

Imperial College London
Department of Materials

**Development of high temperature Thermal History Paints
for reliable off-line measurements**

Daniel Castillo-Gutiérrez

Thesis submitted to Imperial College London for the degree of
PhD of Imperial College London and the Diploma of Imperial College London

Supervisors: Prof. Stephen J. Skinner (Imperial College London)
and Dr Jörg P. Feist (Sensor Coating Systems Ltd., SCS Ltd.)

Submitted for examination:	December 2021
Corrected version re-submitted:	May 2022

**Imperial College
London**

THESIS RESTRICTION

According to the wishes of Sensor Coating Systems Ltd., who sponsored this thesis, with the title “Development of high temperature Thermal History Paints for reliable off-line measurements” written by Daniel Castillo-Gutiérrez, the thesis will be withheld from public use for two years, in an extendable embargo in two-year periods, up to a maximum of six years, until May 2028.

Publication, copying, and viewing are only allowed with the written permission of the abovenamed company and the author.

Daniel Castillo-Gutiérrez, May 2022

DECLARATION OF ORIGINALITY

I, Daniel Castillo-Gutiérrez, certify that the thesis entitled “Development of high temperature Thermal History Paints for reliable off-line measurements” and the work presented herein are my own and any information derived from published or unpublished work of others has been properly acknowledged and a list of references is provided at the end of the thesis.

COPYRIGHT DECLARATION

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence, CC BY-NC-ND v4.0. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform, or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

ABSTRACT

Temperature measurements are of great importance for the operation and maintenance of combustion engines in automotive, aviation and power generation sectors. The development of efficient engines in these sectors will have a decisive impact in the fight against climate change over the coming decades. Conversion technologies, such as gas turbines, can help to reduce CO₂ emissions, while transitioning from fossil fuels to renewable energy sources. In this context, the validation of temperatures in new engine designs is critical, in particular for turbomachinery components exposed to the harsh conditions of the combustion environment. Current techniques show critical limitations measuring temperatures on the surface of complex-shaped components, such as rotating turbine blades. The use of off-line temperature measurement techniques can overcome some of these limitations, delivering the maximum temperature seen on the surface of rotating turbomachinery components in harsh combustion environments.

This investigation focuses on the development of a novel off-line surface temperature technique, Thermal History Paint (THP). This technique consists of a luminescent pigment and a liquid binder, functional to temperatures up to 900 °C on metallic substrates. The behaviour of THP based on potassium silicate binder was studied in this work, revealing the main limitations to high temperature functionality. The obtained results revealed interaction between the pigment and the binder and interaction between the THP layer and the metallic substrates. As improvement points, the pigment and the binder were modified, and several interlayers were evaluated between the THP and stainless-steel substrates. While interlayers did not improve the behaviour of the THP, substituting the binder showed some enhanced behaviour at high temperatures. One binder, Ludox® SM30, showed good attachment to metallic substrates, and good behaviour as a carrier of thermographic phosphors.

The combination of the new binder, Ludox® SM30, and the previous potassium silicate binder was tested in order to obtain a high temperature version of thermal history paint. A new THP formulation containing Ludox® SM30 (47.5 % wt.), potassium silicate (47.5 % wt.) and Y₂SiO₅: Eu³⁺ (5 % wt.) showed a temperature upper limit extended to 950 °C, and low interaction between the pigment and the binder. This formulation delivered reliable temperature measurements, with uncertainties of +/- 8 °C, for 95 % confidence levels. These results demonstrate the utility of thermal history paints as a durable technique for monitoring temperature engine components, with an uncertainty in the same range of thermocouple readings.

PUBLICATIONS

- 75 • S. Araguas-Rodriguez, D. Peral, **D. Castillo-Gutiérrez**, S. Karagiannopoulos, J. P. Feist, C. C. Pilgrim, J. Scheibel, ‘Feasibility of Thermal History Paints for Long Term Exposure in Low Temperature Life Critical Components’, GT2022-80848 in ASME Turbo Expo 2022, Controls, Diagnostics & Instrumentation, Rotterdam, The Netherlands, 2022.
- 80 • S. Karagiannopoulos, **D. Castillo-Gutiérrez**, D. Peral, S. Araguas-Rodriguez, J. P. Feist, M. Rode, ‘Advanced Thermal Profiling of Turbocharger Compressor Wheels Using Phosphorescence Thermal History Coatings’, GT2022-80820 in ASME Turbo Expo 2022, Turbomachinery General Interest, Rotterdam, The Netherlands, 2022.
- 85 • C. Pilgrim, **D. Castillo-Gutiérrez**, S. Araguas-Rodriguez, S. Karagiannopoulos, J. Feist, A. Redwood, Y. Zhang, C. Copeland, J. Scobie, C. Sangan, ‘Thermal Profiling of Cooled Radial Turbine Wheel’, GT2020-14932 in *Proceedings of the ASME Turbo Expo 2020: Turbomachinery Technical Conference and Exposition. Volume 5: Controls, Diagnostics, and Instrumentation; Cycle Innovations; Cycle Innovations: Energy Storage*. Virtual. September 21–25, 2020. V005T05A014. <https://doi.org/10.1115/GT2020-14932>
- 90 • R. Krewinkel, A. Such, A. Oyarbide de la Torre, A. Wiedermann, **D. Castillo-Gutiérrez**, S. Araguas-Rodriguez, J.H. Schleifenbaum, M. Blaswich, ‘Design and Characterization of Additively Manufactured NGVs Operated in a Small Industrial Gas Turbine’, Available via: <https://www.researchgate.net/publication/338555779>, presented at the International Gas Turbine Congress, Tokyo, Japan, 2019.
- 95 • D. Peral, **D. Castillo-Gutiérrez**, S. Araguas-Rodriguez, A. Yáñez -Gonzalez, C. C. Pilgrim, S. Karagiannopoulos, J. P. Feist, S. Skinner., ‘Reliable Temperature Measurement with Thermal History Paints: An Uncertainty Model’ *Proceedings of the ASME Turbo Expo 2019: Turbomachinery Technical Conference and Exposition. Volume 6: Ceramics; Controls, Diagnostics, and Instrumentation; Education; Manufacturing Materials and Metallurgy*. Phoenix, Arizona, USA. June 17–21, 2019. V006T24A022. ASME. <https://doi.org/10.1115/GT2019-92087>
- 100
- 105

Poster Presentations

- 110 • *Validation of a Thermal History Paint on a Turbine Blade in a hot gas rig facility*, **Castillo-Gutiérrez D**, Peral-Jiménez D, Araguas-Rodríguez S, Dehe V, Rabs M, Karagiannopoulos S, et al. In: GT2020-16014, Poster Session, ASME Turbo Expo. London, England, UK; 2020.
- 115 • *Luminescent Thermal Memory Paints*, **D. Castillo-Gutiérrez**, S. Araguas-Rodriguez, A. Leibinger, S. Karagiannopoulos C. Pilgrim, J. Feist, S. Skinner, C. Cavallo, M. Genschmar, D. Peral, ASME Turbo Expo 2018, Lillestroem, Oslo, Norway, June 2018

Awards

- 120 **Warren M. Rohsenow Prize** at the ASME Turbo-Expo 2020 Conference and Exhibition
- 125 The heat-transfer division of the American Society of Mechanical Engineers (ASME) awarded the poster presentation: *Validation of a Thermal History Paint on a Turbine Blade Hot Gas Test Rig Facility*, as the best presentation at a session on heat transfer in gas turbine systems. Video presentation available through the YouTube channel of the Centre of Doctoral Training on Advanced Characterisation of Materials (CDT-ACM): <https://youtu.be/XavD5JSPH0A>

Other presentations and conference participation

- 130 • Second International Phosphor Thermometry Conference, Otto von Guericke University, Magdeburg, Germany, July 2020
- 135 • 10th International Charles Parsons Turbine Conference, Cranfield University, UK, September 2019
- 135 • Inaugural International Conference on Phosphor Thermometry, University of Strathclyde, Glasgow, Scotland, UK, July 2018
- 135 • European Coatings Conference, Future Dialogue, Vincentz Network, Berlin, Germany, November 2017

ACKNOWLEDGEMENTS

In order of appearance...

Many thanks to Prof. Stephen J. Skinner and Dr Jörg P. Feist for interviewing me remotely when it was not that common, back in 2017, and giving me the opportunity to do this PhD thesis. I hope their guidance and patience is properly reflected in these pages.

I will always be grateful to Dr Christopher C. Pilgrim and Dr Silvia Araguas-Rodriguez, technical directors at SCS Ltd., who carefully reviewed endless amounts of results. This work contains the discussions over many meetings during the year 2019.

Special thanks to MAN Energy Solutions, in particular to Dr Robert Krewinkel, Christoph Benninghoven and Dr Ulrich Orth, for their support and collaboration over the years.

A big thank you to the incredible team at SCS Ltd., in particular Dr Solon Karagiannopoulos, Dr David Peral-Jiménez, Inken-Katharina Semmler, Sarah Turner, Dr Marta Ferran-Marques, Elijah Boumhah, Kieron Rai, Abraham Kolawole, Harsh Patel, Mahmood and Ahmed Zaid, Dr James Hickey, Sophie Everett, Joseph Counte (Dr to be), Clem Seyers, Goran Krsic, Mike Connolly, Fleur Conway, Tamanna Begum, Etienne Wiemann, Mike Genschmar, Hannah Puntschuh, Dr Salvador Pacheco-Gutiérrez, Sadiye Isisal, Dr Alexander Leibinger, Claudio Cavallo, ...and the army of interns who walked through the lab during these four and a half years of shared equipment experiences.

Many thanks to all the staff at London East UK, who keep the facilities alive, and those at Imperial College London whose technical expertise were a great help during this thesis, particularly Dr Richard Sweeny and Dr Victoria Bemmer for all their good advice in X-Ray Diffraction, and Dr Mahmoud Ardakani and Dr Ecaterina Ware for their guidance at the electron microscopy suite.

To the ones who were already there...

Deepest thanks to Dr Miguel Cacho-Soblechero and Dr Alvaro Yáñez-Gonzalez, who are guilty of making me move to London and to live surrounded by the rest of the Spanish gang, Julia Gonzalez, Alberto Martinez de Aragon, Cristina Berlanga, Dr Alba Rodriguez-Meira, Ana Pliego, and other beings populating this incredible city.

Finally, this work would not have been possible without the constant support of my family: my parents, Antonio and Maria, my sister Lucia, my grandma Carmen, my aunt Amelia, my uncle Francisco (on my mother side), my uncle Francisco (on my father side) and other relatives and friends. Thank you all for your positive energy and constant check-ups.

And at the very end...a few words about love and distance...

When all this started, distance was the most painful thing to bear. Luckily, that is solved now and tested to the extreme of living a global pandemic together. Thank you for keeping me afloat, Simone Krings (Dr to be) and good luck to us both in the future.

TABLE of CONTENTS

	THESIS RESTRICTED	3
	DECLARATION OF ORIGINALITY.....	3
180	COPYRIGHT DECLARATION	3
	ABSTRACT	4
	PUBLICATIONS	5
	Poster Presentations.....	5
	Awards	6
185	Other presentations and conference participation	6
	ACKNOWLEDGEMENTS.....	7
	TABLE OF CONTENTS.....	8
	LIST OF FIGURES	11
	LIST OF TABLES	20
190	1 INTRODUCTION.....	22
	1.1 Need for temperature measurements	22
	1.1.1 Gas turbines and turbomachinery	23
	1.1.2 Automotive sector and other industrial applications	24
	1.2 Temperature measurement techniques	25
195	1.2.1 On-line temperature measurements	25
	1.2.2 Off-line temperature measurements	28
	1.2.3 Summary of temperature measurements.....	32
	1.3 Objectives	33
	1.4 Thesis outline.....	34
200	2 FUNDAMENTALS OF LUMINESCENCE.....	35
	2.1 Energy levels and luminescence theory	35
	2.1.1 Dynamics of excited states and electronic transitions	38
	2.1.2 Luminescent Materials	41
	2.2 Temporal Luminescence.....	43
205	2.3 Summary of Luminescent Concepts.....	44

3	REVIEW OF PHOSPHORESCENT THERMAL HISTORY SENSORS.....	45
3.1	Definition criteria for thermal history sensor.....	46
3.2	History sensing mechanisms	47
210	3.2.1 Thermal damaging mechanism.....	47
	3.2.2 Thermally driven diffusion.....	48
	3.2.3 Amorphous to crystalline mechanism	49
	3.2.4 Summary of history sensing mechanisms.....	51
3.3	Concepts for thermal history paint	52
215	3.3.1 Luminescent pigment	52
	3.3.2 Deposition methods and binder enclosure	60
3.4	Conclusions on thermal history sensors.....	66
4	MATERIALS AND METHODS	67
4.1	Thermal History Paint.....	67
220	4.1.1 Production of luminescent pigment	67
	4.1.2 Production of thermal history paint	68
	4.1.3 Deposition of thermal history paint	69
4.2	Heat treatment	70
225	4.2.1 Isothermal heat treatment	70
	4.2.2 Furnace calibration	70
	4.2.3 Sample heat treatment	71
	4.2.4 Bar heat treatment.....	71
4.3	Luminescence measurements.....	73
230	4.3.1 Spectral response	74
	4.3.2 Temporal response.....	75
4.4	Material characterization methods	79
	4.4.1 X-Ray Diffraction (XRD).....	79
	4.4.2 Fourier Transform Infra-Red (FTIR).....	81
	4.4.3 Thermal Analysis (TA).....	82
235	4.4.1 Scanning Electron Microscopy (SEM)	83
5	RESULTS: TESTING OF HIGH TEMPERATURE MATERIALS FOR THERMAL HISTORY SENSING.....	85
5.1	Behaviour of thermal history paint at high temperatures.....	85
240	5.1.1 Pigment and binder interaction	85
	5.1.2 Thermal analysis of thermal history paint	92
	5.1.3 Interaction between thermal history paint and substrate.....	93
	5.1.4 Efflorescence of thermal history paint.....	105
	5.1.5 Strategy to reach reliable measurements at high temperatures	108
5.2	Modification of existing binder	115
245	5.2.1 Potassium addition.....	115
	5.2.2 Lithium addition	118
5.3	Substitution of existing binder	120
	5.3.1 High temperature binder candidates	121
	5.3.2 Summary of high temperature binder testing and selection.....	137
5.4	Pigment modification	140
250	5.4.1 Dopant modification	140
	5.4.2 Pigment synthesis modification.....	142

	5.5 Interlayer	153
	5.5.1 Sealmat as interlayer.....	154
255	5.5.2 Durazane® 1800 as interlayer	155
	5.5.3 Ludox® SM30 as interlayer	157
	5.5.4 Summary of results on THP deposited on interlayers.	159
	 6 DEVELOPMENT OF A HIGH-TEMPERATURE THERMAL HISTORY PAINT.161	
	6.1 Optimisation route for THP: Combination of Solutions	161
260	6.1.1 Characterisation of colloidal silica, Ludox® SM30	162
	6.1.2 Combination of solutions: Calcined pigment mixed into potassium silicate and Ludox® SM30 colloidal silica binders.	164
	6.1.3 Binder combination applied on stainless-steel and development of a high-temperature thermal history paint.....	169
265	 7 CONCLUSIONS AND OUTLOOK.....	175
	7.1 Conclusions.....	175
	7.2 Future work.....	176
	 8 REFERENCES.....	177
	 9 APPENDIX.....	203
270	9.1 Supplementary results	203
	9.1.1 Thermal conductivity of thermal history paint	203
	9.1.2 FTIR spectra of Y ₂ SiO ₅ : Eu ³⁺ pigment modified with citric acid addition from 700 °C to 1,300 °C.....	204
	9.1.3 XRD of Y ₂ SiO ₅ : Eu ³⁺ pigment modified with citric acid addition and heated to 900 °C.	205
	9.1.4 Luminescent spectra of Y ₂ SiO ₅ :Eu ³⁺ pigment modified with citric acid	206
275	9.1.5 Luminescent spectra of combination of Ludox ® SM30 and potassium silicate paints	207
	 9.2 Poster presentation, awarded with the Warren M. Rohsenow Prize at the ASME Turbo-Expo 2020	209
	 9.3 Material certificate of stainless steel 316L	210
	 9.4 Permissions for third party copyright.....	212
280	9.4.1 Permission for Figure 1.1, from the Institute of Materials, Minerals and Mining (IOM3).....	213
	9.4.2 Permission for Figure 1.3, from the Institute of Physics, (IOP)	214
	9.4.3 Permission for Figure 2.2, from Elsevier license.....	215
	9.4.4 Permission for Figure 2.7, from Elsevier license.....	216
	9.4.5 Permission for Figure 3.2, from Taylor & Francis group	217
285	9.4.6 Permission for Figure 3.3, from Cambridge University press	217
	9.4.7 Permission for Figure 4.12, from Avantes.....	218
	9.4.8 Permission for Figure 4.13, from ACS publications.....	219
	9.4.9 Permission for Figure 5.7, from John Wiley and sons	219
	9.4.10 Permission for Figure 5.32, from ACS publications	220
290	9.4.11 Permission for Figure 5.40, from ACS publications	221

LIST OF FIGURES

295	FIGURE 1.1 FIRING TEMPERATURES AND EFFICIENCIES IN TURBOMACHINERY, OVER THE LAST DECADES. PLOT EXTRACTED WITH PERMISSION FROM [15]. SOURCES CONSULTED [16–25]. CONFIDENCE OF THE FIT INDICATED AS SHADED AREAS AROUND THE LINES AND DATA POINTS.	23
	FIGURE 1.2 SCHEMATIC DIAGRAM OF A BI-METAL THERMOCOUPLE, CONSISTING OF TWO DISSIMILAR METAL WIRES JOINED IN ONE EXTREME, WHERE THE TEMPERATURE IS MEASURED, AND CONNECTED THROUGH A REFERENCE JUNCTION TO A READER.....	25
300	FIGURE 1.3 THERMAL PAINT TEST APPLIED ON: (A) BUTTERFLY TEST PIECE HEATED BY JOULE EFFECT AND (B) SET OF SAMPLES HEATED IN 10 °C STEPS, BOTH PAINTED WITH ROLLS-ROYCE TP96 THERMAL PAINT. REPRODUCED WITH PERMISSION FROM REFERENCE [89].....	29
	FIGURE 2.1 (LEFT) EXCITATION, EMISSION, AND HEAT RELEASE OF A LUMINESCENT ION, A, IN ITS HOST LATTICE. (RIGHT) EXCITATION AND RELAXATION TRANSITIONS IN AN ENERGY DIAGRAM.....	35
305	FIGURE 2.2 DIAGRAM OF ENERGY LEVEL SPLITTING OF Eu^{3+} ($4f^6$), FROM INTERELECTRONIC CONFIGURATION TERMS, THROUGH SPIN-ORBIT COUPLING LEVELS, TO CRYSTAL-FIELD SUBLEVELS. EXTRACTED WITH PERMISSION FROM [111].	37
	FIGURE 2.3 LUMINESCENCE PROCESS SHOWN FOR EXAMPLE ENERGY LEVELS, INCLUDING EMISSION SPECTRUM, EXTRACTED FROM [115] WITH PERMISSION VIA CC-BY-NC-ND 3.0.	38
310	FIGURE 2.4 ABSORPTION SPECTRA OF Eu^{3+} IN Y_2SiO_5 AT AMBIENT TEMPERATURE, AFTER 30 MIN HEAT TREATMENT AT 900 °C. OBSERVATION WINDOWS KEPT AT 614 NM AND 620 NM, SHOWN WITH AN OFFSET FOR VISUALISATION. SPECTRA PROVIDED BY PHOSPHOR TECHNOLOGY LTD. [119] FROM SAMPLES PRODUCED BY SENSOR COATING SYSTEMS LTD. [105].	39
	FIGURE 2.5 SCHEMATIC REPRESENTATION OF STARK SPLITTING AND BROADENING EFFECT OF OPTICAL EMISSION SPECTRUM. AN IDEALISED CRYSTAL WITH IDENTICAL SITES IS SHOWN ON THE LEFT (A), WHILE DIFFERENT RANDOMISED STARK LEVELS ARE SHOWN ON THE RIGHT (B). REPRODUCED FROM [115] WITH PERMISSION VIA CC-BY-NC-ND 3.0.....	40
	FIGURE 2.6 LUMINESCENT PROCESS INCLUDING ENERGY TRANSFER FOR LUMINESCENT IONS A AND D WITHIN A HOST STRUCTURE.	41
320	FIGURE 2.7 DIEKE DIAGRAM FOR SOME RARE EARTH IONS. THE BLUE SHADED AREA REPRESENTS THE ENERGY GAP BETWEEN THE PRINCIPAL RADIATIVE ENERGY LEVEL AND THE HIGHEST ENERGY GROUND STATE. EXTRACTED WITH PERMISSION FROM [135].	42
	FIGURE 3.1 SCHEMATIC OF AMORPHOUS TO CRYSTALLINE TRANSITION. LUMINESCENT IONS DISPLAYED ALONG THE STRUCTURE AS YELLOW DOTS, WITH EXCITATION INCIDENT LIGHT (BLUE ARROW) AND EMISSION LIGHT (RED ARROW). LIFETIME DECAY VALUES INDICATED AS T ARE GIVEN AS EXAMPLES FOR THE TWO STATES IN THE AMORPHOUS TO CRYSTALLINE TRANSITION.	50
325	FIGURE 3.2 PARTIAL UNIT CELL OF $\text{Y}_2(\text{SiO}_4)\text{O}$. REPRODUCED WITH PERMISSION FROM [228], BASED ON [227].	55
	FIGURE 3.3 EXCITATION AND RELAXATION TRANSITIONS FOR THE ENERGY LEVELS OF Eu^{3+} . DATA OBTAINED FROM REFERENCE [122], ORIGINALLY PUBLISHED BY THE SAME AUTHOR IN [245].	57
330	FIGURE 3.4 EMISSION SPECTRUM OF $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$, AFTER HEAT TREATMENT AT 1,000 °C FOR 30 MINUTES.....	58
	FIGURE 3.5 TEMPERATURE DIAGRAM SHOWING THE RANGE OF USE FOR CURRENT THERMAL HISTORY TECHNOLOGIES ACCORDING TO THE DEPOSITION TECHNIQUE EMPLOYED. THERMAL HISTORY PAINT (THP) ARE APPLIED BY	

	CONVENTIONAL AIR SPRAYING, WHILE THERMAL HISTORY COATINGS (THC) ARE APPLIED BY ATMOSPHERIC PLASMA SPRAY (APS).	62
335	FIGURE 3.6 PHASE DIAGRAM OF THE SiO_2 AND K_2O , EXTRACTED WITH PERMISSION FROM [323]. COMPOSITION OF THE POTASSIUM SILICATE BINDER USED IN THIS INVESTIGATION INDICATED WITH A RED DOTTED LINE.	65
	FIGURE 4.1 SCHEMATIC OF A FUNCTIONING AIR SPRAY GUN, WHERE INDEPENDENT CIRCUITS OF FLUID AND PRESSURIZED AIR ARE MARKED IN RED AND BLUE, RESPECTIVELY.....	69
340	FIGURE 4.2 TUBE FURNACE CALIBRATION OF ACHIEVED TEMPERATURE ON A SAMPLE, AS FUNCTION OF THE TEMPERATURE SET IN THE FURNACE, BETWEEN 250 °C AND 1,150 °C, IN AN ELITE THS12 (LEFT), AND BETWEEN 600 °C AND 1,250 °C IN AN ELITE THS15 (RIGHT). LINEAR FITS AND EQUATIONS INCLUDED.....	71
	FIGURE 4.3 TECHNICAL DRAWING OF 316 STAINLESS STEEL BARS FOR STANDARD CALIBRATION TEST. ALL DIMENSIONS IN MM.	72
345	FIGURE 4.4 (A) PICTURE OF A STAINLESS-STEEL BAR DURING HEAT TREATMENT ON TUBE FURNACE. K-TYPE THERMOCOUPLES INSERTED ALONG THE SIDE OF THE BAR. (B) TEMPERATURE GRADIENT ALONG LENGTH OF THE BAR FOLLOWING A SIGMOIDAL DISTRIBUTION, FITTED WITH A CONTINUOUS LINE AROUND TEMPERATURE DATA POINTS. (C) SCHEMATIC OF BAR INTRODUCED IN THE TUBE FURNACE FROM THE COLD END AT THE EXTREME OF THE TUBE UP TO THE ISOTHERMAL REGION IN THE CENTRE.	73
350	FIGURE 4.5 SCHEMATIC OF SCS INSTRUMENTATION SET-UP TO MEASURE SPECTRAL FEATURES OF PHOSPHOR EMISSIONS	74
	FIGURE 4.6 SCHEMATIC OF AN AVANTES AVASPEC-ULS OPTICAL BENCH DESIGN, INCLUDING A SYMMETRICAL CZERNY-TURNER SPECTROMETER, EXTRACTED WITH PERMISSION FROM AVANTES CATALOG X [298].	75
	FIGURE 4.7 SCHEMATIC OF SCS INSTRUMENTATION DEVICE TO MEASURE LONG LIFETIME DECAY PHOSPHOR EMISSIONS.	76
355	FIGURE 4.8 EXAMPLE OF SINGLE EXPONENTIAL DECAY OF THERMAL HISTORY PAINT MEASURED WITH SCS LTD. INSTRUMENTATION DEVICE. THE INTENSITY (I) DECREASES FROM THE INITIAL INTENSITY (I_0).....	77
	FIGURE 4.9 SCHEMATIC OF INSTRUMENTATION SET-UP TO MEASURE SHORT LIFETIME DECAYS PHOSPHOR EMISSIONS, EXTRACTED FROM [115] WITH PERMISSION VIA CC-BY-NC-ND 3.0.	77
360	FIGURE 4.10 EXAMPLE OF SINGLE EXPONENTIAL OF YSO: EU MEASURED WITH INSTRUMENTATION SET-UP FOR SHORT LIFETIME DECAYS. THE FIT GENERATED ON THE EXPERIMENTAL DATA FROM THE ALGORITHM “ExpDECAY1” FROM ORIGINPRO2020.....	78
	FIGURE 4.11 BRAGG DIFFRACTION ON A CRYSTALLINE LATTICE, WHERE X-RAY RADIATION FINDS THE ATOMS IN THE LATTICE, SCATTERING RADIATION IN A PARTICULAR ANGLE, ACCORDING TO BRAGG’S LAW.....	79
365	FIGURE 4.12 BLOCK DIAGRAM OF THE COMPONENTS OF AN FT-IR SPECTROMETER. REPRINTED WITH PERMISSION FROM REFERENCE [305].	81
	FIGURE 4.13 SCHEMATIC OF DIFFERENTIAL SCANNING CALORIMETRY SETUP, ADAPTED FROM [307], OBTAINED FROM [308].	82
	FIGURE 4.14 SCHEMATIC OF EMITTED SIGNALS FROM A SAMPLE INTERROGATED WITH AN ELECTRON BEAM. ADAPTED FROM [309].	83
370	FIGURE 5.1 LUMINESCENCE SPECTRA OF Y_2SiO_5 : Eu^{3+} PIGMENT AND THERMAL HISTORY PAINT PELLETT (Y_2SiO_5 : Eu^{3+} PIGMENT IN POTASSIUM SILICATE BINDER), OBTAINED AT ROOM TEMPERATURE AFTER EXCITATION WITH 532 NM VISIBLE LIGHT. BOTH SAMPLES WERE HEAT-TREATED AT 1,100 °C FOR 30 MINUTES.	86
	FIGURE 5.2 DIFFRACTION PATTERN OF YTTRIUM ORTHOSILICATE, DOPED WITH Eu^{3+} IONS, AFTER HEAT TREATMENT AT 1,100 °C FOR 30 MINUTES. X1-YSO REFERENCE PATTERN INDICATED WITH RED SQUARES.....	86

375	FIGURE 5.3 DIFFRACTION PATTERN OF THERMAL HISTORY PAINT PELLET, AFTER HEAT TREATMENT TO 1,100 °C FOR 30 MINUTES. MATCHING CANDIDATES INDICATED WITH MARKERS.....	87
	FIGURE 5.4 LUMINESCENT SPECTRA OF $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$ PIGMENT HEAT TREATED AT TEMPERATURES FROM 400 °C TO 1,300 °C.....	90
	FIGURE 5.5 LUMINESCENT SPECTRA OF THP PELLETS HEAT TREATED AT TEMPERATURES FROM 600 °C TO 1,300 °C.	91
380	FIGURE 5.6 THERMAL ANALYSIS OF THERMAL-HISTORY PAINT, INCLUDING THERMO-GRAVIMETRIC ANALYSIS (TGA) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC).....	92
	FIGURE 5.7 LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR THREE THERMAL HISTORY SAMPLES: (A) THP APPLIED ON SAPPHIRE DISCS, 12.5MM IN DIAMETER, HEAT TREATED TO THE INDICATED TEMPERATURE. (B) PIGMENT POWDER, HEAT TREATED TO THE INDICATED TEMPERATURE AND ATTACHED ONTO A GLASS SLIDE. (C)	
385	THP APPLIED ON STAINLESS STEEL 316L TILES, 20X10 MM, HEAT TREATED TO THE INDICATED TEMPERATURE.	94
	FIGURE 5.8 (A) LUMINESCENT EMISSION SPECTRA OF A HEATED METALLIC SUBSTRATE COATED WITH [TOP] THP AND [BOTTOM] BINDER ONLY, AFTER EXCITATION WITH 532 NM LIGHT. (B) NATURAL LOGARITHM OF THE RATIO OF Cr^{3+} AND Eu^{3+} INTENSITY PLOTTED AS A FUNCTION OF RECIPROCAL EXPOSURE TEMPERATURE. EXTRACTED FROM [106] WITH PERMISSION VIA CC-BY-NC-ND 4.0	95
390	FIGURE 5.9 (A) PHOTOGRAPH OF METALLIC SUBSTRATES, COATED WITH THP AND HEAT TREATED FOR THE INDICATED DURATION. LUMINESCENT EMISSION SPECTRA OF THP ON METALLIC SUBSTRATE, HEATED AT 700 °C (B), AT 900 °C (C) AND AT 1,000 °C (D) FOR THE INDICATED DURATION.	96
	FIGURE 5.10 LIFETIME DECAY MEASURED ON THP DEPOSITED ON NICKEL COUPONS AND HEAT TREATED AT THREE TEMPERATURES (700 °C, 900 °C AND 1,000 °C) OVER DIFFERENT EXPOSURE TIMES. LINES LINKING POINTS INCLUDED FOR VISUALIZATION. ERROR BARS CORRESPOND TO THE STANDARD DEVIATION OF FIVE MEASUREMENTS TAKEN ON THE PAINTED SURFACE OF THE SAMPLE. EXCITATION WAS PERFORMED AT 532 NM AND THE EMISSION WAS RECORDED AT 620 +/- 26 NM.	97
395	FIGURE 5.11 LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR THP APPLIED ON INCONEL 738 DISCS AND STAINLESS-STEEL 316L SUBSTRATES (LEFT). PHOTOGRAPHS OF METALLIC SUBSTRATES, COATED WITH THP, AND HEAT TREATED TO 800 °C, 900 °C AND 1,000 °C FOR 30 MINUTES (RIGHT).	99
400	FIGURE 5.12 (LEFT) LUMINESCENT EMISSION SPECTRA OF THP DEPOSITED ON INCONEL 738 DISCS, HEATED AT INDICATED TEMPERATURE. (RIGHT) LUMINESCENT EMISSION SPECTRA OF THP DEPOSITED ON STAINLESS STEEL 316L SUBSTRATES, HEATED AT INDICATED TEMPERATURE.	100
405	FIGURE 5.13 PHOTOGRAPH OF 16 STAINLESS-STEEL SAMPLES, OF DIMENSIONS 20 X 10 X 3 MM, PAINTED WITH THP, HEATED TO 200 °C, 400 °C, 600 °C AND 800 °C AND STORED IN FOUR DIFFERENT STORING CONDITIONS.	105
	FIGURE 5.14 HUMIDITY MEASUREMENTS FOR THE FOUR STORAGE CONDITIONS CONSIDERED TO STUDY EFFLORESCENCE ON THP.....	106
	FIGURE 5.15 EVOLUTION OF LUMINESCENT LIFETIME DECAY OF THP DEPOSITED ON STAINLESS STEEL SAMPLES, HEAT TREATED AT 200 °C, 400 °C, 600 °C AND 800 °C AND THEN STORED FOR 42 DAYS IN DIFFERENT CONDITIONS: STANDARD STORAGE (IN A SEALED PLASTIC BAG), REFRIGERATION STORAGE (SEALED BAG STORED IN A FRIDGE AT AROUND 5 °C), DESICCANT STORAGE (SAMPLES STORED IN SILICA GEL) AND VACUUM STORAGE (SAMPLES STORED IN VACUUM BAGS).....	107
410	FIGURE 5.16 LIFETIME DECAY AS A FUNCTION OF TEMPERATURE FOR POTASSIUM SILICATE BINDER MIXED IN WITH $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$ PIGMENTS, PREVIOUSLY CALCINED AT 250 °C, 400 °C AND 600 °C. MAXIMUM SENSING TEMPERATURES INDICATED FOR CLARITY.	109
415		

	FIGURE 5.17 FTIR SPECTRA OF $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ PIGMENT SAMPLES HEAT-TREATED FOR 30 MINUTES TO THE INDICATED TEMPERATURE. SILICATE AND NITRATE PEAKS IDENTIFIED. EXTRACTED FROM [106] WITH PERMISSION VIA CC-BY-NC-ND 4.0.	111
420	FIGURE 5.18 (A) LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR THP – P600 APPLIED ON SAPPHIRE DISCS. LINES LINKING POINTS ADDED FOR VISUALIZATION (B) LUMINESCENT SPECTRA OF THP – P600 DEPOSITED ON SAPPHIRE DISCS AND HEAT TREATED AT TEMPERATURES FROM 600 °C TO 1,300 °C. THE $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ PIGMENT OF THE THP – P600 WAS CALCINED TO 600 °C PRIOR TO PAINT PRODUCTION. (C) PAINTED SAPPHIRE SUBSTRATES, HEAT TREATED TO THE INDICATED TEMPERATURE.	112
425	FIGURE 5.19 PHOTOGRAPH OF THP DEPOSITED ON A 40 CM LONG STAINLESS-STEEL BAR, AND HEAT-TREATED BETWEEN 200 °C AND 1,100 °C. THE DARKENING OF THE THP, ASSOCIATED WITH THE LTD DROP, APPEARS AT TEMPERATURES ABOVE 900 °C, WHERE THE COLOUR TURNS GREEN. ESTIMATED TEMPERATURE LOCATIONS HAVE BEEN INCLUDED FOR CLARITY.	113
430	FIGURE 5.20 REFERENCE THP DEPOSITED ON A STAINLESS-STEEL BAR, HEAT TREATED AND WHERE LTD WAS MEASURED EVERY 5 MM. THE MONOTONIC INCREASE OF LIFETIME DECAY (TOP) AND THE SENSITIVITY ANALYSIS OF THE MONOTONIC INCREASE (BOTTOM) ARE SHOWN OVER INCREASING TEMPERATURE, BETWEEN 150 °C TO 900 °C FOR THP-P400 (A) AND THP-P600 (B) OVER A TEMPERATURE RANGE, BETWEEN 250 °C AND 1,000 °C.	114
435	FIGURE 5.21 (A) STAINLESS STEEL BAR PAINTED WITH BINDER MODIFIED BY POTASSIUM ADDITION. (B) PHOTOGRAPH OF THE FIRST SECONDS OF HEAT TREATMENT OF A STAINLESS-STEEL BAR PAINTED WITH MODIFIED BINDER, WITH POTASSIUM ADDITION, IN A TUBE FURNACE HEATED UP TO 1,100°C. BUBBLE FORMATION IS VISIBLE AT HOT TEMPERATURES. (C) PHOTOGRAPH AFTER SOME MINUTES OF THE SAME BAR HEAT TREATMENT, WHERE PAINT BLISTERS ARE VISIBLE ALL OVER THE PAINTED SURFACE, FROM HOT TO COLD END OF THE PAINTED BAR.	116
440	FIGURE 5.22 (A) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR LUMINESCENT HISTORY PAINT, MODIFIED BY POTASSIUM ADDITION AND DEPOSITED ON A 40 X 20 X 3 MM STAINLESS-STEEL 316L BAR. DURING HEAT TREATMENT A TEMPERATURE GRADIENT, BETWEEN 150 °C TO 1,100 °C WAS GENERATED ALONG THE BAR, ALLOWING FOR LIFETIME DECAY TO BE MEASURED AFTER HEAT TREATMENT. (B) MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR MODIFIED HISTORY PAINT, BY POTASSIUM ADDITION (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC INCREASE (BOTTOM).	117
445	FIGURE 5.23 (A) PHOTOGRAPH OF POLYMERIZED POTASSIUM SILICATE BINDER MODIFIED BY LITHIUM ADDITION, INTRODUCING ONE EQUIVALENT OF LITHIUM PER SILICA EQUIVALENT, AS RECEIVED BY THE AUTHOR. (B) PHOTOGRAPH OF LITHIUM ENRICHED POTASSIUM SILICATE BINDER, AFTER WATER AND PIGMENT ADDITION. AN OVERHEAD STIRRER WAS USED, AS WELL AS ZIRCONIA BEADS TO FACILITATE THE MIXING.	118
450	FIGURE 5.24 (A) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR TWO MIXES OF LUMINESCENT HISTORY PAINT, MODIFIED BY LITHIUM ADDITION, AND DEPOSITED ON 400 X 20 X 3 MM STAINLESS-STEEL BARS. (B) MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR MODIFIED THP, BY LITHIUM ADDITION (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC INCREASE (BOTTOM). (C) PHOTOGRAPH OF THE BARS PAINTED WITH MODIFIED BINDER, BY LITHIUM ADDITION. COLD END (~200 °C) AND HOT END (~1,100 °C) INDICATED.	119
455	FIGURE 5.25 PHOTOGRAPH OF THE STAINLESS-STEEL PAINTED BAR PAINTED WITH SEALMET® BINDER, LOADED WITH 10 % WT. OF PIGMENT, SHOWN AFTER HEAT-TREATMENT. COLD END (~200 °C) AND HOT END (~1,100 °C) INDICATED.	122
	FIGURE 5.26 LIFETIME DECAY PLOTTED OVER TEMPERATURE, MEASURED ON THP, AND DEPOSITED ON A STAINLESS-STEEL BAR FOR SEALMET® LOADED WITH 5 % WT. PIGMENT (A) AND SEALMET® LOADED WITH 10 % WT. PIGMENT (B). THE MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR THESE THP'S (TOP) AND	

	SENSITIVITY ANALYSIS OF THE MONOTONIC INCREASE (BOTTOM) ARE SHOWN FOR SEALMET® PAINT LOADED	
460	WITH 5 % WT. PIGMENT (C) AND FOR SEALMET® LOADED WITH 10 % WT. PIGMENT (D).	123
	FIGURE 5.27 (LEFT) LTD PLOTTED OVER TEMPERATURE FOR A POTENTIAL LOW TEMPERATURE THP BASED ON	
	SEALMET® AS A BINDER, AND PIGMENT CALCINED TO 350 °C DEPOSITED ON A STAINLESS-STEEL BARS AND HEAT	
	TREATED UP TO 500 °C. (RIGHT) MONOTONIC INCREASE OF LTD OVER TEMPERATURE (TOP) AND SENSITIVITY	
	ANALYSIS OF THE MONOTONIC LIFETIME DECAY INCREASE (BOTTOM).	124
465	FIGURE 5.28 LUMINESCENT EMISSION SPECTRA OF PATTERNS OF (A) Y ₂ SiO ₅ : EU PIGMENT, (B) FIXWOOL® COATING 130	
	ON ITS OWN, AND (C) Y ₂ SiO ₅ : EU PIGMENT MIXED INTO FIXWOOL® COATING 130.	125
	FIGURE 5.29 STAINLESS STEEL BAR PAINTED WITH UNIFRAX FIXWOOL® COATING 130, HEAT TREATED FROM 200 °C	
	(LEFT, COLD EXTREME) TO 1,100 °C (RIGHT, HOT EXTREME). DETACHMENT OF PAINT LAYER WAS OBSERVED FOR	
	TEMPERATURES ABOVE 1,000 °C.	126
470	FIGURE 5.30 LUMINESCENT SPECTRA OF FIXWOOL® COATING HEAT TREATED AT 800 °C, 900 °C, 1000 °C AND 1050 °C.	
		127
	FIGURE 5.31 (LEFT) LIFETIME DECAY, MEASURED THROUGH A 694 NM OPTICAL FILTER, PLOTTED OVER THE HEAT-	
	TREATMENT TEMPERATURE FOR FIXWOOL® COATING 130, DEPOSITED ON 400 X 20 X 3 MM STAINLESS-STEEL BAR	
	AS A SINGLE LAYER OR BY SEVERAL LAYERS, AND HEAT TREATED UP TO 1,100 °C. (RIGHT) MONOTONIC DECREASE	
475	OF LIFETIME DECAY OVER TEMPERATURE FOR FIXWOOL® COATING 130 (TOP) AND SENSITIVITY ANALYSIS OF THE	
	MONOTONIC DECREASE (BOTTOM).	127
	FIGURE 5.32 STAINLESS STEEL BARS PAINTED WITH LITHIUM POLY-SILICATE (TOP BAR), AND LITHISIL®25 LITHIUM	
	SILICATE. BOTH BARS WERE HEAT TREATED FROM 200 °C (RIGHT, COLD END) TO 1,100 °C (LEFT, HOT END). .	129
	FIGURE 5.33 (A) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR LITHIUM POLY-SILICATE, AND LITHIL®25, OF	
480	LUMINESCENT HISTORY PAINT. BOTH PAINTS WERE DEPOSITED ON 400 X 20 X 3 MM STAINLESS-STEEL BARS AND	
	HEAT TREATED UNTIL 1,100 °C. (B) MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR LITHIUM	
	SILICATE PAINTS (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC INCREASE (BOTTOM).	130
	FIGURE 5.34 STAINLESS STEEL BAR PAINTED WITH FFB® 1210 PAINT AND HEAT TREATED FROM 200 °C (LEFT, COLD	
	EXTREME) TO 1,100 °C (RIGHT, HOT EXTREME). DETACHMENT OF PAINT LAYER WAS OBSERVED FOR	
485	TEMPERATURES ABOVE 800 °C.	131
	FIGURE 5.35 STAINLESS STEEL BAR PAINTED WITH IPXX PHOSPHATE BINDER PAINT AND HEAT TREATED FROM 200 °C	
	(LEFT, COLD EXTREME) TO 1,100 °C (RIGHT, HOT EXTREME). DETACHMENT OF PAINT LAYER WAS OBSERVED AT	
	HIGH TEMPERATURES ABOVE 900 °C.	132
	FIGURE 5.36 (A) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR FFB® 1210 AND IPXX PHOSPHATE BASED	
490	LUMINESCENT HISTORY PAINT. BOTH PAINTS WERE DEPOSITED ON 400 X 20 X 3 MM STAINLESS-STEEL BARS AND	
	HEAT TREATED UNTIL 1,100 °C. (B) MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR BOTH	
	PHOSPHATE PAINTS (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC INCREASE (BOTTOM).	132
	FIGURE 5.37 STAINLESS STEEL BAR PAINTED WITH DURAZANE® 1800, POLYSILAZANE POLYMER PAINT, SHOWN BEFORE	
	HEAT TREATMENT (TOP) AND AFTER HEAT TREATMENT (BOTTOM) FROM 200 °C (LEFT, COLD END) TO 1,100 °C	
495	(RIGHT, HOT END).	133
	FIGURE 5.38 LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR DURAZANE® 1800 ORGANIC POLY-SILAZANE	
	POLYMER USED AS BINDER FOR LUMINESCENT HISTORY PAINT, APPLIED ON A 400 X 20 X 3 MM STAINLESS-STEEL	
	BARS AS A SINGLE LAYER OR AS SEVERAL LAYERS, AND HEAT TREATED UNTIL 1,100 °C. NO SENSITIVITY ANALYSIS	
	WAS PERFORMED FOR THIS BINDER.	134

500	FIGURE 5.39 STAINLESS STEEL BARS PAINTED WITH LUDOX® SM 30 (TOP) AND LUDOX® HS 40 (BOTTOM) AS BINDERS FOR LUMINESCENT HISTORY PAINT. RULER WITH SCALE IN CENTI-METRES SHOWN FOR REFERENCE. BOTH BARS WERE PAINTED HALF AS A SINGLE LAYER, AND HALF APPLYING SEVERAL LAYERS OF PAINT. APPEARANCE OF THE PAINT LAYER DID NOT SHOW SIGNIFICANT VARIATIONS BEFORE AND AFTER HEAT TREATMENT.	135
505	FIGURE 5.40 LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR THP, DEPOSITED ON 400 X 20 X 3 MM STAINLESS-STEEL BARS AND HEAT TREATED UP TO 1,100 °C. THE BINDERS USED TO GENERATE THE THP WERE LUDOX® SM30 AND LUDOX® HS40 (A) AND LUDOX® AS30 AND LUDOX® AS40. THE MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC INCREASE (BOTTOM) ARE SHOWN FOR THE THP'S BASED IN LUDOX® SM30 AND LUDOX® HS40 (C) AND LUDOX® AS30 AND LUDOX® AS40 (D).	136
510	FIGURE 5.41 LUMINESCENT SPECTRA OF Y_2SiO_5 DOPED WITH ERBIUM, HEAT TREATED TO 600 °C, 800 °C AND 1,000 °C.	141
	FIGURE 5.42 LIFETIME DECAY OF Y_2SiO_5 DOPED WITH ERBIUM, HEAT TREATED TO 600 °C, 800 °C AND 1,000 °C, MEASURED WITH THE FAST DECAY SET-UP DESCRIBED IN CHAPTER 4, USING AN OPTICAL FILTER 543 +/- 22NM.	141
515	FIGURE 5.43 AVERAGE STOICHIOMETRY OF EDX POINTS MEASURED ON PIGMENTS PRODUCED BY ADDING 10 G AND 25 G OF CITRIC ACID, COMPARED TO THE ORIGINAL PIGMENT PRODUCTION.	144
	FIGURE 5.44 XRD PATTERNS OF Y_2SiO_5 : Eu^{3+} PIGMENTS PRODUCED BY SOL-GEL BY THE SYNTHESIS ROUTE DESCRIBED IN CHAPTER 4 (A), COMPARED TO THE ADDITION OF 10 G OF CITRIC ACID DURING SYNTHESIS (B) AND 25 G OF CITRIC ACID (C), FOR TEMPERATURES BETWEEN 900 °C AND 1,300 °C.	145
520	FIGURE 5.45 CALCULATED RELATIVE CONTENT OF X1 YTTRIUM MONO-SILICATE PHASE, OBTAINED FROM DIFFRACTION PATTERNS OF YTTRIUM MONO-SILICATE SAMPLES PRODUCED BY ADDITION OF CITRIC ACID, AND HEAT TREATED AT TEMPERATURES BETWEEN 1,000 °C AND 1,300 °C.	148
	FIGURE 5.46 LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR PIGMENTS PRODUCED BY ADDING 10 G AND 25 G OF CITRIC ACID, COMPARED TO THE ORIGINAL PIGMENT PRODUCTION.	149
525	FIGURE 5.47 (A) LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR STAINLESS-STEEL BARS PAINTED WITH THP PRODUCED WITH PIGMENT MODIFIED BY ADDING 10 G AND 25 G OF CITRIC ACID, COMPARED TO THE ORIGINAL PIGMENT PRODUCTION, CA0. (B) SENSITIVITY ANALYSIS OF LIFETIME DECAY OVER TEMPERATURE, FOR THP PRODUCED WITH MODIFIED PIGMENTS CA0, CA10 AND CA25, APPLIED AND HEAT-TREATED ON STAINLESS-STEEL BARS.	150
530	FIGURE 5.48 LUMINESCENT SPECTRA OF CA PAINTS AFTER HEAT EXPOSURE AT TEMPERATURES BETWEEN 255 °C AND 1,100 °C.	152
	FIGURE 5.49 (A) SCHEMATIC OF STANDARD THP DEPOSITION ON A METALLIC SUBSTRATE. DIFFUSION ZONES ARE EXPECTED AFTER HIGH TEMPERATURE EXPOSURE, AS WELL AS OXIDATION AND CORROSION OF THE METAL. (B) SCHEMATIC OF THP DEPOSITION ON AN INTERLAYER, COATING A METALLIC SUBSTRATE. DIFFUSION ZONES ARE EXPECTED AFTER HIGH TEMPERATURE EXPOSURE, AS WELL AS OXIDATION AND CORROSION OF THE METAL AND THE INTERLAYER CONSTITUENTS.	153
535	FIGURE 5.50 THP DEPOSITED ON TOP OF A SEALMET INTERLAYER ON A STAINLESS-STEEL BAR AND HEAT-TREATED BETWEEN 150 °C AND 1,100 °C. COLD END OF THE BAR ON THE LEFT-HAND SIDE, AND HOT END ON THE RIGHT-HAND SIDE.	154
540	FIGURE 5.51 (LEFT) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR THP DEPOSITED ON A SEALMET 1800, BOTH DEPOSITED ON A 400 X 20 X 3 MM STAINLESS-STEEL BAR AND HEAT TREATED UP TO 1,100 °C. (RIGHT)	

	MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR THP DEPOSITED ON SEALMET INTERLAYER (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC LIFETIME DECAY INCREASE (BOTTOM).	154
545	FIGURE 5.52 THP DEPOSITED ON A DURAZANE® 1800 INTERLAYER ON A STAINLESS-STEEL BAR AND HEAT-TREATED BETWEEN 200 °C AND 1,100 °C. COLD END OF THE BAR ON THE LEFT-HAND SIDE, AND HOT END ON THE RIGHT-HAND SIDE.....	155
	FIGURE 5.53 (LEFT) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR THP DEPOSITED ON A DURAZANE® 1800 INTERLAYER, BOTH DEPOSITED ON A 400 X 20 X 3 MM STAINLESS-STEEL BAR AND HEAT TREATED UP TO 1,100°C. (RIGHT) MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR THP DEPOSITED ON THE	
550	INTERLAYER (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC LIFETIME DECAY INCREASE (BOTTOM)....	156
	FIGURE 5.54 THP APPLIED ON STAINLESS-STEEL BARS, ON TOP OF A LUDOX® SM30 INTERLAYER (TOP) AND THP APPLIED DIRECTLY ON THE METALLIC SUBSTRATE, SHOWING A DARKER COLOUR (BOTTOM).....	157
	FIGURE 5.55 THP APPLIED ON A STAINLESS-STEEL BAR COATED WITH A LUDOX® SM30 INTERLAYER (TOP) AND THP APPLIED DIRECTLY ON A STAINLESS-STEEL BAR (BOTTOM), AFTER HEAT TREATMENT AT 150 °C FOR ONE HOUR.	
555		157
	FIGURE 5.56 (LEFT) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR THP DEPOSITED ON A LUDOX® SM30 INTERLAYER, BOTH DEPOSITED ON A 400 X 20 X 3 MM STAINLESS-STEEL BAR AND HEAT TREATED BETWEEN 150 °C AND 1,100 °C. (RIGHT) MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR THP DEPOSITED ON THE INTERLAYER (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC LIFETIME DECAY INCREASE (BOTTOM).	
560		158
	FIGURE 5.57 THP DETACHED FROM STAINLESS-STEEL BAR COATED WITH A LUDOXSM30 INTERLAYER, AFTER HEAT TREATMENT AT TEMPERATURES BETWEEN 150 °C AND 1,100 °C. THE WHITER AREAS AT THE COLD END OF THE BAR, ON THE LEFT HAND-SIDE, WHILE THE HIGHEST TEMPERATURES ARE ON THE RIGHT EXTREME, HOT END...	158
	FIGURE 5.58 (LEFT) LIFETIME DECAY PLOTTED OVER TEMPERATURE FOR THP DEPOSITED ON INTERLAYERS OF SEALMET, DURAZANE® 1800 AND LUDOX® SM30 DEPOSITED ON STAINLESS-STEEL BARS AND HEAT TREATED UP TO 1,100 °C. (RIGHT) MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE FOR THP DEPOSITED ON INTERLAYERS (TOP) AND SENSITIVITY ANALYSIS OF THE MONOTONIC LIFETIME DECAY INCREASE (BOTTOM)..	159
565	FIGURE 6.1 LIFETIME DECAY PLOTTED OVER TEMPERATURE OF EXPOSURE OF LUDOX® SM30 BASED THP, DEPOSITED ON A STAINLESS-STEEL BAR AND HEAT TREATED UP TO 1,100 °C. THE LIFETIME DECAY WAS REMEASURED AT THE SAME LOCATIONS AFTER SIX MONTHS OF STORAGE TO EVALUATE THE EFFECT OF EFFLORESCENCE.	162
	FIGURE 6.2 DIFFRACTION PATTERNS OF LUDOX ® SM30 SAMPLES AFTER HEAT TREATMENTS BETWEEN 800 °C AND 1,200 °C. MATCHING SILICA PHASES ARE IDENTIFIED AND INDICATED WITH MARKERS.....	163
	FIGURE 6.3 CALCULATED RELATIVE CONTENT OF SILICA PHASES, CRISTOBALITE AND TRIDYMITE BIPHASIC MIXTURE, OBTAINED FROM DIFFRACTION PATTERNS OF LUDOX®SM30 SAMPLES HEAT TREATED AT TEMPERATURES BETWEEN 800 °C AND 1,200 °C.	163
575	FIGURE 6.4 TERNARY PLOT OF THP PIGMENT ($Y_2SO_5: Eu^{3+}$), LUDOX® SM30 BINDER AND POTASSIUM SILICATE BINDER.	164
	FIGURE 6.5 LIFETIME DECAY OF PAINT PELLETS, HEAT-TREATED BETWEEN 800 °C AND 1,100 °C, COMBINING LUDOX® SM30 AND POTASSIUM SILICATE BINDERS WITH PIGMENT CALCINED AT 600 °C (P600). LINES JOINING POINTS ADDED FOR VISUALIZATION.	165
580	FIGURE 6.6 LUMINESCENT SPECTRA OF PAINT SAMPLES, HEAT-TREATED AT 1,100 °C, COMBINING LUDOX® SM30 AND POTASSIUM SILICATE BINDERS WITH PIGMENT CALCINED AT 600 °C (P600).	167

585	FIGURE 6.7 (LEFT) RATIO BETWEEN THE $^5D_0 \rightarrow ^7F_2$ AND THE $^5D_0 \rightarrow ^7F_1$ TRANSITIONS OF Eu^{3+} , STUDIED IN THE LUMINESCENT SPECTRA OF PAINT PELLETS, HEAT-TREATED AT 1,100 °C, COMBINING LUDOX® SM30 AND POTASSIUM SILICATE BINDERS (INDICATED AS “KSiO” IN THE FIGURE) WITH PIGMENT CALCINED AT 600 °C (P600). (RIGHT) RATIO BETWEEN THE $^5D_0 \rightarrow ^7F_2$ AND THE $^5D_0 \rightarrow ^7F_1$ TRANSITIONS OF Eu^{3+} , EMBEDDED IN OXIDE GLASSES STUDIED BY OOMEN AND VAN DONGEN [368].	168
590	FIGURE 6.8 LUDOX® SM30 BASED PAINTS APPLIED ON STAINLESS-STEEL BARS AND TILES. FROM TOP TO BOTTOM, RUN 3 (CONSISTING OF LUDOX® SM30 (47.5 % WT.), POTASSIUM SILICATE (47.5 % WT.) AND P600 PIGMENT (5 % WT.)), RUN 2 (CONSISTING OF LUDOX® SM30 (72 % WT.), POTASSIUM SILICATE (23 % WT.) AND P600 PIGMENT (5 % WT.)), AND RUN 1 (LUDOX® SM30 (95%W) AND P600 PIGMENT (5 % WT.)).	169
595	FIGURE 6.9 (A) LIFETIME DECAY OBTAINED AFTER HEAT-TREATMENT OF LUDOX® SM30 BASED PAINTS APPLIED ON STAINLESS-STEEL BARS, RUNS 1, 2 AND 3. MAXIMUM TEMPERATURE OF MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE INDICATED WITH VERTICAL LINES AT 850 °C, 900 °C AND 950 °C. (B) PHOTOGRAPH OF 400 X 20 X 3 MM STAINLESS-STEEL BARS PAINTED WITH LUDOX® SM30 BASED PAINTS, AFTER HEAT EXPOSURE FROM 200 °C, COLD SIDE (RIGHT) TO 1,100 °C, HOT SIDE (LEFT). POTASSIUM SILICATE INDICATED AS “KSiO” IN THE LEGEND.	170
600	FIGURE 6.10 PHOTOGRAPH OF 20 X 10 X 3 STAINLESS-STEEL TILES PAINTED WITH LUDOX® SM30 BASED PAINTS, AFTER HEAT EXPOSURE AT 600 °C (A), 700 °C (B), 800 °C (C) AND 900 °C (D). RUNS 1 TO 3 FROM LEFT TO RIGHT.....	171
605	FIGURE 6.11 COMPARISON OF LIFETIME DECAY READINGS, OVER MAXIMUM TEMPERATURE EXPOSURE FOR STAINLESS-STEEL BAR AND SAMPLES PAINTED WITH, LUDOX® SM30 BASED THERMAL HISTORY PAINTS, FOR RUN 1 (A), RUN 2 (B) AND RUN 3 (C). POTASSIUM SILICATE INDICATED AS “KSiO” IN THE LEGEND OF THE FIGURE. SHADED AREAS INDICATE THE END OF THE MONOTONIC INCREASE OF LIFETIME DECAY WITH INCREASING TEMPERATURE.	172
610	FIGURE 6.12 TEMPERATURE DIFFERENCES WITH RESPECT THERMOCOUPLE READINGS AT 600 °C, 700 °C AND 800 °C OF LUDOX® SM30 BASED THERMAL HISTORY PAINTS, RUNS 1, 2 AND 3.....	173
615	FIGURE 6.13 LIFETIME DECAY READINGS ON POTASSIUM-SILICATE THP REFERENCE PAINTS (P400 AND P600), AND LUDOX® SM30 BASED PAINTS (RUNS 1, 2 AND 3) AFTER DEPOSITION AND HEAT-TREATMENT UP TO 1,100 °C ON STAINLESS-STEEL TEST BARS. MAXIMUM TEMPERATURE OF MONOTONIC INCREASE OF LIFETIME DECAY OVER TEMPERATURE INDICATED WITH VERTICAL LINES AT 850 °C, 900 °C AND 950 °C.	174
620	FIGURE 9.1 THERMAL CONDUCTIVITY OVER INCREASING TEMPERATURE ON THP DEPOSITED ON STAINLESS-STEEL 316L AND NIMONIC 75, NICKEL ALLOY.	203
	FIGURE 9.2 FTIR SPECTRA FOR $Y_2SiO_5: Eu^{3+}$ PIGMENTS PRODUCED BY ADDING (B) 10 G AND (C) 25 G OF CITRIC ACID, COMPARED TO (A) THE ORIGINAL PIGMENT PRODUCTION WITHOUT CITRIC ACID, FOR TEMPERATURES BETWEEN 700 °C AND 1,300 °C.	204
	FIGURE 9.3 XRD PATTERNS OF $Y_2SiO_5: Eu^{3+}$ PIGMENTS PRODUCED BY ADDING (B) 10 G AND (C) 25 G OF CITRIC ACID, COMPARED TO (A) THE ORIGINAL PIGMENT PRODUCTION WITHOUT CITRIC ACID ADDITION. ALL SAMPLES WERE HEAT TREATED AT 900 °C. ICDD REFERENCE PATTERN OF YTTRIA (Y_2O_3) 00-043-1036 INDICATED WITH BLUE LINES.....	205
	FIGURE 9.4 LUMINESCENT EMISSION SPECTRA OF PIGMENT SAMPLES MODIFIED WITH CITRIC ACID, COMPARED TO THE EMISSION OF EUROPIUM NITRATE. SPECTRA NORMALISED TO THE MAXIMUM INTENSITY IN THE WHOLE RANGE, FROM 578 NM TO 710 NM.	206
	FIGURE 9.5 LUMINESCENT SPECTRA OF PAINT PELLETS, HEAT-TREATED BETWEEN 800 °C AND 1,100 °C, COMBINING LUDOX ® SM30 AND POTASSIUM SILICATE (KSiO) BINDERS WITH PIGMENT:	208

625	FIGURE 9.6 POSTER NAMED “VALIDATION OF A THERMAL HISTORY PAINT ON A TURBINE BLADE HOT GAS TEST RIG FACILITY” PRESENTED AT THE VIRTUAL ASME TURBO-EXPO 2020.....	209
	FIGURE 9.7 MATERIAL CERTIFICATE OF THE STAINLESS-STEEL 316L BARS ISSUED FROM SOG LTD. DURING 2018. .	210
	FIGURE 9.8 MATERIAL CERTIFICATE OF THE STAINLESS-STEEL 316L BARS ISSUED FROM SOG LTD. DURING 2019. .	211

LIST OF TABLES

630	TABLE 1.1 SUMMARY OF ON-LINE AND OFF-LINE TEMPERATURE MEASUREMENT TECHNIQUES	32
	TABLE 3.1 THERMAL HISTORY SENSORS, CLASSIFIED BY HOST AND LUMINESCENT ION AS REPORTED IN LITERATURE.	45
	TABLE 3.2 STABLE VALENCE STATES OF COMMON RARE EARTH IONS AND TRANSITION METALS	47
	TABLE 3.3 PHOSPHORS UNDER THE AMORPHOUS TO CRYSTALLINE MECHANISM FOR THERMAL HISTORY SENSING, CLASSIFIED BY HOST, DOPANT ION AND TEMPERATURE RANGE EXPLORED IN THE LITERATURE.	51
635	TABLE 3.4 $X_1\text{-Y}_2\text{SiO}_5$ PHOSPHORS DOPED WITH DIFFERENT LUMINESCENT IONS UNDER THE AMORPHOUS TO CRYSTALLINE MECHANISM, CLASSIFIED BY DOPANT ION AND MAXIMUM TEMPERATURE EXPLORED.....	56
	TABLE 3.5 TRANSITIONS OBSERVED IN THE EMISSION SPECTRA OF $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$, IDENTIFICATION ACCORDING TO [122].	58
640	TABLE 3.6 REVIEW OF BINDERS EVALUATED FOR USE IN THERMAL HISTORY PAINTS.	64
	TABLE 4.1 SUMMARY OF CONSTITUENTS, QUANTITIES, AND TIME OF MIXING FOR THE SYNTHESIS OF 50G OF $(\text{Eu}_{0.16}\text{Y}_{0.84})_2\text{SiO}_5$	67
	TABLE 5.1 ANALYSIS OF LUMINESCENT SPECTRA OF PIGMENT AND THP SAMPLES, HEAT TREATED AT 1,100 °C FOR 30 MINUTES.....	88
645	TABLE 5.2 COMPOSITION OF STAINLESS STEEL 316L AND INCONEL 738, NICKEL ALLOY.....	98
	TABLE 5.3 CROSS SECTION OF THP APPLIED ON STEEL AND NICKEL METALLIC SUBSTRATES OBSERVED VIA SCANNING ELECTRON MICROSCOPY (SEM) AFTER HEAT TREATMENT AT 800 °C, 900 °C AND 1,000 °C FOR TWO METAL ALLOYS: INCONEL 738 AND STAINLESS STEEL 316L. SCALE AND SETTINGS USED FOR IMAGE ACQUISITION ARE INCLUDED IN THE LEGEND BELOW EACH IMAGE: WORKING DISTANCE (WD), BEAM VOLTAGE (EHT), TYPE OF SIGNAL/DETECTOR (IN ALL CASES, SECONDARY ELECTRONS, SE2) AND MAGNIFICATION (MAG).	101
650	TABLE 5.4 EDX LINES OVER SEM MICROGRAPHS OF THP DEPOSITED ON INCONEL 738 SAMPLES, AFTER HEAT TREATMENT AT 800 °C, 900 °C AND 1,000 °C. MAIN ELEMENTAL CONSTITUENTS OF THP (SI AND K) AND OF THE INCONEL METALLIC SUBSTRATE (NI AND CR) ARE PLOTTED OVER THE DISTANCE ALONG THE EDX LINE..	102
	TABLE 5.5 EDX LINES OVER SEM MICROGRAPHS OF THP DEPOSITED ON STAINLESS STEEL 316L SAMPLES, AFTER HEAT TREATMENT AT 800 °C, 900 °C AND 1,000 °C. MAIN ELEMENTAL CONSTITUENTS OF THP (SI AND K) AND OF THE STAINLESS-STEEL SUBSTRATE (Fe, CR AND NI) ARE PLOTTED OVER THE DISTANCE ALONG THE EDX LINE.	103
655	TABLE 5.6 SUMMARY OF MAIN OBSERVATIONS ON THP AFTER HEAT TREATMENT AND SUGGESTED SOLUTIONS TO REACH RELIABLE TEMPERATURE MEASUREMENTS AT HIGH TEMPERATURES.....	108
660	TABLE 5.7 SOLID CONTENT, DENSITY, AND pH MEASUREMENTS ON CURRENT THP REFERENCE, USING POTASSIUM SILICATE BINDER.	112
	TABLE 5.8 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR THP REFERENCE.....	115
	TABLE 5.9 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR BINDER MODIFICATION BY POTASSIUM ADDITION.	117
665	TABLE 5.10 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR BINDER MODIFICATION BY LITHIUM ADDITION.	120
	TABLE 5.11 TESTED BINDER CANDIDATES, COMMERCIAL PROVIDERS, AND SUMMARY OF PROPERTIES.	121
	TABLE 5.12 SOLID CONTENT, DENSITY, AND pH MEASUREMENTS ON SEALMET® SILICATE BINDER.....	122
	TABLE 5.13 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR SEALMET® BINDER.....	124

670	TABLE 5.14 SOLID CONTENT, DENSITY, AND PH MEASUREMENTS ON FIXWOOL® COATING 130 ALUMINA-SILICATE BINDER.	125
	TABLE 5.15 SOLID CONTENT, DENSITY, AND PH MEASUREMENTS ON LITHIUM SILICATE BINDERS.	129
	TABLE 5.16 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR LITHIUM SILICATE BINDERS.	130
	TABLE 5.17 SOLID CONTENT, DENSITY, AND PH MEASUREMENTS ON FFB® 1210 MG-PHOSPHATE BINDER.	131
675	TABLE 5.18 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR METALLIC PHOSPHATE BINDERS.	133
	TABLE 5.19 SOLID CONTENT, DENSITY, PH, AND PARTICLE SIZE OF LUDOX® COLLOIDAL SILICA SOLUTIONS.	135
	TABLE 5.20 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR LUDOX® COLLOIDAL-SILICA SOLUTIONS.	137
	TABLE 5.21 SUMMARY OF LUMINESCENT LIFETIME DECAY, TEMPERATURE, SENSITIVITY, AND ATTACHMENT TO METALLIC SUBSTRATES OF THP REFERENCE, BINDER MODIFICATIONS AND BINDER SUBSTITUTIONS.	138
680	TABLE 5.22 SUMMARY OF CITRIC ACID ADDED TO SOL-GEL PIGMENT PRODUCTION	142
	TABLE 5.23 EDX ANALYSIS OF LUMINESCENT HISTORY PIGMENT PRODUCED BY ADDITION OF CITRIC ACID.	143
	TABLE 5.24 PEAK IDENTIFICATION OF XRD SPECTRA OF PIGMENTS PRODUCED BY ADDITION OF CITRIC ACID.	146
	TABLE 5.25 SUMMARY OF XRD PHASES IDENTIFIED ON PIGMENT MODIFIED WITH CITRIC ACID.	147
685	TABLE 5.26 SUMMARY OF ATTACHMENT CAPABILITIES OF PRODUCTS TESTED AS HIGH TEMPERATURE BINDERS.	153
	TABLE 5.27 SUMMARY OF LIFETIME DECAY EVOLUTION OVER TEMPERATURE FOR THP DEPOSITED ON INTERLAYERS.	159
	TABLE 5.28 SUMMARY OF ATTACHMENT AND SENSITIVITY IMPROVEMENT FOR THP APPLIED ON TOP OF INTERLAYERS.	160
690	TABLE 6.1 SUMMARY OF OBSERVED THP BEHAVIOUR AT HIGH TEMPERATURES, DEVELOPMENT ROUTES CONSIDERED AND SELECTED SOLUTIONS FOR THE DESIGN OF A NEW VERSION OF THERMAL HISTORY PAINT	161
	TABLE 6.2 DIFFRACTION PATTERNS OF PAINT PELLETS, HEAT-TREATED BETWEEN 800 °C AND 1,100 °C, COMBINING LUDOX ® SM30 AND POTASSIUM SILICATE BINDERS WITH PIGMENT CALCINED AT 600 °C (P600).	166
	TABLE 9.1 PERMISSIONS FOR THIRD PARTY COPYRIGHT WORKS	212

695

1 Introduction

Climate change has raised concerns worldwide over the last decades. Reduction of CO₂ and greenhouse gas emissions are among the main objectives of current regulations in the automotive and power generation sectors, where new propulsion systems, complying with these new regulations, will undergo major transformations. The global trend in the energy sector is moving towards cleaner and more efficient turbomachines, combining renewable and non-renewable sources for power generation. In this context, gas turbines can provide a transitory alternative to renewables, as a flexible and cost competitive conversion technology [1]. Gas turbines are experiencing constant development and the increase of efficiency in these turbo-engines can have major implications in the global energy supply. In fact, it is estimated that an increase of 1 % in the efficiency of combustion engines worldwide, will be equivalent to saving 7 billion US-dollars in fuel use or, in other words, avoiding the CO₂ emissions of 2 million cars [2].

The gas turbine market, prior to the COVID-19 pandemic, predicted an increasing demand of turbo-engines in the aviation and electricity generation sectors, since gas turbines offer high efficiencies, and flexibility while in operation. The use of bio-fuels and electric/hybrid propulsion systems have been progressively incorporated as well, showcasing reduced emission solutions [2,3]. These offer distinct advantages in electricity generation, and their use will progressively substitute fossil energy sources. The introduction of renewable sources, such as wind and solar, will lead to a progressively decarbonized energy supply as well. However, gas turbines will remain a critical conversion technology during the transition to renewables [1]. In the aerospace sector, the fuel use is a key consideration not only in terms of emissions, but also in terms of cost to the end consumer. In commercial aviation, 50 % of the cost of a flight ticket goes to the cost of the fuel [4]. At the same time, the number of aircraft has been growing steadily worldwide in the last decades, and the global forecast is of strong growth over the next 20 years, according to the pre-pandemic market projections by the main commercial aerospace manufacturers [5,6]. This provides a favourable environment for the incorporation of new designs and new materials in energy, aerospace and other sectors exploiting turbomachinery and combustion engines.

1.1 Need for temperature measurements

Temperature measurements are vital not only in the validation of new designs and new materials, but also for the maintenance of gas turbines and other engines. The need of these temperature measurements is critical in the high temperature combustion environments of automotive, aerospace and power generation sectors. In terms of efficiency, it has been estimated than an increase of 100 °F in the inlet temperature of gas turbines can provide an increase in efficiency between 2 and 4 % [7]. However, the limiting factor for gas turbine manufacturers, is measuring this inlet temperature. While measuring the exhaust gas temperature with thermocouples is relatively straightforward, the inlet temperatures are difficult to measure using intrusive methods. Any loose broken piece of equipment upstream, such as a broken thermocouple, can cause severe damage passing through the turbine blades. In addition, the first stage turbine blades are exposed to the most severe conditions of temperature, corrosion, and stress, and the material design remains

quite challenging. The trend in the industry is moving towards the progressive increase of the inlet temperature, while maintaining an acceptable temperature in the metallic components [7]. These high operating temperatures provide a challenge for the lifing and durability of turbomachinery components in combustion environments. In the extreme conditions supported by blade air-foils, creep will halve the life of turbine blades every 10 - 15 °C increase in the component temperature [8,9].

Therefore, temperature sensing tools are essential for the industry, and their market value in 2020 was USD 6.3 billion. This has been projected to grow to USD 8.8 billion by 2027 [10]. The demand of surface temperature measurements, from the major gas turbines OEMs, has also grown over the last decades, especially for complex-shaped turbomachinery components, often in movement. The obtention of reliable surface temperature measurements is critical for both operation and maintenance stops, where the maximum temperature seen by the component is difficult to be determined. As stated by the Propulsion Instrumentation Working Group (PIWG), temperature measurements over 80 % of the blade air-foil surface of all blades in a gas turbine are necessary for appropriate life monitoring [11].

1.1.1 Gas turbines and turbomachinery

The applications of gas turbines range from power generation to vehicle propulsion. The design criteria may be different, but turbo-engines displaying safe and high efficiencies are always preferred. The social awareness on climate change is affecting the viability of fossil fuels for power generation. While coal and fuel fired plants will be progressively abandoned in the coming decades, gas fired plants are in the energy supply roadmap in the United Kingdom [12] and in the European Union [13,14], and new plants are planned to be installed in the next decades. Simple cycle gas turbine efficiencies have increased from 15 % in the first half of the 20th century, to more than 40 % nowadays [7]. This increasing trend in efficiency is shown in **Figure 1.1** over the last decades, next to the increasing firing temperatures in new gas turbine designs.

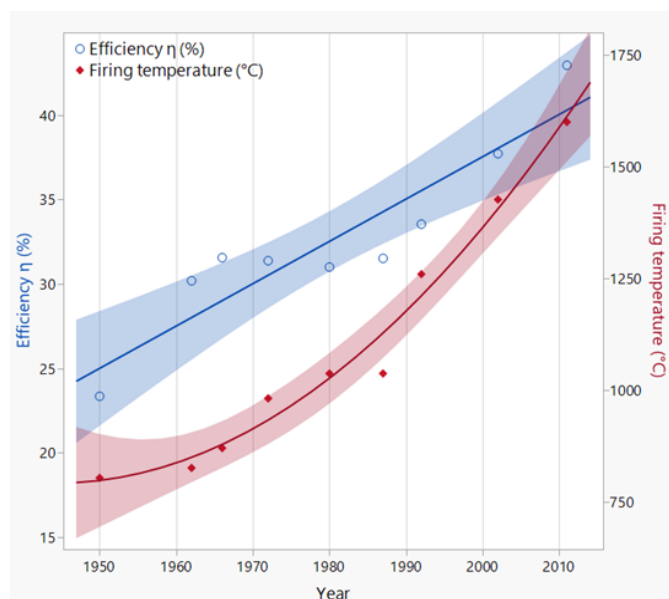


Figure 1.1 Firing temperatures and efficiencies in turbomachinery, over the last decades. Plot extracted with permission from [15]. Sources consulted [16–25]. Confidence of the fit indicated as shaded areas around the lines and data points.

The working principle of a gas turbine consists of the generation of power through fuel burning in compressed air conditions. A simple gas turbine is comprised of three main sections: a compressor, a combustor chamber, and a turbine. After combustion, the expanding air flow is used to drive a turbine and generate work, following a Brayton cycle. The first stage of a gas turbine, after combustion, is the most critical one, determining the inlet temperature and therefore the efficiency of the turbine [7]. Many design improvements have contributed to the increase of the inlet temperature and therefore the increasing efficiency in gas turbines for the last decades, from protective coatings, such as Thermal Barrier Coatings (TBC's) [26–29], to sophisticated internal cooling systems [30–32]. This increased turbine efficiency can be increased by two means, gas compression and temperature increase. The approximation of thermal efficiency of a turbine is expressed in **Equation 1.1**.

$$\eta_t = \frac{1 - \frac{T_{Exh}}{TIT}}{1 - \left(\frac{1}{R_c}\right)^\sigma} \quad (1.1)$$

Where η_t is the turbine efficiency, T_{Exh} is the exhaust temperature (in °R), TIT is the Turbine Inlet Temperature (in °R), R_c is the inverse of R_t , which is the ratio between the turbine inlet pressure and the turbine exhaust pressure. In other words, R_c is the ratio between the turbine exhaust pressure and the turbine inlet pressure. σ is a parameter corresponding to $\sigma = (k-1)/k$, where k is the ratio of specific heats, c_p/c_v . The use of R_c instead of R_t , allows the approximation of the turbine efficiency using intermediate turbine temperatures, instead of turbine inlet temperatures, which are difficult to measure on a long term basis [33].

The extreme conditions in the gas turbine combustion environment make temperature measurements very challenging, but accurate surface temperature measurements on rotating components are vital in the design, material selection and life prediction of turbine blades. Operating temperatures often surpass the melting temperature of frequently used nickel based superalloys [34], so that surface temperature measurements, usually feeding numerical simulations, could validate new designs in turbomachinery [35]. In terms of durability verification, surface temperatures are necessary to prevent creep and other failure mechanisms [36,37].

1.1.2 Automotive sector and other industrial applications

The need to validate new designs can be extended to the automotive industry. New designs in automotive components, exposed to the harsh conditions of the combustion, can be assessed with surface temperature measurements. This is the case of pistons and new cooling systems, specifically on turbocharger components [38,39]. The automotive industry is also driven by the new emission regulations in Europe (*Euro6d*) and China (*China6b*), which have the aim to reduce specifically CO₂ emissions. Other common polluting practices such as fuel enrichment or over-fuelling are widely expected to be banned, according to new *Real Driving Emissions legislation*, as these are highly contaminant methods to lower combustion temperatures [40]. Validation of those new designs and the need for a rapid market entry will require new temperature measurement technologies to provide accurate data across an entire component.

However, elimination of over-fuelling will result in higher thermal loads for components such as exhaust valves, turbochargers, and manifolds. In order to meet durability criteria for these components, several options are considered: firstly, more advanced, and costly materials such as Ni-based super alloys regularly used in the gas turbine industry for regimes up to 1,050 °C, secondly, the reduction of exhaust temperatures to 980 °C by additional cooling technologies, and, thirdly, the introduction of internally cooled components.

The latter concept is common practice in the gas turbine industry as well, as seen before.

1.2 Temperature measurement techniques

In this section, a brief review on the temperature measurement techniques employed in combustion environments are outlined. These methods, can be found in the literature classified as contact, optical, intrusive and non-intrusive [41]. Furthermore, for turbomachinery components, these can be divided into on-line and off-line techniques. On-line methods obtain temperature information during operation, while off-line techniques record the thermal history, mainly maximum temperatures, which can be obtained after operation. Off-line readings are exploited in maintenance monitoring, durability verification, and in dedicated tests to feed and verify numerical simulations [35,42].

1.2.1 On-line temperature measurements

1.2.1.1 Thermocouple thermometry

Thermocouples are considered the benchmark in the industrial temperature sensing field. Among their main advantages are their simplicity, robustness, and low cost. They cover a wide range of temperatures, and their working principle is based on the Seebeck effect. This describes the voltage generated between two conductive metals, such as nickel, chromium, or aluminium, both exposed to the same reference temperature. As shown in **Figure 1.2** below, T_1 represents the temperature to be measured, where the ends of both wires are joined in a junction. The reference temperature is held at a different point in the wire, and the electromagnetic force generated between the wires will be proportional to this temperature difference. Therefore, thermocouples are self-powered and accurate, depending on the type considered (K, N or S, for example) and the manufacturer [43–47]. Properly designed thermocouples can demonstrate accuracies of ± 1 °C, measuring temperatures from -270°C to 2,300 °C, such as chromel/alumel systems [7].

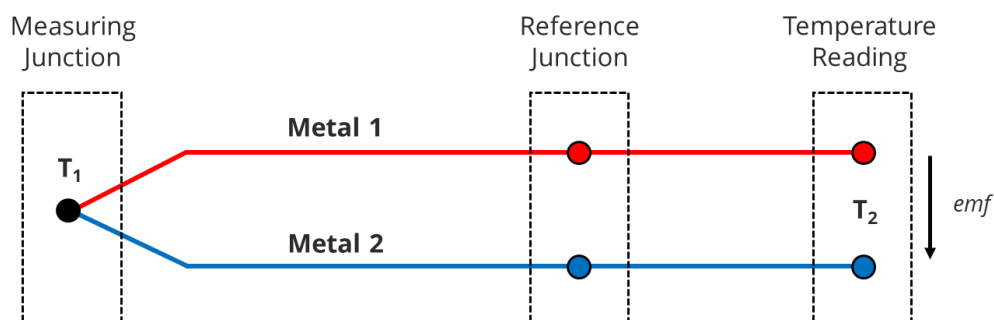


Figure 1.2 Schematic diagram of a bi-metal thermocouple, consisting of two dissimilar metal wires joined in one extreme, where the temperature is measured, and connected through a reference junction to a reader.

Thermocouples are considered an intrusive technique, since they have to be either in contact or embedded in the medium whose temperature is under measurement. In gas turbines, thin film thermocouples can be employed for temperature measurements within the super-alloy metal of the blades [48–50]. These can be used at temperatures higher than 1,000 °C. However, one of the main limitations of thermocouples is the voltage drift at high temperatures [51–53]. Numerical methods are used to study this deviation, which is often considered a systematic error [54,55]. Additionally, temperature measurements near the surface of the metal are quite challenging, since the hot gas path is normally protected by Thermal Barrier Coatings (TBC's), which are quite fragile. Placing thermocouples within these protective layers is quite demanding and costly. Even if standard thermocouples are installed on the surface of a component in the hot gas path of a turbine, the measuring tip can protrude from the TBC layer, disturbing the gas flow. The recorded temperature would suffer an increased associated error as well.

While widely used in industry, alternative techniques to thermocouples are desired in rotating components, such as turbine blades, where Non-Destructive Testing (NDT) methods are highly valued as well [56–58]. Thermocouples provide point measurements, so that in order to monitor a large area, a large number of sensors are required to be installed. Connecting more than a single thermocouple on a relatively small area remains notably challenging, particularly on rotating components. Remote, off-line, and non-contact temperature measuring methods are considered not only in these cases, but also in nuclear reactors, where even thermocouples face increasing challenges such as transmutation by neutron irradiation and subsequent drift and de-calibration, due to material degradation [59–61].

1.2.1.2 Pyrometry

Pyrometry is also known as infrared thermometry. This non-contact temperature measurement technique relies on the observation of thermal radiation released from the surfaces of hot components. The infrared radiation is captured by a detector, not affecting the environment where the temperature measurement is performed. Nevertheless, the detection requires optical access, so that the power of the radiation emission could be assigned to the temperature of the hot body. This is described in **Equation 1.2**, where the spectral radiance is dependent from wavelength and temperature according to Planck's law:

$$E(\lambda, T) = \varepsilon(\lambda, T) \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \quad (1.2)$$

Where E is the spectral radiance (in $\text{W} \cdot \text{m}^{-3}$), ε the spectral emissivity, h the Planck constant ($\text{J} \cdot \text{s}$), c the speed of light ($\text{m} \cdot \text{s}^{-1}$), k_B the Boltzmann constant ($\text{J} \cdot \text{K}^{-1}$), λ the wavelength (m) and T the absolute temperature (K).

Pyrometers have been used in gas turbines for decades, both in engine development and health monitoring [62]. The main limitation of this technique is the emissivity dependence from hot surfaces, and the emission being in an adequate wavelength range of interest. The temperature is determined by comparing signals, from a hot source and a “cold” (or background) surrounding object. The uncertainty of this method is

relatively low [63,64], however it is challenging in a combustion environment where temperatures are overall uniformly high. Radiation can be reflected from other elements in the turbo-engine, such as the nozzle guide vanes. Additionally, the radiation can be absorbed by combustion gases, and the presence of soot, particles and/or flames can distort the optical signal arriving to the detector.

Measurement of complex shapes remains particularly difficult, especially on ceramic-based coatings, which are normally transparent at high temperatures. Emissivity of coatings may change during operation due to the thermal transition undergone by the surfaces, in addition to contamination within the coating layers, which could result in new radiation sources at high temperatures, and therefore a source of significant errors [65,66]. Among the mitigation measures for these challenges, two-colour pyrometers could be used to partially overcome the effect of the unknown emissivity, introducing an intensity ratio [67,68]. These assume constant emissivity at all wavelengths, which is not the behaviour of most materials at high temperatures. Other alternatives are single-wavelength pyrometers [69] and multi-colour pyrometers, using three or more signals at different wavelengths to calculate both temperature and emissivity by means of numerical fitting algorithms [70].

1.2.1.3 Thermographic phosphors

Phosphor thermometry is based on the luminescent properties of certain materials, such as rare earths embedded in a ceramic host. These phosphors act as temperature sensors, which can be excited with external light, emitting light as a response. This emitted light is slightly different to the excitation one, both in intensity and wavelength range, but once detected, the emission can be corresponded to the temperature surrounding the phosphor. Several phosphorescent properties are temperature dependent, for instance, emission intensity and decay time, allowing thermographic phosphors to provide real time temperature information in an operating system. The temperature range recorded through this technique goes from cryogenic conditions [71,72] to a maximum around 1,700 °C [73], exploiting the luminescent changes in thermally stable phosphors. A review on these can be found in references [74–77].

This technique has been traditionally exploited by doping Thermal Barrier Coating materials, such as Yttrium Aluminium Garnet (YAG) or Yttria Stabilized Zirconia (YSZ) [78]. Rare earth optically active ions are introduced within the coating layers, acting as temperature sensors. These doped layers can reveal temperature profiles through the depth of the TBC [79], as well as detecting erosion and degradation of the coating [80,81]. Ceramic phosphors are strong candidates to be used in turbomachinery, given their high melting point [73,82], and the flexibility in deposition methods; from binding the ceramic in a paint [83] to Electron Beam Physical Vapour Deposition (EB-PVD) [84]. However, the major disadvantage of this technique is the need for optical access to the material during operation. If the thermographic phosphor is deposited on an engine component, this will involve an aperture through the casing of the turbomachine, which is not often feasible or desirable.

1.2.1.4 Resistive thermal detectors

Resistive Thermal Detectors (RTD) are based on the temperature dependence of the electrical resistivity of materials. These consist of wired metal, generally platinum, under a constant electric current. The change of the internal resistance, due to temperature variation, can be inferred by a voltage drop, showing higher accuracies than thermocouples. However, RTD's are intrusive and their maximum detection capabilities are limited to 1,000 °C. Platinum is an expensive material, and their response time is slower than thermocouples. This added to heat dissipation challenges in hot environments, make RTD's not really common in turbomachinery temperature measurements [7].

1.2.2 Off-line temperature measurements

1.2.2.1 Thermal paints / Thermo-chromic paints

Thermo-chromic paints or *thermal paints* are temperature sensor layers formed by a variety of reactive metallic compounds, comprised mainly of cobalt, chromium, iron, lead and magnesium, which are mixed in a liquid binder or solvent to form a paint [85]. When exposed to increasing temperatures these compounds change colour permanently depending on the maximum temperature achieved. Heat initiates specific reactions within the paint layer, which results in a colour change, for instance, the oxidation of iron. These permanent changes can be observed after heat exposure [86,87], as the heat activates chemical reactions between the metal compounds and the water molecules or carbon dioxide in the environment [88]. For this reason, these paints are also known as colour-changing-paints.

Thermal paints are sensitive to environment exposure, in particular Red-Ox reactions, which changes the colour of the paint after heat exposure to particular temperatures. The kinetics of the chemical reactions are affected by the presence of oxygen and other reducing elements in the environment, which makes the calibration quite challenging. Painted bowtie or butterfly samples are normally used to generate temperature gradients passing electric current through the painted piece. These and other type of substrates, such as the rectangular ones shown in **Figure 1.3** below, can be heat treated at different target temperatures to obtain a complete calibration colour chart. However, the extraction of reliable temperature information from thermal paints remains quite challenging. Temperature reading involves complete calibrated colour charts to be used by trained and experienced operators. Isothermal lines are often drawn on the component painted surface, in a labour intensive and time-consuming process. The accuracy of the temperature measurement depends on the type of paint used and the database available. Surface colour measurements normally consist of three numbers, mimicking the trichromatic human vision, where one of these values usually estimates the lightness of the surface. This is particularly difficult to determine in glossy surfaces, such as ceramic paints exposed to high temperatures. In the best case scenario, a resolution of 10 °C can be obtained, while in other cases only temperature ranges of 100 °C will be available [89].

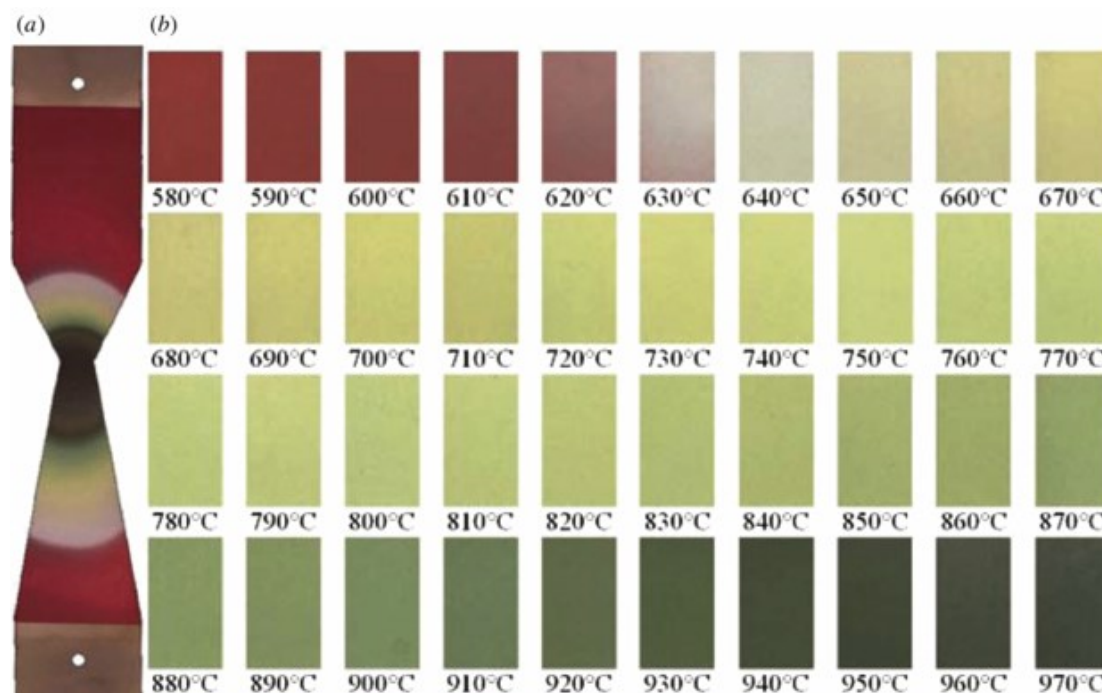


Figure 1.3 Thermal Paint test applied on: (a) butterfly test piece heated by Joule effect and (b) set of samples heated in 10 °C steps, both painted with Rolls-Royce TP96 thermal paint. Reproduced with permission from reference [89].

The exposure time to the target temperature must be carefully controlled, normally under dedicated tests since the durability of thermal paints is quite limited above 5-10 minutes. Longer exposures, even at relatively low temperatures, may lead to undesired colour changes that can limit the dynamic range of the paint. These colour changes are often subtle, so that the interpretation can only be based on large temperature changes, resulting in poor temperature measurement resolution. Efforts have been made to automate the interpretation, using colour models such as Red-Green-Blue (RGB), but external parameters such as ambient lightning can complicate the interpretation of colour changes in complex-shape components [87].

Additionally, thermal paints contain hazardous elements, such as chromium, lead, nickel and cobalt, that in contact with the human body may lead to heavy metals intoxication [86]. Current European Union legislation on chemical substances, Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH) [90], restricts the use of such chemicals. This legislation has been set to continue in the United Kingdom, under the instruction of the Health and Safety Executive (HSE) from the 1st of January 2021 [91]. Therefore, companies employing thermal paints are required to seek alternatives [92].

1.2.2.2 Metallurgical temperature sensors and glass-ceramic sensors

Thermally induced structural changes in a series of metal alloys can be exploited for temperature sensing purposes. For instance, steel alloys display precipitation of certain phases after annealing, and these alterations can be detected via magnetic methods for temperatures up to 900 °C. Monitoring the growth of the Thermally Grown Oxide (TGO) layers is also a widely used method in industry, especially for complex shape metallic components, such as gears. The thickness of this oxide layer is used for temperature

determination, after metal samples are sectioned and observed under a microscope. The exposure temperature can be inferred by mathematical models after assessing the degradation of the metal surface. Among the drawbacks of this method are the destructive nature of this technique and the fact that temperatures are only provided for small sections of the sample, basically point measurements.

Other off-line temperature sensors are:

- **Tem-plugs**, which are composed of steel alloy and shaped as small, screwed plugs. After exposure to increasing temperatures, the steel hardness changes irreversibly, and it can be compared to previous calibrated measurements. Typical exposures times are over 1 hour, with longer times recommended for a full change in hardness. This technique is destructive both for the surface of the component containing the screw hole and for the plug itself, and the accuracy is at best 3%, being the temperature range of use between 60 °C and 850 °C [93].
- **Ferro-plugs** are made of duplex stainless steel, which undergoes permanent phase transformations at high temperatures. The steel changes from an Iron phase to a Chromium rich phase, displaying lower ferromagnetic behaviour. This can be determined with a magnetic susceptometer or a ferritoscope. The sensitive temperature range is in a narrow interval between 400 °C and 600 °C and the accuracies around 3 % for long exposure times, of several thousand hours [94]. Sigma-plugs follow a similar concept, detecting changes in magnetism of intermetallic phases between 600 °C and 900 °C. In the case of stainless steel, the Curie Temperature is measured after heat exposure, to reveal the thermal history. This method requires liquid nitrogen, and it is not normally done in situ.
- **Glass-ceramic arrays** are a type of sensor based on phase transformations as well. Glass ceramics are alkali, alkaline-earth, and transition metal alumina-silicates, obtained by quenching molten components to room temperature. The resultant glass can crystallise sequentially upon heating, changing in the process its optical properties. The transmittance of the glass, displayed as an array of sensors, can detect different exposure temperatures and times. Experimental set-ups were able to detect temperatures up to 900 °C with a resolution of 50 °C [95].

1.2.2.3 Uniform crystal temperature sensors (UCTS)

Crystal temperature sensors are based on diamond or silicon carbide cubic samples, which are exposed to neutron radiation. This generates point defects in the internal structure of the cube, either vacancies or interstitials. The crystals are then heat treated, causing the structure to anneal and recrystallise, so that the lattice is swollen according to the maximum temperature seen by the crystal. This change in the lattice parameter, dependent on time and exposure temperature, can be determined accurately using X-Ray Diffraction [96]. Maximum past exposure temperatures measured with UCTS display an error in the range of 8 °C, for a temperature range between 150 °C and 1,400 °C [97–99].

1005 These crystals are typically introduced into previously drilled holes in the surface of turbomachinery components. The cubic samples are normally cemented into the hole, so that the crystals provide a single point measurement near the surface of the component [100–102]. Given the hole requirement, this technique is considered intrusive and destructive. Moreover, a large number of holes and crystals are necessary to provide a temperature profile over the surface of a component, which may limit the application
1010 of UCTS to dedicated engine tests.

1.2.2.4 Thermal history phosphors

Phosphorescent thermal history sensors were first suggested by Feist *et al.* [103]. This technique is partly
1015 based on the luminescence principles behind on-line thermographic phosphors, where changes in luminescent properties are used to determine the temperature of the phosphor. In thermal history sensors, these luminescent changes are non-reversible, so that the maximum exposure temperature is stored within the material structure [104]. This facilitates the interrogation of the sensor after heat exposure, at room temperatures. Therefore, the optical access to observe the phosphor during operation is no longer necessary.

1020 These sensing phosphors can be applied on the surface of turbomachinery components in the form of a paint, Thermal History Paint (THP), or as a coating, Thermal History Coating (THC). These two embodiments, while based on similar principles, can be selected depending on temperature range, durability, cost, and specific application. This technique provides several advantages over existing
1025 alternatives. It offers a continuous temperature coverage over the surface of normally complex-shaped and rotating components. The method does not require the destruction of the component where it is used on. Additionally, paints and coatings show good durability, and both are REACH compliant, in other words, non-toxic (unlike the thermal paints seen before).

Unlike thermal paints, THP's and THC's use phosphorescent temporal measurements. A laser source is
1030 used to excite the coated surface, and the resulting phosphorescent emission can be detected and fitted to a single exponential decay. The Life-Time Decay (LTD) of the decay curve is the temperature sensing parameter, which allows the correlation to the maximum past temperature seen in a specific location. The fundamentals of this technique are outlined in the following sections, since LTD offers several advantages compared to colour changing paints. The LTD is a single scalar value, which can be correlated to a
1035 temperature value, while colour changes in thermal paints require a more challenging calibration. The temporal nature of the measurement allows certain degree of independence with respect non-uniform excitation sources. In addition, decay curves can normally be measured with low intensity emissions, which can happen due to the contamination of the optics of the instrument and/or the contamination of the surface under measurement. Soot and other carbon deposits are usually present in combustion environments and
1040 can be cleaned from the surface of turbomachinery components once these are at room temperature.

1.2.3 Summary of temperature measurements

A summary of the main on-line and off-line temperature measurement methods is outlined in **Table 1.1**.

Table 1.1 Summary of on-line and off-line temperature measurement techniques

	TEMPERATURE RANGE	BENEFITS	LIMITATIONS
On-Line Temperature Measurement Techniques			
Thermocouples	-270 to 2,300 °C	- Transient temperature measurements - Fast on-line measurement recordings.	- Intrusive - Point measurements. - Access and extensive wiring required. - Costly wiring installation - Bonding to ceramic surfaces - Difficult to install on rotating components. - Calibration required.
Pyrometry	Below 3,000 °C	- Transient temperature measurement - Remote temperature measurement - High speed measurements - Wide temperature range	- Optical access required. - Sensitive to other sources of radiation - Difficulties in measurements due to change in emissivity, translucency and thickness of ceramic coatings and cleanness of optics
Thermographic phosphors	- 160 to 1,700 °C	- Independent of emissivity - Surface measurements possible with good resolution - Robust against strong light	- Decreasing signals with increasing temperature. - Bonding and attachment of phosphors to required surface. - Semi-intrusive - Requires optical access to component. - Not-fully developed.
Off-line Temperature Measurement Techniques			
Thermal Paints	Up to 1,200 °C	- Surface temperature profile	- Limited durability of paint - Toxic constituents - Time consuming interpretation and calibration - Subjective and complex measurements - Poor resolution
Crystal Temperature Sensors	150 to 1,450 °C	- Small dimensions - Wide temperature range - Good accuracy	- Intrusive - Point measurements. - Difficult calibration, dependent of precise data acquisition - Laboratory equipment required
Thermal history phosphors	200 to 900 °C	- Non-destructive - Surface temperature profile - Non-toxic constituents - Materials to be used as a paint or as a coating.	- Semi intrusive technique - Under development

1.3 Objectives

Temperature measurement techniques are important in turbomachinery. From the available methods mentioned in the previous sections, thermocouples are the benchmark in the field, given their relatively low cost. Other techniques such as thermographic phosphors, used for on-line surface temperature measurements, have been an active research field for the past 20 years. However, these methods are difficult to implement, and off-line techniques are often used alternatively. Recent methods such as off-line thermographic phosphors, or thermal history sensors, were first proposed by Feist *et al.* in 2007 [103] as a potential temperature sensing alternative to be used as a coating or as a paint. Both embodiments have been investigated since then.

This investigation focusses on Thermal History Paints (THPs) as an easy-application surface temperature measurement technique, with a lower cost than the alternative Thermal History Coatings (THC's) [105]. Recent work on THPs include the investigation by Araguas-Rodriguez [106], as well as, the proof of concept by Rabhiou [104]. Both authors focused on the temperature range 200 °C to 900 °C, showcasing the benefits of THP's as a more accurate alternative to thermal paints. However, as the efficiency trend in turbomachinery is extending to higher temperatures, the development of a new version of THP for reliable off-line measurements at temperature higher than 900 °C will result beneficial both for the industry and for the reduction of global emissions in automotive and power generation. This thesis will focus on the development of THP examining the formulation suggested by Araguas-Rodriguez [106], selecting the appropriate phosphorescent element, as well as selecting a high temperature liquid binder to embody a new paint formulation able to reach high temperature regimes, above 900 °C. Several binders will be tested as carriers of this phosphorescent element, and sprayed on metallic surfaces, such as stainless-steel and nickel alloys as a first approximation to an industrial application.

1.4 Thesis outline

1070

The structure of this thesis reflects the objectives outlined in the previous section.

Chapter 2 includes an introduction of the theoretical principles in luminescent materials, and how these are used in temperature measurements.

1075

Chapter 3 provides a review of phosphorescent materials used as thermal history sensors, as well as the main concepts behind thermal history mechanisms. Once a thermal history sensing mechanism has been selected, the adequate material selection of pigment and binder is considered for the development of Thermal History Paints (THPs).

1080

Chapter 4 focuses on the materials and methods used during this work. These include a description of the pigment and thermal history paint manufacturing, the instrumentation used for luminescent measurements, as well as the material characterisation techniques employed.

1085

In Chapter 5 the results obtained during the selection and testing of high temperature materials, including the current version of thermal history paint are presented and discussed. Several binders, to embody the THP were evaluated, as well as modifications of the pigment, and several interlayers between the THP and stainless-steel substrates. In Chapter 6, the main outcomes of Chapter 5 are applied to generate a new formulation for a high-temperature thermal history paint.

Lastly, Chapter 7 provides a summary of the main conclusions reached during this thesis, which are used to outline the suggested recommendations for future work.

2 Fundamentals of luminescence

Photoluminescence is a physical process consisting of the absorption of light in a material, after which light is re-emitted from within the material at a different wavelength. These luminescent materials, responsible for the photoluminescent process, are efficiently excited by low-wavelength light, in the Ultra-Violet (UV) and visible ranges. Once the material is excited, radiative emissions from within the material can be immediate or extended in time. Luminescence lasting less than 10^{-8} seconds is usually referred to as fluorescence, while longer decays are classified under phosphorescent processes [107]. Since the investigated luminescent materials in this work show lifetime decays in the range 10^{-5} to 10^{-2} seconds, the name phosphor is considered throughout the text referring to the luminescent materials employed here.

This chapter contains a brief introduction on the physics governing the luminescent processes, followed by the dependence of optical luminescent properties and temperature, which is considered the basis for phosphor thermometry. Finally, the main methods used to perform temperature measurements with phosphors are outlined as well, i.e., temporal luminescence (lifetime decay) and spectral methods.

2.1 Energy levels and luminescence theory

Phosphorescent materials contain small quantities of transition metals or rare-earth ions. These are the elements responsible for the photoluminescence process. The excitation of these luminescent materials, is achieved by low-wavelength (high energy) light, where the absorption is more efficient [107]. In **Figure 2.1** below, the excitation and emission of a luminescent ion (A) within a material is shown for light in the visible range. In this example, green light is used for the excitation, while the ion re-emits red light, which is at a higher wavelength. The energy diagram, also in **Figure 2.1**, shows the process for the electrons in the dopant luminescent ion. The excitation light promotes the electrons to a higher energy state, A^* . When the excitation ceases, the electrons return to the ground energy states via two competitive processes, either radiative or non-radiative. If the optical properties associated with the emission are temperature dependent, the luminescent material is considered a thermographic phosphor.

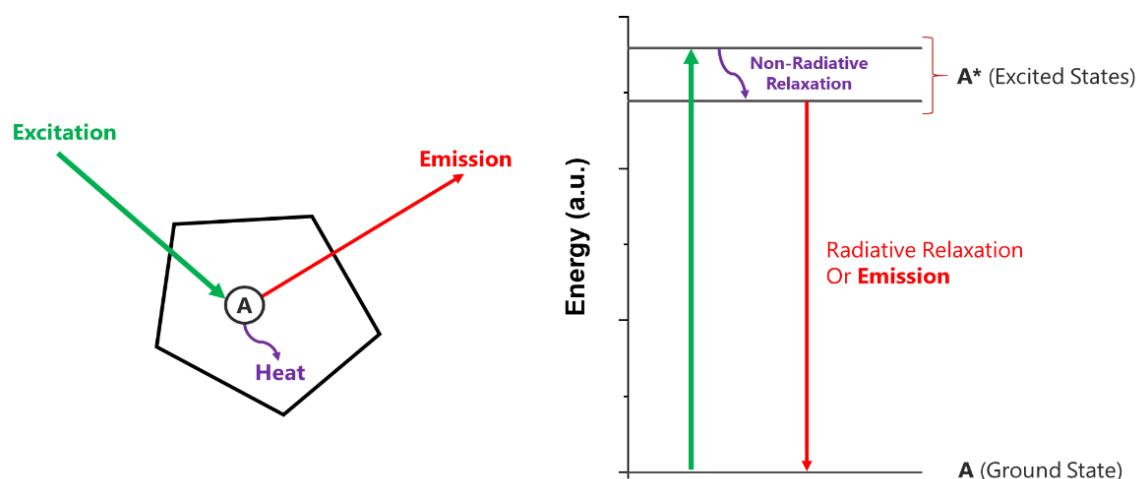


Figure 2.1 (Left) Excitation, emission, and heat release of a luminescent ion, A, in its host lattice. (Right) Excitation and relaxation transitions in an energy diagram.

The luminescent process occurs in the electronic shell of the luminescent ions. Three variables describe, in quantum mechanics, the movement of electrons around the nucleus [108]:

- The Hamiltonian operator (H) describes the kinetic and potential energies in the system, through the time and coordinates of the electrons and nucleus.
- The wavefunction (Ψ_i), describes the movement of the particles in coordinates and time. The square modulus of the wavefunctions ($|\Psi_i|^2$) expresses the probability distribution of an electron within a determined space region. This is called an *orbital*.
- The quantified energy (E_i), associated with a specific wavefunction and independent of the coordinates.

These quantities are related by the Schrödinger equation below, with which the energy states of the electronic shell of an atom can be determined:

$$H \Psi_i = E_i \Psi_i \quad (2.2)$$

Here H corresponds to the Hamiltonian, E_i the energy eigenvalues and Ψ_i the wavefunction of the electrons.

The solutions of the Schrödinger equation are pairs of wavefunctions (Ψ_i) and energy values (E_i). The wavefunctions describe the atomic orbitals. Each orbital can be defined by a discrete energy, E_i . The quantum mechanics of these energy levels and the interactions in the electronic shell are described extensively in reference [109].

The Hamiltonian operator (H) describes the kinetic and Coulombic interactions between the outer electrons and the nucleus, as well as the spin-orbit coupling. Energy splitting caused by Coulomb interactions is in the order of $8,000 \text{ cm}^{-1}$, while spin-orbit coupling represents a finer splitting in the order of $1,000 \text{ cm}^{-1}$ [110]. The order of magnitude of this splitting is represented in **Figure 2.2**, for the Eu^{3+} ion. The Hamiltonian also takes into consideration the ion within a crystal structure. This is the crystal field Hamiltonian, where the ligand ions in the crystal are considered point charges. However it is generally considered that lattice vibrations will not affect the central atom, since electronic motion is faster than the ionic motion (Born-Oppenheimer or adiabatic approximation) [109].

The three quantum numbers describing the energy levels are the principal quantum number, n , the shape of the electron orbital, l , and the orientation of the electron orbital, m . The principal quantum number (n) refers to the overall energy of the electron, describing it with integer values. l represents the orbital angular momentum and takes values $l=0,1,2, \dots (n-1)$. m_l is the z-component of the angular momentum with values in the range $[-l, -(l-1), -(l-2), \dots, (l-2), (l-1), l]$. m_s represents the z-component of the spin angular momentum, s , and takes half integers to describe the orientation of the spin. These are expressed as $+$ or $-1/2$. Alternatively, the representation of the orbitals considers the total angular momentum $j=l+s$. This and its z-component are characterized by the quantum numbers j and m_j , respectively. The number j takes values $l + 1/2$ or $l - 1/2$. On the other hand, m_j values are in the range $[-j, -(j-1), -(j-2), \dots, (j-2), (j-1), j]$ [109].

In atoms containing several electrons, multi-electron states can be defined by a set of total quantum numbers: L , S , M_L and M_S ; or alternatively L , S , J and M_J . Pauli's Exclusion Principle applies to electrons within the same atom, as two electrons cannot occupy identical states or have identical quantum numbers.

- L is the total orbital angular momentum quantum number and takes values $L=0,1,2,\dots$ or S, P, D, F.
- M_L distinguishes the orientations of L and takes the values in the range $[-L, -(L-1), -(L-2), \dots, (L-2), (L-1), L]$. M_S and M_J follow similar rules as M_L .
- S is the total spin quantum number and takes half integer values.
- J is the total angular momentum quantum number that represents the spin orbit coupling, and it is represented by a non-negative integer or half integer value.

$$J = L + S, L + S - 1, \dots, |L - S| \quad (2.6)$$

The value $2S+1$ is termed multiplicity, and it accounts for the electron pairing with the same orbital, relative to the orientation of their spins. For example, two electrons with paired spins cancel each other, and the net spin is zero. This case is called a *singlet*. If the two spins momenta add together, the net spin is not zero, and this case is called *triplet*. The energy levels of the outer electrons in a free atom can be classified by the term symbols including these numbers. The symbols adopt the form $^{2S+1}L_J$, where L , S and J are the total quantum numbers described before. These symbols are used in optical spectroscopy for identification of electronic transitions in the absorption or emission of photons. In the case of europium, the electrons are arranged following the configuration of xenon, then filling the $6s^2$ orbital, where the two electrons contained are a *singlet*, and in the $4f^7$ orbital, where the spin of the seven electrons add their momenta in a *triplet*. More details on quantum mechanical selection rules can be found under references [108,109].

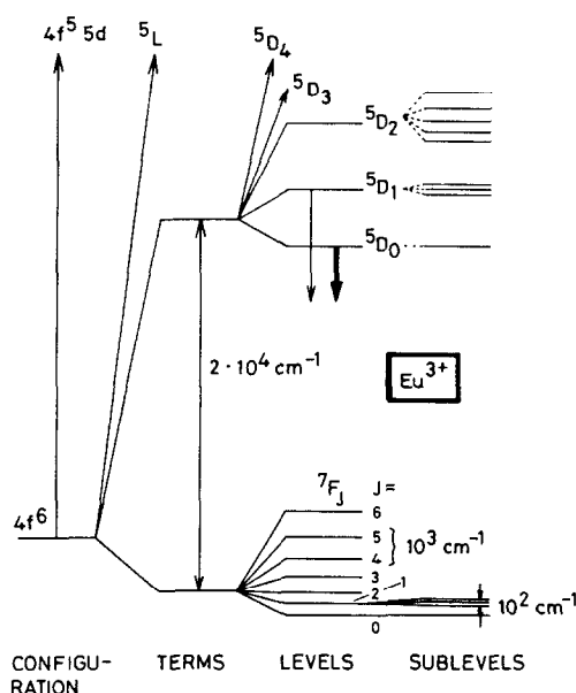


Figure 2.2 Diagram of energy level splitting of Eu^{3+} ($4f^6$), from interelectronic configuration terms, through spin-orbit coupling levels, to crystal-field sublevels. Extracted with permission from [111].

As seen before, absorption and emission processes occur in luminescent ions within solid structures. Luminescence processes take place, energetically speaking, within the band structure of a material, normally in the band gap between the conduction and the valence bands (depending on the electronic configuration of the luminescent element). Dorenbos and other authors have explored the band structure of luminescent ions in several publications [112–114], studying the effect of the host surrounding the luminescent element, as well as the exposure to temperature of the luminescent material.

Electronic transitions can be characterized not only in energy diagrams, but also in the luminescent absorption and emission spectra of luminescent materials. As shown in **Figure 2.3** below, the electronic transitions from ground states (A, D, E) to excited states (B, C) and vice versa, can be attributed to specific wavelengths in the optical spectrum (λ_1 , λ_2). Effects such as the appearance of excitation bands or the broadening of emissions peaks, observed in the luminescence spectra, can be attributed to changes in the electronic splitting, and therefore to changes in the solid structure of the material.

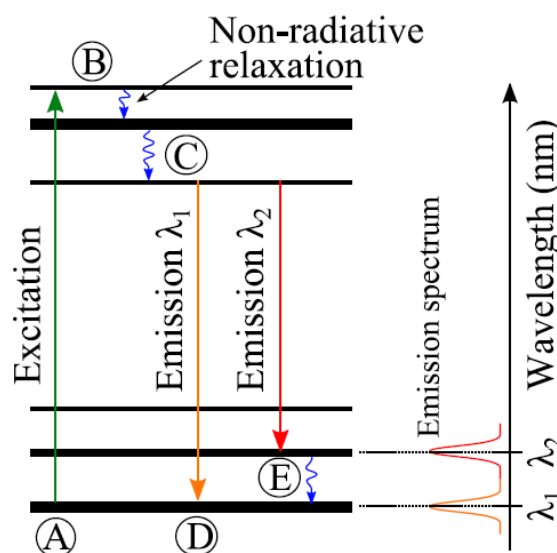


Figure 2.3 Luminescence process shown for example energy levels, including emission spectrum, extracted from [115] with permission via CC-BY-NC-ND 3.0.

2.1.1 Dynamics of excited states and electronic transitions

When an energy pulse, such as excitation via laser, interacts with an electron in the structure of a luminescent material, this can be promoted to an excited energy state. Subsequently, after excitation, the electron returns to the ground energy state through a combination of radiative and non-radiative relaxations. These involve the emission of photons and phonons, respectively. Both relaxations constitute a competitive energy process, whose probabilities depend on the electronic characteristic of the luminescent elements, such as the energy gap between valence and conduction band, as mentioned before. Generally, light emissions from radiative relaxations have their origin in elements with significantly separated energy levels between excited and ground states. Luminescent elements with a large energy gap have a high probability of radiative decay occurring, while the probability of a non-radiative decay is low [116].

2.1.1.1 Selection Rules

Electronic transitions are governed by a set of quantum mechanical selection rules. These determine whether a transition is allowed or forbidden, according to the conservation of the total angular momentum. When a radiative transition occurs, a photon of spin 1 is absorbed or emitted, forcing the electron to an energetic transition compensating for the change in angular momentum [117]. The probability of radiative transitions between electronic states are determined by the quantum mechanics selection rules. In practice, these rules are less strict, given the influence of the crystal field and spin-orbit coupling. It can be considered that a forbidden transition has a low probability, while an allowed transition has a high probability of occurring [108–110]. Further exploration of the selection rules can be found in text books such as Henderson and Imbusch [109].

For example, Charge-Transfer (CT) transitions are allowed by the selection rules in most of the luminescent elements [107]. The process results in a broad absorption band at lower wavelengths, around 300 nm, as shown in **Figure 2.4** below for the Eu^{3+} ion in Y_2SiO_5 . The absorption spectra shown below corresponds to the change in spectral intensity plotted over the excitation wavelength, while keeping the observation window fixed. This can be achieved with two monochromators, as explained in reference [109]. However, this CT provides additional non-radiative routes that could quench the luminescent emission. Excitation at high energies could affect the luminescent transitions at higher wavelengths, normally forbidden by the selection rules. This quenching mechanism was first suggested by Fonger and Struck [118], as an additional electronic state could be found in the 5d orbitals of rare-earth ions, after the promotion of an 4f electron into a 5d orbital. In this thesis, all excitation and detection were performed in the visible range to avoid undesired quenching, as well as to keep laser light visible and safe.

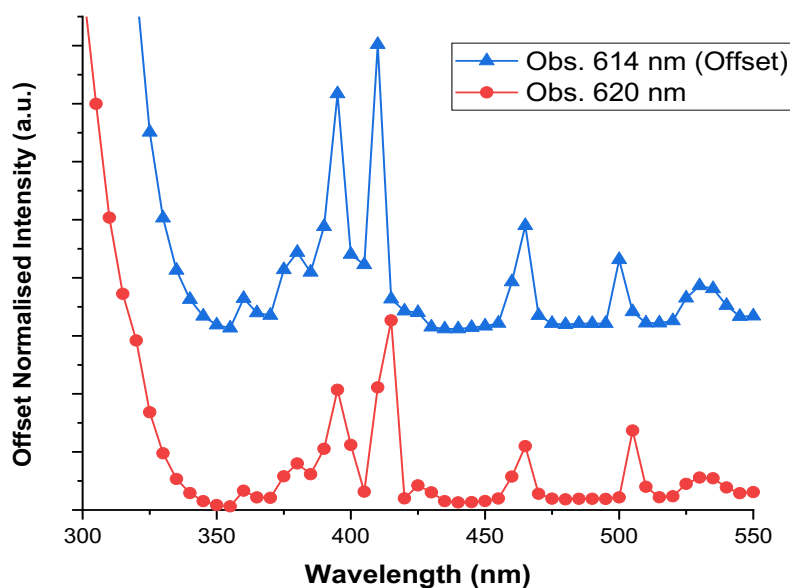


Figure 2.4 Absorption Spectra of Eu^{3+} in Y_2SiO_5 at ambient temperature, after 30 min heat treatment at 900 °C. Observation windows kept at 614 nm and 620 nm, shown with an offset for visualisation. Spectra provided by Phosphor Technology Ltd. [119] from samples produced by Sensor Coating Systems Ltd. [105].

2.1.1.2 Crystal Field Effect

Luminescent ions under external influences, such as the particles of the surrounding host structure, will create splitting and shifting in the luminescent emission spectrum. This is known as the *Stark effect* [109]. The magnitude of this splitting has been determined in the order of 200 - 600 cm^{-1} for ceramic oxides doped with lanthanide rare earths [110,117,120,121]. The crystal structure has an effect on the Stark splitting, but elements within a similar symmetry class will experience identical splitting. For example, transitions for all monoclinic groups will be the same, but selections rules may vary in different point groups depending on the number of allowed transitions. Generally, a low symmetry leads to a more relaxed set of selection rules, and therefore an increased number of allowed transitions. In other words, a specific point group with very low symmetry can result in allowed transitions by the selection rules [122].

The Stark level and sublevel splitting has effects on the optical emission spectrum, as shown in **Figure 2.5** below. Identical Stark splitting, as in an idealised perfect crystal, **Figure 2.5 (a)**, will produce well defined spectral lines and narrower spectral peaks. On the other hand, different ground state levels, such as the ones shown in **Figure 2.5 (b)**, will result in slightly different relaxation transitions, which will generate broad spectral bands. This differentiated broadening due to Stark splitting is commonly observed when comparing crystalline and amorphous host materials.

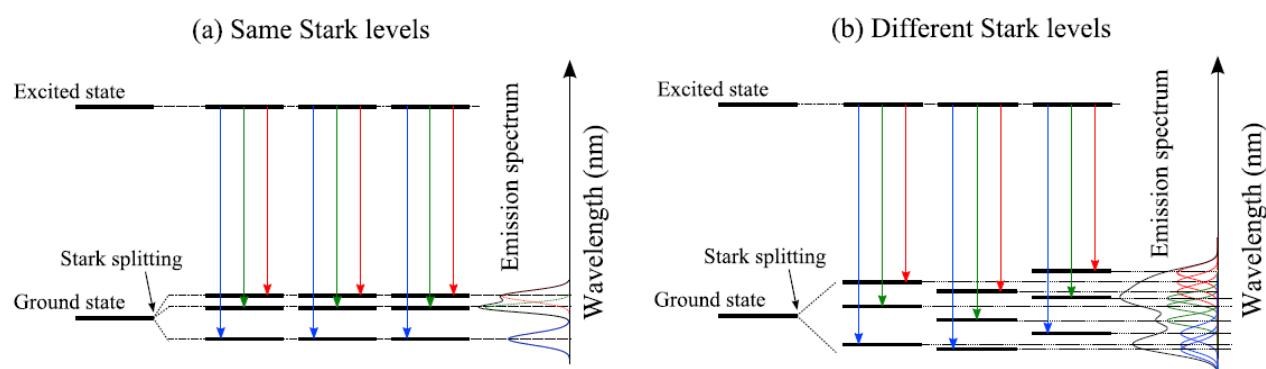


Figure 2.5 Schematic representation of Stark splitting and broadening effect of optical emission spectrum. An idealised crystal with identical sites is shown on the left (a), while different randomised Stark levels are shown on the right (b). Reproduced from [115] with permission via CC-BY-NC-ND 3.0.

2.1.1.3 Energy Transfer

Phosphors contain small amounts of optically active elements. The host lattice can be considered a passive layer surrounding the luminescent centres, but nevertheless defining the location of the luminescent ions, and having an influence on the emission observed. The luminescence process in a phosphor can then be unfolded in the following steps, graphically represented in **Figure 2.6**:

- 1) Excitation
- 2) Absorption
- 3) Energy transfer
- 4) Emission

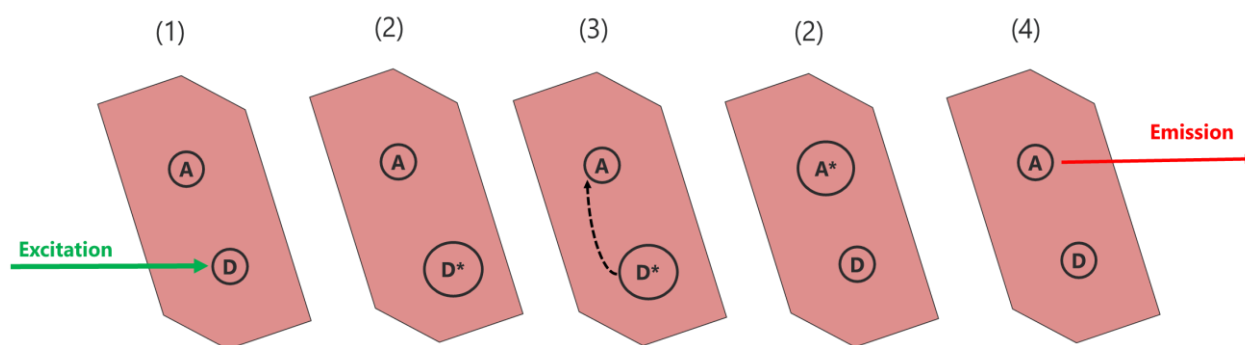


Figure 2.6 Luminescent process including energy transfer for luminescent ions A and D within a host structure.

Luminescent ions in a phosphor are surrounded by other luminescent ions, either identical or not. The probability of energy transfer between an excited centre, or donor, and a secondary centre, or acceptor, will depend on the proximity of both ions. As a response to incident light, the centre D, absorbs the excitation energy, reaching an excited state. This centre D* could relax to its ground state, transferring its excitation to the secondary centre A, which will reach its excited state or A*. This second centre can relax to its ground state either radiatively, as shown in **Figure 2.6**, or non-radiatively, by emitting a phonon.

Energy transfer between optically active centres is strongly dependant on the separation distance between two centres since this mechanism can only take place if some interaction between donor and acceptor centres exists. A high concentration of luminescent ions within the host will result in an enhanced light absorption and emission, as the absorption efficiency increases [116]. However, at a particular concentration, the optical centres are at a critical proximity to each other, and the luminescent emission will decrease. This concentration is known as *quenching concentration* and becomes effective if the centres are in a nanometric distance range, when the average distance between the luminescent centres favours the energy transfer.

The host material defines the optical path-length the excitation light travels. The excitation energy can migrate to a large number of centres, until the transfer finds a defect or impurity, which acts as a acceptor, relaxing the excitation to ground state by multi-phonon emission or cross-over relaxation [116]. Lattice phonons can also assist this process, particularly if these contain the appropriate energy. Then, the process is termed *phonon-assisted energy transfer* [116,123].

2.1.2 Luminescent Materials

The energy levels and emission characteristics of a luminescent material depend on the selection of the luminescent element. Transition metals and rare-earth ions are the most common luminescent ions in phosphor design. The metals consisting of the 4th period in the periodic table, from scandium to manganese, are used as phosphorescent elements, predominantly manganese [124] and chromium [125,126]. However, lanthanide rare-earth ions included in the 6th period of the periodic table are predominantly used [107], given their stable luminescent properties, independent from the surrounding environment, compared to transition metals [127].

Transition metal ions from the 4th period of the periodic table incorporate unfilled 3d electronic shells, whose electrons are responsible for radiative transitions. This outer shell has a strong crystal field interaction, and therefore the energy levels involved in radiative transitions depends on the electronic configuration of the ion, 3dⁿ, and the strength of the crystal field. This dependence between the energy levels and the crystal field strength is represented in the *Tanabe-Sugano* diagrams [107,109], where the different ions, 3dⁿ (n=2...8) are represented for an octahedral crystal field. These diagrams permit the analysis of the emission spectra of a transition metal ion in different host materials, where the visible range spectrum is limited to the 3d³ and 3d⁵ configurations. As a consequence, the transition metals used in commercial phosphors are Cr³⁺ and Mn⁴⁺, with a 3d³ outer shell, and Fe³⁺, which includes the 3d⁵ configuration [107].

The rare-earth ions used in luminescent materials are mainly lanthanide elements found in the 6th period of the periodic table. Their electronic configuration shares the structure [Xe] (6s²) 4f^{*n*} (5d¹), where *n* ranges from 1, in the case of cerium, to 14 for lutetium [122,127]. This characteristic electronic structure ensures an isolation of the 4f orbitals, shielded by the 5s and 5p shells, lowering the influence of the surrounding crystalline field. These lanthanide elements keep a similar energy level diagram either in a compound or as a free ion. The main energy gap of these lanthanides can be represented in Dieke diagrams such as the one shown in **Figure 2.7**, where energy gaps prone to radiative relaxations are marked with inverted triangles and blue shadowing. Further elements can be consulted in an expanded version of this diagram in the thermometry publication by Chambers and Clarke [128], as well as the original publications by Dieke [129,130] and further modifications by Carnall *et al.* [131–134].

Figure 2.7 Dieke diagram for some rare earth ions. The blue shaded area represents the energy gap between the principal radiative energy level and the highest energy ground state. Extracted with permission from [135].

Light emission from trivalent rare earth ions occurs between 4f energy levels with large energy gaps between valence and conduction bands. This gap is rarely bridged by phonon emissions, for example the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} . Additionally, electronic transitions leading to luminescence are mainly electric or magnetic dipole interactions. While magnetic dipole transitions are parity allowed and generally not affected by the surrounding environment [122], electric dipole transitions in the 4f energy levels are forbidden for free ions. These transitions only become partially allowed by mixing orbitals in a randomized host crystal field. Therefore, the emission intensity from these transitions depends on the site symmetry of the host lattice and the selection rules applicable to a particular transition considered.

2.2 Temporal Luminescence

The luminescent response of a phosphor in terms of time, or time-resolved luminescence, represents an interesting sensing parameter for the thermal history of a material. As previously introduced, the relaxation from the excited state to the ground state happens either via radiative decay or non-radiative decay. This two-level system can be described mathematically in terms of time, for a population of N excited ions over a time t , given a probability of depopulation of the excited state, P [107]:

$$\frac{\partial N(t)}{\partial t} = -P \cdot N(t) \quad (2.7)$$

Solving this differential equation and splitting the probability of depopulation into radiative and non-radiative, the following exponential expression is obtained, where N_0 corresponds to the number of excited ions at $t=0$.

$$N(t) = N_0 \cdot e^{-P \cdot t} = N_0 \cdot e^{-(P_R + P_{NR}) \cdot t} \quad (2.8)$$

Therefore, these probabilities of depopulation can be expressed in temporal terms as the inverse of the luminescent decay time. The parameter τ can be found in the literature comprising both depopulation processes as Life-Time Decay (LTD), also expressed as τ .

$$\tau = \frac{1}{P} = \frac{1}{P_R + P_{NR}} \quad (2.9)$$

The number of excited electrons in $N(t)$ can be linked proportionally to the number of emitted photons and therefore the intensity measured with an adequate instrument. The decay can be rewritten as it is shown in the following expression, where τ corresponds to the time elapsed between $I=I_0$ and $I=I_0/e$, this is 36.8% of the initial intensity.

$$I(t) = I_0 \cdot e^{-(t/\tau)} \quad (2.10)$$

The Life-Time Decay (LTD) is frequently used to describe phosphorescent behaviour and it is routinely measured for a variety of applications [122,136]. This life-time of the excited state is a key property of the phosphorescent emission, and while for allowed emission transitions this time is short (10^{-7} to 10^{-8} s), for forbidden transitions in solids this life-time is much longer (in the order of 10^{-3} s) [107].

The equations above show single exponential behaviour. However, luminescent emission is a complex phenomenon, usually exhibiting multi-exponential decays. Single exponentials can be easily identified as straight lines on logarithmic scale plots, while multiple lines indicate a multiexponential behaviour which are transformed into scalar lifetimes [106]. One of the reasons behind the multi-exponential behaviour are the discontinuities in the crystal lattice of the ceramic host, where the luminescent element is contained. These defects and impurities increase the probability of a non-radiative relaxations, which could affect the exponential behaviour of the decay curve [109,123]. For example, residual precursors from the ceramic synthesis, such as water molecules, have also high phonon energies, which could transfer the excitation of the rare-earth and release it through a nearby O-H bond, quenching the luminescent emission of the phosphor [137].

2.3 Summary of Luminescent Concepts

- Luminescent properties for temperature measurements are included under the category of phosphorescent processes, which are slower than fluorescent transitions. Temperature measurement techniques using phosphors are known as *Thermographic phosphors* or *Phosphor Thermometry Techniques*.
- The processes of excitation and emission are covered both from an energetic point of view and from the observations in the luminescent spectra of phosphorescent materials. Effects on the luminescent processes such as the crystal field splitting, and energy transfer are described as well.
- Phosphors used for thermographic measurements are mainly based on rare-earth ions in a solid host structure. Energy diagrams were introduced to understand the luminescent properties of luminescent materials. The energy level splitting, in particular of the 4f levels of rare-earth ions, were discussed, describing the forces acting on the electrons, both from within the atom and the crystal lattice.
- Temporal luminescence was described as the result of radiative and non-radiative relaxation processes, after excitation. The probabilities of these two processes, based on the electron-phonon interactions, are temperature dependent. Non-radiative transitions are the basis of thermographic measurements since temperature affects probability of phonon relaxation.

Lifetime decay measurements and to certain extent **emission spectra** are the parameters used for temperature determination during this thesis. These correspond to the emitted light as a function of time and wavelength, respectively. Temporal luminescence in particular, was proven as a powerful tool to determine the thermal history of luminescent materials after heat exposure.

3 Review of phosphorescent thermal history sensors

Feist, Nichols and Heyes were the first promoters of the concept of phosphorescent thermal history sensor as it is known today [103]. A thermal history sensor reveals the maximum temperature it has been exposed to, by measuring its luminescence properties after heat exposure, at ambient temperature. Thermal history sensing is based on the permanent physical or chemical changes, happening within the sensor material with increasing temperature. These changes can be measured objectively and quantitatively with luminescent methods, either spectroscopic or temporal. An initial classification of phosphors can be done considering ceramic hosts and luminescent ions. Some reported in the literature are shown in **Table 3.1** below.

Table 3.1 Thermal history sensors, classified by host and luminescent ion as reported in literature.

Luminescent ion	Host structure
Eu ³⁺	Al ₂ O ₃ [138], ZrO ₂ [139], YAG [140], Y ₂ O ₃ [141,142], YVO ₄ [143], CaY ₂ Si ₃ O ₁₂ [144], BAM [117,145]
Er ³⁺	SiO ₂ [146], ZrO ₂ [147], GdAlO ₃ [148], Gd ₂ Ti ₂ O ₇ [149], YSZ [150,151]
Tb ³⁺	Y ₂ O ₃ [138,141], Y ₂ SiO ₅ [152–155]
Pr ³⁺	PbO-Sb ₂ O ₃ -B ₂ O ₃ [156]
Ce ³⁺	YAG [157]
Dy ³⁺	YAG [115]

Other examples of materials that could be used for thermal history purposes are displayed in the original patent by Feist, Nichols and Heyes [103]. Investigations on Thermal Barrier Coatings (TBC's) have also led to the discovery of thermal history sensors. This was the case of YSZ: Sm³⁺ [158,159], explored by Pin *et al.* in collaboration with Southside Thermal Sciences, STS Ltd. [159], the precursor company of Sensor Coating Systems, SCS Ltd. [105].

This chapter aims to give an overview on materials and mechanisms used in thermal history sensing. The first section contains a list of criteria for the development of a high-temperature thermal history paint, followed by a summary of the pigment sensing mechanisms and a review of high temperature commercial binders and deposition methods. These will proof the robustness and versatility of phosphorescent materials and methods as superficial thermal history sensors. For example, some of the sensors reported in **Table 3.1** show an increase of the emission intensity with increasing temperature. This can be considered a thermal history sensing parameter since the emission intensity has its origin within the material structure. The amorphous, or semi-crystalline, structure present in a material at low temperatures, normally delivers a low intensity signal. An increase in the degree of crystallinity, after heat exposure, will significantly increase this intensity of the emission signal. In parallel, emission spectra from the luminescent ions will show sharpening of the emission peaks, and lifetime decay readings will also increase after heat exposure. In summary, sensing parameters based on luminescence offer a great deal of detail on the thermal history of a material.

3.1 Definition criteria for thermal history sensor

In this section, criteria for successful thermal history sensors are introduced with a view to develop Thermal History Paints, THP's. These are composed of a phosphorescent pigment mixed into a liquid binder or carrier. The pigment presents quantitative measuring features, while the binder provides a medium for the pigment to be applied. Paints are usually sprayed, which implies a liquid structure being atomized into small droplets to be deposited on the surface of interest.

Thermal history sensors can be defined by the final use, such as operational conditions and temperature range covered. The sensing capability of the luminescent thermal history pigments, which are used not fully crystallised, would be a critical parameter, since a high temperature working range is preferred (above 900 °C), to cover the current trends in the industry. Other selection criteria for high temperature paints are summarized below:

- The new version of THP should have non-reversible, gradual temperature sensing capabilities above 900 °C, which should reflect on the luminescence properties of the history sensor. Therefore, easily made luminescence measurements should be observable before and after heat-treatment.
- The pigment should be chemically inert and preferably, remain unresponsive to the surrounding environment, except for temperature sensing purposes. The substrate and the THP share a large surface of contact, compared to the volume of the paint. The interphase between the two materials is where reactions will have a bigger impact. In the case of the pigments embedded in the paint, interactions with the surrounding binder can also be detrimental to thermal sensing purposes.
- All materials conforming the sensor must be safe to handle and REACH compliant [160], unlike alternative colour-changing thermochromic paints. Reference legislative guidelines are available through European Union REACH legislation and through the United Kingdom Health and Safety Executive [161], where chemicals can be evaluated in terms of toxicity, hazards to the environment and safe handling.
- While heat exposure will influence the crystallization of ceramic phosphor materials, the required sensor should have a high sensitivity to the maximum temperature reached, and a low sensitivity to the duration of the heat exposure. Both effects should preferably be easily deconvoluted by an appropriate calibration. A material system consisting of irreversible and gradually changing crystallographic phases, having an influence in the luminescent properties, is envisioned as an ideal sensor for a wide temperature range.
- The sensor, when applied as a paint, should permit an easy deposition over complex shapes. This would enable the representation of temperature information over 3D plots. Thickness should be kept to a target 30 µm, for dry films, in order to minimize thermal gradients through the thickness of the paint, while guaranteeing good emission intensity through a wide temperature range.

1460

- Thermal history sensors in the form of paint should remain attached to the required substrate at temperatures above 900 °C for at least 30 minutes. No clear degradation of the paint should be visible. This includes paint turning to dark colour that may undermine luminescence measurements, such as, bubbling, dispatchment from the surface and/or melting.

1465

- Preferably, luminescent excitation and emission should be in the visible range in reason of safety requirements when taking luminescent measurements.

3.2 History sensing mechanisms

1470

Different thermally driven processes have been identified as cause of permanent changes in a phosphorescent material. Feist, Nichols and Heyes introduced some of these mechanisms [103], which have been further exploited with the view to develop robust thermal history sensors.

3.2.1 Thermal damaging mechanism

1475

The term *thermal damaging* embodies different luminescence sensitive processes occurring in the structure of materials with increasing temperature. Luminescent properties are sensitive to gradual structural changes before full crystallization in metals and ceramics, but irreversible changes are not normally exploited for temperature sensing purposes. However, luminescent properties can be tailored to exploit changes beyond crystallization. This is the case of phosphor oxidation, which depends on the valence of the luminescent ion. **Table 3.2** below lists common luminescent elements and their valence states.

1480

Table 3.2 Stable valence states of common rare earth ions and transition metals

TRANSITION METALS											
Luminescent element	Mn	Cu	Zn								
Highest Valence State	4+	2+	2+								
LANTHANIDES / RARE EARTH IONS											
Luminescent element	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er	Tm	Yb
Highest Valence State	4+	4+	3+	3+	3+	3+	4+	3+	3+	3+	3+

1485

A common practice to retain certain colour emissions at higher temperatures consists in heat-treating phosphorescent materials in reducing or inert environments. This enables the luminescent ion to adopt a particular valence state and the host structure to remain at a particular phase. This is the case of BaMgAl₁₀O₁₇ doped with Eu²⁺, or BAM: Eu²⁺ for short, which exhibits different emissions depending on its oxidation state. This phosphor has been widely used in the lighting industry [162,163], and only recently employed as thermal history sensor [117,145]. BAM: Eu²⁺ undergoes a degradation process for temperatures above 500 °C, which offer sensor capabilities. Its crystallographic structure consists of spinel

blocks in which the diffusion of cations is favoured [164]. The europium ion oxidizes from Eu^{2+} to Eu^{3+} with increasing temperature [162,165–167] and it has been speculated that the Eu, while more stable as a trivalent ion, might migrate outside the host structure [168]. This degradation involves the reduction of the luminous efficiency of the phosphor and a colour shift from the emission band of Eu^{2+} to a less intense emission from Eu^{3+} [152]. The lifetime decay also varies when measured from different ions. Reported Eu^{2+} decays are around $1\ \mu\text{s}$ [169], while Eu^{3+} lifetime decays in the same host for higher temperatures are several orders of magnitude faster.

High temperature changes in crystallised phosphors can correspond to phase changes as well. Exposure to high temperatures after synthesis might initiate phase transition in the host and consequently change the luminescent properties. This has been used to identify crystalline structure of the host [170]. Phosphors such as $\text{CaSO}_4:\text{Dy}$, are also subjected to thermal damage due to phase change [171]. This limits its application in plasma displays to temperatures below $750\ ^\circ\text{C}$. Neodymium-doped crystals also suffer irreversible changes when heated above $750\ ^\circ\text{C}$ [172]. From the luminescence perspective, this crystallographic variation is important since the symmetry of the host structure around the luminescent dopant ion determines whether a forbidden transition might take place. The distance between the dopant and the host molecule determines the energy of the charge transfer. For oxy-sulphates containing rare-earth ions, the thermal decomposition at high temperatures displaces the sulphur outside the host structure, creating a sulphur-free phosphor [173]. Another thermal history sensor studied by Rabhiou was $\text{Y}_2\text{O}_3\text{S}:\text{Eu}$ [104,152]. This phosphor contains sulphur, which is mixed with yttria in a reducing atmosphere. When heat treated in an oxidizing environment the sulphur leaves the host to form sulphur oxide, SO_2 . This oxidation changes progressively the host structure and the luminescent properties of the europium.

3.2.2 Thermally driven diffusion

Another mechanism for thermal history sensing consists of gradual, permanent changes in the phosphor through diffusion of elements affecting the luminescence properties. These species diffuse mainly from the substrate to the luminescent layer applied on the surface, in a time and temperature dependent process. The most significant parameter is the incorporation of dopants, or other optically active elements into the host matrix. The concentration of the luminescent element has a direct influence on the luminescent properties. Metallic substrates incorporate transition metals, or even rare-earth ions, which can have a substantial effect on the luminescent properties. These ions, once introduced in the sensing layer, may enhance, or decrease the emission intensity or the lifetime decay values, as sensitizers or quenchers [107], respectively. Quenching is normally induced by transition metal ions, such as Fe^{2+} , Ni^{2+} or Co^{2+} , and can alter the emission by energy transfer [116]. Other effect might be the absorption of the excitation light, which might not reach the dopant ion with enough energy. The concentration of these quenchers determines the influence on the luminescent layer.

The impurities introduced in the thermal history layer might have different origins, emerging either from the substrate or from an interlayer, between the substrate and the sensing layer. At high temperatures, Bond-Coats (BC) and/or Thermal Barrier Coatings (TBC's) are expected on the surface of components exposed to harsh combustion conditions. Thermal history layers should be applied on top of these, as the outer layer in contact with the hot atmosphere. Another possibility is the intentional addition of an impurity as a compound in the sensor layer. These would diffuse at a certain activation temperature, which is the prime factor in the diffusion process. There are several examples in the literature of this co-doping, where impurities affect previously doped matrices [174–176]. However, this mechanism makes the sensor highly sensitive to diffusion of undesired elements from the substrate and/or the conforming materials of the thermal history paint, usually ceramic host, and binder.

Some other examples on thermally driven mechanism can be found in the literature. Gu *et al.* [177] linked the calcining temperature and the concentration of dopants to the emission intensity of the phosphor. At an optimum concentration maximum emission intensity was produced, while lower or higher concentrations quench the luminescence to lower intensities. Han *et al.* [178] doped the same host structure of $\text{La}_{9.33}(\text{SiO}_6)_4\text{O}_2$ with Eu^{3+} , Tb^{3+} and Ce^{3+} . Varying the concentration of the three dopants, analysing emission intensity and lifetime decays, the authors identified optimum emission points. Bhatti *et al.* [179] prepared ZnS:Mn , co-doped with Cobalt, Iron and Nickle. While on its own the phosphor is an efficient green emitter, small amounts of impurities decreased lifetime decays due to energy transfer from the host to the impurities. These changes in lifetime decay were proportional to the concentration of the impurities. Liu *et al.* [180] co-doped $\text{SrSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ with sensitizers Ce^{3+} , Dy^{3+} and Mn^{2+} . This co-doping showed some enhancement of the emission intensity, from the energy transfer between the Eu^{2+} and the sensitizers.

3.2.3 Amorphous to crystalline mechanism

Lanthanide activators emit light from the transitions of their $4f$ orbitals in their electronic structure. These are normally isolated by the $5s^2$ and $5p^6$ shells, limiting perturbations from outer elements [127]. In the amorphous state, the electronic band structure is not well defined, and the crystal field is not uniform. There is a great diversity of local symmetry, which affects the energy level distribution. This is the reason behind the broadening of the spectral peaks and the multi-exponential character of the lifetime decays. In addition, defects and impurities in the crystallographic structure could generate non-radiative relaxation voids. These contribute quenching the intensity of the signal, reducing the lifetime decays. Thus, emission properties are dependent on the crystallinity of the material. The crystallization process harmonizes this environment surrounding luminescent ions, which can be integrated in crystalline blocks. The structural defects disappear steadily over the crystallization with increasing temperature, increasing the signal intensity, sharpening and differentiating emission peaks and increasing lifetime decay values [152,181]. A schematic exemplifying this process is shown in **Figure 3.1**.

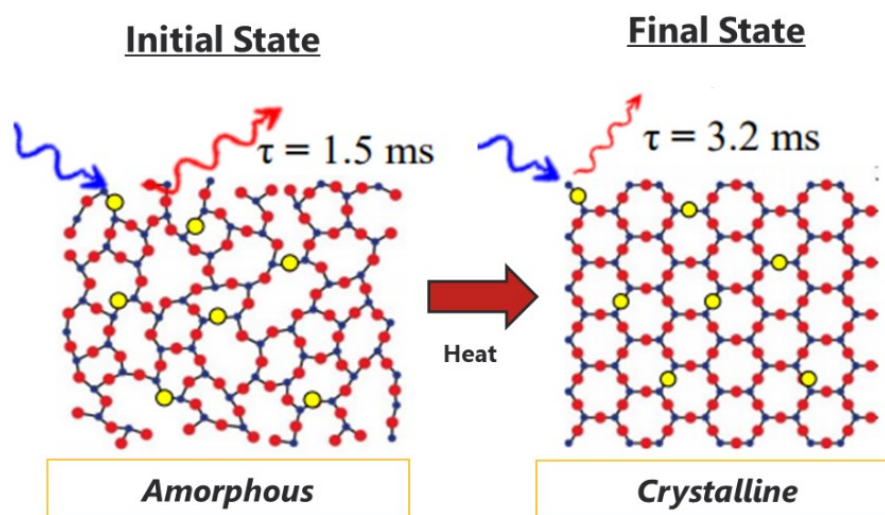


Figure 3.1 Schematic of amorphous to crystalline transition. Luminescent ions displayed along the structure as yellow dots, with excitation incident light (blue arrow) and emission light (red arrow). Lifetime decay values indicated as τ are given as examples for the two states in the amorphous to crystalline transition.

Repeated local environment in an ordered lattice can help to homogenize the energy splitting and the energy levels of the luminescent ions. These rearrange into energetically favourable positions with increasing temperature, where luminescent ions are in equivalent sites. This crystallization process represents a substantial change in the local environment of the dopant ions, which consequently has an influence in the luminescent properties as well. The reduction of the concentration of defects, normally associated with grain growth inside the phosphor particles, narrows the emission lines and increases the lifetime decay. The radiative and non-radiative competitive process, which determines the lifetime decay, skews towards the radiative, as the probability of non-radiative emission is lower in a crystalline material compared to an amorphous one.

Phosphors are routinely produced in an amorphous state [116], and then heat-treated to high temperatures to increase their efficiency and emission intensity. Residual impurities from the production, often organic or solvent species such as H_2O , $(\text{NO}_3)^-$, CO_2 or OH^- can quench the luminescent emission. These species have high phonon energies, between 2,000 and 3,500 cm^{-1} , which can absorb part of the excitation radiation and therefore reduce the energy transfer to the luminescent ion. The emission is severely quenched in presence of these impurities.

As part of the heat-treatment, most of these impurities are not incorporated into the host matrix, abandoning the phosphor at temperatures between 200 and 600 °C depending on the phosphor and the impurity. This allows the phosphor to emit more effectively, making the amorphous to crystalline transition a promising mechanism for thermal history sensing. Some of the phosphors reported in the literature under this mechanism are reported in **Table 3.3**. Europium is the luminescent ion explored more extensively, with a large temperature range exploited in different hosts. Yttrium orthosilicate (Y_2SiO_5) is the most common host, employed for many luminescent ions.

Table 3.3 Phosphors under the amorphous to crystalline mechanism for thermal history sensing, classified by host, dopant ion and temperature range explored in the literature.

Luminescent dopant ion	Host structure	Temperature range (°C)
Ce ³⁺	LaPO ₄ [182], Y ₂ SiO ₅ [183–185], YAG [157]	900-1,300
Sm ³⁺	Gd ₂ O ₃ [186], YVO ₄ [187], Y ₂ SiO ₅ [188]	400-1,300
Eu ³⁺	Al ₂ O ₃ [138], ZrO ₂ [139], Y ₂ O ₃ [142], YVO ₄ [143], SrAl ₂ O ₄ [189], LaPO ₄ [182], Lu ₂ O ₃ [190], Gd ₂ O ₃ [191], YAG [140], Ca ₂ Y ₈ (SiO ₄) ₆ O ₂ [192], Li(MoO ₄) ₂ [193], ZnO [194], La _{9.33} (SiO ₆) ₄ O ₂ [178], Y ₂ SiO ₅ [195–203], YSZ [84,204]	500-1,400
Tb ³⁺	Y ₂ O ₃ [138,141], Y ₂ SiO ₅ [152–155], LaPO ₄ [182], YAl ₃ (BO ₃) ₄ [205]	800-1,400
Dy ³⁺	Gd ₂ O ₃ [186], YVO ₄ [187], YAG [115]	400-900
Er ³⁺	YVO ₄ [187], YSZ [115,150,151]	400-800

3.2.4 Summary of history sensing mechanisms

Some of the structural changes associated to luminescence properties and used to record the thermal history are summarized in the following list:

- Transition to a crystalline phase with temperature [170]
- Oxidation of dopant ions and thermal damaging [117,145,206]
- Diffusion of activator ions or inhibitor/sensitizers [153,174,178,179]
- Increase of degree of crystallinity [152,181,207–209]

These are considered the main mechanisms affecting the luminescence emission permanently. Crystalline phase transitions and oxidation of dopants are part of the thermal damaging mechanism since these are one-off transformations in the material. thermal history sensing capabilities are considered after these permanent changes. However, thermal damaging shows some disadvantages such as the low emission intensities obtained after thermal degradation, and the nature of structural change limiting the dynamic range in temperature and wavelength of the phosphor. Therefore, thermal damaging has been avoided in this investigation, focusing on the investigation of trivalent luminescent ions, not susceptible to oxidation, and host structures with a high temperature endurance.

Thermally driven diffusion is a mechanism highly dependent on time and, particularly, temperature. The nature of the process makes it highly susceptible to diffusion of deleterious impurities, even in the case of co-doping. In the presence of undesired impurities, the luminescence emission might be quenched, degrading the intensity of the signal and, consequently, result in low-quality temperature measurements. Given these disadvantages, thermally driven diffusion was not the main focus of this investigation.

The amorphous to crystalline mechanism has shown a high potential, considering the great number of phosphors described in the literature, see **Table 3.3**. Heat treatments have an effect on the luminescence properties of the phosphor, which can be rapidly analysed by intensity ratio or lifetime decay methods. The

increase of the degree of crystallinity is of particular interest for ceramic hosts produced via sol-gel methods, which are inexpensive and relatively simple. Phosphors obtained by sol-gel are routinely exposed to temperature in order to reduce the gel to a ceramic powder, allowing for a customized starting point in temperature sensing. This is regularly reported in the literature as annealing, calcining, baking or simply heat-treating.

Considering all the above, the **amorphous to crystalline** mechanism has been the preferred for this investigation. The amorphous or semi-crystalline structures obtained from the jellification are good starting points for temperature detection since sol-gel manufacturing involves low manufacturing temperatures, typically lower than 600 °C. This mechanism will be used in the selection of an adequate pigment for a high temperature thermal history paint, as explored in the following sections.

3.3 Concepts for thermal history paint

Once a thermal history sensing mechanism has been selected, the development of Thermal History Paints requires an adequate material selection of pigment and binder. The pigment will be selected among phosphors undergoing the amorphous to crystalline mechanism, thus phosphors with varying luminescent properties with temperature are discussed as potential pigments. Several binders are also reviewed in this section.

3.3.1 Luminescent pigment

Several phosphors have been explored in the literature with different luminescent properties at various temperatures. A summary on the considered phosphors is outlined in the following sections including an expansion on the selected pigment.

3.3.1.1 Selection of luminescent pigment

A pigment for a high temperature thermal history paint should be a phosphor among the amorphous to crystalline category described before. A summary of the phosphors among this sensing mechanism were introduced in **Table 3.3** and some examples are described in the following paragraphs. The effects of heat treatment on the luminescence properties of these phosphors are evaluated according to the criteria for a high temperature history pigment and associated thermal history paint.

Lu₂O₃: Eu was produced in film form by Guo *et al.* [190]. The films were generated in a sol-gel and dip coating process, and then heated at different temperatures from 400 to 900 °C. The heat treatments were 1 hour long, allowing the structure to crystallize. The samples were then characterized by x-ray diffraction, where the patterns revealed a small degree of crystallinity for lower heat treatment temperatures, while sharp and crystalline peaks were observed for the high temperature samples. The authors also accounted for particle size growth with increasing temperature and fewer quenching elements. Lu₂O₃ could be included as a history sensor under thermal damaging mechanism as well, since this phosphor may be subjected to phase transformations between 700 and 1,000 °C, depending on the particle packing density.

For temperatures above 700 °C the history sensing detected with temporal response was quite limited and the phase transformation degraded in general the luminescent emission from the europium. This phosphor did not satisfy the high temperature condition set in the criteria.

$A\text{Eu}(\text{MoO}_4)_2$ phosphors, where A is a monovalent ion such as Li^+ , Na^+ , K^+ or Ag^+ , were also reported in the literature by Guo *et al.* [193]. The phosphors were produced through the sol-gel method, dried at 500 °C for 5 hours and subsequently heat treated to a final temperature between 500 and 900 °C for another 5 hours. X-ray diffraction revealed an increase in crystallinity with increasing temperature, linking this to significant variations in the luminescent properties. The emission intensity improved with temperature for all samples, except $\text{KEu}(\text{MoO}_4)_2$, which underwent a phase change at 800 °C, displaying a decrease in intensity at higher temperatures. This group of phosphors displayed good structural and luminescent evolution with temperature, in particular $\text{LiEu}(\text{MoO}_4)_2$. However, the authors outlined absorption in the ultraviolet range, which would have changed the visible range requirements of the phosphor. This phosphor was therefore, not selected.

$\text{Gd}_2\text{O}_3: \text{Eu}^{3+}$ was produced by spray pyrolysis by Kang *et al.* [191] in a hot-wall reactor for temperatures between 500 and 1,600 °C. The luminescence intensity improved with increasing temperature up to 1,400 °C. At higher temperatures, a phase transition was observed, with poor crystallinity at 1,600 °C and associated luminescent decrease. Giving the demanding production method, investigations with this phosphor were not initiated.

$\text{ZrO}_2: \text{Eu}^{3+}$ was also considered as a phosphor candidate, as produced via spray drying by Quan *et al.* [139]. After preparation, samples were annealed between 400 and 900 °C for 2 hours. Crystallization was observed at 500 °C and luminescence properties were not noticeable for temperatures lower than 600 °C. The authors assumed that the luminescent ion was not well integrated in the host structure. In addition, below 600 °C, impurities remained present, which could act as quenchers of the luminescence. A similar evaluation can be made for europium in Ytria Stabilized Zirconia (YSZ). This host has been recently investigated for temperature detection via intensity ratio [204], and lifetime decay analysis [151]. In both cases, temperature detection was restricted to temperatures higher than 800 °C. The production of YSZ was reported by the authors as an involved and exclusive process, both for europium and erbium doped YSZ [115,150,151]. Since the luminescent ion should remain in the host structure at lower temperatures, these phosphors were not selected for the development of thermal history paints.

$\text{Y}_2\text{O}_3: \text{Eu}^{3+}$ was produced through sol-gel by Zhang *et al.* [142]. The phosphor samples were heat treated between 500 and 1,250 °C for 3 hours. At 600 °C and higher temperatures, the phosphor displayed crystallinity, and improved luminescence was observed. Similar results were obtained for the same host with different luminescent ions by Pilgrim, who experimented with $\text{Y}_2\text{O}_3: \text{Er}^{3+}/\text{Yb}^{3+}$ [115]. Thermal history sensing capabilities in all cases were achieved by the change in crystallite size, which was limited to a temperature range between 600 and 900 °C. This was considered too narrow, and therefore, this phosphor was not selected.

Y₃Al₅O₁₂ (YAG) is a popular host for luminescent ions. It is vastly used in laser equipment, due to its stable optical properties. This may result in a challenge for thermal sensing, however YAG has been used as a thermographic phosphor in TBC systems [84] and tested extensively with different dopant ions [104,115]. Zhou *et al.* [140] manufactured YAG: Eu through citric-gel. Phosphor samples were heat treated to temperatures between 700 and 1,200 °C. After full characterization, the authors outlined that crystallinity and luminescent intensity improved with increasing temperatures. The emission from the phosphor showed different patterns for low and high temperatures, which hindered a continuous temperature sensing. The lifetime decay method was employed at higher temperatures, with a poor temperature resolution between 700 and 1,200 °C, but in all cases with consistent monotonic increase. Pilgrim [115] and Rabhiou [104] have reported other monotonic ranges, for temperatures between 700 and 875 °C. This has been attributed to formation of YAP phase at intermediate temperatures and therefore YAG was not considered for a high temperature thermal history paint.

YAl₃(BO₃)₄: Tb was considered due to its high luminescence efficiency. Yoo *et al.* [205] prepared this phosphor via solid state reaction. The temperature was varied from 900 °C to 1,250 °C, and the crystallinity and luminescence intensity investigated. Unfortunately, above 1,235 °C, the phosphor suffered phase decomposition. This last candidate and YVO₄ [143,187] hosts displayed interesting temperature sensing capabilities. However elements such as Boron or Vanadium raise toxicity concerns [160], and therefore were discarded for a thermal history Paint investigation.

Al₂O₃ doped with europium was studied by Stenders *et al.* [138], as a sol-gel deposited thermographic phosphor. This phosphor was sprayed on silicon wafers, heat treated and interrogated via X-Ray Diffraction (XRD), spectral and temporal luminescent methods. Several phases of the alumina were revealed through the XRD patterns. At 800 °C the alumina remained amorphous, while a mix of alumina phases was detected between 900 °C and 1,400 °C. This crystallisation of the host materials was associated with a change in behaviour of the lifetime decay. When the phosphor was annealed for the first time, the lifetime decay increased with increasing temperature up to 800 °C, point where the lifetime decreased with increasing temperature. This would lead to ambiguous results if this phosphor were employed as a thermal history sensor. Additionally, the authors considered a second annealing for this phosphor, at 900 °C, after which the lifetime decay was obtained at higher temperatures. The lifetime decay showed a monotonic decrease with increasing temperatures, but no thermal evaluation could be made at temperatures lower than 900°C. This phosphor was therefore discarded for further investigation.

Yttrium Orthosilicate (Y₂SiO₅) has been studied in detail by several authors. Rabhiou *et al.* [104,145,152,181] considered Y₂SiO₅: Tb a promising host candidate, since it exhibited a wide temperature range between 400 and 1,250 °C both in powder and paint forms. The crystallization of Y₂SiO₅: Eu also displays gradual and monotonic changes in lifetime decay with increasing temperature and has been studied as a thermal history phosphor in Paints [106,210] and Coatings [208,209] for particular industrial applications. Yttrium silicates were therefore selected for this investigation and Y₂SiO₅ is reviewed in the following section as pigment for a high temperature thermal history paint.

3.3.1.2 Yttrium orthosilicate in thermal history paint

Y_2SiO_5 shows potential as thermal history pigment due its progressive changes in lifetime decay with increasing temperature. It can be manufactured by sol-gel means in an inexpensive synthesis process, while offering several doping options. Yttrium orthosilicate based phosphors have been studied extensively as temperature sensors, but not explored at the high temperature ranges aimed in the selection criteria. An overview of the temperature sensing capabilities of yttrium silicate is outlined in the following paragraphs, as well as the selection of the optimum doping element for the considered host structure, Y_2SiO_5 .

Yttrium silicates, Y-Si-O oxides, are considered in the Yttrium Oxide (Y_2O_3) – Silicon Oxide (SiO_2) binary system, such as the one shown in reference [222], based in [223,224]. This system englobes two yttrium mono-silicate phases, X1 and X2, six polymorphs of yttrium di-silicate (α , β , γ , δ , η and ζ) as well as an Apatite phase, $Y_{4.67}(SiO_4)_3O$, shown in the diagram as YAS. These Y-Si-O ceramics present a high melting point, above 1,775 °C, and a low thermal conductivity, below 3 W/m•K [211,212] at temperatures higher than 500 K. These properties have gathered interest in several industrial sectors, particularly as high temperature multifunctional coatings. Yttrium silicates have been employed as Thermal Barrier Coatings (TBC's) [213], Environmental Barrier Coatings (EBC's) [214–220] and oxidation resistant coatings [221].

Yttrium Mono-silicate, Y_2SiO_5 , can crystallize into two possible monoclinic phases, either X1 phase in the $P2_1/c$ space group, or X2 phase, in the $B2/b$ space group [225,226]. Yttrium silicates are considered rare-earth silicates, since yttrium can be substituted in the silicate structure by a rare-earth element, mainly Lanthanides. The stability of these structures depends on the substitution of yttrium by a lanthanide ion and, most importantly, on the temperature the silicate has been exposed to [222,227]. The X1 phase has been reported to change to X2 phase only at high temperatures, above 1,200 °C [106,225]. This offers a wide temperature range for thermal sensing purposes, from production to the X1-X2 phase change. A model of a partial unit cell of Y_2SiO_5 is shown in **Figure 3.2** below.

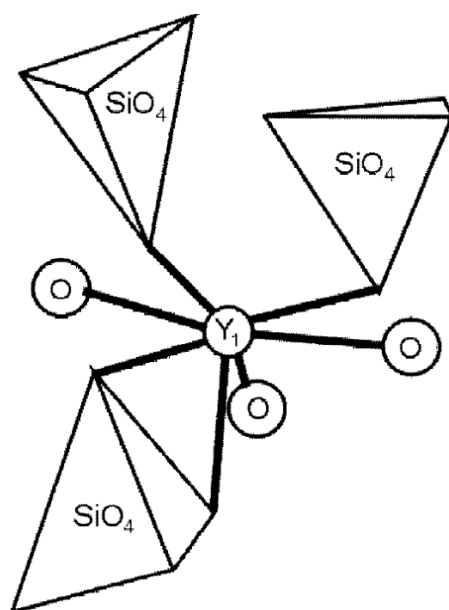


Figure 3.2 Partial unit cell of $Y_2(SiO_4)O$. Reproduced with permission from [228], based on [227].

To mention a few cases, Y_2SiO_5 doped with Ce^{3+} provides an intense blue emission [184], and it is used as a phosphor in solid state lighting and lasers [229]. Tb^{3+} doped Y_2SiO_5 displays efficient green emission under electron beam and UV excitation [155], while $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ emits in the red region and it is used for display devices and Light Emitting Diodes, LED's [230]. The X2 phase of Y_2SiO_5 has been reported to provide more intense emissions for all lanthanide dopants [226,231,232]. However, the appearance of this phase at temperatures higher than 1,200 °C, makes it inconvenient for thermal sensing purposes. On the other hand, the X1 phase can be synthesised from the amorphous state via sol-gel route, which is quite convenient for a phosphor under the amorphous to crystalline sensing mechanism. While literature on the X2 phase of Y_2SiO_5 is more abundant [155,229,233], the focus of this investigation is on the X1 phase. A summary of the luminescent ions found in the literature in the X1 phase of Y_2SiO_5 is displayed in **Table 3.4**.

Table 3.4 X1- Y_2SiO_5 phosphors doped with different luminescent ions under the amorphous to crystalline mechanism, classified by dopant ion and maximum temperature explored.

Dopant ion	References	Maximum temperature
Tb^{3+}	[152–155]	1,400 °C
Eu^{3+}	[195–203]	1,300 °C
Sm^{3+}	[188]	1,300 °C
Ce^{3+}	[183–185,229]	1,400 °C
Co-doping	Ce / Tb [234], Ce / Tb / Eu [233]	150 °C

Co-doping luminescent ions within Y_2SiO_5 were discarded due to the low temperature range supported by host and dopant system. Among the explored luminescent ions, Tb^{3+} is excited via electron beam or UV light, which falls outside the excitation requirements under selection criteria. Similar difficulties on the excitation wavelengths for Sm^{3+} and Ce^{3+} are observed, since light sources outside the visible range are needed. Giving these practical excitation and detection requirements, europium was selected as the luminescent ion. It has been extensively explored in the literature, can be excited in the visible range and its luminescent parameters, spectrum and lifetime decay, can be exploited in Y_2SiO_5 under amorphous to crystalline sensing mechanism [111,235–243].

The energy level structure of the europium trivalent ion, Eu^{3+} is shown in **Figure 3.3**. Excitation from the ground state levels is possible from a light source in the visible range, 532 nm green light in this case. europium can also be excited with light in the UV range [196,198,199,201,244], which might result in excitation to a higher energy level, such as $^5\text{D}_3$. In that case, non-radiatively relaxation to the $^5\text{D}_0$ is expected [122]. A similar transition from $^5\text{D}_2$ to $^5\text{D}_0$ is shown in **Figure 3.3**. At this point, the europium energy gap between valence and conduction band allows for a relaxation involving a radiative emission. This light emission occurs from the excited estate $^5\text{D}_0$ to the J levels of the ground term, $^7\text{F}_J$, where J goes from 0 to 6.

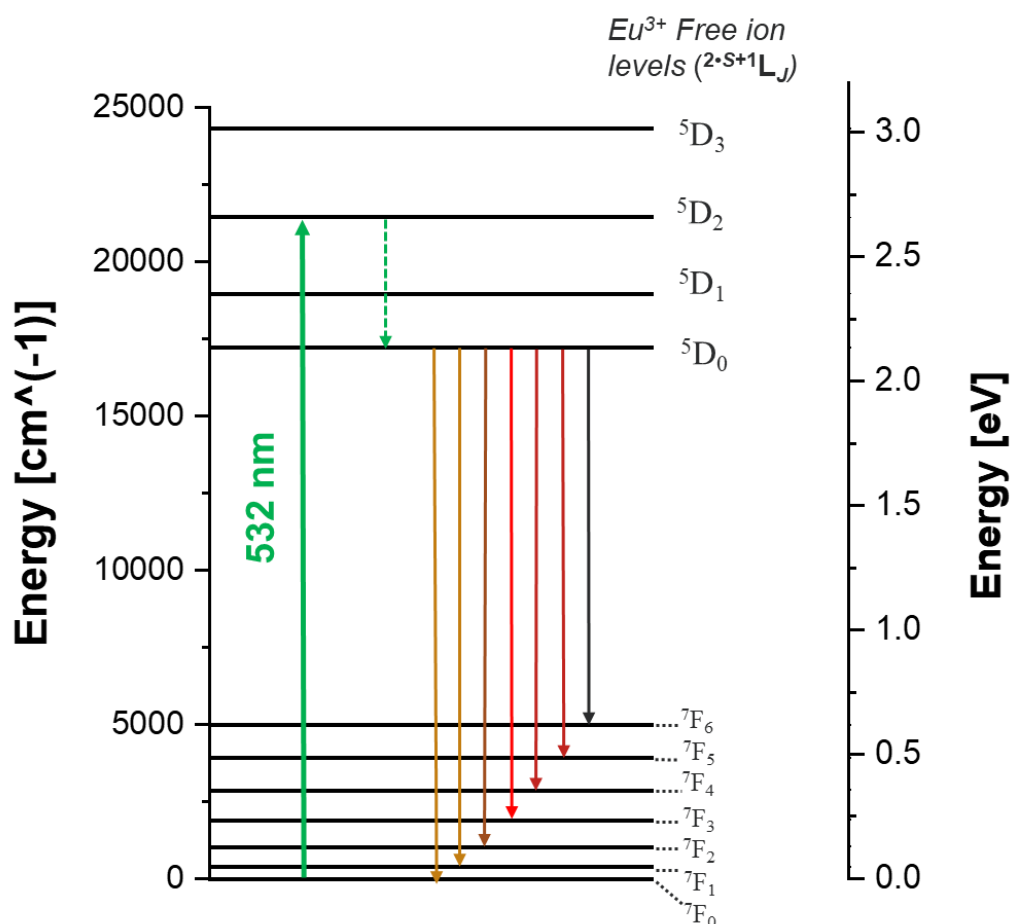


Figure 3.3 Excitation and relaxation transitions for the energy levels of Eu^{3+} . Data obtained from reference [122], originally published by the same author in [245].

These forbidden transitions from the excited states to the ground states give a fair amount of information on the surrounding environment since the symmetry of the rare-earth ion within the host structure reflects into the emission spectra. The case of the ${}^7\text{F}_0$ ground state and the main excited state ${}^5\text{D}_0$ is particularly interesting since these states are non-degenerate and largely unaffected by the crystal-field splitting [106]. Another advantage of europium is the uncommon overlap between the separated ${}^7\text{F}_J$ levels during emission. This characteristic allows to analyse structural transitions, such as crystallization with increasing temperature.

The absorption spectrum of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ has been reported in the literature as a broad band between 200 and 350 nm followed by sharp lines between 350 and 550 nm [196,200]. The broad features correspond to allowed charge transfer transitions, arising from the interactions of the Eu^{3+} and O^{2-} ions. The sharp peaks correspond to the forbidden f-f transitions within the Eu^{3+} . These transitions, displayed in the Eu^{3+} emission spectrum, have already been introduced in **Figure 3.3** and are further explored in **Table 3.5** and **Figure 3.4**. The transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ is defined in the literature as *hypersensitive* since the emission of the europium is more influenced by the local symmetry of the ion and the nature of the ligands [122].

Table 3.5 Transitions observed in the emission spectra of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$, identification according to [122].

Transition	Dipole Character	Wavelength range	Notes
$^5\text{D}_0 \rightarrow ^7\text{F}_0$	Electric Dipole	570 – 585 nm	
$^5\text{D}_0 \rightarrow ^7\text{F}_1$	Magnetic Dipole	585 – 600 nm	Independent of surrounding environment
$^5\text{D}_0 \rightarrow ^7\text{F}_2$	Electric Dipole	610 – 630 nm	Hypersensitive transition, very dependent on surrounding environment
$^5\text{D}_0 \rightarrow ^7\text{F}_3$	Electric Dipole	640 – 660 nm	
$^5\text{D}_0 \rightarrow ^7\text{F}_4$	Electric Dipole	680 – 710 nm	Dependent of surrounding environment, but not hypersensitive
$^5\text{D}_0 \rightarrow ^7\text{F}_5$	Electric Dipole	740 – 770 nm	
$^5\text{D}_0 \rightarrow ^7\text{F}_6$	Electric Dipole	810 - 810 nm	Very weak intensity

While the intensity in the emission spectra of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ may vary between samples and equipment used in the literature, common trends can be identified. The transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ shows the most intense emission, and given its hypersensitive nature, it marks a promising wavelength range to obtain parameters such as lifetime decay. This and other transitions are indicated in **Figure 3.4**, where the emission of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ (at room temperature) are shown after excitation with a 532 nm solid state laser. The phosphor powder sample was previously heat treated at 1,000 °C for 30 minutes. The transitions $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ show very low intensities, which can be expected for low-energy excitations in the visible range. $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions display medium intensities, since one is a magnetic dipole transition and the other depends on the environment, but it is not hypersensitive. A more in depth explanation on the physical phenomena behind the emission spectra of Eu^{3+} can be found in the review paper by Binnemans [122].

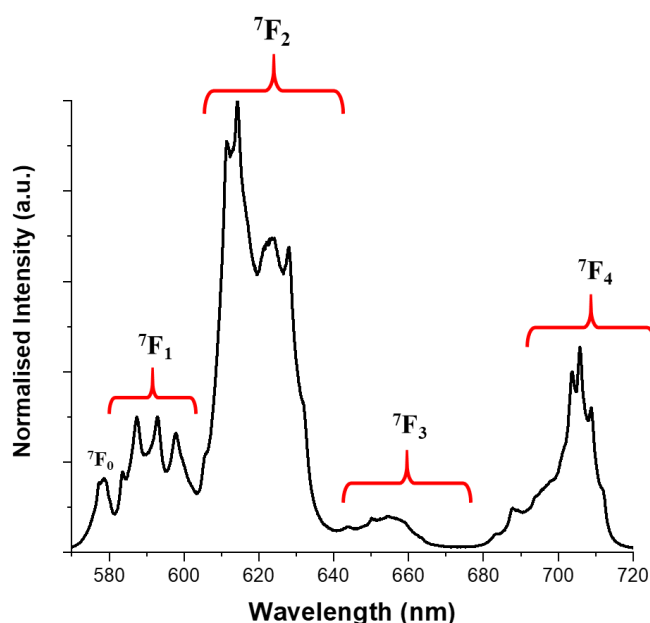


Figure 3.4 Emission spectrum of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$, after heat treatment at 1,000 °C for 30 minutes. Main transitions marked according to Table 3.5. All transitions originated at $^5\text{D}_0$ level.

Synthesis of Y_2SiO_5

Y_2SiO_5 can be synthesized through a wide variety of methods. The choice of a synthesis route over another can have an important influence on the structural properties of these glassy-silicate structures, in particular Yttrium silicates. The phase diagram of the Yttrium Oxide (Y_2O_3) – Silicon Oxide (SiO_2) binary system, shown in reference [222], displays metastable phases as single vertical lines at a given composition. This is the case of $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$, apatite, which is extremely dependant on the stoichiometry of yttrium and silicon. Phase mixtures should be carefully considered, especially for rare-earth doping of yttrium silicates. Parameters such as Y_2SiO_5 powder particle morphology and/or particle size, can have a great influence on the luminescent properties of the phosphor, and therefore, their temperature sensing capabilities [222]. The main synthesis routes of yttrium silicates are solid state, Czochralski method, hydrothermal synthesis, and sol-gel.

Solid state reaction involves the mixing of yttrium oxide and silica via ball milling, followed by heat treatment at high temperatures, between 1,400 and 2,200 °C, for hundreds of hours [246–249]. The resulting sintered particles are then crushed into the desired smaller powder particle sizes. This method remains challenging for the manufacturing of specific compositions, such as $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$ [248,250]. Some drawbacks are the non-reaction of constituents in the ball mill, the high temperatures required, the high cost and energy use. Uniform grains and crystallinities are difficult to obtain, and several grinding and heating cycles are required to achieve a complete reaction. The mechanical process can damage the particle surface as well, which ultimately leads to poor luminescence emission. Giving the characteristics of this production method, solid state reaction was not considered for phosphor manufacturing within this thesis.

The molten salt flux method, also known as Czochralski, is widely employed for the obtention of single crystals. Powder constituents, in this case of Y_2O_3 and SiO_2 , are mixed and melted in a crucible. The seed of a single crystal is pulled slowly from the melt, while the system rotates. Single crystal samples of 40 - 140 mm in diameter and up to 150 mm in length have been manufactured from Yttrium silicates and reported in the literature [251–255]. Some of the drawbacks of this method are the high costs involved and high purity of material required. A high temperature is also required to keep the materials melted, and this might reduce the temperature dynamic range of the sensor. The Czochralski method was not selected for this investigation.

The hydrothermal synthesis of yttrium silicate involves suspending the Yttrium precursor, mainly Yttrium Nitrate ($\text{Y}(\text{NO}_3)_3$), in a clay or layered silicate. The system is then heated in a hydrothermal tank for an extended time, in the order of 100 days [256–259]. The long preparation time, and the addition of impurities from the natural clay makes this method impractical for the manufacturing of thermal history sensors.

Finally, sol-gel is an inexpensive wet chemical synthesis route, which satisfies the low temperature production requirement of thermal history sensors. The precursors used for the pigment, in nitrate or chlorate forms, are dissolved in water and other organic solvents. The hydrolysis of these precursors results in the suspension or *solution* of the reactants in a liquid. To condensate the solution into a solid material, a gelation agent can be added until a closed network *gel* is formed. The excess of water is dried in subsequent

heat treatments, which results in a dense ceramic powder [260]. Some of the advantages of the sol-gel method over other production techniques are the obtention of a homogeneous material, where the particle size can be controlled. The risk of contamination during manufacturing is reduced, and the post-operations such as heat treatments and grinding can be done in a standard chemical laboratory. Sol-gel has been widely used in the production of yttrium silicates. The silicon is added as jellification agent, mainly as Tetra-Ethyl Ortho-Silicate (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$ [222]. The Yttrium precursor most often used is $\text{Y}(\text{NO}_3)_3$ in aqueous solution, which can be easily matched with an equivalent dopant nitrate, such as $\text{Ce}(\text{NO}_3)_3$ or $\text{Eu}(\text{NO}_3)_3$ [261]. Once the precursors have been mixed into a transparent sol, the gel can be dried at temperatures below 600 °C in several progressive steps if necessary.

From the phosphor synthesis methods suggested above, sol-gel has been reported previously in the literature as a successful route to obtain thermal history sensors [104,106,115]. The selected sensing mechanism, amorphous-to-crystalline, aligns well with the sol-gel production method. The low temperatures achieved in manufacturing allow for gradual structural changes at higher temperatures. These structural changes can be interrogated with several characterization techniques, including luminescent methods, for temperature sensing purposes.

3.3.2 Deposition methods and binder enclosure

The deposition of a ceramic phosphor on a substrate can represent a challenge giving the relatively low adhesive forces of ceramic powders at high temperatures. The attachment and application of these type of materials has been studied in ceramic applications, such as water-based refractories. However, the low temperature requirements of thermal history sensors result in a quite limited amount of deposition techniques suitable for these type of material systems. A brief recap of the considered deposition methods is displayed in the paragraphs bellow, followed by a review on high temperature binders for the development of a new version of thermal history paint.

3.3.2.1 Deposition considerations

Phosphor embodiments and deposition methods are linked to particular applications. For instance, Yttrium silicates have been used as oxidation and erosion protection layers on Ceramic Matrix Composites (CMCs), both carbon [262,263] and silicon based [264]. The deposition techniques explored in the literature focus on maximising the performance of the yttrium silicate layer optimising the deposition technique [221,249,265–268], since a good quality coating can increase the efficiency of gas turbine components [269]. Low conductivity, low density ceramic coatings are desired for components exposed to high temperatures, since the *thrust-to-weight-ratio* increases in turbine operation [270]. The durability of protective coatings and turbine components are important factors to consider, but thermal history sensors require a different design approach. Yttrium silicate coatings, exploiting *amorphous-to-crystalline* mechanism, should be applied onto the component surface in an amorphous state, allowing for progressive transition to crystallinity.

Among the low-cost, low-temperature deposition methods, Y-Si-O coatings can be applied via dip-coating introducing the component into an organic slurry. This is an efficient and relatively simple method, well suited to large size components, where high volumes of slurry are required [221,271,272]. The slurry contains a mixture of silicon and yttrium oxides, in addition to different proportions of synthesised yttrium mono and di-silicate. An optimum slurry fluidity is required to cover the surface of a component. This must be dipped, dried, and exposed to high temperatures to allow the slurry particles to coalesce through sintering. Because of this last step in the process, slurry coatings are not ideal for thermal history sensors.

Another considered deposition technique is Atmospheric Plasma Spraying (APS), which allows homogeneous coatings to be formed in the surface of components [249]. Semi-molten ceramic powder particles are sprayed onto the components prior heating in the plasma gun. This usually contains a heating chamber, where the powder particles are fed to. The chamber is at a sufficient high temperature to melt the powder particles, which are accelerated and directed to the surface of the component. The molten particles land on the substrate as splats or lamellar units, which superimpose forming the coating. This deposition route poses a clear disadvantage to the *amorphous-to-crystalline* mechanism since the application depends on the melting of the deposited material. However, this method has been considered both for YAG and yttrium silicate hosts doped with several luminescent ions [104,115], with temperature sensing resolution above 600 °C. Investigations on APS deposition have been recently resumed for YAG [273] and yttrium silicate. For example, a parallel research program on APS yttrium silicate coatings, used as thermal history sensors, is under development at the time of the writing of this thesis, with two recent publications already released [208,209].

Chemical Vapour Deposition (CVD) was considered as well. This technique requires a hot substrate where the coating can “grow” as it contacts a vapour flow carrying the precursors. For the deposition of yttrium silicate coatings, silicon substrates have been used in the past [274]. Laser CVD has been found in the literature as well, where TEOS and yttrium dipivaloyl-methane are used as precursors [275]. This method provides a good control over the thickness and the final microstructure of the coating; however, it is a costly technique, and the hot substrate may represent a challenge for the thermal history sensor. CVD was not considered further.

Other deposition techniques reportedly used for yttrium silicates coatings are electrophoretic deposition [276–279], RF magnetron sputtering [280], microwave sintering [281] and pulsed laser deposition [282]. Yttria-Stabilized-Zirconia (YSZ) coatings have also been applied via EB-PVD [283] but this route was discarded for similar reasons to the CVD case. All techniques previously mentioned require expensive equipment and complex deposition processes, which are unsuitable not only under the scope of this thesis but also for quick application of thermal history sensors on large turbomachinery components. The deposition technique has a great impact on the sensing temperature range, which ideally should go from room temperature to the highest temperature possible. After careful considerations on the possible deposition techniques and their influence on the phosphor itself, the application was narrowed to the dispersion of the semi-amorphous ceramic phosphor in a liquid solution. This paint could be easily spread

and attached to the surface of a turbomachinery component, allowing for low-cost mixing of the phosphor into the paint, rapid in-house deposition, and a large temperature sensing range. The proof of concept of this thermal history paints was developed by Rabhiou [104] and further explored by Araguas - Rodriguez [106]. Yttrium silicate phosphors were selected as the pigment of the paint and dispersed into a liquid carrier or binder. This allowed to temperature sensing from 150 °C to 900 °C. The temperature range overlap of this technique with other deposition techniques is shown in **Figure 3.5**, where Thermal History Paints (THP) and Thermal History Coatings (THC) are displayed over a temperature diagram.

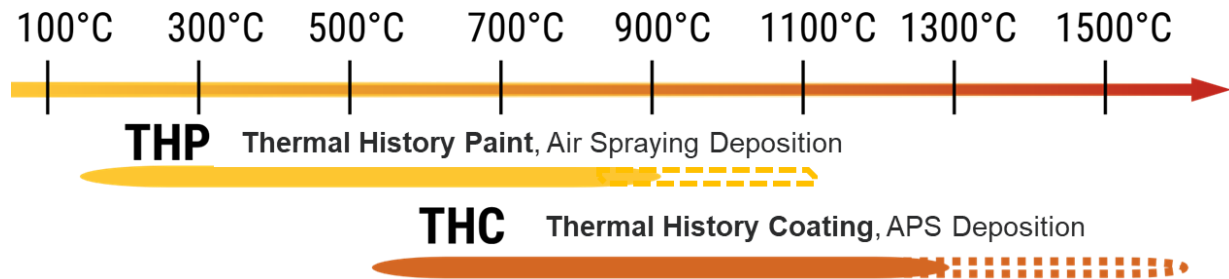


Figure 3.5 Temperature diagram showing the range of use for current thermal history technologies according to the deposition technique employed. Thermal History Paint (THP) are applied by conventional air spraying, while Thermal History Coatings (THC) are applied by Atmospheric Plasma Spray (APS).

Several deposition techniques were considered for the application of thermal history paints, prior dispersion of the phosphorescent pigment into a liquid binder. Among the methods examined, spraying/gunning of the liquid solution, pouring and drying on a surface, as well as the use of caulking guns were down selected. Moulding, paint brushing, paint rolling and other Do-It-Yourself (DIY) solutions, such as the use of trowel and spatula on cement type materials were discarded due to the high viscosity needed in the final product, which could also require a relatively high application thickness. Thin phosphorescent paint layers are critical to control the amount of phosphor deposited on a given surface, as well as to avoid thermal gradients. Therefore, the paint thickness should be controlled during application of the paint, as well as, before and after operation of the component in turbomachinery conditions. Some of the methods suggested for the control of the thickness are interferometry or eddy-current gauges, which will be further considered in the following chapter.

The complex shape of turbomachinery components remains a challenge even for professional painters, especially if a low-thickness layer is required all-over the surface of the component. To maximise the control over the deposited layer, air-gun-spraying was the chosen technique for the deposition of thermal history paints. Conventional air spray guns allow control over the amount of paint projected to the component, as well as over the air flow used to atomize the paint. These characteristics make spraying the ideal method to obtain thin luminescent layers, while minimising errors from the operator.

3.3.2.2 Review of high temperature binders

Once air spraying was selected as the most promising deposition technique, a liquid solution must be identified to contain the luminescent pigment, spreading the paint over the surface of interest, while withstanding high operation temperatures. The ideal binder should have good adhesion on a substrate, while remaining inert. Chemical interaction between the pigment and the binder, or between the binder and the substrate, are not desired since it can affect the temperature sensing capabilities of the phosphor embedded within.

The first use of binders for the embodiment of a ceramic phosphor was described by Allison *et al.* [284]. YAG: Eu was mixed into several high temperature binders and tested on aeronautical grade nickel alloy substrates. The evaluated binders were commercial products provided by Zyp Coatings Inc. [285], VHT [286] and Sauereisen [287]. Some of the produced paints peeled off the substrate and turned chalky after thermal exposure at 800 °C. Only one of the tests provided acceptable adhesion, a mix of Zyp Coating products, containing 50 % Magnesium-aluminium silicate (HPC) and 50 % Lithium-potassium-silicon oxide (LK). The evaluated binders were exposed to temperature and cooled down slowly to avoid thermal shocks, which is not always the case in turbomachinery components.

Goedeke *et al.* [288] experimented with Zyp Coating mixes and Cotronics Corp. [289] products as well. These showed good survivability for temperatures up to 1,500 °C, under similar thermal cycles to the ones applied by Allison *et al.* [284]. The authors also reported a reduction on the luminescence intensity under increasing cycling temperatures. Similar remarks have been described by Bergeron *et al.* [290], whose investigation focused on Cotronics Corp. products. Unfortunately, no explanation was provided for the intensity degradation observed.

The attenuation of luminescence intensity has been related to the irreversible changes experienced by the paint in each thermal cycle [104]. The exposure to high temperatures affects the paint through changes happening in the operating atmosphere and the substrate. For instance, glassy binders are mainly transparent, and could reflect the oxidation of the metallic substrate underneath. If the binder becomes less transparent, the emission by the phosphor contained within is expected to lower as well. Degradation of the metal surface at high temperatures, i.e., high temperature corrosion, is also a contributing factor to the darkening of the metal surface, which can affect the emission of a phosphor applied on top.

If the produced paints are subjected to thermal shocks, the attachment of the paint layer to the substrate is greatly affected. High temperature binders are based in glass-ceramic materials with a low expansion coefficients, in the order of $10^{-7} \text{ (}^\circ\text{C)}^{-1}$, while typical metal alloys acting as a substrate have slightly higher values, in the order of $10^{-5} \text{ (}^\circ\text{C)}^{-1}$ for steel, copper or nickel alloys [291]. This mismatch between the expansion coefficients can lead to poor adhesion of the paint to metallic substrates at high temperatures. This situation can be aggravated by the oxidation of the metal. Thermal expansions and tensions created during the growth of the oxide layer, can affect the paint layer applied on top, particularly if the metallic component has a complex shape.

Paints based on Zyp Coatings products have been reported to have 40 to 60 % open porosity [117], which might influence the interaction between the pigment and the binder, particularly at high temperatures. Feist [110] experimented brushing mixtures of Zyp Coatings Inc. binders, reporting poor adhesion and poor high temperature resistance, particularly to thermal cycling. The requirements on high temperature binders focused on products able to withstand thermal shocks, as thermal history paints might face in real applications. In this regard, Rabhiou suggested several luminescent paints [104], which could be sprayed with a conventional air gun. In his investigation, the phosphor $\text{Y}_2\text{SiO}_5:\text{Tb}^{3+}$ was mixed in products by Zyp Coatings Inc. and Cotronics Corp. binders. The produced paints displayed very weak emission at all wavelengths and the obtained measurements did not show regular intensities, which could be exploited for thermal sensing purposes. The commercial names of the tested binders and other details found in the literature, are displayed in **Table 3.6** below.

Table 3.6 Review of binders evaluated for use in thermal history paints.

Provider Company	Commercial Name	Composition	Max. working temperature (°C)	References
Saureisen	Thinning Liquid # 14	Sodium silicate	1,200	[284,287]
Zyp Coatings Inc.	HPC	Magnesium-aluminium silicate	1,500	[104,285]
	LRC	Aluminium oxide	1,900	
	LK	Lithium-potassium-silicon oxide	1,100	[284]
	BNSL	Glassy carbon / Aluminium silicate	1,600	
	ZAP	Phosphor and aluminium oxide	1,800	[292]
Cotronics Corp,	Resbond 791	Silicate glass	1,650	[284,288,290]
	Resbond 792	Silicate glass	1,650	
	Resbond 793	Silicate oxide	1,760	
Indestructible Paint Ltd.	IP66	Potassium silicate	900	[106,117]

Indestructible Paint Ltd. [293] supplies the branded product IP66, a potassium silicate solution, based on the Kasil 66 solution offered by PQ Corporation [294]. This product has been tested extensively in the thesis by Araguas-Rodriguez [106], and it is used regularly in commercial thermal history paints produced by Sensor Coating Systems Ltd. [105]. The phase diagram of the system $\text{K}_2\text{O}-\text{SiO}_2$ is shown in **Figure 3.6**, where the composition of the binder was identified by Araguas-Rodriguez as $0.55 \pm 0.03 \text{ SiO}_2$ molar fraction, which falls between the phases $\text{K}_2\text{Si}_2\text{O}_5$ and $\text{K}_2\text{Si}_4\text{O}_9$ in the diagram, both exhibiting partial melting above 741 °C.

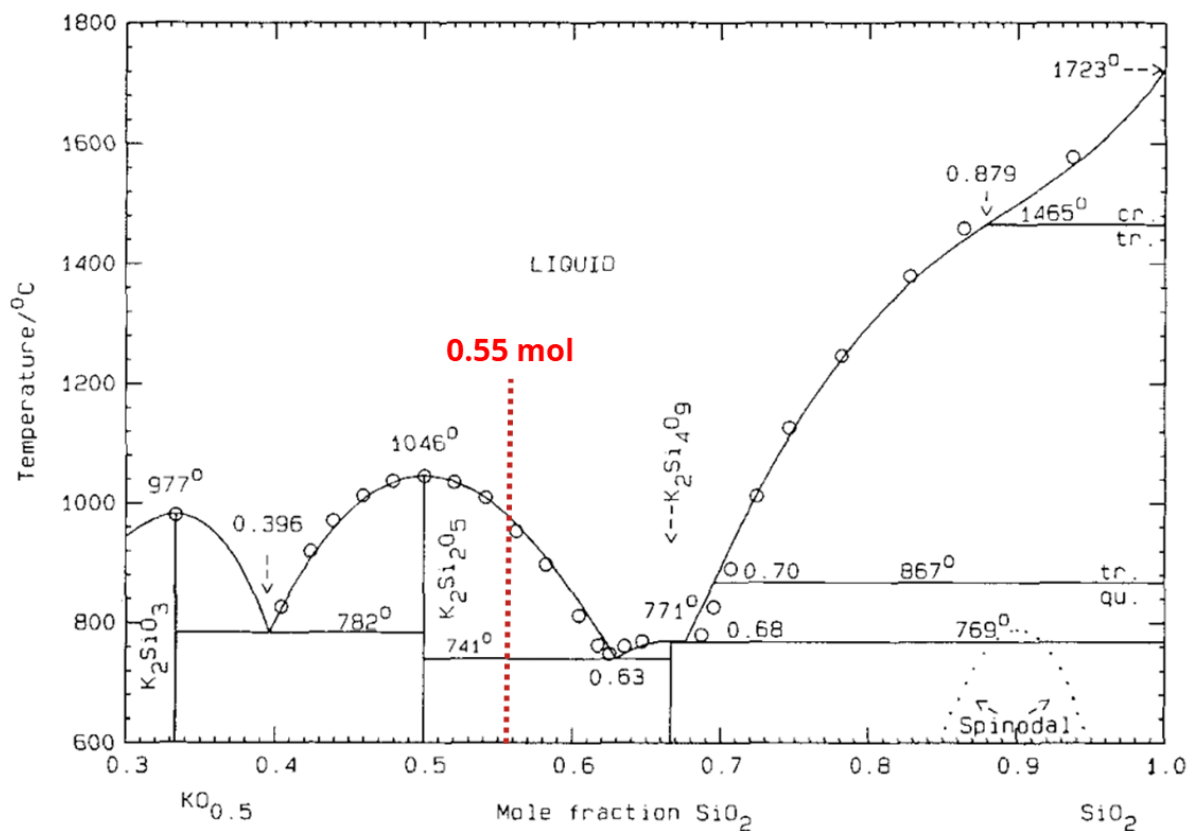


Figure 3.6 Phase diagram of the SiO_2 and K_2O , extracted with permission from [323]. Composition of the potassium silicate binder used in this investigation indicated with a red dotted line.

The luminescent measurements obtained from multiple phosphors embedded within this potassium silicate binder showed good emission intensities up to 900 $^{\circ}\text{C}$ and linear, monotonic trends for lifetime decay readings at different temperatures. The adhesion of the produced paints with this binder also resulted satisfactory, according to the internal results obtained at Sensor Coating Systems Ltd. [105]. Therefore, this binder was suggested as starting point and reference in this thesis, and it will be retaken under *Chapter 5, Results*.

3.4 Conclusions on thermal history sensors

- Among the thermal history mechanisms described in the literature *amorphous-to-crystalline* shows greater potential as it has been tested extensively in the literature. Synthesis and deposition methods for particular phosphors are discussed, since the methods employed may limit the temperature sensing range. **Sol-gel** was concluded to be the ideal manufacturing technique for this kind of mechanism, as well as being low cost and customizable to the process temperature and phosphor employed.
- The low temperature phase of **Yttrium Orthosilicate**, Y_2SO_5 , could be exploited for thermal sensing purposes, as it is a host structure susceptible for doping with multiple luminescent ions. The X1 phase of Y_2SO_5 , present at temperatures below 1,250 °C, allows for amorphous-to-crystalline transition so that the thermal history can be obtained through luminescent methods, typically spectral or temporal.
- **Europium** was identified as the most promising dopant, as excitation and emissions of this element are normally in the visible range. Eu^{+3} has been extensively studied in the literature, showing distinct luminescent peaks for a wide temperature range. Other parameters, such as lifetime decay, can be exploited within Y_2SiO_5 for an amorphous to crystalline thermal sensing mechanism.
- The embodiment of the phosphor into a **paint** was considered the preferred route for the manufacturing of a low temperature sensor. The ceramic phosphor can be dispersed in a liquid solution while still in an amorphous state, so that the phosphor could crystallize in a gradual manner once deposited on a surface. **Air spraying** was identified as the most promising deposition method, since it allows for application of thermal history paints at room temperature, controlling the deposited thickness, which is an advantage when compared to other deposition techniques.
- Among the liquid carriers or binders reviewed in the literature, potassium silicate has been tested and employed in the past and will be among the high temperature products tested under this investigation.

4 Materials and methods

In this chapter, methods, materials, and instrumentation relevant to the development of this work are discussed. Firstly, the manufacturing of Thermal History Paint (THP) is explored, followed by the description of the heat treatment methods, and employed equipment. Then, luminescence-based characterisation methods are briefly introduced, as well as other materials characterization techniques used during this investigation.

4.1 Thermal History Paint

As seen in previous chapters, Thermal History Paints (THP's) were developed to obtain thermal profiles on surfaces of interest, applying phosphorescent temperature sensors embedded in a paint layer. These temperature sensors must withstand the exposure temperatures, with a reliable bonding to the substrate, while enabling the phosphor particles to receive and emit light.

4.1.1 Production of luminescent pigment

Phosphorescent compounds that could be used as a pigment have been reviewed in *Chapter 3*. The compound $(\text{Eu}_x\text{Y}_{1-x})_2\text{SiO}_5$ was selected as the best available thermal history pigment, as seen in previous investigations of thermal history sensors [104,106]. This orthosilicate can be produced in a number of ways. Given the potential use of this pigment in industrial applications, low cost and repeatable manufacturing processes were preferred. The synthesis route chosen to produce this phosphor was sol-gel, as several sol-gel procedures at room temperature were reported in literature [197,295,296]. The steps adopted to produce 50 g of $(\text{Eu}_{0.16}\text{Y}_{0.84})_2\text{SiO}_5$ are shown in **Table 4.1** below.

Table 4.1 Summary of constituents, quantities, and time of mixing for the synthesis of 50g of $(\text{Eu}_{0.16}\text{Y}_{0.84})_2\text{SiO}_5$

Step	Compound	Mol	Mass (g)	Volume (ml)	Time mixing with previous compounds
1	Yttrium nitrate $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0.41	154.4	-	
2	Water H_2O	2.78	-	50	10 minutes
3	Europium nitrate $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0.07	34.3	-	
4	Water H_2O	2.78	-	50	10 minutes
5	Ethanol $\text{C}_2\text{H}_5\text{O}$	4.79	-	281.6	20 minutes
6	TEOS $\text{Si}(\text{OC}_2\text{H}_5)_4$	0.24	-	54.6	
FINAL	Europium doped yttrium orthosilicate $(\text{Eu}_{0.16}\text{Y}_{0.84})_2\text{SiO}_5$		50		48 hours

Yttrium nitrate hexahydrate, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (Alpha Aesar, 99.9% purity) and europium nitrate Hexahydrate, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (VWR International Ltd. 99.9% purity) were used as precursors. Tetra-ethyl-ortho-silicate, (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Merck), was used as silicon source, while ethanol, $\text{C}_2\text{H}_6\text{O}$, (VWR International Ltd., 99.8% absolute) was used as solvent. Yttrium and europium nitrates were dissolved in 50 ml of de-ionized water (VWR International Ltd.) and stirred at room temperature for 10 minutes each, in consecutive steps. Ethanol was added to the solution and mixed for further 20 minutes. Lastly, the TEOS was added in small amounts every 20 seconds. The resulting clear solution was mixed with a magnetic stirrer in air at room temperature until a clear gel was formed. This gelation process lasted around 48 hours for the quantities reported in **Table 4.1**, without using catalysts or increasing the temperature of the reaction. The gel was dried in a decomposition oven (Elite BAF6/18, Elite Thermal Systems Ltd.) at 250 °C for 12 hours, given the volatilization of the species from the Ethanol and the other precursors. Depending on the application, subsequent heat treatments were carried out in the same decomposition furnace, typically up to 400 °C and/or 600 °C, or in tube furnaces for higher temperatures.

4.1.2 Production of thermal history paint

The production of the thermal history paints involved the mixing of phosphor particles in a liquid binder or carrier. Traditionally, chemical binders have been explored, given their adhesive properties, their ability to bind particles and remain attached to surfaces. However, THP's have more demanding thermal requirements, and chemical binders with high melting temperatures were preferably considered. Products such as water-based silicates, inorganic colloidal suspensions, and water -mix refractories were examined for this investigation.

Thermal history paints examined in this investigation were mixed using an overhead stirrer (IKA, Eurostar) equipped with a metallic propeller. 2.5 g of pigment powder were prepared by manual grinding with pestle and mortar and subsequently mixing with 6 g of deionized water with 60 g of mixing media. This method ensured the adequate mixing and grinding of the pigment particles, creating a uniform pigment suspension in the liquid carrier. The selected mixing media were 2 mm diameter zirconia beads. The pigment, the beads and water were stirred for 10 minutes at 250 rpm. In a separate beaker, 47 g of binder were measured. The metallic propeller stirred the solution at a low speed, 100 rpm, while the water and pigment mixture were slowly incorporated into the binder beaker. The final ratio of pigment to binder was 5 % of the total weight of the paint batch, not considering the zirconia beads or the water as active compounds of the paint. Once the total amount of pigment and water was completely incorporated into the binder, the propeller speed was increased to 450 rpm. The mixture was stirred for 45 minutes, followed by 180 seconds of ultrasonication, in order to break any remaining agglomerates. This procedure yielded a low-viscosity white dispersion of phosphorescent pigment, suitable for application as a conventional paint. The zirconia beads remain embedded in the solution, only to be filtered out before paint spraying.

2125

4.1.3 Deposition of thermal history paint

4.1.3.1 Surface preparation and adherence

2130

As a standard metallic substrate, stainless-steel 316L was employed for the deposition of THP, either on test bars, 400 x 20 x 3 mm, and tiles, 20 x 10 x 3 mm (both issued from SOG Ltd., material certificate included in the *Appendix*). Other substrates such as nickel super-alloys, alumina tiles, or sapphire discs (12.5 mm diameter, 0.6 mm thickness, SAPPH-WIND-0139, Pi-Kem) were employed for experiments at temperatures above 900 °C, discussed in *Chapter 5*.

2135

All surfaces were prepared prior to paint application, by sandblasting to remove all scales, oil, and dirt, and to obtain a uniform surface roughness, between 2 and 2.5 μm Ra. A Euro blast 6SF Grit Blaster Yr. 2016 (Ser No. 508976, Gyson International Ltd.), was used for the surface preparation. Saftgrit white blasting media was employed, with a grit size ranging from 120 to 220 μm . A nozzle of 1 cm inner diameter was employed, with a projection pressure of 40 psi (2.75 bars). Finally, a cloth with acetone (VWR International Ltd, Ref No. 20065.293) was used to clean the grit-blasted surfaces removing any residual contamination.

2140

4.1.3.2 Atomization and spraying

2145

THP paint layers were applied with a High Volume Low Pressure (HVLP) air spray gun (Sri Pro gravity fed, DeVilbiss, Carlisle Fluid Technologies [297]). Compressed air was used for the atomization of the paint, which was fed to the gun through a gravity cup. Paint and pressurized air were introduced into the gun via independent circuits. These merge at the front-end of the gun, where the paint was atomised and projected forward. A schematic of this is shown in **Figure 4.1** below.

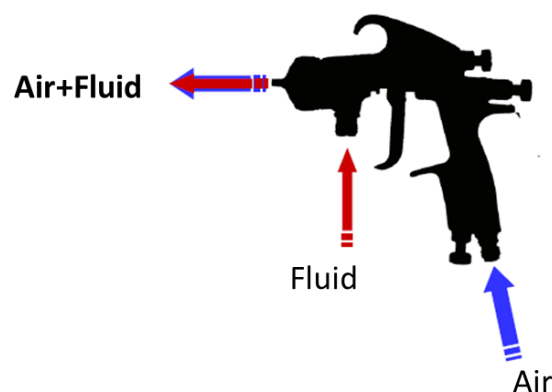


Figure 4.1 Schematic of a functioning air spray gun, where independent circuits of fluid and pressurized air are marked in red and blue, respectively.

2150

4.1.3.3 Dry film thickness determination

During the painting process, the thickness of the paint was monitored using an eddy current gauge (Elcometer 456 FNFSS Coating Thickness Gauge, Elcometer Ltd.). This gauge included a coil probe, which created a magnetic field and therefore eddy currents in the metallic substrate. These eddy currents created magnetic fields as well, which in turn changed the electrical impedance of the coil. This allowed to determine the paint thickness once the probe was calibrated on a bare metallic surface.

The paint was sprayed for several layers, allowing drying between steps. The wet thickness, measured immediately after painting, was recorded up to a target thickness of at least 40.0 μm , according to the accuracy of the instrument. After drying in air for at least one hour, the painted substrates were subjected to a heat treatment of 150 $^{\circ}\text{C}$ for one hour in a conventional electric oven (Elite GPO 300/240, Elite Thermal Systems Ltd.). The oven was pre-heat treated to the target temperature, and subsequently the samples were introduced for the desired heat-treatment time. This curing process removed trapped water between the paint layers and allowed the structure of the paint to rearrange. The target dry thickness at this stage was 30.0 μm , measured after extraction and cooling in ambient conditions. Other thickness measurement techniques considered by other authors [117], such as interferometry, were not tested in this thesis.

4.2 Heat treatment

4.2.1 Isothermal heat treatment

The luminescent thermal history of painted samples with THP was investigated after heat treatment in air. Pigment and paint samples were isothermally heat treated to determine the evolution of the luminescent properties at different temperature. To this end, two tube furnace types were used, an Elite THS12 for temperatures up to 1,200 $^{\circ}\text{C}$ and an Elite TSH15 for temperatures up to 1,500 $^{\circ}\text{C}$.

4.2.2 Furnace calibration

The tube furnaces used during this thesis displayed differences between the temperature set in the controller of the furnace and the temperature finally obtained during the heat treatment. Therefore, a calibration of the tube furnaces was performed. N-type thermocouples (TC Direct, Product number 405-231) in the centre of the working tube were placed in the centre of the tube. The temperature of the furnace was set to different values between 250 $^{\circ}\text{C}$ and 1,150 $^{\circ}\text{C}$ for the THS12 and between 600 $^{\circ}\text{C}$ and 1,250 $^{\circ}\text{C}$ for the THS15. The temperature was allowed to settle at every step for more than half an hour, and eventually, recorded. The temperature was considered stable when the recorded temperature oscillated ± 1 $^{\circ}\text{C}$ of the target temperature. The calibrations for both furnaces are shown in **Figure 4.2**. The relationship between the target temperature and the temperature set in both furnaces show a clear linear trend. This relationship was used to control the furnace and ensure accurate target temperatures.

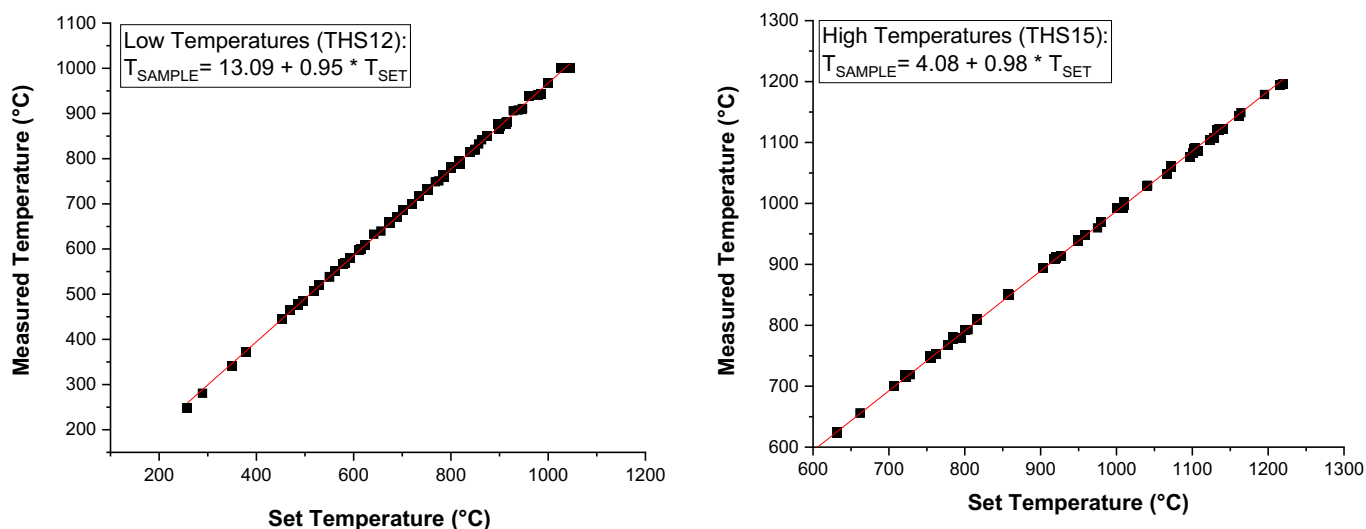


Figure 4.2 Tube furnace calibration of achieved temperature on a sample, as function of the temperature set in the furnace, between 250 °C and 1,150 °C, in an Elite THS12 (Left), and between 600 °C and 1,250 °C in an Elite THS15 (Right). Linear fits and equations included.

4.2.3 Sample heat treatment

Both powder samples and painted metallic substrates were heat treated in one of the two types of tube furnaces described before. The procedure involved introducing the sample through one of the extremes of the tube either on a ceramic or a metallic boat. The tube furnaces were set to the desired temperature and allowed to reach a steady state. After stabilization, the samples were fed into the tube furnace, where an N-type thermocouple was placed in the tube alongside the sample, monitoring the temperature of the sample in-situ. The thermocouple was in contact with the sample. Once the sample was located in the middle, isothermal, section of the working tube, the heat treatment was considered started after the sample reached 98 % of the target temperature. The standard heat treatment time was 30 minutes. Once the time at the desired temperature was completed, the sample was removed from the furnace and allowed to cool outside the furnace.

4.2.4 Bar heat treatment

Bar calibration tests were used to evaluate paints over a surface for a broad temperature range in a single experiment. Bars of stainless-steel 316L, certified by Shanxi Taiyan Stainless Steel Co. Ltd., in 2018, and Marcegaglia Specialties, in 2019, were manufactured to dimensions 400 x 20 x 3mm, and inserted in the tube furnace Elite THS12. A technical drawing of the bar is shown in **Figure 4.3**.

2240

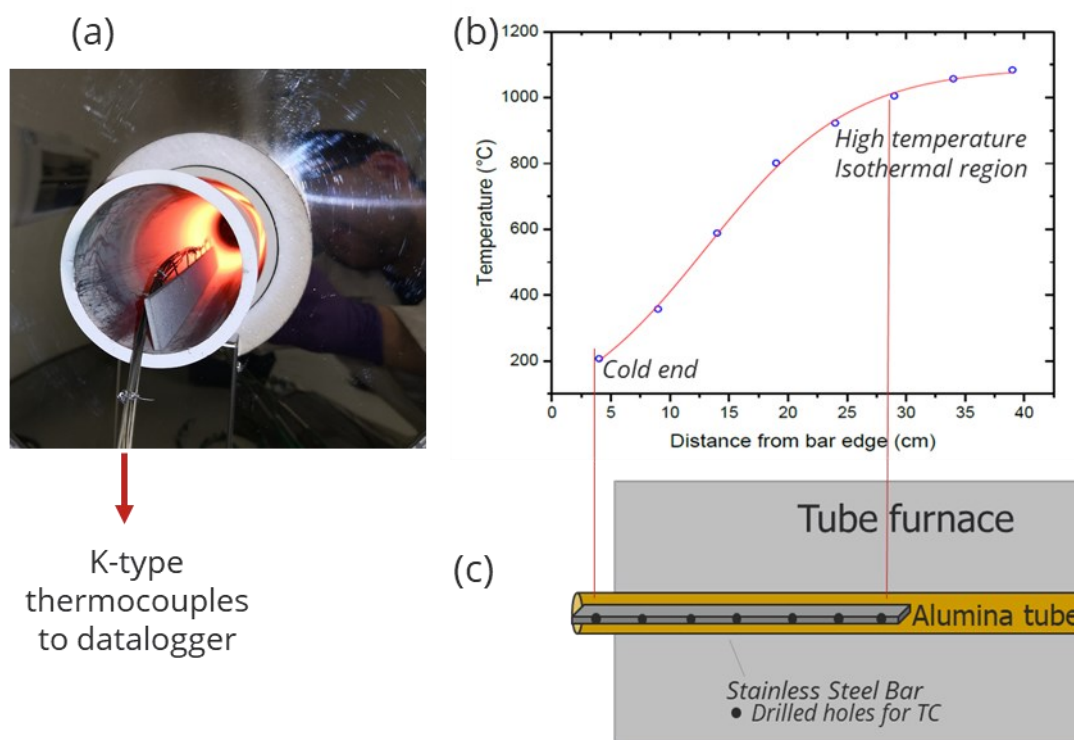


Figure 4.4 (a) Picture of a stainless-steel bar during heat treatment on tube furnace. K-type thermocouples inserted along the side of the bar. (b) Temperature gradient along length of the bar following a sigmoidal distribution, fitted with a continuous line around temperature data points. (c) Schematic of bar introduced in the tube furnace from the cold end at the extreme of the tube up to the isothermal region in the centre.

2245

Any given location of the bar can then be correlated to the maximum temperature previously exposed to. The heat treatment of the bar was considered started once the bar was inserted into the furnace, and the thermocouple in the hottest extreme, centre of the furnace, reached 98 % of the expected maximum temperature. Then the timer for the heat treatment was started, for a standard time of 30 minutes.

2250

4.3 Luminescence measurements

A typical set-up to measure luminescent properties of powder, coating or paint samples comprises of an excitation source, optics to direct the light to the phosphor material and a second set of optics to guide the emitted luminescence to an optical detector, which is normally connected to a data acquisition card and this to a computer. Two variations of this overall configuration were used to capture luminescence as temporal and spectral responses, always considering point measurements over the surface of phosphorescent materials.

2260

4.3.1 Spectral response

2265 An alternative measurement technique records the emission spectrum rather than the decay time of the phosphorescent sample. A schematic setup is shown in **Figure 4.5**. The SCS instrumentation device and the optical fibre bundle were used to lead the excitation light to the sample as in the long lifetime decay case.

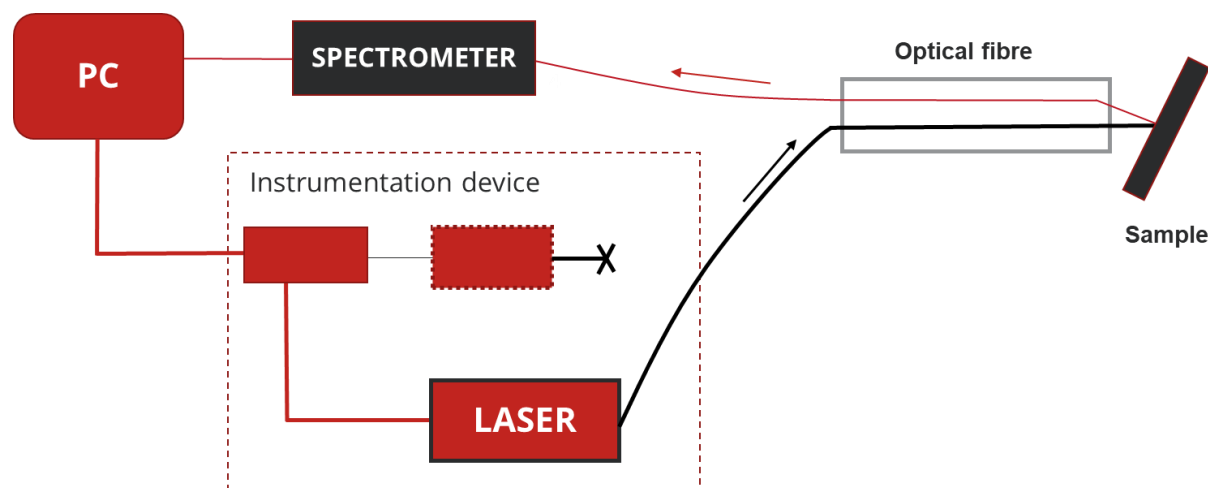


Figure 4.5 Schematic of SCS instrumentation set-up to measure spectral features of phosphor emissions

The difference between this set up and that for the lifetime decay is the collection of the phosphorescent emission. The optical fibre bundle was connected to an AVANTES Spectrometer (AVASPEC-
2275 ULS4096CL-EVO-RS). The emitted spectra were digitised and sent to a computer which also controlled the laser in the SCS instrumentation device. The obtained wavelength range was between 200 and 1,100 nm. The phosphorescent emission has a different wavelength to the excitation light; however, the wavelength collection was cut-off for 550 nm of lower emissions to block the laser wavelength (532 nm) entering the spectrometer.

2280 This *AvaSpec* spectrometer included an optical bench developed in a symmetrical Czerny-Turner design. The light entered the optical bench through a standard SMA-904 connector, and it was collimated by a spherical mirror. A plain grating diffracted the collimated light and second spherical mirror focused the resulting diffracted light, projecting it onto a 1-dimensional linear detector array [298]. A schematic of the functioning of a Czerny-Turner spectrometer is shown in **Figure 4.6**.



- | | |
|------------------------|--------------------|
| 1. Detector | 7. Focusing mirror |
| 2. SMA Connector | 8. CPC light traps |
| 3. Grating | 9. CPC light traps |
| 4. Slit, mode stripper | 10. DCL-UV/VIS |
| 5. 2nd mode stripper | 11. OSC-filter |
| 6. Collimating mirror | |

Figure 4.6 Schematic of an AVANTES Avaspec-ULS optical bench design, including a symmetrical Czerny-Turner spectrometer, extracted with permission from AVANTES Catalog X [298].

The entrance slit, $10\mu\text{m}$, was selected for a high resolution in combination with the grating of 600 lines/mm and the CMOS detector with 4,096 pixels. The final resolution in the obtained spectra was less than 1 nm, which is lower than expected in the crystal field of the host material. The exposure time of the CMOS array was programmable and set depending on the sample under investigation, which guaranteed the repeatability of the spectral measurements obtained for the same maximum intensity detected. In all cases background subtraction was performed in post-processing, in order to remove extraneous light from the obtained spectra. All luminescent spectra shown in this thesis are the average of three intensity values per emission wavelength, which were checked within the sample itself, or with similar samples, i.e., samples heat treated at the same temperature.

4.3.2 Temporal response

As seen in the *Chapter 2*, the phosphorescent emission decay time can give information on past temperatures of a luminescent material. Furthermore, it has the advantage of being less sensitive to low intensity emissions [299]. In this thesis, the decaying emission intensity with time was reduced to a mono-exponential function. This is a simplification since luminescent ions such as europium can often emit multi-exponential decays. The original decay curves, for potential post-processing, were obtained for all measurements taken and examined further if considered necessary. This simplification depends on the acquisition conditions and receives some research attention in the field of phosphor thermometry [76,300]. Two set-ups were used during in this thesis, one for long lifetime decay emissions and one for short lifetime decays.

4.3.2.1 Set-up for long lifetime decays

A schematic of the instrumentation to obtain long lifetime decays is shown in **Figure 4.7** and it is briefly described below.

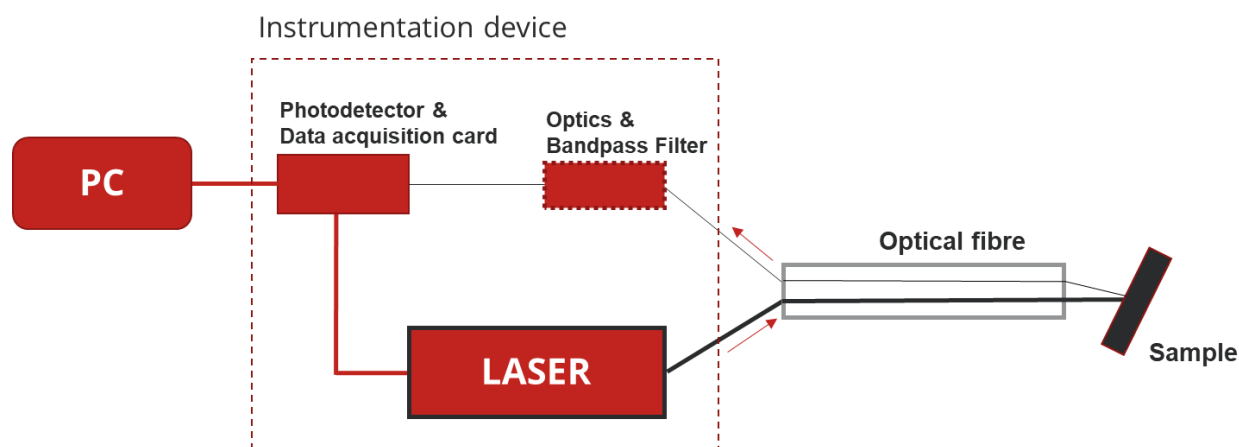


Figure 4.7 Schematic of SCS instrumentation device to measure long lifetime decay phosphor emissions.

The measurement device included a light source, a Diode-Pumped Solid State (DPSS) laser emitting at 532 nm in a pulsed mode. The maximum operation output was 250mW. The laser light was directed towards the sample surface with a probe at the end of an optical fibre bundle. The light illuminated the surface of the sample, exciting the phosphor, which resulted in luminescence emission. The emitted light was collected by the optical fibre, which was custom designed to deliver the laser light to the sample and collect the emitted light back to the device. Once the light travelled from the sample, through the optic fibre bundle, back to the device, it passed several optical filters before reaching the detector, a silicon photomultiplier. Complete details on the instrumentation used in this work cannot be disclosed for the sake of confidentiality.

The first bandpass filter selected the light-wavelength range for investigation. This depended on the material under study. The standard filter used for investigation of standard thermal history paint was centred at 620 nm, with the bandpass collecting 52 nm of the optical spectrum around the centre. The filtered light then went through a series of optics, in order to modulate the intensity of the light. When the light finally reached the silicon photomultiplier, it was converted to an electric signal and amplified. This signal was then digitised and sent to a PC via a data acquisition card. This allowed the manipulation of the data with the adequate software. The obtained decay curves comprised more than 7,000 intensity points each, recorded at a sample rate of 400 kHz. The window span considered for the fitting was fixed at 16,000 μ s, which was estimated to be between 6 and 16 times the length of the decay parameter, τ . This optimal size of the window was explored with Montecarlo simulations by Dowell and Gilles [301].

Lifetime decay (τ) is defined as the time taken from the emission intensity (I) to decrease $1/e$ of the initial intensity (I_0). The discrete data recorded during the decay of the phosphor emission is normally fitted to a single exponential by using the non-linear least squares Levenberg-Marquardt algorithm [302], as exemplified in **Figure 4.8**. Theoretically, τ is independent of the initial intensity (I_0), as it constitutes a

relative decrease in intensity. However, due to instrumentation signal distortions such as the non-linearity of the detector, this independence is not guaranteed in the instrumentation set-up used in this investigation. Other effects, such as the number of repeats, have been explored in publications associated with this research [210] and will be discussed further when considering specific results.

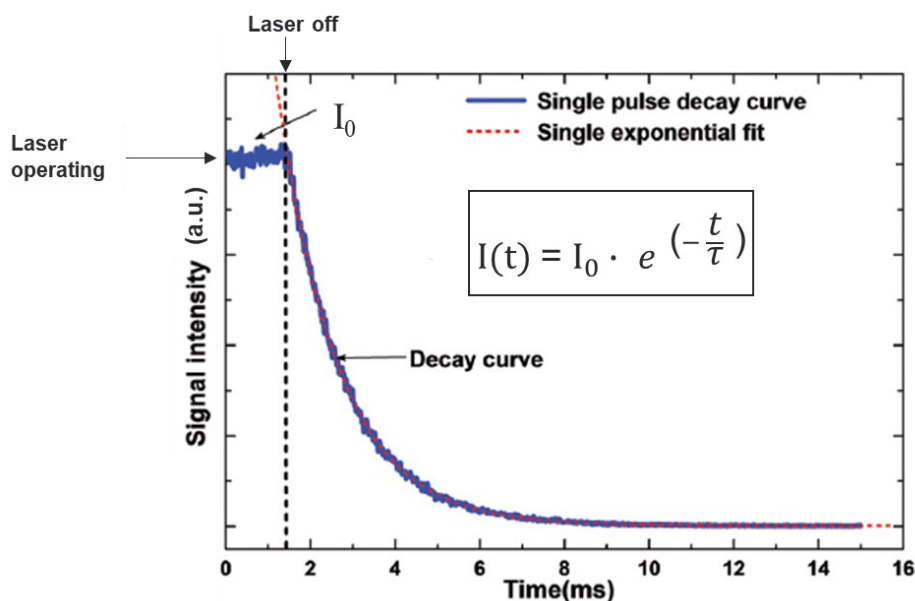


Figure 4.8 Example of single exponential decay of thermal history paint measured with SCS Ltd. instrumentation device. The intensity (I) decreases from the initial intensity (I_0).

4.3.2.2 Set-up for short lifetime decays

A schematic of a more complex set-up for short lifetime decay measurements is shown in **Figure 4.9** below. This same system was employed by Pilgrim [115], including the Optical Energy Transfer System (OPETS), which allows for a certain angle and distance flexibility when the emitted light from the sample reached the first optics. This system also ensured a uniform observation volume, collecting light and coupling it into an optical fibre bundle. This was a non-imaging probe, with an opening of 23 mm, including a high pass filter with a cut-off wavelength of 405 nm to block UV light.

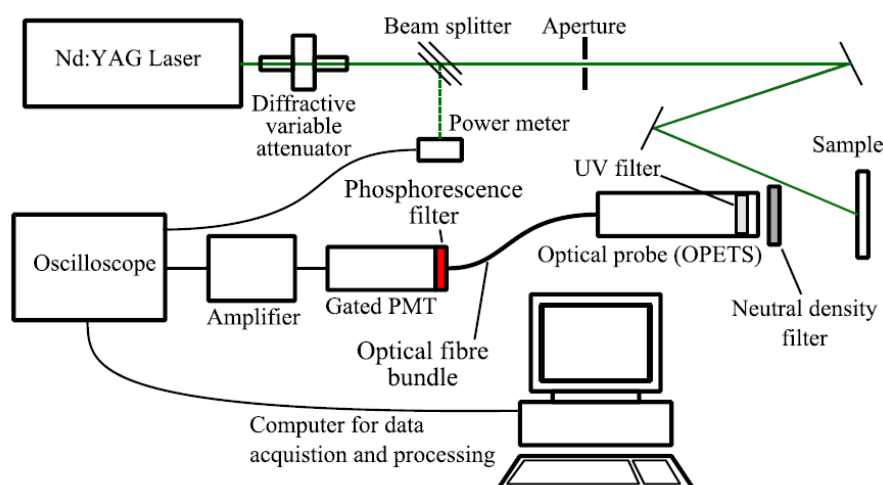


Figure 4.9 Schematic of instrumentation set-up to measure short lifetime decays phosphor emissions, extracted from [115] with permission via CC-BY-NC-ND 3.0.

The laser used was a YAG: Nd Quantel Brilliant B, from Quantel Laser. The laser light passed through a Diffractive Variable Attenuator (DVA, CLWS300IAE, Micron Co.), a beam splitter and an aperture. The laser was operated in a pulse mode with a flashlamp / Q-switch delay setting at or below 330 μs . The output laser wavelength was 532 nm, as in the previous lifetime decay set-up. The DVA was used to manually set the final intensity impinging on the sample. Once the emission from the sample was detected, the DVA allowed a fine control of the signal intensity, between 98 % and 100 % of the dynamic range of the oscilloscope, right from the excitation source.

Then, the light was directed towards the sample using wavelength selective mirrors. The phosphorescence was delivered through the optical fibre bundle to a Photo-Multiplier Tube (PMT). This had a gate function to switch it on and off (H10304, Hamamatsu Photonics), for the duration of the laser pulse, avoiding laser light reflection artefacts. The output voltage of the PMT was kept below 45 mV, using a set of Neutral density filters to attenuate between 0.01 % and 93 % of the light transmission. This PMT converted the phosphorescence light into an electrical signal, which was amplified and passed to an oscilloscope (MDO3034 Tektronix) where it was digitised. All lifetime decay data were recorded using the same digitisation settings, showing differences of less than 1 % between identical decay measurements. The resultant data was analysed in a commercial data processing software (OriginPro2020, Origin Lab). An example of the data analysis performed on the decay curves obtained from the PMT is shown in **Figure 4.10**.

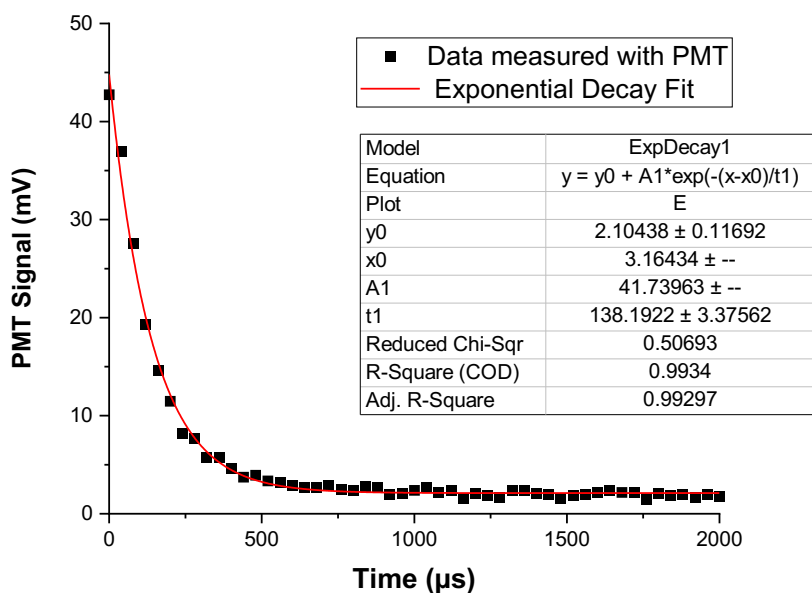


Figure 4.10 Example of single exponential of YSO: Eu measured with instrumentation set-up for short lifetime decays. The fit generated on the experimental data from the algorithm “ExpDecay1” from OriginPro2020

2380

4.4 Material characterization methods

4.4.1 X-Ray Diffraction (XRD)

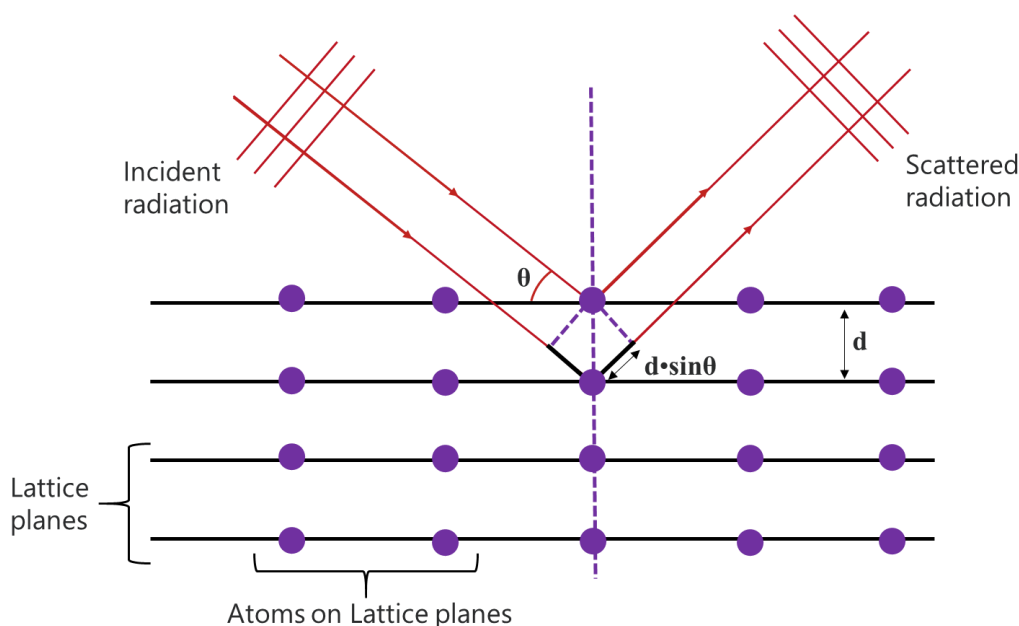
2385

X-Ray Diffraction or XRD is a widely used characterization technique employed for the structural investigation of materials, phase identification and crystallographic analysis [303]. This technique is based on the elastic scattering of X-ray radiation directed to a sample of interest. Bragg's law, describes this scattering process, as shown in **Equation 4.2** below:

$$2 d \sin\theta = n \lambda \quad (4.2)$$

2390

Incident radiation is scattered by the atoms in the crystal lattice planes, which are separated by a regular distance d . The scattered radiation waves will interfere constructively the path between two waves ($2 d \sin\theta$), where θ is the scattering angle. This will enhance the intensity of the scattered radiation, detected at particular integer numbers (n) of the wavelength (λ). This scattering process is schematically represented in **Figure 4.11** below.



2395

Figure 4.11 Bragg diffraction on a crystalline lattice, where X-ray radiation finds the atoms in the lattice, scattering radiation in a particular angle, according to Bragg's law.

2400

When these scattered waves interact constructively, a strong intensity peak is obtained at a particular angle in the diffraction pattern, traditionally represented as an independent variable. This pattern can be related to the atomic and molecular structure of a crystal, allowing the sample identification. While crystalline materials show sharp peaks in the pattern, amorphous materials show broad “humps” due to the irregularity of the d spacing. The crystalline state can be understood as long-range order in the lattice structure, which can be detected via X-ray diffraction, while amorphous state will show short range order at particular points in an overall disordered lattice. This will lead to poor resolution peaks in the pattern, with broad features due to the randomized local order. The transition from broad peaks to sharp features offers the possibility

to study the change from amorphous to crystalline using XRD diffraction patterns, in particular in thermal history sensors, which crystallize in a non-reversible process. Thermal processes will change the structure of the material, and the maximum past temperature unveiled with XRD and luminescence methods.

X-Ray diffractometers generally consists of an X-ray source, a sample holder, and a detector, which collects the scattered X-rays. Source and detector rotate around the sample, collecting intensity at a series of 2θ scanning angles. For this investigation, XRD patterns were collected from powder samples of pigment and dried paint pellets, previously crushed with a mortar. The random orientation of the powder grains guarantees a good coverage of the crystallographic planes. A PANalytical X'Pert diffractometer (MRD with $\text{Cu}\alpha_{1,2}$ -radiation) was used for the pattern collection. The generator settings were 40 mA and 40 kV, and the angular range was between 6° and 90° . The step size in 2θ was 0.042° and the scan step time 112.000 s. The software employed for the pattern fitting was X'Pert High Score Plus, PANalytical B.B.

4.4.2 Fourier Transform Infra-Red (FTIR)

FTIR is a standard characterisation technique, which uses Infra-Red (IR) light and interferometry for identification of materials [304]. The IR beam of light reveals the vibrational frequencies of bonding between atoms, as it passes through a compound. Some of the IR radiation are absorbed, and some are transmitted. The resulting spectrum enables the identification of the chemical structure of the sample. Moreover, the vibrational energies detected by FTIR correspond to the available high phonon energies within the sample.

For this thesis, a NicoletS10 spectrometer, Thermo Fisher, was used to measure the transmittance spectra between 400 and 4,000 ($\times 10^3$) cm^{-1} . The number of scans taken per sample was 32, with a spectral resolution better than 0.4 wavenumber, according to equipment supplier, Thermo Fisher Scientific. A high refractive index crystal was in contact with the sample and reflected the infra-red light in an Attenuated Total Reflectance (ATR) mode. The internal reflectance of the crystal guarantees that an evanescent field enters a few microns into the sample. Therefore, a few milligrams of powder samples were sufficient to cover the high refractive crystal. A schematic of an interferometer for FTIR is shown in **Figure 4.12**.

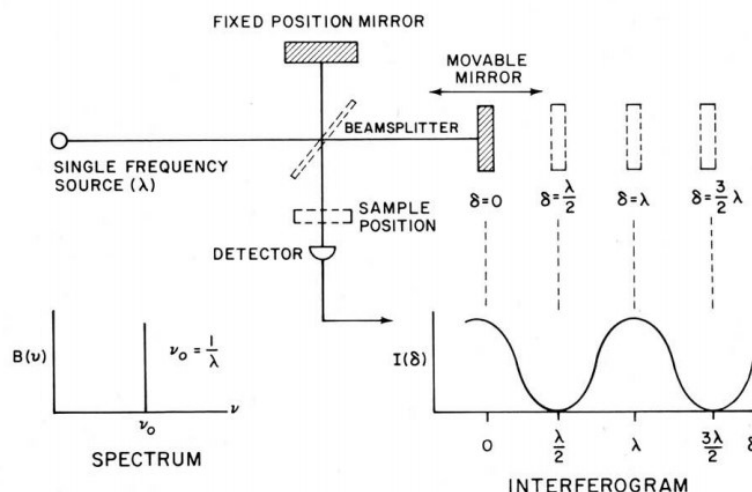


Figure 4.12 Block Diagram of the components of an FT-IR spectrometer. Reprinted with permission from reference [305].

In FTIR, a broad band light is used, which eventually generates the disruption in the evanescent field. The light is split in two paths, one with fixed length and another of adjustable length. After the light finds the sample, it is recombined including constructive and destructive interference. This builds the interferogram, where information on all infrared frequencies is recorded [306]. Using the Fourier Transform, the frequency information can be translated into wavenumbers. Therefore, phonon information from the material was recorded for a range of wavenumbers, between 400 and 4,000 ($\times 10^3$) cm^{-1} , i.e., between 25 and 2.5 nm. A background signal was recorded as well to account for the instrumental absorption. The ratio of the sample signal to the background signal gave the percentage of transmittance with respect to the wavenumber, which was the output of the measurement.

4.4.3 Thermal Analysis (TA)

Thermal Analysis methods are a series of techniques used to reveal the behaviour of materials with temperature. For this thesis, two techniques were simultaneously used, Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA). For both techniques, a pair of crucibles are used. One is left empty as reference, while the material sample under investigation is placed in the other. A heating element is located beneath each crucible, heating both simultaneously, which allows control of the temperature and the heat flow supplied to each of them. DSC measures heat flow variations with temperature, while TGA measures mass changes with temperature. Both methods were recorded with a Netzsch STA 449 F1 Jupiter, Netzsch GmbH. A schematic of a DSC setup is shown in **Figure 4.13**.

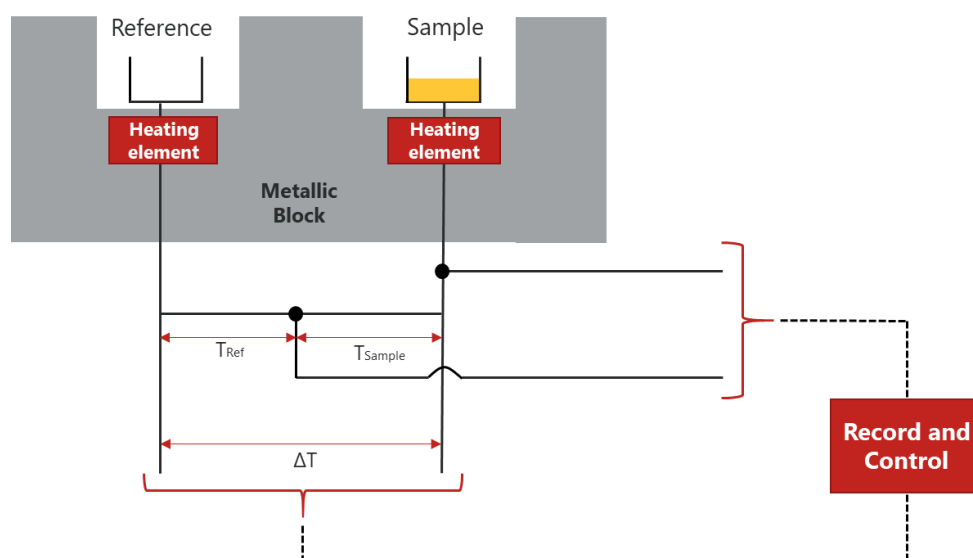


Figure 4.13 Schematic of Differential Scanning Calorimetry setup, adapted from [307], obtained from [308].

Qualitative and quantitative data are obtained from the exothermic and endothermic processes that the sample undergoes with increasing temperature. For instance, DSC measures the amount of energy released or absorbed when the sample is heated. This provides critical information on the properties of the material, such as, melting temperature, heat of reaction, glass transitions or crystalline phase transitions among others [304]. Heat treatments are performed under controlled atmospheres at constant pressures, so that the heat flow can be linked to the enthalpy variation from the sample to the reference. This can be negative or positive depending on the nature of the process. For endothermic processes, the sample will absorb heat with respect to the reference, while the opposite will happen in an exothermic process.

On the other hand, TGA can give information on the weight variation with increasing temperature. This reveals physical phenomena, such as phase changes (vaporization, sublimation) or chemical phenomena (dehydration, decomposition, or oxidation). The instrument heats the sample while continuously measuring the weight of the sample. As the sample increases temperature, mass gain or loss are expected. In conjunction with DSC, the main processes occurring within the material can be quantified and identified.

4.4.1 Scanning Electron Microscopy (SEM)

SEM is a microscopy technique that uses an electron beam at high voltage, under vacuum conditions, to construct images of the surface of samples down to a nanometric resolution. SEM can reveal images to higher resolution than optical microscopes since the reading is not limited by the photon wavelengths in the visible range. The electron beam directs a constant flux of electrons towards the surface of the sample. After hitting the sample, the electrons bounce back in the vacuum chamber, where the electrons are detected. Depending on the angle, energy and origin, electrons undergo several transformations generating different signals. A schematic of the emitted signals is shown on **Figure 4.14**.

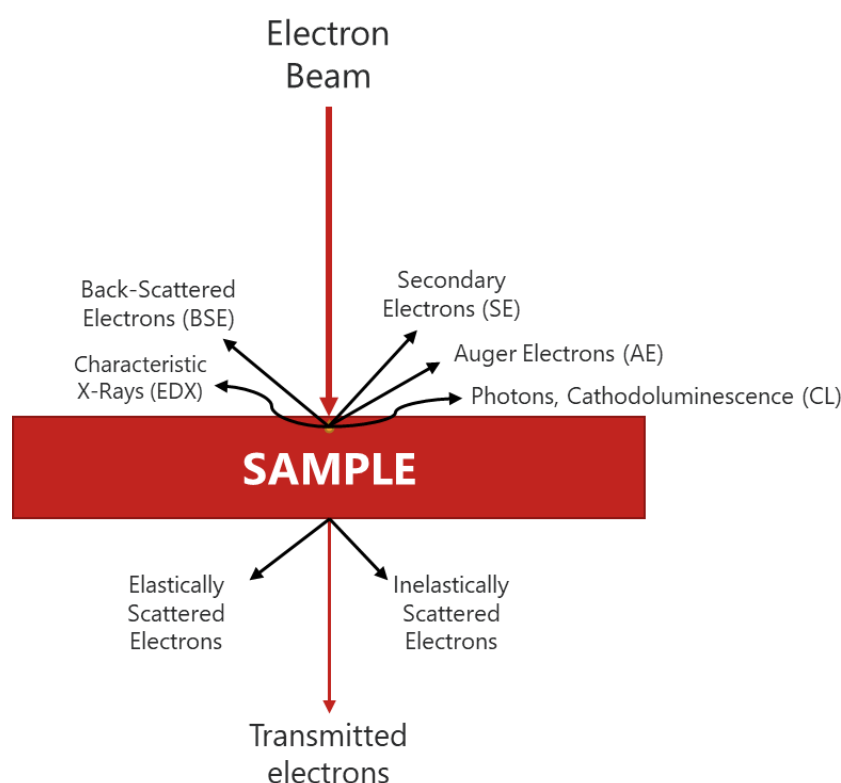


Figure 4.14 Schematic of emitted signals from a sample interrogated with an electron beam. Adapted from [309].

Secondary electrons are generated from inelastic scattering. The intensity is related to the atomic number of the elements in the sample, which provides information about the sample composition. Back-Scattered electrons result from elastic scattering. Their intensity is dependent on the angle of scattering and therefore, the topography of the sample. Characteristic X-rays arise from radiative transitions in the shell of excited atoms in the sample, after interaction with electrons in the beam. These X-rays are characteristic of each element and identify and quantify the composition of the sample under analysis. The study of these X-rays within SEM is called Energy Dispersive X-Ray Spectroscopy (EDX or EDS). A more detailed explanation on EDX and SEM in general can be found in references [309–313].

The SEM used for this investigation was the JEOL JSM 6010 LA, both for topological imaging and elemental analysis. Oxford Instruments INCA software was used for the EDX analysis. Vacuum pressure was below 10^{-5} Torr in all cases, with electron beam voltages between 5 and 20kV. The quality of the SEM images and the EDS analysis depends on the correct preparation of the samples. Cross-sections of painted metallic substrates were prepared for SEM investigation following this procedure. A cold setting resin was used to embody the samples. The substrates were introduced in 25mm ID SamplKups cups (20-9177, Buehler). The remaining volume of the cup was filled with a mix of Epoxy-Cure 2 Resin (20-3430-064, Buehler) and Epoxy-Cure 2 Hardener (20-3432-016, Buehler) in a proportion 4 to 1. Typical quantities used were 20ml and 5ml, respectively. Setting time at ambient temperature for this type of resins was approximately 6 hours. Mould-Release spray was also used on the empty cups prior to use (20-3050-008, Buehler).

Grinding and polishing followed the mounting of the samples in resin. The procedure was similar to the one employed for TBC coatings on metal samples [314]. Firstly, the mounted samples were moved manually over SiC abrasive papers of grades 320, 600, 800 and 1200, with water as lubricant. Secondly, 3 μ m and 1 μ m diamond solutions were used over synthetic cloths. Finally, a submicron colloidal silica water solution was used over a dense cloth. Deionized water was used to clean the surface between steps. Acetone and ethanol were used as a last step to rinse the polished surface and remove all attached dirt. Prior to introduction to the SEM vacuum chamber, a gold layer of tenths of nanometres was sputtered onto the surface of the sample, allowing the characterization of the non-conductive components of the sample. On the other hand, powder samples were prepared by deposition on adhesive carbon fibre. A gold layer was also sputtered on these samples to avoid over charging of the particles.

5 Results: Testing of high temperature materials for thermal history sensing

As successfully demonstrated by Rabhiou [104], Yáñez-Gonzalez [117] and Araguas-Rodriguez [106], phosphorescent ceramic sensor materials can be employed mixed into high temperature binders as Thermal History Paints (THPs). Following the selection criteria in *Chapter 3*, Yttrium Ortho-Silicate ($\text{X1-Y}_2\text{SiO}_5$) was selected as a pigment for the testing of high temperature materials and the expansion of THP to higher temperature regimes. This silicate host was doped with europium (Eu^{3+}), and excited in the visible spectrum with a 532 nm light source, as explained in *Chapter 4*.

The first section of this chapter (5.1) describes the behaviour of the current version of THP at high temperature regimes, above 900 °C, providing a development route to extend the use of THP to higher temperatures. The second section of this chapter (5.2) covers some of the modifications applied to the current binder, potassium silicate. In section 5.3 some binder substitution alternatives are outlined and tested, while in section 5.4 the pigment is subjected to modifications. In section 5.5, interlayers between the metallic substrate and the THP layer are also tested. The results in these sections will lead to the further development of THP formulations, presented in *Chapter 6*.

5.1 Behaviour of thermal history paint at high temperatures

While the selected pigment, Y_2SiO_5 doped with Eu^{3+} , has shown potential temperature sensing over a wide temperature range (from 250 °C to 1,250 °C, as seen in *Chapter 3*), once it is introduced into a potassium silicate binder to form a paint, the working temperature range narrows to temperatures between 250 °C up to 900 °C. The reason behind this temperature range shrinkage has been hypothesised [106], linking this behaviour to interactions between the pigment and the binder and interactions between the THP and the substrate it is applied on. The following sub-sections cover some of the observations for pigment and paint exposed at high temperatures.

5.1.1 Pigment and binder interaction

As outlined in *Chapter 2*, emission spectra can provide an insight in the material structure. Luminescent emission from pigment and paint were taken after heat treatment at 1,100 °C for 30 minutes and are shown in **Figure 5.1**. As a reminder, the current version of THP, includes Y_2SiO_5 : Eu^{3+} pigment heat treated to 400 °C, and then mixed into potassium silicate binder. A sample of this paint was dried at 150 °C for 1.5 hours, subsequently heat treated to 1,100 °C, for 30 minutes, and then compared to the pigment.

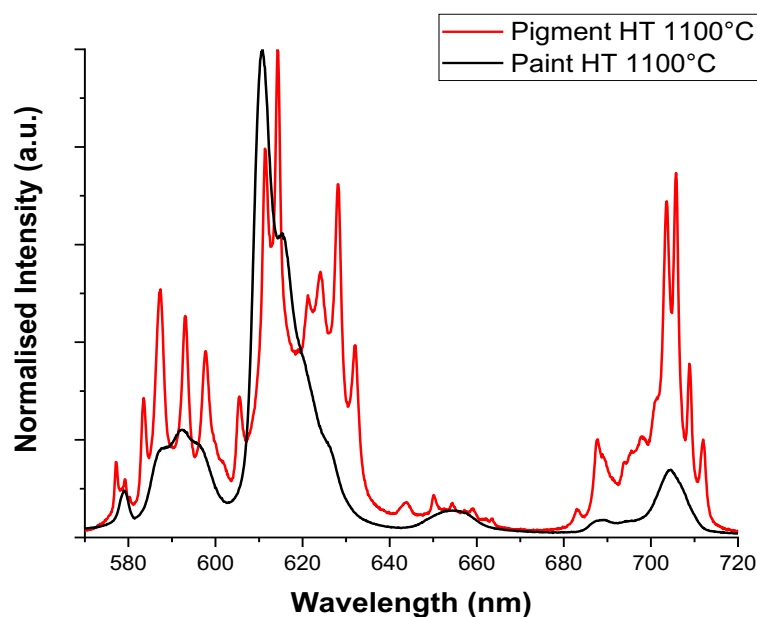


Figure 5.1 Luminescence spectra of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ pigment and thermal history paint pellet ($\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ pigment in potassium silicate binder), obtained at room temperature after excitation with 532 nm visible light. Both samples were heat-treated at 1,100 °C for 30 minutes.

While the spectrum of the $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ pigment, in **Figure 5.1**, showed a multitude of emission lines, the paint spectrum showed broad emission peaks and a considerably lower number of emission lines. These differences in the emission spectra from both samples, observed after heat treatment at a relatively high temperature (1,100 °C) indicated that the emission of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ differs after dispersion in a liquid silicate binder, and subsequently heat treatment. This suggested an interaction between pigment and binder. Emission spectra from both samples have their origin in the Eu^{3+} within the Y_2SiO_5 host, but the environment from which the europium emits is different. In order to reveal the material surroundings of the phosphor, both samples were measured using XRD. The obtained diffraction patterns are shown in **Figures 5.2** and **5.3** for pigment and paint, respectively.

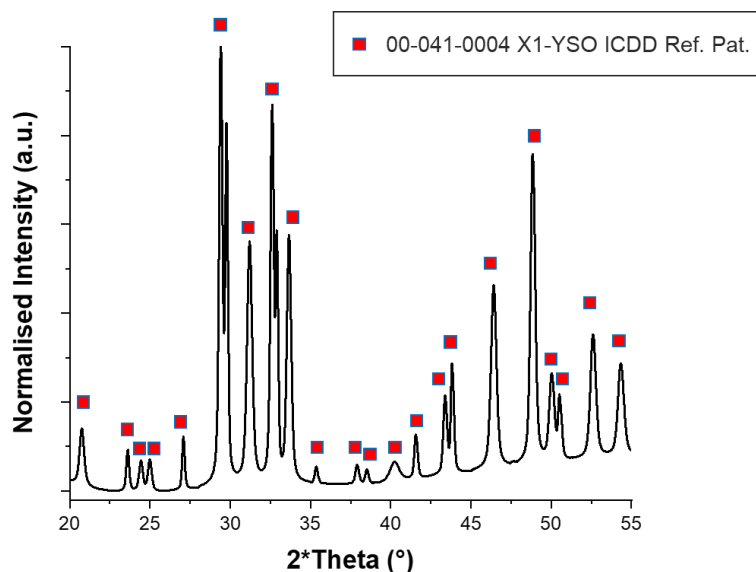


Figure 5.2 Diffraction pattern of yttrium orthosilicate, doped with Eu^{3+} ions, after heat treatment at 1,100 °C for 30 minutes. X1-YSO reference pattern indicated with red squares.

The diffraction pattern of the pigment, $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$, showed a good agreement with the $\text{X1-Y}_2\text{SiO}_5$, ICDD reference pattern 00-041-004 (*X'Pert High Score Plus*, PDF reference database). This indicated that the europium included in the structure does not alter the crystallization of yttrium orthosilicate, as demonstrated by Araguas-Rodriguez [106]. On the other hand, the diffraction pattern obtained from the thermal history paint, shown in **Figure 5.3** below, matched two candidates in the PDF reference database. The obtained pattern, could be identified with the composition of the potassium silicate binder, forming 95 % weight of the paint composition, and matched with the ICDD reference pattern 00-020-0886 potassium hydrogen carbonate hydrate, $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5 \text{H}_2\text{O}$. The presence of water and carbonates can be explained by the interaction between the paint after heat treatment to atmospheric air. CO_2 and water present in the atmosphere could have interacted with the binder after the heat treatment since presence of carbon in the paint after heat exposure to $1,100^\circ\text{C}$ resulted unlikely. The pattern also showed yttrium oxide silicate or apatite phase, $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$. The obtained pattern showed a low signal-to-noise ratio, which corresponds to an amorphous material, in particular the broad “hump” around 28° .

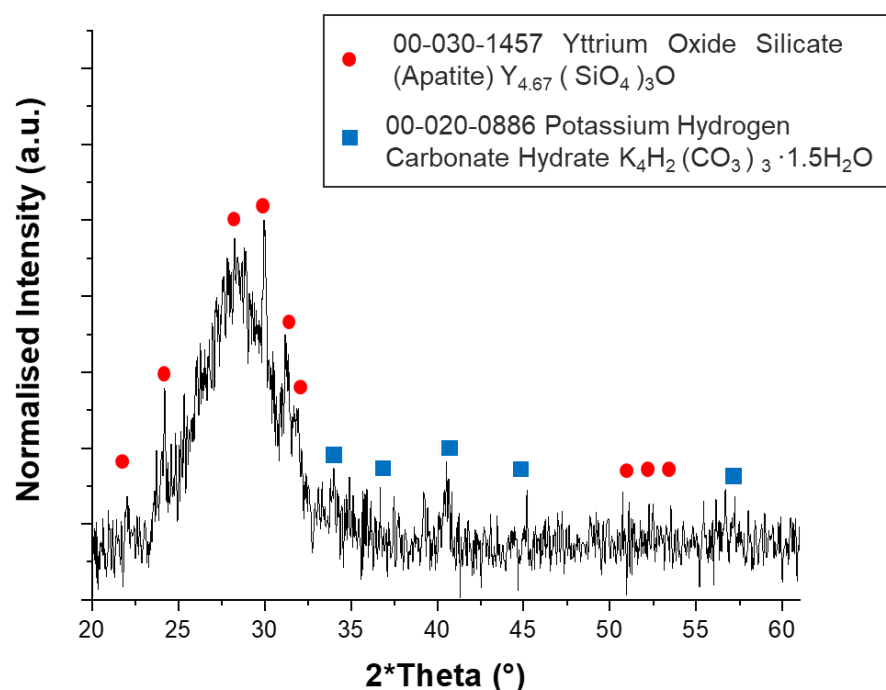
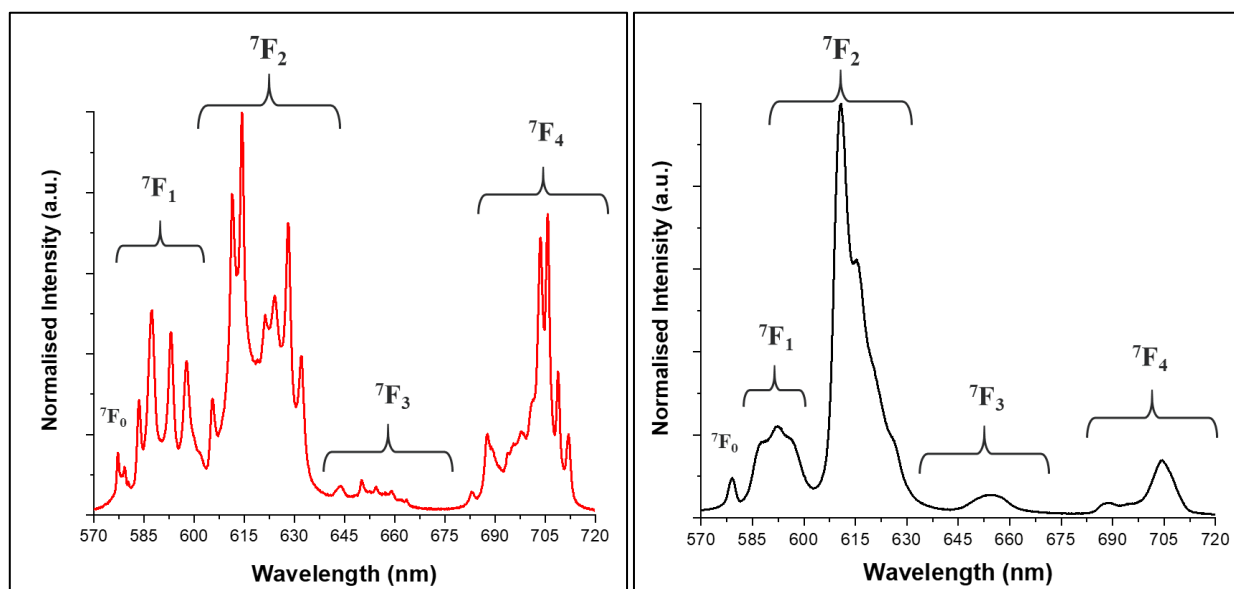


Figure 5.3 Diffraction pattern of thermal history paint pellet, after heat treatment to $1,100^\circ\text{C}$ for 30 minutes. Matching candidates indicated with markers.

The presence of $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$ apatite phase at a temperature of $1,100^\circ\text{C}$, without a pattern corresponding to $\text{X1-Y}_2\text{SiO}_5$ could explain the difference in the luminescent emission observed in **Figure 5.1**. However, XRD did not reveal the pigment structure in detail, as the examined paint contained 5 % weight of the pigment. The low signal-to-noise ratio of the obtained pattern also raised uncertainty around the XRD results. However, the differences in luminescence spectra between pigment and paint, can be explained through the optical spectra itself, since it contains the same luminescent material, $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$.

A full spectral analysis is displayed in **Table 5.1** below, where the peaks in the Eu^{3+} luminescent spectrum are identified for both samples. To identify the main transitions ($^5\text{D}_0 \rightarrow ^7\text{F}_{0...4}$), reference [122] (already explored in *Chapter 3*) was followed, while for crystal field splitting and associated peaks, references [106,195,315] were used. No high temperature X2- Y_2SiO_5 phase was observed in these spectra below 1,300 °C [202,231].

Table 5.1 Analysis of luminescent spectra of pigment and THP samples, heat treated at 1,100 °C for 30 minutes.



Pigment HT 1,100 °C			Paint HT 1,100 °C		
Transition $^5\text{D}_0 \rightarrow ^7\text{F}_0$			Transition $^5\text{D}_0 \rightarrow ^7\text{F}_0$		
Wavelength (nm)	Phase	Site	Wavelength (nm)	Phase	Site
577	X1	Y2	579	X1	Y1
579	X1	Y1			
Transition $^5\text{D}_0 \rightarrow ^7\text{F}_1$			Transition $^5\text{D}_0 \rightarrow ^7\text{F}_1$		
Wavelength (nm)	Phase	Site	Wavelength (nm)	Phase	Site
584	X1	Y2	587	X1	Y1
587	X1	Y1	593	X1	Y1
593	X1	Y1	597	X1	Y1
597	X1	Y1			
Transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$			Transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$		
Wavelength (nm)	Phase	Site	Wavelength (nm)	Phase	Site
605	X1	Y2	611	X1	Y1
611	X1	Y1	615	X1	Y1
614	X1	Y2	625	X1	Y1
621	X1	Y1			
624	X1	Y1			
628	X1	Y2			
632	X1	Y2			
Transition $^5\text{D}_0 \rightarrow ^7\text{F}_3$			Transition $^5\text{D}_0 \rightarrow ^7\text{F}_3$		
Wavelength (nm)	Phase	Site	Wavelength (nm)	Phase	Site
643	X1	Y2	655	X1	Y1
650	X1	Y1			
655	X1	Y1			
659	X1	Y2			

Transition $^5D_0 \rightarrow ^7F_4$			Transition $^5D_0 \rightarrow ^7F_4$		
Wavelength (nm)	Phase	Site	Wavelength (nm)	Phase	Site
683	X1	Y2	688	X1	Y1
687	X1	Y1			
698	X1	Y1			
703	X1	Y1	705	X1	Y1
705	X1	Y1			
708	X1	Y2			
711	X1	Y2			

The *Phase* and *Site* categories, displayed in **Table 5.1**, correspond to the two known crystalline emission of the Y_2SiO_5 , X1 phase, and the two non-equivalent sites of yttrium (Y1 and Y2). Both sites present low local symmetry (C_1), with a different oxygen Coordination Number (CN). The X1- Y_2SiO_5 phase, site 1 (Y1) is coordinated to three free oxygen ions and four silicon-bonded oxygens: a total coordination number of 7. Site 2 (Y2) is coordinated to one free oxygen and eight silicon-bonded oxygens, a total CN of 9 [195,231,316–318]. During the silicate formation, the Eu^{3+} ion occupies the Y^{3+} sites in the Y_2SiO_5 since the ionic radius of europium (0.0947 nm) is similar to the yttrium one (0.0900 nm) [319]. X1- Y_2SiO_5 is the only phase present at 1,100 °C, as expected for the crystallization process of $(Eu_xY_{1-x})_2SiO_5$, where $x=0.16$.

This crystallization can also be observed in the luminescent spectra of the pigment after exposure at different temperatures, shown in **Figure 5.4**. The main observations were explained by Araguas-Rodriguez [106] and are summarized in the following bullet-point-list:

- For temperatures below 950 °C, the luminescent spectra show broad peaks, corresponding to amorphous material structure.
- Between 950 °C and 1,000 °C, the phase X1- Y_2SiO_5 , starts forming.
- Between 1,000 °C and 1,100 °C, spectral peaks from the two non-equivalent sites (Y1, 7 folded, and Y2, 9 folded) are observed, in particular in the $^5D_0 \rightarrow ^7F_0$ transition.
- At 1,100 °C emissions from Y1 and Y2 have similar intensity.
- Between 1,150 °C and 1,200 °C, the transition from the X1 phase to the X2 phase in the Y_2SiO_5 can be observed. This generates some disorder in the crystalline structure, which has been attributed to the presence of apatite phase, or $Y_{4.67}(SiO_4)_3O$ [202].
- At 1,250 °C, the sample displays a mixture of phases X1- Y_2SiO_5 , X2- Y_2SiO_5 and $Y_{4.67}(SiO_4)_3O$.

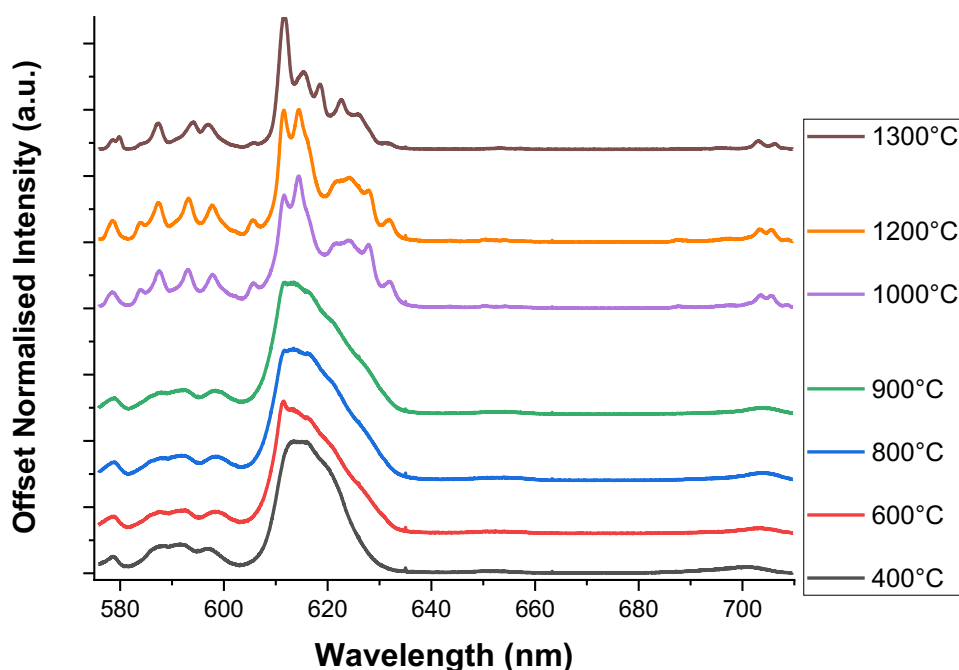


Figure 5.4 Luminescent spectra of $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment heat treated at temperatures from 400 °C to 1,300 °C.

As described in *Chapter 4*, the $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment is mixed in a 5 % weight proportion in a potassium silicate binder, so it can be easily applied as a paint. The emission spectra of the paint, shown in **Figure 5.5**, is different to the pigment emission seen in **Figure 5.4**. Both sets of spectra originate from the same phosphor, $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$, but the differences observed can be attributed to the interaction between pigment and binder. The X1- Y_2SiO_5 emission peaks identified in **Table 5.1**, can be used as a guide for both. While the emission peaks present slight differences in relative intensities, the location of the peaks remained unchanged for all the samples, in particular for the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$, between 610 and 630 nm. As seen in *Chapter 4*, lifetime decay measurements are normally taken at 620 +/- 26 nm.

For the paint samples, shown in **Figure 5.5**, no variations were observed at temperatures higher than 1,100 °C. Luminescent spectra from samples heat treated at 1,100 °C, 1,200 °C and 1,300 °C are remarkably similar, in particular for the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$, between 610 and 630 nm, where the lifetime decay measurements are taken. Emission peaks are limited to those of the Eu^{3+} , substituting yttrium almost exclusively in the Site 1 (Y1) of the X1- Y_2SiO_5 phase. No high temperature X2- Y_2SiO_5 phase was observed, and more surprisingly, no emission peak could be identified as site 2 (Y2) above 1,000 °C in the paint samples. The expected crystallization of the Y_2SiO_5 pigment is somehow inhibited once it is introduced in the binder, according to the luminescent spectra. The paint emission spectra also show broader and fewer peaks, compared to the sharp and multiple peaks observed for the pigment.

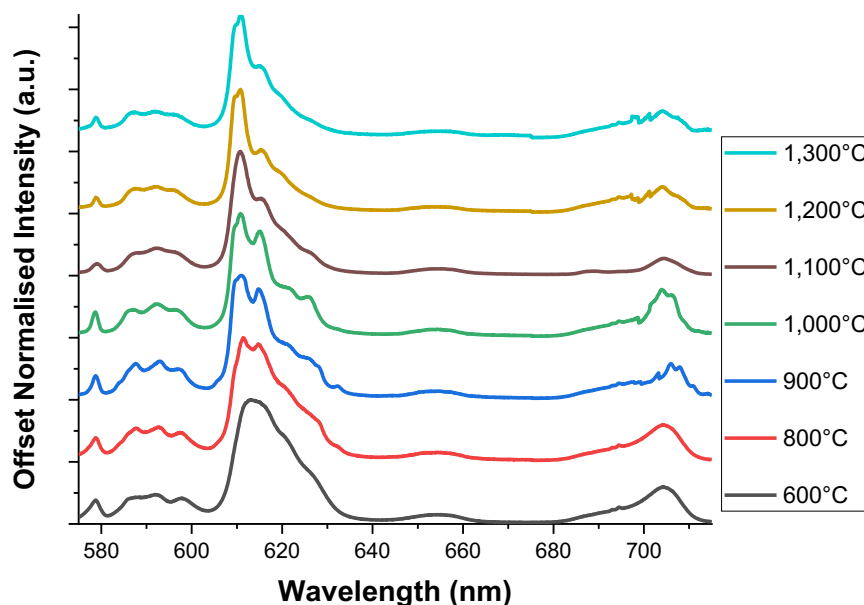


Figure 5.5 Luminescent spectra of THP pellets heat treated at temperatures from 600 °C to 1,300 °C.

The luminescent spectra of the $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ within the THP, after high temperature exposure, corresponds to the emission from an amorphous environment. The main constituent of the paint is the potassium silicate binder, which is known to maintain an amorphous structure after exposure to high temperatures [106]. The XRD results from the paint after heat treatment at 1,100 °C, also revealed the presence of apatite phase, $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$, shown in **Figure 5.3**. This meta-stable phase can be found as a second phase only in particular environments containing metallic ions [222]. In these circumstances, distortion in the lattice surrounding the emitting Eu^{3+} ion is expected after exposure at high temperatures [122], forming an amorphous environment. While the luminescent spectra of the THP showed some evolution in the emission from Eu^{3+} between 600 °C and 1,100 °C, as observed in the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$, (610 to 630 nm, in **Figure 5.5**). The transition $^5\text{D}_0 \rightarrow ^7\text{F}_4$, between 680 and 710 nm, while also sensitive to the environment of the europium, displayed ambiguous results and it was not considered further in this thesis for temperature determination.

The differences observed in the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition were less evident at higher temperatures, where an improved version of THP should provide other parameters to yield a satisfactory thermal history sensor. As explained in *Chapter 4*, all luminescent spectra shown in this thesis are the average of three intensity values per emission wavelength, and always compared to similar samples exposed to the same temperature.

5.1.2 Thermal analysis of thermal history paint

XRD and luminescent spectral analysis of pigment and paint revealed different crystallization environments for the phosphor at high temperatures. Further information on the underlying material processes was sought via thermal analysis. Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) were used to analyse the behaviour of a dried paint pellet from room temperature to 1,500 °C. Given the wide temperature range to analyse, the heating rate used was 10 K/min on a 22 mg sample. Both TGA and DSC traces are shown in **Figure 5.6**, and each reading is represented on an independent vertical axis.

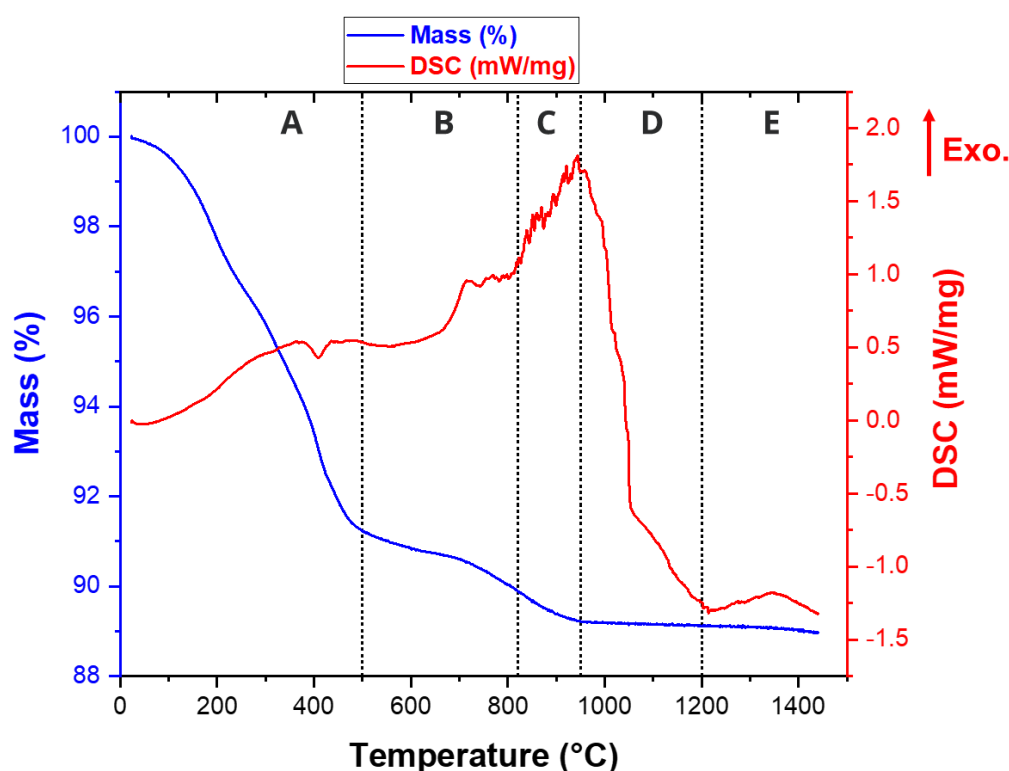


Figure 5.6 Thermal analysis of thermal-history paint, including Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

The TGA trace recorded the mass of the sample as it was heat treated. Overall, the mass reduced around 12 %, but this weight variation changed differently over the temperature range considered. From room temperature to almost 500 °C, most of the mass loss occurred, around 8 %. This is region A in the graph. From 500 °C to 950 °C, regions B and C, the mass reduction represents around 3% of the total loss. At higher temperatures, the mass remained stable.

The DSC trace starts at room temperature, showing an increase of energy in the sample with increasing temperatures. The trace stabilizes around 400 °C, at the end of the region A, where a small endothermic peak is observed. This corresponds to the removal of structural water, released with the polymerization of silanol groups (-Si-OH) into siloxane groups (-Si-O-Si) [320–322]. At 500 °C the mass drop slows down, entering in region B, where the DSC trace stabilizes until 600 °C. Between 600 °C and 730 °C the energy

increases exponentially, followed by a flattening until the end of the region at 825 °C. This behaviour can be explained by a phase transition within the potassium silicate binder and simultaneous melting of the phase $K_2Si_4O_9$ of the potassium silicate binder.

Region C in **Figure 5.6**, between 825 °C and 950 °C, shows increasing energy within the sample with increasing temperature. This increase occurs in an oscillating or *noisy* trend, identified with bubbling or boiling in a fully liquid silicate, as suggested by the technical team at the characterization suite of the Department of Materials at Imperial College London.

Finally, regions D (between 950 °C and 1,200 °C) and E (from 1,200 °C to 1,440 °C) show a drop and stabilization of energy, respectively. This has been observed in similar silicates [320,324], and explained by vitrification and densification of the silicate. This can explain the amorphous structure revealed in the diffraction pattern in **Figure 5.3** for a THP sample heat treated at 1,100 °C, which corresponded to vitrified silicate with a low order in its internal structure.

5.1.3 Interaction between thermal history paint and substrate

Thermal history paints have been used in several industrial applications, mostly in gas turbine and automotive components [32,39,325]. The temperature sensing parameter used in these cases is the Life-Time Decay (LTD) of the phosphor after excitation, as explained in *Chapter 4*. This LTD shows a variation with increasing temperature exposure, which allows calibrations to be performed for the working temperature range of the THP, between 150 °C and 900 °C, with an estimated uncertainty of 6.3 °C and 13 °C for 67 % or 95 % confidence levels, respectively. This uncertainty range was calculated comparing the temperature obtained from thermal history paint measurements, adequately calibrated, and thermocouple readings, and their respective uncertainties, following the uncertainty determination model in the publication by Peral *et al.* [210].

THP is deposited, namely, on metallic substrates, which are the main material constituents of turbomachinery components. The metal underneath the THP layer may have an influence on the luminescent measurements, especially when the system THP-substrate is exposed at high temperatures. The lifetime decay of THP on two different substrates, stainless-steel and sapphire, was explored after heat exposure for 30 minutes at the indicated temperatures. The results are plotted in **Figure 5.7** below. Lifetime decay of the pigment, deposited on glass slides after temperature exposure, is shown for comparison.

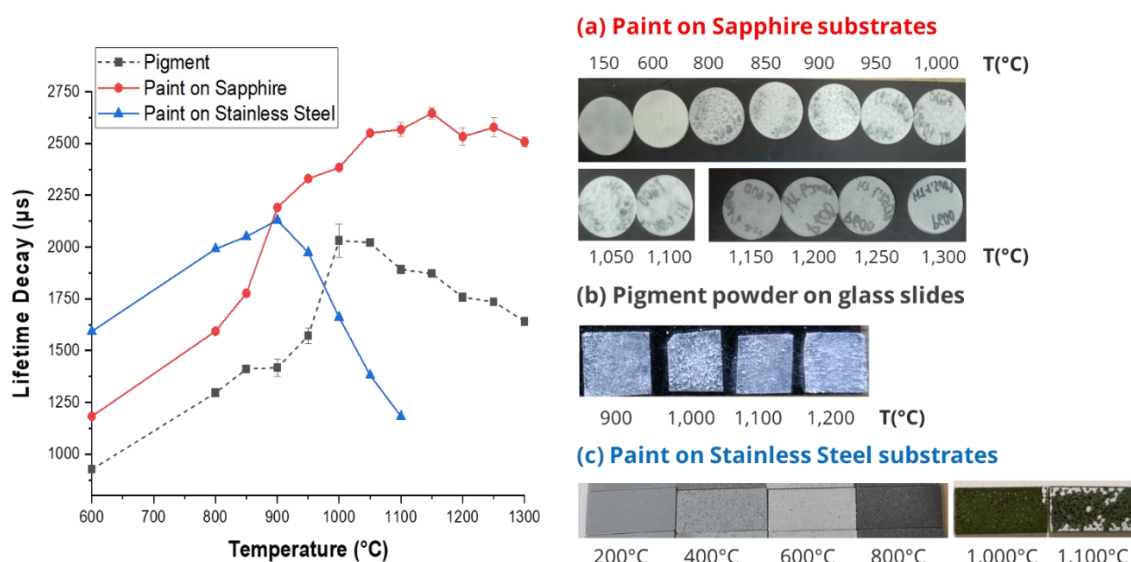


Figure 5.7 Lifetime decay evolution over temperature for three thermal history samples:

- (a) THP applied on sapphire discs, 12.5mm in diameter, heat treated to the indicated temperature.**
- (b) Pigment powder, heat treated to the indicated temperature and attached onto a glass slide.**
- (c) THP applied on Stainless Steel 316L tiles, 20x10 mm, heat treated to the indicated temperature.**

The lifetime decay results of the three types of samples considered in **Figure 5.7** show a monotonic increase with increasing temperature up to 900 °C. As expected by the composition of the THP, at 800 °C the paint started melting. This can be observed on the painted sapphire discs, where some bubbling and change in transparency is visible on the painted discs heat-treated from 800 °C to 1,050 °C. Above this temperature, the THP is completely molten and transparent. The letters written underneath the sapphire discs can be easily seen after heat exposure at 1,300 °C, while for temperatures below 1,100 °C both disc and paint are not completely transparent.

The glass formed after the melting of the potassium silicate binder is not the whole cause of the lifetime decay change above 900 °C. While the lifetime decay of the THP on sapphire continues increasing to temperatures up to 1,150 °C, the THP applied on stainless-steel showed some structural changes from 800 °C, mainly darkening in the colour of the paint, as well as some bubbling, shown in **Figure 5.7**. While no interaction between the THP layer and sapphire substrates was detected, the stainless-steel had a clear effect on the THP. The lifetime decay shows a maximum at 900 °C, after which it drops. The darkening of the THP applied on metal can also hinder luminescent measurements, as the emitted signal from dark samples show low intensity. An interaction between the THP and the metallic substrate was hypothesised by Araguas-Rodriguez [106] and it is developed in the following sections.

For the pigment, the maximum LTD was found at 1,000 °C, decreasing after exposure at higher temperatures. This is in agreement with the crystallization process explained in previous sections. The LTD stops increasing monotonically with increasing temperature as soon as the $X1-Y_2SiO_5$ starts forming, and the europium emits from both non-equivalent sites of the X1 phase (Y1 and Y2). In addition, the appearance of the pigment does not change with increasing temperatures, as similarly observed for the THP on sapphire.

5.1.3.1 THP on metallic substrates

Life-Time Decay (LTD) is an appropriate temperature sensing parameter for THP on any substrate, for temperatures between 150 °C and 900 °C. In order to expand this temperature sensing range of the THP, the drop in the monotonic increase of LTD with temperature must be explained. Several hypotheses have been developed in the past, in particular for THP on metallic substrates. Araguas-Rodriguez observed the luminescent spectra on THP and on binder layers applied on stainless-steel after high temperature exposure [106]. While most of the spectral lines could be attributed to the europium, lines at 694 nm on THP and binder were detected as well. These were attributed to emission from chromium ions, Cr^{3+} [326], potentially coming from the metal substrate where the paint layer was deposited on. In **Figure 5.8**, the spectral measurements from both THP and binder are shown. Emission lines from both europium and chromium are indicated, for samples exposed at different temperatures.

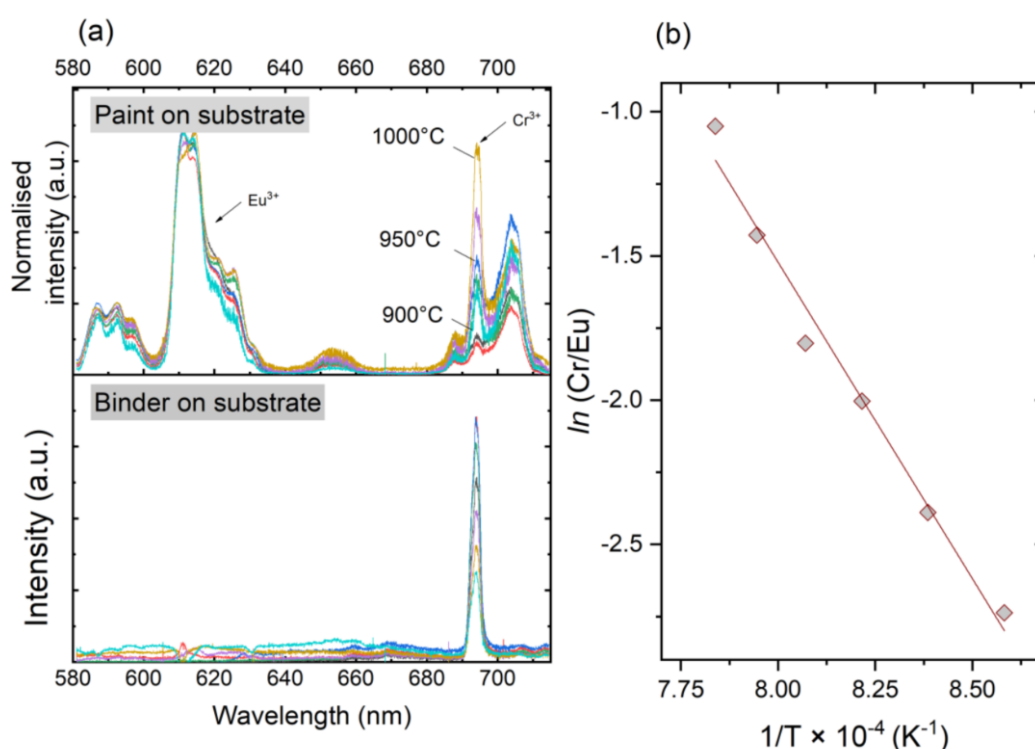


Figure 5.8 (a) Luminescent emission spectra of a heated metallic substrate coated with [top] THP and [bottom] binder only, after excitation with 532 nm light. (b) Natural logarithm of the ratio of Cr^{3+} and Eu^{3+} intensity plotted as a function of reciprocal exposure temperature. Extracted from [106] with permission via CC-BY-NC-ND 4.0

Chromium is a common constituent of steel and nickel alloys. Araguas-Rodriguez hypothesized that the detection of chromium in the luminescent emission of THP and binder might indicate migration of chromium species into the paint layer, following the oxidation of the metallic substrate at high temperatures [106]. This process might be facilitated by the progressive melting of the paint at temperatures higher than 741 °C. The natural logarithm of the Cr^{3+} over the Eu^{3+} intensity, plotted as a function of the reciprocal temperature in **Figure 5.8**, suggested that it is a thermally induced process, and therefore described by the Arrhenius equation.

This *diffusion* mechanism of chromium into the paint is mainly driven by temperature, but exposure time to temperature has also an influence. A short experiment was performed to study the effect of exposure time on THP deposited on coupons of a nickel alloy containing chromium. 21 of these coupons were exposed to three temperatures (700 °C, 900 °C and 1,000 °C) for seven different exposure times (3, 4, 5, 6, 10, 30 and 60 minutes). Photographs of the coupons and luminescent spectra recorded on the painted surfaces are shown in **Figure 5.9** below.

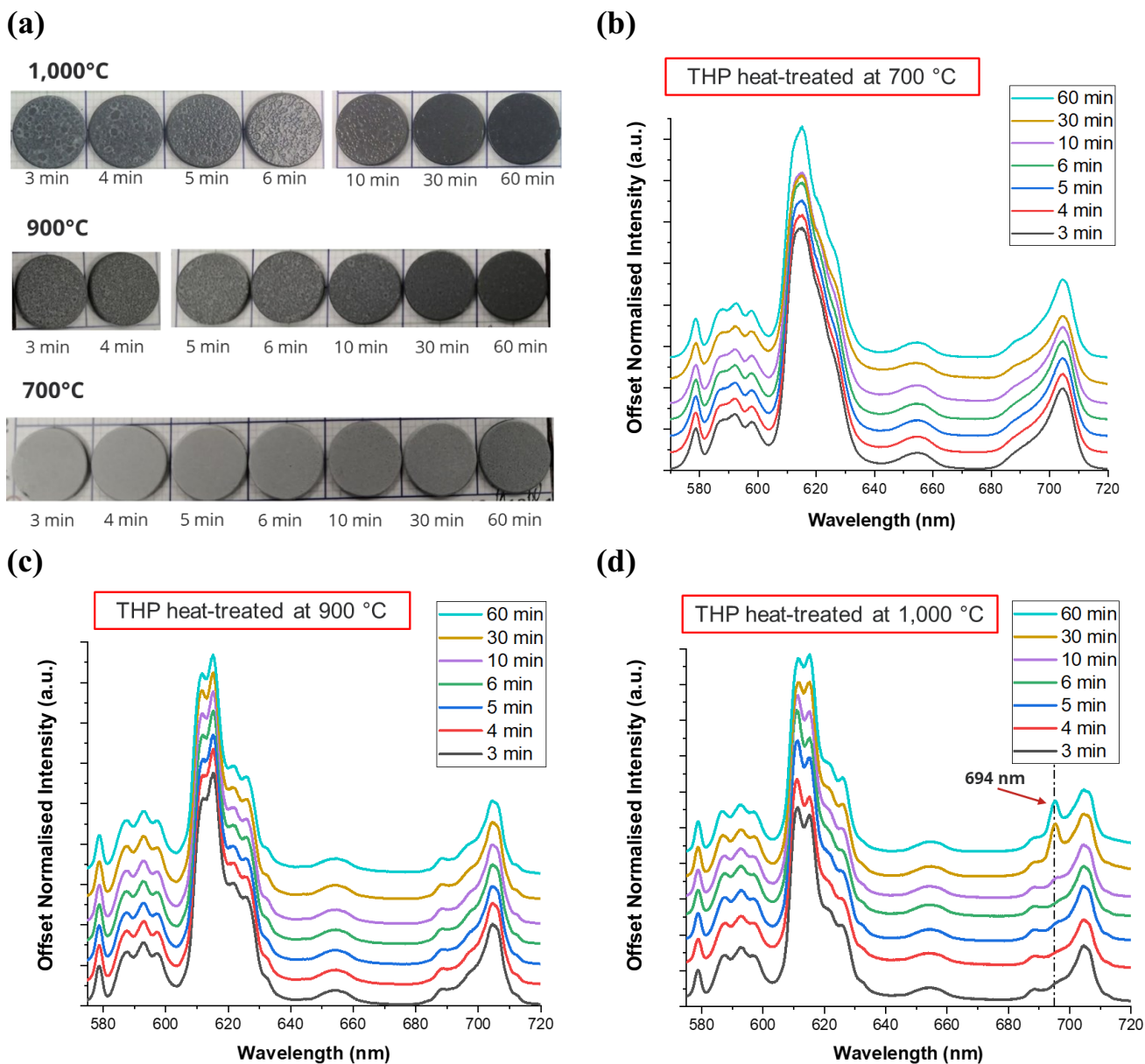


Figure 5.9 (a) Photograph of metallic substrates, coated with THP and heat treated for the indicated duration. Luminescent emission spectra of THP on metallic substrate, heated at 700 °C (b), at 900 °C (c) and at 1,000 °C (d) for the indicated duration.

Overall, the spectral behaviour of THP remained unaltered for each given temperature, in particular observing the transition $^5D_0 \rightarrow ^7F_2$, between 610 and 630 nm, in all samples. Chromium emission was only detected on coupons heat treated to 1,000 °C for exposure times between 10 and 60 minutes. In these cases, a relatively broad peak was recorded at 694 nm, while for the rest of the samples this emission was not

detected. This delayed chromium emission was identified in the luminescent spectra but could not be the main factor associated to LTD decrease at high temperatures. LTD measurements on these painted nickel coupons are shown in **Figure 5.10**.

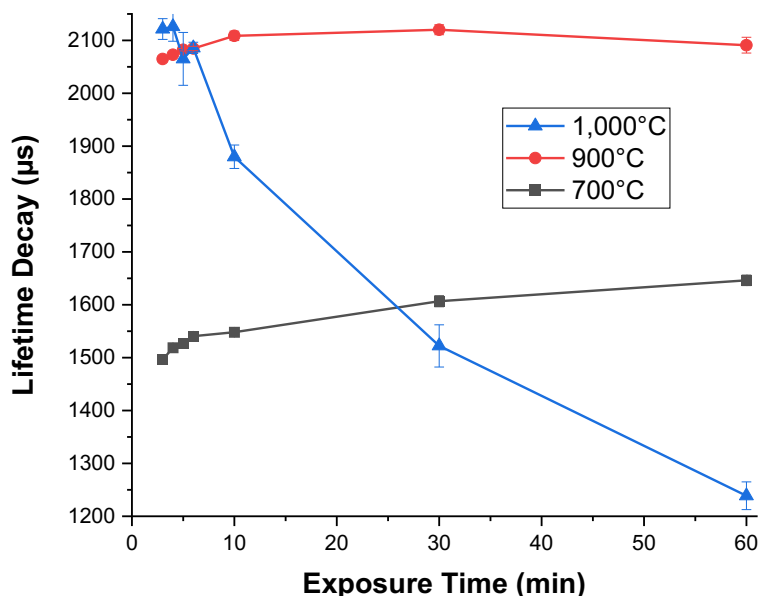


Figure 5.10 Lifetime Decay measured on THP deposited on nickel coupons and heat treated at three temperatures (700 °C, 900 °C and 1,000 °C) over different exposure times. Lines linking points included for visualization. Error bars correspond to the standard deviation of five measurements taken on the painted surface of the sample. Excitation was performed at 532 nm and the emission was recorded at 620 +/- 26 nm.

The lifetime decay values obtained on samples heat treated at 700 °C increased with longer exposure times. Two sensitivity regimes were observed, a high sensitivity region, up to 6 minutes of exposure time, and a low sensitivity region for longer exposure times. The LTD changed at a range of 14.1 μs/min and 6.1 μs/min, respectively. These could lead to temperature measurement variations of 6.2 °C/min and 2.7 °C/min, respectively. Samples heat treated at 900 °C showed the high sensitivity regime for exposure times below 10 minutes, where the sensitivity was estimated 6.1 μs/min and 2.7 °C/min for LTD and temperature variations, respectively. The maximum LTD recording at 900 °C was after 30 minutes of heat exposure. For longer exposure times at 900 °C, the LTD decreased. The effect of the exposure time can be considered a secondary factor with respect to temperature in this case, while no chromium emissions were detected. However, this limits the maximum time of exposure of the THP to 30 minutes at 900 °C, and longer exposure times considered ambiguous.

For the samples heated to 1,000 °C, the lifetime decay increase was not sustained. While LTD measurements on samples heated for 3 and 4 minutes showed values higher than the ones measured on samples heated at 900 °C, the LTD decreased for longer exposure times. The standard deviation of measurements taken on the surface of these samples also increased for longer exposure times, pointing to the degradation of the paint layer, as observed in the photograph of the coupons in **Figure 5.9 (a)**. The paint

turned to a dark green colour, possibly influenced by the oxidation of the metal underneath, and bubbles were visible for all the exposure times considered. While LTD measurements from paint exposed at 1,000 °C could be potentially used, calibrating a decreasing trend of LTD over increasing temperature, extending the monotonic increase of LTD was the preferred strategy in this thesis, avoiding the ambiguity of having a maximum point in a calibration curve.

5.1.3.2 Electron Microscopy observation of the THP-substrate interface

To study the interaction between the THP and the metal substrate underneath, three samples of two common metal alloys were painted and heat treated to 800 °C, 900 °C and 1,000 °C. Rectangular stainless-steel 316L samples of dimensions 20 x 10 x 3 mm were used, as well as cylindrical samples of Inconel 738, 40 mm in diameter and 3 mm thickness. The composition of the stainless steel 316L and Inconel 738, used for this study are shown in **Table 5.2** below.

Table 5.2 Composition of Stainless Steel 316L and Inconel 738, nickel alloy.

(wt. %) →	C	Si	Mn	Ti	Al	Co	W	Mo	Cr	Ni	Fe
Stainless Steel 316L	0.02	0.40	1.10	-	-	-	-	2.12	16.73	10.20	Rest
Inconel 738	0.15	0.30	0.20	3.50	3.50	8.50	2.66	1.50	16.00	Rest	0.50

The Inconel 738 cylindrical samples were cut in half before THP deposition to facilitate handling and further characterisation via electron microscopy. Prior to spraying, a thin strip of masking tape was laid at approximately the middle of the sample and removed after deposition of the paint layer. This allowed the metal substrate to be exposed to the hot atmosphere during the heat treatment, while the most part of the surface of interest remained painted, and therefore a direct comparison between bare metal and painted metal exposed to temperature could be established. One half of the Inconel 738 samples were used for luminescent measurements, while the other half were embedded in resin and observed under the electron microscope. In the case of the stainless-steel samples, double the needed number of samples were painted and heat treated for the same purposes. The samples and luminescent lifetime decay obtained after heat treatment are shown in **Figure 5.11** below. Three measurements were taken on the surface of every sample, both for luminescent spectra and LTD. While between 800 °C and 900 °C the LTD increased, it decreased at higher temperatures. Differences observed between the samples, could lead to an explanation on the LTD drop at high temperatures on these two metallic alloys.

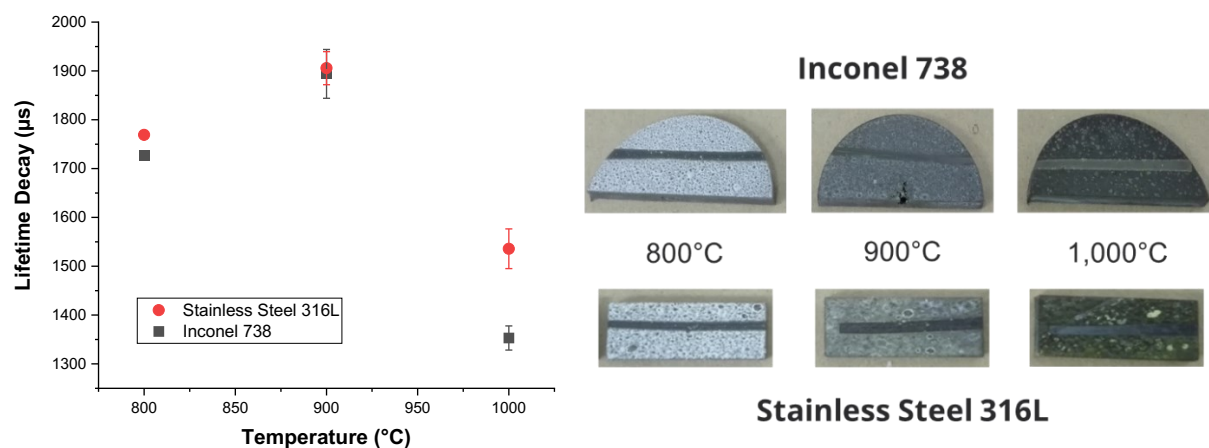


Figure 5.11 Lifetime decay evolution over temperature for THP applied on Inconel 738 discs and stainless-steel 316L substrates (left). Photographs of metallic substrates, coated with THP, and heat treated to 800 °C, 900 °C and 1,000 °C for 30 minutes (right).

Luminescent spectra of the samples were also recorded after heat treatment and shown in **Figure 5.12** for the three temperatures and two metals considered. On both substrates, luminescent emission peaks change according to the temperature exposed to, from broad peaks observed at 800 °C to sharper emission lines at 900 °C and 1,000 °C. While spectra at 800 °C and 900 °C are similar for both metal substrates, subtle differences can be observed in the transition $^5D_0 \rightarrow ^7F_2$, between 610 and 630 nm, at 1,000 °C. The THP on Inconel showed a single peak at around 614 nm and two less intense peaks at 622 nm and 626 nm. THP on stainless-steel, after heat exposure at 1,000 °C, showed a double peak, less intense at 611 nm and more intense at 614 nm, corresponding to the sites Y1 and Y2 of the $X_1-Y_2SiO_5$ phase, as seen previously in **Table 5.1**. This broad emission peak also showed a shoulder between 620 nm and 630 nm on stainless-steel, while on Inconel this shoulder plateaued above 615 nm.

These differences can be explained by the degradation of the paint structure. In the photographs of the samples in **Figure 5.11**, bubbling of the paint after heat treatment can be observed. This could have exposed the metal underneath to luminescence interrogation. Spectra from the two samples heat treated at 1,000 °C show an emission peak at around 694 nm, which could originate either from the metal underneath the THP layer or from metal incorporation into the paint layer.

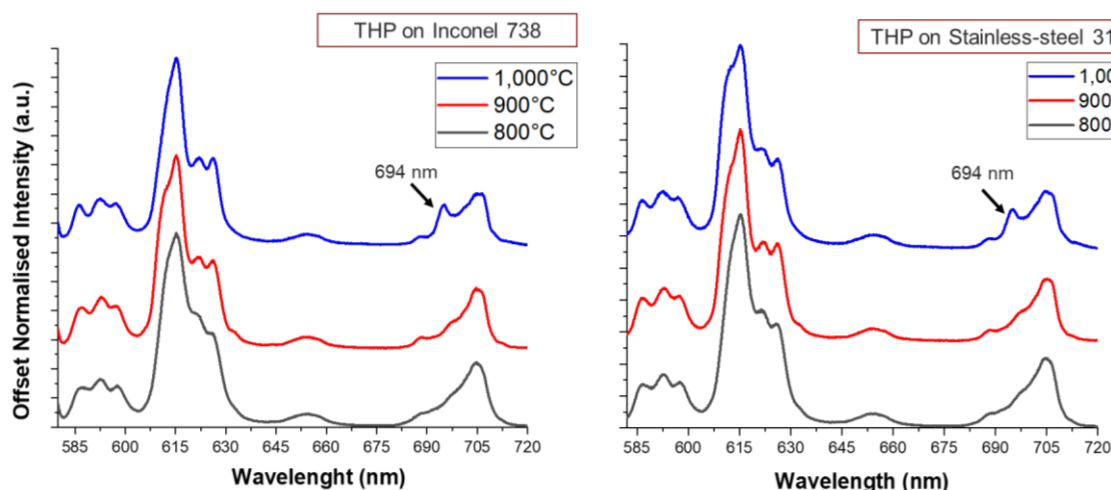
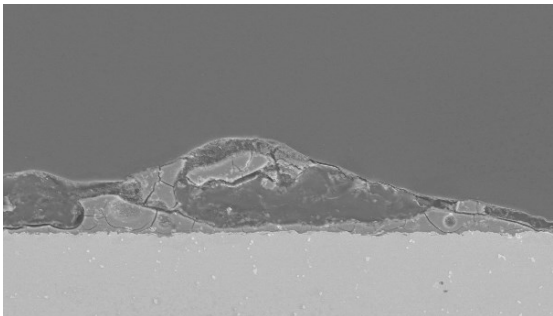
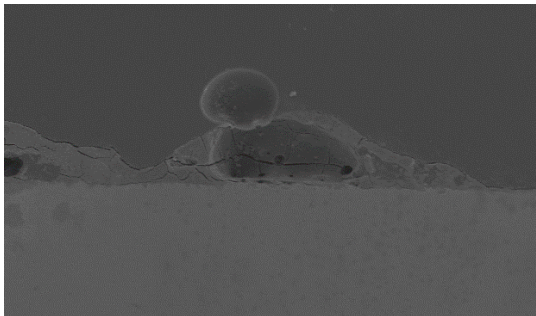
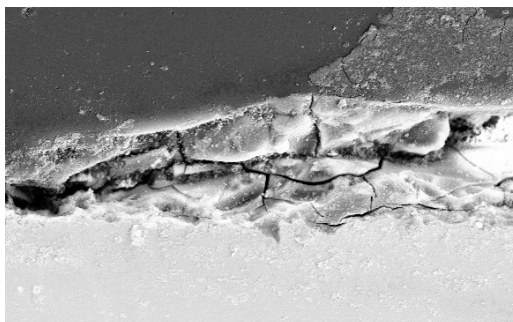
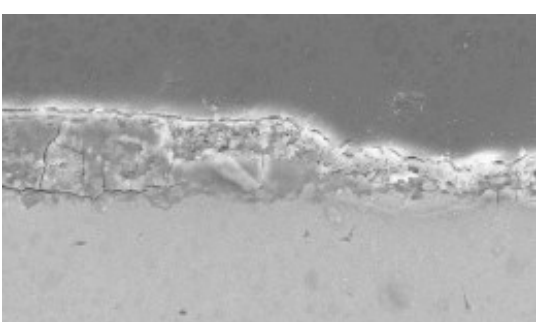
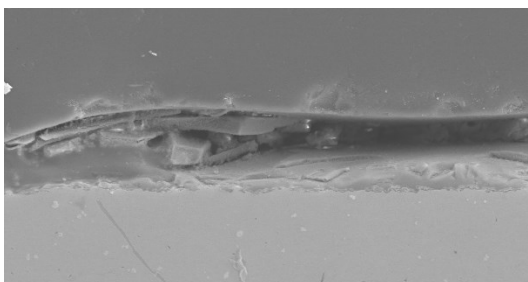
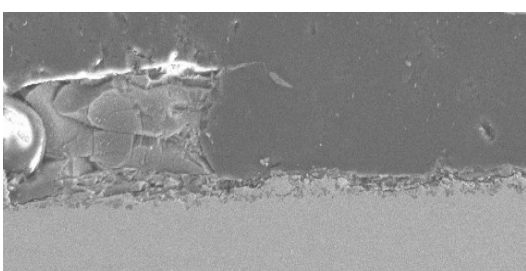


Figure 5.12 (Left) Luminescent emission spectra of THP deposited on Inconel 738 discs, heated at indicated temperature. (Right) Luminescent emission spectra of THP deposited on Stainless Steel 316L substrates, heated at indicated temperature.

For the purpose of this study, characterization via electron microscopy was carried out, with a focus on the contact zone between paint and metal. Cross sections of both type of substrates were explored via Scanning Electron Microscopy (SEM) after exposure at 800 °C, 900 °C and 1,000 °C. A summary of all six interfaces considered, and the settings of the SEM are shown in **Table 5.3**.

2930 **Table 5.3** Cross section of THP applied on steel and nickel metallic substrates observed via Scanning Electron Microscopy (SEM) after heat treatment at 800 °C, 900 °C and 1,000 °C for two metal alloys: Inconel 738 and Stainless Steel 316L. Scale and settings used for image acquisition are included in the legend below each image: Working Distance (WD), beam voltage (EHT), type of signal/detector (in all cases, Secondary Electrons, SE2) and Magnification (Mag).

2935

	Inconel 738	Stainless Steel 316L
800°C	 100 μm EHT = 20.00 kV Signal A = SE2 WD = 11.9 mm Mag = 500 X	 100 μm EHT = 15.00 kV Signal A = SE2 WD = 11.3 mm Mag = 500 X
900°C	 10 μm EHT = 20.00 kV Signal A = SE2 WD = 12.8 mm Mag = 2.00 K X	 100 μm EHT = 20.00 kV Signal A = SE2 WD = 10.5 mm Mag = 500 X
1,000°C	 20 μm EHT = 20.00 kV Signal A = SE2 WD = 9.7 mm Mag = 750 X	 100 μm EHT = 20.00 kV Signal A = SE2 WD = 10.0 mm Mag = 500 X

EDX line scans were performed across the paint layer applied on top of the base metal. These are shown in yellow in the SEM micrographs for Inconel in **Table 5.4**, and on Stainless Steel in **Table 5.5**. The tables include the elements detected from the paint layer (top of every line) to the metal substrate (end of the line) in every case. The paint contains silicon (Si), potassium (K) and high contents of oxygen (O), while the metal substrate contains mostly chromium (Cr) and nickel (Ni) in the case of the Inconel 738, and iron (Fe) and chromium (Cr) in the case of Stainless Steel 316L.

2940

Table 5.4 EDX lines over SEM micrographs of THP deposited on Inconel 738 samples, after heat treatment at 800 °C, 900 °C and 1,000 °C. Main elemental constituents of THP (Si and K) and of the Inconel metallic substrate (Ni and Cr) are plotted over the distance along the EDX line.

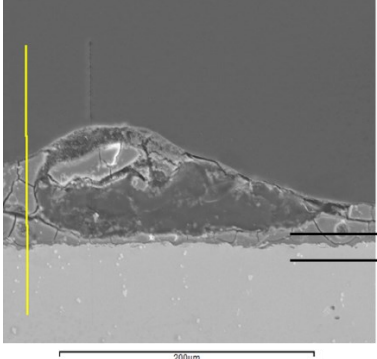
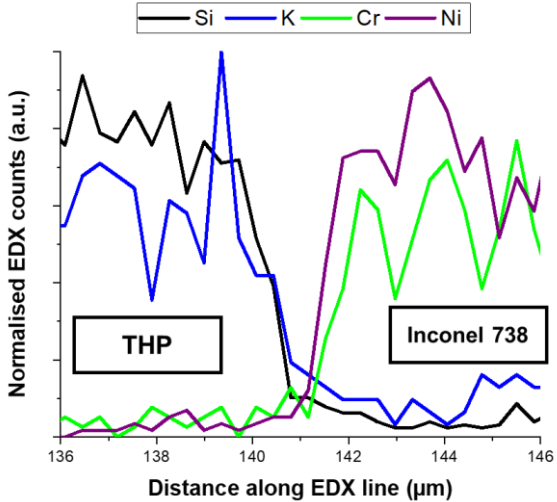
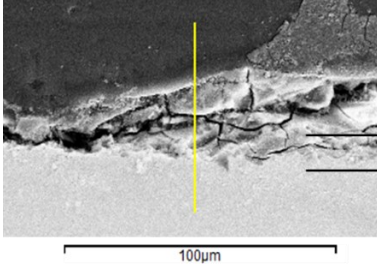
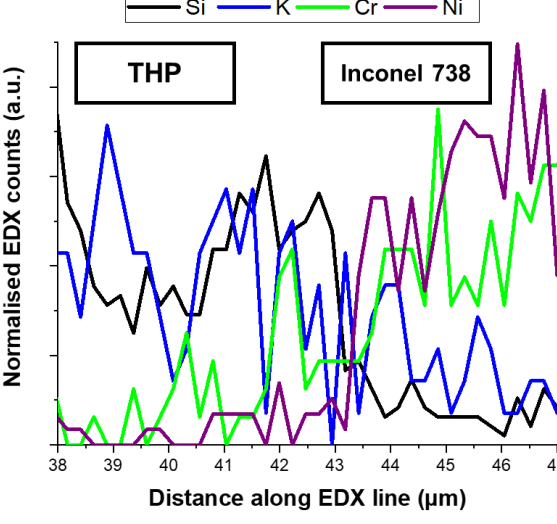
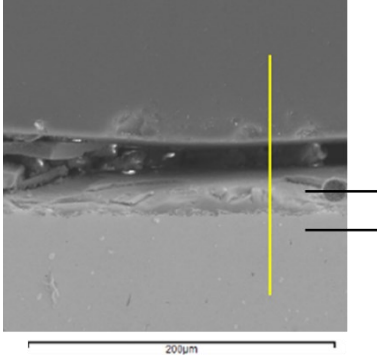
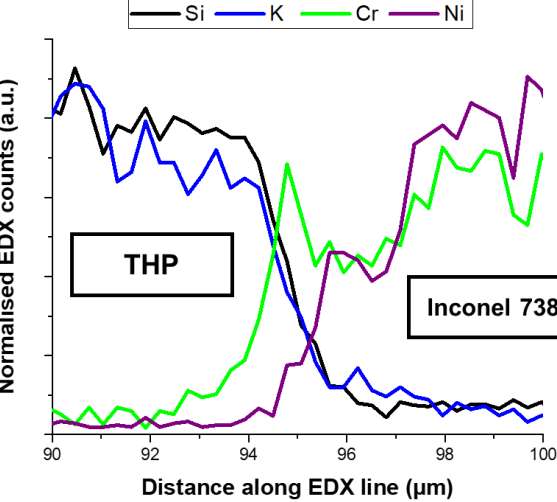
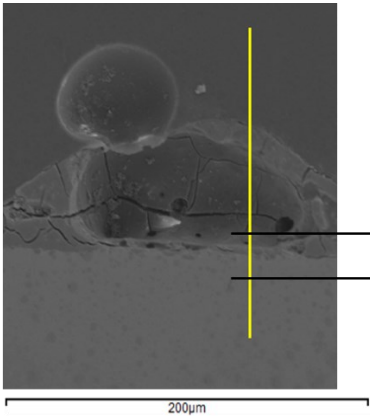
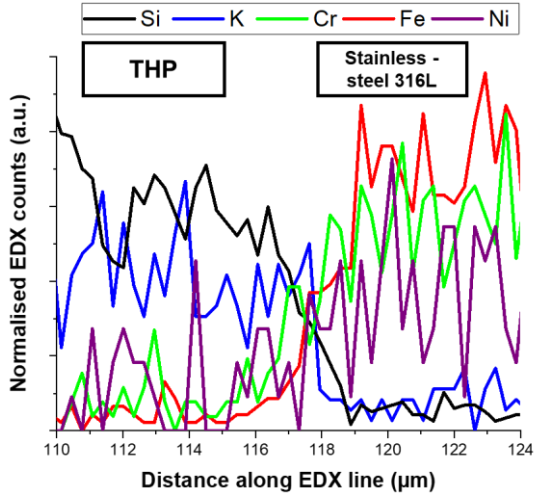
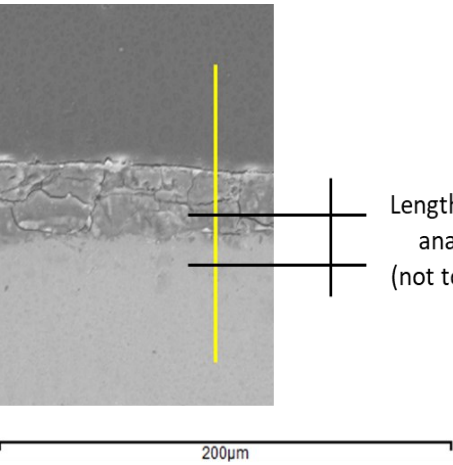
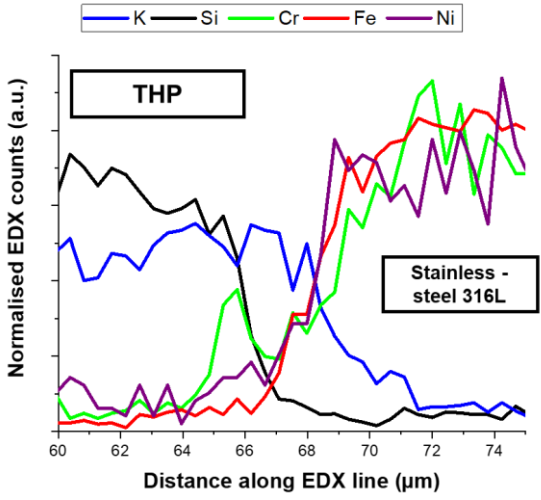
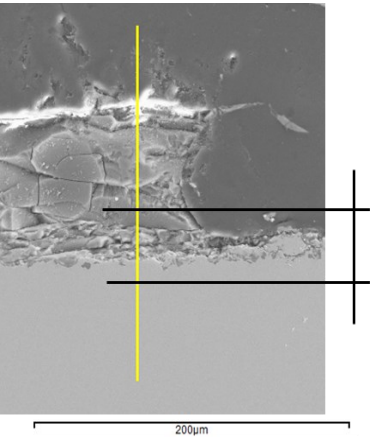
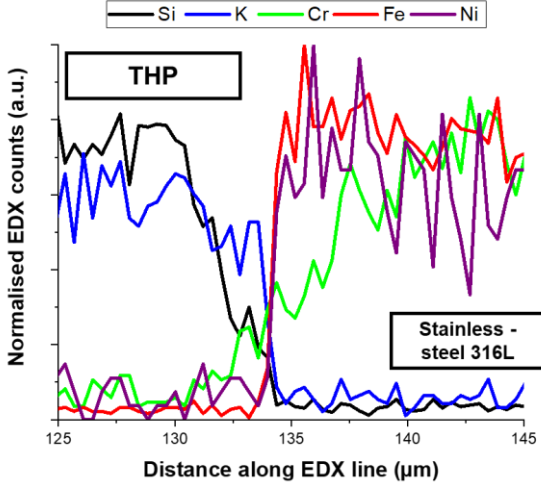
	Inconel 738	THP-Metal Interface
800°C	 Total length of the line: 184.95µm Line resolution: 0.36 µm	
900°C	 Total length of the line: 60.84 µm Line resolution: 0.24 µm	
1,000°C	 Total length of the line: 147.20 µm Line resolution: 0.28 µm	

Table 5.5 EDX lines over SEM micrographs of THP deposited on Stainless Steel 316L samples, after heat treatment at 800 °C, 900 °C and 1,000 °C. Main elemental constituents of THP (Si and K) and of the Stainless-Steel substrate (Fe, Cr and Ni) are plotted over the distance along the EDX line.

	Stainless Steel 316L	THP-Metal Interface
800°C	 Total length of the line: 159.44 µm Line resolution: 0.31 µm	
900°C	 Total length of the line: 114.04 µm	 Line resolution: 0.44 µm
1,000°C	 Total length of the line: 201.96 µm	 Line resolution: 0.39 µm

The detected elements in the EDX lines are shown in the right-hand side graphs in **Tables 5.4** and **5.5**, where the contact interface between paint and metal is augmented for visualization. The transition from the paint into metal is shown from the left-hand side to the right-hand side, respectively in every graph, for increasing length across the EDX lines in all cases, as shown in the graphs on the right-hand side. Therefore, THP is found at lower distances across the EDX line, and metal at higher distances. The scanning direction was from top to bottom across the yellow line shown in all micrographs. The length of the lines varied from 60 μm to 201 μm and the spatial resolution from 0.24 μm to 0.44 μm . In all six cases, there is a transition from the THP layer to metal substrate, detected in the 10 to 20 μm of the paint-substrate interface, which can be observed in the elements in the EDX lines. Metallic species were detected with a sudden increase of the EDX counts, nickel and iron, within a smaller length than the paint constituents, and well over the noise level observed in the EDX line of every element. In other words, while silicon and potassium faded gradually through the interface paint-metal, metallic elements such as, iron or nickel, show up in the detector counts in shorter lengths, in all cases between 1 μm and 4 μm .

To confirm the lifetime decay and spectral features, shown in **Figures 5.11** and **5.12**, the EDX results obtained around the paint-metal interface were considered. Chromium was detected, within the paint layer in some of the cases shown in **Tables 5.4** and **5.5**, at relatively small distance from the interface, around 2 μm away from the transition paint-metal. This is the case of stainless-steel and Inconel 738 heat-treated at 1,000 $^{\circ}\text{C}$. The presence of chromium can explain the decrease in LTD seen on both substrates, as well as the emission at 694 nm seen in the spectra for these samples. In the other extreme case, samples heated at 800 $^{\circ}\text{C}$, chromium was not detected within the paint layer, and a clear transition was observed from paint to metal on the EDX lines, in particular for the Inconel 738. However, the most interesting case was found on stainless-steel heat-treated at 900 $^{\circ}\text{C}$, where chromium was detected within the paint layer, but could not be correlated to an effect in luminescence, either in LTD or in spectra. As an additional note, not all the metals constituting the substrates were detected, nor the other constituent elements of the paint, such as yttrium or europium.

While the results shown here might not be conclusive due to the detection limits of this technique [312], the presence of chromium was detected within THP deposited on common metallic substrates exposed to temperatures of 900 $^{\circ}\text{C}$ and 1,000 $^{\circ}\text{C}$. The effect of the heat exposure can be observed in the pictures of the painted samples in **Figure 5.11**, in the luminescent results shown in **Figures 5.11** and **5.12**, and these can be correlated to presence of chromium within the paint layer, shown in **Tables 5.4** and **5.5**, e.g., THP on stainless-steel and Inconel 738 heat-treated at 1,000 $^{\circ}\text{C}$, where chromium was detected in the EDX scans, chromium emission was detected in the spectra and a drop in the LTD of at least 400 μs was appreciated on both substrates with respect samples exposed at 900 $^{\circ}\text{C}$.

Low levels of chromium impurities within the paint layer can be enough to produce an effect in LTD and luminescence spectra. Araguas-Rodriguez examined different chromium concentrations in paint batches, concluding that an effect on the lifetime decay could be observed for concentrations as low as 0.02 % wt. of chromium oxide (Cr_2O_3) mixed into the THP [106].

5.1.4 Efflorescence of thermal history paint

Efflorescence refers to the deposition of salts on the surface of a porous material. On silicate-based materials, certain types of chemical reactions can lead to this phenomenon. The hydroxy groups (-OH) in the silicate can react with the CO₂ in the atmosphere to generate a carbonate. This mechanism has been observed in construction materials [327], wall paintings and monuments [328] and studied in detail for sodium, potassium and lithium silicates [329]. The main parameters affecting efflorescence are:

- Amount of CO₂
- Humidity
- Temperature, at which the chemical reaction occurs.

Efflorescence was proven by Araguas-Rodriguez [106] to have an effect on the shelf life of the THP. The main constituent of THP is potassium silicate, which is a material reported in the literature to exhibit these kind of reactions [329]. In this investigation, structural changes could be observed on the surface of painted samples, in particular after temperature exposure. The appearance of the THP turned white and displayed a powdery consistence. Depending on the exposure temperature, the paint layer became brittle and, in some areas, detached from the surface of the substrate. Furthermore, efflorescence was found to influence the luminescent results obtained from samples heat treated to different temperatures. The first observations reported by Araguas-Rodriguez [106] showed variations in lifetime decay measured on the same samples over 34 days. The lifetime decay values decreased in the first 15 days of the study, after which the trend stabilised.

An experiment was devised to test the effect of efflorescence on THP. 16 stainless-steel samples were painted, and heated to four different temperatures: 200 °C, 400 °C, 600 °C and 800 °C. After heat treatment, one sample of each temperature was stored in one of four different storage conditions, in sealed plastic bags: exposed to ambient conditions (standard storage), inside a fridge (at a temperature around 5 °C), in a bag with silica-gel desiccant and in a sealed vacuum bag. Since the vacuum bags had to be re-open regularly to extract the samples, imperfect vacuum was obtained and the results from these samples can be considered equivalent to standard storage in sealed plastic bags. The heat-treated samples are shown in **Figure 5.13** below, after one week of storage.

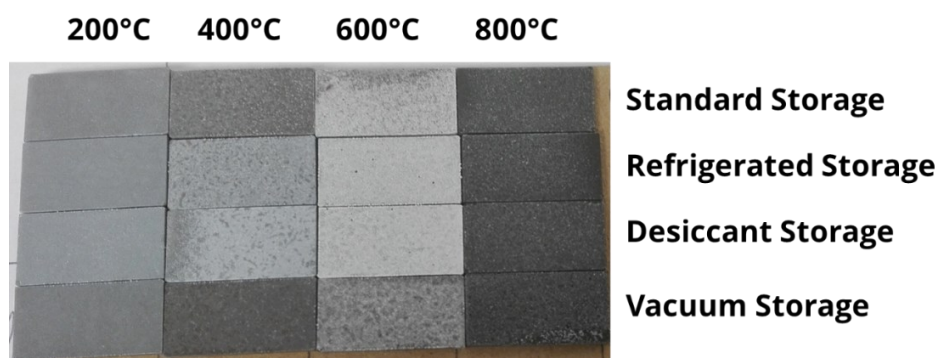


Figure 5.13 Photograph of 16 stainless-steel samples, of dimensions 20 x 10 x 3 mm, painted with THP, heated to 200 °C, 400 °C, 600 °C and 800 °C and stored in four different storing conditions.

Humidity was found to be a critical parameter, as it has an influence on the kinetics of the chemical reaction associated with efflorescence [330]. The ambient humidity surrounding the samples was measured regularly with a HM01 humidity meter, Tack-life tools, which allowed for simultaneous Relative Humidity (RH) readings and ambient temperature readings. The instrument displayed the % RH dew point wet bulb readings with an accuracy of 3 %. Humidity and luminescent measurements were recorded every 3.5 days and plotted in **Figures 5.14** and **5.15**, respectively. The humidity values shown in **Figure 5.14** below correspond to the first 21 days of the experiment. The total duration of the experiment was 42 days, but as the humidity recorded in the desiccant storage bag increased overtime, the desiccant was substituted on day 21. The humidity values obtained for the rest of the days are equivalent to the first 21 days.

Humidity was found to be relatively stable for the samples stored in plastic bags. “Standard” and “vacuum” can therefore be considered equivalent storage conditions. The recorded humidity values, between 50 and 70 % RH, correspond to the atmospheric conditions in London, United Kingdom. This humidity was higher for the cold storage storing condition, where the relative humidity was around 70 %. Finally, the samples stored in a plastic bag with desiccant were exposed to humidity lower than 40 %. The desiccant incorporated ambient humidity as the bags were opened and the samples extracted for luminescent measurements. This explains the increasing trend of the relative humidity for the desiccant values in **Figure 5.14** below, and why the silica-gel desiccant was substituted on day 21 of the experiment.

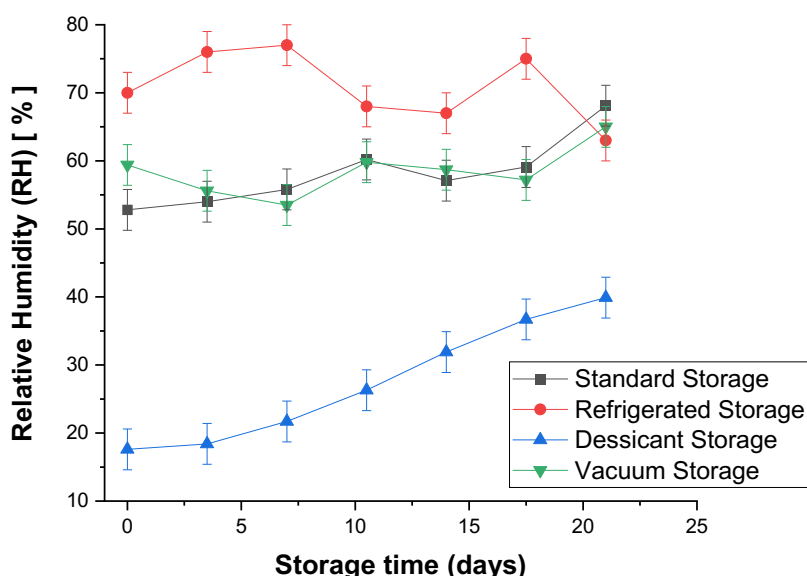


Figure 5.14 Humidity measurements for the four storage conditions considered to study efflorescence on THP.

Life-Time Decay (LTD) recordings on the 16 samples considered, are shown in **Figure 5.15** over 42 days. LTD ranges for the four storage conditions are clearly differentiated according to the heat treatment temperature the samples were subjected to. Samples heated to 800 °C show LTD values of around 1,800 μ s, while samples heated to 600 °C exhibit values below 1,600 μ s. Decreasing temperature and LTD, samples heated to 400 °C display LTD around 1,200 μ s and finally samples subjected to heat treatment at 200 °C have LTD values around 800 μ s.

Clear differences can be observed between samples stored at different conditions as well. While samples stored in desiccant or in a fridge show relatively stable LTD values for the whole storage duration, samples stored in standard conditions and in vacuum bags at ambient temperature, show clear decreasing trends of LTD over the storage time. These effects can be linked to the presence of carbonates, which were found in the diffraction patterns of THP shown in **Figure 5.3**, after heat treatment at 1,000 °C. The presence of carbon residuals in the pigment or the binder is unlikely after heat exposure at those high temperatures, while chemical reaction on the surface of the paint with the CO₂ and the humidity in the air are more likely. In agreement with Araguas-Rodriguez [106], the biggest changes occur in the first 15 days of storage for the intermediate temperatures, 400 °C and 600 °C.

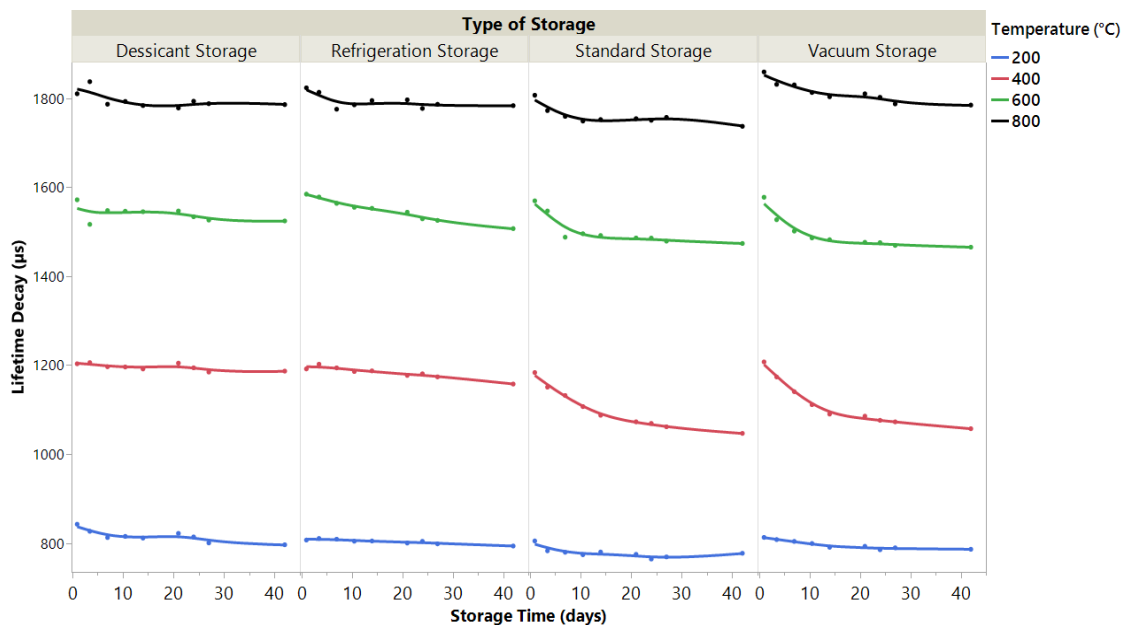


Figure 5.15 Evolution of luminescent lifetime decay of THP deposited on stainless steel samples, heat treated at 200 °C, 400 °C, 600 °C and 800 °C and then stored for 42 days in different conditions: Standard storage (in a sealed plastic bag), Refrigeration storage (sealed bag stored in a fridge at around 5 °C), Desiccant storage (samples stored in silica gel) and Vacuum storage (samples stored in vacuum bags).

The lifetime decay results shown in **Figure 5.15** led to the identification of cold and dry storage conditions, in a fridge and in silica-gel desiccant, respectively, as the two conditions that could mitigate the effect of the efflorescence in the luminescent behaviour of THP. The decrease in LTD in cold and dry conditions is less steep than for standard and vacuum, in particular in the first 15 days of storage. However, the ideal storage conditions for deposited THP, under low storage temperature, low humidity, and low CO₂ atmospheres, might proof impractical in a real turbomachinery application. Large component would be difficult to store in desiccant or in cold environments, such as fridge. Hence, a development of the THP towards minimising the impact of the efflorescence would be immediately advantageous to this technique.

In an industrial application of THP, the efflorescence effect in lifetime decay could be reduced by storing the painted turbomachinery components and calibration samples for the same duration. However, slight delays in the heat treatment of the calibration samples with respect to the engine operation could result in a mismatch in the temperature determination.

5.1.5 Strategy to reach reliable measurements at high temperatures

After reviewing the behaviour of conventional Thermal History Paint (THP) in the previous sections, and identifying the main challenges, a strategy was devised to act on the performance of the THP as a temperature sensor. A summary of the observed THP behaviour and associated actions is displayed in **Table 5.6** below. The black dots represent expected improvement effects on every challenge. These actions will be developed experimentally in the following sections.

The action with the highest expected impact is the binder substitution, which could solve most of the ambiguity around the THP, from the efflorescence to the pigment-binder interaction. A binder with a high melting point and with little interaction with the substrate will be surveyed from among commercially available products. The current binder and pigment will also be modified in order to reach higher temperature capabilities. Finally, a series of interlayers between the THP and the metallic substrate will be explored to reduce the interaction between the paint and the metallic substrate.

Table 5.6 Summary of main observations on THP after heat treatment and suggested solutions to reach reliable temperature measurements at high temperatures.

THP behaviour at high temperatures → ----- Suggested solutions ↓	1. Interaction Pigment - Binder	2. Binder melting	3. Interaction with metallic substrates / THP structural degradation	4. Efflorescence / Shelf life
1. Binder modification	●	●		
2. Binder substitution	●	●	●	●
3. Pigment modification	●		●	
4. Interlayer			●	

5.1.5.1 Pigment calcination

To obtain enhanced THP behaviour at high temperatures, the pigment calcination temperature must be considered. The THP version, used by Araguas-Rodriguez [106], contains $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ pigment, produced via sol-gel, and calcined at 400 °C for 1 hour. The paint produced with this pigment delivers monotonic measurements between luminescent lifetime decay and temperature for a range between 150 °C and 900 °C. For the purposes of this thesis, narrower and higher temperature ranges are preferred, and higher calcination temperatures were investigated.

Three batches of paint were produced with three pigments calcined at different temperatures: 250 °C, 400 °C and 600 °C. Three stainless-steel bars were painted and exposed to temperature gradients from 150 °C to 1,100 °C in a tube furnace for 30 min, as indicated in *Chapter 4*. The lifetime decay values obtained along the bar are plotted in **Figure 5.16** below for the maximum temperature seen at every location along the bar.

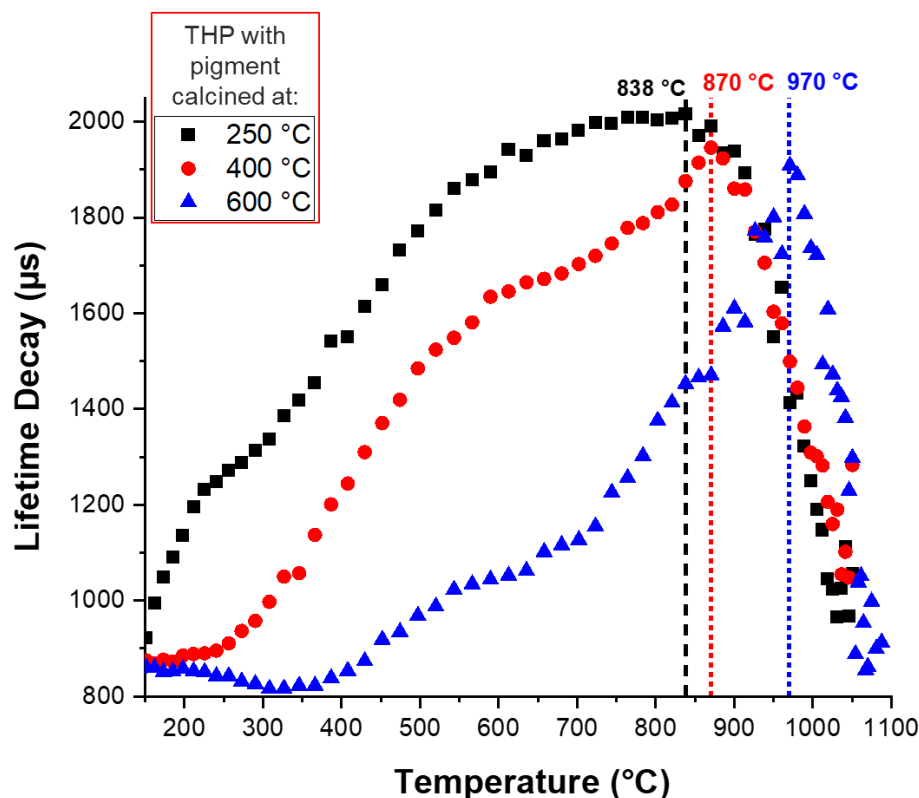


Figure 5.16 Lifetime decay as a function of temperature for potassium silicate binder mixed in with $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ pigments, previously calcined at 250 °C, 400 °C and 600 °C. Maximum sensing temperatures indicated for clarity.

The three curves display a similar general behaviour. For the 250 °C and 400 °C cases the lifetime decay increases monotonically from 100 °C, until a certain point (indicated with vertical bars). The 600 °C case is slightly different since the pigment was calcined at a higher temperature. The lifetime decay decreases between 100 °C and 300 °C, experiencing a monotonic increase between 300 °C and 970 °C, indicated as a vertical line. This can be considered the maximum sensing or working point, after which the lifetime decay drops with increasing temperature. The luminescent readings at higher temperatures, after the drop in LTD, are not normally considered in the temperature determination of painted turbomachinery components, as a single lifetime decay value could represent two temperatures and lead to incorrect temperature sensing.

Overall, the monotonic increasing trend of the lifetime decay over temperature can be explained with the luminescence fundamentals introduced in *Chapter 2*. The temporal luminescent behaviour of phosphors can be summarised with the Equation 5.1, below.

$$\tau = \frac{1}{P_R + P_{NR}} \quad (5.1)$$

where LTD (or τ) is inversely proportional to the probability of radiative decay (P_R) and the probability of non-radiative (P_{NR}) decay of an electronic transition from an excited state to a ground state. The probability of non-radiative decay, P_{NR} , includes all possible quenching mechanisms that could prevent radiative emissions. These can be residual species with high phonon energy, such as defects within the structure. In the case of THP, synthesis residuals (NO_3^- , OH^- and carbonates among others) will gradually leave the structure of the paint with increasing temperature. The pigment and paint silicate structures will start forming, densifying, and reducing the overall defect concentration. The removal of all these quencher species will reduce the P_{NR} , which in turn will lead to an increase of LTD values.

As seen in **Figure 5.16**, the temperature-lifetime decay behaviour of THP's with pigments calcined at different temperatures shifts with calcination temperature. A high calcination temperature of the pigment (600 °C) was found to increase the upper bound of the monotonic increasing range of the calibration curve up to 970 °C. This behaviour can be explained considering the local environment of the emitting ions of each paint. The calcination temperature affects the local structure surrounding the Eu^{3+} ions, shifting the low probability of non-radiative decay to higher temperatures. The Eu^{3+} ion, in pigment calcined at a higher temperature, is more protected from quenching mechanisms once is mixed into the binder. Conversely, at lower temperatures the paint behaviour for higher calcination temperatures, plateaus proportionally to this calcination temperature. For the pigment calcined at 600 °C, the temperature sensing resolution starts at 350 °C, while for lower calcination temperatures the THP resolution starts earlier.

Additionally, as shown in **Figure 5.16**, the paint with the pigment calcined to 250 °C shows higher LTD values than pigments calcined at higher temperatures. This pigment shows an offset of around 150 μs with respect to the paint with the pigment calcined at 400 °C, and an offset of around 500 μs with respect to the paint with the pigment calcined at 600 °C. These differences suggest an intrinsic difference in the luminescent emission of the Eu^{3+} ions, which are in different environments in each paint. Araguas-Rodriguez [106] hypothesized, from observations of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, that a higher calcination temperature resulted in an easier dispersion of the pigment into the THP. Up to 350 °C the pigment showed traces of nitrates, which conforms a more regular environment for an emitting Eu^{3+} ion, compared to the amorphous silica network of the binder. The structure of the $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment was described with the FTIR spectra shown in **Figure 5.17**, where silicate species cannot be observed below 400 °C.

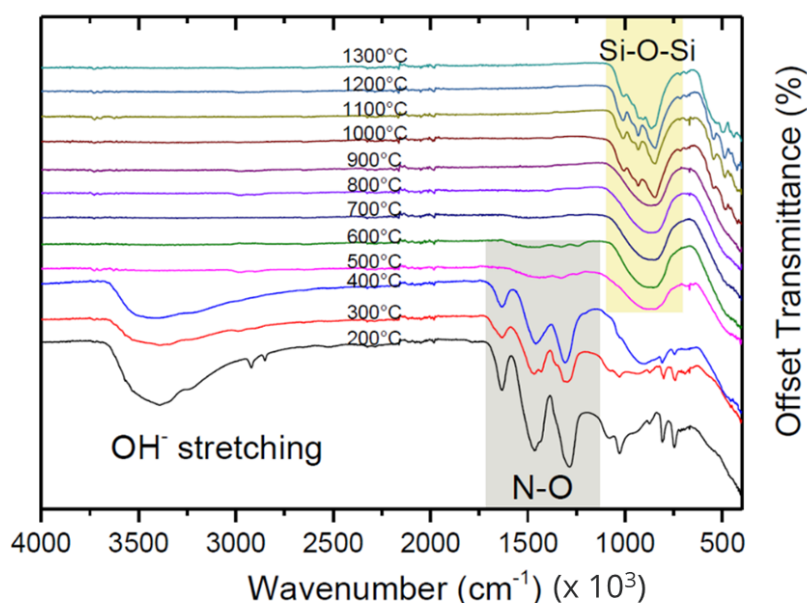


Figure 5.17 FTIR spectra of $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment samples heat-treated for 30 minutes to the indicated temperature. Silicate and nitrate peaks identified. Extracted from [106] with permission via CC-BY-NC-ND 4.0.

In the same way that high calcination temperatures (600 °C) expand the monotonic increase of lifetime decay to temperatures up to 970 °C, low calcination temperatures of the pigment (250 °C) result in a reduced maximum working temperature of the THP, to 838 °C, as seen in **Figure 5.17**. The compromise solution found by Araguas-Rodriguez [106] consisted of pigment calcined at 400 °C, which gave the widest temperature range with monotonic increase of lifetime decay between 200 °C and 900 °C. For the purposes of this thesis, the $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment calcined to 400 °C and 600 °C were used as references, both mixed into the standard binder, and tested in alternative binders. Standard THP produced with these binders are referred in the following sections as THP-P400 and THP-P600, respectively.

Sapphire single crystal discs were painted with the THP-P600 version, to observe its behaviour on a non-metallic substrate, similar to the THP-P400 version shown in **Figure 5.7**, in *Section 5.1.3*. Lifetime decay and spectral measurements were taken on the painted discs after heat treatment between 800 °C and 1,300 °C. Photographs of the discs after heat treatment, and associated results are shown in **Figure 5.18**.

Both LTD and spectra results are similar to the ones discussed for THP-P400 in *Sections 5.1.1 and 5.1.3*. The monotonic increase of lifetime decay with temperature was maintained up to 1,150 °C. This trend differed from the behaviour of the pigment on its own, that showed a maximum of lifetime decay at 1,000 °C, indicated with vertical lines in **Figure 5.18 (a)**. The temperature range of the monotonic increase of the pigment expanded once it was introduced in the binder. The luminescent spectra of the THP-P600 showed the expected emission lines, with small variations above 1,000 °C with respect to the spectra shown in *section 5.1.1* for THP-P400, analysed peak by peak in **Table 5.1**.

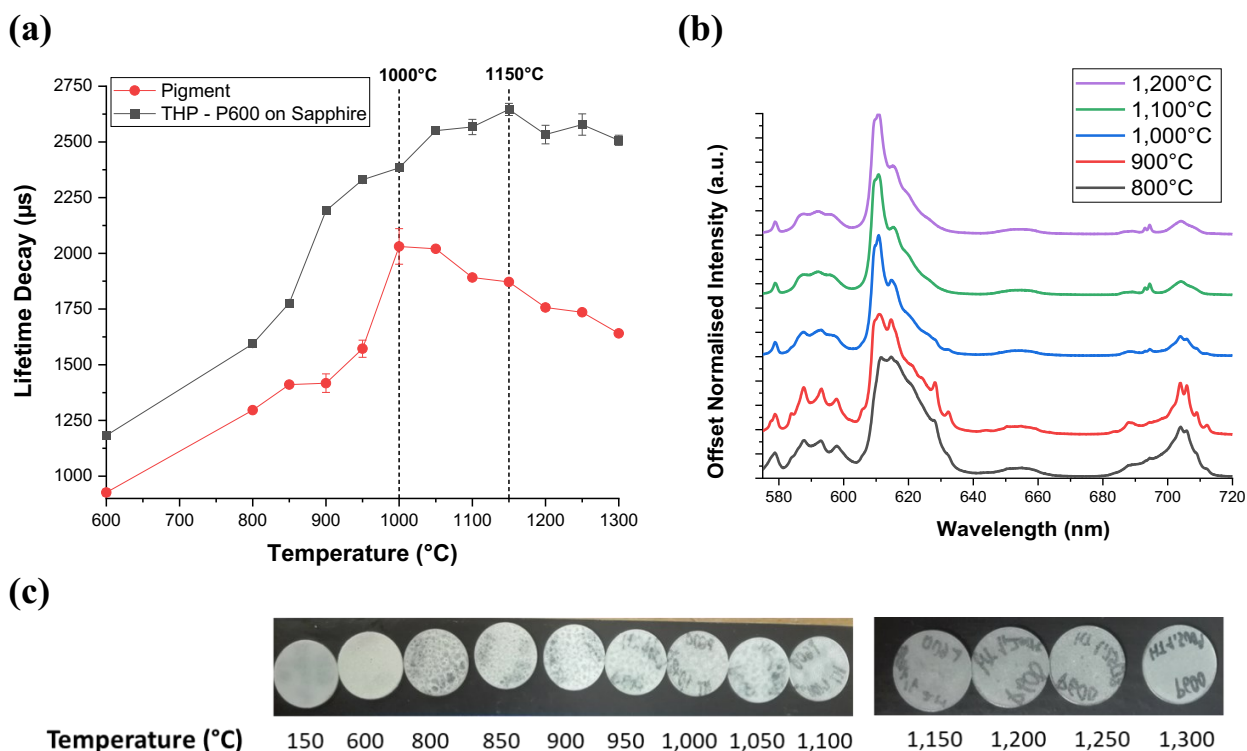


Figure 5.18 (a) Lifetime decay evolution over temperature for THP – P600 applied on sapphire discs. Lines linking points added for visualization (b) Luminescent spectra of THP – P600 deposited on sapphire discs and heat treated at temperatures from 600 °C to 1,300 °C. The $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment of the THP – P600 was calcined to 600 °C prior to paint production. (c) Painted sapphire substrates, heat treated to the indicated temperature.

5.1.5.2 THP References

Once the pigment calcination temperature has been taken into consideration, a reference test was devised to compare THP modifications with existing references. The bar test described in *Chapter 4* was considered the more appropriate testing method, as it allows measurements across a wide temperature range in a single experiment. Two 400 x 20 x 3 mm stainless-steel bars, issued from SOG Ltd., were cleaned and the surface of one the long sides, grit blasted and painted with the reference THP's, consisting of potassium silicate binder (95 % wt.) and $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment calcined at 400 °C or 600 °C (5 % wt.). These are THP-P400 and THP-P600, respectively.

The reference binder was ordered from Indestructible Paint Ltd. [293], which markets this potassium silicate solution under the name *IP66*. The original manufacturer of the binder is PQ Corporation [294], which gave the name *Kasil® 6* or *K6* to this particular composition of potassium silicate. The solid content, density and pH of this binder are summarized in **Table 5.7** below.

Table 5.7 Solid content, density, and pH measurements on current THP reference, using potassium silicate binder.

Binder	Solid Content (%)	Density (g/ml)	pH
IP66 / K6 (PQ Corp)	36.9 +/- 0.2	1.6 +/- 0.2	8.6

Once the painted bar was heat treated in a tube furnace, the THP was exposed to a wide temperature range, from below 200 °C at its cold end up to 1,100 °C at the hot end. The change in colour of the THP, deposited on stainless-steel, is shown in **Figure 5.19**. The paint displayed a light grey colour at low temperatures,

turning white at around 500 °C, where the highest intensity is detected [106]. However, at higher temperatures the THP becomes progressively darker, showing a dark green colour near the hot end, where the intensity of the luminescent emission is lower.

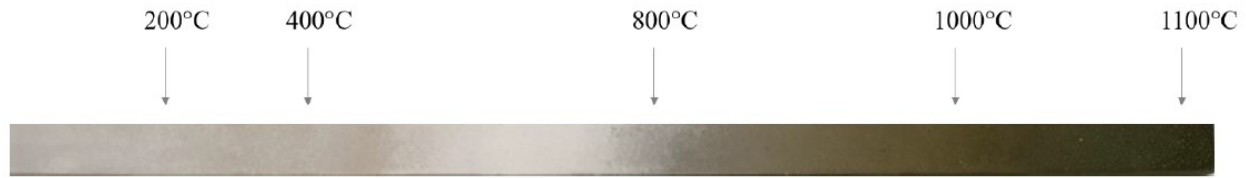


Figure 5.19 Photograph of THP deposited on a 40 cm long stainless-steel bar, and heat-treated between 200 °C and 1,100 °C. The darkening of the THP, associated with the LTD drop, appears at temperatures above 900 °C, where the colour turns green. Estimated temperature locations have been included for clarity.

Lifetime decay measurements were obtained every 5 mm along the bar and plotted against the maximum temperature seen at every location. The results are displayed in **Figure 5.20** for both THP-P400 and THP-P600 references. For a better analysis of the monotonic increase of the LTD with temperature, a sensitivity analysis was performed on the lifetime decay evolution over temperature. Sensitivity has been defined by Dramicanin [331] as the quotient between the change of a luminescent parameter, lifetime decay in this case, and the associated change in temperature. This definition was based on the International Vocabulary of Metrology (VIM) [332], adapted for temporal luminescent thermometry measurements, and described in **Equation 5.2**.

$$S = \frac{\partial \tau}{\partial T} \quad (5.2)$$

where:

- τ or LTD, Luminescent Lifetime Decay, measurand or indication of the luminescent emission [μs], measurand or indication, luminescent sensing parameter leading to a temperature measurement.
- T , exposure temperature [$^{\circ}\text{C}$ or K]
- S , Sensitivity, quotient of change in the indication, or LTD in this case, over temperature [$\mu\text{s} / ^{\circ}\text{C}$]

The choice of the first derivative of the LTD-Temperature curve, as a sensitivity parameter, was influenced by metrology standards [332], and has been used to determine the sensitivity of thermographic phosphors in the past [331]. The temperature values used to plot the LTD values can be used to plot the first derivative as well, maintaining the same interpolation range. More specifically, Peral *et al.* [210] used a model based in the LTD-Temperature curve to determine the uncertainty of the temperature measurement obtained from THP. The first derivative of the LTD-Temperature curve was used as a sensitivity coefficient in the uncertainty propagation model. The estimated uncertainty of the THP was $\pm 3 - 6 ^{\circ}\text{C}$, for 67 % confidence levels, with a maximum uncertainty of $\pm 13 ^{\circ}\text{C}$ for 95 % confidence levels. These are in the same order of magnitude as the uncertainties of thermocouple readings.

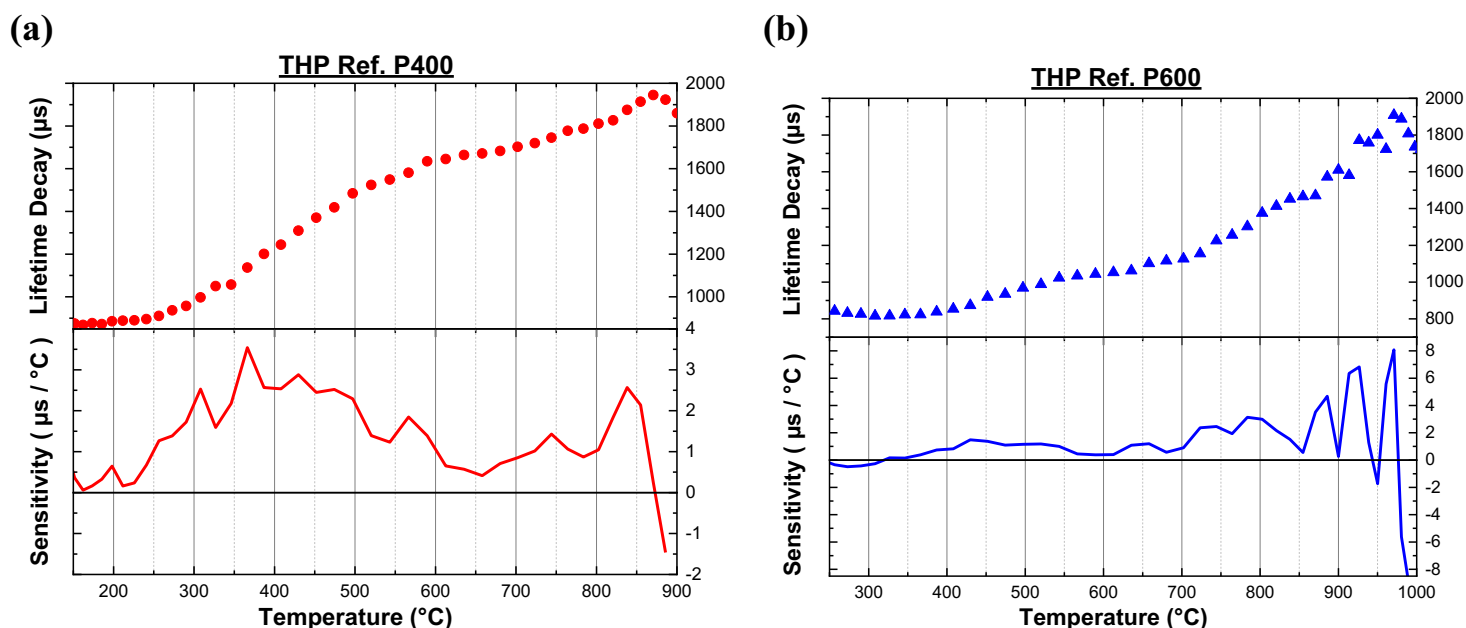


Figure 5.20 Reference THP deposited on a stainless-steel bar, heat treated and where LTD was measured every 5 mm. The monotonic increase of lifetime decay (top) and the sensitivity analysis of the monotonic increase (bottom) are shown over increasing temperature, between 150 °C to 900 °C for THP-P400 (a) and THP-P600 (b) over a temperature range, between 250 °C and 1,000 °C.

In **Figure 5.20 (a)** the monotonic increase of the lifetime decay of the reference paint THP-P400 is shown between 150 °C and 900 °C. The sensitivity analysis is shown in at the bottom of the same figure, with values above 1 $\mu\text{s}/^\circ\text{C}$ from 200 °C to 870 °C. The minimum value measured of lifetime decay was 872.0 μs and the maximum 1,945.1 μs . In **Figure 5.20 (b)** the monotonic increase of the lifetime decay of the reference paint THP-P600 was analysed from 250 °C to 1,000 °C. The sensitivity is shown at the bottom of the same figure and can be divided into three regions. For temperatures below 500 °C, the sensitivity remains below 2 $\mu\text{s}/^\circ\text{C}$, while for higher temperatures the sensitivity increases up to 3 $\mu\text{s}/^\circ\text{C}$. Above 900 °C, the lifetime decay shows a noisy monotonic increase up to the maximum around 960 °C.

In terms of luminescent lifetime decay, the minimum value measured was 963.6 μs and the maximum 2,105.3 μs . This wide range of lifetime decay leads to an average sensitivity of 2.1 $\mu\text{s}/^\circ\text{C}$ between 250 °C and 960 °C., which is slightly different for the different temperature regions described before. These parameters, and the monotonic increase temperature range for both P400 and P600 reference paints, are summarized in **Table 5.8** and will be used as a comparison for the subsequent binders tested in this chapter.

Table 5.8 Summary of lifetime decay evolution over temperature for THP reference.

	Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range ($^{\circ}\text{C}$)	Sensitivity ($\mu\text{s}/^{\circ}\text{C}$)
THP Ref. P400	872.0	1,945.1	1073.1	From 200 $^{\circ}\text{C}$ to 870 $^{\circ}\text{C}$	1.4 +/- 1.0
THP Ref. P600	963.6	2,105.3	1141.7	From 250 $^{\circ}\text{C}$ to 960 $^{\circ}\text{C}$	2.1 +/- 1.7

5.2 Modification of existing binder

The potassium silicate binder currently used to produce THP presents some limitations at high temperatures, as shown in *section 5.1* of this chapter. Some of the improvement points are the binder melting temperature and the interaction between the pigment and the binder. The use of this potassium silicate binder limits the temperature detection range to 900 $^{\circ}\text{C}$ or 970 $^{\circ}\text{C}$ on metallic substrates, depending on the calcination temperature of the pigment.

In this section, two modifications of the existing binder are tested in order to increase the melting point of the THP and widen its temperature detection range above 900 $^{\circ}\text{C}$. Firstly, potassium hydroxide was added to the current binder, in order to increase the amount of potassium in the binder solution, and therefore increase the melting temperature of the THP. Secondly, lithium hydroxide was added the standard potassium silicate expecting less effects of efflorescence, as described by Veinot *et al.* [329]. These modifications are part of the first action to reach better measurement reliability with THP.

5.2.1 Potassium addition

The current THP formulation is comprised of a 95 % weight of a potassium silicate binder. Araguas-Rodriguez [106] found that the silica (SiO_2) content of this binder was around 0.55 % mol, which falls between the compounds $\text{K}_2\text{Si}_2\text{O}_5$ and $\text{K}_2\text{Si}_4\text{O}_9$, as shown in the potassium oxide – silicon oxide phase diagram in **Figure 3.6**. Considering these extremes of the binder composition the temperature capabilities of the current silicate binder could be expanded by increasing the melting temperature. The simplest way to increase the melting temperature, according to the phase diagram, would be to increase the potassium content, towards the 1,046 $^{\circ}\text{C}$ melting point of $\text{K}_2\text{Si}_2\text{O}_5$. To this end, potassium hydroxide, KOH, was added to the binder solution. This task was performed in collaboration with Dr Violaine Mendez and Richard Banks at Indestructible Paint [293]. The addition of KOH to the binder solution resulted in one extra equivalent of potassium per silica (SiO_2) in the silicate network. This new binder formulation was used to manufacture THP with a standard P400 pigment, as described in *Chapter 4*.

A bar test was performed with this modified version of the binder. A 40-cm long stainless-steel bar was cleaned, grit-blasted and painted with the modified binder, as shown in **Figure 5.21 (a)** below. While the paint remained in good state both in liquid solution and applied onto the stainless-steel bar, during heat-treatment, the paint showed bubbling and detachment from the metallic substrate, as shown in **Figure 5.21 (b) and (c)** below. This might indicate a lack of chemical stability in the silicate. Potassium silicates are known to be hygroscopic, and the absorbed moisture could have introduced inhomogeneities in the paint structure [333].

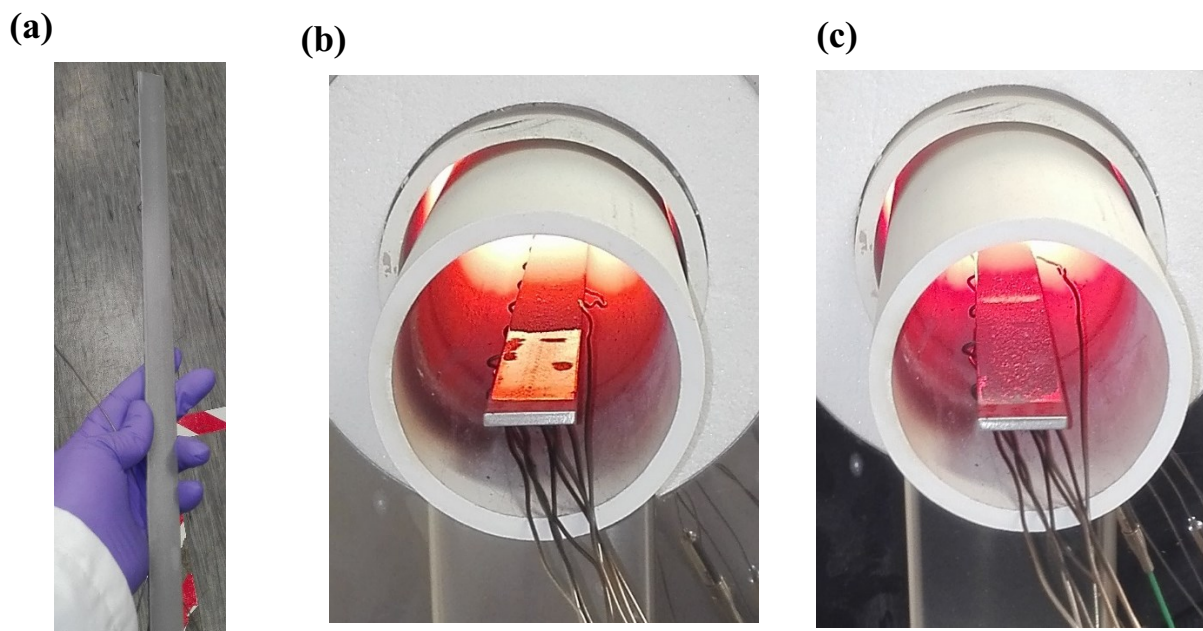


Figure 5.21 (a) Stainless steel bar painted with binder modified by potassium addition. **(b)** Photograph of the first seconds of heat treatment of a stainless-steel bar painted with modified binder, with potassium addition, in a tube furnace heated up to 1,100°C. Bubble formation is visible at hot temperatures. **(c)** Photograph after some minutes of the same bar heat treatment, where paint blisters are visible all over the painted surface, from hot to cold end of the painted bar.

Despite the paint detachment from the surface, luminescent lifetime decay measurements could be obtained on the surface of the bar after heat-treatment. Measurements were taken every 5 mm from the cold to the hot end of the bar and plotted against the maximum temperature seen at every location. These results are displayed in **Figure 5.22 (a)** below. The monotonic increase of the LTD with temperature is further examined via a sensitivity analysis of the paint between 200 °C and 900 °C and shown in **Figure 5.22 (b)**. Overall, the sensitivity values obtained are above 1 $\mu\text{s}/^\circ\text{C}$, with a stable increase between 400 and 700 °C. However, from 800 °C the paint detached severely from the metal and the lifetime decay showed a noisy trend from 900 °C.

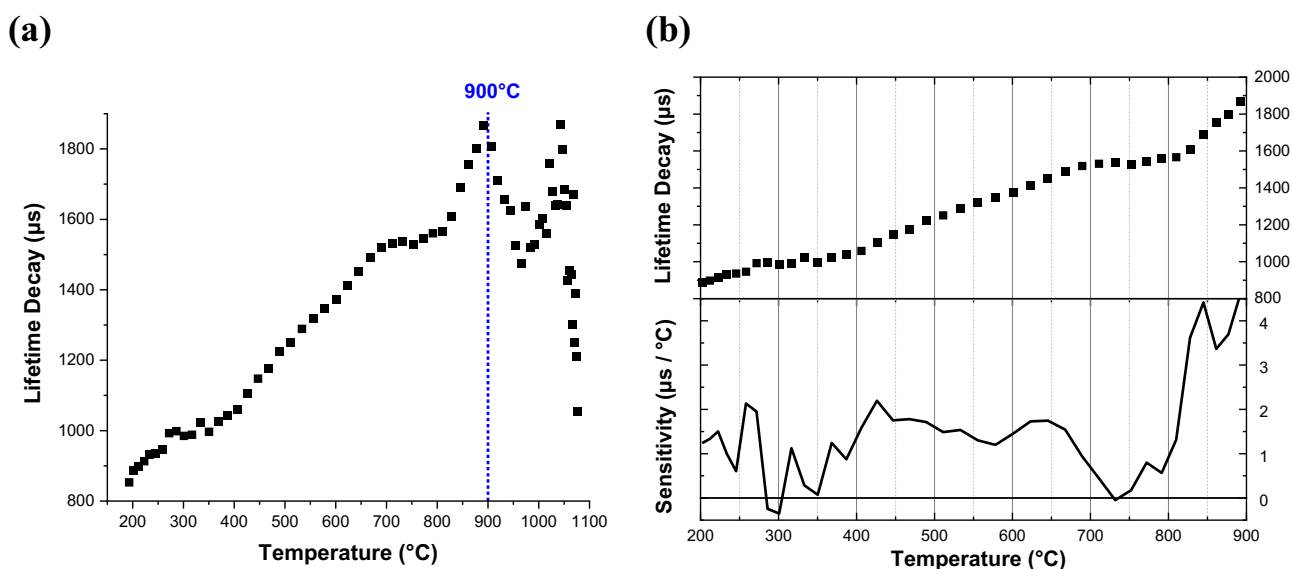


Figure 5.22 (a) Lifetime Decay plotted over temperature for luminescent history paint, modified by potassium addition and deposited on a 40 x 20 x 3 mm stainless-steel 316L bar. During heat treatment a temperature gradient, between 150 °C to 1,100 °C was generated along the bar, allowing for lifetime decay to be measured after heat treatment. (b) Monotonic increase of lifetime decay over temperature for modified history paint, by potassium addition (top) and sensitivity analysis of the monotonic increase (bottom).

In terms of luminescent lifetime decay, the minimum value measured was 853.3 μs and the maximum 1,870.5 μs . This wide range of lifetime decay is effectively limited at 800 °C. At this point the detachment of the paint became noticeable. Measurements at higher temperatures were not considered, despite the apparent improvement in sensitivity between 800 °C and 900 °C. The drop in LTD at temperatures higher than 900 °C produces some ambiguity if LTD is the only parameter available for temperature determination. Further interpretation can be made via analysis of the luminescent spectra and/or through visual inspection. For example, the oxidation of metallic surfaces is quite evident at these high temperatures compared to metals exposed at 800 °C, which could be easily differentiated from metals exposed at 1,100 °C. The THP also changes colour at high temperatures, as shown in **Figure 5.19** for the reference paints. All the sensitivity parameters obtained from the THP enriched with potassium are summarized in **Table 5.9** below.

Table 5.9 Summary of lifetime decay evolution over temperature for binder modification by potassium addition.

	Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range (°C)	Sensitivity ($\mu\text{s}/^\circ\text{C}$)	Attachment to metallic substrate
Binder modification, Potassium addition	853.3	1807.5	954.2	From 193 °C to 905 °C	1.11 +/- 0.69 (until 800 °C)	Bubbling observed during heat treatment. Paint flaking off during cooling.

3345

5.2.2 Lithium addition

Lithium silicates belong to the same group of water-based systems as sodium and potassium silicates: soluble silicate solutions [334]. Lithium silicate on its own is explored as an alternative binder in *section* 5.3, however lithium addition to the current potassium silicate binder was suggested by the binder provider, Indestructible Paint, and performed by Dr Violaine Mendez at their facilities. Lithium hydroxide, LiOH, was added to the solution in a similar way to the potassium hydroxide. Two new binder formulations were produced: one containing half lithium equivalent per silica (SiO_2) in the solution and a second mix containing one lithium equivalent per silica. These two mixtures were named 37 and 24 respectively and tested as binders to manufacture THP. A standard P400 pigment was used.

3350

3355

After production, the binders with Lithium added were found to polymerise. The inside of one of the bottles received by the author is shown in **Figure 5.23 (a)** below. Nevertheless, 47g of both formulations were extracted from the respective bottles and mixed with P400 pigment and water to produce sprayable THP. After mixing both binders with an overhead stirrer and zirconia beads, as explained in *Chapter 4*, two sprayable formulations were produced and tested on two stainless-steel bars. The THP production process is shown in **Figure 5.23 (b)** below.

3360

(a)**(b)**

Figure 5.23 (a) Photograph of polymerized potassium silicate binder modified by lithium addition, introducing one equivalent of lithium per silica equivalent, as received by the author. **(b)** Photograph of lithium enriched potassium silicate binder, after water and pigment addition. An overhead stirrer was used, as well as zirconia beads to facilitate the mixing.

3365

Two 40-cm long stainless-steel bars were painted with the modified binder formulations, 24 and 37. Lifetime decay measurements were taken along the bar, after heat-treatment, from the cold to the hot end and plotted against the maximum exposure temperature seen at every location. These results are displayed in **Figure 5.24 (a)** below. The monotonic increase of both LTD's over temperature are further examined with a sensitivity analysis between 150 °C and 750 °C and shown in **Figure 5.24 (b)**. A photograph of the two tested bars is displayed in **Figure 5.24 (c)**, where the cold and hot ends are indicated for clarity.

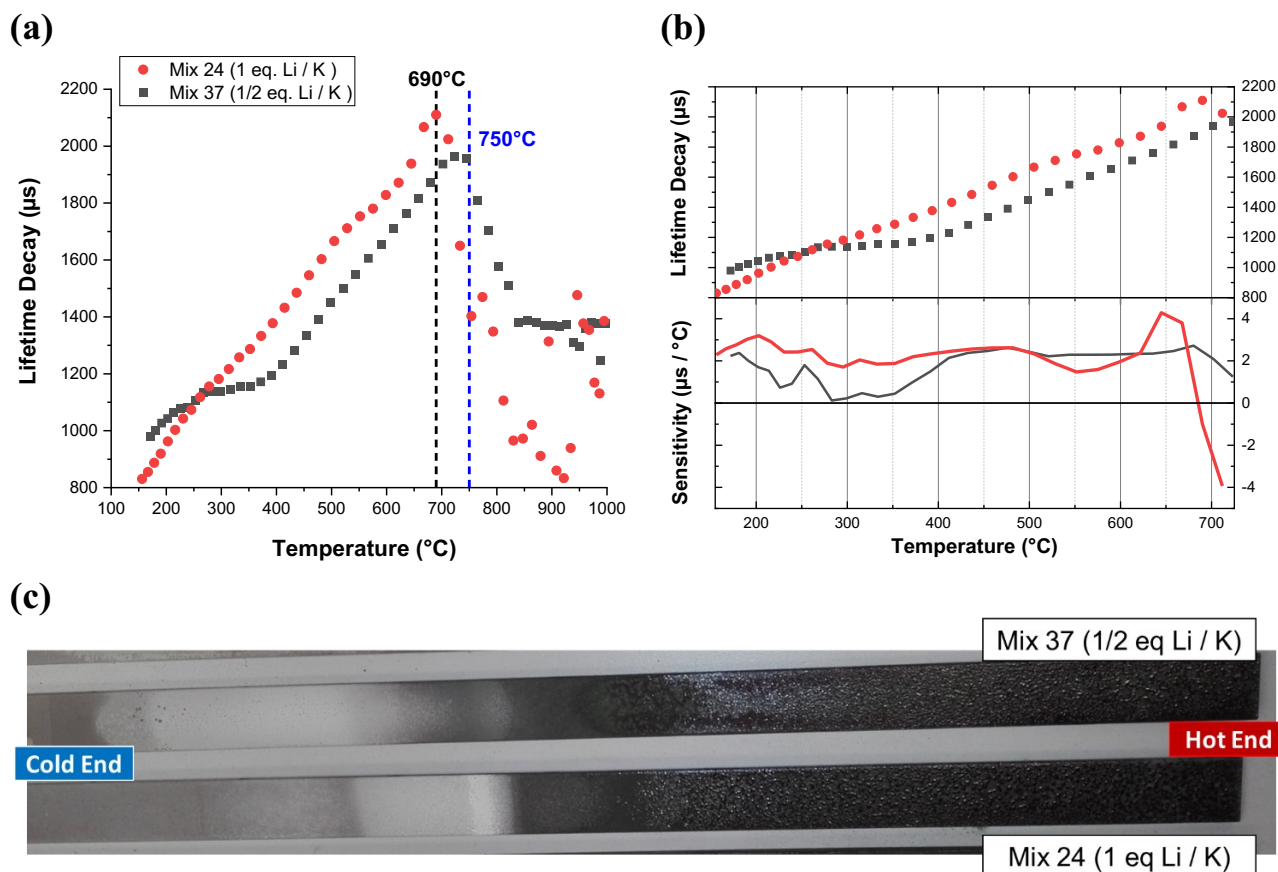


Figure 5.24 (a) Lifetime Decay plotted over temperature for two mixes of luminescent history paint, modified by lithium addition, and deposited on 400 x 20 x 3 mm stainless-steel bars. **(b)** Monotonic increase of lifetime decay over temperature for modified THP, by lithium addition (top) and sensitivity analysis of the monotonic increase (bottom). **(c)** Photograph of the bars painted with modified binder, by lithium addition. Cold end (~ 200 $^{\circ}\text{C}$) and hot end ($\sim 1,100$ $^{\circ}\text{C}$) indicated.

The luminescent lifetime decay of the two binders ranges from a minimum of 830.7 μs and 980.0 μs for *Mix 24* and *Mix 37*, respectively, to a maximum of 2,110.2 μs and 1,963.7 μs , respectively. This wide range in lifetime decay does not correspond to a wide temperature range, since both mixes have their maximum LTD around 700 $^{\circ}\text{C}$. This is substantially below the 900 $^{\circ}\text{C}$ upper limit of the standard THP.

In terms of sensitivity, both binders exhibit constant values around 2 $\mu\text{s} / ^{\circ}\text{C}$ along the working temperature range, from 200 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$. Measurements at higher temperatures were not considered. All the sensitivity parameters analysed are summarized in **Table 5.10** and will be compared with the rest of binders tested in this chapter.

3390 **Table 5.10 Summary of lifetime decay evolution over temperature for binder modification by lithium addition.**

	Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range (°C)	Sensitivity (μs/°C)	Additional Comments
<i>Mix 37,</i> ½ eq. Li / K	980.0	1963.7	983.7	From 162 °C to 702 °C	1.70 +/- 0.81	Polymerisation of the binder while in storage.
<i>Mix 24,</i> 1 eq. Li / K	830.7	2110.2	1279.5	From 167 °C to 712 °C	2.30 +/- 0.44 (until 650 °C)	Polymerisation of the binder and THP produced.

3395 Lithium addition to potassium silicate liquid solution did not achieve the extended temperature regime intended. As a matter of fact, the maximum temperature achieved for a monotonic increase of the lifetime decay over was found around 700 °C for the two mixtures tested. This temperature limit was almost 200 °C below the 900 °C upper limit of the potassium silicate on its own. The degradation of this lithium-potassium-silicate system can be associated with the melting temperature of the material system and the chemical stability observed before the addition of the pigment. The binder polymerised on its own and only long stirring times and water addition resulted in a sprayable paint. Despite the advantages expected from lithium-based binders, addition of lithium was discarded as a promising route to produce a new version of THP.

3400

5.3 Substitution of existing binder

Following the binder modifications explored previously, the focus of this section is on the binder substitution altogether. As explained in *section 5.1*, the current version of THP presents some limitations, in particular the binder behaviour at high temperatures. Substituting the current binder could improve all the areas of interest in a new THP formulation. To this end, more than 35 providers of commercially available paints, and other liquid solutions, were contacted for the development of this section. 10 products were found to produce viable paints, and therefore tested as THP binders.

3405

The criteria followed for the enquiry of commercially available high temperature binders included the following points:

3410

- High functional temperature, preferably above 1,200 °C.
 - Resistance to thermal exposure, over 30 minutes at a given temperature.
 - Low reactivity with ceramic/silicate pigments, and with metallic substrates.
 - No organic/plastic constituents.
 - Low viscosity, so that spraying with an air-pressure-gun remains possible.
 - Long shelf life both as a liquid solution and once applied on a surface.
- 3415

Further expectations of a novel high temperature binder included health and safety requirements, as all tested products were REACH compliant [90,91], as well as good adherence to the substrate these were applied on (stainless-steel 316L). Good control of the dry film thickness was also preferred, as some variability is expected as a result of the paint deposition via air-spraying, wet deposition, and subsequent drying.

5.3.1 High temperature binder candidates

After a thorough market survey, following the criteria outlined previously, six groups of commercially available products were identified and tested as potential high temperature binders. The behaviour assessment was evaluated via the bar test, presented in *Chapter 4*, and via sensitivity analysis as performed for the binder modifications presented in the previous section. In **Table 5.11**, the commercial name of the candidate products, provider company, basic composition, and maximum working temperature (as indicated in the respective technical datasheets) are summarised.

Table 5.11 Tested binder candidates, commercial providers, and summary of properties.

	Product Commercial Name	Provider Company	Main constituents	Maximum working temperature (°C)
0.	THP Reference IP66 / Kasil 6	Indestructible Paint [293] / PQ Corporation [294]	Potassium silicate water-based solution	900
1.	Sealmet®	Zyp-Coatings [285]	Sodium-potassium-aluminium silicate	1,300
2.	Fixwool® Coating 130	Unifrax [335]	Alumina and silicate	1,500
3.	Lithium Polysilicate	Grace & Co. [336]	Lithium poly-silicate (~4 %w Li ₂ O)	-
	LithiSil®25	PQ Corporation [294]	Lithium poly-silicate (~2.5%w Li ₂ O)	-
4.	Fabutit, FFB® 1210	Budenheim KG [337]	Mono-magnesium phosphate solution	1,210
5.	Durazane ® 1800	Merck Group [338]	Poly-silazane polymer	1,800
6.	Ludox® SM 30	Grace & Co. [336]	Colloidal silica (contains sodium)	1,650
	Ludox® HS 40		Colloidal silica (contains sodium)	1,650
	Ludox® AS 30		Colloidal silica (contains ammonium)	1,650
	Ludox® AS 40		Colloidal silica (contains ammonium)	1,650

5.3.1.1 Silicate based solution

As reported in *Chapter 3*, several silicate binders have been used in the past to embody THP, allowing phosphor-based paints to be sprayed on the surface of turbomachinery components. Among the products used in previous investigations, the high temperature coatings provided by Zyp Coatings, Inc. [285] were surveyed, as these products were used by several authors in the past [110,117,339]. A particular water-based coating stood out from the Zyp Coatings catalogue, Sealmet®. This product consists of a mix of ceramic oxides, specially intended for application on metallic substrates, in particular stainless-steel. The temperature upper limit indicated in the technical datasheet was 1,300 °C, which made Sealmet® an interesting candidate for high temperature exposure. Solid content, density and pH of this binder candidate were measured upon reception of the Sealmet® sample. These parameters are summarised in **Table 5.12**.

Table 5.12 Solid content, density, and pH measurements on Sealmet® silicate binder.

Product Commercial Name	Solid Content (%)	Density (g/ml)	pH
Sealmet ® - Zyp Coatings	67.7 +/- 0.8	1.1 +/- 0.2	9.2

Pigment preheated to 400 °C (P400) was mixed into the Sealmet® following the standard procedure described in *Chapter 4* for paint manufacturing. Two THP batches were generated with different pigment contents. The first batch comprised 5 % wt. of pigment and the second 10 % wt. For the second case, to guarantee a good miscibility, 10 g of water was premixed with 5 g of pigment, and then 35 g of Sealmet® was introduced to complete the single paint batch. This batch was sprayed onto two stainless-steel test bars. One bar was sprayed through the standard THP procedure, applying several paint layers onto the metal (between 10 and 15 layers). The second bar was sprayed on a single stroke, opening the paint valve of the spray gun, to obtain the same desired dry paint thickness, 30 µm. This application procedure was discussed with Zyp Coatings, as single layer deposition improved considerably the attachment to the metal substrate. The third stainless-steel bar, painted with a single layer of 10%w pigment mixed in Sealmet® THP, is shown in **Figure 5.25** below, after heat-treatment. One of the concerns using Sealmet® as a binder was the dark colour displayed after heat treatment. Despite the efforts to lighten the colour of the Sealmet® binder by introducing more pigment and water in the THP mixed, the painted surface of the bar remained quite dark, in particular at the hot end of the bar after heat treatment.

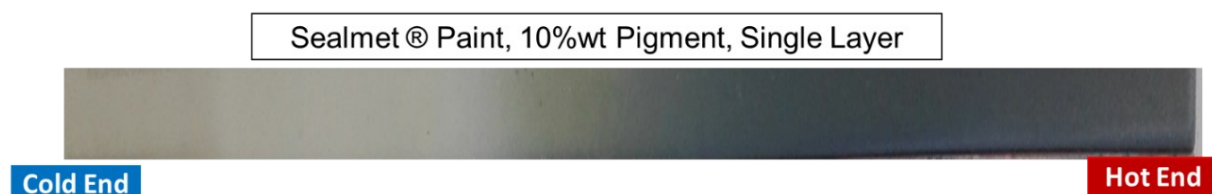


Figure 5.25 Photograph of the stainless-steel painted bar painted with Sealmet® binder, loaded with 10 % wt. of pigment, shown after heat-treatment. Cold end (~200 °C) and Hot end (~1,100 °C) indicated.

The three stainless-steel bars were heat-treated and measured for luminescent lifetime decay, from cold to hot end. The obtained LTD was plotted against the maximum exposure temperature seen at every location. The obtained results are displayed in **Figure 5.26 (a)** for Sealmet® with 5%wt. pigment and in **Figure 5.26 (b)** for Sealmet® with 10 % wt., both applied as several layers and as a single layer. The results from the three bars were subjected to a sensitivity analysis up to the maximum of the monotonic increase in LTD and shown in **Figures 5.26 (c) and (d)**.

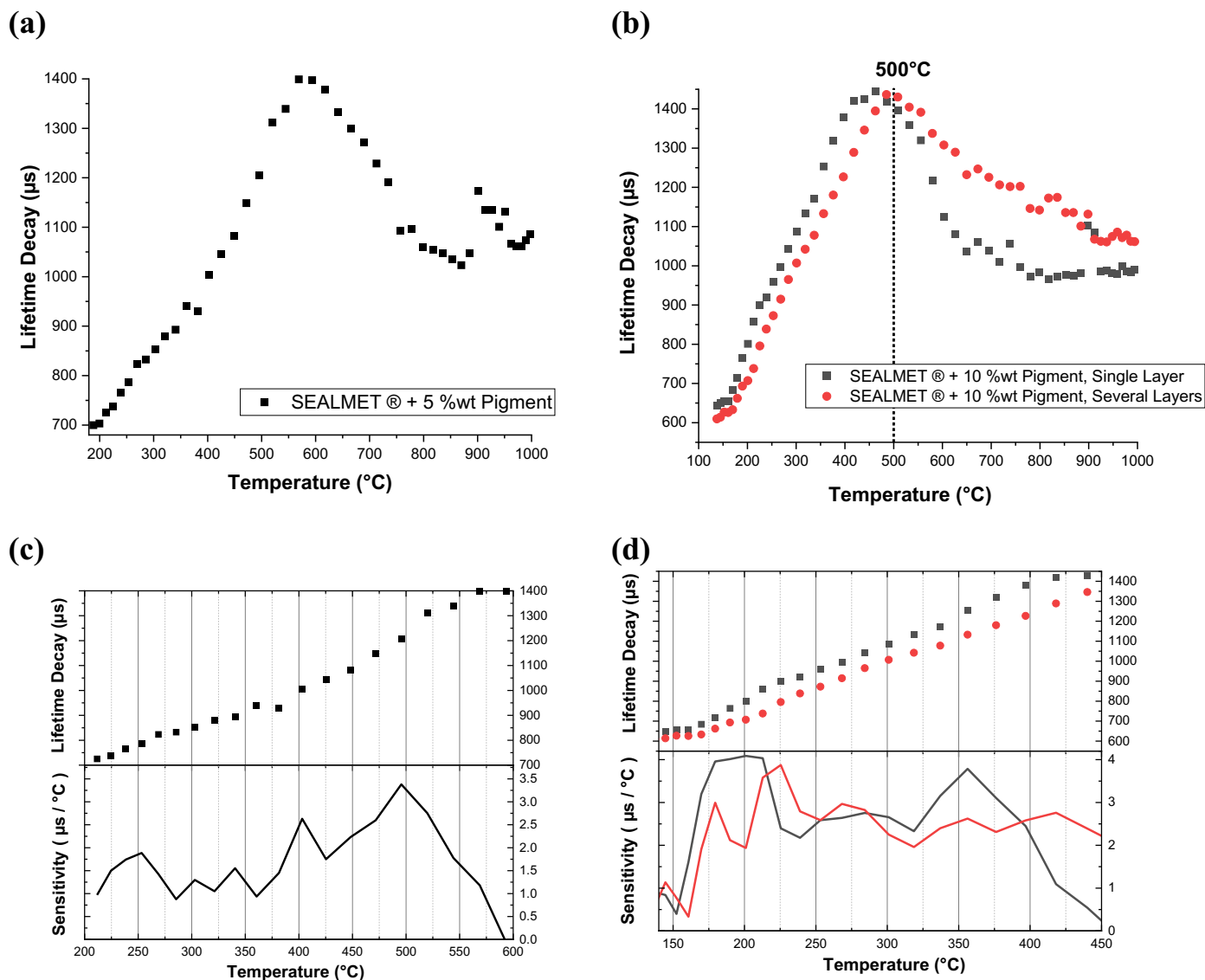


Figure 5.26 Lifetime decay plotted over temperature, measured on THP, and deposited on a stainless-steel bar for Sealmet® loaded with 5 % wt. pigment (a) and Sealmet® loaded with 10 % wt. pigment (b). The monotonic increase of lifetime decay over temperature for these THP's (top) and sensitivity analysis of the monotonic increase (bottom) are shown for Sealmet® paint loaded with 5 % wt. pigment (c) and for Sealmet® loaded with 10 % wt. pigment (d).

The Sealmet® with 5 % wt. pigment displayed a monotonic increase in lifetime decay up to 568 °C, point where the LTD dropped for higher temperatures. This is a relatively low temperature limit, while the standard THP shows functionality up to 900 °C. The luminescent lifetime decay of the two other bars showed similar behaviour between them, but a low monotonic behaviour range of the lifetime decay up to 462 °C and 485 °C for the for Sealmet® with 10 % wt., applied as a single layer and as several layers, respectively. All these parameters are summarized in **Table 5.13** below.

The lifetime decay ranged from 600 μs to 1,400 μs for the three cases considered. Unfortunately, this wide range in lifetime decay does not correspond to a wide temperature range. In terms of sensitivity, both binders exhibit constant values around 2 $\mu\text{s}/^\circ\text{C}$ along the working temperature range, from 130 $^\circ\text{C}$ to 600 $^\circ\text{C}$. Given this reduced temperature range Sealmet® was discounted from further evaluation.

Table 5.13 Summary of lifetime decay evolution over temperature for Sealmet® binder.

		Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range ($^\circ\text{C}$)	Sensitivity ($\mu\text{s}/^\circ\text{C}$)
Sealmet® Silicate solution, Zyp Coatings	5 % wt. Pigment	689.2	1399.1	709.9	From 158 $^\circ\text{C}$ to 568 $^\circ\text{C}$	1.65 +/- 0.79
	10 % wt. Pigment - Single layer	643.0	1445.0	802.0	From 138 $^\circ\text{C}$ to 462 $^\circ\text{C}$	2.23 +/- 0.86
	10 % wt. Pigment – Several layers	609.7	1436.6	827.1	From 138 $^\circ\text{C}$ to 485 $^\circ\text{C}$	2.23 +/- 1.43

Sealmet® as a binder for low temperature sensing

The possibility of obtaining temperature measurements with THPs from ambient temperatures was observed for the first time when testing binders at relatively low temperatures [38]. Sealmet®, containing 7.5 % wt. of pigment calcined at 350 $^\circ\text{C}$, was tested in a bar heat-treatment where the hot end was at a maximum of 500 $^\circ\text{C}$. A high linearity in lifetime decay with increasing temperature was observed. The LTD evolution with increasing temperature, including the sensitivity analysis, is shown in **Figure 5.27** below. This indicates the potential of thermal history paints for temperature sensing from ambient temperature. Sealmet® is therefore a suitable binder candidate for a future low temperature THP.

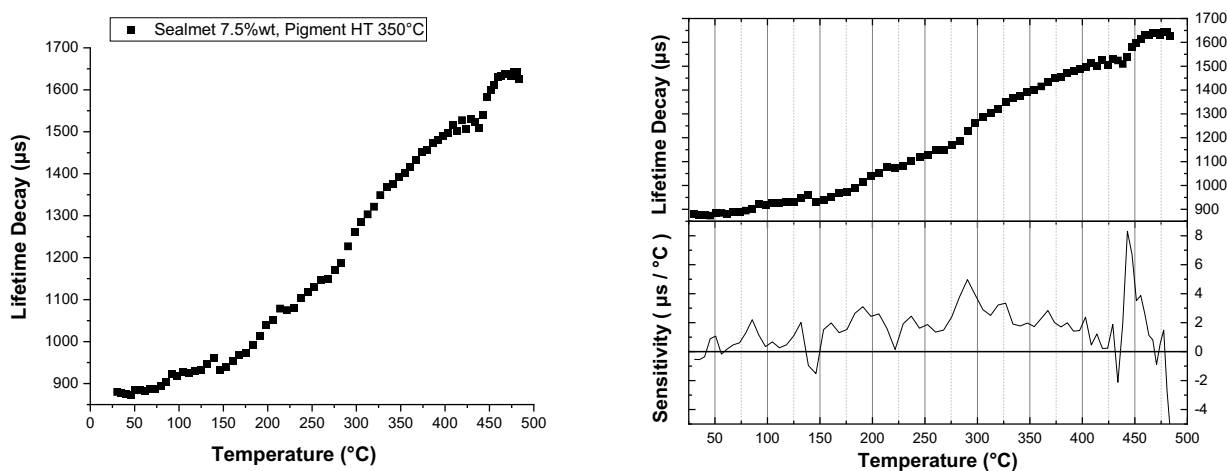


Figure 5.27 (Left) LTD plotted over temperature for a potential low temperature THP based on Sealmet® as a binder, and pigment calcined to 350 $^\circ\text{C}$ deposited on a stainless-steel bars and heat treated up to 500 $^\circ\text{C}$. (Right) Monotonic increase of LTD over temperature (top) and sensitivity analysis of the monotonic lifetime decay increase (bottom).

5.3.1.2 Alumina and silicate solution

As a second substitution binder, an alumina-silicate solution was tested as embodiment for the phosphorescent $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment. Several providers of water-based refractories were contacted and the company Unifrax Ltd. [335] pointed to the Fixwool® Coatings in their catalogue as potential high temperature binders. This group of air-drying coatings are used to insulate and protect metallic surfaces as well as to resist hot gas erosion in furnaces and other hot environments. Among the Fixwool® Coating range of products offered by Unifrax Ltd., only Fixwool® Coating 130 was selected and tested during this investigation, given its white colour and temperature limit of 1,300 °C. The solid content, density, and pH of the binder as received are summarised in **Table 5.16** below.

Table 5.14 Solid content, density, and pH measurements on Fixwool® coating 130 alumina-silicate binder.

Product Commercial Name	Solid Content (%)	Density (g/ml)	pH
Fixwool® Coating 130	42.5 +/- 1.9	1.4 +/- 0.1	7.2

The introduction of the $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment into the binder was performed, as explained in *Chapter 4*, through a two-step process, mixing first the binder into water and then introducing this mix into the binder. The generated paint showed low emission intensities around 620 nm, where the most intense Eu^{3+} peak is normally found. This made impossible analysis via lifetime decay at those wavelengths, and therefore this binder was immediately discarded. Nevertheless, a luminescent spectral analysis was performed to investigate the causes of the low emission around 620 nm. The pigment, the Fixwool® Coating 130 on its own, and the generated paint were interrogated at room temperatures. The resulting luminescent spectra are shown in **Figure 5.28** below.

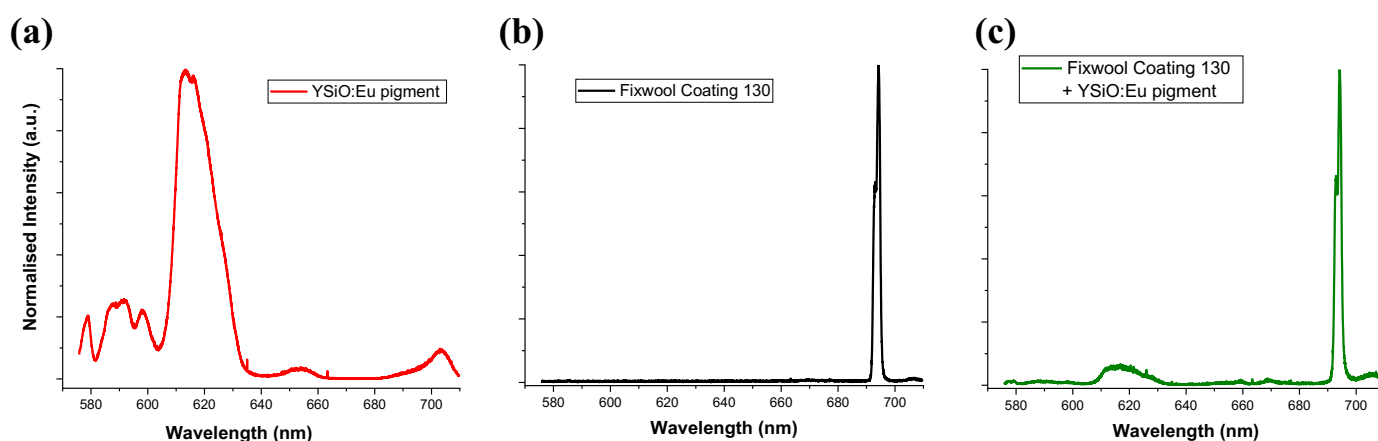


Figure 5.28 Luminescent emission spectra of patterns of (a) $\text{Y}_2\text{SiO}_5:\text{Eu}$ pigment, (b) Fixwool® Coating 130 on its own, and (c) $\text{Y}_2\text{SiO}_5:\text{Eu}$ pigment mixed into Fixwool® Coating 130.

The luminescent spectrum obtained from the pigment, shown in **Figure 5.28 (a)**, corresponds to the broad spectral features of Eu^{3+} , as seen in previous sections. Surprisingly, the spectra of the Fixwool® Coating displayed an intense emission peak around 694 nm, as shown in **Figure 5.28 (b)**. This emission peak can

be attributed to emissions from chromium species, specifically from the Cr^{3+} ion [326]. Chromium was not reported by Unifrax Ltd. as a constituent of this aluminosilicate coating [340]. Moreover, chromium has been hypothesized to have detrimental effects in the Eu^{3+} emission, as discussed in *section 5.1*. The luminescent spectra obtained after mixing the europium-based pigment into the Fixwool® Coating is shown in **Figure 5.28 (c)**, where the chromium emission intensity remained unaffected, while the europium intensity decreased considerably. Most of the Eu^{3+} spectral peaks were not visible, except for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at around 620 nm. This peak displayed an intensity 90% lower than the one observed in the pigment. This decrease can be attributed to energy transfer from the Eu^{3+} ions to the Cr^{3+} ions in the same environment, as previously reported for trivalent lanthanide ions and transition metals [341–343].

Araguas-Rodriguez demonstrated experimentally the detrimental effect of chromium species in contact with THP, both in a liquid solution as well as applied on a metallic substrate [106]. The chromium displayed a thermally active luminescent behaviour, where the Cr^{3+} emission lines were more intense after exposure to higher temperatures, as seen in **Figure 5.8**. This evidence led to the arrangement of not performing a bar test with the produced paint. Alternatively, an investigation was carried out to use the Fixwool® Coating on its own, as a chromium-based luminescent sensor. This is elaborated in the following section.

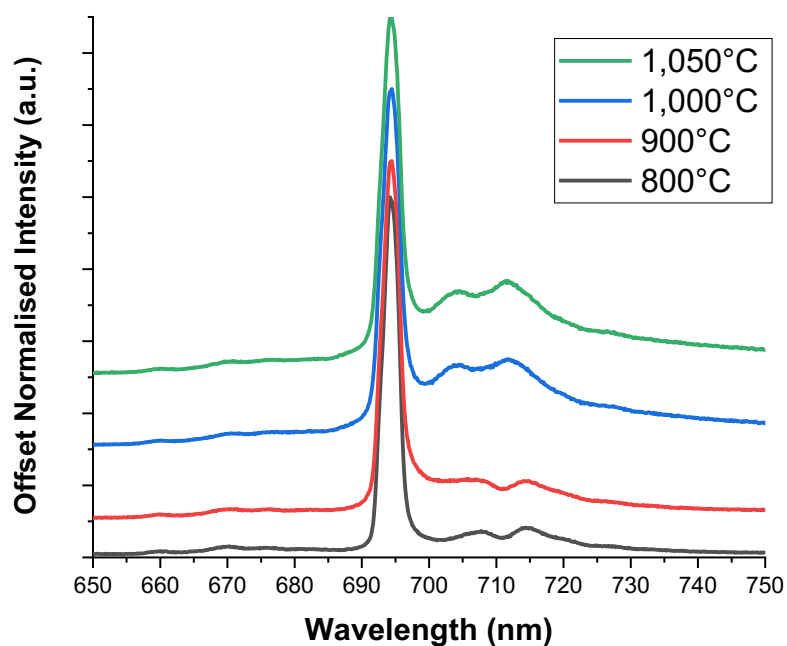
Fixwool® Coating 130 as an alternative chromium-based temperature sensor

Since the Fixwool® Coating 130 was discarded as a carrier of the $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$ pigment, a bar test was performed with the coating on its own. Half of a standard 40-cm stainless steel bar was sprayed with Fixwool® Coating 130 as a single layer, and a second half sprayed with multiple layers (10 to 15 layers). Then the bar was heat treated in a tube furnace up to 1,100 °C. A picture of the painted test bar after heat treatment is shown in **Figure 5.29** below, where the thermocouples for temperature monitoring are still introduced in the side of the bar. The Fixwool® Coating 130 detached from the metallic substrate in the hot end of the bar, but at lower temperatures the coating remained in a good state.



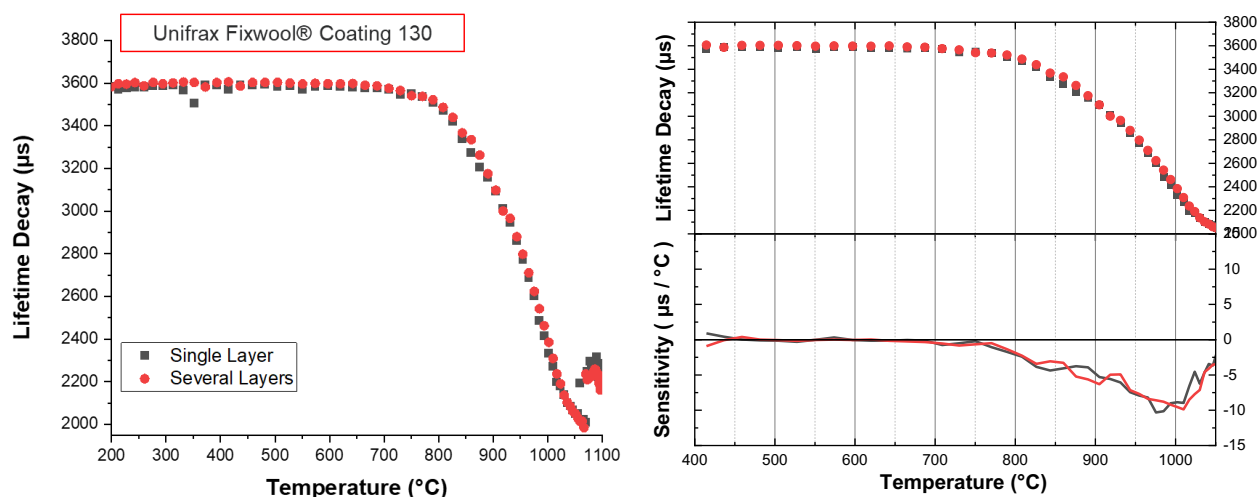
Figure 5.29 Stainless steel bar painted with Unifrax Fixwool® Coating 130, heat treated from 200 °C (left, cold extreme) to 1,100 °C (right, hot extreme). Detachment of paint layer was observed for temperatures above 1,000 °C.

The luminescent spectra of the Fixwool® Coating 130 on the heated bar was examined at different exposure temperatures. The emission spectra recorded between 800 °C and 1,050 °C are displayed in **Figure 5.30**. The main Cr^{3+} emission peak at 694 nm was visible at all temperatures, while slight changes were observed in the emission peaks at higher wavelengths, between 700 and 720 nm. These spectral changes were considered insufficient to build a temperature sensor based on spectral features, but lifetime decay readings were taken filtering the emitted light around the 694 nm peak.



3570 **Figure 5.30** Luminescent spectra of Fixwool® Coating heat treated at 800 °C, 900 °C, 1000 °C and 1050 °C.

Lifetime decay readings were recorded along the painted bar with Fixwool® Coating 130 using a 694 nm optical filter. In **Figure 5.31** below, the LTD results are plotted against the corresponding maximum exposure temperature, both for the single and several layers painted halves. A sensitivity analysis was performed over the monotonic decrease observed in lifetime decays at higher temperatures.



3580 **Figure 5.31** (Left) Lifetime decay, measured through a 694 nm optical filter, plotted over the heat-treatment temperature for Fixwool® Coating 130, deposited on 400 x 20 x 3 mm stainless-steel bar as a single layer or by several layers, and heat treated up to 1,100 °C. (Right) Monotonic decrease of lifetime decay over temperature for Fixwool® Coating 130 (top) and sensitivity analysis of the monotonic decrease (bottom).

The lifetime decay trends observed for the Fixwool® Coating 130 in **Figure 5.31**, applied both as a single layer and as several layers are remarkably similar. Two regions can be clearly differentiated in both cases: at temperatures below 800 °C, the LTD readings remain constant around 3,600 µs, while at temperatures higher than 800 °C the lifetime decay values decrease monotonically to a minimum of 2,000 µs at 1,050 °C. LTD at higher temperatures are not considered given the detachment of the Fixwool® Coating 130 from the metallic substrate. The sensitivity of the coating decreased accordingly with increasing temperature, down to a value of -10 µs/°C at 1,000 °C.

Despite the high temperature sensing range of the Fixwool® Coating 130, and its interesting lifetime decay evolution between 800 °C and 1,050 °C, no further tests were performed with this product. Among the reasons to stop testing with Fixwool® Coating 130 the following are the most important:

- Insufficient luminescent spectral features compared to the $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$ pigment.
- Detachment from stainless-steel at high temperatures.
- LTD sensitivity limited to the range 800 °C to 1,050 °C.

Further investigation to ascertain the presence and concentration of chromium within the Fixwool® Coatings was not carried out during this thesis. Atomic Layer Deposition (ALD) was discussed as a potential method to create a controlled layer of chromium, but due to lack of time and funding it was not performed in this work.

5.3.1.3 Lithium silicate solutions

Lithium silicates are among the most important commercially available soluble silicates, in addition to sodium and potassium silicates [329,334]. This group of materials was explored during this investigation given their relatively high melting point at all potential compositions. Liquid phases are not present below 1,024 °C, as shown in the phase diagram in of the system SiO₂ and Li₂O [344].

Commercially available lithium silicates were surveyed among paint and binder manufacturers. Two similar products were found, and samples ordered from Grace & Co. [336] and PQ Corporation [294], respectively. The commercial names of these two products were lithium poly-silicate, provided by Grace & Co., and LithiSil®25, provided by PQ Corporation. Both products consist of a water-based solution of silica, that amounts around 20 % of the dry solid content, and lithium oxide (Li₂O), that amounts to the rest of the solid content, around 5 % for the lithium poly-silicate and 2.5 % for the LithiSil®25. The solid content, density and pH of both products are summarized in **Table 5.15**.

Table 5.15 Solid content, density, and pH measurements on lithium silicate binders.

Product Commercial Name	Solid Content (%)	Density (g/ml)	pH
Lithium poly-silicate	24.2 +/-0.5	1.3 +/- 0.1	11.1
LithiSil®25	22.6 +/-1.3	1.4 +/- 0.2	8.2

Two paint batches were produced by mixing P600 pigment into the two binders considered. Two stainless steel bars were sprayed with the respective mixes and then heat-treated between 200 °C and 1,100 °C, to obtain a temperature gradient along the bars. A picture of the two bars after heat exposure is shown in **Figure 5.32** below, where the darker areas indicate the higher exposure temperatures, and the lighter/whiter areas indicate the low exposure temperatures.



Figure 5.32 Stainless steel bars painted with lithium poly-silicate (top bar), and LithiSil®25 lithium silicate. Both bars were heat treated from 200 °C (right, cold end) to 1,100 °C (left, hot end).

The luminescent properties of the bars after heat exposure were measured by the standard lifetime decay readings along the bar, from cold to hot temperatures. The obtained LTD values are plotted against the exposure temperature in **Figure 5.33 (a)**. A sensitivity analysis was performed for the monotonic increase of lifetime decay over temperature, between 200 °C and 900 °C, and represented in **Figure 5.33 (b)**.

Given the pigment pre-heat treated to 600 °C used in these bar tests, low sensitivity was expected below 300 °C. However, between 300 °C and 800 °C, both lithium silicate solutions displayed a monotonic increase in LTD with increasing exposure temperature, with sensitivities around 2 $\mu\text{s} / ^\circ\text{C}$, between 400 °C and 600 °C, and around 3 $\mu\text{s} / ^\circ\text{C}$, between 700 °C and 800 °C. At higher temperatures, the LTD behaviour of the lithium poly-silicate paint became irregular and was not further considered. The LTD recorded on the Lithil®25 paint dropped from 850 °C with increasing temperature, in a similar behaviour to the standard THP based on potassium silicate.

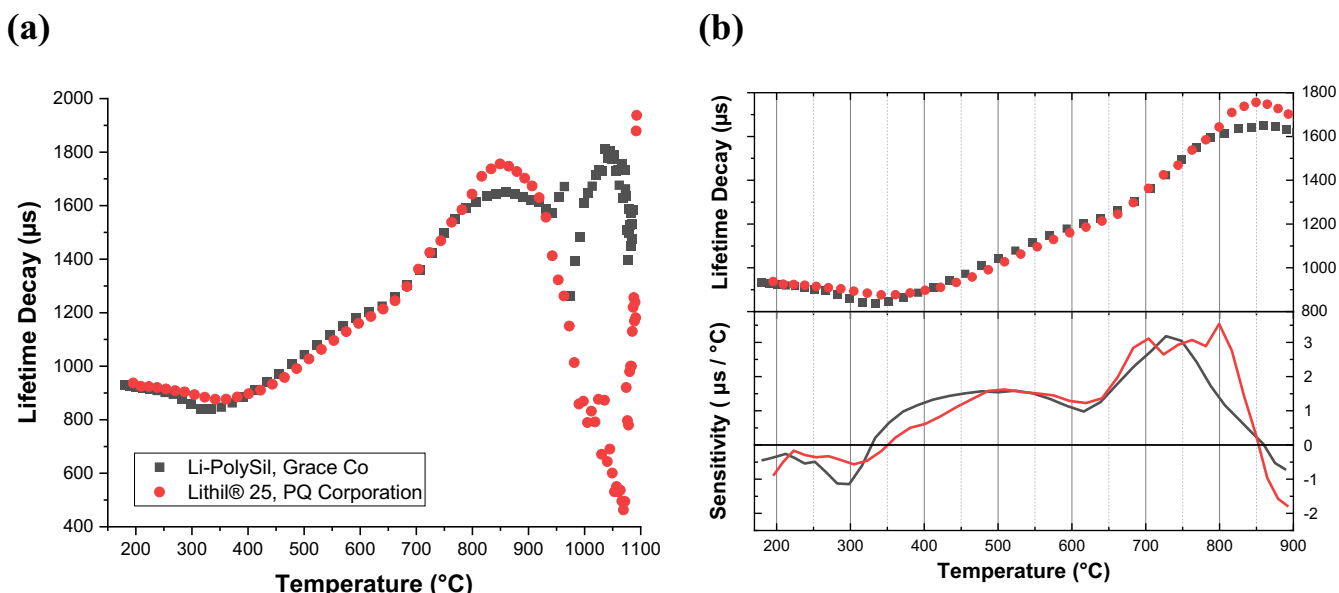


Figure 5.33 (a) Lifetime Decay plotted over temperature for lithium poly-silicate, and Lithil®25, of luminescent history paint. Both paints were deposited on 400 x 20 x 3 mm stainless-steel bars and heat treated until 1,100 °C. (b) Monotonic increase of lifetime decay over temperature for lithium silicate paints (top) and sensitivity analysis of the monotonic increase (bottom).

The lithium silicates tested as high temperature binders did not enhance the LTD-temperature behaviour of the standard THP with P600 pigment. The luminescent parameters and ranges are summarized in **Table 5.16** below. Both products display similar ranges in lifetime decay, between 930 μs and 1,600 μs , and temperature, from 170 °C to 900 °C. Given the polymerization observed when lithium oxide was added into the standard potassium silicate binder, discussed in *section 5.2.2*, as well as the erratic LTD behaviour observed at high temperatures, these lithium silicate solutions were not selected as high temperature binders.

Table 5.16 Summary of lifetime decay evolution over temperature for lithium silicate binders.

	Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range ($^\circ\text{C}$)	Sensitivity ($\mu\text{s}/^\circ\text{C}$)
Lithium poly-silicate	931.4	1619.5	688.1	From 170 °C to 904 °C	1.18 +/- 0.77
LithiSil® 25	937.3	1747.2	864.7	From 182 °C to 865 °C	1.42 +/- 0.93

5.3.1.4 Metallic phosphate solutions

Metallic phosphates are an interesting group of materials, commercially available as water-based solutions, and able to withstand high temperatures, given the high melting point of their metallic constituents. Two phosphate solutions were found among paint and chemical manufacturers, Fabutit FFB® 1210, produced by Budenheim KG [337], and a metallic phosphate produced expressly for this thesis by Indestructible Paint [293]. The composition of this second binder was not fully disclosed but among the constituents were phosphoric acid (10-20 % wt.), molybdenum trioxide (3-5 % wt.), magnesium oxide (3-5 % wt.), silicon dioxide powder (1-3 % wt.) and potassium permanganate (1 % wt.). On the other hand, Fabutit, FFB® 1210, is a mono-magnesium phosphate solution.

Other commercially available phosphates were considered as potential binders as well. Among others, Gardobond® AL produced by BASF / Chemetall [345], an aluminium phosphate solution with the chemical formula $\text{Al}(\text{H}_2\text{PO}_4)_3$. This product was not selected for testing due to Health and Safety concerns, even though it was reported to be used in industrial processes mixed with another binder considered in *section 5.3.1.6*, Ludox® SM30. The specific risk assessment conducted for the Indestructible Paint phosphate binder, raised some doubts on the compliance with the REACH legislation [90,91]. Experimentation with this product was kept to a minimum, and only a bar test was performed with it. This binder was named IPXX for internal process at Indestructible Paint [293], respectively. On the other hand, the solid content, density, and pH of Fabutit FFB® 1210 are reported in **Table 5.17** below, as this was the only product consider safe for laboratory handling.

Table 5.17 Solid content, density, and pH measurements on FFB® 1210 Mg-phosphate binder.

Product Commercial Name	Solid Content (%)	Density (g/ml)	pH
Fabutit FFB® 1210	42.5 +/- 1.9	1.4 +/- 0.1	7.2

Pigment pre-heat-treated to 600°C (P600) was mixed into both binder candidates, generating two paint batches. The pigment was not easily mixed into the binders, falling to the bottom of the container after being stirred into the binder, especially for Fabutit FFB® 1210. Nevertheless, the two produced paints were sprayed onto two stainless steel bars and heat-treated in a tube furnace between 200 °C and 1,100 °C. The pictures of both bars after heat treatment are shown in **Figures 5.34** and **5.35** below.



Figure 5.34 Stainless steel bar painted with FFB® 1210 paint and heat treated from 200 °C (left, cold extreme) to 1,100 °C (right, hot extreme). Detachment of paint layer was observed for temperatures above 800 °C.

3685



Figure 5.35 Stainless steel bar painted with IPXX phosphate binder paint and heat treated from 200 °C (left, cold extreme) to 1,100 °C (right, hot extreme). Detachment of paint layer was observed at high temperatures above 900 °C.

3690

Both paints considered detached from the metallic substrate at high temperatures, while for temperatures lower than 800 °C the paint remained in a good state, attached to the stainless-steel bar. Luminescent interrogation was performed on both bars. Lifetime decay measurements obtained on the surface of the paint and plotted against the maximum exposure temperature per location and shown in **Figure 5.36 (a)** below. A sensitivity analysis on the lifetime decay behaviour over temperature was also performed and shown in **Figure 5.36 (b)**.

3695

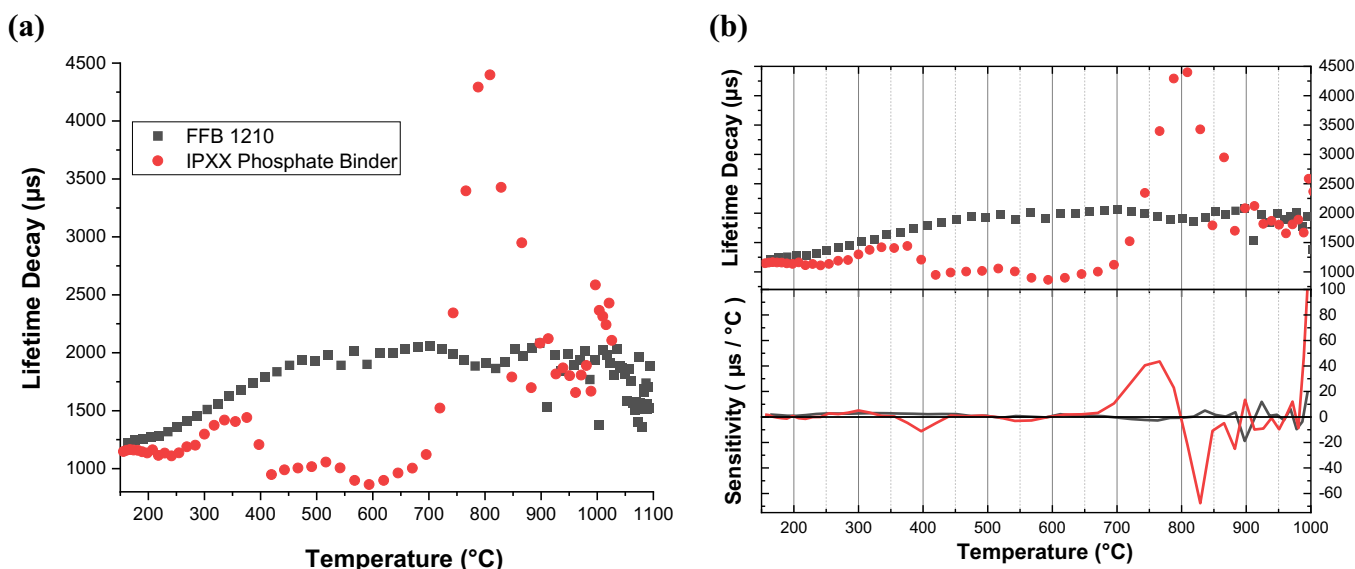


Figure 5.36 (a) Lifetime Decay plotted over temperature for FFB® 1210 and IPXX phosphate based luminescent history paint. Both paints were deposited on 400 x 20 x 3 mm stainless-steel bars and heat treated until 1,100 °C. **(b)** Monotonic increase of lifetime decay over temperature for both phosphate paints (top) and sensitivity analysis of the monotonic increase (bottom).

3700

The paint produced from Fabutit FFB® 1210 showed a monotonic behaviour in lifetime decay for temperatures between 150 °C and 500 °C. From 500 °C up to 1,000 °C the LTD plateaus at a value around 2,000 μs showing no sensing capabilities for temperature changes. The second phosphate binder, IPXX, showed an irregular trend of lifetime decay with increasing temperatures, with a peculiar increment between 700 °C and 800 °C of more than 3,000 μs. The sensitivity fluctuated between $\pm 50 \mu\text{s} / ^\circ\text{C}$, so that neither the IPXX nor the Fabutit FFB® 1210 were selected for further investigation as high temperature binders. A summary of the sensitivity analysis, obtained from both tested phosphate solutions, is shown in **Table 5.18**.

3705

3710 **Table 5.18 Summary of lifetime decay evolution over temperature for metallic phosphate binders.**

	Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range (°C)	Sensitivity (μs/°C)	Attachment to metallic substrate
Fabutit FFB® 1210	1220.3	2083.4	863.1	From 150°C to 500°C	1.05 +/- 5	Paint layer flaked off after heat treatment
IPXX Phosphate Binder	862.9	4398.3	3535.4	From 400°C to 863°C	3.31 +/- 23.5	Paint layer flaked off after heat treatment

5.3.1.5 Poly-silazane polymer

3715 Durazane® 1800, an organo-poly-silazane polymer, produced by Merck Performance Materials [338] was considered for testing under this investigation. This product is composed a poly-silazane polymer, and its main commercial application is as a paint or coating of metallic surfaces in order to create protective barriers against corrosion or gas diffusion. Given the high temperature limit claimed by the manufacturer, 1,800 °C, and the deposition method recommended, spraying the Durazane® 1800 with an airgun, a small amount of this product was ordered and tested as a high temperature binder.

3720 The use of Durazane® 1800 requires several health and safety precautions, since it is a flammable product, and therefore was kept away from heat sources until after deposition on a stainless-steel bar. A single stainless-steel bar was sprayed and subsequently cured in a decomposition furnace (with the appropriate ventilation). Poly-silazane is known to release hydrogen and ammonia when heat-treated. The bar was heat-treated at 250 °C for five hours, after which it was introduced into a tube furnace for heat-treatment between 3725 200 °C and 1,100 °C. A picture of the bar before and after heat-treatment is shown in **Figure 5.37** below.



Figure 5.37 Stainless steel bar painted with Durazane® 1800, polysilazane polymer paint, shown before heat treatment (top) and after heat treatment (bottom) from 200 °C (left, cold end) to 1,100 °C (right, hot end).

3730 Luminescent lifetime decay was measured on the surface of the painted bar. Half of the bar was painted applying a single layer of Durazane® 1800 paint, and a second half applying several layers. The obtained results, plotted against the maximum exposure temperature, are shown in **Figure 5.38**. No clear trend could be distinguished from the lifetime decay measurements. While at low temperatures, between 150 °C and 500 °C the values seem to plateau at around 1,000 μs, for temperatures higher than 500 °C, the lifetime decay showed a random scattering between 1,000 and 1,250 μs.

Durazane® 1800 was not tested further as a high temperature binder, in particular considering the safety implications of its use. A further application is developed in *section 5.5*, where the Durazane® 1800 is used as an interlayer between standard THP and the stainless-steel substrate.

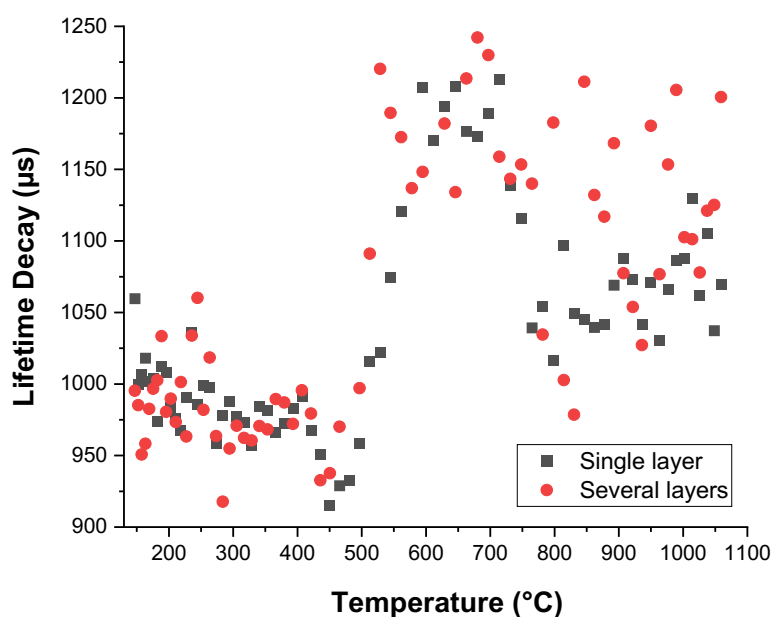


Figure 5.38 Lifetime decay plotted over temperature for Durazane® 1800 organic poly-silazane polymer used as binder for luminescent history paint, applied on a 400 x 20 x 3 mm stainless-steel bars as a single layer or as several layers, and heat treated until 1,100 °C. No sensitivity analysis was performed for this binder.

5.3.1.6 Colloidal silica solutions

Among the products considered as high temperature binders, the focus of the market survey was on materials with high melting point. Silica (SiO_2) is known to have a high melting point, displaying three transitions with increasing temperature: quartz, tridymite and cristobalite [346].

Colloidal silica solutions are commercially available products, with a high silica content, that could be used as high temperature binders. Four grades of the Ludox® colloidal silica solutions were found in the catalogue of the company Grace & Co [336], and samples were requested for testing during this investigation. The main application of this water-based solution of silica nanoparticles is in catalysis, but its versatility allows other uses within the temperature limit of 1,650 °C.

The four Ludox® grades provided by Grace are summarized in **Table 5.19**, with their respective solid content, density, pH, and particle size. Ludox® SM 30 and Ludox® HS 40 contain Na_2O in their liquid solution while Ludox® AS 30 and Ludox® AS 40 contain ammonia. The particle size is the main difference between the different grades considered.

Table 5.19 Solid content, density, pH, and particle size of Ludox® colloidal silica solutions.

Product Commercial Name	Solid Content (%)	Density (g/ml)	pH	Particle Size (nm)
Ludox® SM 30	25.7 +/- 1.4	1.2 +/- 0.2	9.9	7
Ludox® HS 40	27.7 +/- 2.1	1.2 +/- 0.1	9.7	12
Ludox® AS 30	33.5 +/- 0.5	1.4 +/-0.1	9.5	12
Ludox® AS 40	43.3 +/-0.12	1.6 +/- 0.2	9.2	22

Paint batches were manufactured with the four Ludox® grades, using pigment calcined at 600°C (P600). Two stainless-steel bars were sprayed with the produced paints, half of the bar as a single layer, and the other half of the bar applying several layers (between 10 and 15) until the desired 30 µm dry film thickness was obtained. In **Figure 5.39** below the two bars painted with Ludox® SM30 (top) and Ludox® HS40 (bottom) are shown for comparison. The appearance of the four bars after heat-treatment was very similar.

The attachment to the metal substrate of the ammonia grades after heat treatment, Ludox® AS30 and Ludox® AS40, was relatively worse than for the Ludox® containing Na₂O. The paint layer could be easily scratched from the metallic substrate for the higher particle sizes considered Ludox® AS40 and HS40.

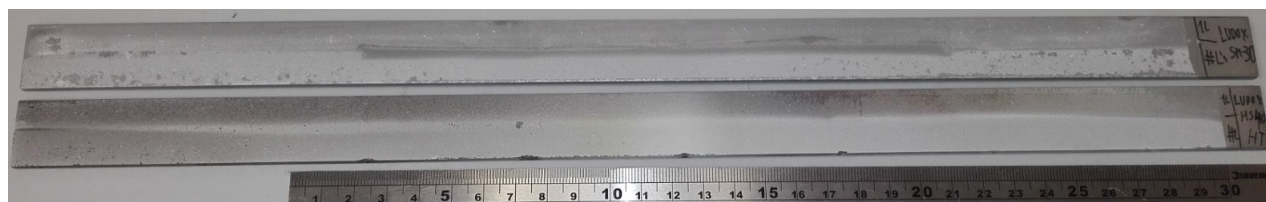


Figure 5.39 Stainless steel bars painted with Ludox® SM 30 (top) and Ludox® HS 40 (bottom) as binders for luminescent history paint. Ruler with scale in centi-metres shown for reference. Both bars were painted half as a single layer, and half applying several layers of paint. Appearance of the paint layer did not show significant variations before and after heat treatment.

The four bars painted with Ludox® showed similar results on the “single” and “several layers” halves. In **Figure 5.40** below only the halves sprayed with several layers are shown. The sensitivity analysis of the four paints was performed for the monotonic increase of lifetime decay with temperature, between 400 °C and 950 °C. In all four cases, a similar behaviour to the standard THP can be observed. The lifetime decay increased monotonically to temperatures slightly higher than 900 °C, dropping at higher temperatures.

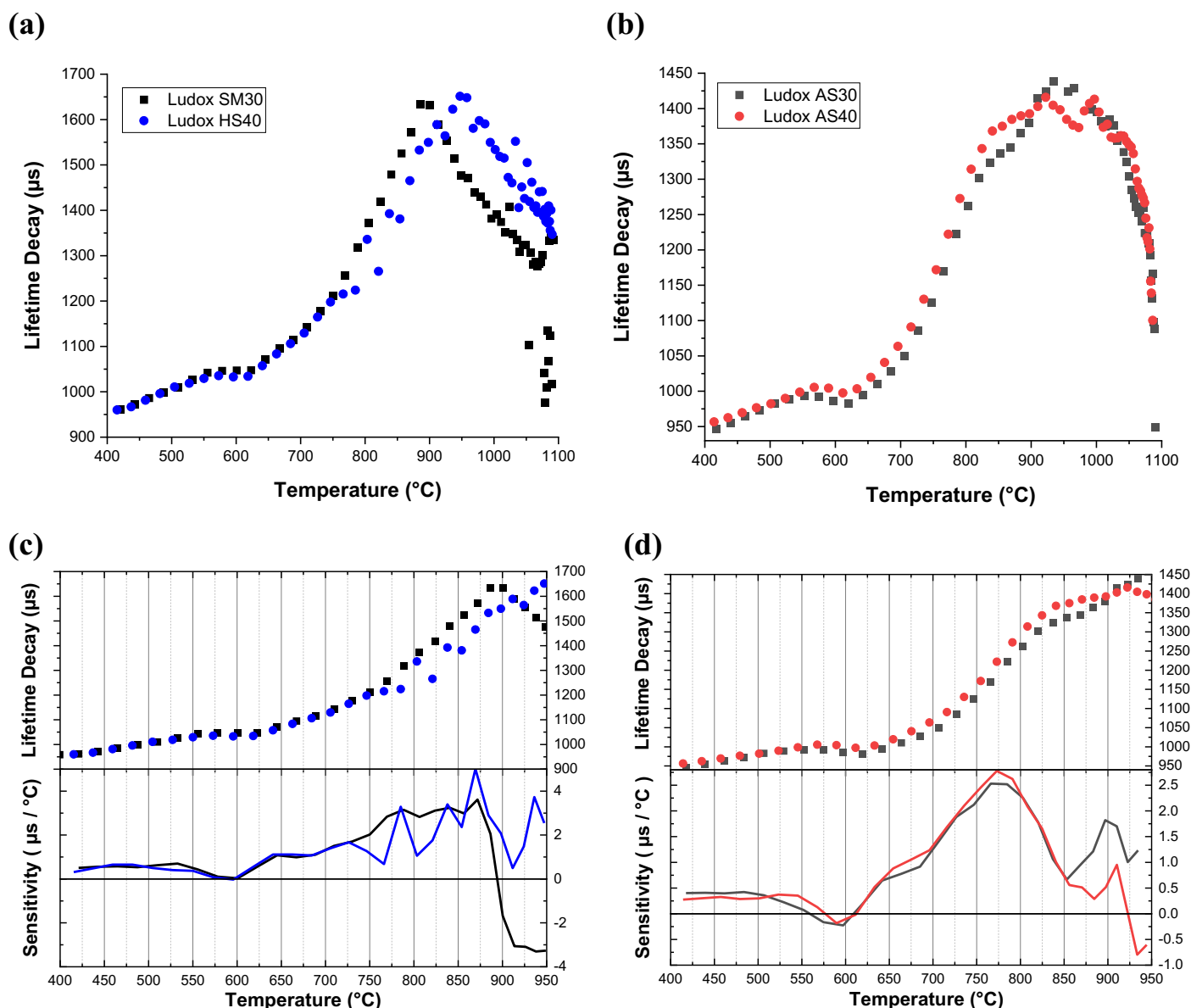


Figure 5.40 Lifetime decay plotted over temperature for THP, deposited on 400 x 20 x 3 mm stainless-steel bars and heat treated up to 1,100 °C. The binders used to generate the THP were Ludox® SM30 and Ludox® HS40 (a) and Ludox® AS30 and Ludox® AS40. The monotonic increase of lifetime decay over temperature for (top) and sensitivity analysis of the monotonic increase (bottom) are shown for the THP's based in Ludox® SM30 and Ludox® HS40 (c) and Ludox® AS30 and Ludox® AS40 (d).

The sensitivities of the sodium grades, shown in **Figure 5.40**, fluctuate between 1 μs / °C and 2 μs / °C, with lower values at temperatures below 600 °C, as expected for the P600 pigment employed in these tests. The sensitivity of the ammonia grades, Ludox® AS30 and AS40, was lower than the sodium grades, particularly at temperatures higher than 800 °C, from a maximum of 2.5 μs / °C the sensitivity dropped to 1 μs / °C. The lifetime decay measured on one of the ammonia grades plateaued from 800 °C, to finally drop at temperatures higher than 950 °C. On the other hand, the sodium Ludox® grades, dropped abruptly at 900 °C, with a rectilinear decrease of lifetime decay at higher temperatures.

The lifetime decay and temperature ranges of the four Ludox® paints were very similar. The luminescent readings can be grouped according to the composition, where the lifetime decay ranged from 950 μs to

1,600 μs for Ludox® SM30 and HS40 (containing sodium) and from 940 μs to 1,400 μs for Ludox® AM30 and AS40 (containing ammonia). Given the use of P600 pigment, the temperature ranged from a minimum around 400 °C to over 900 °C in all cases. These parameters, and the average sensitivity obtained from the paints, are summarised in **Table 5.20** below.

Table 5.20 Summary of lifetime decay evolution over temperature for Ludox® colloidal-silica solutions.

	Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range (°C)	Sensitivity ($\mu\text{s}/^\circ\text{C}$)	Attachment to metallic substrate
Ludox® SM 30	958.8	1633.4	674.6	From 400 °C to 900 °C	1.41 +/- 1.3	Good, for dry film thickness around 30 μm
Ludox® HS 40	953.6	1651.3	697.7	From 400 °C to 947 °C	1.46 +/- 1.2	Paint flaked off after heat treatment at intermediate temperatures
Ludox® AS 30	937.9	1457.8	519.9	From 400 °C to 984 °C	1.02 +/- 0.8	Paint layer flaked off after heat treatment
Ludox® AS 40	953.2	1415.9	462.7	From 400 °C to 922 °C	0.9 +/- 0.8	Paint layer flaked off after heat treatment

Considering the luminescent and temperature ranges obtained, as well as the sensitivity values, the Ludox® colloidal-silica solutions showed promising behaviour at high temperatures, keeping a white colour from ambient temperature up to 1,100 °C. A uniform colour results in an enhanced luminescent signal, and in more reliable lifetime decay measurements at high temperatures. The Ludox® water-based solutions are a good environment both for silica nano particles in suspension and for phosphorescent ceramic pigments, such as $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$.

5.3.2 Summary of high temperature binder testing and selection

Once all the high temperature binders were used as paint batches, containing $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment, and tested in a wide temperature range up to 1,100 °C, the main observations could be summarised in **Table 5.21** below. The lifetime decay, temperature and sensitivities are explored individually for every binder, as well as the attachment to the metallic substrate.

Table 5.21 Summary of luminescent lifetime decay, temperature, sensitivity, and attachment to metallic substrates of THP reference, binder modifications and binder substitutions.

			LTD Range (μ s)	Maximum Temperature (°C)	Sensitivity (μ s/°C)	Attachment to metallic substrate
THP REFERENCE	Potassium silicate + P400 pigment		1073.1	870	1.4	Good
	Potassium silicate + P600 pigment		1141.7	963	2.1	Good
BINDER MODIFICATION	Potassium addition		954.2	905	1.1 (until 800°C)	Bubbling and flaking off observed.
	Lithium addition, Mix 37, ½ eq. Li / K		983.7	702	1.7	Good
	Lithium addition, Mix 24, 1 eq. Li / K		1279.5	711	2.3 (until 650°C)	Good
BINDER SUBSTITUTION	Sealmet ® + 5%wt Pigment		709.9	568	1.7	Good
	Sealmet ® + 10%wt Pigment - 1 <i>layer</i>		802.0	462	2.2	Good
	Sealmet ® + 10%wt Pigment – # <i>layers</i>		827.0	485	2.2	Good
	Lithium Polysilicate		688.1	904	1.2	Good
	FFB® 1210		863.1	500	1.1	Paint layer flaked off after heat treatment
BINDER SUBSTITUTION	IPXX Phosphate Binder		3535.4	863	3.3	Paint layer flaked off after heat treatment
	LithiSil ® 25		864.67	864	1.4	Good
	Ludox® SM 30		674.6	900	1.4	Good

	Ludox® HS 40		697.7	947	1.5	Paint flaked off after heat treatment
	Ludox® AS 30		519.9	984	1.1	Paint layer flaked off after heat treatment
	Ludox® AS 40		462.7	922	0.9	Paint layer flaked off after heat treatment

The most critical parameter to consider for the selection of a high temperature binder is the maximum temperature reached while the sensing parameter, lifetime decay, increases monotonically with temperature. These maximum temperatures are marked in bold in **Table 5.21** above. All the binders considered displayed maximum temperatures below 1,000 °C, which result in a moderate improvement with respect to the capability of the standard THP, with a maximum around 900 °C.

Secondly, the attachment to the metallic substrate must be considered, as a bar test in laboratory conditions represents an environment less aggressive than any engine test. The attachment to the substrate is a good indication of a promising binder behaviour at high temperatures. A good attachment to the metal was reported for the lithium modifications of the binder, the lithium silicate alternative binders, LithiSil® 25 and lithium poly-silicate, and only one of the Ludox® colloidal silica grades, **Ludox® SM30**.

Ludox® SM30 was selected for further investigation given the good attachment to stainless-steel at high temperatures, the white colour displayed over a wide temperature range (up to 1,100 °C) and the promising sensitivity values observed for the monotonic increase of lifetime decay over temperature. Further results are shown in section 5.6.

Four grades of Ludox® have been tested as high temperature binders in this thesis, two liquid solutions with sodium counter ions and two with ammonia counter ions. While the pH and the density of all the versions were equivalent, Ludox® SM30 was the tested version containing particles of the lowest size, 7 nm in diameter. This could explain the favourable environment of Ludox® SM30 to contain ceramic phosphor pigments and to guarantee a good attachment to metallic surfaces. Unfortunately, due to lack of time and funding, further investigation in the adhesion of Ludox® paints was not performed in this thesis. To design new versions of Ludox® based THP's, the mixing of different Ludox® versions was considered, in combination with further characterisation of the paint-substrate interlayer with advanced techniques, such as TEM. These last two tasks fell outside the scope of this work.

5.4 Pigment modification

After testing several high temperature binder candidates, the focus in this section shifts towards the pigment. Despite the advantages of using $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ as THP pigment, which were presented in *Chapter 3*; two modifications of the current pigment are tested in this section: the modification of the dopant and the modification of the host. These are included among the suggested solutions to improve the THP behaviour at higher temperatures, seen in *Section 5.1*.

5.4.1 Dopant modification

The first efforts to modify the current pigment focused on changing the phosphorescent dopant in the Y_2SiO_5 host. While europium has shown advantages with respect to other dopants, such as the exploitation as an amorphous-to-crystalline sensor over a wide temperature range, there are some disadvantages that could be solved by changing phosphorescent element. Among others, the interaction with metallic substrates reported in *Section 5.1* is of key importance.

Keeping Y_2SiO_5 as host structure, erbium was explored as a potential dopant element. Erbium was chosen among other luminescent elements, since it could be excited in the visible range with the instrumentation described in *Chapter 4*. The emission of erbium occurs at lower wavelengths than the one of europium, in a reduced wavelength range, which could reduce the interaction between the phosphor and the chromium emission from metallic substrates. The sol-gel process, reported in *Chapter 4*, was employed to produce this pigment following a conventional synthesis route. 50 g of pigment were produced, using Erbium nitrates as a precursor, instead of europium nitrate.

5.4.1.1 Yttrium mono-silicate as erbium carrier

Once the Erbium doped pigment was synthesized and calcined at 400 °C, pigment samples were heat treated to 600 °C, 800 °C and 1,000 °C for one hour. Luminescent spectra were obtained on the three samples, after excitation with 532 nm light. These are shown in **Figure 5.41**. The three patterns obtained show similar emission lines, with an enhanced intensity with increasing temperature.

The transitions observed could be identified using the Dieke diagram discussed in *Chapter 2*. The excited state reached in a free erbium ion, illuminated with a 532 nm wavelength, can be located between the states $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$. The relaxation to the ground level, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, has been estimated to have an emission peak around 545 nm [115]. This is not observed in the emission spectra obtained for the Y_2SiO_5 doped with erbium. The following transition, $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$, has a radiative emission estimated around 660 nm, which was not visible in the obtained spectra. The recorded spectra shown in **Figure 5.41** could not be identified, despite differences in the emission could be observed with increasing temperature. Contamination with an unidentified luminescent element was hypothesized but not pursued.

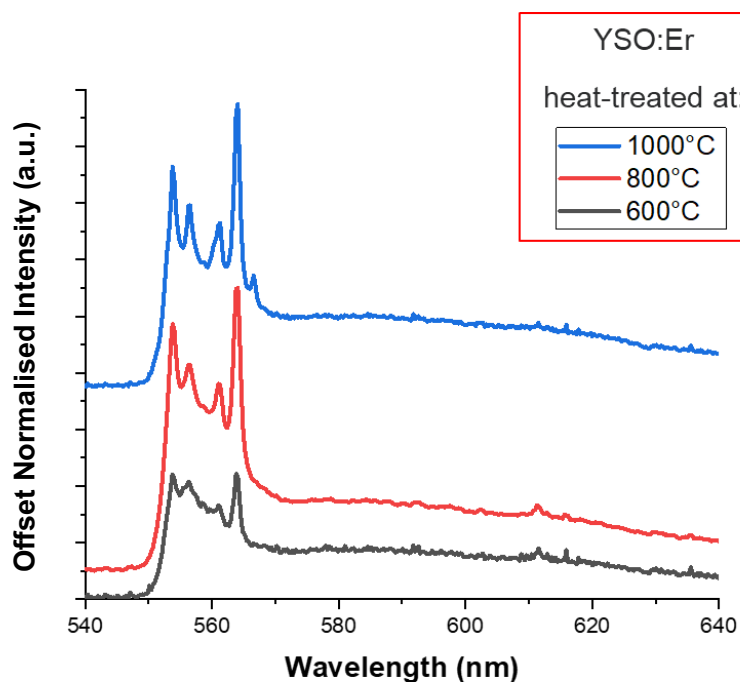


Figure 5.41 Luminescent spectra of Y_2SiO_5 doped with erbium, heat treated to 600 °C, 800 °C and 1,000 °C.

Despite the difficult identification of the emission peaks obtained in the luminescent spectra, lifetime decay measurements were taken using a 543 nm $\pm$ 22nm optical filter. The decay curves were obtained with the *fast decay set-up* described in Chapter 4 to ensure a low interaction of the laser excitation, which uses pulses of 10 ns. The decay curves obtained are shown in Figure 5.42 below. The decay values (τ) were obtained with a mono-exponential fitting, using a Levenberg-Marquardt algorithm in the software OriginPro2021.

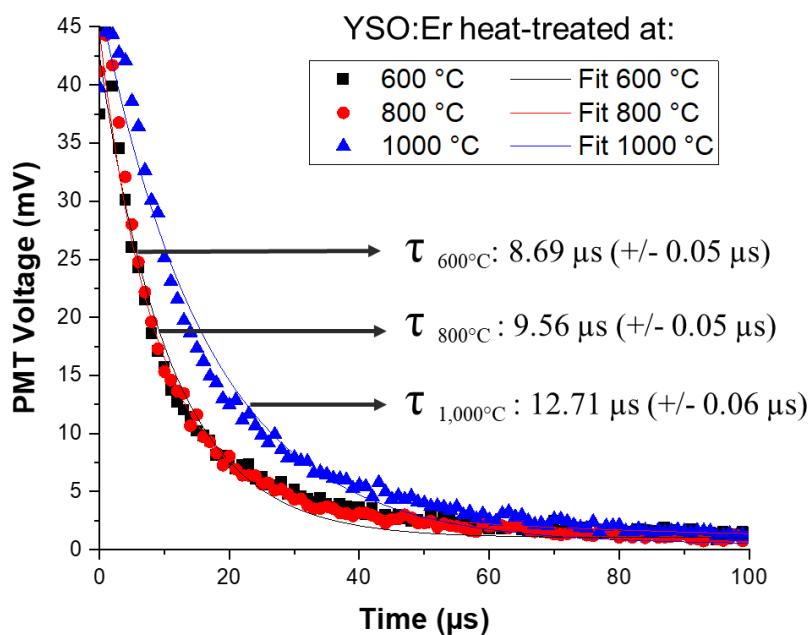


Figure 5.42 Lifetime decay of Y_2SiO_5 doped with Erbium, heat treated to 600 °C, 800 °C and 1,000 °C, measured with the fast decay set-up described in Chapter 4, using an optical filter 543 $\pm$ 22nm.

The obtained life-time decay values, shown in **Figure 5.42**, increase from low to high temperatures. The sensitivity obtained was not regular, as less than 1 μs difference was observed between the sample heat treated at 600 $^{\circ}\text{C}$ and the sample heat treated at 800 $^{\circ}\text{C}$. The decay is slightly longer for the sample heat treated at 1,000 $^{\circ}\text{C}$, but all the decays obtained were relatively fast, tenths of microseconds, compared to the Y_2SiO_5 doped with europium explored in previous versions of pigment and paints. These usually range from 500 μs to 2,200 μs .

The fast decays obtained, represent a challenge in terms of instrumentation, since a faster laser excitation must be employed on these phosphors. The low sensitivity at temperatures below 1,000 $^{\circ}\text{C}$ and the uncertainty of the transitions observed in the spectra lead to the conclusion to stop using Y_2SiO_5 doped with erbium as a potential pigment for THP.

5.4.2 Pigment synthesis modification

The second pigment modification consisted of changing the synthesis route to obtain europium doped Y_2SiO_5 . The sol-gel route, explored in *Chapter 4*, was modified by adding different amounts of citric acid (0529-500G, VWR International Ltd.) as a last constituent in the solution. Citric acid is used generally as a chelating agent in the Pechini sol-gel method [347,348], usually employed in the production of yttrium mono-silicate (Y_2SiO_5) and yttrium disilicate ($\text{Y}_2\text{Si}_2\text{O}_7$) [349]. The Pechini method has some advantages compared to standard sol-gel processes, such as low cost, easy control of the stoichiometry, and good homogeneity of the obtained materials, in addition to low synthesis temperature required [349–352]. These advantages are explored to produce luminescent pigments in this thesis, since the sol-gel route employed is carried out at room temperature, as described in *Chapter 4*. Citric acid is also used as fuel during the combustion of sol-gel formed metal complexes [353–356], as well as a retardant in the crystallization of oxide phases from organic precursors [357–360].

Three pigment batches were synthesised for this investigation, one of them following the standard sol-gel process, and two additional batches were generated adding different amounts of citric acid. The batch without citric acid was named CA0, a second batch where 10 g of citric acid was added was named CA10 and finally a third batch with 25g of citric acid was named CA25. The summary of added quantities and pH measured on the three solutions generated are shown in **Table 5.22** below.

Table 5.22 Summary of citric acid added to sol-gel pigment production

	Citric acid (g)	pH
CA0	0	6
CA10	10	5
CA25	25	4

5.4.2.1 Electron microscopy observation of modified pigment powders

Samples of the three pigment batches, after synthesis and calcination at 400 °C, were observed via Scanning Electron Microscopy (SEM) and the elemental composition obtained through Energy-Dispersive X-ray Spectroscopy (EDX or EDS). Seven random locations were selected in each pigment batch. The micrographs and molar composition of the selected points are summarised in **Table 5.23** below. As expected, the main constituents detected were carbon (C), oxygen (O), silicon (Si) and yttrium (Y). Other elements, such as gold (Au) are present due to the nanolayer coating covering these non-conductive ceramic samples.

Table 5.23 EDX analysis of luminescent history pigment produced by addition of citric acid.

	EDX Points	Element Composition (% mol)																																																																
CA0		<table><thead><tr><th></th><th>C</th><th>O</th><th>Si</th><th>Y</th><th>Au</th></tr></thead><tbody><tr><td>1</td><td>21.91</td><td>61.9</td><td>3.02</td><td>13.18</td><td></td></tr><tr><td>2</td><td>18.77</td><td>65.68</td><td>7.13</td><td>8.42</td><td></td></tr><tr><td>3</td><td>18.72</td><td>66.23</td><td>5.73</td><td>9.32</td><td></td></tr><tr><td>4</td><td>21.25</td><td>65.38</td><td>1.34</td><td>12.03</td><td></td></tr><tr><td>5</td><td>18.66</td><td>65.1</td><td>6.69</td><td>9.56</td><td></td></tr><tr><td>6</td><td></td><td>75.79</td><td>2.88</td><td>19.08</td><td>1.85</td></tr><tr><td>7</td><td>21.96</td><td>66.13</td><td></td><td>1.84</td><td>10.07</td></tr></tbody></table>		C	O	Si	Y	Au	1	21.91	61.9	3.02	13.18		2	18.77	65.68	7.13	8.42		3	18.72	66.23	5.73	9.32		4	21.25	65.38	1.34	12.03		5	18.66	65.1	6.69	9.56		6		75.79	2.88	19.08	1.85	7	21.96	66.13		1.84	10.07																
	C	O	Si	Y	Au																																																													
1	21.91	61.9	3.02	13.18																																																														
2	18.77	65.68	7.13	8.42																																																														
3	18.72	66.23	5.73	9.32																																																														
4	21.25	65.38	1.34	12.03																																																														
5	18.66	65.1	6.69	9.56																																																														
6		75.79	2.88	19.08	1.85																																																													
7	21.96	66.13		1.84	10.07																																																													
CA10		<table><thead><tr><th></th><th>C</th><th>O</th><th>Si</th><th>Y</th><th>Au</th><th>Ni</th><th>Al</th></tr></thead><tbody><tr><td>1</td><td>28.3</td><td>58.77</td><td>4.04</td><td>8.88</td><td></td><td></td><td></td></tr><tr><td>2</td><td>28.44</td><td>57.9</td><td>4.52</td><td>9.14</td><td></td><td></td><td></td></tr><tr><td>3</td><td>23.53</td><td>60.82</td><td>5.81</td><td>9.16</td><td>0.68</td><td></td><td></td></tr><tr><td>4</td><td>23.74</td><td>60.15</td><td>4.61</td><td>11.5</td><td></td><td></td><td></td></tr><tr><td>5</td><td>30.03</td><td>45.56</td><td>8.11</td><td>16.29</td><td></td><td></td><td></td></tr><tr><td>6</td><td>38.36</td><td>45.06</td><td>4.62</td><td>7.27</td><td>6.87</td><td>1.84</td><td></td></tr><tr><td>7</td><td>28.22</td><td>48.02</td><td>8.79</td><td>13.61</td><td></td><td></td><td>1.36</td></tr></tbody></table>		C	O	Si	Y	Au	Ni	Al	1	28.3	58.77	4.04	8.88				2	28.44	57.9	4.52	9.14				3	23.53	60.82	5.81	9.16	0.68			4	23.74	60.15	4.61	11.5				5	30.03	45.56	8.11	16.29				6	38.36	45.06	4.62	7.27	6.87	1.84		7	28.22	48.02	8.79	13.61			1.36
	C	O	Si	Y	Au	Ni	Al																																																											
1	28.3	58.77	4.04	8.88																																																														
2	28.44	57.9	4.52	9.14																																																														
3	23.53	60.82	5.81	9.16	0.68																																																													
4	23.74	60.15	4.61	11.5																																																														
5	30.03	45.56	8.11	16.29																																																														
6	38.36	45.06	4.62	7.27	6.87	1.84																																																												
7	28.22	48.02	8.79	13.61			1.36																																																											
CA25		<table><thead><tr><th></th><th>C</th><th>O</th><th>Si</th><th>Y</th><th>Au</th></tr></thead><tbody><tr><td>1</td><td>30.19</td><td>50.5</td><td>6.2</td><td>13.11</td><td></td></tr><tr><td>2</td><td>30.31</td><td>52.26</td><td>5.39</td><td>12.04</td><td></td></tr><tr><td>3</td><td>30.39</td><td>56.34</td><td>4.36</td><td>8.91</td><td></td></tr><tr><td>4</td><td>32.79</td><td>52.08</td><td>5.81</td><td>9.32</td><td></td></tr><tr><td>5</td><td>28.92</td><td>58.19</td><td>4.91</td><td>7.97</td><td></td></tr><tr><td>6</td><td>32.3</td><td>56.23</td><td>3.34</td><td>8.13</td><td></td></tr><tr><td>7</td><td>35.23</td><td>53.18</td><td>2.94</td><td>7.91</td><td>0.74</td></tr></tbody></table>		C	O	Si	Y	Au	1	30.19	50.5	6.2	13.11		2	30.31	52.26	5.39	12.04		3	30.39	56.34	4.36	8.91		4	32.79	52.08	5.81	9.32		5	28.92	58.19	4.91	7.97		6	32.3	56.23	3.34	8.13		7	35.23	53.18	2.94	7.91	0.74																
	C	O	Si	Y	Au																																																													
1	30.19	50.5	6.2	13.11																																																														
2	30.31	52.26	5.39	12.04																																																														
3	30.39	56.34	4.36	8.91																																																														
4	32.79	52.08	5.81	9.32																																																														
5	28.92	58.19	4.91	7.97																																																														
6	32.3	56.23	3.34	8.13																																																														
7	35.23	53.18	2.94	7.91	0.74																																																													

The average mole fraction of each powder batch was calculated considering the elemental stoichiometry of seven points per sample. These are plotted in **Figure 5.43** below, where the associated standard deviations are indicated with an interval bar. As expected, the pigment batch where the largest amount of citric acid was added, CA25, showed the biggest amount of carbon (31.29 % +/- 3.05 %), followed by the CA10 batch (28.66 % +/- 4.95 %). These are relatively high values compared to the batch without citric acid, CA0, where the amount of carbon detected was 20.21 % +/- 1.66 %. Checking the molar content of the elements in the produced samples was important to guarantee the combustion carbon in subsequent heat treatments of the samples. This extra energy generated in the environment of the pigment was hypothesised to alter the crystallization of the oxide phases, and therefore extend the monotonic increase of the lifetime decay to higher temperature regimes.

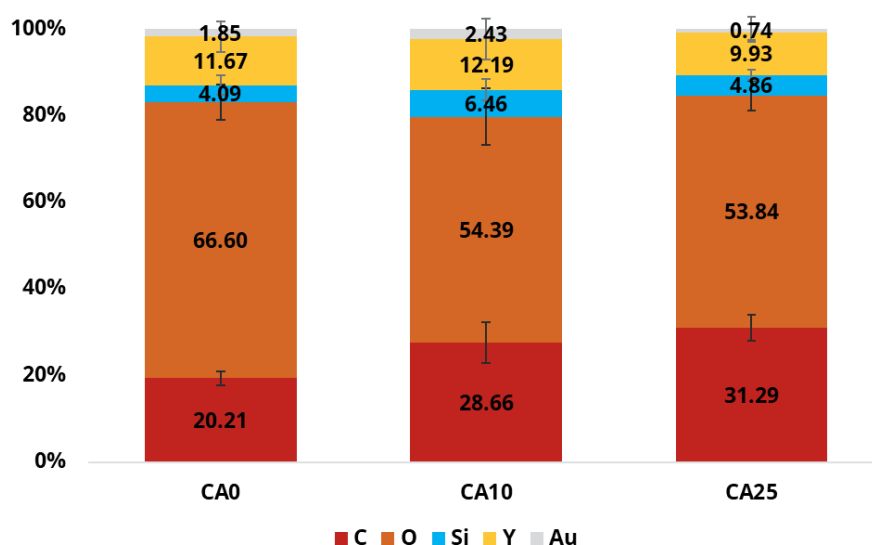


Figure 5.43 Average stoichiometry of EDX points measured on pigments produced by adding 10 g and 25 g of citric acid, compared to the original pigment production.

5.4.2.2 XRD characterization of modified pigment powder

The characterization of the pigment batches with electron microscopy was followed by characterisation via X-Ray Diffraction (XRD). Samples of the three powder batches were heat treated for one hour at temperatures from 900 °C to 1,300 °C, in intervals of 100 °C. The diffraction patterns for samples at lower temperatures showed no crystalline peaks, except an amorphous halo centred around 29 ° two-theta, expected in amorphous silica-based structures [106]. The samples heat treated at 900 °C displayed broad peaks, with low intensity, which are identified in the *Appendix, section 9.1.3*. All the obtained diffraction patterns are plotted together in **Figure 5.44** below, in increasing order of temperature exposure. The peak identification, and summary of the phases observed, are shown in **Tables 5.24** and **5.25**.

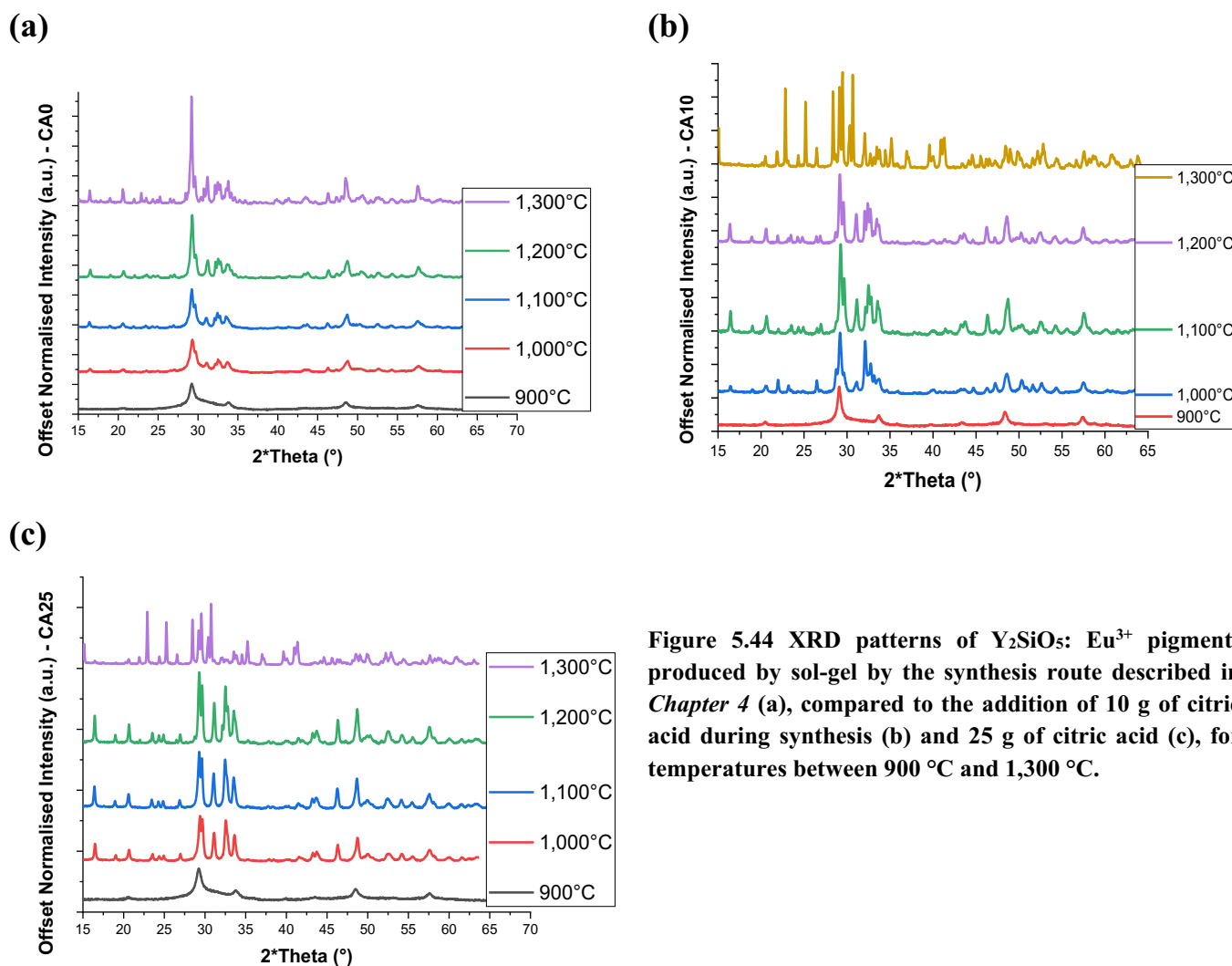
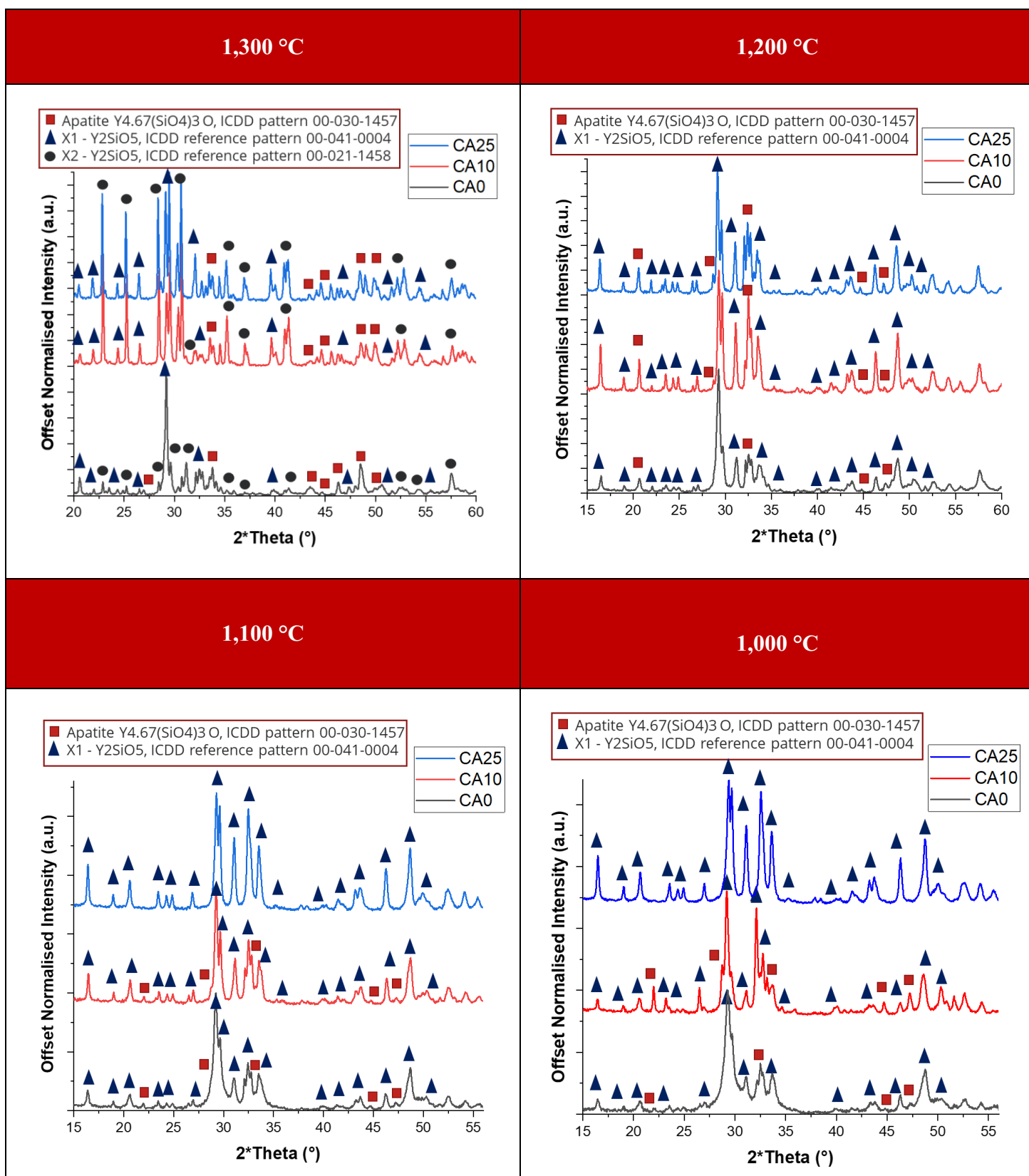


Figure 5.44 XRD patterns of $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ pigments produced by sol-gel by the synthesis route described in *Chapter 4* (a), compared to the addition of 10 g of citric acid during synthesis (b) and 25 g of citric acid (c), for temperatures between 900 °C and 1,300 °C.

The diffraction patterns are identified individually in **Table 5.24**. As a general comment, the CA0 batch showed consistently a high intensity peak at 29 ° two-theta, at all temperatures, compared to the rest of the peaks in the pattern. This might indicate that a predominant silicate is formed at low temperatures. The addition of citric acid does not change substantially the phases present in the structure, since all the peaks in the pattern can be identified. However, the peak at 29 ° two-theta, in the CA10 and CA25 batches, have a similar intensity to the other peaks in the patterns, especially for the CA25 case.

Table 5.24 Peak identification of XRD spectra of pigments produced by addition of citric acid.



3990 The three phases detected in all XRD patterns are the following:

- Apatite, $Y_{4.67}(SiO_4)_3 O$, ICDD reference pattern 00-030-1457.
- Phase X1 of yttrium mono-silicate, Y_2SiO_5 , ICDD reference pattern 00-041-0004.
- Phase X2 of yttrium mono-silicate, Y_2SiO_5 , ICDD reference pattern 00-021-1458.

3995 One or two of the phases are normally found together at temperatures below 1,200 °C, in particular Apatite ($Y_{4.67}(SiO_4)_3 O$) and X1-YSO. Only at 1,300 °C, a mixture of the three phases is detected. The phases identified in **Table 5.24** are summarized in **Table 5.25** below including a colour code for visualization.

Table 5.25 Summary of XRD phases identified on pigment modified with citric acid.

	CA0	CA10	CA25
1,300 °C	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO X2-YSO	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO X2-YSO	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO X2-YSO
1,200 °C	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO
1,100 °C	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO	X1-YSO
1,000 °C	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO	$Y_{4.67}(SiO_4)_3 O$ Apatite X1-YSO	X1-YSO

4000

In the pigment batches with low amounts of citric acid, CA0 and CA10, a mixture of X1 phase of yttrium mono-silicate (YSO or Y_2SiO_5) and apatite ($Y_{4.67}(SiO_4)_3 O$) can be observed after heat treatment at 1,000 °C. The batch including 25 g of citric acid shows only X1 phase at this temperature, delaying the appearance of apatite up to 1,200 °C, compared to the other pigment batches. However, at 1,300 °C, the three batches display a mixture of phases: X1 yttrium mono-silicate, X2 yttrium mono-silicate and apatite. While that the addition of citric acid does not have an influence on the formation of the X2 phase at 1,300 °C, it has an influence in the amount of X1 phase present at lower temperatures. The relative content of the X1 phase, which is the only one present at all temperatures, was calculated by comparing the area of the peaks identified as X1 in the diffraction pattern (ICDD reference pattern 00-041-0004) over the area of all the other peaks. This relative content, in percentage, is shown in **Figure 5.45** for temperatures between 1,000 °C and 1,300 °C.

4010

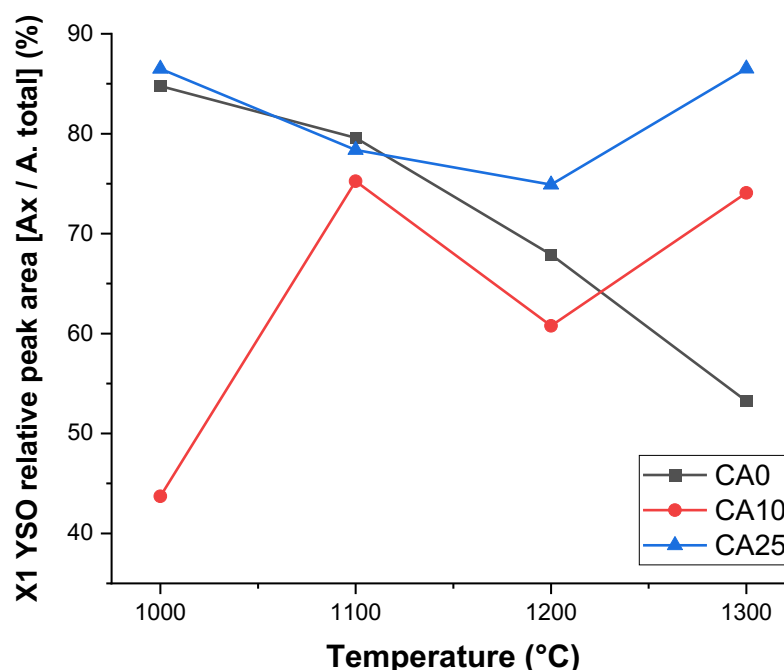


Figure 5.45 Calculated relative content of X1 yttrium mono-silicate phase, obtained from diffraction patterns of yttrium mono-silicate samples produced by addition of citric acid, and heat treated at temperatures between 1,000 °C and 1,300 °C.

The relative content of X1-YSO in the CA10 pigment is different to the other two sets, CA0 and CA25, after heat exposure at 1,000 °C. While the X1 content in the CA10 phosphor was 43 %, the other two cases showed around 85 %, after heat exposure at 1,000 °C. Then the X1 content in the CA10 pigment increased to almost an 80 % at 1,100 °C, which is in the same range of the CA0 and the CA25 samples. In the CA0 case, the content of X1 showed a decreasing trend with increasing temperature, which is not observed when citric acid is included in the pigment synthesis. In the CA10 and CA25 cases, the X1 content decreased from 1,100 °C to 1,200 °C, when apatite phase was first detected in the XRD patterns. The X1 content in the CA10 and CA25 samples then increased between 1,200 °C and 1,300 °C, where the X2 phase was present. This indicates the more effective conversion of apatite and X1 phase to X2 phase when no citric acid is added during the synthesis. The different content of X2 phase can be observed in the diffraction patterns in **Table 5.24** and **Figure 5.44**, for the samples heat treated at 1,300 °C. Following the same procedure than for the X1, considering the area under the X2 peaks, the content of this phase was almost 20 % in the CA0 pigment, 7 % in the CA10 pigment and almost negligible in the CA25 case.

The addition of 10 g of citric acid in the sol-gel synthesis of Y_2SiO_5 doped with Eu^{3+} revealed a delay in the formation of the X1 phase up to 1,100 °C. At temperatures higher than 1,100 °C the presence of X1 phase in the three samples stayed at similar levels, between 60 and 80 %, but with different increasing and decreasing trends in the X1 phase content, depending on the other phases present: apatite and/or X2 phase. The effect of low and high amounts of X1 phase in the three pigments studied here can be compared to the luminescent properties of the same samples, presented in the following sections.

5.4.2.3 Luminescent characterisation of modified pigment and paints

Luminescent properties, such as emission spectra and lifetime decay, were obtained both from the pigment on its own, as well as from the paint produced with these pigments. As explained in *Chapter 4*, Thermal History Paint (THP) was produced with pigment pre-heat treated to 400 °C in order to imitate the capabilities of standard THP. 2.5 g of each batch, CA0, CA10 and CA25, were mixed into potassium silicate binder and sprayed onto stainless-steel bars. The lifetime decay and the spectra of these samples are shown in the following sections, and in the *Appendix*.

Lifetime decay of modified pigment

Luminescent lifetime decay was measured on pigment samples heat-treated between 600 °C and 1,300 °C for more than one hour. These samples were previously explored with X-Ray diffraction. The results are shown in **Figure 5.46** below, where the results of the three batches (CA0, CA10 and CA25) are shown after exposure to the same temperatures.

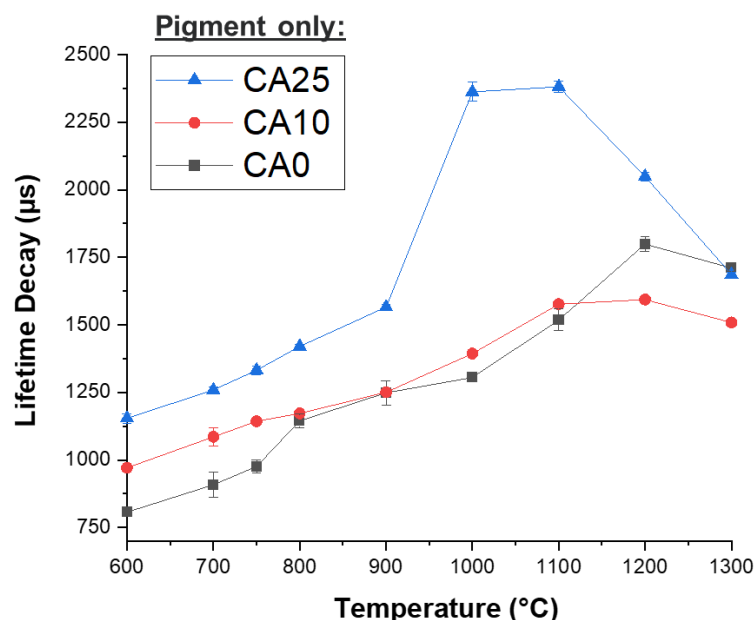


Figure 5.46 Lifetime Decay evolution over temperature for pigments produced by adding 10 g and 25 g of citric acid, compared to the original pigment production.

The first general observation is the offset in lifetime decay between the three batches at temperatures below 800 °C. This is a similar phenomenon to the one observed in the pigment calcination, *Section 5.1.5.1*. The luminescent Eu^{3+} ion emits from a different environment, in this case more dispersed in the CA25 pigment due to the high content of citric acid. The pathlength of the luminescent emission is longer in this case since the Eu^{3+} ions are at further away from each other than in the other two cases. This increases the lifetime decay of the CA25 pigment, specially at low temperatures, compared to the CA0 and CA10 cases. Above 800 °C, the lifetime decay values for the CA0 and CA10 batches are relatively similar, showing a maximum lifetime decay at 1,200 °C, and clearly dropping between 1,200 °C and 1,300 °C, where the presence of X2-YSO was detected during the XRD characterisation in the previous section.

The CA25 batch shows a different lifetime decay behaviour to the other two batches with less citric acid. The sensitivity remained uniform up to 900 °C, increased between 900 °C and 1,000 °C, and dropped between 1,000 °C and 1,100 °C (interval where the maximum can be found). The sensitivity is negative above 1,100 °C, or in other words, the lifetime decay decreases with increasing temperature above 1,100 °C. The CA25 pigment shows a shorter monotonically increasing temperature range and a non-uniform sensitivity above 900 °C, which corresponds to the lack of apatite at temperatures between 900 °C and 1,100 °C. However, the increase in lifetime decay observed in the CA25 powders, between 1,000 °C and 1,100 °C, does not have an immediate correlation with the observations in the XRD diffraction patterns.

Lifetime decay of THP bar test with modified pigment

Three paint batches were generated with the three pigments modified with citric acid, CA0, CA10 and CA25. As previously explained, the pigment samples were pre-heat treated to 400 °C in order to compare with the standard THP. The three paint batches were sprayed onto three stainless-steel bars and heat treated in a tube furnace up to 1,100 °C, as explained in *Chapter 4*. Lifetime decay measurements were obtained over the painted surface and plotted over the maximum exposure temperature along the bar. The results are shown in **Figure 5.47** below, including the sensitivity analysis of the three bars.

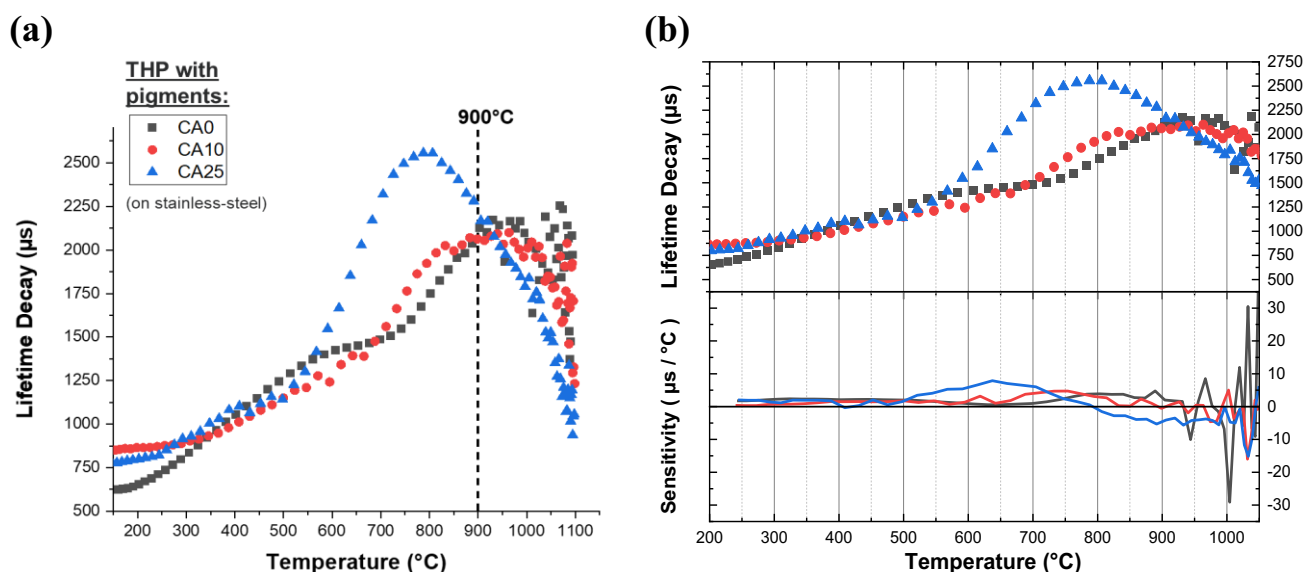


Figure 5.47 (a) Lifetime Decay evolution over temperature for stainless-steel bars painted with THP produced with pigment modified by adding 10 g and 25 g of citric acid, compared to the original pigment production, CA0. (b) Sensitivity analysis of lifetime decay over temperature, for THP produced with modified pigments CA0, CA10 and CA25, applied and heat-treated on stainless-steel bars.

The lifetime behaviour over increasing temperatures for the three paint batches considered are very similar at low and medium temperatures. Below 400 °C, CA10 and CA25 paints show a slight offset respect the paint without citric acid, CA0. However, the three bars display an increasing lifetime decay trend with increasing temperatures. The sensitivity and absolute lifetime decay values obtained are relatively similar for the three paints below 600 °C, and in the case of the CA0 and CA10 batches the similarity continues through the whole temperature range, up to around 900 °C, where both bars show their maximum lifetime decay values. The CA25 paint, differs from the other two batches, with a similar behaviour to the one observed in the pigment-only, shown in **Figure 5.46**. The sensitivity increased at temperatures above 500 °C, up to a maximum at 800 °C. At higher temperatures, the lifetime decay dropped consistently with increasing temperature. The paint batch with the highest amount of citric acid, CA25, displayed the shortest working temperature range and an irregular sensitivity compared to the other paints generated in this section.

Comparing the LTD of the pigment on its own, **Figure 5.46**, and the pigment embedded on the potassium silicate binder (THP), **Figure 5.47**, a shift in the temperature where the maximum LTD can be appreciated. Once the pigment is introduced in the binder the monotonic increase of LTD shrinks around 100 °C for the three pigments considered. This has also been observed for standard THP, where the interaction between the pigment and the binder and the interaction with the metallic substrate limit the sensing capability of the phosphor at high temperatures, i.e., above 900 °C.

Luminescent spectra of THP bar test with modified pigment

Spectra were obtained on the painted bars after heat treatment, for temperatures between 255 °C and 1,100 °C. These luminescent spectra are plotted in **Figure 5.48** below, for the three paint batches considered (CA0, CA10 and CA25) over increasing temperature. The spectral features observed do not differ from the ones observed in standard THP, analysed in detail in *section 5.1*. However, some observations can be made:

- The spectra obtained on CA25 paint show chromium emissions, at 694 nm, at temperatures of 1,000 °C and 1,100 °C. This paint batch is more susceptible to interaction with metallic substrates than the other two batches considered.
- The main differences between paint batches can be observed in the ${}^7F_2$ transition, at wavelengths between 610 nm and 630 nm.
 - CA0 paint showed a single broad peak at temperatures below 800 °C, which transformed at higher temperatures. CA10 and CA25 show a less defined peak following similar transformations above 800 °C,
 - The three paint batches show similar spectral features at 1,100 °C.

4130

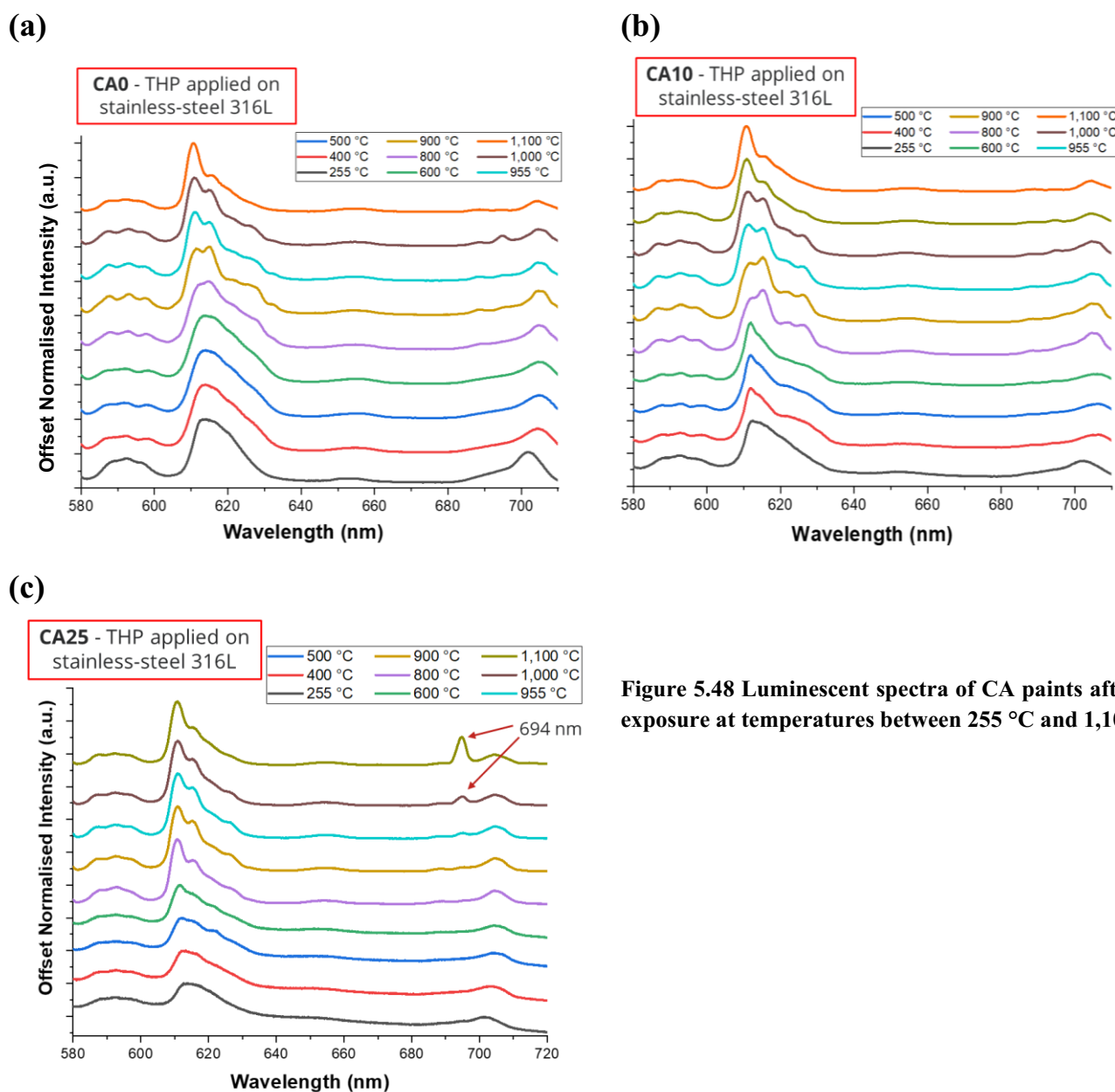


Figure 5.48 Luminescent spectra of CA paints after heat exposure at temperatures between 255 °C and 1,100 °C

5.4.2.4 Conclusions on pigment synthesis modification

4135

After modifying the pigment synthesis route, adding citric acid as a last step in the sol-gel process, some differences were observed on the XRD diffraction patterns of the samples after temperature exposure between 900 °C and 1,300 °C, and compared to samples following the standard synthesis route (CA0). The addition of 25 g of citric acid delayed the generation of apatite phase in the pigment at temperatures below 1,100 °C, but this did not result in an extended working temperature range either of the pigment on its own or mixed into potassium silicate binder, as a thermal history paint. Furthermore, the citric acid might increase the interaction between the paint and the metallic substrate, since chromium luminescent emission was visible on painted samples treated above 1,000 °C. The modifications of the pigment synthesis via citric acid addition did not lead to an extension of the temperature range of THP.

4140

5.5 Interlayer

In *section 5.3*, a series of high temperature products were surveyed and tested as potential binders to contain thermal history pigment. Independently, to the results obtained previously, these products were intended to be used at high temperatures, and therefore considered as potential interlayers. From the strategic point of view, the utilization of an interlayer will mitigate the interaction of the THP with the metallic substrate, particularly the chromium migration into the paint layer. The interlayers could be applied directly onto the metallic substrate with a layer of THP deposited on top. Two schematics are shown in **Figure 5.49** below, one for the standard deposition of THP and a second depicting the interlayer case.

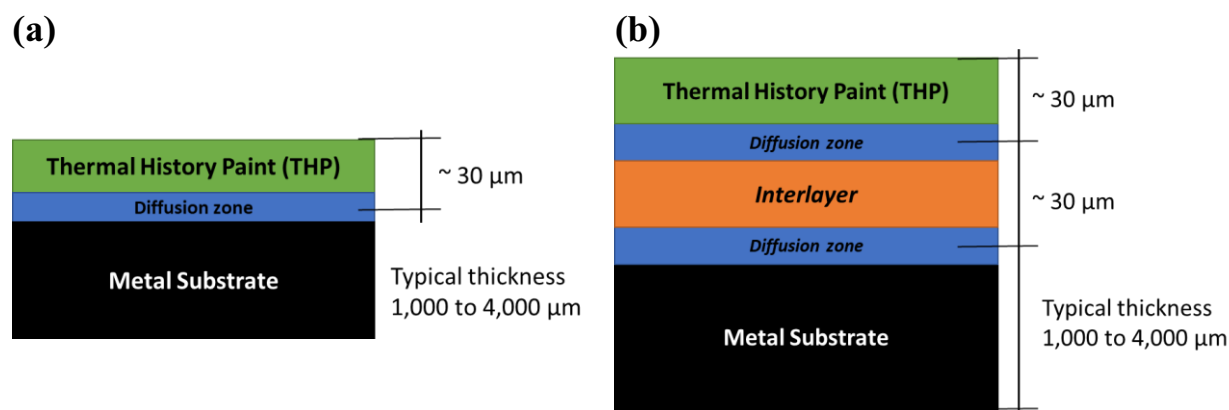


Figure 5.49 (a) Schematic of standard THP deposition on a metallic substrate. Diffusion zones are expected after high temperature exposure, as well as oxidation and corrosion of the metal. (b) Schematic of THP deposition on an interlayer, coating a metallic substrate. Diffusion zones are expected after high temperature exposure, as well as oxidation and corrosion of the metal and the interlayer constituents.

In order to evaluate a suitable interlayer, some of the previously considered high temperature binders in this thesis were tested. The experiments shown in this section consist of a first approximation to obtain an Interlayer-THP diffusion zone which does not result detrimental to the behaviour of the THP at high temperatures. The diffusion of chromium is the main limitation in the use of THP above 900 °C. If the chromium diffusion could occur within the interlayer, without affecting the THP layer, the temperature range of the thermal history paint could be extended to higher temperature regimes. The binder candidates were classified according to the attachment to metallic substrates at high temperatures, as a first selection criterion. The binders that could be used as interlayers are compiled in **Table 5.26** below, with a simple evaluation on the adhesive properties observed in *section 5.3*.

Table 5.26 Summary of attachment capabilities of products tested as high temperature binders.

Commercial Name	Provider Company	Attachment to metal substrate above 900°C
Sealmet	Zyp Coatings, Inc.	✓
Durazane ® 1800	Merck Group / AZ Products	✓
Ludox ® SM 30	Grace GmbH & Co	✓
Fixwool Coatings	Unifrax Ltd.	X
Fabutit 1210	Budenheim KG	X

The commercially available products that could be used as potential interlayers are Sealmat, Durazane ® 1800 and Ludox ® SM30.

5.5.1 Sealmat as interlayer

As seen in *Section 5.3*, Sealmat is a water-based silicate solution commercialised by Zyp Coatings, Inc. A relatively thick layer of this product, over 50 µm, was sprayed onto a stainless-steel bar in a single pass, as recommended by the manufacturer. After drying, conventional THP was sprayed on top of the Sealmat layer until an additional paint film of 30 µm in thickness was deposited, as explained in *Chapter 4*. Then this painted bar was heat-treated in a tube furnace between 150 °C and 1,100 °C. A picture of the bar after heat-treatment is shown in **Figure 5.50** below.



Figure 5.50 THP deposited on top of a Sealmat interlayer on a stainless-steel bar and heat-treated between 150 °C and 1,100 °C. Cold end of the bar on the left-hand side, and hot end on the right-hand side.

The THP deposited on top of the Sealmat showed the standard grey-white colour expected after heat-treatment. At temperatures above 1,000 °C, near the hot end, the painted bar displayed a blue colour. This is probably a result of the metal oxides present in the Sealmat and exposed to high temperatures, visible through the THP layer.

Lifetime decay measurements were taken on the heat-treated THP deposited on the Sealmat. The results were plotted over the thermocouple temperature trace recorded during the heat treatment, to match the lifetime decay values with their corresponding temperatures, as explained in *Chapter 4*. The results are displayed in **Figure 5.51** below, next to the sensitivity analysis performed on the obtained results.

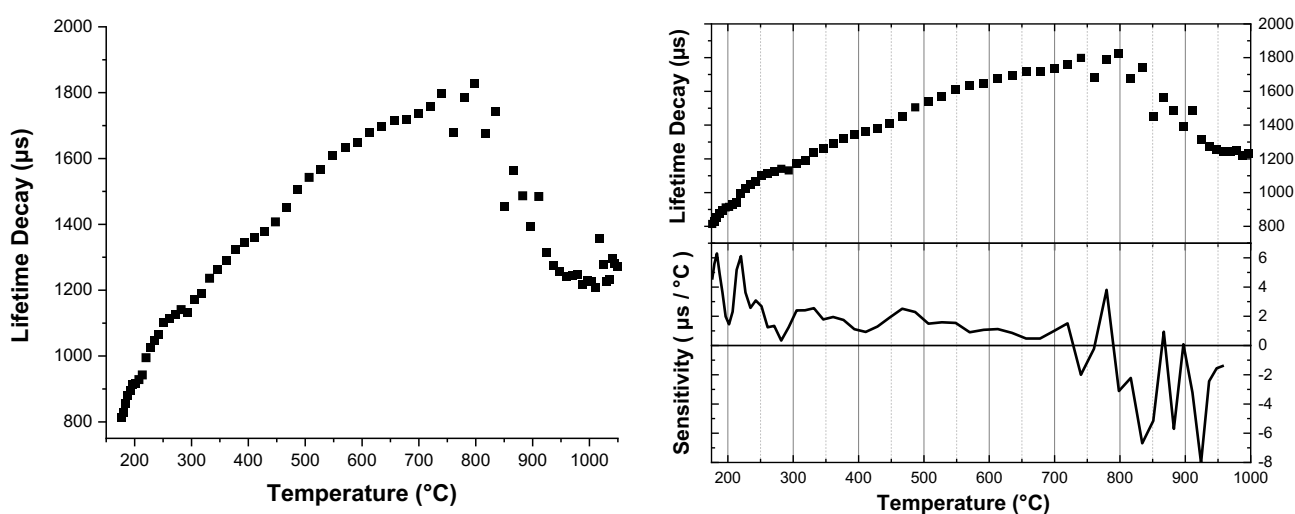


Figure 5.51 (Left) Lifetime Decay plotted over temperature for THP deposited on a Sealmat 1800, both deposited on a 400 x 20 x 3 mm stainless-steel bar and heat treated up to 1,100 °C. (Right) Monotonic increase of lifetime decay over temperature for THP deposited on Sealmat interlayer (top) and sensitivity analysis of the monotonic lifetime decay increase (bottom).

4195

4200

Overall, the THP shows a stable monotonic increase with increasing temperatures from 150 °C up to 800 °C, with a stable sensitivity between 300 °C and 700 °C. The maximum lifetime decay recorded was obtained at around 800 °C, but some changes in the sensitivity are noticeable from 700 °C. At temperatures above 800 °C, the lifetime decay decreases with increasing temperatures, setting the working range of this painted interlayer between 154 °C and 800 °C. The attachment of the THP to the Sealmet is not perfect, and some paint detachment can be observed in some areas in **Figure 5.50**. In conclusion, the obtained results are similar to the THP directly applied onto the metal substrate, with no clear improvement in attachment or extended temperature range.

4205

5.5.2 Durazane® 1800 as interlayer

4210

4215

A layer of Durazane® 1800 was sprayed onto a stainless-steel 316L bar and cured in a decomposition furnace as explained in section 5.3.1.5. On top of this Durazane® 1800 layer, 30 µm of THP were sprayed and cured at 150 °C for more than one hour. This bar was then heat treated in a tube furnace, to generate a temperature gradient between 200 °C and 1,100 °C. A picture of this bar after heat treatment is shown in **Figure 5.52** below. Both the Durazane ® and the THP remained in a light white colour at low temperatures, turning transparent (with a glossy appearance) at higher temperatures. The metal underneath oxidized with the temperature exposure, turning into a dark colour, observable below the transparent painted layers near the hot end.



Figure 5.52 THP deposited on a Durazane® 1800 interlayer on a stainless-steel bar and heat-treated between 200 °C and 1,100 °C. Cold end of the bar on the left-hand side, and hot end on the right-hand side.

4220

4225

Lifetime Decay measurements were taken on top of the painted bar, matching each measurement with the maximum exposure temperature seen at every point, as explained in *Chapter 4*. The results are plotted in **Figure 5.53**, where both the lifetime decay – temperature plot, and the sensitivity analysis of the interlayer system are shown. The monotonic increase of the lifetime decay with increasing temperature is remarkably linear, with a stable sensitivity above 1 µs / °C from 200 °C to almost 900 °C, where the maximum lifetime decay value was measured. Above 900 °C, the LTD values drop with increasing temperature, similarly to conventional THP applied directly on metal.

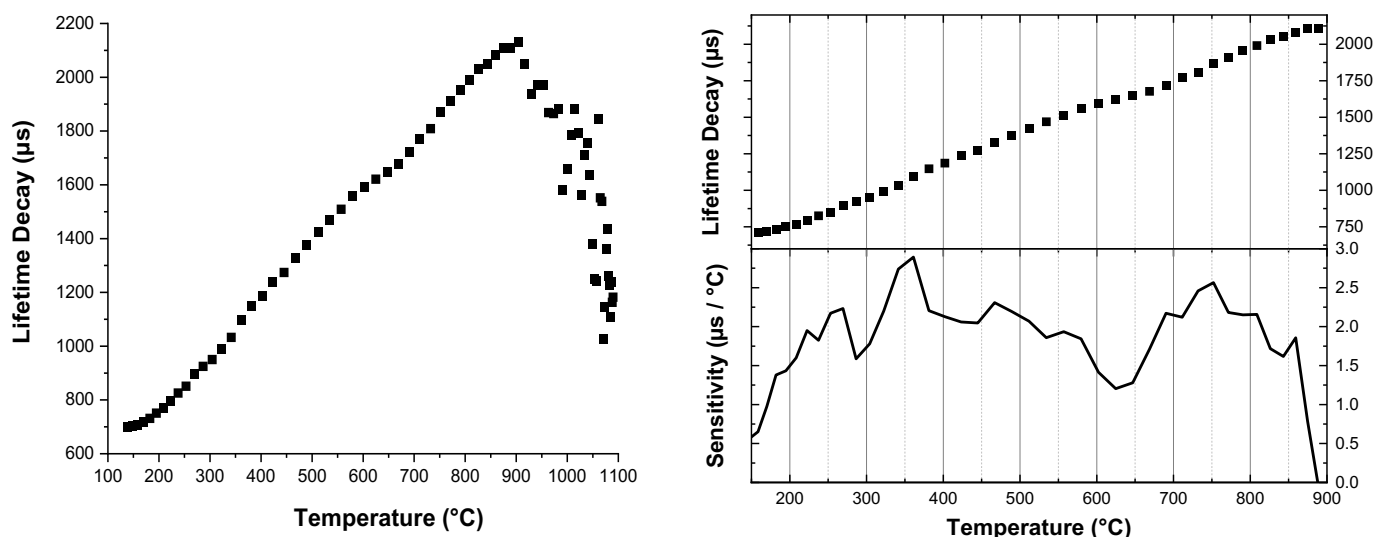


Figure 5.53 (Left) Lifetime Decay plotted over temperature for THP deposited on a Durazane® 1800 interlayer, both deposited on a 400 x 20 x 3 mm stainless-steel bar and heat treated up to 1,100°C. (Right) Monotonic increase of lifetime decay over temperature for THP deposited on the interlayer (top) and sensitivity analysis of the monotonic lifetime decay increase (bottom).

4230

5.5.3 Ludox® SM30 as interlayer

Ludox® SM30 was applied on a stainless-steel 316L bar as explained in *Chapter 4*. A second layer of standard THP was applied on top of the Ludox® SM30 layer, while in parallel a second bar without interlayer was sprayed as well. This enabled the direct comparison of the same THP with and without interlayer. The as-sprayed bars are shown in **Figure 5.54** below.

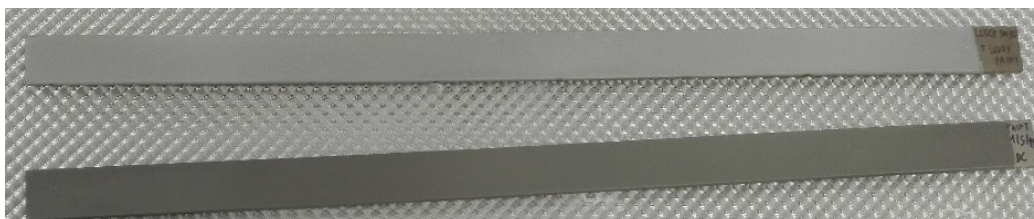


Figure 5.54 THP applied on stainless-steel bars, on top of a Ludox® SM30 interlayer (top) and THP applied directly on the metallic substrate, showing a darker colour (bottom).

Both bars were cured in an electric furnace at 150 °C for over one hour. In **Figure 5.55**, the two painted bars are shown after curing, with the distinctive white appearance of conventional THP. While the paint layer deposited directly on stainless-steel was uniform, showing good general appearance, the paint deposited on Ludox® SM30 displayed some blisters and overall detachments. This effect has been hypothesised as the *thickness limit* or *Critical Cracking Thickness (CCT)* of the Ludox® SM30 and the THP system, but has not been further investigated in this work [361–363].



Figure 5.55 THP applied on a stainless-steel bar coated with a Ludox® SM30 interlayer (top) and THP applied directly on a stainless-steel bar (bottom), after heat treatment at 150 °C for one hour.

The two bars were subsequently heat-treated in a tube furnace, generating a temperature gradient up to 1,100°C. The LTD values obtained along the bars are plotted against the corresponding maximum temperature in **Figure 5.56** below, where the sensitivity analysis is also included. The LTD readings of the THP deposited directly on metal and of the THP deposited on top of the Ludox® interlayer are very similar. Both bars show a monotonic increase of lifetime decay with increasing temperature, up to 900 °C, with a relatively stable sensitivity around 2 $\mu\text{s} / ^\circ\text{C}$. Above this temperature, the LTD values dropped at higher temperatures. No significant differences were found in the LTD readings from the THP applied directly on stainless-steel and on a Ludox® SM30 interlayer.

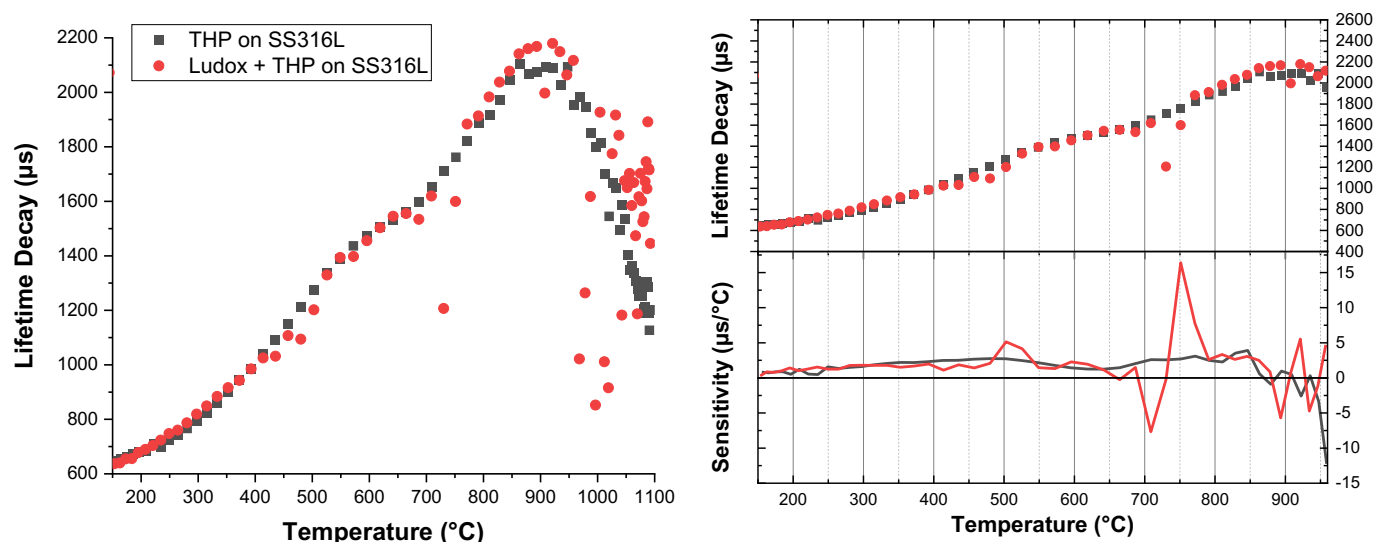


Figure 5.56 (Left) Lifetime Decay plotted over temperature for THP deposited on a Ludox® SM30 interlayer, both deposited on a 400 x 20 x 3 mm stainless-steel bar and heat treated between 150 $^{\circ}\text{C}$ and 1,100 $^{\circ}\text{C}$. (Right) Monotonic increase of lifetime decay over temperature for THP deposited on the interlayer (top) and sensitivity analysis of the monotonic lifetime decay increase (bottom).

Unfortunately, the THP on top of the Ludox ® SM30 did not show a good attachment to the interlayer. As shown in **Figure 5.57** below, the THP was barely attached to the Ludox ® SM30 after heat treatment. This effect and the lack of improvement with respect conventional THP applied directly on metallic substrates, stopped further investigation of Ludox ® SM30 as an interlayer for conventional THP.



Figure 5.57 THP detached from stainless-steel bar coated with a LudoxSM30 interlayer, after heat treatment at temperatures between 150 $^{\circ}\text{C}$ and 1,100 $^{\circ}\text{C}$. The whiter areas at the cold end of the bar, on the left hand-side, while the highest temperatures are on the right extreme, hot end.

5.5.4 Summary of results on THP deposited on interlayers.

The LTD – Temperature curves of the three interlayers tested are plotted together in **Figure 5.58** below, with the corresponding sensitivity analysis. The three bars were painted with the same batch of THP, so the sensitivities obtained are very similar in the three cases, oscillating around $2 \mu\text{s} / ^\circ\text{C}$. The only source of variability is the THP detachment from the Ludox[®] SM30 interlayer, that generates high and low sensitivity values between 700°C and 800°C .

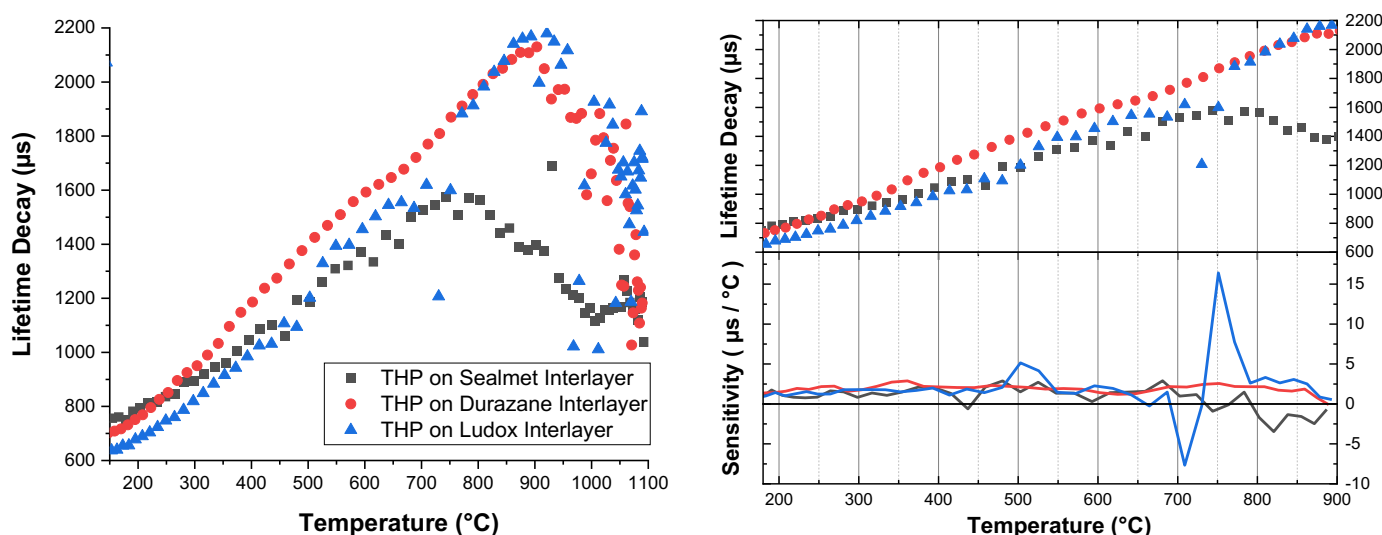


Figure 5.58 (Left) Lifetime Decay plotted over temperature for THP deposited on interlayers of Sealmet, Durazane[®] 1800 and Ludox[®] SM30 deposited on stainless-steel bars and heat treated up to $1,100^\circ\text{C}$. (Right) Monotonic increase of lifetime decay over temperature for THP deposited on interlayers (top) and sensitivity analysis of the monotonic lifetime decay increase (bottom).

A summary of the LTD analysis has been gathered in **Table 5.27**. However, other parameters can be considered in the evaluation of an interlayer, such as the mitigation in the interaction with metallic substrates or the improvement in the linearity of the THP.

Table 5.27 Summary of lifetime decay evolution over temperature for THP deposited on interlayers.

	Min LTD (μs)	Max LTD (μs)	LTD Range (μs)	Temperature Range ($^\circ\text{C}$)	Sensitivity ($\mu\text{s}/^\circ\text{C}$)
THP on Sealmet	694.3	1689.6	995.3	From 154°C to 800°C	1.1 ± 1.0
THP on Durazane[®] 1800	698.9	2129.6	1430.7	From 137°C to 903°C	1.8 ± 0.6
THP on Ludox[®] SM30	637.2	2149.5	1512.3	From 135°C to 934°C	1.6 ± 0.9 (until 700°C)

The values in **Table 5.27** above, are similar to the THP references reported in **Table 5.8**. The sensitivity of the three tested interlayers increased compared to the references, and the temperature range expanded in the low temperature regime, below 200 °C in all cases. The THP references start the temperature working range around 200 °C (P400) or higher, for the P600 pigment case (See *Section 5.1.5.1, Pigment calcination*). A start of the LTD monotonic increase at temperatures below 200 °C can be considered an expansion of the working temperature range and it is suggested as an area of future investigation in *Chapter 7, Future Work*.

Qualitatively, the three tested interlayers can be evaluated according to the attachment to the THP and the improvement in the LTD-temperature sensitivity. These parameters are summarised in **Table 5.28** below. The Durazane® 1800 is the only product offering a good attachment between the THP and the interlayer, while improving the sensitivity, compared to the THP reference paints presented in *section 5.1.5.2*, from 1.4 µs / °C to 1.8 µs / °C. This constitutes an advantage over some of the binders tested and presented in **Table 5.21**. However, given the nature of Durazane® 1800 and the precautions needed for its use (see *section 5.3.1.5*), the use of this interlayer was discarded to extend the use of THP into higher temperature regimes.

Table 5.28 Summary of attachment and sensitivity improvement for THP applied on top of interlayers.

	THP attachment to Interlayer	LTD-Temp. sensitivity improvement
Sealmet	✓	X
Durazane® 1800	✓	✓
Ludox® SM30	X	X

6 Development of a high-temperature thermal history paint

After exploring different strategies to expand the working range of THPs to higher temperatures, a route combining several successful findings was tested, leading to the development of a new version of thermal history paint.

6.1 Optimisation route for THP: Combination of Solutions

The first observations made on THP at high temperatures (*Section 5.1*) led to different testing routes to explore the mitigation of some of the detrimental effects of high temperature exposure (*Sections 5.2 to 5.5*). Some of the selected solutions gave way to a potential development of the THP into higher temperature regimes, while some other routes do not show a clear improvement above 900 °C. All the development routes, and the main outcomes after testing, are summarised in **Table 6.1** below.

Table 6.1 Summary of observed THP behaviour at high temperatures, development routes considered and selected solutions for the design of a new version of thermal history paint

THP behaviour at high temperatures (> 900°C)		Development route	<u>Selected solution</u>
1. Interaction Pigment -Binder effect on luminescent properties 2. Binder melting 3. Interaction with metallic substrate / THP structural degradation 4. Efflorescence / Shelf Life		1. Binder modification	
		2. Binder substitution	Ludox ® SM 30
		3. Pigment modification	Pigment Calcination
		4. Interlayer	

Modifying the current liquid binder showed clear limitations as these silicate solutions became chemically unstable after slightly changing the composition. The use of interlayers did not show improvements, neither expanding the temperature range above 900 °C nor improving the attachment of the THP layer to the substrate. On the other hand, during the pre-test considerations of the pigment, the calcination of the pigment at 600 °C expanded the working range of the THP to temperatures above 900 °C.

From the evaluated binder candidates as a substitute for the potassium silicate, only one displayed potential enhanced behaviour at high temperatures, Ludox® SM30. This binder retained a white appearance after exposure to temperatures above 900 °C, improving the emission of the phosphorescent pigment embedded in the paint. The attachment to the metallic substrate was good, and fewer effects of efflorescence were observed after measuring the same painted stainless-steel bar, after six months in storage, as shown in **Figure 6.1** below. A minimal effect of efflorescence is extremely beneficial to improve the reliability of lifetime decay measurements, reducing the uncertainty of the measurement and obtaining reliable measurements at high temperatures, as seen in *section 5.1.4*.

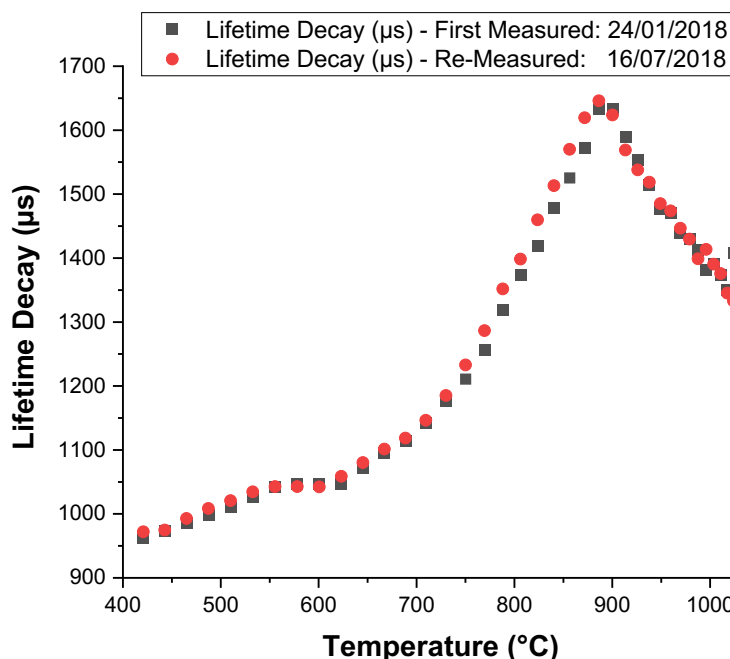


Figure 6.1 Lifetime Decay plotted over temperature of exposure of Ludox® SM30 based THP, deposited on a stainless-steel bar and heat treated up to 1,100 °C. The Lifetime decay was remeasured at the same locations after six months of storage to evaluate the effect of efflorescence.

6.1.1 Characterisation of colloidal silica, Ludox® SM30

Ludox® SM30 samples were characterised via X-Ray diffraction (XRD) after being exposed to temperatures up to 1,200 °C for one hour. Below 800 °C, no crystalline features were observed, and the main characterisation efforts were focused on the samples heated between 800 °C and 1,200 °C. The diffraction patterns of these samples are shown in **Figure 6.2**, where the silica phases are identified and indicated with markers.

All the samples show a mixture of cristobalite (01-082-1553 and 01-082-1410 PDF ICDD reference patterns) and tridymite (00-042-1401 and 01-082-1559 PDF ICDD reference patterns), tetragonal and orthorhombic silica phases, respectively. The main cristobalite peak located at 22 ° two-theta, is observed from 800 °C up to 1,200 °C, while the main tridymite peaks located at 21 ° and 23 ° can only be observed at 900 °C or higher temperatures.

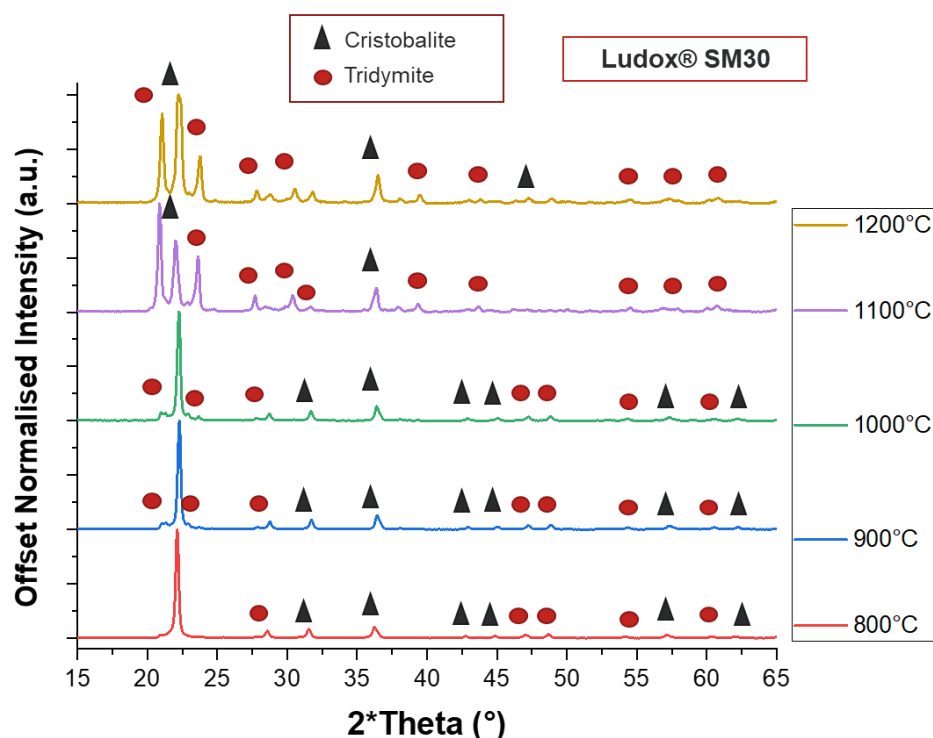


Figure 6.2 Diffraction patterns of Ludox ® SM30 samples after heat treatments between 800 °C and 1,200 °C. Matching silica phases are identified and indicated with markers.

The area of the main peaks of the cristobalite and the tridymite were analysed and plotted as a percentage over the total area of the peaks, over the exposure temperature. This is shown in **Figure 6.3** below. The obtained mixture of phases has been observed by other authors in silica products contaminated with metals [364]. In the case of Ludox ® SM30, sodium counter-ions are part of the colloidal silica solution, and the manufacturing process might result in the presence of cristobalite at relatively low temperatures [365,366].

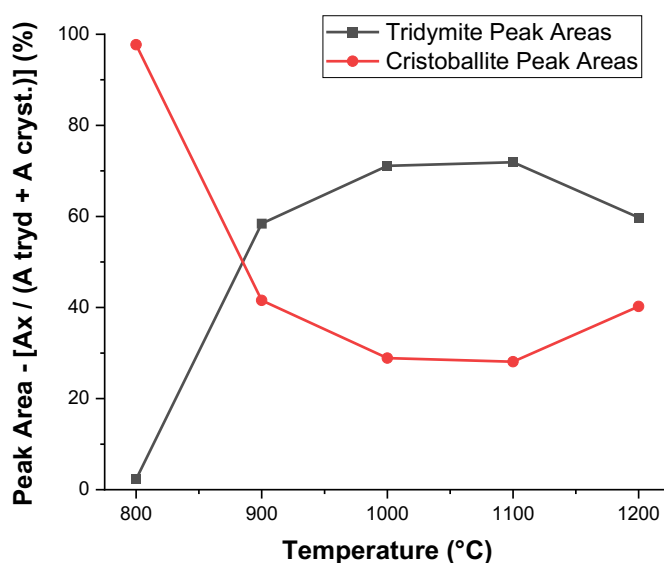


Figure 6.3 Calculated relative content of silica phases, cristobalite and tridymite biphasic mixture, obtained from diffraction patterns of Ludox®SM30 samples heat treated at temperatures between 800 °C and 1,200 °C.

6.1.2 Combination of solutions: Calcined pigment mixed into potassium silicate and Ludox® SM30 colloidal silica binders.

Given the promising results obtained using Ludox ® SM30, this product was identified as a potential high temperature binder for a new version of thermal history paint. However, Ludox ® SM30 was tested with a pigment calcined at 600 °C, which once it was mixed into the binder led to a maximum operative temperature of 900 °C. The same pigment, mixed into potassium silicate, extended this maximum operative temperature to 960 °C. The combination of both binders could lead to an intermediate improved behaviour, and therefore the combination of these was tested in this section, for different concentrations of Ludox ® SM30 and potassium silicate (IP66). The concentration of pigment was kept constant at 5 % wt., as described in *Chapter 4*. The produced compositions, summarised in the ternary plot in **Figure 6.4**, are:

- Run 1: Ludox ® SM30 (95 % wt.) and P600 pigment (5 % wt.)
- Run 2: Ludox ® SM30 (72 % wt.), potassium silicate (23 % wt.) and P600 pigment (5 % wt.)
- Run 3: Ludox ® SM30 (47.5 % wt.), potassium silicate (47.5 % wt.) and P600 pigment (5 % wt.)
- Run 4: Ludox ® SM30 (23 % wt.), potassium silicate (72 % wt.) and P600 pigment (5 % wt.)
- THP-P600 (Reference): potassium silicate (95 % wt.) and P600 pigment (5 % wt.)

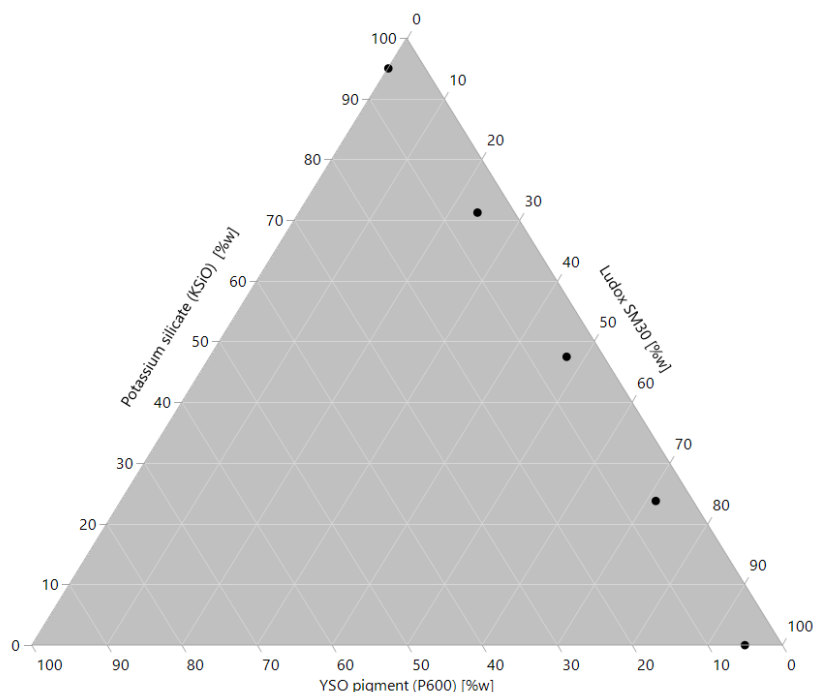


Figure 6.4 Ternary plot of THP pigment ($\text{Y}_2\text{SO}_5: \text{Eu}^{3+}$), Ludox® SM30 binder and potassium silicate binder.

Once the paint batches were produced, as explained in *Chapter 4*, a few drops of every paint were dried in an oven at 150 °C. The obtained paint pellets were deposited on alumina tiles and then heat-treated to temperatures between 800 °C and 1,100 °C. The samples were scratched from the alumina tiles when necessary, and characterised by luminescent lifetime decay and spectra, as well as X-Ray diffraction. The lifetime decay results of the different runs are plotted against the maximum exposure temperature in **Figure 6.5**.

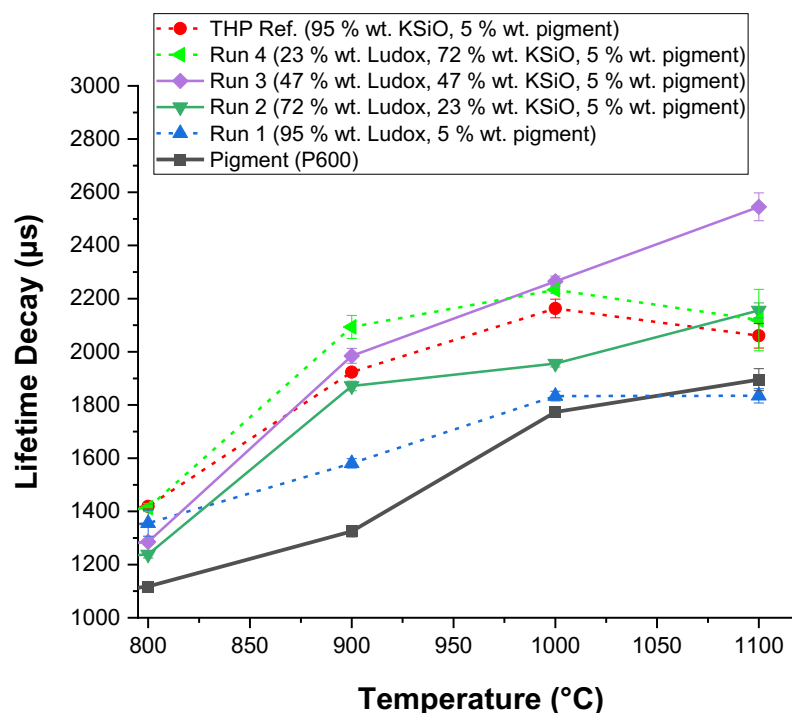


Figure 6.5 Lifetime decay of paint pellets, heat-treated between 800 °C and 1,100 °C, combining Ludox® SM30 and potassium silicate binders with pigment calcined at 600 °C (P600). Lines joining points added for visualization.

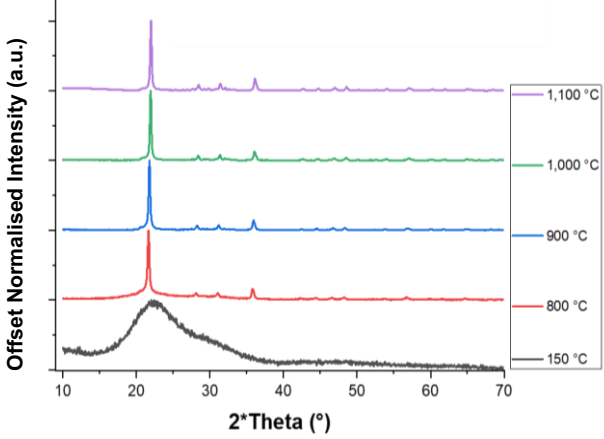
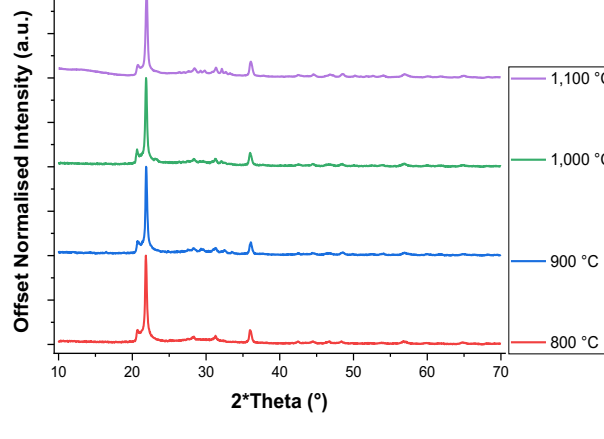
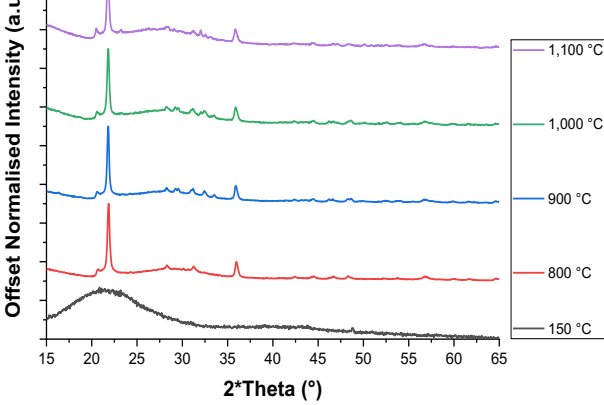
Three of the six samples considered show a monotonic increase of lifetime decay with increasing temperature between 800 °C and 1,100 °C:

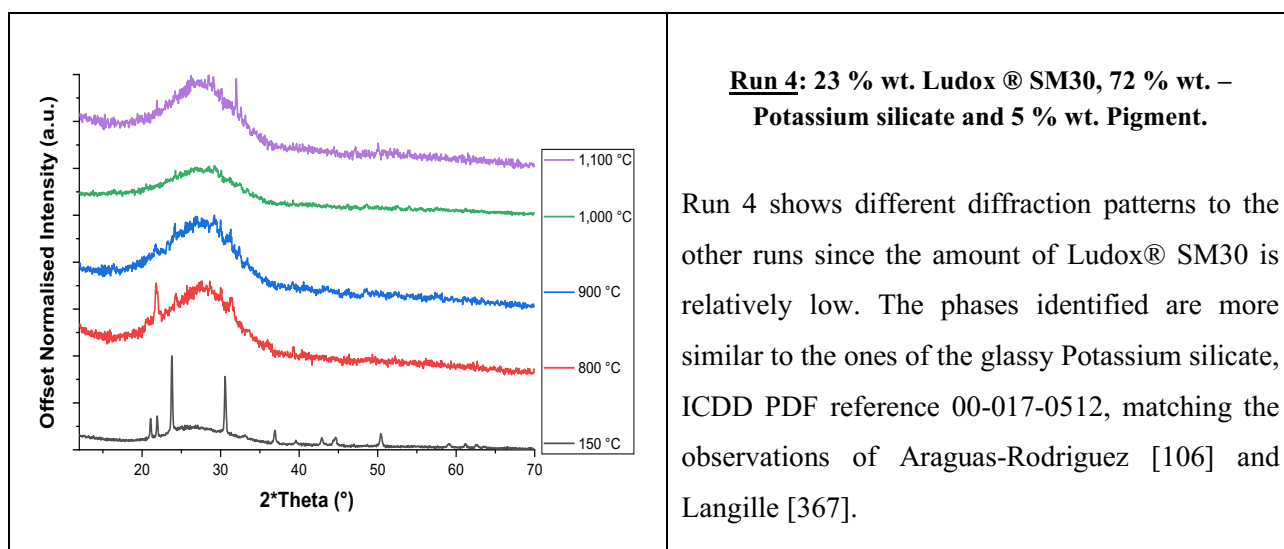
- The P600 pigment on its own, pre-calcined to 600°C.
- Run 2: Ludox ® SM30 (72 % wt.), potassium silicate (23 % wt.) and P600 pigment (5 % wt.)
- Run 3: Ludox ® SM30 (47.5 % wt.), potassium silicate (47.5 % wt.) and P600 pigment (5 % wt.)

This behaviour indicates that the mixture of Ludox® SM30 and potassium silicate could result in an improved working temperature range in a new version of THP, when the proportion of Ludox® SM30 is equal or higher than that of potassium silicate. Unfortunately, the presence of potassium silicate results necessary to improve the behaviour of the pigment on its own, which it is not observed in Run 1. This was discussed in *section 5.1*, where the interaction between the pigment and the potassium silicate binder extended the operative temperature of the pigment on its own, as seen in **Figure 5.8**. Some of the detrimental effects of the potassium silicate, such as the efflorescence, are expected to remain in a version of THP which includes potassium silicate binder. This has not been investigated further in this section.

The samples of the runs 1 to 4 were characterised by XRD and the results are summarised in **Table 6.2**.

Table 6.2 Diffraction patterns of paint pellets, heat-treated between 800 °C and 1,100 °C, combining Ludox ® SM30 and potassium silicate binders with pigment calcined at 600 °C (P600).

	Run 1: 95 % wt. Ludox ® SM30, 5 % wt. Pigment. As discussed in the characterisation of the Ludox® SM30 on its own, in the previous section, the sample showed an amorphous pattern below 800 °C. The diffraction pattern was identified with Cristobalite (01-082-1553 and 01-082-1410 ICDD PDF reference patterns) at temperatures above 800 °C. Unlike the Ludox® SM30 on its own, no transition to tridymite was observed at 1,100 °C.
	Run 2: 72 % wt. Ludox ® SM30, 23 % wt. – Potassium silicate and 5 % wt. Pigment. All the diffracted patterns obtained between 800 °C and 1,100 °C are very similar, showing a stable mixture of cristobalite and tridymite. This might be caused by the presence of the pigment and the potassium silicate, affecting the more intense peaks of the Ludox® SM30, which can be clearly identified.
	Run 3: 47.5 % wt. Ludox ® SM30, 47.5 % wt. – Potassium silicate and 5 % wt. Pigment. Run 3 shows a similar mixture of cristobalite and tridymite to the one observed in the samples of the Run 2. The background of these samples is more pronounced, as a consequence of the increase in potassium silicate in the composition.

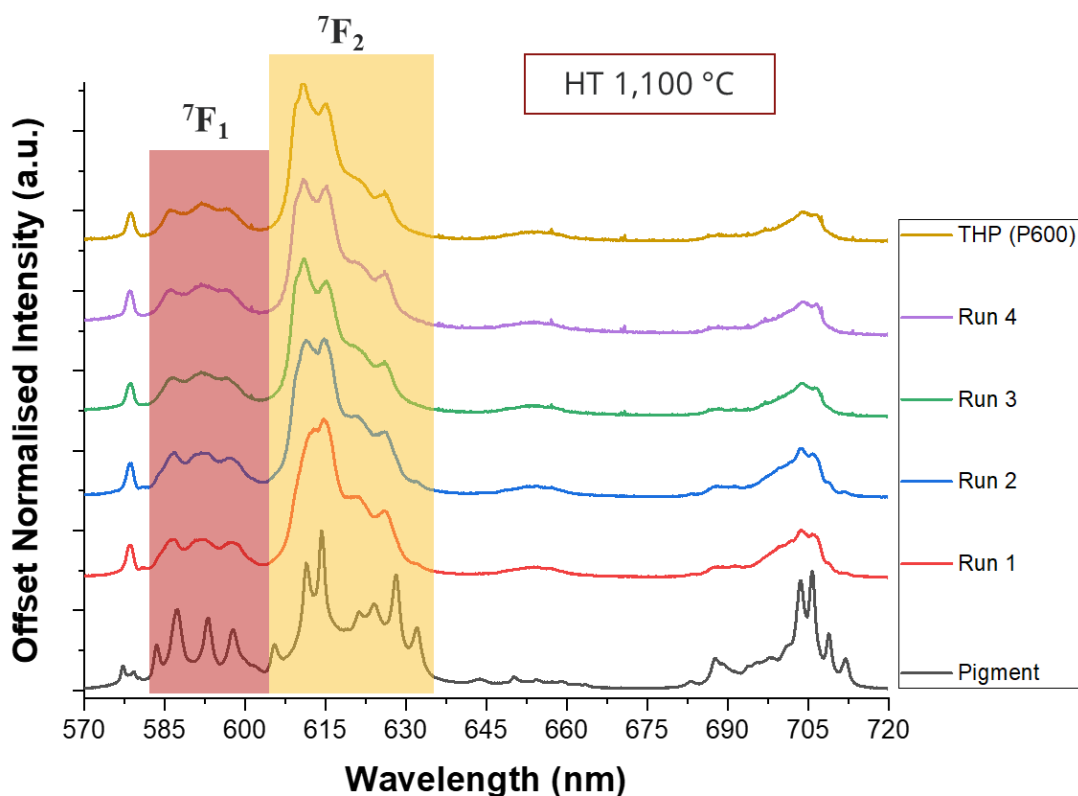


4440

6.1.2.1 Luminescent spectra of the Ludox® SM30 and Potassium silicate combination

The luminescent spectra of all the samples considered in the previous section were obtained and can be consulted in the *Appendix*. However, the spectra obtained from all the samples heat-treated to 1,100 °C are included in this section, to observe the differences in the europium emission after heat exposure at the same temperature. In particular the transitions $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$, marked in **Figure 6.6** below, were compared and analysed through an intensity ratio.

4445



4450

Figure 6.6 Luminescent spectra of paint samples, heat-treated at 1,100 °C, combining Ludox® SM30 and potassium silicate binders with pigment calcined at 600 °C (P600).

The spectra of the Runs 2 to 4, show similar $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ emission peaks, in particular the shoulder between 620 nm and 635 nm, while the pigment on its own and the Run 1 differ slightly from the other spectra, for emission lines centred at 611 nm and 614 nm. The areas under the curve of the $^7F_1$ and $^7F_2$ transitions were obtained from all the samples and the intensity ratio plotted in **Figure 6.7** below. The same ratio of the emission from europium embedded in oxide glasses studied by Oomen and van Dongen [368] was plotted for comparison.

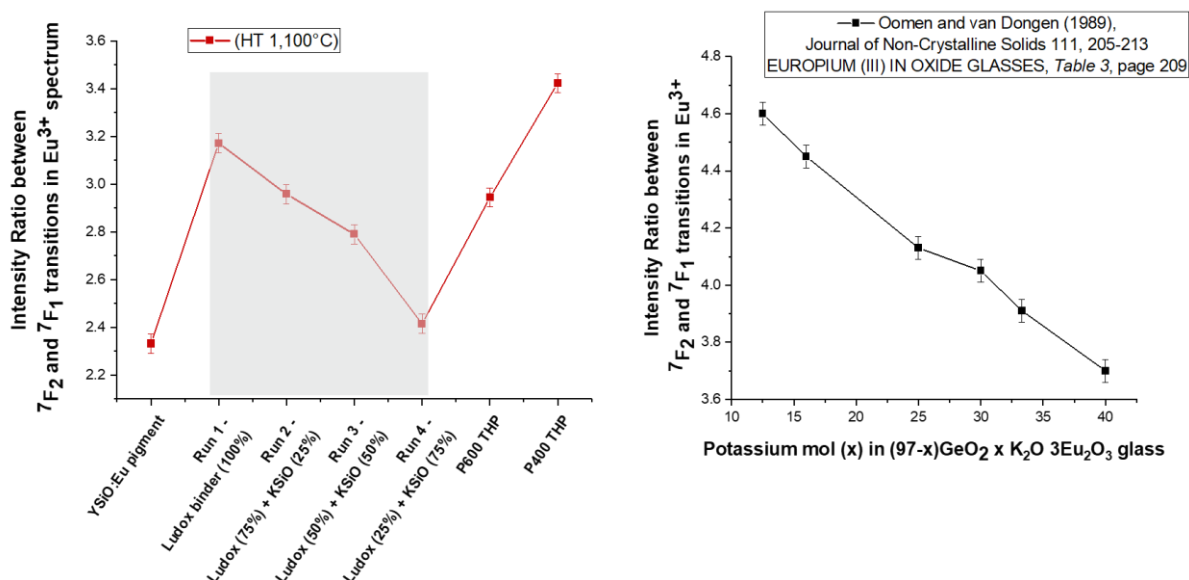


Figure 6.7 (Left) Ratio between the $^5D_0 \rightarrow ^7F_2$ and the $^5D_0 \rightarrow ^7F_1$ transitions of Eu^{3+} , studied in the luminescent spectra of paint pellets, heat-treated at 1,100 °C, combining Ludox® SM30 and potassium silicate binders (indicated as “KSiO” in the figure) with pigment calcined at 600 °C (P600). **(Right)** Ratio between the $^5D_0 \rightarrow ^7F_2$ and the $^5D_0 \rightarrow ^7F_1$ transitions of Eu^{3+} , embedded in oxide glasses studied by Oomen and van Dongen [368].

The intensity ratios from the europium emission of the two cases are in the same order of magnitude. A similar decreasing trend was obtained when comparing the Runs 1 to 4, marked in **Figure 6.7 (Left)** Oomen and van Dongen [368], studied the europium in glass, surrounded by an increasing amount of potassium ions, where the same decreasing trend was observed for an increasing amount of potassium. The increase of number of modifiers, i.e., potassium ions, in the silicate network, surrounding the europium, led to a decrease in the intensity ratio $^5D_0 \rightarrow ^7F_2$ over $^5D_0 \rightarrow ^7F_1$. In this case, increasing the proportion of potassium surrounding the europium, produced a decrease in the ratio in both cases.

As explained in *Chapters 2 and 3*, the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition depends on the structural changes in the vicinity of the emitting Eu^{3+} ion. Changes in the glass structure, modified by alkali and Eu^{3+} ions will influence the symmetry of the glass and therefore the emission from the europium. For low alkali concentrations, the ions are incorporated into the voids of the glass network. These do not normally include the voids in the vicinity of the Eu^{3+} ion, due to the repulsion of the positive charges. For higher alkali concentrations, however, it is inevitable that voids in the vicinity of the Eu^{3+} are occupied. The glass network forming units can include two non-bridging oxygens, which can influence the symmetry and covalency at the Eu^{3+} emission site [368].

6.1.3 Binder combination applied on stainless-steel and development of a high-temperature thermal history paint

The combination of Ludox® SM30 and potassium silicate binders showed promising results as stand-alone samples, heat treated on alumina substrates and then interrogated via luminescent techniques. Therefore, the formulations explored in the previous section were tested on stainless-steel. A set of three 400 x 20 x 3 mm stainless-steel bars and several 20 x 10 x 3 mm samples were painted with the Runs 1 to 3 of the paints previously produced. A picture of the painted bars and samples, after curing at 150 °C, is shown in **Figure 6.8** below.

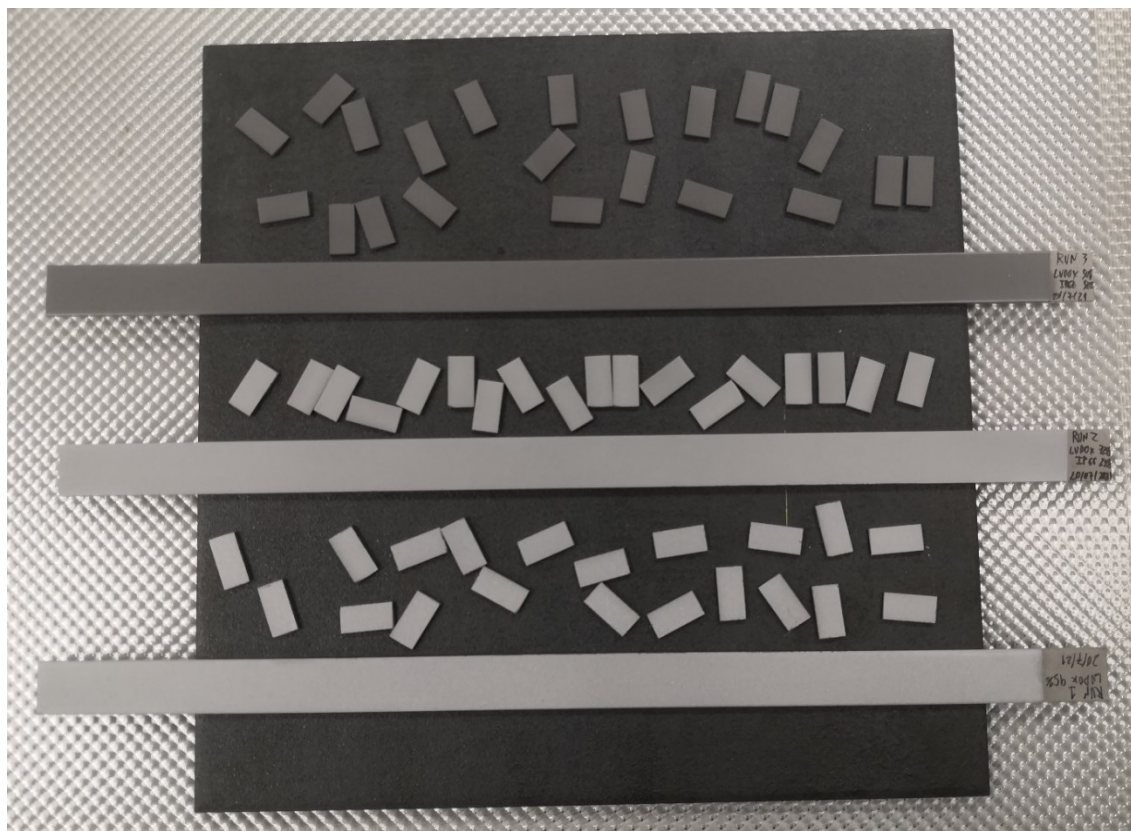
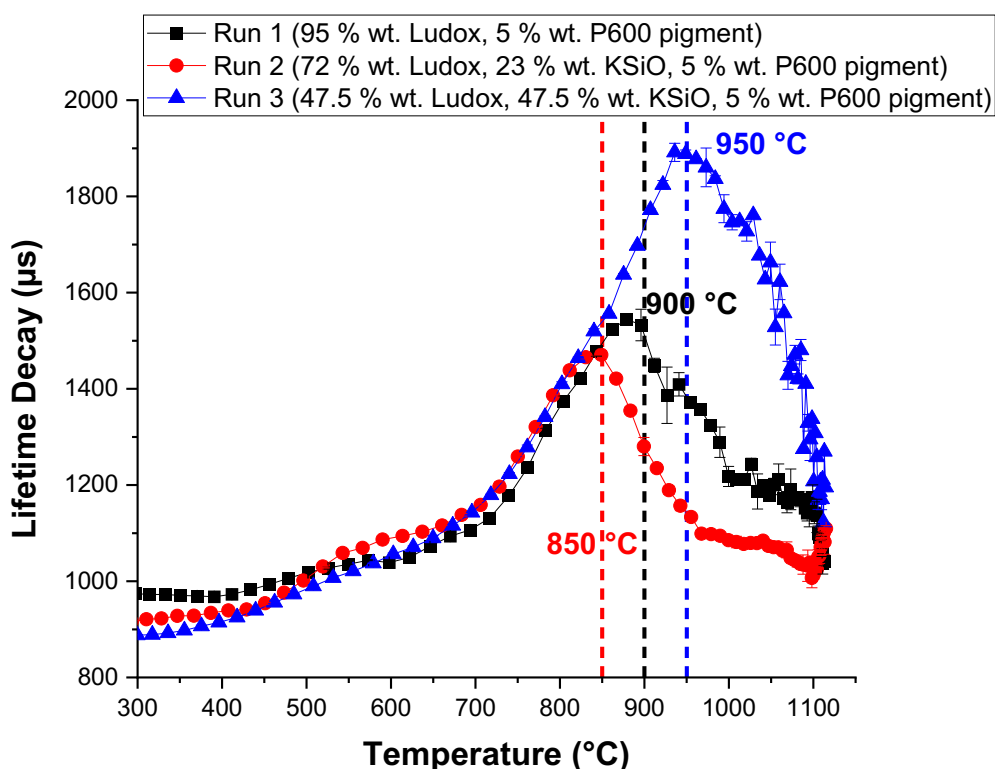


Figure 6.8 Ludox® SM30 based paints applied on stainless-steel bars and tiles. From top to bottom, Run 3 (consisting of Ludox® SM30 (47.5 % wt.), potassium silicate (47.5 % wt.) and P600 pigment (5 % wt.)), Run 2 (consisting of Ludox® SM30 (72 % wt.), potassium silicate (23 % wt.) and P600 pigment (5 % wt.)), and Run 1 (Ludox® SM30 (95%w) and P600 pigment (5 % wt.)).

The bars were heat-treated following the standard bar test procedure described in *Chapter 4*, to produce a profile between 200 °C and 1,100 °C. A picture of the heat-treated bars and the lifetime decay values obtained after heat exposure are shown in **Figure 6.9**. The three paints were produced with pigment heat treated at 600 °C. However, the highest lifetime decay values of the three paints were obtained at three different temperatures, where the monotonic increase of lifetime decay with increasing temperature stopped. As indicated in the figure, Run 1 (containing only Ludox® SM30 as a binder) reached 900 °C before dropping in lifetime decay. The bar painted with the Run 2 paint, showed its maximum at 850 °C, and Run 3, with an equal 47.5 % wt. of Ludox ® SM30 and potassium silicate, extended the monotonic increase of the lifetime decay up to 950 °C.

The same pigment reached different maximum temperatures depending on the binder surrounding it, once it is deposited on the same metallic substrate. As discussed in *Chapter 5*, this maximum working temperature depends on the interaction between pigment and binder, and on the detrimental effect of the metallic substrate in the luminescent properties of the paint layer, especially metallic substrates containing chromium (which is the case of stainless-steel and most of the nickel alloys used in turbomachinery components). Nevertheless, luminescent measurements at temperatures higher than these maximum working points could be used for temperature determination, using the data of these test bars for calibration.

(a)



(b)

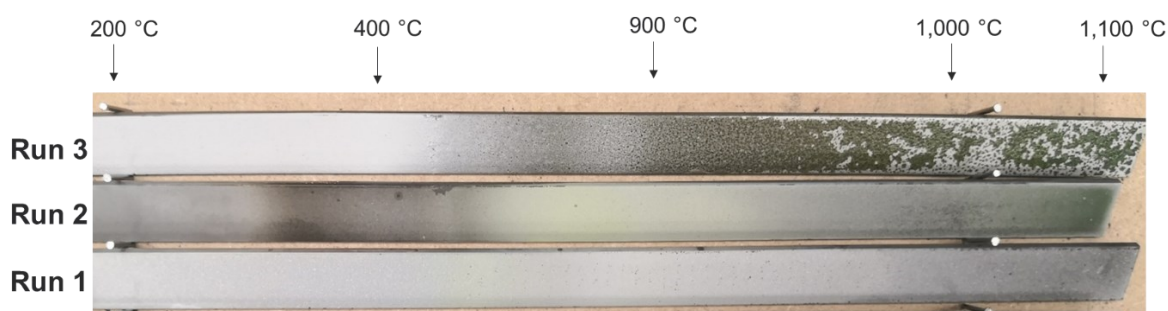


Figure 6.9 (a) Lifetime decay obtained after heat-treatment of Ludox® SM30 based paints applied on stainless-steel bars, Runs 1, 2 and 3. Maximum temperature of monotonic increase of lifetime decay over temperature indicated with vertical lines at 850 $^{\circ}\text{C}$, 900 $^{\circ}\text{C}$ and 950 $^{\circ}\text{C}$. **(b)** Photograph of 400 x 20 x 3 mm stainless-steel bars painted with Ludox® SM30 based paints, after heat exposure from 200 $^{\circ}\text{C}$, cold side (right) to 1,100 $^{\circ}\text{C}$, hot side (left). Potassium silicate indicated as “KSiO” in the legend.

Three samples, which were painted with the paint runs seen before, were heat treated to four different temperatures, 600 °C, 700 °C, 800 °C and 900 °C for the same time (30 minutes), and compared to the results from the test bars, which also lasted 30 minutes at maximum exposure temperature. Pictures of the 20 x 10 x 3 mm stainless-steel bars painted with these Ludox® SM30 based paints are shown in **Figure 6.10** below, after heat exposure to the indicated temperatures. The colour displayed on the samples was similar to the one shown on the bars, indicating consistency between the bar and the samples painting and heat-treatments, as would happen in a turbo-engine test employing thermal history paints.

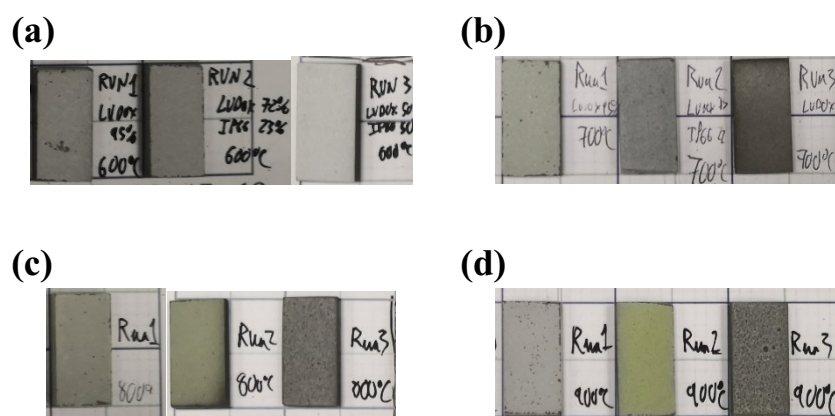


Figure 6.10 Photograph of 20 x 10 x 3 stainless-steel tiles painted with Ludox® SM30 based paints, after heat exposure at 600 °C (a), 700 °C (b), 800 °C (c) and 900 °C (d). Runs 1 to 3 from left to right.

Using the bar tests as calibration curves and the samples as a replacement for a turbomachinery component, the heat treatment temperatures of the samples were calculated by linear interpolation. Both bars and samples consisted of the same substrate material, and were painted in the same session, by the same operator. The heat treatments were carried out in the same furnace equipment, and temperature measurements during the procedure obtained from the same type K thermocouples for both bars and sample heat treatments. Other sources of uncertainty in the temperature determination with thermal history paints were considered, following the publication by Peral *et al.* [210]. These included corrections for the thermocouple readings, from the wires and datalogger, among others, as well as statistical considerations from the lifetime decay measurements, both for the calibration and the “component”.

For better visualization, the values obtained from samples and bar tests were plotted together for each paint run and shown in **Figure 6.11** below. For simplification, only three of the temperatures considered for the samples were included in the uncertainty analysis, 600 °C, 700 °C and 800 °C. The samples heat treated at 900 °C fell outside the monotonic increasing range of lifetime decay with increasing temperature for Runs 1 and 2 and therefore were discarded from the uncertainty analysis. On the other hand, samples and bars painted with Run 3 displayed a continuous increase of lifetime decay at 900 °C and higher temperatures.

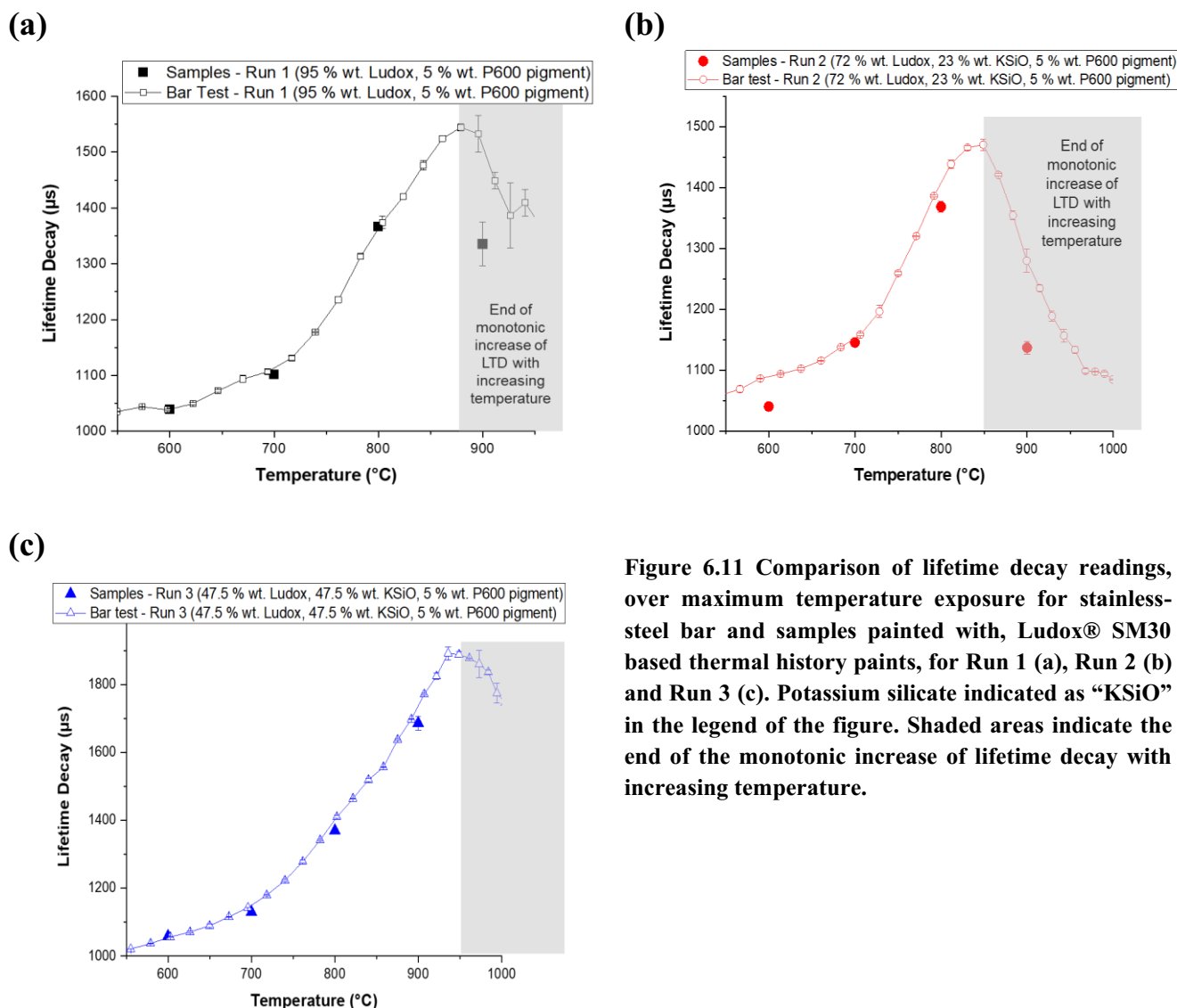


Figure 6.11 Comparison of lifetime decay readings, over maximum temperature exposure for stainless-steel bar and samples painted with, Ludox® SM30 based thermal history paints, for Run 1 (a), Run 2 (b) and Run 3 (c). Potassium silicate indicated as “KSiO” in the legend of the figure. Shaded areas indicate the end of the monotonic increase of lifetime decay with increasing temperature.

While the differences in lifetime decay between samples and bars can be observed in the graphs in **Figure 6.11**, temperature differences between the thermocouple readings during the heat treatment of the samples and those obtained from the LTD from the samples are more relevant in the development of a high-temperature version of thermal history paint. The lifetime decay measurements from the “component” were compared to the calibration curves, or bar test, performing a linear interpolation between known pairs of lifetime decay and temperatures. This returned temperature differences between 1 °C and 15 °C, in absolute terms, for all cases except Run 2 at 600 °C, where the resolution of the paint flattens the calibration curve. In these conditions the effect of the efflorescence can become critical, so components and calibration samples should be measured at the same time after heat treatment and stored in identical conditions. However, more importantly than the temperature differences, shown in **Figure 6.12** below, are the uncertainties of these temperature measurements, both for thermocouple and lifetime decay readings.

Following the uncertainty estimation model developed by Peral *et al.* [210], the uncertainty of the thermocouples was calculated for the readings at 600 °C, 700 °C and 800 °C. This uncertainty ranged between 5 °C and 8 °C, as shown in **Figure 6.12** below. For the three cases, the readings obtained from the thermocouples were considered the obtained value as well. The temperature difference was therefore 0 °C in the three cases. However, the uncertainty of these thermocouple measurements was not 0 °C, as represented with the error bands in the figure below. For the temperatures obtained from the luminescent measurements, the uncertainty ranged between 1 °C and 8 °C, but more importantly, there was an overlap between the temperature readings obtained from both techniques. This indicates that temperature measurements from thermal history paints and thermocouple readings are in the same order of magnitude for a 95 % confidence, with an overlap of the uncertainty bands of all the measurements from both techniques. These three runs of Ludox® based thermal history paints could be considered the foundation of a high temperature version of THP, based on the same pigment, P600.

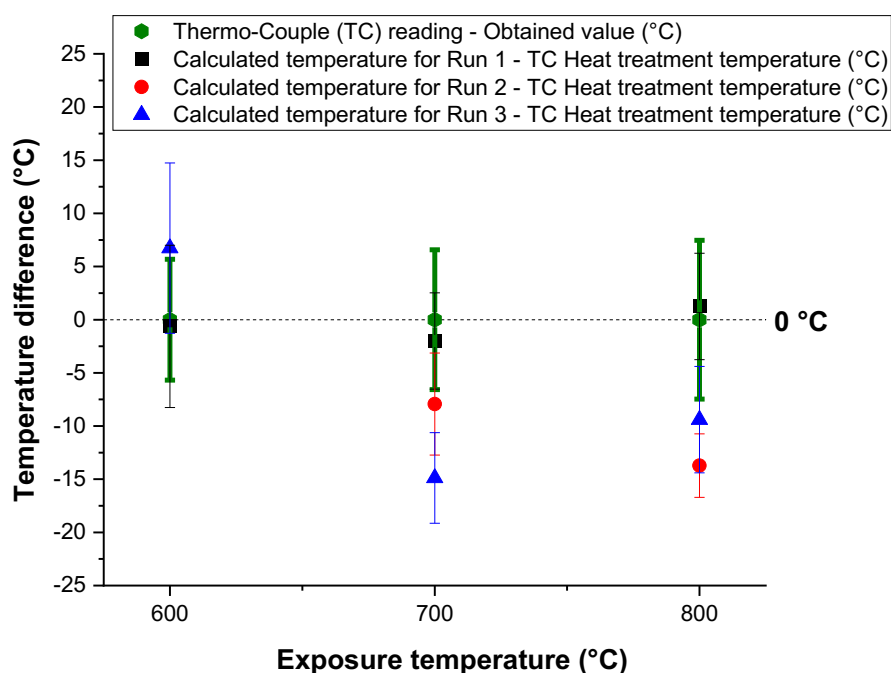


Figure 6.12 Temperature differences with respect thermocouple readings at 600 °C, 700 °C and 800 °C of Ludox® SM30 based thermal history paints, Runs 1, 2 and 3.

As a summary of the previously used THP versions, and the new findings in this thesis, a lifetime decay over temperature graph including the bar tests of the three Ludox® based paints, and the THP references are plotted in **Figure 6.13**. The three temperature upper limits observed for the paints using pigment calcined at 600 °C are indicated as vertical lines at 850 °C, 900 °C and 950 °C. The standard thermal history paint, THP Ref. P400, shows a maximum working temperature at 900 °C before the lifetime decay drops with increasing temperature. This paint also shows an offset of lifetime values with respect to the paints containing P600 pigment, as discussed in *section 5.1*.

The main improvement of using pigment calcined at 600 °C was the extended temperature range observed when mixed in the potassium silicate binder, up to 950 °C once applied on stainless-steel. However, this improvement was not observed when a new binder was used, Ludox ® SM30, or when a higher proportion of this binder was used in combination with potassium silicate. These cases are Runs 1 and 2, respectively. The maximum temperature of monotonic increase of lifetime decay with increasing temperature for Run 1, Ludox® SM30 (95 % wt.) and P600 pigment (5 % wt.), and Run 2, Ludox® SM30 (72 % wt.), potassium silicate (23 % wt.) and P600 pigment (5 % wt.), are 900 °C and 850 °C, respectively.

The most promising version of thermal history paint is therefore Run 3, containing Ludox® SM30 (47.5 % wt.), potassium silicate (47.5 % wt.) and P600 pigment (5 % wt.), since the temperature range extended to 950 °C, as expected for a paint containing P600 pigment. This formulation provides advantages from the two binders included in the mixture: low interaction between the pigment and the binder and less effect of metallic substrates.

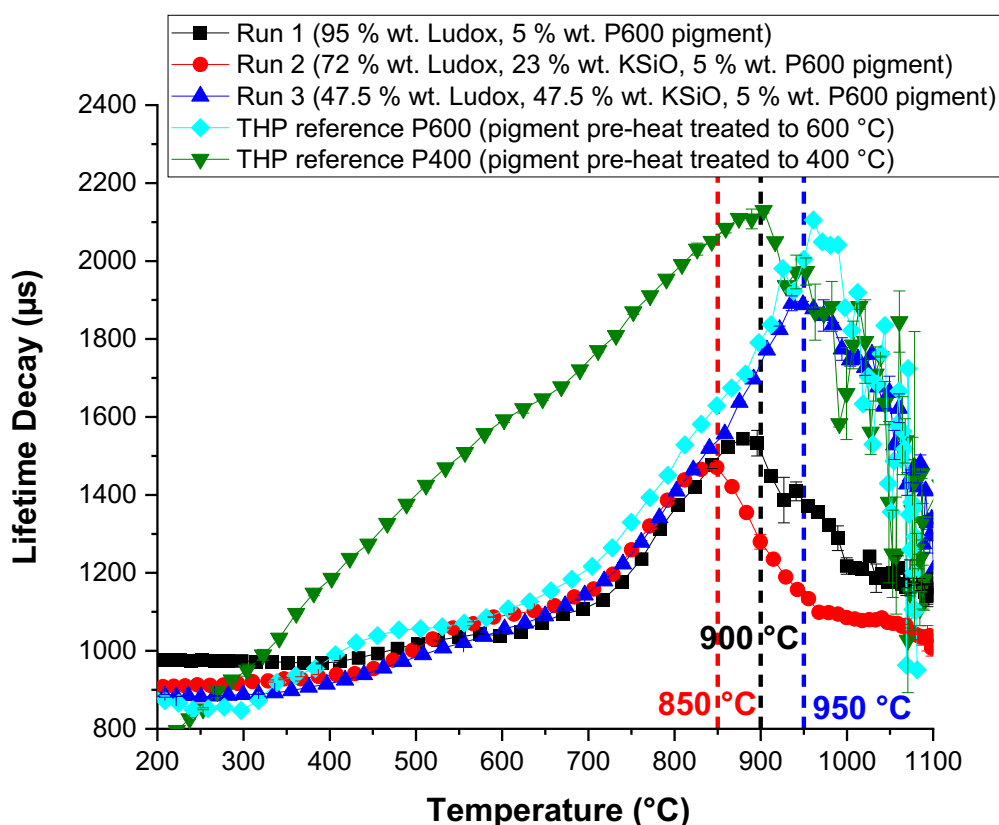


Figure 6.13 Lifetime decay readings on potassium-silicate THP reference paints (P400 and P600), and Ludox® SM30 based paints (Runs 1, 2 and 3) after deposition and heat-treatment up to 1,100 °C on stainless-steel test bars. Maximum temperature of monotonic increase of lifetime decay over temperature indicated with vertical lines at 850 °C, 900 °C and 950 °C.

4610

7 Conclusions and outlook

7.1 Conclusions

4615

This work has improved the understanding of thermal history sensing, and the behaviour at high temperatures of phosphorescent materials, based on the amorphous-to-crystalline mechanism. The focus of the investigation was on developing Thermal History Paints (THP's), an easily applied surface temperature technique, selecting the appropriate pigment and binders to embody a new paint formulation functional at temperatures above 900 °C.

4620

The behaviour of THP based on a potassium silicate binder was studied, revealing the main limitations to high temperature functionality. The obtained results revealed interaction between the pigment and the binder, interaction between the paint layer and the metallic substrate, and the melting of the potassium silicate binder, as some of the disadvantages of the THP material system. As potential solutions, the binder and pigment were modified and/or substituted, and several interlayers were tested between the THP and stainless-steel substrates. While binder modifications and interlayers did not show improved behaviour of the THP, calcinating the pigment to 600 °C and substituting the binder to Ludox® SM30, a colloidal silica solution, showed improved behaviour to temperatures up to 1,100 °C.

4625

4630

The combination of the calcined pigment, the new binder Ludox® SM30, as well as the previous potassium silicate binder were characterised in order to produce a reliable version of thermal history paint. A new THP formulation containing Ludox® SM30 (47.5 % wt.), potassium silicate (47.5 % wt.) and $\text{Y}_2\text{SiO}_5: \text{Eu}^{3+}$ pigment calcined at 600 °C (5 % wt.) showed an extended temperature range to 950 °C, and low interaction between the pigment and the binder. This formulation delivered reliable temperature measurements, in the same range of thermocouple readings, with a maximum uncertainty of ± 8 °C, for 95 % confidence levels. The results shown in this work demonstrate the utility of thermal history paints as validation tools for thermal models in turbomachinery, as well as a being a durable method to monitor engine components at temperatures 50 °C higher than previous versions of thermal history paints.

4635

4640

7.2 Future work

The results offered in this work show the versatility of thermal history paints for surface temperature measurements. The combination of binders has been experimented for the first time, offering an optimal route for the development of THP for high and low temperature regimes. Further characterisation of paints combining Ludox® SM30 and potassium silicate will be required to explain the luminescent behaviour of the pigment in these environments. In particular, thermal analysis of paints having potassium silicate in excess, over 50 % wt. Run 4, indicated in *Chapter 6*, could be a good starting point.

More investigation in the effect of surface roughness and oxidation of metallic substrates [369] on THP will be required as well. The oxidation processes of typical chromia and alumina former alloys [370] should be explored, as well as the potential influence on THP temperature readings. The thickness of the THP layer might also have an influence in the luminescent properties explored in this work, such as the lifetime decay.

Characterisation of THP with advanced techniques, suited for inorganic silicate materials at low temperatures, could give further details on the crystallisation of the paint layer, in particular those features not revealed with standard XRD or FTIR, such as the ones shown in the *Appendix*. For example, Nuclear Magnetic Resonance (NMR) could give a clearer insight in the atomic structure of silicates, and it has been employed before on Yttrium Silicate compounds [250,371] and other silicates [372].

The design of new THPs, for specific applications, with other luminescent pigments and other binders is still a fascinating research topic. For high temperatures applications, elements with high melting points, such as Magnesium and Calcium, should be investigated for the development of new THP versions. For low temperature applications, which could potentially avoid the pre-heat-treatment of the paint at 150 °C after deposition, some of the binders tested in this work are good starting points. For example, Sealmet® and Ludox® are versatile binders which just need a standard air-drying process at room temperature. A first attempt of a low temperature THP was presented in *section 5.3.1.1*, for a Sealmet® based THP, with a low calcination temperature pigment, tested up to 500 °C. Another alternative could be testing more interlayers between the THP layer and the metallic substrate.

Given the easy application of thermal history paints and the substitution of colour changing paints, with alternative off-line techniques, THPs are a popular temperature method among turbomachinery and automotive OEMs around the world. The use of THP, and the results obtained in this work for the development of superficial temperature sensors, are having an impact in the turbomachines being designed today, and the ones that will be used in the coming decades.

8 References

- 4680 1. European Turbine Network (ETN), Bjoerkqvist C. Gas Turbines: Important Conversion Technology for The Future, R&D recommendation report. Chaussée de Charleroi 146-148/20, 1060 Brussels, Belgium: ETN Global; 2021 [Last accessed: 2021 Dec 14] <https://etn.global/about-etn/gas-turbine-technology/about-gas-turbines/>
- 4685 2. Kavandi JL, Lammas A ‘John’, Alley T. Turbomachines for Clean Power and Propulsion Systems, Keynote Theme, ASME Turbo Expo 2019, Phoenix, AZ, USA. 2019 [Last accessed: 2020 Aug 25]. <https://event.asme.org/Turbo-Expo-2019/Program/Keynote>
3. Asadullah M. Barriers of commercial power generation using biomass gasification gas: A review. *Renewable and Sustainable Energy Reviews*. 2014 Jan 1; 29:201–15. <http://www.sciencedirect.com/science/article/pii/S136403211300614X>
- 4690 4. Castillo D, Ferran-Marques M, Semmler IK, Feist JP. Gas turbines in a changing world. 2019 [Last accessed: 2020 Aug 25] <https://www.linkedin.com/pulse/gas-turbines-changing-world-daniel-castillo/>
5. Boeing. Current Market Outlook 2019-2038. 2019 [Last accessed: 2020 Aug 25]. <http://www.boeing.com/commercial/market/current-market-outlook-2017/>
6. Airbus. Global Market Forecast 2019-2038. [Last accessed: 2020 Aug 27]. <http://www.airbus.com/aircraft/market/global-market-forecast.html>
- 4695 7. Boyce MP. Gas Turbine Engineering Handbook. 4th ed. Elsevier Science; 2012. <https://books.google.co.uk/books?id=owLqP3prEmsC>
8. Peters M, Leyens C, Schulz U, Kaysser WA. EB-PVD Thermal Barrier Coatings for Aeroengines and Gas Turbines. *Advanced Engineering Materials*. (2001);3(4):193–204. [https://doi.org/10.1002/1527-2648\(200104\)3:4<193::AID-ADEM193>3.0.CO;2-U](https://doi.org/10.1002/1527-2648(200104)3:4<193::AID-ADEM193>3.0.CO;2-U)
- 4700 9. Schulz U, Leyens C, Fritscher K, Peters M, Saruhan-Brings B, Lavigne O, Dorvaux J-M, Poulain M, Mévrel R, Caliez M. Some recent trends in research and technology of advanced thermal barrier coatings. *Aerospace Science and Technology*. 2003 Jan 1;7(1):73–80. <http://www.sciencedirect.com/science/article/pii/S1270963802000032>
- 4705 10. Markets and Markets. Temperature Sensor Market by Product Type, Global Forecast to 2027. [Last accessed: 2020 Aug 22]. <https://www.marketsandmarkets.com/Market-Reports/temperature-sensor-market-522.html>
11. Propulsion Instrumentation Working Group (PIWG). Propulsion Instrumentation Working Group (PIWG), ‘Sensor Specifications, Surface temperature mapping’. 2020 [Last accessed: 2020 Aug 16]. <http://www.piwg.org/sensor/>
- 4710 12. Updated energy and emissions projections: 2018, Projections of greenhouse gas emissions and energy demand from 2018 to 2035. GOV.UK, Publications, Environment, Climate change and energy, Energy, and climate change: evidence and analysis, Research, and analysis. 2019 May. <https://www.gov.uk/government/publications/updated-energy-and-emissions-projections-2018>
- 4715 13. Capros P, De Vita A, Höglund Isaksson L, Winiwarter W, Purohit P, Bottcher H, Frank S, Havlik P, Gusti M, Witzke H. EU energy, transport and GHG emissions trends to 2050-Reference scenario 2013. European Commission; 2013. <https://op.europa.eu/en/publication-detail/-/publication/ed961fc9-ade8-4f00-9a5f-76e91ba56bfd/language-en>
14. Capros P, De Vita A, Tasios N, Siskos P, Kannavou M, Petropoulos A, Evangelopoulou S, Zampara M, Papadopoulos D, Nakos C. EU Reference Scenario 2016-Energy, transport and GHG emissions

- 4720 Trends to 2050. 2016; https://ec.europa.eu/energy/data-analysis/energy-modelling/eu-reference-scenario-2016_en
15. Feist JP, Araguas-Rodriguez S, Semmler IK, Zaid A, Straka MS, Castillo D. Meeting Future Emission Standards. *Materials World*, IOM3. 2020 May [Last accessed: 2020 Jun 23]; <https://www.iom3.org/materials-world-magazine/feature/2020/apr/30/meeting-future-emission-standards>
- 4725 16. Boyce MP. Advanced industrial gas turbines for power generation (Chapter 2). In: Rao AD, editor. *Combined Cycle Systems for Near-Zero Emission Power Generation*. Woodhead Publishing; 2012. p. 44–102. <http://www.sciencedirect.com/science/article/pii/B978085709013350002X>
17. Mazareanu E, IATA Airline Industry Economic Performance. Statista, Transportation & Logistics, Aviation, Total fuel consumption of commercial airlines worldwide between 2005 and 2021 (in billion gallons). Original data from: <https://www.iata.org/en/iata-repository/pressroom/fact-sheets/fact-sheet---industry-statistics/>. 2020 [Last accessed: 2020 Aug 22]. <https://www.statista.com/statistics/655057/fuel-consumption-of-airlines-worldwide/> <https://www.iata.org/en/iata-repository/pressroom/fact-sheets/fact-sheet---industry-statistics/>
- 4730 18. Sönnichsen N. Statista, Energy & Environmental Services, Electricity, Installed natural gas power generation capacity worldwide from 2018 to 2050 (in gigawatts), Survey from EIA, US Gov, International Energy Outlook 2019. 2019 [Last accessed: 2020 Aug 22]. <https://www.statista.com/statistics/217252/global-installed-power-generation-capacity-of-natural-gas/>
- 4735 19. Index Mundi Commodity Prices. Jet Fuel Daily Price. [Last accessed: 2020 Aug 22]. <https://www.indexmundi.com/commodities/?commodity=jet-fuel&months=120>
- 4740 20. Patel S. GE Unveils New H-Class Gas Turbine—and Already Has a First Order. *PowerMag, News & Technology for the Global Energy Industry*. 2019 [Last accessed: 2020 Aug 22]. <https://www.powermag.com/ge-unveils-new-h-class-gas-turbine-and-already-has-a-first-order/>
21. Bristot A. Aero engine efficiency: how far can we really get? UoN Blogs / INNOVATE – Novel Aerospace Technologies. [Last accessed: 2020 Aug 22]. <https://blogs.nottingham.ac.uk/innovate/2015/01/08/aero-engine-efficiency-how-far-can-we-really-get/>
- 4745 22. Mitsubishi Heavy Industries (MHI). MHI Achieves 1,600°C Turbine Inlet Temperature in Test Operation of World’s Highest Thermal Efficiency ‘J-Series’ Gas Turbine. [Last accessed: 2020 Aug 22]. <https://www.mhi.com/news/story/1105261435.html>
- 4750 23. US Energy Information Administration, Independent Statistics & Analysis (EIA US GOV). What is the efficiency of different types of power plants? [Last accessed: 2020 Aug 22]. <https://www.eia.gov/tools/faqs/faq.php?id=107&t=3>
24. U.S. Energy Information Administration 2011, Annual Energy Review. [Last accessed: 2020 Jun 23]. https://www.eia.gov/totalenergy/data/annual/pdf/sec8_17.pdf
- 4755 25. U.S. Energy Information Administration (2020) Monthly Energy Review, May 2020. [Last accessed: 2020 Jun 23] p. 129. <https://www.eia.gov/totalenergy/data/monthly/pdf/mer.pdf>
26. Vaßen R, Jarligo MO, Steinke T, Mack DE, Stöver D. Overview on advanced thermal barrier coatings. *Surface and Coatings Technology*. 2010;205(4):938–42.
- 4760 27. Padture NP, Gell M, Jordan EH. Thermal Barrier Coatings for Gas-Turbine Engine Applications. *Science*. 2002 Apr 12;296(5566):280. <http://science.sciencemag.org/content/296/5566/280.abstract>

28. Bose S, DeMasi-Marcin J. Thermal barrier coating experience in gas turbine engines at Pratt & Whitney. *Journal of Thermal Spray Technology*. 1997 Mar 1;6(1):99–104.
<https://doi.org/10.1007/BF02646318>
- 4765 29. DeMasi-Marcin JT, Gupta DK. Protective coatings in the gas turbine engine. *Surface and Coatings Technology*. 1994 Dec 1;68–69:1–9.
<http://www.sciencedirect.com/science/article/pii/0257897294901295>
30. Singh K. Advanced Materials for Land Based Gas Turbines. *Transactions of the Indian Institute of Metals*. 2014 Oct 1;67(5):601–15. <https://doi.org/10.1007/s12666-014-0398-3>
- 4770 31. Saini A, Pollock T. High-temperature materials increase efficiency of gas power plants. *MRS Bulletin*. 2012;37(6):550–1. <https://www.cambridge.org/core/article/hightemperature-materials-increase-efficiency-of-gas-power-plants/A4E6A955FC4C6D6B506D5FC4CF6168B0>
- 4775 32. Krewinkel R, Färber J, Orth U, Frank D, Lauer M, Pilgrim C, Gonzalez AY, Feist J, Saggese R, Berthier S, Araguas-Rodriguez S. Validation of Surface Temperature Measurements on a Combustor Liner Under Full-Load Conditions Using a Novel Thermal History Paint. *Journal of Engineering for Gas Turbines and Power*. 2016 Nov 2;139(4):041508–041508–8.
<http://dx.doi.org/10.1115/1.4034724>
33. Giampaolo T. The gas turbine handbook: Principles and practices. Second Edition. The Fairmont Press, Inc.; 2003.
- 4780 34. Seraffon M, Simms NJ, Sumner J, Nicholls JR. The development of new bond coat compositions for thermal barrier coating systems operating under industrial gas turbine conditions. *Surface and Coatings Technology*. 2011 Dec 25;206(7):1529–37.
<http://www.sciencedirect.com/science/article/pii/S0257897211006256>
- 4785 35. Chang J, Güralp O, Filipi Z, Assanis D, Kuo T-W, Najt P, Rask R. New Heat Transfer Correlation for an HCCI Engine Derived from Measurements of Instantaneous Surface Heat Flux. *SAE Transactions*. 2004 [Last accessed: 2020 Aug 27]; 113:1576–93.
<http://www.jstor.org/stable/44723615>
- 4790 36. J. Sumner, A. Encinas-Oropesa, M. Seraffon, N. J. Simms, J. R. Nicholls. Lifetime prediction for gas turbine materials in power generation. In: *International Conference on Sustainable Power Generation and Supply (SUPERGEN 2012)*. 2012. p. 1–6.
37. Rybnikov A, Getsov L, Leontiev S. Failure Analysis of Gas Turbine Blades. *Microscopy and Microanalysis*. 2005/08/01 ed. 2005;11(S02):222–3.
- 4795 38. Karagiannopoulos S, Castillo-Gutierrez D, Peral-Jimenez D, Araguas Rodriguez S, Rode M, Feist JP. Advanced Thermal Profiling of Turbocharger Compressor Wheels Using Phosphorescence Thermal History Coatings. GT2022-80820. ASME Turbo Expo 2022, Rotterdam, The Netherlands (Turbomachinery-General Interest).
39. Pilgrim CC, Castillo D, Araguás-Rodríguez S, Karagiannopoulos S, Feist JP, Redwood A, Zhang Y, Copeland C, Scobie J, Sangan C. Thermal Profiling of Cooled Radial Turbine Wheel. In 2020 [Last accessed: 2021 Apr 12]. <https://doi.org/10.1115/GT2020-14932>
- 4800 40. Baumgarten H, Görgen M, Balazs A, Nijs M, Lehn H, Scharf J, Thewes M, Böhmer M, Alt N, Claßen J. New Lambda = 1 Gasoline Powertrains New technologies, and their interaction with connected and autonomous driving. In Graz, Austria: AVL, Motor & Umwelt; 2018.
<https://www.avl.com/documents/10138/8682805/14+Baumgarten.pdf>
- 4805 41. Ramgade R, Thak U, Pidurkar H, Kathale L. Literature Review on Innovative Technologies for Measurement of Aero-Engine Components. *International Research Journal of Engineering and*

Technology (IRJET). 2018 Apr;05(04):2361–7.
<http://www.academia.edu/download/56822062/IRJET-V5I4524.pdf>

42. Findeisen E, Woerz B, Wieler M, Jeschke P, Rabs M. Evaluation of Numerical Methods to Predict Temperature Distributions of an Experimentally Investigated Convection-Cooled Gas-Turbine Blade. 2017;(50886): V05BT22A012. <http://dx.doi.org/10.1115/GT2017-64205>
43. Literature, Product Guides and Downloads, Lab-facility, Temperature and Process Technology. [Last accessed: 2020 Aug 31]. <https://www.labfacility.com/downloads>
44. Pentronic news 2020-2 • VOL. 12. [Last accessed: 2020 Aug 31]; https://www.pentronic.se/wp-content/uploads/2020/05/pn-eng_-2-20-1.pdf
45. TC Direct, Reference Guide. [Last accessed: 2020 Aug 31]. <https://www.tcdirect.co.uk/>
46. Shannon K, Butler B. 7B.4 A review of error associated with thermocouple temperature measurement in fire environments. In: Proceedings of the 2nd International Wildland Fire Ecology and Fire Management Congress. 2003. p. 16–20.
https://ams.confex.com/ams/FIRE2003/techprogram/paper_67056.htm
47. Knappe C. Phosphor Thermometry on Surfaces - A Study of its Methodology and its Practical Applications [Doctoral thesis]. [Sweden]: Lund University; 2013 [Last accessed: 2020 Aug 31].
[https://portal.research.lu.se/portal/en/publications/phosphor-thermometry-on-surfaces--a-study-of-its-methodology-and-its-practical-applications\(cc23fc4d-9dce-4202-af54-79b5ddf38dcb\).html#Overview](https://portal.research.lu.se/portal/en/publications/phosphor-thermometry-on-surfaces--a-study-of-its-methodology-and-its-practical-applications(cc23fc4d-9dce-4202-af54-79b5ddf38dcb).html#Overview)
48. Tougas IM, Gregory OJ. Thin film platinum–palladium thermocouples for gas turbine engine applications. *Thin Solid Films*. 2013 Jul 31; 539:345–9.
<http://www.sciencedirect.com/science/article/pii/S0040609013008912>
49. Marshall R, Atlas L, Putner T. The preparation and performance of thin film thermocouples. *Journal of Scientific Instruments*. 1966 Mar;43(3):144–9. <http://dx.doi.org/10.1088/0950-7671/43/3/305>
50. Tszeng TC, Saraf V. A Study of Fin Effects in the Measurement of Temperature Using Surface-Mounted Thermocouples. *Journal of Heat Transfer*. 2003 Sep 23;125(5):926–35.
<http://dx.doi.org/10.1115/1.1597622>
51. Scervini M. Progress in the Development of Low Drift Nickel Based Thermocouples for High Temperature Applications. In: GT2015. Volume 6: Ceramics; Controls, Diagnostics, and Instrumentation; Education; Manufacturing Materials and Metallurgy; Honours and Awards; 2015 [Last accessed: 2020 Sep 7]. <https://doi.org/10.1115/GT2015-42652>
52. Scervini M, Rae C. The contributions to drift of positive and negative thermoelements in type K MIMS thermocouples. *AIP Conference Proceedings*. 2013 Sep 10 [Last accessed: 2020 Jul 9];1552(1):570–5. <https://aip.scitation.org/doi/abs/10.1063/1.4819604>
53. Bentley RE. Long-term drift in mineral-insulated Nicrosil-sheathed type K thermocouples. *Sensors and Actuators A: Physical*. 1990 May 1;24(1):21–6.
<http://www.sciencedirect.com/science/article/pii/0924424790800435>
54. Franco GA, Caron E, Wells MA. Quantification of the Surface Temperature Discrepancy Caused by Subsurface Thermocouples and Methods for Compensation. *Metallurgical and Materials Transactions B*. 2007 Dec 1;38(6):949–56. <https://doi.org/10.1007/s11663-007-9100-z>
55. Li DI, Wells MA. Effect of subsurface thermocouple installation on the discrepancy of the measured thermal history and predicted surface heat flux during a quench operation. *Metallurgical and Materials Transactions B*. 2005 Jun 1;36(3):343–54. <https://doi.org/10.1007/s11663-005-0064-6>

- 4850 56. Mevissen F, Meo M. A Review of NDT/Structural Health Monitoring Techniques for Hot Gas Components in Gas Turbines. *Sensors*. 2019;19(3).
57. Scervini, Rae, Page, Rudkin, O'Dell, Loveless, Marchais. The ALPHET project: A new approach to improve the lifing methodology for thermocouple probes used in gas turbines. In: *EVI-GTI Conference on Gas Turbine Instrumentation (GTI 2017)*. 2017. p. 1–10.
- 4855 58. Scervini M, Rae C, Page R, Rudkin M, Loveless D, O'Dell S. Towards an Improved Lifing Methodology for Thermocouple Probes Used in Gas Turbines. In: *GT2018. Volume 6: Ceramics; Controls, Diagnostics, and Instrumentation; Education; Manufacturing Materials and Metallurgy; 2018* [Last accessed: 2020 Sep 7]. <https://doi.org/10.1115/GT2018-76221>
- 4860 59. Palmer, Haggard, Herter, Scervini, Swank, Knudson, Cherry. Summary of thermocouple performance during advanced gas reactor fuel irradiation experiments in the advanced test reactor and out-of-pile thermocouple testing in support of such experiments. In: *2015 4th International Conference on Advancements in Nuclear Instrumentation Measurement Methods and their Applications (ANIMMA)*. 2015. p. 1–9.
- 4865 60. Scervini M, Rae C. Low drift type N thermocouples for nuclear applications. In: *2013 3rd International Conference on Advancements in Nuclear Instrumentation, Measurement Methods, and their Applications (ANIMMA)*. 2013. p. 1–7.
61. Scervini M, Rae C, Lindley B. Transmutation of thermocouples in thermal and fast nuclear reactors. In: *2013 3rd International Conference on Advancements in Nuclear Instrumentation, Measurement Methods, and their Applications (ANIMMA)*. 2013. p. 1–8.
- 4870 62. Douglas J, Smith CA, Taylor SJR. An integrated approach to the application of high bandwidth optical pyrometry to turbine blade surface temperature mapping. In: *ICIASF 99 18th International Congress on Instrumentation in Aerospace Simulation Facilities Record (Cat No99CH37025)*. 1999. p. 4/1-4/6.
63. Magunov AN. Spectral pyrometry (Review). *Instruments and Experimental Techniques*. 2009 Jul 1;52(4):451–72. <https://doi.org/10.1134/S0020441209040010>
- 4875 64. Magunov AN, Pylnev MA, Lapshinov BA. Spectral pyrometry of objects with unknown emissivities in a temperature range of 400–1200 K. *Instruments and Experimental Techniques*. 2014 Jan 1;57(1):86–90. <https://doi.org/10.1134/S0020441214010072>
- 4880 65. Kerr C, Ivey P. An overview of the measurement errors associated with gas turbine aeroengine pyrometer systems. *Measurement Science and Technology*. 2002 May 7;13(6):873–81. <http://dx.doi.org/10.1088/0957-0233/13/6/307>
66. Siegel R, M. Spuckler C. Analysis of thermal radiation effects on temperatures in turbine engine thermal barrier coatings. *Materials Science and Engineering* 1;245(2):150–9. <http://www.sciencedirect.com/science/article/pii/S0921509397008459>
- 4885 67. Gentleman MM, Lugh V, Nychka JA, Clarke DR. Noncontact Methods for Measuring Thermal Barrier Coating Temperatures. *International Journal of Applied Ceramic Technology*. 2006 Mar 1 [Last accessed: 2020 Sep 1];3(2):105–12. <https://doi.org/10.1111/j.1744-7402.2006.02069.x>
- 4890 68. Anselmi-Tamburini U, Campari G, Spinolo G, Lupotto P. A two-colour spatial-scanning pyrometer for the determination of temperature profiles in combustion synthesis reactions. *Review of Scientific Instruments*. 1995 Oct 1 [Last accessed: 2020 Sep 1];66(10):5006–14. <https://doi.org/10.1063/1.1146124>
69. Sami D. Alaruri, Lisa Bianchini, Andrew Brewington. Emissivity measurements for YSZ thermal barrier coating at high temperatures using a 1.6-um single-wavelength pyrometer. *Optical Engineering*. 1998 Feb 1;37(2):683–7. <https://doi.org/10.1117/1.601868>

- 4895 70. Cassady L, Choueiri E. High accuracy multi-colour pyrometry for high temperature surfaces. Princeton University. 2003.
71. Cai T, Kim D, Kim M, Liu YZ, Kim KC. Two-dimensional thermographic phosphor thermometry in a cryogenic environment. *Measurement Science and Technology*. 2016 Nov 24;28(1):015201. <http://dx.doi.org/10.1088/1361-6501/28/1/015201>
- 4900 72. Kim D, Kim M, Kim KC. Effect of frost on phosphorescence for thermographic phosphor thermometry. *Measurement Science and Technology*. 2017 Nov 15;28(12):125202. <http://dx.doi.org/10.1088/1361-6501/aa8894>
73. Cates M, Allison S, Jaiswal S, Beshears D. YAG: Dy and YAG: Tm Fluorescence Above 1400 C. *Proceedings of the International Instrumentation Symposium*. 2003 Jan 1;49.
- 4905 74. Allison SW, Gillies GT. Remote thermometry with thermographic phosphors: Instrumentation and applications. *Review of Scientific Instruments*. 1997;68(7):2615–50.
75. Kontis K. A review of some current research on pressure sensitive paint and thermographic phosphor techniques. *The Aeronautical Journal* (1968). 2007;111(1122):495–508. <https://www.cambridge.org/core/article/review-of-some-current-research-on-pressure-sensitive-paint-and-thermographic-phosphor-techniques/98A36774710AA95AF4FBAC4E8450E929>
- 4910 76. Brübach J, Pflitsch C, Dreizler A, Atakan B. On surface temperature measurements with thermographic phosphors: A review. *Progress in Energy and Combustion Science*. 2013 Feb 1;39(1):37–60. <http://www.sciencedirect.com/science/article/pii/S0360128512000433>
- 4915 77. Aldén M, Omrane A, Richter M, Särner G. Thermographic phosphors for thermometry: A survey of combustion applications. *Progress in Energy and Combustion Science*. 2011 Aug 1;37(4):422–61. <http://www.sciencedirect.com/science/article/pii/S0360128510000560>
78. Choy K-L, Heyes AL, Feist J. Thermal barrier coating with thermoluminescent indicator material embedded therein. Google Patents; US6974641B1, 2005.
- 4920 79. Eldridge JI, Bencic TJ, Allison SW, Beshears DL. Depth-penetrating temperature measurements of thermal barrier coatings incorporating thermographic phosphors. *Journal of Thermal Spray Technology*. 2004 Mar 1;13(1):44–50. <https://doi.org/10.1007/s11666-004-0048-0>
80. Pilgrim CC, Sollazzo PY, Berthier S, Feist JP, Biswas SK, Nicholls JR. Thermal barrier sensor coatings - sensing damage and ageing in critical components. In: *IET & ISA 60th International Instrumentation Symposium 2014*. 2014. p. 1–8. 10.1049/cp.2014.0558
- 4925 81. Pilgrim CC, Berthier S, Feist JP, Wellman RG, Heyes AL. Photoluminescence for quantitative non-destructive evaluation of thermal barrier coating erosion. *Surface and Coatings Technology*. 2012 Sep 25; 209:44–51. <http://www.sciencedirect.com/science/article/pii/S0257897212008006>
82. Abell JS, Harris IR, Cockayne B, Lent B. An investigation of phase stability in the Y2O3-Al2O3 system. *Journal of Materials Science*. 1974;9(4):527–37. <https://doi.org/10.1007/BF02387524>
- 4930 83. Allison SW, Beshears DL, Gadfort T, Bencic T, Eldridge J, Hollerman WA, Boudreaux P. High temperature surface measurements using lifetime imaging of thermographic phosphors: bonding tests. In: *ICIASF 2001 Record, 19th International Congress on Instrumentation in Aerospace Simulation Facilities* (Cat No01CH37215). 2001. p. 171–6.
- 4935 84. Steenbakker RJL, Feist JP, Wellman RG, Nicholls JR. Sensor Thermal Barrier Coatings: Remote in Situ Condition Monitoring of EB-PVD Coatings at Elevated Temperatures. *Journal of Engineering for Gas Turbines and Power*. 2009 Apr 10 [Last accessed: 2020 Jan 30];131(041301). <https://doi.org/10.1115/1.3077662>

85. Cowling JE, King P, Alexander AL. Temperature-Indicating Paints. *Ind Eng. Chem.* 1953 Oct 1;45(10):2317–20. <https://doi.org/10.1021/ie50526a047>
86. Hodgkinson EC, Watson HM. Temperature indicating paint, Patent US20030049467A1. 2004.
- 4940 87. Smith MD. Interpretation of thermal paint, Patent EP0947813A1. 1998.
88. Neely A, Tjong W. Calibration of Thermal Paints for Hypersonic Flight Test. In: 15th AIAA International Space Planes and Hypersonic Systems and Technologies Conference. American Institute of Aeronautics and Astronautics; 2008 [Last accessed: 2020 May 19]. (International Space Planes and Hypersonic Systems and Technologies Conferences). <https://doi.org/10.2514/6.2008-2664>
- 4945 89. Lempereur C, Andral R, Prudhomme JY. Surface temperature measurement on engine components by means of irreversible thermal coatings. *Measurement Science and Technology.* 2008 Aug 27;19(10):105501. <http://dx.doi.org/10.1088/0957-0233/19/10/105501>
- 4950 90. European Commission. Regulation (EC) No 1907/2006 - Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). <https://echa.europa.eu/regulations/reach/legislation>
91. Gov.UK, HSE. How to comply with REACH chemical regulations. [Last accessed: 2020 Sep 7]. https://www.gov.uk/guidance/how-to-comply-with-reach-chemical-regulations?utm_source=613460fe-fbec-4ce9-992c-ca7bdb6abacc&utm_medium=email&utm_campaign=govuk-notifications&utm_content=immediate
- 4955 92. Marsh N. The impact of REACH on the aerospace sector - a DU's perspective & response. 2007 [Last accessed: 2020 Sep 7]. <https://www.hse.gov.uk/reach/events/nigelmarsh.pdf>
93. Tem-plug, Testing Engineers INC. [Last accessed: 2020 Sep 7]. <http://www.testing-engineers.com/templug.html>
- 4960 94. Lo KH, Shek CH, Lai JKL. Metallurgical temperature sensors. *Recent Patents on Mechanical Engineering.* 2008;1(3):225–32. 10.2174/2212797610801030225
95. Fair GE, Kerans RJ, Parthasarathy TA. Thermal history sensor based on glass-ceramics. *Sensors and Actuators A: Physical.* 2008 Feb 15;141(2):245–55. <http://www.sciencedirect.com/science/article/pii/S0924424707006656>
- 4965 96. Annerfeldt M, Shukin S, Björkman M, Karlsson A, Jönsson A, Svistounova E. GTX100 Turbine section measurement using a temperature sensitive crystal technique. A comparison with 3D thermal and aerodynamic analysis, Demag Delaval Industrial, Turbomachinery AB, (Siemens Turbomachinery AB, Finspong, Sweden). PowerGen Europe, Barcelona. 2004 [Last accessed: 2020 Sep 7]; <https://pdfs.semanticscholar.org/2b8b/c55e77a77f497f2acaf831da21f8d772cea9.pdf>
- 4970 97. Bachuchin IV, Zabusov OO, Morozov VA, Nikolaenko VA, Saltykov MA. Temperature measurement with irradiated materials. *Atomic Energy.* 2011 Jul 1;110(3):178–83. <https://doi.org/10.1007/s10512-011-9408-2>
- 4975 98. Volinsky AA, Ginzburgsky L. Irradiated cubic single crystal SiC as a high temperature sensor. *MRS Proceedings.* 2011/02/01 ed. 2003;792: R5.3. <https://www.cambridge.org/core/journals/mrs-online-proceedings-library-archive/article/irradiated-cubic-single-crystal-sic-as-a-high-temperature-sensor/404E356EADBA1CC1A7D5E35824D5E7C4>
99. Sheth A, Thomas A. Uniform Crystal Temperature Sensor (UCTS) Application to Validation, Verification and Technical Comparison Processes. UC DRC. 2015 [Last accessed: 2020 Aug 31]; <https://pdfs.semanticscholar.org/3f11/9b4f082dc565223c281065f15c728199d712.pdf>

- 4980 100. Thomas A. LG Tech-Link Global. LG Tech-Link Inc. [Last accessed: 2020 Aug 24].
<http://www.lgtechlink.com>
101. DeVoe J, Odom S, Ginzburgsky L. Uniform Crystal Temperature Sensor Accuracy Under Transient Conditions. In: GT2012. Volume 4: Heat Transfer, Parts A and B; 2012 [Last accessed: 2020 Aug 31]. p. 79–87. <https://doi.org/10.1115/GT2012-68197>
- 4985 102. DeVoe J, Thomas A, DeVoe R, Ginzburgsky E. Gas Temperature Measurement in Engine Conditions Using Uniform Crystal Temperature Sensors (UCTS). In: GT2018. Volume 5B: Heat Transfer; 2018 [Last accessed: 2020 Aug 31]. <https://doi.org/10.1115/GT2018-76890>
103. Feist JP, Nicholls JR, Heyes AL. Determining thermal history of components, Patent WO/2009/083,729. US8746969B2, US Patent 8,746,969, 2007.
- 4990 104. Rabhiou A. Phosphorescent Thermal History Sensing for Advanced Condition Monitoring in High Temperature Environment [PhD Thesis]. Imperial College London; 2012.
<https://doi.org/10.25560/39125>
105. Sensor Coating Systems Ltd. [Last accessed: 2020 Jun 15]. <http://www.sensorcoatings.com/>
106. Araguas-Rodriguez S. Optimisation of luminescent thermal history sensors [PhD Thesis, Restricted Access]. [Department of Materials]; Imperial College London; 2018.
- 4995 107. Blasse, Grabmaier BC. Luminescent materials. Springer-Verlag; 1994.
<https://books.google.co.uk/books?id=zMDvAAAAMAAJ>
108. Bünzli J-CG, Eliseeva SV. Basics of Lanthanide Photophysics. Lanthanide Luminescence. 2010; 7:1–45. http://infoscience.epfl.ch/record/174014/files/Springer_Series_Basics-10.pdf
- 5000 109. Henderson B, Imbusch GF. Optical spectroscopy of inorganic solids. Vol. 44. Oxford University Press; 1989.
110. Feist JP. Development of phosphor thermometry for gas turbines. Imperial College London; 2001.
111. Bünzli JG. The europium (III) ion as spectroscopic probe in bioinorganic chemistry. *Inorganica Chimica Acta*. 1987;139(1):219–22.
<http://www.sciencedirect.com/science/article/pii/S0020169300840840>
- 5005 112. Dorenbos P. Systematic behaviour in trivalent lanthanide charge transfer energies. *Journal of Physics: Condensed Matter*. 2003 Nov 25;15(49):8417–34. <http://dx.doi.org/10.1088/0953-8984/15/49/018>
- 5010 113. Bessière A, Dorenbos P, Eijk CWE van, Pidol L, Krämer KW, Güdel HU. Spectroscopy and anomalous emission of Ce doped elpasolite Cs₂LiYCl₆. *Journal of Physics: Condensed Matter*. 2004 Mar 1;16(10):1887–97. <http://dx.doi.org/10.1088/0953-8984/16/10/019>
114. Pidol L, Kahn-Harari A, Viana B, Ferrand B, Dorenbos P, Haas JTM de, Eijk CWE van, Virey E. Scintillation properties of Lu₂Si₂O₇:Ce₃, a fast and efficient scintillator crystal. *Journal of Physics: Condensed Matter*. 2003 Mar 17;15(12):2091–102. <http://dx.doi.org/10.1088/0953-8984/15/12/326>
- 5015 115. Pilgrim CC. Luminescence for the non-destructive evaluation of thermal barrier coatings [Eng. Thesis]. Imperial College London; 2014. <https://spiral.imperial.ac.uk/handle/10044/1/42252>
116. Solé J, Bausa L, Jaqué D. An introduction to the optical spectroscopy of inorganic solids. John Wiley & Sons; 2005.
117. Yáñez Gonzalez A. Phosphorescent thermal history sensors for extreme environments [PhD Thesis]. Imperial College London; 2015. <https://doi.org/10.25560/44732>

- 5020 118. Fonger WH, Struck CW. Eu³⁺ 3D Resonance Quenching to the Charge-Transfer States in Y₂O₃S, La₂O₃S, and LaOCl. *J Chem Phys*. 1970 Jun 15 [Last accessed: 2020 Jun 24];52(12):6364–72. <https://doi.org/10.1063/1.1672952>
119. Phosphor Technology Ltd., Spectral Analysis. [Last accessed: 2020 Aug 5]. <https://www.phosphor-technology.com/spectral-analysis/>
- 5025 120. Heber J, Hellwege KH, Köbler U, Murmann H. Energy levels and interaction between Eu³⁺-ions at lattice sites of symmetry C₂ and symmetry C_{3i} in Y₂O₃. *Zeitschrift für Physik a Hadrons and nuclei*. 1970 Jun 1;237(3):189–204. <https://doi.org/10.1007/BF01398633>
121. Hellwege KH, Hüfner S, Schinkmann M, Schmidt H. Optical absorption spectrum and crystal field of erbium aluminium garnet (ErAlG). *Physik der kondensierten Materie*. 1966 Feb 1;4(5):397–403. <https://doi.org/10.1007/BF02422758>
- 5030 122. Binnemans K. Interpretation of europium (III) spectra. *Coordination Chemistry Reviews*. 2015 Jul 1; 295:1–45. <http://www.sciencedirect.com/science/article/pii/S001085451500065X>
123. Dexter DL, Schulman JH. Theory of Concentration Quenching in Inorganic Phosphors. *J Chem Phys*. 1954 Jun 1 [Last accessed: 2020 Jul 6];22(6):1063–70. <https://doi.org/10.1063/1.1740265>
- 5035 124. Brübach J, Feist JP, Dreizler A. Characterization of manganese-activated magnesium fluorogermanate with regards to thermographic phosphor thermometry. *Measurement Science and Technology*. 2008 Jan 14;19(2):025602. <http://dx.doi.org/10.1088/0957-0233/19/2/025602>
125. Kinsman KM, McKittrick J, Sluzky E, Hesse K. Phase Development and Luminescence in Chromium-Doped Yttrium Aluminium Garnet (YAG: Cr) Phosphors. *Journal of the American Ceramic Society*. 1994 Nov 1 [Last accessed: 2020 Jul 4];77(11):2866–72. <https://doi.org/10.1111/j.1151-2916.1994.tb04516.x>
- 5040 126. Bessière A, Jacquart S, Priolkar K, Lecointre A, Viana B, Gourier D. ZnGa₂O₄:Cr³⁺: a new red long-lasting phosphor with high brightness. *Opt Express*. 2011 May 23;19(11):10131–7. <http://www.opticsexpress.org/abstract.cfm?URI=oe-19-11-10131>
- 5045 127. Binnemans K. Lanthanide-Based Luminescent Hybrid Materials. *Chem Rev*. 2009 Sep 9;109(9):4283–374. <https://doi.org/10.1021/cr8003983>
128. Chambers MD, Clarke DR. Doped Oxides for High-Temperature Luminescence and Lifetime Thermometry. *Annu Rev Mater Res*. 2009 Jul 6 [Last accessed: 2019 Dec 18];39(1):325–59. <https://doi.org/10.1146/annurev-matsci-112408-125237>
- 5050 129. Dieke GH, Crosswhite HM, Crosswhite H. Spectra and energy levels of rare earth ions in crystals. 1968.
130. DeShazer LG, Dieke GH. Spectra and Energy Levels of Eu³⁺ in LaCl₃. *J Chem Phys*. 1963 May 1 [Last accessed: 2020 Jun 19];38(9):2190–9. <https://doi.org/10.1063/1.1733949>
- 5055 131. Carnall WT. Chapter 24 The absorption and fluorescence spectra of rare earth ions in solution. In: *Handbook on the Physics and Chemistry of Rare Earths*. Elsevier; 1979. p. 171–208. <http://www.sciencedirect.com/science/article/pii/S0168127379030075>
132. Carnall WT, Fields PR, Rajnak K. Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr³⁺, Nd³⁺, Pm³⁺, Sm³⁺, Dy³⁺, Ho³⁺, Er³⁺, and Tm³⁺. *J Chem Phys*. 1968 Nov 15 [Last accessed: 2020 Jul 5];49(10):4424–42. <https://doi.org/10.1063/1.1669893>
- 5060 133. Carnall WT, Fields PR, Wybourne BG. Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. I. Pr³⁺, Nd³⁺, Er³⁺, Tm³⁺, and Yb³⁺. *J Chem Phys*. 1965 Jun 1 [Last accessed: 2020 Jul 5];42(11):3797–806. <https://doi.org/10.1063/1.1695840>

134. Carnall WT, Goodman GL, Rajnak K, Rana RS. A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3 . *J Chem Phys*. 1989 Apr 1 [Last accessed: 2020 Jul 1];90(7):3443–57. <https://doi.org/10.1063/1.455853>
135. Clarke DR, Gentleman MM. Luminescence sensing of temperatures in thermal barrier coatings. *Surface and Coatings Technology*. 2007 Dec 15;202(4):681–7. <http://www.sciencedirect.com/science/article/pii/S0257897207006135>
136. Lakowicz JR. Principles of fluorescence spectroscopy. Springer science & business media; 1999.
137. Stavola M, Isganitis L, Sceats MG. Cooperative vibronic spectra involving rare earth ions and water molecules in hydrated salts and dilute aqueous solutions. *J Chem Phys*. 1981 Apr 15 [Last accessed: 2021 Aug 26];74(8):4228–41. <https://doi.org/10.1063/1.441664>
138. D. Stenders, I. Karadagli, C. Pflitsch, B. Atakan. Sol-gel deposited thermographic phosphors as possible thermal history coatings. In: IET & ISA 60th International Instrumentation Symposium 2014. 2014. p. 1–6.
139. Quan ZW, Wang LS, Lin J. Synthesis, and characterization of spherical $\text{ZrO}_2\text{:Eu}^{3+}$ phosphors by spray pyrolysis process. *Materials Research Bulletin*. 2005 May 18;40(5):810–20. <http://www.sciencedirect.com/science/article/pii/S0025540805000498>
140. Zhou YH, Lin J, Wang SB, Zhang HJ. Preparation of $\text{Y}_3\text{Al}_5\text{O}_{12}$: Eu phosphors by citric–gel method and their luminescent properties. *Optical Materials*. 2002 Aug 1;20(1):13–20. <http://www.sciencedirect.com/science/article/pii/S0925346702000204>
141. Erdei S, Roy R, Harshe G, Juwhari H, Agrawal D, Ainger F, White W. The effect of powder preparation processes on the luminescent properties of yttrium oxide-based phosphor materials. *Materials research bulletin*. 1995;30(6):745–53.
142. Zhang J, Tang Z, Zhang Z, Fu W, Wang J, Lin Y. Synthesis of nanometre Y_2O_3 : Eu phosphor and its luminescence property. *Materials Science and Engineering* 2002; 334(1):246–9. <http://www.sciencedirect.com/science/article/pii/S0921509301018123>
143. Zhou YH, Lin J. Morphology control and luminescence properties of YVO_4 : Eu phosphors prepared by spray pyrolysis. *Optical Materials*. 2005 May 1;27(8):1426–32. <http://www.sciencedirect.com/science/article/pii/S0925346704003799>
144. Bandi VR, Nien Y-T, Lu T-H, Chen I-G. Effect of Calcination Temperature and Concentration on Luminescence Properties of Novel $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$: Eu Phosphors. *Journal of the American Ceramic Society*. 2009 Dec 1 [Last accessed: 2020 Apr 27];92(12):2953–6. <https://doi.org/10.1111/j.1551-2916.2009.03308.x>
145. Rabhiou A, Kempf A, Heyes A. Oxidation of divalent rare earth phosphors for thermal history sensing. *Sensors and Actuators B: Chemical*. 2013 Feb 1; 177:124–30. <http://www.sciencedirect.com/science/article/pii/S0925400512010362>
146. Cattaruzza E, Back M, Battaglin G, Trave E. Unexpected behaviour of the 1.54 μm luminescence in Er-doped silica films. *Journal of Non-Crystalline Solids*. 2014 Oct 1; 401:186–90. <http://www.sciencedirect.com/science/article/pii/S0022309314000295>
147. Martínez-Hernández A, Guzmán-Mendoza J, Rivera-Montalvo T, Sánchez-Guzmán D, Guzmán-Olgún JC, García-Hipólito M, Falcony C. Synthesis and cathodoluminescence characterization of $\text{ZrO}_2\text{:Er}^{3+}$ films. *Journal of Luminescence*. 2014 Sep 1; 153:140–3. <http://www.sciencedirect.com/science/article/pii/S0022231314001604>

- 5105 148. Deng T, Yan S, Hu J. Effect of Calcination Temperature on Up-Conversion Photoluminescence of the GdAlO_3 : Er^{3+} , Yb^{3+} Phosphor. *ECS Journal of Solid-State Science and Technology*. 2014 Dec 31;4(3): R48–53. <http://dx.doi.org/10.1149/2.0101503jss>
149. Ting C-C, Chien Y-C, Sung W-F. Erbium Doping Effects on the Structural and Infrared Luminescence Properties of $\text{Gd}_2\text{Ti}_2\text{O}_7$ Nanocrystals. *ECS Journal of Solid-State Science and Technology*. 2013;2(6): R105–10. <http://dx.doi.org/10.1149/2.015306jss>
- 5110 150. Copin EB, Massol X, Amiel S, Sentenac T, Le Maout Y, Lours P. Novel erbia-yttria co-doped zirconia fluorescent thermal history sensor. *Smart Materials and Structures*. 2016 Nov 17;26(1):015001. <http://dx.doi.org/10.1088/0964-1726/26/1/015001>
- 5115 151. Amiel S, Copin E, Sentenac T, Lours P, Le Maout Y. On the thermal sensitivity and resolution of a YSZ: Er^{3+} /YSZ: Eu^{3+} fluorescent thermal history sensor. *Sensors and Actuators A: Physical*. 2018; 272:42–52. <http://www.sciencedirect.com/science/article/pii/S0924424717302182>
152. Rabhiou A, Feist J, Kempf A, Skinner S, Heyes A. Phosphorescent thermal history sensors. *Sensors and Actuators A: Physical*. 2011 Sep 10;169(1):18–26. <http://www.sciencedirect.com/science/article/pii/S092442471100269X>
- 5120 153. Rabhiou A, Feist J, Kempf A, Skinner S, Heyes A. Concept for a Phosphorescent Thermal History Sensor. In: GT2010. Volume 3: Controls, Diagnostics, and Instrumentation; Cycle Innovations; Marine; 2010 [Last accessed: 2020 Apr 28]. p. 343–51. <https://doi.org/10.1115/GT2010-23517>
- 5125 154. Kang YC. Luminescence Characteristics of Y_2SiO_5 : Tb Phosphor Particles Directly Prepared by the Spray Pyrolysis Method. *Journal of The Electrochemical Society*. 1999;146(3):1227. <http://dx.doi.org/10.1149/1.1391750>
155. Fan D, Yang S, Wang J, Zheng A, Song X, Yu D. Synthesis, and cathodoluminescent properties of Y_2SiO_5 :Tb $^{3+}$ phosphors prepared from uniform precursor. *Journal of Luminescence*. 2012 May 1;132(5):1122–5. <http://www.sciencedirect.com/science/article/pii/S0022231311006788>
- 5130 156. Satyanarayana T, Brik MG, Venkatramaiah N, Kityk IV, Plucinski KJ, Ravikumar V, Veeraiah N. Influence of Crystallization on the Luminescence Characteristics of Pr^{3+} Ions in $\text{PbO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3$ Glass System. *Journal of the American Ceramic Society*. 2010 Jul 1 [Last accessed: 2020 Apr 27];93(7):2004–11. <https://doi.org/10.1111/j.1551-2916.2010.03696.x>
- 5135 157. LIU C, YU R, XU Z, CAI J, YAN X, LUO X. Crystallization, morphology, and luminescent properties of YAG: Ce^{3+} phosphor powder prepared by polyacrylamide gel method. *Transactions of Nonferrous Metals Society of China*. 2007 Oct 1;17(5):1093–9. <http://www.sciencedirect.com/science/article/pii/S1003632607602313>
158. Pin L, Pilgrim C, Feist J, Le Maout Y, Ansart F, Lours P. Characterisation of thermal barrier sensor coatings synthesised by sol–gel route. *Sensors and Actuators A: Physical*. 2013 Sep 1; 199:289–96. <http://www.sciencedirect.com/science/article/pii/S0924424713001398>
- 5140 159. Pin L. Renforcement et fonctionnalisation de barrières thermiques aéronautiques élaborées par voie sol-gel: comportement en oxydation cyclique et diagnostic thermique. Université de Toulouse; 2012.
160. European Commission. Regulation (EC) No 1907/2006 - Registration, Evaluation, Authorisation and Restriction of CHemicals (REACH).
- 5145 161. Gov.UK. Control of Substances Hazardous to Health (COSHH), Health & Safety Executive. <https://www.hse.gov.uk/coshh/index.htm>
162. Oshio S. Mechanism of Luminance Decrease in $\text{BaMgAl}[\text{sub-10}]\text{O}[\text{sub-17}]:\text{Eu}[\text{sup 2+}]$ Phosphor by Oxidation. *Journal of The Electrochemical Society*. 1998;145(11):3903. <http://dx.doi.org/10.1149/1.1838891>

163. Lacanilao A, Wallez G, Mazerolles L, Dubot P, Binet L, Pavageau B, Servant L, Buissette V, Le Mercier T. Structural analysis of thermal degradation and regeneration in blue phosphor BaMgAl₁₀O₁₇:Eu²⁺ based upon cation diffusion. *Solid State Ionics*. 2013 Dec 15; 253:32–8. <http://www.sciencedirect.com/science/article/pii/S0167273813003809>
164. Dunn B, Farrington GC. Fast divalent ion conduction in Ba⁺⁺, Cd⁺⁺ and Sr⁺⁺ beta" aluminas. *Materials Research Bulletin*. 1980 Dec 1;15(12):1773–7. <http://www.sciencedirect.com/science/article/pii/0025540880901968>
165. Kim K-B, Koo K-W, Cho T-Y, Chun H-G. Effect of heat treatment on photoluminescence behaviour of BaMgAl₁₀O₁₇: Eu phosphors. *Materials Chemistry and Physics*. 2003 Jun 26;80(3):682–9. <http://www.sciencedirect.com/science/article/pii/S025405840300110X>
166. Sohn K-S, Kim SS, Park HD. Luminescence quenching in thermally treated barium magnesium aluminate phosphor. *Appl Phys Lett*. 2002 Aug 26 [Last accessed: 2020 Apr 22];81(10):1759–61. <https://doi.org/10.1063/1.1504866>
167. Bizarri G, Moine B. On BaMgAl₁₀O₁₇:Eu²⁺ phosphor degradation mechanism: thermal treatment effects. *Journal of Luminescence*. 2005 Jun 1;113(3):199–213. <http://www.sciencedirect.com/science/article/pii/S0022231304004430>
168. Wu Z, Cormack AN. Defects in BaMgAl₁₀O₁₇: Eu²⁺ Blue Phosphor. *Journal of Electroceramics*. 2003 Jul 1;10(3):179–91. <https://doi.org/10.1023/B:JECR.0000011216.01346.03>
169. Särner G, Richter M, Aldén M. Investigations of blue emitting phosphors for thermometry. *Measurement Science and Technology*. 2008 Oct 17;19(12):125304. <http://dx.doi.org/10.1088/0957-0233/19/12/125304>
170. Salek G, Demourgues A, Jubera V, Garcia A, Gaudon M. Mn²⁺ doped Zn₃(PO₄)₂ phosphors: Irreversible thermochromic materials useful as thermal sensors. *Optical Materials*. 2015 Sep 1; 47:323–7. <http://www.sciencedirect.com/science/article/pii/S0925346715003456>
171. Bakshi AK, Patwe SJ, Bhide MK, Sanyal B, Natarajan V, Tyagi AK, Kher RK. Thermoluminescence, ESR and x-ray diffraction studies of CaSO₄: Dy phosphor subjected to post preparation high temperature thermal treatment. *Journal of Physics D: Applied Physics*. 2007 Dec 21;41(2):025402. <http://dx.doi.org/10.1088/0022-3727/41/2/025402>
172. Zhang ZY, Grattan KTV, Palmer AW, Meggitt BT. Potential for temperature sensor applications of highly neodymium-doped crystals and fibre at up to approximately 1000 °C. *Review of Scientific Instruments*. [Last accessed: 2020 Apr 30];68(7):2759–63. <https://doi.org/10.1063/1.1148191>
173. Melnikov P, Nascimento VA, Consolo LZZ, Silva AF. Mechanism of thermal decomposition of yttrium nitrate hexahydrate, Y(NO₃)₃·6H₂O and modelling of intermediate oxynitrates. *Journal of Thermal Analysis and Calorimetry*. 2013;111(1):115–9. <https://doi.org/10.1007/s10973-012-2236-3>
174. Arai K, Namikawa H, Kumata K, Honda T, Ishii Y, Handa T. Aluminium or phosphorus co-doping effects on the fluorescence and structural properties of neodymium-doped silica glass. *Journal of Applied Physics*. 1986;59(10):3430–6.
175. Jang HS, Im WB, Lee DC, Jeon DY, Kim SS. Enhancement of red spectral emission intensity of Y₃Al₅O₁₂:Ce³⁺ phosphor via Pr co-doping and Tb substitution for the application to white LEDs. *Journal of Luminescence*. 2007 Oct 1;126(2):371–7. <http://www.sciencedirect.com/science/article/pii/S0022231306006284>
176. Su Y, Li L, Li G. Synthesis and Optimum Luminescence of CaWO₄-Based Red Phosphors with Codoping of Eu³⁺ and Na⁺. *Chem Mater*. 2008 Oct 14;20(19):6060–7. <https://doi.org/10.1021/cm8014435>

177. Gu F, Wang SF, Lü MK, Zhou GJ, Liu SW, Xu D, Yuan DR. Effect of Dy³⁺ doping and calcination on the luminescence of ZrO₂ nanoparticles. *Chemical Physics Letters*. 2003 Oct 13;380(1):185–9.
5195 <http://www.sciencedirect.com/science/article/pii/S0009261403015495>
178. Han X, Lin J, Xing R, Fu J, Wang S, Han Y. Preparation, patterning, and luminescent properties of oxyapatite La_{9.33}(SiO₆)₄O₂: A (A= Eu³⁺, Tb³⁺, Ce³⁺) phosphor films by sol–gel soft lithography. *Journal of Physics: Condensed Matter*. 2003;15(12):2115.
179. Bhatti HS, Sharma R, Verma NK. Laser-induced down-conversion parameters of singly and doubly doped ZnS phosphors. *Pramana*. 2005 Sep 1;65(3):541–6. <https://doi.org/10.1007/BF02704213>
5200
180. Liu R-S, Liu Y-H, Bagkar NC, Hu S-F. Enhanced luminescence of SrSi₂O₂N₂:Eu²⁺ phosphors by codoping with Ce³⁺, Mn²⁺, and Dy³⁺ ions. *Appl Phys Lett*. 2007 Aug 6 [Last accessed: 2020 May 5];91(6):061119. <https://doi.org/10.1063/1.2768916>
181. Heyes AL, Rabhiou A, Feist JP, Kempf A. Thermal history sensing with thermographic phosphors. *AIP Conference Proceedings*. 2013 Sep 10 [Last accessed: 2020 Apr 27];1552(1):891–6.
5205 <https://aip.scitation.org/doi/abs/10.1063/1.4821412>
182. Yu M, Lin J, Fu J, Zhang HJ, Han YC. Sol–gel synthesis and photoluminescent properties of LaPO₄: A (A = Eu³⁺, Ce³⁺, Tb³⁺) nanocrystalline thin films. *J Mater Chem*. 2003;13(6):1413–9.
<http://dx.doi.org/10.1039/B302600K>
183. Coetsee E, Terblans JJ, Ntwaeaborwa OM, Swart HC. Luminescent mechanism of Y₂SiO₅: Ce phosphor powder. *Physica B: Condensed Matter*. 2009 Dec 1;404(22):4426–30.
5210 <http://www.sciencedirect.com/science/article/pii/S092145260901103X>
184. Muresan LE, Oprea BF, Cadis AI, Perhaita I, Ponta O. Studies on Y₂SiO₅: Ce phosphors prepared by gel combustion using new fuels. *Journal of Alloys and Compounds*. 2014 Dec 5; 615:795–803.
5215 <http://www.sciencedirect.com/science/article/pii/S0925838814016156>
185. Saha S, Chowdhury PS, Patra A. Luminescence of Ce³⁺ in Y₂SiO₅ Nanocrystals: Role of Crystal Structure and Crystal Size. *J Phys Chem B*. 2005 Feb 1;109(7):2699–702.
<https://doi.org/10.1021/jp0462106>
186. Pang ML, Lin J, Fu J, Xing RB, Luo CX, Han YC. Preparation, patterning, and luminescent properties of nanocrystalline Gd₂O₃: A (A=Eu³⁺, Dy³⁺, Sm³⁺, Er³⁺) phosphor films via Pechini sol–gel soft lithography. *Optical Materials*. 2003 Sep 1;23(3):547–58.
5220 <http://www.sciencedirect.com/science/article/pii/S092534670300020X>
187. Yu M, Lin J, Wang Z, Fu J, Wang S, Zhang HJ, Han YC. Fabrication, Patterning, and Optical Properties of Nanocrystalline YVO₄: A (A = Eu³⁺, Dy³⁺, Sm³⁺, Er³⁺) Phosphor Films via Sol–Gel Soft Lithography. *Chem Mater*. 2002 May 1;14(5):2224–31. <https://doi.org/10.1021/cm011663y>
5225
188. Ramakrishna G, Nagabhushana H, Prashantha SC, Sharma SC, Nagabhushana BM. Role of flux on morphology and luminescence properties of Sm³⁺ doped Y₂SiO₅ nanopowders for WLEDs. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015 Feb 5; 136:356–65.
<http://www.sciencedirect.com/science/article/pii/S1386142514013997>
189. Liu Y, Xu C-N. Influence of Calcining Temperature on Photoluminescence and Triboluminescence of Europium-Doped Strontium Aluminate Particles Prepared by Sol–Gel Process. *J Phys Chem B*. 2003 May 1;107(17):3991–5. <https://doi.org/10.1021/jp022062c>
5230
190. Guo H, Yin M, Dong N, Xu M, Lou L, Zhang W. Effect of heat-treatment temperature on the luminescent properties of Lu₂O₃: Eu film prepared by Pechini sol–gel method. *Applied surface science*. 2005;243(1–4):245–50.
5235

191. Kang YC, Park S, Lenggoro I, Okuyama K. Gd₂O₃: Eu phosphor particles with sphericity, submicron size and non-aggregation characteristics. *Journal of Physics and Chemistry of Solids*. 1999;60(3):379–84.
- 5240 192. Yu M, Lin J, Wang SB. Sol–gel derived silicate oxyapatite phosphor films doped with rare earth ions. *Journal of Alloys and Compounds*. 2002 Oct 7;344(1):212–6.
<http://www.sciencedirect.com/science/article/pii/S0925838802003432>
193. Guo C, Wang S, Chen T, Luan L, Xu Y. Preparation of phosphors AEu (MoO₄)₂ (A = Li, Na, K and Ag) by sol-gel method. *Applied Physics A*. 2009 Feb 1;94(2):365–71.
<https://doi.org/10.1007/s00339-008-4811-9>
- 5245 194. Panatarani C, Wuled Lenggoro I, Okuyama K. The crystallinity and the photoluminescent properties of spray pyrolyzed ZnO phosphor containing Eu²⁺ and Eu³⁺ ions. *Journal of Physics and Chemistry of Solids*. 2004 Nov 1;65(11):1843–7.
<http://www.sciencedirect.com/science/article/pii/S0022369704001775>
- 5250 195. Yin M, Zhang W, Lou L, Xia S, Krupa J-C. Spectroscopic properties of Eu³⁺ ions in X₁–Y₂SiO₅ at nanometric scale. *Physica B: Condensed Matter*. 1998 Nov 2;254(1):141–7.
<http://www.sciencedirect.com/science/article/pii/S0921452698004281>
196. Yin M, Zhang W, Xia S, Krupa J-C. Luminescence of nanometric scale Y₂SiO₅:Eu³⁺. *Journal of Luminescence*. 1996 Jul 1;68(6):335–9.
<http://www.sciencedirect.com/science/article/pii/0022231396000324>
- 5255 197. Zhang W, Xie P, Duan C, Yan K, Yin M, Lou L, Xia S, Krupa J-C. Preparation, and size effect on concentration quenching of nanocrystalline Y₂SiO₅: Eu. *Chemical Physics Letters*. 1998 Jul 31;292(1):133–6. <http://www.sciencedirect.com/science/article/pii/S0009261498006563>
198. Krsmanovic R, Andric Z, Marinovic-Cincovic M, Zekovic I, Dramicanin MD. Optical and Thermal Investigation of Sol-Gel Derived Eu³⁺: Y₂SiO₅ Nanoparticles.
- 5260 199. Ha MG, Han K-R, Jeong J-S, Bae JS, Jeong ED, Hong K, Bae BS, Bae DS, Yang H-S. Characterization, and optical properties of Y₂SiO₅: Eu³⁺ phosphors prepared by using the reverse micelle and the sol-gel processes. *Journal of the Korean Physical Society*. 2012;61(6):858–61.
200. Huang H, Yan B. In situ sol–gel composition of multicomponent hybrid precursors to luminescent novel unexpected microrod of Y₂SiO₅:Eu³⁺ employing different silicate sources. *Solid State Communications*. 2004 Dec 1;132(11):773–7.
<http://www.sciencedirect.com/science/article/pii/S0038109804008105>
- 5265 201. Duan C-K, Yin M, Yan K, Reid MF. Surface and size effects and energy transfer phenomenon on the luminescence of nanocrystalline X₁–Y₂SiO₅:Eu³⁺. *Journal of Alloys and Compounds*. 2000 May 24;303–304:371–5. <http://www.sciencedirect.com/science/article/pii/S0925838800006435>
- 5270 202. Cannas C, Mainas M, Musinu A, Piccaluga G, Enzo S, Bazzoni M, Speghini A, Bettinelli M. Structural investigations, and luminescence properties of nanocrystalline europium-doped yttrium silicates prepared by a sol–gel technique. *Optical Materials*. 2007 Feb 1;29(6):585–92.
<http://www.sciencedirect.com/science/article/pii/S0925346705004842>
- 5275 203. A. M. Chinie, S. Georgescu, C. Stoicescu, A. S. Stefan, M. Bercu, E. Borca. Synthesis and characterization of Eu³⁺-doped orthosilicates (Y₂SiO₅) nanocrystalline powders. In 2007.
<https://doi.org/10.1117/12.729588>
204. Wang H, Mao Q, Lan B, Zhou S. Visualized thermal history sensor based on the rare-earth-doped zirconia. *Opt Lett*. 2020 May 1;45(9):2608–11. <http://ol.osa.org/abstract.cfm?URI=ol-45-9-2608>

- 5280 205. Yoo HS, Im WB, Kang JH, Jeon DY. Preparation, and photoluminescence properties of $\text{YAl}_3(\text{BO}_3)_4$: Tb^{3+} , Bi^{3+} phosphor under VUV/UV excitation. *Optical Materials*. 2008 Oct 1;31(2):131–5. <http://www.sciencedirect.com/science/article/pii/S0925346708000414>
206. Cornu L, Duttine M, Gaudon M, Jubera V. Luminescence switch of Mn-Doped ZnAl_2O_4 powder with temperature. *J Mater Chem C*. 2014;2(44):9512–22. <http://dx.doi.org/10.1039/C4TC01425A>
- 5285 207. Feist JP, Karmakar Biswas S, Pilgrim CC, Sollazzo PY, Berthier S. Off-Line Temperature Profiling Utilizing Phosphorescent Thermal History Paints and Coatings. *Journal of Turbomachinery*. 2015 May 12;137(10):101003–101003–8. <http://dx.doi.org/10.1115/1.4030259>
208. Araguás-Rodríguez S, Ferran-Marqués M, Pilgrim CC, Kamnis S, Feist JP, Nicholls JR. Thermal History Coatings: Part I — Influence of Atmospheric Plasma Spray Parameters on Performance. In 2020 [Last accessed: 2021 Apr 12]. <https://doi.org/10.1115/GT2020-16004>
- 5290 209. Ferran-Marqués M, Araguás-Rodríguez S, Pilgrim C, Lee K, Larose J, Feist J, Nicholls JR. Thermal History Coatings: Part II — Measurement Capability up to 1500 °C. In 2020 [Last accessed: 2021 Apr 12]. <https://doi.org/10.1115/GT2020-16209>
- 5295 210. Peral D, Castillo D, Araguas-Rodriguez S, Yáñez-Gonzalez A, Pilgrim C, Karagiannopoulos S, Feist JP, Skinner S. Reliable Temperature Measurement with Thermal History Paints: An Uncertainty Estimation Model. In: GT2019. Volume 6: Ceramics; Controls, Diagnostics, and Instrumentation; Education; Manufacturing Materials and Metallurgy; 2019 [Last accessed: 2019 Nov 29]. <https://doi.org/10.1115/GT2019-92087>
- 5300 211. Sun Z, Li M, Li Z, Zhou Y. Hot corrosion of $\gamma\text{-Y}_2\text{Si}_2\text{O}_7$ in strongly basic Na_2CO_3 molten salt environment. *Journal of the European Ceramic Society*. 2008 Jan 1;28(1):259–65. <http://www.sciencedirect.com/science/article/pii/S095522190700386X>
212. Wu Z, Sun L, Wang J. Progresses on the Optimal Processing and Properties of Highly Porous Rare Earth Silicate Thermal Insulators. *J Korean Ceram Soc*. 2018 Nov 27;55(6):527–55. <https://doi.org/10.4191/kcers.2018.55.6.12>
- 5305 213. Eaton Jr HE, Allen WP, Jacobson NS, Lee KN, Opila EJ, Smialek JL, Wang H, Meschter PJ, Luthra KL. Silicon based substrate with yttrium silicate environmental/thermal barrier layer. Google Patents; US6296941B1, 2001.
214. Deng J, Lu B, Hu K, Li H, Wang J, Fan S, Zhang L, Cheng L. Interaction between Y-Al-Si-O glass-ceramics for environmental barrier coating materials and Ca-Mg-Al-Si-O melts. *Ceramics International*. 2020 May 6; <http://www.sciencedirect.com/science/article/pii/S0272884220313225>
- 5310 215. García E, Nistal A, Martín de la Escalera F, Khalifa A, Sainz MA, Osendi MI, Miranzo P. Thermally Sprayed $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ Coatings for High-Temperature Protection of SiC Ceramics. *Journal of Thermal Spray Technology*. 2015 Jan 1;24(1):185–93. <https://doi.org/10.1007/s11666-014-0178-y>
- 5315 216. Jang B-K, Feng F-J, Lee K-S, García E, Nistal A, Nagashima N, Kim S, Oh Y-S, Kim H-T. Thermal behaviour, and mechanical properties of Y_2SiO_5 environmental barrier coatings after isothermal heat treatment. *Surface and Coatings Technology*. 2016 Dec 25; 308:24–30. <http://www.sciencedirect.com/science/article/pii/S0257897216310982>
- 5320 217. Lange A, Braun R, Mechnich P, Büttner CC, Schulz U, Portebois L, Mathieu S, Vilasi M, Drawin S. Y_2SiO_5 environmental barrier coatings for niobium silicide-based materials. *Materials at High Temperatures*. 2015 Jan 1;32(1–2):74–80. <https://doi.org/10.1179/0960340914Z.00000000079>
218. Vaßen R, Bakan E, Gatzert C, Kim S, Mack DE, Guillon O. Environmental Barrier Coatings Made by Different Thermal Spray Technologies. *Coatings*. 2019;9(12):784.

219. Kakisawa H, Nishimura T. A method for testing the interface toughness of ceramic environmental barrier coatings (EBCs) on ceramic matrix composites (CMCs). *Journal of the European Ceramic Society*. 2018 Feb 1;38(2):655–63.
http://www.sciencedirect.com/science/article/pii/S0955221917306465
220. Raghunandan S, Kumar RS, Kamaraj M, Gandhi AS. Role of water in the sol-gel synthesis of yttrium monosilicate. *Ceramics International*. 2019 Mar 1;45(4):4487–92.
http://www.sciencedirect.com/science/article/pii/S0272884218332462
221. Aparicio M, Durán A. Yttrium Silicate Coatings for Oxidation Protection of Carbon–Silicon Carbide Composites. *Journal of the American Ceramic Society*. 2000 Jun 1 [Last accessed: 2020 May 23];83(6):1351–5. <https://doi.org/10.1111/j.1151-2916.2000.tb01392.x>
222. Sun Z, Li M, Zhou Y. Recent progress on synthesis, multi-scale structure, and properties of Y–Si–O oxides. *International Materials Reviews*. 2014 Sep 1;59(7):357–83.
<https://doi.org/10.1179/1743280414Y.0000000033>
223. Levin EM, Robbins CR, McMurdie HF. *Phase Diagrams for Ceramists*, The American Ceramic Society. Inc, Columbus, Ohio. 1964;601.
224. Martin Nikl. Silicate Glass-Based Nanocomposite Scintillators. In: Daniel Nižanský, editor. *Advances in Nanocomposite Technology*. Rijeka: IntechOpen; 2011 [Last accessed: 2020 May 9]. p. Ch. 9. <https://doi.org/10.5772/19981>
225. Fukuda K, Matsubara H. Anisotropic thermal expansion in yttrium silicate. *Journal of Materials Research*. 2003;18(7):1715–22. <https://www.cambridge.org/core/article/anisotropic-thermal-expansion-in-yttrium-silicate/B50D3F9214014EEB2D9DADFB83B71A0A>
226. Shin SH, Jeon DY, Suh KS. Emission Band Shift of the Cathodoluminescence of Y₂SiO₅: Ce Phosphor Affected by Its Activator Concentration. *Japanese Journal of Applied Physics*. 2001 Jul 15;40(Part 1, No. 7):4715–9. <http://dx.doi.org/10.1143/JJAP.40.4715>
227. Felsche J. The crystal chemistry of the rare-earth silicates. In: *Rare earths*. Springer; 1973. p. 99–197.
228. Nowok J, Kay J, Kulas R. Thermal expansion, and high-temperature phase transformation of the yttrium silicate Y₂SiO₅. *Journal of materials research*. 2001;16(8):2251–5.
229. Aitasalo T, Hölsä J, Lastusaari M, Legendziewicz J, Niittykoski J, Pellé F. Delayed luminescence of Ce³⁺ doped Y₂SiO₅. *Optical Materials*. 2004 Jul 1;26(2):107–12.
<http://www.sciencedirect.com/science/article/pii/S0925346703003264>
230. Parganiha Y, Kaur J, Dubey V, Chandrakar D. Synthesis, characterization, thermoluminescence and optical studies of Eu³⁺ doped Y₂SiO₅ phosphor. *Superlattices and Microstructures*. 2015 Jan 1; 77:152–61. <http://www.sciencedirect.com/science/article/pii/S0749603614004273>
231. Lin J, Su Q, Zhang H, Wang S. Crystal structure dependence of the luminescence of rare earth ions (Ce³⁺, Tb³⁺, Sm³⁺) in Y₂SiO₅. *Materials Research Bulletin*. 1996 Feb 1;31(2):189–96.
<http://www.sciencedirect.com/science/article/pii/0025540895001786>
232. Marsh PJ, Silver J, Vecht A, Newport A. Cathodoluminescence studies of yttrium silicate: cerium phosphors synthesised by a sol–gel process. *Journal of Luminescence*. 2002 Jun 1;97(3):229–36.
<http://www.sciencedirect.com/science/article/pii/S0022231302002296>
233. Zhang X, Zhou L, Pang Q, Shi J, Gong M. Tunable Luminescence and Ce³⁺ → Tb³⁺ → Eu³⁺ Energy Transfer of Broadband-ExLast accessed: and Narrow Line Red Emitting Y₂SiO₅:Ce³⁺, Tb³⁺, Eu³⁺ Phosphor. *J Phys Chem C*. 2014 Apr 10;118(14):7591–8. <https://doi.org/10.1021/jp412702g>

234. Gonzalez-Ortega JA, Perea N, Hirata GA. White light emission from Y_2SiO_5 : Ce, Tb films exLast accessed: by electroluminescence. *Optical Materials*. 2006 Oct 1;29(1):47–50. <http://www.sciencedirect.com/science/article/pii/S092534670600108X>
- 5370 235. Pires AM, Davolos MR, Stucchi EB. Eu^{3+} as a spectroscopic probe in phosphors based on spherical fine particle gadolinium compounds. *International Journal of Inorganic Materials*. 2001 Nov 1;3(7):785–90. <http://www.sciencedirect.com/science/article/pii/S1466604901000411>
- 5375 236. Pisarski WA, Pisarska J, Dominiak-Dzik G, Ryba-Romanowski W. Transition metal (Cr^{3+}) and rare earth (Eu^{3+} , Dy^{3+}) ions used as a spectroscopic probe in compositional-dependent lead borate glasses. *Journal of Alloys and Compounds*. 2009 Sep 18;484(1):45–9. <http://www.sciencedirect.com/science/article/pii/S0925838809009670>
237. Horrocks WD, Sudnick DR. Lanthanide ion luminescence probes of the structure of biological macromolecules. *Acc Chem Res*. 1981 Dec 1;14(12):384–92. <https://doi.org/10.1021/ar00072a004>
- 5380 238. Szuszkiewicz W, Keller B, Guzik M, Aitasalo T, Niittykoski J, Hölsä J, Legendziewicz J. Application of lanthanide (Eu, Nd) spectroscopy as a structural probe of diluted double phosphates. *Journal of Alloys and Compounds*. 2002 Jul 17;341(1):297–306. <http://www.sciencedirect.com/science/article/pii/S0925838802000282>
239. Montini T, Speghini A, Rogatis LD, Lorenzut B, Bettinelli M, Graziani M, Fornasiero P. Identification of the Structural Phases of CexZr1-xO2 by Eu (III) Luminescence Studies. *J Am Chem Soc*. 2009 Sep 16;131(36):13155–60. <https://doi.org/10.1021/ja905158p>
- 5385 240. Jia G, Tanner PA, Duan C-K, Dexpert-Ghys J. Eu^{3+} Spectroscopy: A Structural Probe for Yttrium Orthoborate Phosphors. *J Phys Chem C*. 2010 Feb 18;114(6):2769–75. <https://doi.org/10.1021/jp910329k>
- 5390 241. Yanes AC, Del-Castillo J, Méndez-Ramos J, Rodríguez VD, Torres ME, Arbiol J. Luminescence, and structural characterization of transparent nanostructured Eu^{3+} -doped $\text{LaF}_3\text{-SiO}_2$ glass-ceramics prepared by sol-gel method. *Optical Materials*. 2007 Apr 1;29(8):999–1003. <http://www.sciencedirect.com/science/article/pii/S0925346706001376>
- 5395 242. Bueno LA, Gouveia-Neto AS, da Costa EB, Messaddeq Y, Ribeiro SJL. Structural and spectroscopic study of oxyfluoride glasses and glass-ceramics using europium ion as a structural probe. *Journal of Physics: Condensed Matter*. 2008 Mar 4;20(14):145201. <http://dx.doi.org/10.1088/0953-8984/20/14/145201>
243. Pisarski WA, Pisarska J, Dominiak-Dzik G, Mączka M, Ryba-Romanowski W. Compositional-dependent lead borate-based glasses doped with Eu^{3+} ions: Synthesis and spectroscopic properties. *Journal of Physics and Chemistry of Solids*. 2006 Dec 1;67(12):2452–7. <http://www.sciencedirect.com/science/article/pii/S0022369706003593>
- 5400 244. Qin X, Ju Y, Bernhard S, Yao N. Europium-doped yttrium silicate nanophosphors prepared by flame synthesis. *Materials Research Bulletin*. 2007 Aug 7;42(8):1440–9. <http://www.sciencedirect.com/science/article/pii/S002554080600448X>
245. Binnemans K. A comparative spectroscopic study of Eu^{3+} in crystalline host matrices. *Bulletin des societés chimiques belges*. 1996;105(12):793–8.
- 5405 246. Parmentier J, Bodart PR, Audoin L, Massouras G, Thompson DP, Harris RK, Goursat P, Besson J-L. Phase Transformations in Gel-Derived and Mixed-Powder-Derived Yttrium Disilicate, $\text{Y}_2\text{Si}_2\text{O}_7$, by X-Ray Diffraction and ^{29}Si MAS NMR. *Journal of Solid-State Chemistry*. 2000 Jan 1;149(1):16–20. <http://www.sciencedirect.com/science/article/pii/S0022459699984748>

247. Noerlund C, Hazell R, Hewat A. Synthesis, crystal growth and structure investigations of rare-earth disilicates and rare-earth oxyapatites. *Acta Chemica Scandinavica* (1989). 1997; 51:37–43.
5410 http://actachemscand.org/pdf/acta_vol_51_p0037-0043.pdf
248. Kumar S, Drummond CH. Crystallization of various compositions in the Y₂O₃–SiO₂ system. *Journal of Materials Research*. 2011/01/31 ed. 1992;7(4):997–1003.
5415 <https://www.cambridge.org/core/journals/journal-of-materials-research/article/crystallization-of-various-compositions-in-the-y2o3sio2-system/470515CBBED7C3583A92AA9B0DBEF177>
249. Seifert HJ, Wagner S, Fabrichnaya O, Lukas HL, Aldinger F, Ullmann T, Schmücker M, Schneider H. Yttrium Silicate Coatings on Chemical Vapor Deposition-SiC-Precoated C/C–SiC: Thermodynamic Assessment and High-Temperature Investigation. *Journal of the American Ceramic Society*. 2005 Feb 1 [Last accessed: 2020 May 7];88(2):424–30. <https://doi.org/10.1111/j.1551-2916.2005.00077.x>
5420
250. Parmentier J, Liddell K, Thompson DP, Lemerrier H, Schneider N, Hampshire S, Bodart PR, Harris RK. Influence of iron on the synthesis and stability of yttrium silicate apatite. *Solid State Sciences*. 2001 May 1;3(4):495–502.
<http://www.sciencedirect.com/science/article/pii/S1293255801011517>
- 5425 251. Stein A, Keller SW, Mallouk TE. Turning Down the Heat: Design and Mechanism in Solid-State Synthesis. *Science*. 1993 Mar 12;259(5101):1558.
<http://science.sciencemag.org/content/259/5101/1558.abstract>
- 5430 252. Leonyuk NI, Belokoneva EL, Bocelli G, Righi L, Shvanskii EV, Henrykhson RV, Kulman NV, Kozhvakhteeva DE. Crystal Growth and Structural Refinements of the Y₂SiO₅, Y₂Si₂O₇ and LaBSiO₅ Single Crystals. *Crystal Research and Technology*. 1999 Nov 1 [Last accessed: 2020 May 7];34(9):1175–82. [https://doi.org/10.1002/\(SICI\)1521-4079\(199911\)34:9<1175::AID-CRAT1175>3.0.CO;2-2](https://doi.org/10.1002/(SICI)1521-4079(199911)34:9<1175::AID-CRAT1175>3.0.CO;2-2)
- 5435 253. Shoudu Z, Siting W, Xingda S, Haobing W, Heyu Z, Shunxing Z, Jun X. Czochralski growth of rare-earth orthosilicates–Y₂SiO₅ single crystals. *Journal of Crystal Growth*. 1999 Mar 1;197(4):901–4. <http://www.sciencedirect.com/science/article/pii/S0022024898005533>
254. Pang H, Zhao G, Jie M, Xu J, He X. Study on the growth, etch morphology and spectra of Y₂SiO₅ crystal. *Materials Letters*. 2005 Dec 1;59(28):3539–42.
<http://www.sciencedirect.com/science/article/pii/S0167577X05006191>
- 5440 255. Zorenko Yu, Gorbenko V, Zorenko T, Malinowski P, Jary V, Kucerkova R, Beitlerova A, Mares JA, Nikl M, Fedorov A. Luminescent and scintillation properties of Bi³⁺ doped Y₂SiO₅ and Lu₂SiO₅ single crystalline films. *Journal of Luminescence*. 2014 Oct 1; 154:525–30.
<http://www.sciencedirect.com/science/article/pii/S0022231314003226>
- 5445 256. Becerro AI, Naranjo M, Perdígón AC, Trillo JM. Hydrothermal Chemistry of Silicates: Low-Temperature Synthesis of γ-Yttrium Disilicate. *Journal of the American Ceramic Society*. 2003 Sep 1 [Last accessed: 2020 May 25];86(9):1592–4. <https://doi.org/10.1111/j.1151-2916.2003.tb03519.x>
257. Becerro AI, Naranjo M, Alba MD, Trillo JM. Structure-directing effect of phyllosilicates on the synthesis of γ-Y₂Si₂O₇. Phase transitions in Y₂Si₂O₇. *J Mater Chem*. 2003;13(7):1835–42.
<http://dx.doi.org/10.1039/B302276E>
- 5450 258. Trusty PA, Chan KC, Ponton CB. Synthesis of sinteractive single-phase microstructure yttrium disilicate precursor powder using hydrothermal processing. *Journal of Materials Research*. 2011/01/31 ed. 1998;13(11):3135–43. <https://www.cambridge.org/core/article/synthesis-of-sinteractive-singlephase-microstructure-yttrium-disilicate-precursor-powder-using-hydrothermal-processing/8521CFB7B45143ADA2FBE75A1E62A181>

- 5455 259. Whittingham MS. Hydrothermal synthesis of transition metal oxides under mild conditions. *Current Opinion in Solid State and Materials Science*. 1996 Apr 1;1(2):227–32. <http://www.sciencedirect.com/science/article/pii/S1359028696800891>
260. Brinker CJ, Scherer GW. *Sol-gel science: the physics and chemistry of sol-gel processing*. Academic press; 2013.
- 5460 261. Lin C, Wang H, Kong D, Yu M, Liu X, Wang Z, Lin J. Silica Supported Submicron $\text{SiO}_2@Y_2\text{SiO}_5:\text{Eu}^{3+}$ and $\text{SiO}_2@Y_2\text{SiO}_5:\text{Ce}^{3+}/\text{Tb}^{3+}$ Spherical Particles with a Core–Shell Structure: Sol–Gel Synthesis and Characterization. *European Journal of Inorganic Chemistry*. 2006 Sep 1 [Last accessed: 2020 May 25];2006(18):3667–75. <https://doi.org/10.1002/ejic.200600256>
- 5465 262. Webster JD, Westwood ME, Hayes FH, Day RJ, Taylor R, Duran A, Aparicio M, Rebstock K, Vogel WD. Oxidation Protection Coatings for C/SiC based on Yttrium Silicate. *Journal of the European Ceramic Society*. 1998 Dec 1;18(16):2345–50. <http://www.sciencedirect.com/science/article/pii/S0955221998002416>
263. Fitzer E, Huttner W. Structure, and strength of carbon/carbon composites. *Journal of Physics D: Applied Physics*. 1981;14(3):347.
- 5470 264. Lee KN, Fox DS, Bansal NP. Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si_3N_4 ceramics. *Journal of the European Ceramic Society*. 2005 Jan 1;25(10):1705–15. <http://www.sciencedirect.com/science/article/pii/S095522190400531X>
265. García E, Miranzo P, Osendi MI. The Prospect of Y_2SiO_5 -Based Materials as Protective Layer in Environmental Barrier Coatings. *Journal of Thermal Spray Technology*. 2013 Jun 1;22(5):680–9. <https://doi.org/10.1007/s11666-013-9917-8>
- 5475 266. Jian-Feng H, Xie-Rong Z, He-Jun L, Xin-Bo X, Ye-wei F, Min H. SiC/yttrium silicate multi-layer coating for oxidation protection of carbon/carbon composites. *Journal of Materials Science*. 2004 Dec 1;39(24):7383–5. <https://doi.org/10.1023/B:JMSC.0000048756.96547.bf>
- 5480 267. Zhang J-P, Fu Q-G, Zhuang L, Li H-J, Sun C. Preparation and Ablation Properties of Y_2SiO_5 Coating for SiC-Coated C/C Composites by Supersonic Plasma Spraying. *Journal of Thermal Spray Technology*. 2015 Aug 1;24(6):994–1001. <https://doi.org/10.1007/s11666-015-0256-9>
268. Huang J-F, Zhang Y-T, Zeng X-R, Cao L-Y, Deng F, Wu J-P. Hydrothermal electrophoretic deposition of yttrium silicate coating on SiC–C/C composites. *Materials Technology*. 2007 Sep 1;22(2):85–7. <https://doi.org/10.1179/175355507X214140>
- 5485 269. Kaya H. The application of ceramic-matrix composites to the automotive ceramic gas turbine. *Composites Science and Technology*. 1999 May 1;59(6):861–72. <http://www.sciencedirect.com/science/article/pii/S0266353899000160>
270. Ohnabe H, Masaki S, Onozuka M, Miyahara K, Sasa T. Potential application of ceramic matrix composites to aero-engine components. *Composites Part A: Applied Science and Manufacturing*. 1999 Apr 1;30(4):489–96. <http://www.sciencedirect.com/science/article/pii/S1359835X98001390>
- 5490 271. Kondo M, Ogura Y, Morimoto T. Chemical stability between Y_2SiO_5 and SiC in an oxidation protection system for carbon/carbon composites. *Materials Transactions, JIM*. 1998;39(11):1146–51.
- 5495 272. Smeacetto F, Salvo M, Ferraris M, Casalegno V, Canavese G, Moskalewicz T, Ellacott S, Rawlings RD, Boccaccini AR. Erosion protective coatings for low density, highly porous carbon/carbon composites. *Carbon*. 2009 May 1;47(6):1511–9. <http://www.sciencedirect.com/science/article/pii/S0008622309000645>

273. Puntschuh H. Microstructural and luminescence characterisation of lanthanide-doped and atmospheric plasma sprayed YAG coatings [Master Thesis, Access Restricted]. [SCS (London, UK) and Kiel, Germany]: Christian-Albrechts-Universität zu Kiel; 2019.
- 5500 274. Gordon RG, Becker J, Hausmann D, Suh S. Vapor deposition of metal oxides, silicates and phosphates, and silicon dioxide. 2005 Nov 29.
275. Ito A, Endo J, Kimura T, Goto T. Eggshell- and fur-like microstructures of yttrium silicate film prepared by laser chemical vapor deposition. *Materials Chemistry and Physics*. 2011 Jan 1;125(1):242–6. <http://www.sciencedirect.com/science/article/pii/S0254058410007418>
- 5505 276. Argirusis C, Damjanović T, Stojanović M, Borchardt G. Synthesis, and electrophoretic deposition of an yttrium silicate coating system for oxidation protection of C/C-Si-SiC composites. In *Trans Tech Publ*; 2005. p. 451–6.
- 5510 277. Argirusis Chr, Damjanović T, Borchardt G. Yttrium silicate coating system for oxidation protection of C/C–Si–SiC composites: Electrophoretic deposition and oxygen self-diffusion measurements. *Journal of the European Ceramic Society*. 2007 Jan 1;27(2):1303–6. <http://www.sciencedirect.com/science/article/pii/S0955221906003542>
278. Argirusis Chr, Damjanović T, Schneider O. An impedance study of the electrophoretic deposition from yttrium silicate suspensions. *Journal of Materials Science*. 2006 Dec 1;41(24):8059–67. <https://doi.org/10.1007/s10853-006-0417-9>
- 5515 279. Grosse-Brauckmann J, Damjanović T, Argirusis C. Galvanostatic Electrophoretic Deposition of Yttriumsilicate on C/C-Si-SiC Composites. *Key Engineering Materials - KEY ENG MAT*. 2009 Jun 1; 412:243–8.
280. Mechnich P. Y₂SiO₅ coatings fabricated by RF magnetron sputtering. *Surface and Coatings Technology*. 2013 Dec 25; 237:88–94. <http://www.sciencedirect.com/science/article/pii/S0257897213007792>
- 5520 281. Zheng XH, Du YG, Xiao JY, Zhang WJ, Zhang LC. Double layer oxidation resistant coating for carbon fiber reinforced silicon carbide matrix composites. *Applied Surface Science*. 2009 Jan 15;255(7):4250–4. <http://www.sciencedirect.com/science/article/pii/S0169433208023672>
282. Sun XW, Kwok HS. Pulsed laser deposition of silicate phosphor thin films. *Applied Physics A*. 1999 Dec 1;69(1): S39–43. <https://doi.org/10.1007/s003399900260>
- 5525 283. Steenbakker RJL, Wellman RG, Nicholls JR, Feist JP. Sensor TBCs: Remote In-Situ Condition Monitoring of EB-PVD Coatings at Elevated Temperatures. In: *GT2008. Volume 1: Aircraft Engine; Ceramics; Coal, Biomass and Alternative Fuels; Manufacturing, Materials and Metallurgy; Microturbines and Small Turbomachinery*; 2008 [Last accessed: 2020 Aug 6]. p. 269–78. <https://doi.org/10.1115/GT2008-51192>
- 5530 284. Allison S, Beshears D, Bencic T, Hollerman W, Boudreaux P. Development of temperature-sensitive paints for high-temperature aeropropulsion applications. In: *37th Joint Propulsion Conference and Exhibit. American Institute of Aeronautics and Astronautics*; 2001 [Last accessed: 2020 Apr 27]. (Joint Propulsion Conferences). <https://doi.org/10.2514/6.2001-3528>
285. ZypCoatings Inc. [Last accessed: 2020 Jun 12]. <http://www.zypcoatings.com/>
- 5535 286. VHT Paint, a division of Dupli-Color, Inc., a Sherwin-Williams Company. [Last accessed: 2020 Jun 14]. <https://www.vhtpaint.com/>
287. Saureisen. [Last accessed: 2020 Jun 14]. <https://www.sauereisen.com/>

288. Goedeke SM, Hollerman WA, Bergeron NP, Allison SW, Cates MR, Bencic TJ, Mercer CR, Eldridge JI, Bhandarkar S. Study of Resbond® Ceramic Binders Used for High Temperature Non-Contact Thermometry. In: Advances in photonic materials and devices, CERAMIC TRANSACTIONS, Symposium, Advances in photonic materials and devices. American Ceramic Society; 2005. p. 115–25. <https://www.tib.eu/de/suchen/id/BLCP%3ACN057854661>
289. Cotronics Corp. [Last accessed: 2020 Jun 12]. <http://www.cotronics.com>
290. Bergeron N, Hollerman W, Goedeke S, Allison S, Cates M, Bencic T, Mercer C, Eldridge J. Effect of Adding MgO₂ to a Selection of Resbond® Thermally Sensitive Paints. In: Proceedings of the 50th Annual International Instrumentation Symposium, San Antonio, TX. Citeseer; 2004. <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.546.9935&rep=rep1&type=pdf>
291. Beall G. Design and properties of glass-ceramics. Annual Review of Materials Science. 1992;22(1):91–119.
292. Hollerman W, Guidry R, Womack F, Bergeron N, Allison S, Beshears D, Goedeke S, Bencic T, Eldridge J, Mercer C. Use of Phosphor Coatings for High Temperature Aerospace Applications. In: 39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit. American Institute of Aeronautics and Astronautics; 2003 [Last accessed: 2018 May 31]. (Joint Propulsion Conferences). <https://doi.org/10.2514/6.2003-4585>
293. Indestructible Paint Ltd. [Last accessed: 2020 Jun 12]. <http://www.indestructible.co.uk/>
294. PQ Corporation. [Last accessed: 2020 Jun 15]. <https://www.pqcorp.com/>
295. Cannas C, Mainas M, Musinu A, Piccaluga G, Speghini A, Bettinelli M. Nanocrystalline luminescent Eu³⁺-doped Y₂SiO₅ prepared by sol–gel technique. Optical Materials. 2005 Jul 1;27(9):1506–10. <http://www.sciencedirect.com/science/article/pii/S0925346705000364>
296. Yan B, Huang H-H. In-situ sol–gel synthesis of luminescent Y₂SiO₅: Tb³⁺ nanophosphors derived from an assembly of hybrid precursors. Journal of Materials Science. 2004 May [Last accessed: 2020 Apr 19];39(10):3529–31. <http://link.springer.com/10.1023/B:JMSC.0000026969.87323.53>
297. SRi Pro Lite, DeVilBiss, Carlisle, Bournemouth, UK. Technical Literature. <https://www.carlisleleft.eu/en/products/product/devilbiss-sri-pro-lite-gravity-spray-gun1>
298. Avantes. Theoretical background: Spectrometers. [Last accessed: 2020 Apr 13]. <https://www.avantes.com/support/theoretical-background/spectrometers>
299. Khalid HA, Kontis K. Thermographic Phosphors for High Temperature Measurements: Principles, Current State of the Art, and Recent Applications. Sensors. 2008;8(9).
300. Knappe C, Lindén J, Abou Nada F, Richter M, Aldén M. Investigation, and compensation of the nonlinear response in photomultiplier tubes for quantitative single-shot measurements. Review of Scientific Instruments. 2012 Mar 1 [Last accessed: 2020 Apr 8];83(3):034901. <https://doi.org/10.1063/1.3693618>
301. Dowell LJ, Gillies GT. Errors caused by baseline offset and noise in the estimation of exponential lifetimes. Review of Scientific Instruments. 1991 Jan 1 [Last accessed: 2020 Apr 12];62(1):242–3. <https://doi.org/10.1063/1.1142322>
302. Marquardt DW. An algorithm for least-squares estimation of nonlinear parameters. Journal of the society for Industrial and Applied Mathematics. 1963;11(2):431–41.
303. Cullity BD. Elements of X-ray Diffraction. Addison-Wesley Publishing; 1956.

- 5580 304. Skoog D, Holler F, Nieman T. Principles of Instrumental Analysis. Fifth Edition. Saunders College Publishing, New York; 1997.
305. Perkins WD. Fourier transform-infrared spectroscopy: Part I. Instrumentation. J Chem Educ. 1986 Jan 1;63(1): A5. <https://doi.org/10.1021/ed063pA5>
- 5585 306. Fisher T. Introduction to Fourier transform infrared spectrometry, Nicolet. A Thermo Electron Business. 2001;1–8.
307. Martín JMA, Cintas AM, Miranda T, Serratos JM. Introducción a la ciencia de materiales: técnicas de preparación y caracterización. Vol. 20. Editorial CSIC-CSIC Press; 1993.
308. Gonzalez-Benito FJ. Caracterización de Materiales, Open Course Ware (OCW) Universidad Carlos III de Madrid. 2008 [Last accessed: 2020 Apr 16]. <http://ocw.uc3m.es/cursos-archivados/caracterizacion-de-materiales>
- 5590 309. Erdman N, Bell DC. Chapter 7 Scanning Electron and Ion Microscopy of Nanostructures. In: Nanocharacterisation (2). The Royal Society of Chemistry; 2015. p. 300–50. <http://dx.doi.org/10.1039/9781782621867-00300>
310. Jeol A. Guide to Scanning Microscope Observation. Jeol, Japan. 2006;4–35.
- 5595 311. Rahul Mehta ED1 - Viacheslav Kazmiruk. Interactions, Imaging and Spectra in SEM. In: Scanning Electron Microscopy. Rijeka: IntechOpen; 2012 [Last accessed: 2020 Apr 18]. p. Ch. 2. <https://doi.org/10.5772/35586>
312. Quantitative EDS X-ray microanalysis using SEM, My Scope Training, Microscopy Australia. 2020. <https://myscope.training/legacy/analysis/eds/>
- 5600 313. Oatley CW, Nixon WC, Pease RFW. Scanning Electron Microscopy. In: Marton L, editor. Advances in Electronics and Electron Physics. Academic Press; 1966. p. 181–247. <http://www.sciencedirect.com/science/article/pii/S0065253908610100>
314. Kelly M, Singh J, Todd J, Copley S, Wolfe D. Metallographic techniques for evaluation of Thermal Barrier Coatings produced by Electron Beam Physical Vapor Deposition. Materials Characterization. 2008 Jul 1;59(7):863–70. <http://www.sciencedirect.com/science/article/pii/S1044580307002562>
- 5605 315. Lin J, Su Q, Wang S, Zhang H. Influence of crystal structure on the luminescence properties of bismuth (III), europium (III) and dysprosium (III) in Y₂SiO₅. J Mater Chem. 1996;6(2):265–9. <http://dx.doi.org/10.1039/JM9960600265>
- 5610 316. Yin M, Zhang W, Xia S, Krupa J-C. Luminescence of nanometric scale Y₂SiO₅:Eu³⁺. Journal of Luminescence. 1996 Jul 1;68(6):335–9. <http://www.sciencedirect.com/science/article/pii/0022231396000324>
317. Ghosh P, Sadhu S, Patra A. Preparation, and photoluminescence properties of Y₂SiO₅:Eu³⁺ nanocrystals. Physical Chemistry Chemical Physics. 2006;8(28):3342–8.
- 5615 318. Wang J, Tian S, Li G, Liao F, Jing X. Preparation and X-ray characterization of low-temperature phases of R₂SiO₅ (R = rare earth elements). Materials Research Bulletin. 2001 Jul 15;36(10):1855–61. <http://www.sciencedirect.com/science/article/pii/S002554080100664X>
319. Li Guan, Litao Jin, Guoqi Jia, Xu Li, Zhiping Yang, Qinglin Guo, Guangsheng Fu. Synthesis of Eu³⁺ doped yttrium orthosilicate phosphor by sol-combustion method. In 2010. <https://doi.org/10.1117/12.871775>

- 5620 320. Xu L, Hu Y, Mu Y, Zhang F, Wang J, Chen W, Li Y, Zu C. Kinetics of foaming process of potassium silicate gel at high temperature. *Materials Letters*. 2020 Dec 15; 281:128614. <http://www.sciencedirect.com/science/article/pii/S0167577X20313215>
321. Maniar PD, Navrotsky A, Rabinovich EM, Ying JY, Benziger JB. Energetics, and structure of sol-gel silicas. *Journal of Non-Crystalline Solids*. 1990 Sep 1;124(1):101–11. <http://www.sciencedirect.com/science/article/pii/0022309390910867>
- 5625 322. Sassi M, Gramlich V, Miéhe-Brendlé J, Josien L, Paillaud J-L, Benggedach A, Patarin J. Synthesis, and characterization of a new one-dimensional sodium silicate named Mu-29. *Microporous and Mesoporous Materials*. 2003 Oct 3;64(1):51–61. <http://www.sciencedirect.com/science/article/pii/S1387181103004050>
- 5630 323. Wu P, Eriksson G, Pelton AD. Optimization of the Thermodynamic Properties and Phase Diagrams of the Na₂O–SiO₂ and K₂O–SiO₂ Systems. *Journal of the American Ceramic Society*. 1993 Aug 1 [Last accessed: 2020 Jan 12];76(8):2059–64. <https://doi.org/10.1111/j.1151-2916.1993.tb08333.x>
324. Prud'homme E, Michaud P, Joussein E, Peyratout C, Smith A, Rossignol S. In situ inorganic foams prepared from various clays at low temperature. *Applied Clay Science*. 2011 Jan 1;51(1):15–22. <http://www.sciencedirect.com/science/article/pii/S0169131710003443>
- 5635 325. Araguás Rodríguez S, Jelinek T, Michálek J, Yáñez González Á, Schulte F, Pilgrim C, Feist J, Skinner SJ. Accelerated thermal profiling of gas turbine components using luminescent thermal history paints. *J Glob Power Propuls Soc*. 2018 Apr 25; 2:344–61. <https://journal.gpps.global/a/S3KTGK/>
- 5640 326. Shionoya S, Yen WM, Yamamoto H. *Phosphor Handbook*. CRC Press, Taylor & Francis Group; 2006.
327. Brocken H, Nijland TG. White efflorescence on brick masonry and concrete masonry blocks, with special emphasis on sulphate efflorescence on concrete blocks. *Construction and Building Materials*. 2004 Jun 1;18(5):315–23. <https://www.sciencedirect.com/science/article/pii/S0950061804000285>
- 5645 328. Zehnder K, Arnold A. Crystal growth in salt efflorescence. *Journal of Crystal Growth*. 1989 Sep 2;97(2):513–21. <https://www.sciencedirect.com/science/article/pii/0022024889902340>
329. Veinot DE, Langille KB, Nguyen DT, Bernt JO. Efflorescence of soluble silicate coatings. *Journal of Non-Crystalline Solids*. 1991 Feb 1;127(2):221–6. <http://www.sciencedirect.com/science/article/pii/002230939190146W>
- 5650 330. Cotton FA, Wilkinson G, Murillo CA, Bochmann M, Grimes R. *Advanced inorganic chemistry*. Vol. 6. Wiley New York; 1988.
331. Dramićanin MD. Sensing temperature via downshifting emissions of lanthanide-doped metal oxides and salts. A review. *Methods and Applications in Fluorescence*. 2016 Oct 11;4(4):042001. <http://dx.doi.org/10.1088/2050-6120/4/4/042001>
- 5655 332. BIPM (2008). *International vocabulary of metrology: Basic and general concepts and associated terms (VIM)*. Joint Committee for Guides in Metrology. Technical report; 2008.
333. Kracek F, Brown N, Morey G. Equilibrium relations and factors influencing their determination in the system K₂SiO₃–SiO₂. *Journal of Physical Chemistry*. 1937;41(9):1183–93.
- 5660 334. Weldes HH, Lange KRobert. Properties of Soluble Silicates. *Ind Eng. Chem*. 1969 Apr 1;61(4):29–44. <https://doi.org/10.1021/ie50712a008>
335. Unifrax, High Temperature-Performance Products. [Last accessed: 2018 May 31]. <https://www.unifrax.com/>

336. Grace, High-Performance Specialty Chemicals and Materials. [Last accessed: 2018 May 31].
<https://grace.com/en-us/Pages/Ludox-Colloidal-Silica.aspx>
- 5665 337. Budenheim KG, Chemische Fabrik. [Last accessed: 2018 May 31].
<https://www.budenheim.com/en/>
338. Merck, Performance Materials. [Last accessed: 2018 May 31]. <http://www.merck-performance-materials.de/de/durazane/durazane.html>
- 5670 339. Goedeke S, Hollerman W, Bergeron N, Allison S, R. Cates M, Bencic T, Mercer C, Eldridge J. Study of Resbond® Ceramic Binders Used for High Temperature Non-Contact Thermometry. Vol. 163. 2005.
340. Unifrax Fixwool Coatings, Document datasheets U-681 EN. [Last accessed: 2021 Dec 4].
<https://www.unifrax.com/wp-content/uploads/2018/08/Fixwool-Coatings-EN.pdf>
- 5675 341. Blasse G, Bril A. Energy transfer from trivalent rare earth ions to Cr³⁺. *Physics Letters A*. 1967 Jul 17;25(1):29–30. <http://www.sciencedirect.com/science/article/pii/0375960167903210>
342. Blasse G, Bril A. Some Observations on the Cr³⁺ Fluorescence in the Huntite Structure. *physica status solidi (b)*. 1967 Jan 1 [Last accessed: 2020 Jan 3];20(2):551–6.
<https://doi.org/10.1002/pssb.19670200215>
- 5680 343. Weber MJ, Sharp EJ, Miller JE. Optical spectra, relaxation, and energy transfer of Eu³⁺ and Cr³⁺ in a europium phosphate glass. *Journal of Physics and Chemistry of Solids*. 1971 Jan 1;32(10):2275–84. <http://www.sciencedirect.com/science/article/pii/S0022369771802226>
344. Kracek FC. The Binary System Li₂O–SiO₂. *J Phys Chem*. 1930 Dec 1;34(12):2641–50.
<https://doi.org/10.1021/j150318a001>
345. BASF / Chemetall. [Last accessed: 2021 Feb 27]. <https://www.chemetall.com/>
- 5685 346. Kracek FC. The System Sodium Oxide-Silica. *J Phys Chem*. 1930 Jul 1;34(7):1583–98.
<https://doi.org/10.1021/j150313a018>
347. Pechini MP. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor. Google Patents; US3330697A, 1967.
- 5690 348. Dimesso L. Pechini processes: an alternate approach of the sol–gel method, preparation, properties, and applications. *Handbook of Sol-Gel Science and Technology*. 2016; 2:1–22.
349. Wang YH, Wang ZS, Jiang Y, Wang X, Cheng JG. Characterization and Formation of Yttrium Disilicate Nanocrystalline Powders by EDTA–Citric Acid Complexing Process. *International Journal of Applied Ceramic Technology*. 2016 Jul 1 [Last accessed: 2021 May 18];13(4):736–42.
<https://doi.org/10.1111/ijac.12551>
- 5695 350. Shao J, Tao Y, Wang J, Xu C, Wang WG. Investigation of precursors in the preparation of nanostructured La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3–δ} via a modified combined complexing method. *Journal of Alloys and Compounds*. 2009 Sep 18;484(1):263–7.
<https://www.sciencedirect.com/science/article/pii/S0925838809007968>
- 5700 351. Zhang C, Zhang Y, Wang J, Wang D, He D, Xia Y. Li₄Ti₅O₁₂ prepared by a modified citric acid sol–gel method for lithium-ion battery. *Journal of Power Sources*. 2013 Aug 15; 236:118–25.
<https://www.sciencedirect.com/science/article/pii/S0378775313001924>
352. Li F, Weng L-Q, Xu G-Y, Song S-H, Yu J. Synthesis, and characterization of microwave dielectric BaTi₄O₉ ceramics via EDTA–citrate gel process. *Materials Letters*. 2005 Oct 1;59(23):2973–6.
<https://www.sciencedirect.com/science/article/pii/S0167577X05004519>

- 5705 353. Kakihana M, Arima M, Nakamura Y, Yashima M, Yoshimura M. Spectroscopic Characterization of Precursors Used in the Pechini-Type Polymerizable Complex Processing of Barium Titanate. *Chem Mater*. 1999 Feb 1;11(2):438–50. <https://doi.org/10.1021/cm9806681>
354. Cannas C, Musinu A, Peddis D, Piccaluga G. New Synthesis of Ferrite–Silica Nanocomposites by a Sol–Gel Auto-Combustion. *Journal of Nanoparticle Research*. 2004 Jun 1;6(2):223–32. <https://doi.org/10.1023/B:NANO.0000034679.22546.d7>
- 5710 355. Cannas C, Musinu A, Peddis D, Piccaluga G. Synthesis and Characterization of CoFe_2O_4 Nanoparticles Dispersed in a Silica Matrix by a Sol–Gel Autocombustion Method. *Chem Mater*. 2006 Aug 1;18(16):3835–42. <https://doi.org/10.1021/cm060650n>
356. Anedda R, Cannas C, Musinu A, Pinna G, Piccaluga G, Casu M. A two-stage citric acid–sol/gel synthesis of ZnO/SiO_2 nanocomposites: study of precursors and final products. *Journal of Nanoparticle Research*. 2008 Jan 1;10(1):107–20. <https://doi.org/10.1007/s11051-007-9235-5>
- 5715 357. Gülgün MA, Popoola OO, Kriven WM. Chemical Synthesis and Characterization of Calcium Aluminate Powders. *Journal of the American Ceramic Society*. 1994 Feb 1 [Last accessed: 2021 May 27];77(2):531–9. <https://doi.org/10.1111/j.1151-2916.1994.tb07026.x>
- 5720 358. Liu Y, Zhang Z-F, Halloran J, Laine RM. Yttrium Aluminum Garnet Fibres from Metalloorganic Precursors. *Journal of the American Ceramic Society*. 1998 Mar 1 [Last accessed: 2021 May 27];81(3):629–45. <https://doi.org/10.1111/j.1151-2916.1998.tb02383.x>
359. Cinibulk MK. Synthesis of Yttrium Aluminum Garnet from a Mixed-Metal Citrate Precursor. *Journal of the American Ceramic Society*. 2000 May 1 [Last accessed: 2021 May 18];83(5):1276–8. <https://doi.org/10.1111/j.1151-2916.2000.tb01367.x>
- 5725 360. Cinibulk MK. Effect of Precursors and Dopants on the Synthesis and Grain Growth of Calcium Hexaluminate. *Journal of the American Ceramic Society*. 1998 Dec 1 [Last accessed: 2021 May 27];81(12):3157–68. <https://doi.org/10.1111/j.1151-2916.1998.tb02751.x>
361. White LR. Capillary rise in powders. *Journal of Colloid and Interface Science*. 1982 Dec 1;90(2):536–8. <http://www.sciencedirect.com/science/article/pii/0021979782903198>
- 5730 362. Murray M. Cracking in coatings from colloidal dispersions: An industrial perspective. *Proceedings Rideal Lecture*, London. 2009.
363. Routh AF. Drying of thin colloidal films. *Reports on Progress in Physics*. 2013 Mar 18;76(4):046603. <http://dx.doi.org/10.1088/0034-4885/76/4/046603>
- 5735 364. Arahori T, Suzuki T. Transformation of tridymite to cristobalite below 1470° C in silica refractories. *Journal of Materials Science*. 1987 Jun 1;22(6):2248–52. <https://doi.org/10.1007/BF01132967>
365. Chaklader A. X-Ray Study of Quartz-Cristobalite Transformation. *Journal of the American Ceramic Society*. 1963 Feb 1 [Last accessed: 2021 Jun 20];46(2):66–71. <https://doi.org/10.1111/j.1151-2916.1963.tb11677.x>
- 5740 366. Chaklader A., Roberts A. Transformation of Quartz to Cristobalite. *Journal of the American Ceramic Society*. 1961 Jan 1 [Last accessed: 2021 Jun 20];44(1):35–41. <https://doi.org/10.1111/j.1151-2916.1961.tb15344.x>
- 5745 367. Langille KB, Nguyen D, Bernt JO, Veinot DE, Murthy MK. Mechanism of dehydration and intumescence of soluble silicates. *Journal of Materials Science*. 1991 Feb 1;26(3):704–10. <https://doi.org/10.1007/BF00588307>

-
368. Oomen EWJL, van Dongen AMA. Europium (III) in oxide glasses: Dependence of the emission spectrum upon glass composition. *Journal of Non-Crystalline Solids*. 1989 Nov 1;111(2):205–13. <http://www.sciencedirect.com/science/article/pii/0022309389902822>
- 5750 369. Nowak JW, Ochał K, Wierzba P, Gancarczyk K, Wierzba B. Effect of Substrate Roughness on Oxidation Resistance of an Aluminized Ni-Base Superalloy. *Metals*. 2019;9(7).
370. Jönsson B, Westerlund A. Oxidation Comparison of Alumina-Forming and Chromia-Forming Commercial Alloys at 1100 and 1200 °C. *Oxidation of Metals*. 2017 Oct 1;88(3):315–26. <https://doi.org/10.1007/s11085-016-9710-4>
- 5755 371. Parmentier J, Bodart PR, Audoin L, Massouras G, Thompson DP, Harris RK, Goursat P, Besson J-L. Phase Transformations in Gel-Derived and Mixed-Powder-Derived Yttrium Disilicate, $Y_2Si_2O_7$, by X-Ray Diffraction and ^{29}Si MAS NMR. *Journal of Solid-State Chemistry*. 2000 Jan 1;149(1):16–20. <http://www.sciencedirect.com/science/article/pii/S0022459699984748>
- 5760 372. Stebbins JF, Bista S. Pentacoordinated and hexacoordinated silicon cations in a potassium silicate glass: Effects of pressure and temperature. *Journal of Non-Crystalline Solids*. 2019 Feb 1; 505:234–40. <http://www.sciencedirect.com/science/article/pii/S0022309318306562>

9 Appendix

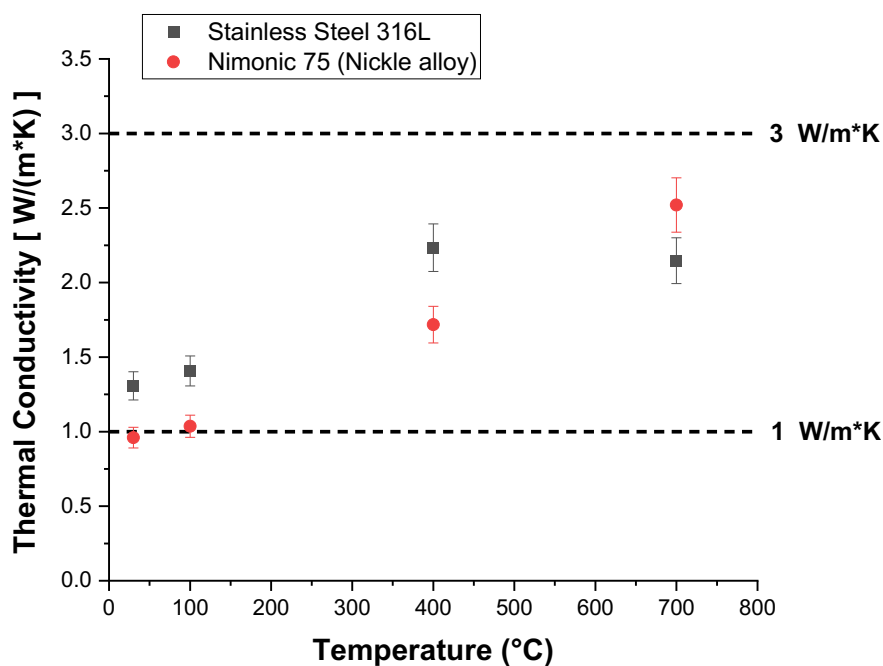
5765

9.1 Supplementary results

9.1.1 Thermal conductivity of thermal history paint

5770

Stainless-steel 316L and Nimonic 75 tiles, of dimensions 20 x 10 x 3 mm, were painted with conventional P400-THP and sent to the University of Sheffield, through the Henry Royce Institute to obtain the thermal conductivity of the paint layer. Measurements were taken via Laser Flash Analysis (LFA) within the temperature range of the paint, between 30 °C and 700 °C. Results are shown in **Figure 9.1** below, where the thermal conductivity shows an increasing trend with increasing temperature, for a film thickness of 30 μm . All the values obtained fell between 1 and 3 W / m $^{\circ}\text{K}$.



5775

Figure 9.1 Thermal Conductivity over increasing temperature on THP deposited on stainless-steel 316L and nimonic 75, nickel alloy.

5780 9.1.2 FTIR spectra of $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigment modified with citric acid addition from 700 °C to 1,300 °C.

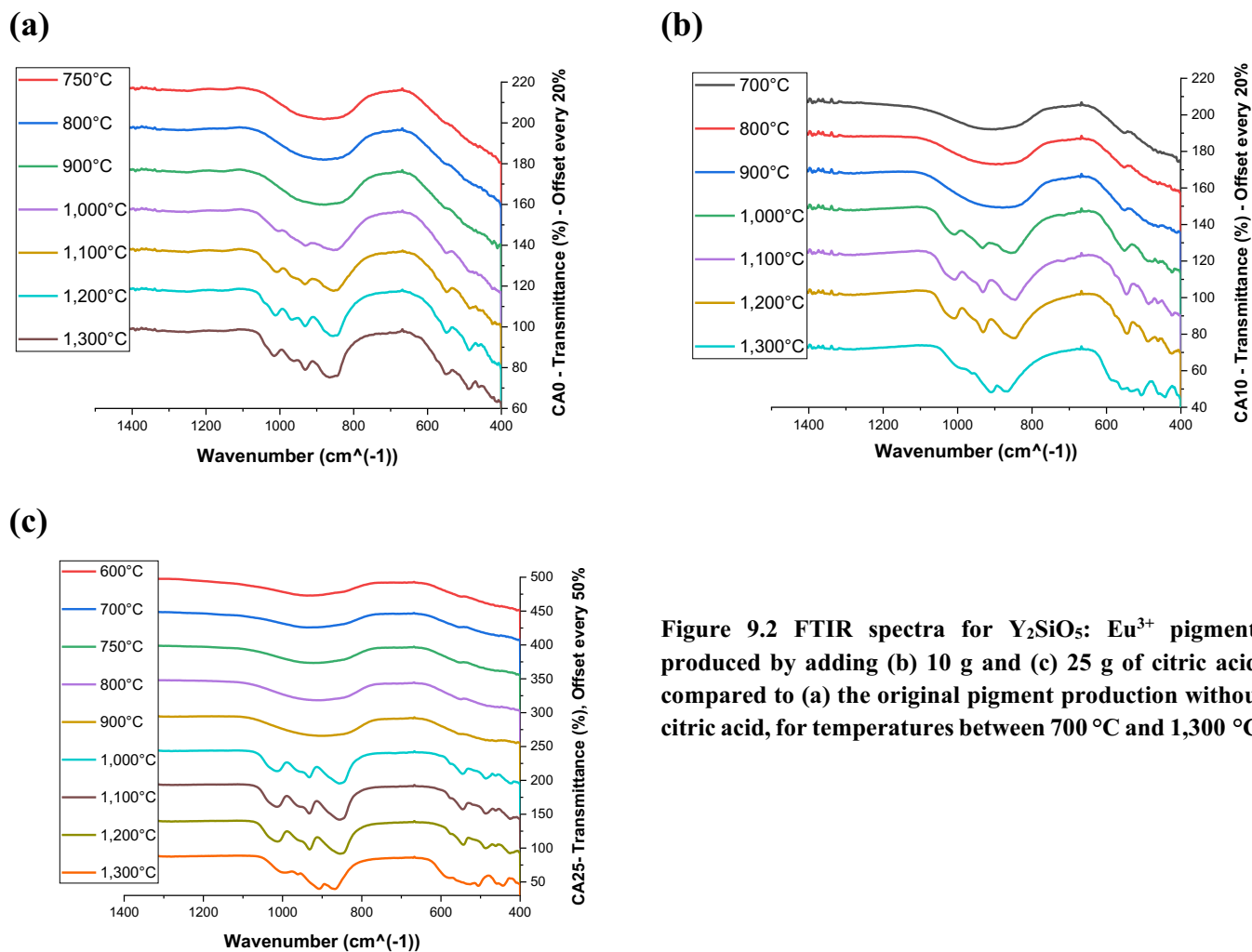


Figure 9.2 FTIR spectra for $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$ pigments produced by adding (b) 10 g and (c) 25 g of citric acid, compared to (a) the original pigment production without citric acid, for temperatures between 700 °C and 1,300 °C.

5785

5790

5795

9.1.3 XRD of $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$ pigment modified with citric acid addition and heated to 900 °C.

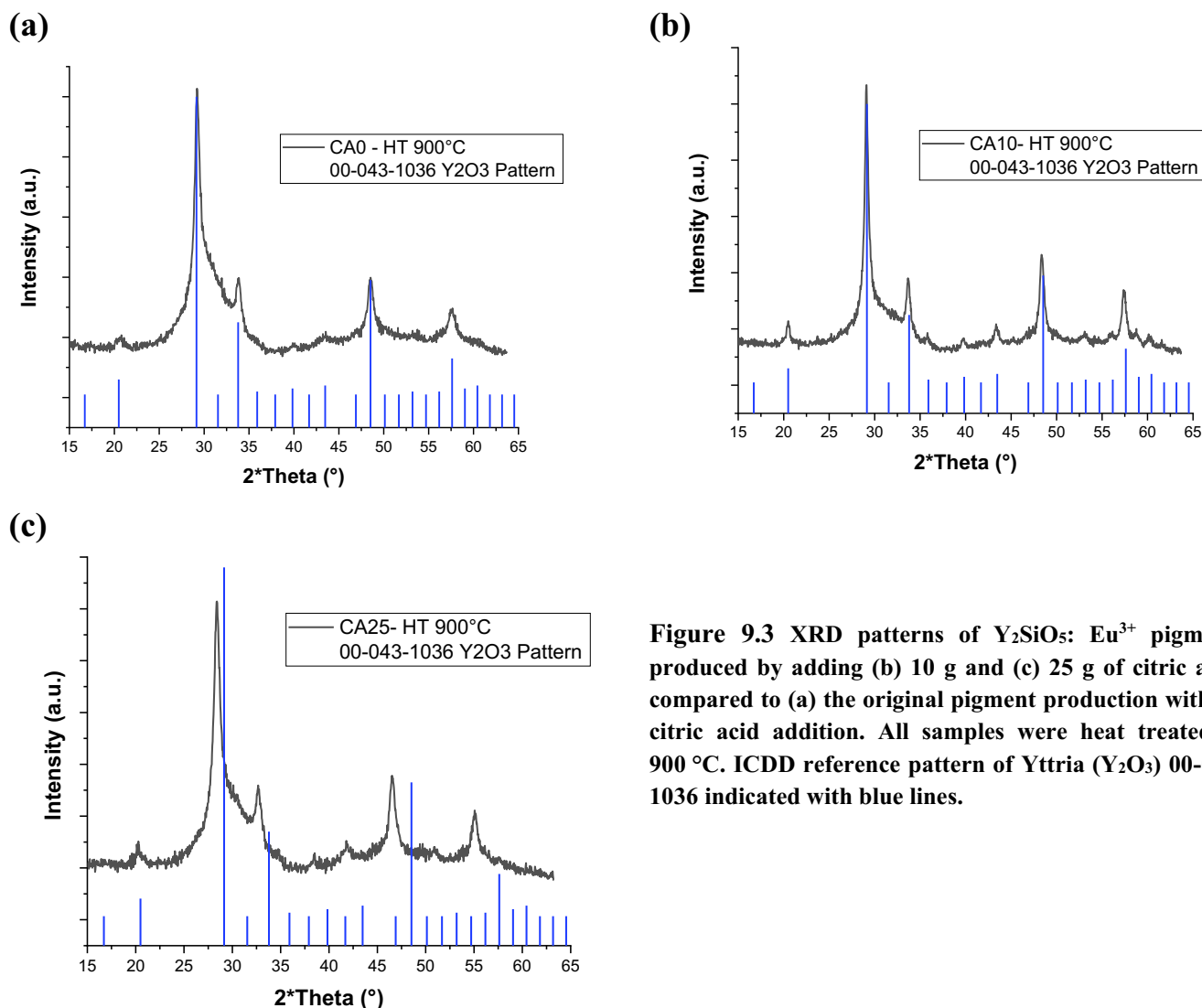


Figure 9.3 XRD patterns of $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$ pigments produced by adding (b) 10 g and (c) 25 g of citric acid, compared to (a) the original pigment production without citric acid addition. All samples were heat treated at 900 °C. ICDD reference pattern of Yttria (Y_2O_3) 00-043-1036 indicated with blue lines.

5800

5805

5810

5815

9.1.4 Luminescent spectra of $\text{Y}_2\text{SiO}_5\text{:Eu}^{3+}$ pigment modified with citric acid

The luminescent spectra of the pigments modified with citric acid were obtained at room temperature and compared to the emission of europium nitrate ($\text{Eu}(\text{NO}_3)_3$) for the four main transitions of europium $^5\text{D}_0 \rightarrow ^7\text{F}_n$, where n are the transitions 0 to 4, explained in *Chapter 3*. The sub-divided peaks are shown in **Figure 9.4** below.

5820

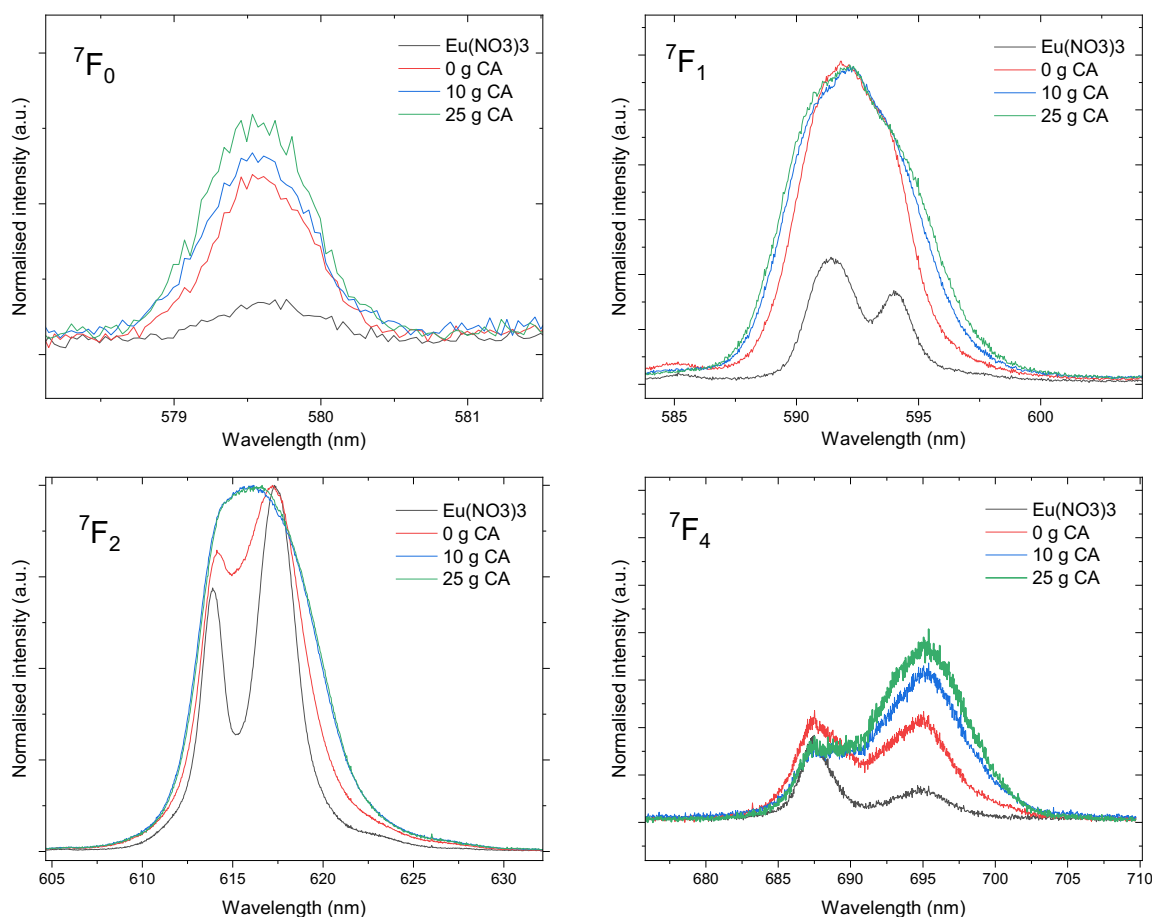


Figure 9.4 Luminescent emission spectra of pigment samples modified with citric acid, compared to the emission of europium nitrate. Spectra normalised to the maximum intensity in the whole range, from 578 nm to 710 nm.

5825

The emission from the $\text{Eu}(\text{NO}_3)_3$ is consistently different to the other samples, and has been reported elsewhere [106]. On the other hand, the emission from the yttrium mono-silicate samples modified with citric acid, CA10 and CA25, are very similar, considering all the emission peaks. The pigment batch without citric acid (CA0) shows an intermediate emission between the europium nitrate and the citric acid pigments.

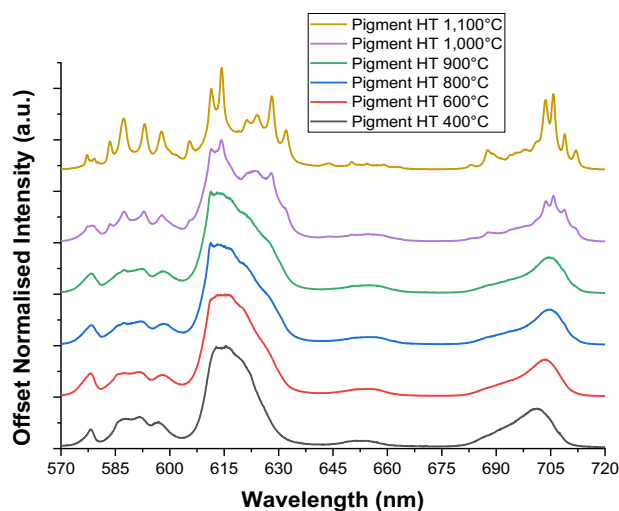
5830

The clearest examples are the transitions $^7\text{F}_2$ and $^7\text{F}_4$.

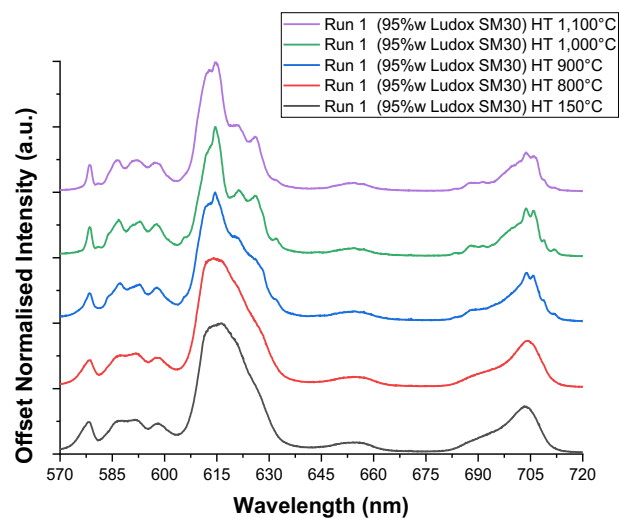
In the $^7\text{F}_2$ transition, the europium nitrate shows two emission peaks at two differentiated wavelengths, 611 and 617 nm. The CA0 batch shows two semi-merged peaks, where the two tips can still be distinguished at the same wavelengths. Finally, for the CA10 and CA25 samples, the $^7\text{F}_2$ transition is a broad and convoluted peak, indicating an amorphous environment for the europium emission.

9.1.5 Luminescent spectra of combination of Ludox ® SM30 and potassium silicate paints

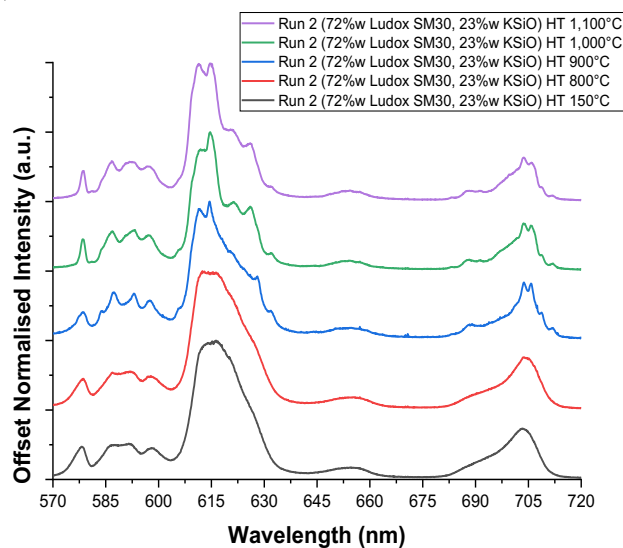
(a)



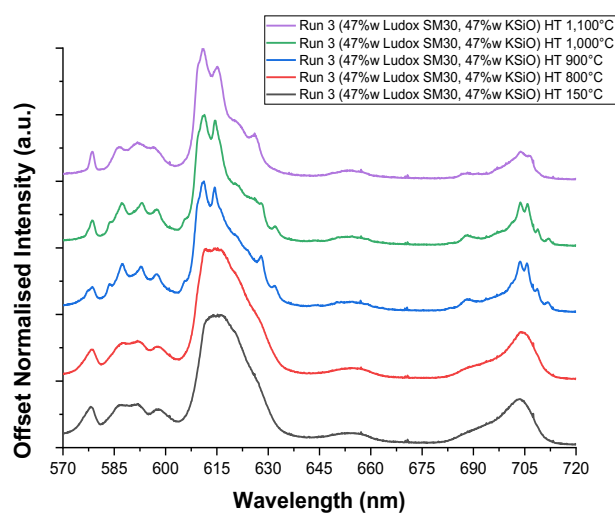
(b)



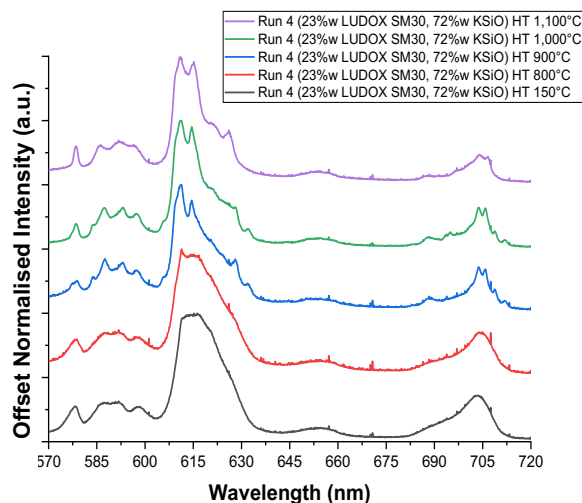
(c)



(d)



(e)



(f)

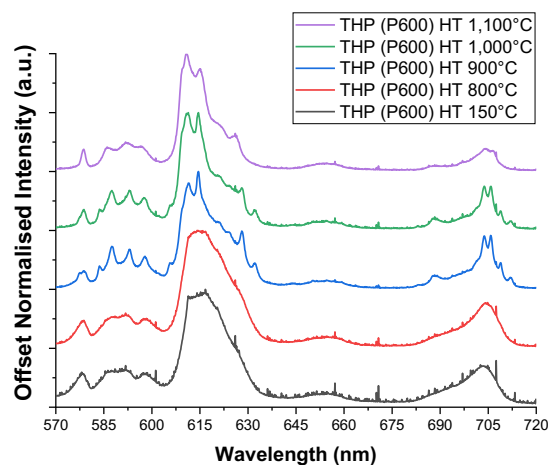


Figure 9.5 Luminescent spectra of paint pellets, heat-treated between 800 °C and 1,100 °C, combining Ludox ® SM30 and Potassium silicate (KSiO) binders with pigment:

- (a) Y_2SiO_5 : Eu pigment calcined at 600 °C (P600).
- (b) Run 1: Ludox ® SM30 (95 % wt.) and P600 pigment (5 % wt.)
- (c) Run 2: Ludox ® SM30 (72 % wt.), Potassium Silicate (23 % wt.) and P600 pigment (5 % wt.)
- (d) Run 3: Ludox ® SM30 (47.5 % wt.), Potassium Silicate (47.5 % wt.) and P600 pigment (5 % wt.)
- (e) Run 4: Ludox ® SM30 (23 % wt.), Potassium Silicate (72 % wt.) and P600 pigment (5 % wt.)
- (f) THP-P600 (Reference): Potassium Silicate (95 % wt.) and P600 pigment (5 % wt.)

5850 9.2 Poster presentation, awarded with the Warren M. Rohsenow Prize at the ASME Turbo-Expo 2020

5855 The poster “Validation of a Thermal History Paint on a Turbine Blade Hot Gas Test Rig Facility” presented at the ASME (The American Society of Mechanical Engineers) Turbo-Expo 2020 virtual conference, won the Warren M. Rohsenow Prize for the best presentation at a session on heat transfer in gas turbine systems. The poster is shown in **Figure 9.6** below. The winner video presentation is available through the YouTube channel of the Centre of Doctoral Training on Advanced Characterisation of Materials (CDT-ACM): <https://youtu.be/XavD5JSPH0A>

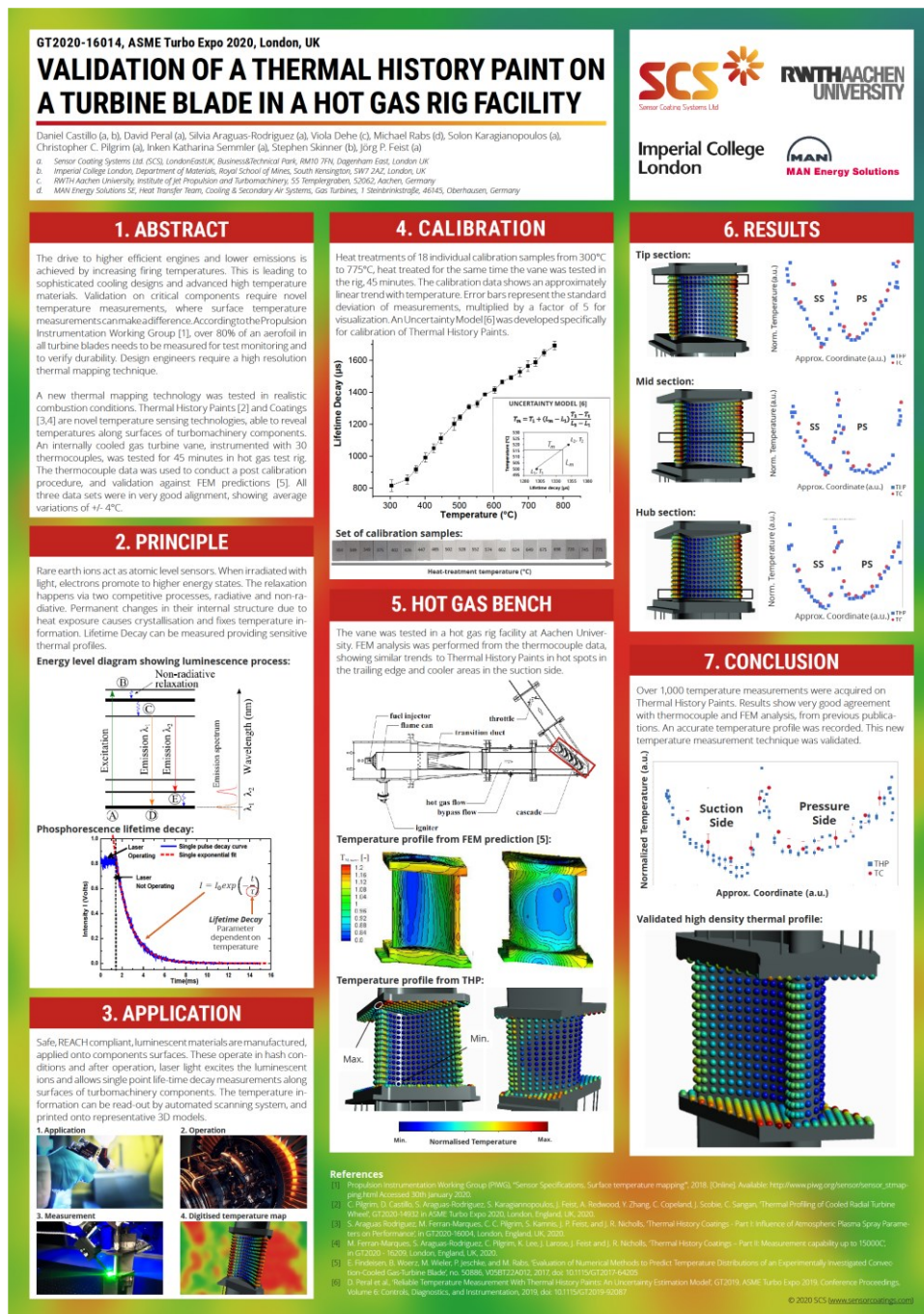


Figure 9.6 Poster named “Validation of a Thermal History Paint on a Turbine Blade Hot Gas Test Rig Facility” presented at the virtual ASME Turbo-Expo 2020

9.3 Material certificate of stainless steel 316L

N° Certificado:

8814

8121806-07

Pagina: 1

22/11/2007 17:48 FAX

022



Certified in accordance to Pressure Equipment Directive 97/23/EC Annex I,
Paragraph 4.3 by TÜV Anlagentechnik GmbH (Notified Body Identification No.0035)
Inspection Certificate EN10204-3.1

Shanxi Taigang Stainless Steel CO.,LTD Member of Taiyuan Iron and Steel (Group) Co.,LTD				MILL TEST CERTIFICATE								
NO.2 jiancaoping, Taiyuan, Shanxi, P.R.China				MATERIAL 1.4401/1.4404/316/316L NO.1 FINISH								
TEL: (0351)3013328 FAX: (0351)3017816				SPECIFICATION ASTM A240/A240M EN10088-2								
http://www.tisco.com.cn				L/C NO.								
E-mail: tgbxg@tisco.com.cn				CERTIFICATE NO. S-1-1								
CUSTOMER S.I.P.L.S.P.A.				DATE OF ISSUE / /								
CONTRACT NO. D711PSI0061				DATE OF 2007/11/31								
Product		Melting furnace		Inspection stamp		Mark of the Manufacturer						
COIL		E+VOD				Shanxi Taiyuan Stainless Steel Co., Ltd						
NO.	Heat No.	Coil No.	Quantity	Dimensions (mm)		Weight (kg)						
1	A1608116	KA70362630K10	1	5.000 × 1500 × C		14200						
2	A2700343	KA70366352	1	10.000 × 1500 × C		14510						
3	A2700314	FA70303340K20	1	3.000 × 1500 × C		11540						
Total:			3			40250						
Chemical Composition												
Heat No.	C	Si	Mn	P	S	Cr	Ni	Cu	Al	Mo	N	Ti
A1608116	0.017	0.410	1.140	0.028	0.004	16.410	10.370			2.160		
A2700343	0.019	0.356	1.201	0.027	0.006	16.723	10.253			2.209		
A2700314	0.023	0.327	1.248	0.025	0.002	17.491	10.191			2.122		
Mechanical Properties												
Test No.	Tensile R _m N/mm ²	R _{0.2} Yield strength N/mm ²	R _{p1.0} Yield strength N/mm ²	Elongation A 5(%)	Corrosion Tests	Hardness						
						HRB	HV	HRC				
87001124-T	630	316	345	56		88						
87F00544-T	598	301	323	53		84						
87002256-T	584	301	323	53		84						
Surface and dimensions controlled: O.K.												
Work Inspector:												

Page 1 of 1

This to declare that the material as described in here has been cut to :
PIATTO CES.316L 4000X20X3
and remarked with steelgrade, heat n°, workinspector's stamp CC

Figure 9.7 Material certificate of the stainless-steel 316L bars issued from SOG Ltd. during 2018.



MARCEGAGLIA
SPECIALTIES

Registered seat and Administration offices:
Via Cassanese 16
40040 Castiglione degli Ippoliti
Modena Italy
Tel. +39 - 0376 685 1
Fax. +39 - 0376 685 600
www.marcegaglia.com

Customer UK MARCEGAGLIA SPECIALTIES RAP 8 TH FLOOR-THAVES INN HOUSE ECTN 2HB 3-4 HOLBORN CIRCUS - LOND GB		Consignee ND THE METAL CENTRE WESTERN WAY-WEDNESBURY WS10 7BW WEST MIDLANDS GB		Type Number Issued On		Delivery Nn OI Delivery note nr		Quality Control O.M.D./O.M. L.Sobazzi Plant Of Ozalordo		Pages 4/4	
--	--	---	--	-----------------------------	--	---------------------------------------	--	---	--	--------------	--

Identification Nr	Quantity	Heat	C (%)	SI (%)	Mn (%)	P (%)	S (%)	Cr (%)	Ni (%)	Mo (%)	N (%)	Rm [N/mm²]	Rp 0.2 [N/mm²]	A HRB
19NWJ001888	507 KG	1900948	.027	.390	.850	.0340	.0018	16.73010.1202.120	.0340	623	424	513	51.0	87
19NWJ001889	507 KG	1900948	.027	.390	.850	.0340	.0018	16.73010.1202.120	.0340	623	424	513	51.0	87
54000034 PXP 30x5x4000 A316L EN 1.4404X2CrNiMo17-12-2. WNR1.4404. A316L / AISI316. X5CrNiMo17-12-2. WNR1.4401. A316 EN10028-7.EN10088-2.EN10088-4. ASTM A240. ASME SA240. ASTM A480. ASME SA480 1591856395/10 C60192 OCTOBER Date 10/10/2019														
19NW0003357	498 KG	0456689	.021	.330	1.120	.0330	.0010	16.57010.0502.100	.0450	588	301	365	54.0	81
19NW0003376	504 KG	0456692	.021	.370	1.070	.0300	.0010	16.54010.0502.020	.0450	641	451	531	49.0	91
19NW0003377	452 KG	0456692	.021	.370	1.070	.0300	.0010	16.54010.0502.020	.0450	640	451	530	49.4	91
54000083 PXP 60x5x4000 A316L EN 1.4404X2CrNiMo17-12-2. WNR1.4404. A316L / AISI316. X5CrNiMo17-12-2. WNR1.4401. A316 EN10028-7.EN10088-2.EN10088-4. ASTM A240. ASME SA240. ASTM A480. ASME SA480 1591856395/20 C60192 OCTOBER Date 10/10/2019														
19NS004953	526 KG	0456152	.019	.330	1.010	.0290	.0010	16.60010.0902.000	.0450	602	322	375	54.4	82

Remarks: - We certify that products listed above comply with order requirements - Document validated acc. EN10204 par. 5 - Durability: NPD - Regulated Substances: NPD - Intended Uses: Building Constructions or Civil Engineering - DoP available at http://www.marcegaglia.com/brochure/quality/top.html	0474 MARCEGAGLIA Via Cassanese 16 40040 Castiglione degli Ippoliti Modena Italy EN 10088-4:2003 CE
--	--

Figure 9.8 Material certificate of the stainless-steel 316L bars issued from SOG Ltd. during 2019.

9.4 Permissions for third party copyright

These permissions were requested and granted during the years 2020 and 2021 for their reproduction on this thesis.

Table 9.1 Permissions for third party copyright works

Type of work	Source work	Ref.	Copyright holder	Licence number	Page number
Figure 1.1	Meeting Future Emission Standards. Materials World, IOM3 [Internet]. 2020 May https://www.iom3.org/materials-world-magazine/feature/2020/apr/30/meeting-future-emission-1315-standards	[15]	SCS Ltd. / IOM3	-	
Figure 1.3	Surface temperature measurement on engine components by means of irreversible thermal coatings. Measurement Science and Technology; 19(10): 105501. http://dx.doi.org/10.1088/0957-0233/19/10/105501	[89]	Institute of Physics, IOP Publishing Ltd.	1071217	
Figure 2.2	The europium (III) ion as spectroscopic probe in bioinorganic chemistry. Inorganica Chimica Acta. 1987; 139(1): 219–22. DOI: 10.1016/S0020-1693(00)84084-0	[111]	Elsevier	4855420625551	
Figure 2.7	Luminescence sensing of temperatures in thermal barrier coatings. Surface and Coatings Technology. 2007, 15; 202 (4): 681–7. DOI: 10.1016/j.surfcoat.2007.05.092	[135]	Elsevier	4855410229263	
Figure 3.2	Recent progress on synthesis, multi-scale structure, and properties of Y–Si–O oxides. International Materials Reviews. 2014 September 1; 59 (7): 357–83. DOI: 10.1179/1743280414Y.0000000033	[222]	Taylor & Francis	-	
Figure 3.3	Thermal expansion and high-temperature phase transformation of the yttrium silicate Y ₂ SiO ₅ . Journal of materials research. 2001; 16(8):2251–5	[228]	Cambridge University Press	4837100917575	
Figure 4.7	AVANTES website, Theoretical background section, Schematic of an AVANTES Avaspec-ULS optical bench design, including a symmetrical Czerny-Turner spectrometer	[298]	AVANTES NG	-	
Figure 4.13	Fourier transform-infrared spectroscopy: Part I. Instrumentation, 1986, Journal of Chemical Education, https://doi.org/10.1021/ed063pA5	[305]	The Journal of Chemical Education		
Figure 5.7	Optimization of the Thermodynamic Properties and Phase Diagrams of the Na ₂ O–SiO ₂ and K ₂ O–SiO ₂ Systems, 1993 DOI: 10.1111/j.1151-2916.1993.tb08333.x	[323]	Journal of the American Ceramic Society	4997050061333	
Figure 5.32	The Binary System Li ₂ O–SiO ₂ , 1930 The Journal of Physical Chemistry, 34, 12, 2641-2650 DOI: 10.1021/j150318a001	[344]	The Journal of Physical Chemistry		
Figure 5.40	The System Sodium Oxide-Silica <i>The Journal of Physical Chemistry</i> 1930 34 (7), 1583-1598 https://doi.org/10.1021/j150313a018	[346]	The Journal of Physical Chemistry		

9.4.1 Permission for Figure 1.1, from the Institute of Materials, Minerals and Mining (IOM3)

Email communication

From: Katherine Williams <Katherine.Williams@iom3.org>

Sent: 17 May 2021 11:12

To: Castillo, Daniel <d.castillo17@imperial.ac.uk>

Subject: RE: Permission to use Figure published in Materials World

Dear Daniel,

Of course, you can use that in your thesis. I hope the write up goes well.

Regards,

Katherine



Katherine Williams

Head of Content

Institute of Materials, Minerals & Mining

297 Euston Road, London, NW1 3AD

020 7451 7323 | www.iom3.org

From: Castillo, Daniel <d.castillo17@imperial.ac.uk>

Sent: 17 May 2021 10:45

To: Katherine Williams <Katherine.Williams@iom3.org>

Subject: Permission to use Figure published in Materials World

Hi Katherine,

I am a PhD student at Imperial College, I am writing my thesis at the moment, and I would like to use one of the figures published in the Materials World magazine. The Figure was published in May 2020 and submitted the 30th of April 2020 by Jörg Feist and Silvia Araguas-Rodriguez, both ex-Imperial and currently working at Sensor Coating Systems Ltd.

The title of the feature was Taking the heat / Meeting future emission standards.

It can be found in the IOM3 website under: <https://www.iom3.org/resource/meeting-future-emission-standards.html>

Could you grant the permission for me to use this figure in my thesis?

I can provide a permission request form if necessary.

Thank you very much.

Best Regards

Daniel Castillo

9.4.2 Permission for Figure 1.3, from the Institute of Physics, (IOP)

5920

1. Measurement Science and Technology

0.00 GBP

Order license ID	Pending	Publisher	IOP Publishing
ISSN	0957-0233	Portion	Image/photo/illustration
Type of Use	Republish in a thesis/dissertation		

LICENSED CONTENT

Publication Title	Measurement Science and Technology	Country	United Kingdom of Great Britain and Northern Ireland
Author/Editor	Institute of Physics (Great Britain)	Rightsholder	IOP Publishing, Ltd

ADDITIONAL DETAILS

Order reference number	N/A	The requesting person / organization to appear on the license	Imperial College London
------------------------	-----	---	-------------------------

REUSE CONTENT DETAILS

Title, description or numeric reference of the portion(s)	Figure 1	Title of the article/chapter the portion is from	Surface temperature measurement on engine components by means of irreversible thermal coatings
Editor of portion(s)	N/A	Author of portion(s)	Institute of Physics (Great Britain)
Volume of serial or monograph	N/A	Issue, if republishing an article from a serial	N/A
Page or page range of portion	4	Publication date of portion	2008-01-18

5925 9.4.3 Permission for Figure 2.2, from Elsevier license

ELSEVIER LICENSE

TERMS AND CONDITIONS

Jun 24, 2020

5930 This Agreement between Imperial College London -- Daniel Castillo ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Centre.

License Number 4855420625551

5935 License date Jun 24, 2020

Licensed Content Publisher Elsevier

Licensed Content Publication Inorganica Chimica Acta

Licensed Content Title The europium (III) ion as spectroscopic probe in bioinorganic chemistry

Licensed Content Author Jean-Claude G. Bünzli

5940 Licensed Content Date Dec 1, 1987

Licensed Content Volume 139

Licensed Content Issue 1-2

Licensed Content Pages 4

Start Page 219

5945 End Page 222

Type of Use reuse in a thesis/dissertation

Portion figures/tables/illustrations: 24/06/2020 Rights Link Printable License

5950 Number of figures/tables/illustrations: 1

Format both print and electronic

Are you the author of this Elsevier article? No

Will you be translating? No

5955 Institution name: Imperial College London

Portions Figure 1

Requestor Location: Imperial College London, United Kingdom

Publisher Tax ID GB 494 6272 12

5960 Total 0.00 GBP

9.4.4 Permission for Figure 2.7, from Elsevier license

5965 24/06/2020 Rights Link Printable License

ELSEVIER LICENSE, TERMS AND CONDITIONS

5970 Jun 24, 2020, This Agreement between Imperial College London -- Daniel Castillo ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Centre.

License Number 4855410229263

License date Jun 24, 2020

Licensed Content Publisher Elsevier

5975 Licensed Content Publication Surface and Coatings Technology

Licensed Content Title Luminescence sensing of temperatures in thermal barrier coatings

Licensed Content Author D.R. Clarke, M.M. Gentleman

Licensed Content Date Dec 15, 2007

Licensed Content Volume 202

5980 Licensed Content Issue 4-7, Pages 7, Start Page 681, End Page 687

Type of Use reuse in a thesis/dissertation

Portion figures/tables/illustrations

Number of figures/tables/illustrations: 1

5985

Institution name: Imperial College London

Publisher Tax ID GB 494 6272 12

Total 0.00 GBP

5990

9.4.5 Permission for Figure 3.2, from Taylor & Francis group

09/05/2020

Rightslink® by Copyright Clearance Center



RightsLink®



Home



Help



Email Support



Sign in



Create Account

Taylor & Francis
Taylor & Francis Group

Recent progress on synthesis, multi-scale structure, and properties of Y-Si-O oxides

Author: Ziqi Sun, , Meishuan Li, et al

Publication: International Materials Reviews

Publisher: Taylor & Francis

Date: Sep 1, 2014

Rights managed by Taylor & Francis

Thesis/Dissertation Reuse Request

Taylor & Francis is pleased to offer reuses of its content for a thesis or dissertation free of charge contingent on resubmission of permission request if work is published.

BACK

CLOSE

© 2020 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions
Comments? We would like to hear from you. E-mail us at customercare@copyright.com

5995 9.4.6 Permission for Figure 3.3, from Cambridge University press

7/05/2020 Rights Link Printable License

CAMBRIDGE UNIVERSITY PRESS LICENSE, TERMS AND CONDITIONS, May 27, 2020

6000 This Agreement between Imperial College London -- Daniel Castillo ("You") and Cambridge University Press ("Cambridge University Press") consists of your license details and the terms and conditions provided by Cambridge University Press and Copyright, Clearance Centre.

6005 License Number 4837100917575
License date May 27, 2020
Licensed Content Publisher Cambridge University Press
Licensed Content Publication Journal of Materials Research
Licensed Content Title Thermal expansion and high-temperature phase
6010 transformation of the yttrium silicate Y₂SiO₅
Licensed Content Author J. W. Nowok, J. P. Kay, R. J. Kulas
Licensed Content Date Jan 31, 2011
Licensed Content Volume 16
Licensed Content Issue 8, Start page 2251, End page 2255
6015 Type of Use Dissertation/Thesis

Portions Figure 5

Requestor: Imperial College London, South Kensington Campus, London, SW7 2BP, UK

Publisher Tax ID GB823847609

6020 Total 0.00 GBP

9.4.7 Permission for Figure 4.12, from Avantes

E-theses letter: request to reproduce an extract from a third party's published work

06/04/20

Dear Chantal Elout,

I am completing my PhD thesis at Imperial College London entitled 'Development of a second generation of Thermal History Paints for reliable offline high temperature measurements'.

I seek your permission to reprint, in my thesis an extract from your: **AVANTES website, Theoretical Background Section**. The extract to be reproduced is the **Optical Bench Design**, under: <https://www.avantes.com/support/theoretical-background/spectrometers/958-introduction-spectrometers/442-optical-bench-design>.

I would like to include the extract in my thesis which will be added to Spiral, Imperial's institutional repository <http://spiral.imperial.ac.uk/> and made available under a CC BY-NC-ND Creative Commons Licence.

If you are happy to grant me all the permissions requested, please return a signed copy of this letter. If you wish to grant only some of the permissions requested, please list these and then sign.

Yours sincerely,

Daniel Castillo

PhD Candidate at Department of Materials, Imperial College London

Permission granted for the use requested above:

I confirm that I am the copyright holder of the extract above and hereby give permission to include it in your thesis which will be made available, via the internet, for non-commercial purposes under the terms of the user licence.

[please edit the text above if you wish to grant more specific permission]

Signed:



Name: *B. J. ODERKERK*

Organisation: *Avantes BV*

Job title: *CEO*

9.4.8 Permission for Figure 4.13, from ACS publications

Fourier transform-infrared spectroscopy: Part I. Instrumentation

Author: W. D. Perkins
 Publication: Journal of Chemical Education
 Publisher: American Chemical Society
 Date: Jan 1, 1986
 Copyright © 1986, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

9.4.9 Permission for Figure 5.7, from John Wiley and sons

**JOHN WILEY AND SONS LICENSE
 TERMS AND CONDITIONS**
 Jan 27, 2021

This Agreement between Imperial College London -- Daniel Castillo ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Centre.

License Number	4997050061333
License date	Jan 27, 2021
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Journal of the American Ceramic Society
Licensed Content Title	Optimization of the Thermodynamic Properties and Phase Diagrams of the Na ₂ O–SiO ₂ and K ₂ O–SiO ₂ Systems
Licensed Content Author	Ping Wu, Gunnar Eriksson, Arthur D. Pelton
Licensed Content Date	Jul 11, 2005
Licensed Content Volume	76
Licensed Content Issue	8
Licensed Content Pages	6
Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic

Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title	Development of Thermal History Paints
Institution name	Imperial College London
Expected presentation date	Jan 2021
Portions	Figure 1 Imperial College London South Kensington Campus
Requestor Location	London, SW7 2BP United Kingdom Attn: Imperial College London
Publisher Tax ID	EU826007151
Total	0.00 GBP

9.4.10 Permission for Figure 5.32, from ACS publications




[Home](#)
[Help](#)
[Email Support](#)
[Sign in](#)
[Create Account](#)

The Binary System Li₂O-SiO₂
 Author: F. C. Kracek
 Publication: The Journal of Physical Chemistry A
 Publisher: American Chemical Society
 Date: Jan 1, 1929
 Copyright © 1930, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

[BACK](#)
[CLOSE WINDOW](#)

This service provides permission for reuse only. If you do not have a copy of the portion you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving RightsLink.

ⓘ If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

Note: Individual Scheme and Structure reuse is free of charge and does not require a license. If the scheme or structure is identified as a "Figure" in the article, permission is required.

ⓘ Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

If credit is given to another source for the material you requested, permission must be obtained from that source.

6035

6040

9.4.11 Permission for Figure 5.40, from ACS publications



The System Sodium Oxide-Silica
 Author: F. C. Kracek
 Publication: The Journal of Physical Chemistry A
 Publisher: American Chemical Society
 Date: Jan 1, 1929
 Copyright © 1930, American Chemical Society

Quick Price Estimate

This service provides permission for reuse only. If you do not have a copy of the portion you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving RightsLink.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

Note: Individual Scheme and Structure reuse is free of charge and does not require a license. If the scheme or structure is identified as a Figure in the article, permission is required.

Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

6045

