

*Experimental determination and modelling of
various thermo-physical properties of nuclear
materials above 1500 K*

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Declaration of originality

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Abstract

In the framework of improving nuclear power plant safety during accidents, the current study is focused on developing and applying a new technique for the high temperature determination of thermal conductivity, specific heat, thermal diffusivity, spectral and total hemispherical emissivity, as well as the melting points of nuclear materials.

The new inverse method is based on the laser flash approach. The novel use of a finite element analysis (FEA) model (as part of the inverse method) allows accurate description of complex boundary conditions and has led to an improved accuracy of the evaluated properties. The inverse method has been tested for use with two devices – a pyrometer and an infrared camera. All experimental results are complemented by novel and existing solid state theory.

The results obtained on isotropic, isostatically pressed, graphite (neutron moderator) are in good agreement with literature values (available to around 1500 K) and extend the available data up to 2800 K.

Values are reported of specific heat, thermal conductivity and thermal diffusivity of UO_2 from 1500 K to 2900 K. The specific heat model and measurements show, for the first time that a gradual pre-melting transition is consistent with high temperature literature values – enthalpy increment measurements and independently measured high temperature oxygen defect concentrations.

Experimental results are also presented for the thermal conductivity, specific heat, thermal diffusivity, spectral and total hemispherical emissivity of ThO₂ from 2000 K to 3050 K. It is the first time direct measurements of thermal conductivity and total hemispherical emissivity have been carried out on ThO₂ at such high temperatures. All new results commit to a better understanding of the properties of nuclear materials, in particular nuclear fuel, under extreme conditions. Hence, this work will contribute towards improved predictions of nuclear core behaviour during an accident (using fuel performance or severe accident codes).

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Table of Contents

Chapter 1	: Introduction.....	23
1.1	From nuclear fission to power generation	24
1.2	Brief history of nuclear reactor design and the evolution of concepts.....	27
1.3	Nuclear accidents and the birth of Accident Tolerant Fuel (ATF) concepts.....	32
1.4	Project goal.....	36
Chapter 2	: Techniques for measuring material thermo-physical properties.....	39
2.1	Comparison of techniques	40
2.1.1	Thermal conductivity	40
2.1.2	Specific heat capacity	43
2.1.3	Thermal diffusivity	46
2.1.4	Emissivity (spectral and total)	48
2.1.5	Melting Point	50
2.2	Brief review of advancements in the laser flash method	52
Chapter 3	: Theory of condensed matter.....	57
3.1	Specific heat.....	58
3.1.1	Harmonic specific heat	58
3.1.2	Electronic specific heat due to localised electrons	60
3.1.3	Electronic specific heat due to free electrons.....	61
3.1.4	Specific heat due to defect formation	61
3.1.5	Conversion from c_V to c_P	68
3.2	Thermal and electrical conductivity theory	69
3.2.1	Thermal conductivity due to free electrons.....	69
3.2.2	Lattice thermal conductivity	70
3.2.3	Ionic thermal and electrical conductivity	72
3.2.4	Polaron thermal and electrical conductivity.....	73
3.3	Thermal expansion.....	74
3.3.1	Lattice contribution.....	74
3.3.2	Defect contribution.....	75
3.4	Thermal diffusivity	76
3.5	Emissivity	76
Chapter 4	: Experimental methods.....	79
4.1	New inverse method (based on the laser-flash technique).....	80
4.1.1	Laser flash equipment and measurement procedure.....	80
4.1.2	Devices and calibrations.....	82
4.1.3	Computational methodology	89

Table of Contents

4.1.4	Noise filtering	91
4.1.5	Finite Element Analysis (FEA).....	93
4.1.6	FEA convergence criteria	95
4.1.7	Optimisation algorithm	99
4.1.8	Impact of the laser beam's spatial profile.....	103
4.1.9	Impact of noise filtering.....	106
4.1.10	Heat losses due to vapourisation	107
4.1.11	Convective heat transfer coefficient.....	108
4.1.12	Fitting approximations.....	110
4.2	Spectral emissivity (640 nm).....	114
4.3	X-ray diffraction (XRD)	116
4.4	Scanning Electron Microscopy (SEM)	116
Chapter 5	: Testing and validation of the new inverse method.....	117
5.1	Sensitivity analysis and correlation between parameters	118
5.1.1	Pyrometer method.....	120
5.1.2	Camera method	123
5.2	Synthetic data tests	127
5.2.1	Pyrometer method.....	128
5.2.2	Camera method	128
5.3	Experimental data tests	133
5.3.1	Pyrometer method.....	133
5.3.2	Camera method	134
5.4	Error analysis.....	136
5.4.1	Specific heat, thermal conductivity and thermal diffusivity.....	137
5.4.2	Measured temperature and spectral emissivity.....	140
5.5	Summary.....	144
Chapter 6	: Isostatic graphite.....	145
6.1	Introduction	146
6.2	Samples.....	147
6.3	Spectral emissivity	148
6.4	Specific heat capacity.....	149
6.5	Thermal conductivity.....	153
6.6	Thermal diffusivity	156
6.7	Summary.....	157
Chapter 7	: Uranium dioxide.....	159
7.1	Introduction	160
7.2	Samples.....	162
7.3	Vapourisation heat losses.....	164
7.4	Experimental measurements	167

Table of Contents

7.5	Phonon density of states	175
7.6	Defect concentrations.....	176
7.7	Specific heat.....	182
7.8	Thermal expansion.....	183
7.9	Electrical conductivity	185
7.10	Thermal conductivity.....	186
7.11	Thermal diffusivity	188
7.12	Summary.....	190
Chapter 8 : Thorium dioxide.....		193
8.1	Introduction	194
8.2	Samples.....	197
8.3	Vapourisation heat losses.....	200
8.4	Experimental results	203
8.5	Phonon density of states.....	210
8.6	Defect concentrations.....	212
8.7	Specific heat.....	215
8.8	Thermal expansion.....	216
8.9	Thermal conductivity.....	218
8.10	Total hemispherical emissivity.....	222
8.11	Summary.....	225
Chapter 9 : Discussion.....		226
9.1	New methodology.....	227
9.1.1	Pyrometer method.....	227
9.1.2	Infrared camera	228
9.2	Graphite.....	228
9.2.1	Specific heat	229
9.2.2	Thermal conductivity.....	229
9.3	Uranium dioxide	230
9.3.1	Defects.....	230
9.3.2	Specific heat	231
9.3.3	Thermal conductivity.....	233
9.3.4	Model analysis of other thermo-physical properties (not measured in this work)	234
9.3.5	Relevance for fuel performance and safety	236
9.4	Thorium dioxide.....	236
9.4.1	Defects.....	237
9.4.2	Specific heat, melting and pre-melting transition.....	237
9.4.3	Thermal conductivity.....	239
9.4.4	Total hemispherical emissivity	240
9.4.5	Thermal expansion	242

Table of Contents

9.4.6	Relevance of new results for fuel performance.....	242
Chapter 10	: Conclusions and future work.....	245
10.1	New methods	246
10.1.1	Pyrometer method.....	246
10.1.2	Infrared camera method	247
10.2	Measurements and interpretation	247
10.2.1	Graphite.....	248
10.2.2	UO ₂	248
10.2.3	ThO ₂	249
10.2.4	Comparing UO ₂ and ThO ₂	251
10.3	Future work	253

List of Figures

Figure 1-1: A) Schematic of the fission chain reaction; B) Graph of the binding energy per nucleon (MeV) as a function of element atomic mass (Courtesy of the educational publisher Pearson Prentice Hall).....	25
Figure 1-2: Schematic of a pressurized water reactor power plant and associated machinery and equipment involved during the electricity generation process ³	27
Figure 1-3: Timeline of the evolution of reactor design. ⁶	31
Figure 4-1: Schematic of the laser flash experimental set-up.	82
Figure 4-2: TRUMPF laser power vs. measured voltage. The black solid line represents the calibration curve when a sapphire window was absent, while the red dotted line takes into account the effect of the sapphire window.	83
Figure 4-3: The space-time variation of the laser power: A) Normalised power as a function of normalized beam spot radius (nominal); B) Normalised power as a function of time. The blue dots represent the measured profiles, while the red dotted lines represent the functional approximation of the measured profiles.....	85
Figure 4-4: Voltage vs. inverse temperature obtained via tungsten ribbon lamp calibration: A) Russpyro; B) HS01. Black line represent absence of sapphire window during calibration, while red dotted lines represent the calibration with a sapphire window (between tungsten lamp and pyrometers).	86
Figure 4-5: Ln(signal) vs. inverse temperature obtained via high temperature black body calibration: A) NUC D; B) NUC F.	87
Figure 4-6: Logic diagram of triggering procedure. Solid green lines represent the standard devices used and standard information transfer sequence. Dotted green lines represent the devices used and the sequence of information transfer when using the infrared camera. The blue lines represents the spectropyrometer as a stand-alone device, where data is transferred directly to the PC.....	89
Figure 4-7: Logic scheme of the computer programs developed for the infrared camera and pyrometer measurements.....	91
Figure 4-8: Relative error vs. fractional band width of the FFT filter obtained from least square optimisation of filtered synthetic thermograms. Red line shows the band width chosen for filtering all experimental results.	92
Figure 4-9: Example geometry of the axisymmetric model and the mesh used in FlexPDE. The red dashed line denotes the axis of symmetry at $r = 0$	95
Figure 4-10: Relative error (RE) vs. time (duration of simulation, i.e computed thermogram) calculated via equation (4-8) for various numbers of grid points. A) Calculations of RE performed on the rear side of the axisymmetric geometry at the	

central radial location ($r/r_p=0$); B) Calculations of RE were performed on the rear side of the axisymmetric geometry at the central radial location ($r/r_p=0.5$).....	97
Figure 4-11: Relative error (RE) vs. time (duration of simulation, i.e computed thermogram) calculated via equation (4-9) for various numbers of grid points.; A) Calculations of RE performed on the rear side of the axisymmetric geometry at the central radial location ($r/r_p=0$); B) Calculations of RE were performed on the rear side of the axisymmetric geometry at the central radial location ($r/r_p=0.5$).....	98
Figure 4-12: Example of a thermogram (temperature vs. time graph) obtained from experiment compared to the model thermogram obtained via least squares minimisation.	101
Figure 4-13: Steady state and transient measurements recorded using an infrared camera. (A) Example of a 3-D steady state temperature profile of a UO_2 sample. The magnitudes of the x and y axes are indices and not metric quantities.; (B) the axisymmetric steady state temperature distribution deduced from (A); (C) example of radially distributed thermograms for a UO_2 sample measured by the infrared camera compared to the optimised finite element (FEA) solution. (D) Radially distributed synthetic thermograms (produced via the FEA model with perturbed input parameters and added artificial noise) compared to the optimised finite element solution.	103
Figure 4-14: The calibrated spatial profile (blue dashed line) of the laser compared to a top hat approximation of the spatial laser profile (red line). $P(r)$ represents the calibrated or measured power as a function of radius, while P_{max} represents the integral power.	105
Figure 4-15: Calculated heat transfer coefficient for a cylindrical pellet of graphite in Argon as a function of temperature at a pressure of 1 bar.	110
Figure 4-16: Approximation of thermal conductivity (k) as a function of radius for the pyrometer method. The box on top represents the axisymmetric geometry of the sample with the axis of symmetry at $r = 0$. A constant value (a_0) is used to describe the radial dependence of the evaluated property (e.g. k – thermal conductivity).....	111
Figure 4-17: Approximation of thermal conductivity (k) as a function of radius (infrared camera method). The box on top represents the axisymmetric geometry of the sample with the axis of symmetry at $r = 0$ on the graph below. In this case an $(N-1)^{th}$ order polynomial is used to describe the radial dependence of the evaluated property. The respective fitting parameters are N constants a_{i-1}	112
Figure 4-18: Schematic of the first three iterations of the iterative gradient (IG) method. In black are all the values, which are allowed to vary during the optimisation procedure of the respective iteration, while in red are the values which have been stored and fixed as a result of prior iterations.	114
Figure 4-19: Inverse temperature as a function of wavelength measured by a 256 channel spectropyrometer (example from a measurement on isostatically pressed graphite at 1933 K).....	115

Figure 5-1: Sensitivity coefficients (K) vs. time at the central rear location of the axisymmetric geometry. Examined parameters include thermal conductivity (k), specific heat capacity (c_p), convective heat transfer coefficient (HTC), the total hemispherical emissivity (ϵ_{tot}), spatial laser beam profile ($P(r)$), absorptivity (ϵ_{1064}) and thickness (t_s).	122
Figure 5-2: Sensitivity coefficients S (K) on the rear boundary as a function of time computed using the thermo-physical properties of UO_2 for various parameters (thermal conductivity (k), specific heat (c_p), convective heat transfer coefficient (HTC), the total hemispherical emissivity (ϵ_{tot}), spatial laser beam profile ($P(r)$), absorptivity (ϵ_{1064}) and thickness (t_s). A) radial location $r=0$; B) radial location $r= r_B/2$; C) radial location $r=r_B$; D) radial location $r=r_B + (r_P - r_B)/2$; E) radial location $r=r_P$; (r_B – beam spot radius (m), r_P – sample radius (m)). The range of each x-axis in each subplot is identical to the one shown in E).	124
Figure 5-3: (A) Integral sensitivity coefficients as a function of the relative radial location (r/r_P). Examined parameters include thermal conductivity (k), specific heat capacity (c_p), convective heat transfer coefficient (h), the total hemispherical emissivity (ϵ_{tot}), spatial laser beam profile ($P(r)$), absorptivity (ϵ_{1064}) and sample thickness (t_s); (B) zoom-in of the lower right corner of (A).	125
Figure 5-4: The correlation (Pearson coefficient) of parameter pairs vs. relative radial position. The chosen parameters are based on equation (5-3) and are thermal conductivity (k), specific heat (c_p), convective heat transfer coefficient (h) and total hemispherical emissivity (ϵ_{tot})	127
Figure 5-5: Summary of synthetic data tests. A) specific heat vs. normalised radius; B) thermal conductivity vs. normalised radius. Both plots compare the output of the two approximations (Iterative gradient (IG) approximation vs. polynomial (PNOM) approximation) to the exact solution (the exact solutions are the property profiles used to generate the synthetic thermograms, which were then used to test the approximations). The two property profiles were obtained from independent runs of the IG and PNOM approximations (i.e. the two properties were not fitted simultaneously); C) specific heat vs. temperature; D) thermal conductivity vs. temperature. Graphs C and D were obtained by assigning the known temperature at each radial position to the corresponding property value at the same radial coordinate.	132
Figure 5-6: Experimental evaluation of thermal conductivity (k) vs. temperature using the camera method. A) Results for UO_2 using PNOM and IG approximations compared to recommendation of Fink; B) Results for isostatically pressed graphite using PNOM and IG approximations compared to recommendation of Pavlov, et al. ¹³¹	136
Figure 5-7: Histogram of specific heat values (top left) with its respective quantile – quantile plot (bottom left), thermal conductivity values (top middle) with its respective quantile – quantile plot (bottom middle) and thermal diffusivity values (top right) with its respective quantile – quantile plot (bottom right)	139

Figure 5-8: Absolute measurement error (K) vs. temperature (K) for different spectral emissivities at 645 nm. A) spectral emissivity (ϵ) = 0.1; B) spectral emissivity (ϵ) = 0.3; C) spectral emissivity (ϵ) = 0.5; D) spectral emissivity (ϵ) = 0.7; E) spectral emissivity (ϵ) = 0.9. Various deviations from the correct spectral emissivity are represented by the different colored lines. The range of each x-axis in each plot is identical to the ones shown in D) and E).....	142
Figure 5-9: Absolute measurement error (K) vs. temperature (K) for different values of spectral emissivity: A) spectral emissivity (ϵ) = 0.1; B) spectral emissivity (ϵ) = 0.3; C) spectral emissivity (ϵ) = 0.5; D) spectral emissivity (ϵ) = 0.7; E) spectral emissivity (ϵ) = 0.9. The different colored lines represent different wavelengths. The measurement error represents the difference between the implicit numerical solution to Planck's law and Wien's approximation. The range of each x-axis in each plot is identical to the ones shown in D) and E).....	143
Figure 6-1: Crystal structure of graphite. A) primitive unit cell; B) carbon Frenkel pair introduced in unit cell; C) Left: top down view of a defect free primitive (perfect) unit cell (c direction points out of the viewing plane); C) Right: possible interstitial positions (marked by solid red circles) in close proximity to the empty plane at $c = 0.5c_0$ shown via the 2-D hexagonal lattice (the dotted lines mark the primitive unit cell in 2-D). The interstitial positions have been assigned based on the work of Li et al. ¹³⁶	147
Figure 6-2: Spectral emissivity at a wavelength of 640 nm for fine grained polycrystalline graphite.	149
Figure 6-3: Measured specific heat capacity as a function of temperature for polycrystalline graphite, compared to the calculated specific heat capacity using equation (6-5). The literature data (green triangles and red rhombohedra) has been taken from Hay, et al. ¹³⁷ . The error bars on the blue data points correspond to two standard deviations and are equivalent to 15.2% relative error (for details on error analysis refer to Section 5.4).	152
Figure 6-4: Thermal conductivity of isotropic graphite as a function of temperature. Experimental data is compared to the model described in this work. The error bars on the blue data points correspond to two standard deviations and are equivalent to 19.4% relative error (for details on error analysis refer to Section 5.4).	156
Figure 6-5: Thermal diffusivity of isotropic graphite as a function of temperature. The error bars on the blue data points correspond to two standard deviations and are equivalent to 15% relative error (for details on error analysis refer to Section 5.4).....	157
Figure 7-1: Crystal structure of UO_2 : A) Perfect unit cell; B) Unit cell containing an oxygen Frenkel pair; C) Unit cell containing a Schottky trio (tri-vacancy defect); D) Unit cell containing a uranium Frenkel pair.....	162
Figure 7-2: Comparison of the partial pressures calculated via the Rand-Markin model and those predicted by FactSage ¹⁶⁷ at 1 bar ambient pressure. (A) Comparison of the relative errors of the 3 dominant vapour species; (B) Relative error of the total vapour pressure. The dotted red line represents 4% relative error and is intended for visual guidance.....	166

Figure 7-3: The heat loss dominance diagram for UO_2 calculated according to the equations described in sections 4.1.5, 4.1.10 and 4.1.11 of Chapter 4. The solid black lines indicate where the dominant heat flux loss transitions from one mechanism to another. The dotted red line indicates the melting point of the UO_2	167
Figure 7-4: X-ray diffraction spectra of four different UO_2 samples compared with the Rietveld refinement used for determining the respective lattice parameters. (A) UO_2 specimen subjected to a maximum temperature of 2780 K; (B) UO_2 specimen subjected to a maximum temperature of 2450 K; (C) UO_2 subjected to a maximum temperature of 2340 K; (D) UO_2 specimen held at room temperature (300 K).....	168
Figure 7-5: Temperature (left) vs. time and laser power (right) vs. time after subjecting a UO_2 sample to a laser pulse. Melting point has been identified from the thermal arrest observed upon cooling.....	170
Figure 7-6: Temperature vs. time graph (thermogram) recorded after applying a laser pulse to both sides of a UO_2 sample simultaneously (with optical fiber splitting of 50%) under 100 bar He. The small temperature vs. time graph (upper centre) shows a zoom-in of the thermogram indicating a plateau at 2960 K. The two SEM images (right) show the melting pool (the darker central region). The black dot surrounded by a black dotted circle (lower right) indicate the approximate pyrometer spot location and nominal spot size, respectively.	171
Figure 7-7: An example cooling curve for a 2mm thick UO_2 sample under He at 100 bar (recorded by switching off the laser, which was heating both sides of the disc shaped sample). Each number corresponds to a zoom-in of the respective region on the cooling curve indicated by black dotted lines. No observable arrest in temperature drop can be seen.....	172
Figure 7-8: (A) Specific heat vs. temperature measured in this work compared to Hiernaut et al. ¹⁷³ and Ronchi et al. ¹⁵⁹ ; (B) Thermal diffusivity vs. temperature measured in this work compared to Ronchi et al. ⁶⁵ ; (C) Thermal conductivity vs. temperature measured in this work compared to Ronchi et al. ⁶⁵ ; and (D) Spectral emissivity at 640 nm vs. temperature measured in this work compared to Bober et al. ¹⁶²	174
Figure 7-9: Phonon density of states (PDOS or DOS) vs. frequency - comparison between the proposed model for the phonon density of states and the experimental data of Dolling et al. ¹⁷⁵	176
Figure 7-10: Convergence scheme for defect concentration calculations following from equations (7-9) to (7-12).	178
Figure 7-11: Matrix plot of defect type vs. concentration, specific heat contribution and enthalpies of formation as a function of temperature. Each column of the matrix plot represents a defect type (graphs A, D, G – Frenkel pairs; graphs B, E, H – Schottky trios, graphs C, F, I – polaron pairs). The implicit solution is compared to the explicit approximation of equations (7-9) to (7-11).....	181

Figure 7-12: (A) Oxygen Frenkel pair concentration vs. temperature. The model output is compared to the measured data of Hutchings et al. ¹⁸¹ ; (B) Arrhenius plot of A.....	182
Figure 7-13: (A) Specific heat capacity vs. temperature comparing the experimental results obtained in this work with the model output and fit to literature data. Red dashed lines denote a 95% confidence range based on Fink's function. (B) Enthalpy increment vs. temperature comparing the model output to the experimental data collected by Fink ¹⁵⁸	183
Figure 7-14: Model prediction for certain dimensional properties of UO ₂ as a function of temperature. Each graph shows the lattice contribution to the particular property as well as the combined contributions of the lattice and defect terms: (A) Volumetric thermal expansion coefficient as a function of temperature; (B) Theoretical density as a function of temperature; (C) Lattice parameter as a function of temperature; (D) Thermal expansion vs. temperature. The model results are compared to available experimental data ^{187,188}	184
Figure 7-15: Plot of electrical conductivity vs. temperature. (A) the model proposed in this work compared to experimental data ^{190,191} and various fits to the respective literature data ^{65,117,190} ; (B) the contributions to electrical conductivity based on the dominant defect species and their concentrations estimated in this work; (C) Arrhenius plot of A; (D) Arrhenius plot of B.....	186
Figure 7-16: Thermal conductivity vs. temperature. (A) the experimental data measured in this work compared with the proposed model and established literature fits ^{65,132} . (B) lattice and electronic contributions to thermal conductivity estimated via the model proposed in this work compared with the estimates from fits reported in the literature ^{65,132} . The 95% confidence interval is obtained from a polynomial fit to the absolute residual difference between all reported data by Fink ¹³² and the suggested fit by the same author. The acronym τ_{SP} stands for the spin – phonon scattering relaxation time.....	187
Figure 7-17: A plot of thermal diffusivity vs. temperature, comparing experimental data from this work with the model output and the literature fit proposed by Ronchi et al. ⁶⁵	189
Figure 8-1: Comparison of the partial pressures calculated via the Rand-Markin model and those predicted by FactSage ¹⁶⁷ at 1 bar ambient pressure. (A) comparison of the relative errors of the 3 dominant vapour species (B) the relative error of the total vapour pressure.....	201
Figure 8-2: The heat loss dominance diagram for ThO ₂ calculated according to the methodology in sections 4.1.5, 4.1.10 and 4.1.11 of Chapter 4. The solid black lines indicate where the dominant heat flux loss transitions from one mechanism to another. The dotted red line represents the melting point of the material.	202
Figure 8-3: X-ray diffraction spectra of three different ThO ₂ samples compared with the Rietveld refinement used for determining the respective lattice parameters. (A) ThO ₂ specimen subjected to a maximum temperature of 2500 K; (B) ThO ₂ specimen	

held at room temperature (300 K); (C) ThO ₂ specimen subjected to a maximum temperature of 3000 K.	204
Figure 8-4: (A) Temperature vs. truncated time showing the melting plateau of ThO ₂ ; the melting point is indicated via a solid red line; SEM image of the melting pool presented above the red dashed line. Red dashed lines indicate the confidence limits of the measured melting point. (B) Temperature vs. truncated time plots for two thermograms measured in this work compared to the thermogram reported by Ronchi et al. ²⁰⁹	205
Figure 8-5: Specific heat evaluated in this work compared to the measurements of Dash, et al. ²⁰⁷ , Banerjee, et al. ²⁰⁸ , Ralph, et al. ²¹⁰ and Ronchi, et al. ²⁰⁹ . The blue line is the recommended curve by Konings, et al. ²²¹ , based on the derivative of a fit to enthalpy data collected from literature.	206
Figure 8-6: Spectral emissivity at 645 nm and total hemispherical emissivity as a function of temperature measured in this work. Spectral emissivity is compared to the measurements by Ronchi, et al. ²⁰⁹ at 960 nm. The solid and dashed lines are fitted to the data in this work for guidance.....	207
Figure 8-7: Thermal conductivity as a function of temperature for ThO ₂ corrected to 95% TD. Measurements in this work compared to the data of Murabayashi ²¹² , Cozzo et al. ²¹¹ , Murti et al. ²²³ , Jain et al. ²²⁴ , Pillai et al. ²²² and Weilbacher ²¹³	209
Figure 8-8: Thermal diffusivity as a function of temperature measured in this work compared to the experimental measurements of Murabayashi ²¹² , Cozzo et al. ²¹¹ , Murti et al. ²²³ , Jain et al. ²²⁴ , Pillai et al. and, Weilbacher ²¹³	210
Figure 8-9: Phonon density of states (PDOS) vs. frequency - comparison between the proposed model for the phonon density of states and the DFT data of Wang et al. ²²⁵	212
Figure 8-10: Plot of defect type (the title of each column) vs. the respective concentrations, excess specific heat and formation enthalpies. (A), (C), (E) represent the temperature dependent concentration, excess specific heat and formation enthalpy of oxygen Frenkel pairs respectively, while (B), (D), (F) show the temperature dependent concentration, excess specific heat and formation enthalpy of Schottky trios.	214
Figure 8-11: (A) Measurements of specific heat as a function of temperature compared to the model results and the fit recommended by Konings et al. ²²¹ (B) Enthalpy increment data collected by Fink ²²⁹ compared to the model output.....	216
Figure 8-12: Experimental and model results for dimensional property parameters of ThO ₂ as a function of temperature. (A) Volumetric thermal expansion coefficient as a function of temperature; (B) Theoretical density as a function of temperature; (C) Lattice parameter as a function of temperature and (D) Thermal expansion vs. temperature. The model results have been compared to available experimental data ¹⁹⁶ and the recommended correlation ²¹⁷ . The dashed black lines show only the lattice contribution to thermal expansion, while the solid black lines represent the combined contributions of lattice and defects.....	217

Figure 8-13: Schematic of the ThO ₂ band gap free of defects (left) and the possible donor (1) or acceptor energy levels (2) (right). E_{CB} is the energy of the conduction band edge, E_{VB} is the valence band edge energy, while E_A and E_D are the possible acceptor and donor energy levels, respectively.	219
Figure 8-14: (A) Thermal conductivity as a function of temperature measured in this work compared to: the experimental data of Murabayashi ²¹² , Cozzo et al. ²¹¹ , Murti et al. ²²³ , Jain et al. ²²⁴ , Pillai et al. ²²² , Weilbacher ²¹³ , the current model results and the fit proposed in this work; (B) The lattice term of thermal conductivity calculated by the model compared to the lattice and electronic terms obtained from the fit.	221
Figure 8-15: Total hemispherical emissivity measured in this work plotted together with the experimental results of Pirani ²³⁹ , the measurements by Sully et al. ²³⁸ and the semi-empirical model proposed in this work. The red dashed lines represent the indicative 95% confidence intervals of the model calculation.....	224
Figure 10-1: Comparison of the recommended fits of thermal conductivity of UO ₂ and ThO ₂ from 500 K up to melting point. The UO ₂ curve is plotted based on the study of Fink ¹³² , while the ThO ₂ curve as well as both melting points are recommended based on the current work.....	252

List of Tables

Table 1-1: Summary of some of the core components corresponding to different reactor types, currently or previously in operation.....	31
Table 2-1: Summary of techniques for measuring thermo-physical properties. GHP – guarded hot plate; HW – hot wire; RM – radial method; DEH – direct electrical heating; AC – adiabatic calorimetry; DC – drop calorimetry; DSC – differential scanning calorimetry; LF – laser flash; WM – wave method; LP – laser polarimetry; BBC – black body cavity; ISR – integrating sphere reflectometry; MWP – multi-wavelength pyrometry; CM – comparative method; LH – laser heating; IFH – inductive furnace heating. N/L – no limit.	55
Table 4-1: A comparison between the calculated properties (thermal conductivity (k) and specific heat (c_p)) using the calibrated and top hat laser profiles at pressure $p = 0.4$ MPa. Furthermore, results are compared to the values obtained by Hay et al. ⁸⁵	106
Table 4-2: Comparison of the effect of noise filtering for a thermogram at temperature $T = 2219$ K and pressure $p = 0.4$ MPa. The examined parameters include: the fitted properties (thermal conductivity and specific heat capacity); signal to noise ratio (SNR); computational time (t_{comp}) for a single core processor of 2.6 GHz frequency and RAM (random-access memory) 8 GB.....	107
Table 5-1: Correlation matrix for the possible fitting parameters for the rear central thermogram.....	123
Table 5-2: Comparison of the evaluated and exact properties using synthetic thermograms (computed using the properties of 95% dense UO_2 reported by Fink ¹³²) and the isothermal approximation for the central radial location.....	128
Table 5-3: Comparison of the relative standard deviation (RSD) and the coefficient of determination (R^2) for the output of each approximation.	130
Table 5-4: Comparison of evaluated and reference properties for UO_2 at 1562 K and isostatically pressed graphite at 1536 K.	134
Table 5-5: Summary of the output uncertainty of specific heat (Δc_F), thermal conductivity (Δk) and thermal diffusivity ($\Delta \alpha$) for a thermogram at temperature $T = 2050$ K and at a pressure $p = 0.4$ MPa.	140
Table 6-1: Material properties of isostatically pressed graphite (measured at 0.1 MPa).....	148
Table 6-2: Summary of the measured graphite sample characteristics and laser beam parameters.	148
Table 6-3: Summary of parameters used in the specific heat capacity and thermal conductivity models.	155

Table 7-1: Summary of UO ₂ sample characteristics and laser beam parameters.....	163
Table 7-2: Material properties of UO ₂ used as input in the FEA model.	164
Table 7-3: Summary of standard formation enthalpies and entropies. The subscript corresponds to the respective reaction number in equations (7-1) to (7-5).....	165
Table 7-4: Lattice parameter of UO ₂ (derived from refined XRD spectra in Figure 7-4) for different exposure temperatures. The uncertainty on the lattice parameter has been approximated to be of the order of $\pm 0.001 \text{ \AA}$ (95% confidence interval).....	169
Table 7-5: Summary of input parameters for PDOS model.....	176
Table 7-6: Summary of input parameters for the defect concentration calculation. All parameters are expressed per molecule of UO ₂	179
Table 7-7: Summary of input parameters for the calculation of thermal and electrical conductivity.	190
Table 8-1: Summary of ThO ₂ sample characteristics and laser beam parameters.....	199
Table 8-2: Material properties of ThO ₂ used as input in the FEA model.	199
Table 8-3: Summary of standard formation enthalpies and entropies. The subscript corresponds to the respective reaction number in equations (8-2) to (8-6).....	201
Table 8-4: Lattice parameter of ThO ₂ (derived from refined XRD spectra in Figure 8-3) for different exposure temperatures. The uncertainty on the lattice parameter has been approximated to be of the order of $\pm 0.001 \text{ \AA}$ (95% confidence interval).....	204
Table 8-5: Summary of input parameters for the phonon density of states model.....	211
Table 8-6: Summary of input parameters for the defect concentration calculation.....	214
Table 8-7: Summary of input parameters for the calculation of thermal conductivity of ThO ₂	222

Chapter 1 : Introduction

- *“Perplexity is the beginning of knowledge.”* -

Khalil Gibran, poet

This chapter begins by introducing the reader to the underlying mechanisms enabling nuclear fission reactors. Various reactor designs are briefly outlined and compared. This leads on to the description of four significant nuclear accidents and the rise of accident tolerant fuels (ATF). Finally, the goal of the current work is stated, which is directly linked to nuclear accident scenarios and hence to improving the safety of nuclear fission reactors.

1.1 From nuclear fission to power generation

Nuclear fission is the underlying mechanism which drives conventional nuclear power stations to produce heat and hence electricity. The enormous energy density of this process is one of the main reasons for the development of nuclear reactors. The amount of energy which can be extracted from 1kg of U-235 is 2 to 3 million times greater than the amount of energy, which can be harvested from the same amount of oil, gas or coal¹.

Nature has enabled nuclear fission by creating elements of different binding energies per nucleon. When a heavy element is bombarded with neutrons it can split into two lighter elements (Figure 1-1A). These lighter elements (with higher atomic mass than Fe^{56}) have larger binding energies per nucleon compared to the original heavy isotope (see Figure 1-1B). Hence, such a nuclear splitting or fission reaction yields a positive net binding energy per nucleon (products minus reactants), which corresponds to an energy release.

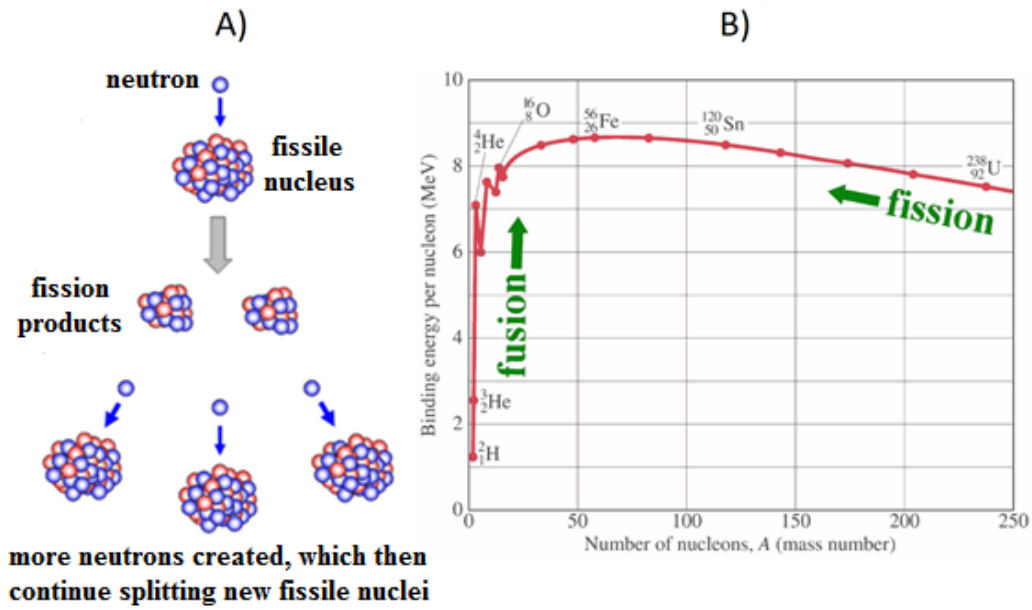


Figure 1-1: A) Schematic of the fission chain reaction; B) Graph of the binding energy per nucleon (MeV) as a function of element atomic mass (Courtesy of the educational publisher Pearson Prentice Hall).

In order to sustain a nuclear fission chain reaction (Figure 1-1A), it is necessary that the heavy element material is fissile (can sustain a fission reaction via thermal neutrons) and that the average number of neutrons released by the splitting of the heavy atom must be greater than 1. From an engineering viewpoint, this number has to be often greater than 2, since various loss mechanisms (e.g. neutron absorption by reactor structural materials or fertile fission products) are responsible for neutron leakage.

In order to controllably harness the tremendous amount of energy locked in fissile materials, nuclear reactors are required. Various reactor designs exist, which are summarised in the following section. An example of the currently most widely adopted design is the pressurized water reactor (PWR). A schematic of a PWR power station is shown in Figure 1-2. Different reactor designs require different power plant features, however certain

concepts related to the operation and functionality of the power plant tend to be common. The fissile material or fuel can be in metallic, ceramic or salt form (the latter in a liquid state). The nuclear fuel (in the case of the metallic or ceramic type) is typically encapsulated in a metallic shell (cladding) and is located in the reactor core. In order to control the nuclear reaction, control rods are inserted (e.g. dropped) or mechanically extracted from the core. These are made of neutron absorbing materials (e.g. Ag-In-Cd alloys or boron carbide encapsulated in metallic cladding²), which when inserted in the core, decrease the average number of neutrons available per fission event. Other reaction control mechanisms are also available, such as the injection of boric acid within the reactor core coolant (in the case of PWRs). The heat produced by the fuel is extracted via a coolant; in most reactors the coolant is water, however it can also be a gas, liquid metal or a molten salt. The reactor core and coolant are placed in a steel pressure vessel, which is connected via an inlet and outlet leg to a heat exchanger. The resulting circuit is called the primary loop.

The primary loop in a PWR is then passed through a heat exchanger. The heat transferred through the heat exchanger is used to convert water into steam in the secondary loop of a PWR power plant. The hot water vapour drives a turbine, cools down, condenses within the condenser and then is pumped back into the heat exchanger. Finally, the turbine is connected to a generator. The generated electricity is passed through a transformer and then transmitted via an electrical grid to the end customers (households, industry, etc.).

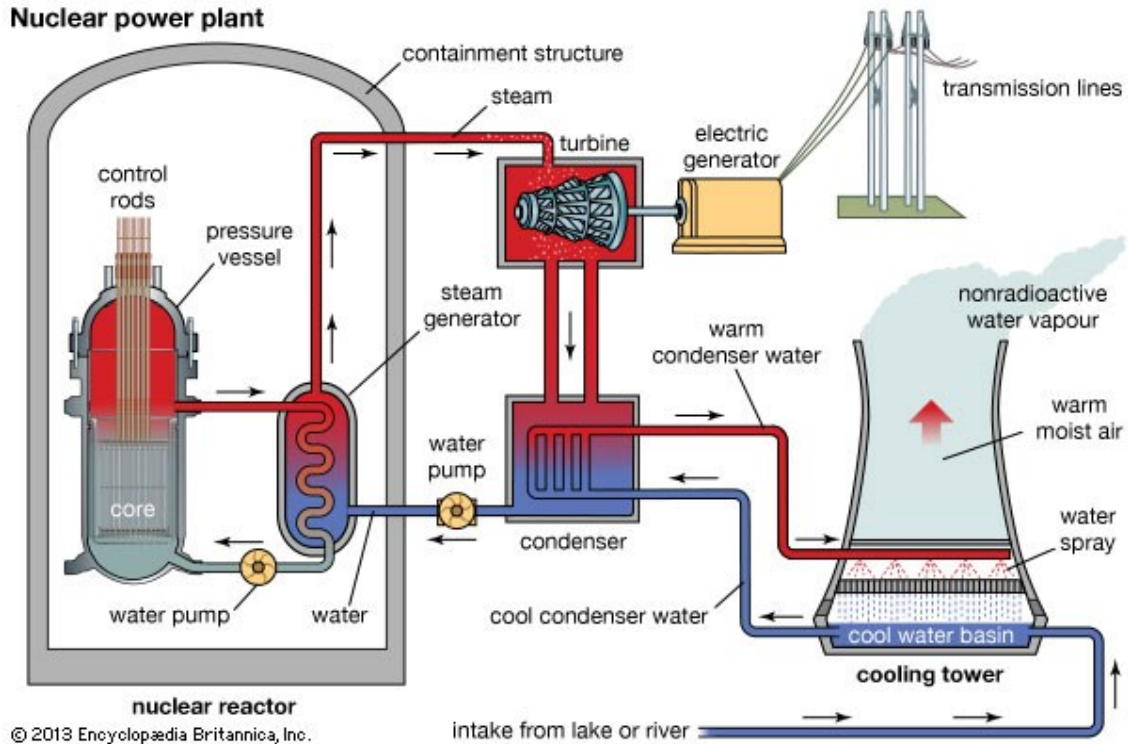


Figure 1-2: Schematic of a pressurized water reactor power plant and associated machinery and equipment involved during the electricity generation process³.

1.2 Brief history of nuclear reactor design and the evolution of concepts

In the 1950s the promise of nuclear energy solving the energy needs of the human race was put to the test. In 1951 the first reactor to produce electricity was commissioned and its name was the Experimental Breeder Reactor (EBR-I)⁴. This reactor served as the proof of concept generating nuclear energy in a controlled manner and producing electricity from it. Even though the EBR-I could only power as few as four light bulbs, it was a breakthrough which led to the first generation of reactors⁵. These marked the beginning of the boiling water reactor (BWR) series (Dresden – I, 1959), the pressurized water reactor

(PWR) series (Shippingport, 1957) and the gas-cooled reactor designs (Calder Hall, 1956), which were capable of producing several 10s of MW electrical power.

The pursuit of economies of scale led to further developing these concepts into reactors supplying 100s of MW electrical power to electrical grids around the world (Generation II).

The PWR technology was developed by the US navy, initially for propelling nuclear submarines and later adapted for civilian electricity generation. The BWR reactor concept was developed by researchers at Argonne National Laboratory in the USA. In the meantime the Soviet Union developed their own variation of the PWR with hexagonally arranged fuel bundles and horizontal heat generators and named their design Vodo-Vodyanoi Energetichesky Reaktor (VVER or Water-Water Power Reactor). Furthermore, they also deployed the graphite moderated, water cooled 'Reaktor Bolshoy Moshchnosti Kanalnyy (RBMK)' reactor design. The United Kingdom continued investing in a new fleet of gas cooled reactors, known as the Advanced Gas-cooled Reactors (AGR). These promised commercial competitiveness, due to high operating temperatures (i.e. higher efficiency) and the possibility of online refueling, which proved problematic due to severe turbulences within the reactor pressure vessel. France initially followed a programme similar to the British one, however eventually shifted to PWR designs. Canada developed the Canada Deuterium Uranium (CANDU) design, which operates using pressure tubes with fuel bundles instead of a pressure vessel, heavy water as moderator and coolant and natural uranium fuel. The CANDU design was largely motivated by Canada not having access to the enrichment technology needed in some of the other designs as well as a lack of industry experience and capability in producing large pressure vessels.

In the mid-1990s a new generation of nuclear reactors was conceived – Generation III. These new series of reactor concepts offered improved safety, greater thermal efficiency, longer operational life and use of advanced fuel materials. Westinghouse shifted from active safety to passive safety in their advanced PWRs or AP reactors, relying on natural processes to cool the reactor building and vessel in the case of an accident. In the meantime AREVA developed the European Pressurized Water Reactor (EPR) introducing 300% redundancies (four independent cooling systems, each of which capable of extracting residual decay heat after reactor shutdown) and a corium catcher (corium is the term used for the mixture of molten fuel and cladding in the event of a reactor meltdown) for severe accidents involving core meltdown. The final commercialised generation III design was the Advanced Boiling Water Reactor (ABWR). Improvements include integrated water pumps inside the reactor pressure vessel for improved water recirculation performance and an improved emergency cooling system.

Since the early 2000s, research programmes have explored the viability of 6 reactor concepts as part of the Generation IV initiative. These include the molten salt reactor (MSR), sodium-cooled fast reactor (SFR), lead-cooled fast reactor (LFR), gas-cooled fast reactor (GFR), very high temperature reactor (VHTR) and super critical water reactor (SCWR). Some of the aims of these evolutionary designs are to reduce the life of radioactive waste from hundreds of thousands of years to centuries, increase the energy yield per unit mass of nuclear fuel, introduce additional safety features (e.g. low or near ambient pressure in reactor pressure vessel for LFR, SFR and MSR) and capability of deploying a wider range of fuel types. A timeline of the discussed reactor evolution is presented in Figure 1-3, while

a comparison of some of the key structural components of different reactor types is shown in Table 1-1.

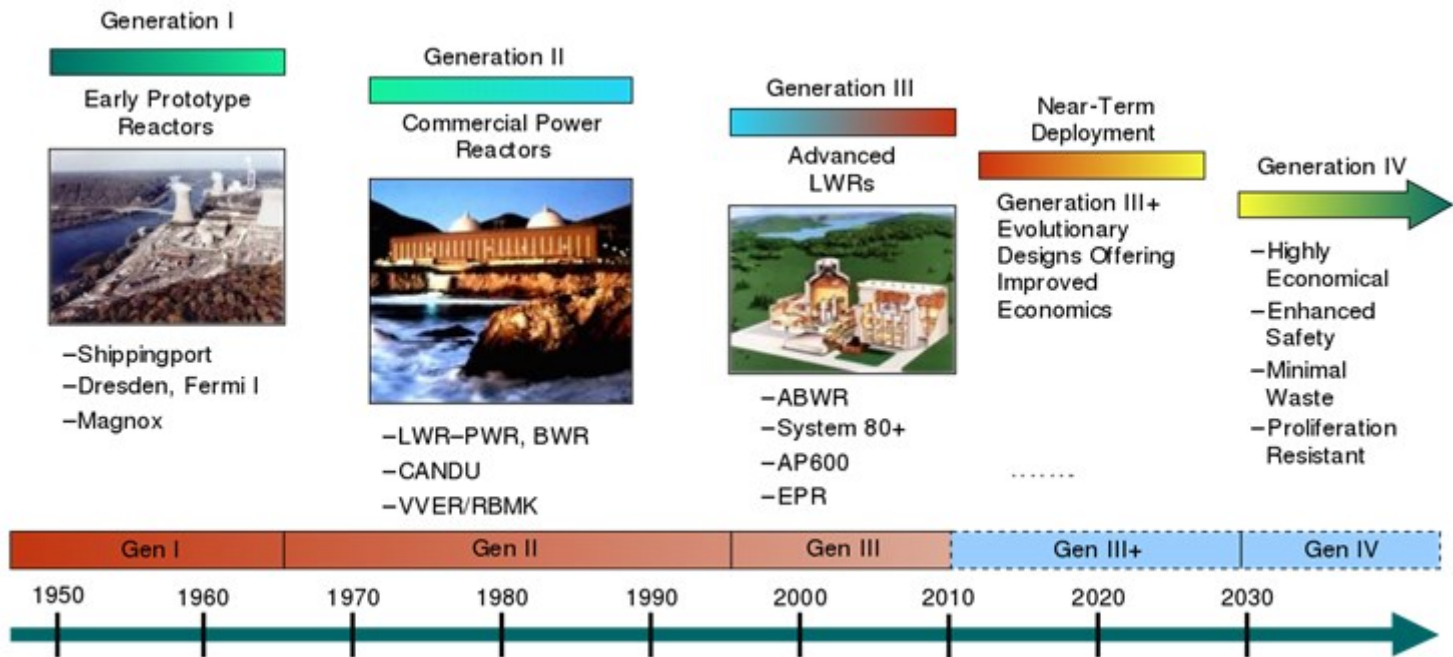


Figure 1-3: Timeline of the evolution of reactor design.⁶

Table 1-1: Summary of some of the core components corresponding to different reactor types, currently or previously in operation.

	PWR	BWR	Magnox	AGR	CANDU	FBR	VVER	RBMK
fuel	UO ₂ * / MOX ⁺	UO ₂ * / MOX ⁺	UO ₂	UO ₂ *	UO ₂	U ²³⁵ alloy* (seed) UO ₂ (blanket)	UO ₂ *	UO ₂
cladding	Zircalloy	Zircalloy	Mg-Al alloy	Steel	Zr-2.5 Nb alloy	Zr alloy	Zr alloy	Zr alloy
moderator	water	water	graphite	graphite	heavy water	none	water	graphite
coolant	water	water	CO ₂ gas	CO ₂ gas	heavy water	liquid metal	water	water

* enrichment with fissile isotopes required

⁺ MOX – mixed oxide fuel (i.e. (U,Pu)O₂)

1.3 Nuclear accidents and the birth of Accident Tolerant Fuel (ATF) concepts

By now it has become evident that nuclear safety has always been of paramount importance in the history of nuclear engineering design. This has been greatly influenced by the occurrence of severe nuclear accidents, some of which can be considered as tragic catastrophes⁷. There are four major nuclear accidents, which have changed our perception of nuclear power plant safety – Windscale, Three Mile Island (TMI), Chernobyl and Fukushima.

On October 10th 1957, the first major nuclear power plant accident occurred at the Windscale nuclear facility in Sellafield, UK^{8,9}. The operators had ordered a Wigner release (the process of annealing graphite, in which metastable radiation induced defects are relaxed to their original low energy states and heat is released controllably across the material; the core stabilises as a result). Unexpectedly this procedure led to an increase of the core temperature in some fuel channels. Attempts of cooling the reactor were made by increasing the rate of air flow through the core, however instead of decreasing, the reactor temperature continued to increase. Parts of the reactor core (i.e. certain fuel canisters and surrounding graphite moderator) had caught fire and significant amounts of radioactive species began to escape through the reactor building chimney. After failed attempts of using liquid CO₂ to extinguish the fire, finally by pumping water through the core and by shutting off all air supply feeding

the flames, the reactor was successfully cooled down. The significant release of radioactive species in the environment has made this nuclear accident the worst in UK history.

More than two decades after the Windscale fire, another series of events led to the Three Mile Island accident¹⁰. On March 28th 1979 the TMI-2 reactor was shut down. However, a pressure relief valve had failed to close and since there was no instrumentation mounted to check the actual position of the valve, the operators were unaware of it. This led to depressurization of the reactor pressure vessel (RPV) and resulted in boiling of the water coolant. As water was being lost, high pressure pumps injected water into the pressurizer. The misled operators were convinced the pressurizer was full as a result of a too high coolant quantity in the reactor pressure vessel. Hence, they reduced the flow of water into the RPV and sped up the loss of coolant. The core was uncovered and severely damaged as a result of the progressively higher temperatures. Hours into the accident, the erroneously open valve was spotted and closed. However, the re-flooding of the RPV was obstructed by the generated steam. Until the cooling was fully re-established, the core had already partially melted and radioactivity had been released to the reactor building, but only relatively small amounts of inert gases escaped into the environment.

Less than a decade after TMI, the world experienced, what many consider, the greatest and most tragic nuclear accident of our time¹¹. On April 26th 1986 near Pripjat, Ukraine the Chernobyl power plant was stabilised at low power with most

control rods fully extracted from the core and a low void percentage in the coolant voids under a high coolant flow¹². The reactor was, then, subjected to a turbine trip stress test. The recirculation pumps of the reactor were switched off. As a result the reactor coolant heated up and the void content in the coolant began to increase. The positive temperature coefficient of reactivity (dominated by the large void coefficient inherent to the RBMK reactor design when operated at lower powers and hence reactivity coefficient increases as water boils) led to the fuel heating up, which led to a further reactivity increase. As a result the power of the reactor increased almost instantaneously and led to a reactivity initiated accident. A steam explosion followed as a result of direct interaction of fuel particles or melt with superheated water droplets. This destroyed the reactor building and led to the release of tremendous amounts of radioactive species into the environment in the weeks following the explosion. This accident is considered to be the worst amongst all nuclear power plant disasters.

In the subsequent decades nuclear energy regained public confidence and the industry's prospects seemed to be improving at an accelerated rate globally. This positive outlook was halted on March 11th, 2011. One of the strongest earthquakes ever recorded struck near the east coast of Japan close to the Fukushima Daiichi nuclear power plant¹³. Reportedly, all reactors on site survived the primary tremor without experiencing any significant damage. The problems began less than an hour later, once a tsunami wave, more than 14 m in height, hit the plant¹⁴. All emergency

generators were drowned and became dysfunctional, disabling the reactor core recirculation pumps. Sea water pumps were also damaged, which obstructed heat removal through the condensers. As a result of these events and other failed procedures, decay heat accumulated in units 1-3, boiling off the vital coolant and hence uncovering and accelerating the heating of the reactor core. The high temperatures provided the driving force for the conversion of steam to hydrogen and zirconium dioxide via an exothermic reaction on the surface of the zirconium cladding. This had two abrupt consequences – hydrogen accumulation leading to explosions and a temperature increase accelerated by the exothermic nature of the reaction. As a result all three units experienced a melt-down and significant releases of radioactive material into the environment.

Each of these accidents have identified specific issues related to nuclear power plant safety. As a result power plant design and safety culture have been continuously improving over time. However, after the Fukushima accident it became evident that a different approach to safety was needed - an approach, which did not only provide measures to deal with an emergency situation, once it has occurred, but one that would help prevent or at least significantly retard the devastating effects of a severe accident scenario. This new approach arrived in the form of novel nuclear fuel and cladding concepts, named as Accident Tolerant Fuel (ATF)^{15,16}. These aim to provide longer coping time (elapsed time prior to an irrecoverable fuel and cladding distortion); higher fission product retention capabilities, both during accident and

operating conditions; elimination of adverse fuel/cladding side effects (e.g. hydrogen production on the Zr alloy surface). In order to select the best possible concept, it is thus paramount to examine all related material properties (mechanical, chemical, microstructural, thermo-physical, etc.) not only up to operating temperatures, but also beyond, in a temperature range representative of an accident scenario.

1.4 Project goal

It is clear by now that the nuclear industry aims to be able to prevent or at least contain nuclear accidents. Hence, major research efforts are dedicated towards an improved understanding of the accident conditions and as a result a greater ability to predict accident scenarios. The prediction of the fuel's behaviour during off-normal conditions is particularly fundamental, as the fuel matrix comprises the first barrier to the release of radioactive substances. However, a cornerstone for being able to predict the fuel performance during accidents are the material properties. Most of the thermo-physical properties of the fuel are relatively well known up to 1500 K, as there are numerous appropriate measurement techniques for their determination (further elaborated in Chapter 2). The aim of this study will be, however, to increase the availability and improve the quality of measurements of high temperature thermo-physical properties, where few techniques and hence, measurements are available. The measured properties include thermal conductivity, specific heat, thermal diffusivity, melting point spectral and total hemispherical emissivity. Hence,

the current work's goal is threefold: i) development and testing of a new experimental methodology for the measurement of the aforementioned properties above 1500 K (described in Chapter 4 and Chapter 5); ii) application of the new methodology by measuring the previously stated properties for three nuclear materials - graphite, UO_2 and ThO_2 (presented in Chapter 6, Chapter 7 and Chapter 8, respectively); iii) discussion of the underlying mechanisms in terms of new and established condensed matter physics (introduced in Chapter 3 and applied in Chapter 6, Chapter 7 and Chapter 8).

Chapter 2 : Techniques for measuring material thermo-physical properties

– *“It is in literature that the concrete outlook of
humanity receives its expression.”* –

Alfred North Whitehead, mathematician

In the framework of nuclear accident conditions and the experimental determination of thermo-physical properties of nuclear materials at elevated temperatures (up to melting), it is vital to determine which technique or techniques are suited for measurements at such extreme temperatures. In this chapter various techniques for the determination of thermal conductivity, thermal diffusivity, specific heat capacity, emissivity and melting point are reviewed. Their principles are briefly explained, however the review is focused on the critical assessment of the applicability and limitations of each technique. Finally, the laser flash method is reviewed in greater details, as it is the basis for the newly developed methodology introduced in this work.

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2.1 Comparison of techniques

This review compares the available experimental techniques for the measurement of five thermo-physical properties – thermal conductivity, specific heat, thermal diffusivity, spectral emissivity and melting point. The determination of these properties is of immense importance not only for the nuclear industry^{17,18} but also in other material science applications – for example aerospace¹⁹, heat engines²⁰ and civil engineering²¹.

2.1.1 Thermal conductivity

Thermal conductivity describes the ratio between the rate of thermal energy flowing through a material per unit area and the temperature gradient normal to that area. Various techniques exist for the determination of thermal conductivity – guarded hot plate²², hot-wire technique²³, radial method²⁴ and direct electrical heating method²⁵.

The guarded hot plate (GHP) method is a steady-state technique. The sample is subjected to an isothermal boundary on one side and controlled surface heat flux on the opposite side. The temperature increase on the side of the heater is also monitored. Based on these temperature measurements and Fourier's law, the thermal conductivity of the sample can be obtained. The main advantages of this method is its simple design and accuracy at low temperatures²⁶. Among some of the disadvantages are big sample sizes and long equilibration time²⁷. It is also limited to

temperatures generally below 1400 K²⁶, given errors due to heat losses at higher temperatures²⁸.

The hot wire (HW) technique utilises a wire source to heat a block of material. The wire is of a known thermal conductivity and is machined into a hole in the middle of a sample material of unknown thermal conductivity. Two thermocouples are also placed inside the sample (in solid samples holes are machined for the thermocouples), which measure the temperature, as a function of time, at two radial positions. From the linear heat rating and the respective transient temperature response measured by the thermocouples, the thermal conductivity of the sample can be calculated. Among the method's strengths are its wide applicability to gases, liquids as well as solids²⁹, but also relatively short measurement times compared to steady state methods. Common limitations include: thermal resistance at the wire-sample interface^{30,31}, capacity effects of the wire (whereby high thermal inertia per unit length of the wire can lead to relatively long measurement times^{30,31}), finite sample geometry (the analytical solution assumes an infinite medium³²) and necessity for relatively long samples in order to minimise axial heat transfer (most solutions assume purely radial transfer of heat)^{32,33}.

The radial method (RM) can be thought of as a steady state version of the hot-wire method. Based on the linear heat rating of the wire source, the temperatures and respective positions of two thermocouples placed along the sample radius, the thermal

conductivity can be evaluated²⁴. The advantages of this technique are its diverse applicability to solids, liquids and gases³⁴, and high temperature capability. However, radial methods require relatively large samples, long equilibration times and are prone to increasing uncertainty with increasing temperature, due to radiative heat losses³⁵.

An important application of the RM can be found inside nuclear fuel in nuclear test reactors (however, the linear heat rating is a consequence of fission rather than wire heat source). Thermal conductivity can be measured during reactor operation via in-pile methods. The advantage of steady-state in-pile methods is the direct determination and surveillance of this nuclear fuel property under real reactor conditions, incorporating the thermal conductivity degradation, due to radiation damage, composition variations and microstructural changes. Due to the high radiation dose produced by nuclear fuel this method is amongst the very few available options for the direct determination of the fuel's thermal conductivity³⁶. Among the main limitations are errors due to the calculation of an effective thermal conductivity, averaged over a significant temperature range, and errors due to fuel composition variation, microstructural phenomena and most notably due to variations and uncertainties associated with the fuel-cladding gap³⁷. Other limitations can arise from uncertainty in the thermocouple position, limited temperature range (< 1900 K), uncertainty in the thermal resistance between the thermocouple and the surrounding fuel¹⁹ and de-calibration due to irradiation^{38,39}.

The direct electrical heating (DEH) method, also known as the Kohlrausch method²⁵ passes current through a wire shaped sample in order to heat up the specimen. Thermocouples measure the temperature and potential difference at various axial positions along the wire. From these measured quantities, one can calculate the product of electrical resistivity and thermal conductivity⁴⁰. Additionally, the electrical resistivity can be evaluated separately from the heating current and voltage drop along the length of the wire. The advantages of this technique include facilitating measurements at high temperatures and relatively good precision (5-8%)⁴¹. However, this technique is generally limited to good electrical conductors^{41,42}. Another limitation is the assumption of constant electrical resistivity, which for many materials is temperature dependent.

2.1.2 Specific heat capacity

The specific heat capacity describes the amount of energy required to raise one unit of material mass by one unit of temperature. Hence, making it an equivalently important property for high temperature applications, similar to the ones stated above. Current measurement techniques include adiabatic calorimetry, drop calorimetry⁴³, differential scanning calorimetry⁴⁴ and direct electrical heating⁴⁵.

Adiabatic calorimetry (AC) measures the temperature change in the system (furnace and specimen) due to a measured heat flow. Based on these quantities and the measured mass of the specimen, the specific heat can be obtained. The advantages

of this method are its high degree of accuracy ($<0.2\%$) in the temperature range 100 K – 800 K^{46,47} and low temperature measurement capability (down to 2 K)^{48,49}. The main limitations are deteriorating accuracy above 1000 K due to deviation from adiabatic conditions (a result of surging radiative heat losses)⁴⁷ and loss of precision at low temperatures due to thermometer insensitivity⁴⁸.

The drop calorimetry (DC) method is based on consecutive drops of reference material and sample material inside a furnace from room temperature to the furnace temperature. Once the sample/reference is dropped, an additional heat flux is supplied to bring the system back to the original furnace temperature. Based on the supplied energy, the heat capacity of the reference sample, the weights and molar masses of the two materials, one can calculate the sample's enthalpy increment and obtain a fit of enthalpy vs. temperature. The derivative of the fitted function yields the specific heat capacity⁴³. Alternatively, if the calorimeter is accurately calibrated for drops from particular temperatures, a reference sample is not needed⁵⁰. Among its strengths is its accuracy at lower temperatures and intermediate temperatures (470 - 1570 K)^{51,52} and its tested high temperature capability⁵³. Limitations include deteriorating accuracy with increase in temperature, relatively long equilibration times at high temperatures (20-30 minutes)⁵⁰ and possible sample contamination at elevated temperatures due to contact with capsules⁵⁰. Furthermore, uncertainties in the enthalpy increment data amplify and lead to larger relative uncertainties when

converted to specific heat capacity⁵⁴. Hence, the specific heat capacity is very sensitive to the type of fitted function and its confidence intervals.

Differential scanning calorimetry (DSC) measures the difference in the rate of heat supplied to a measured material and a reference required to keep the two samples at the same temperature. This is also known as power compensated DSC. From the measured heat flow rates (calibrated for equipment asymmetry) and scanning rate (inverse of heating rate) one can calculate the heat capacity⁵⁵. Alternatively, heat flux DSC subjects both sample and reference to a constant heat flux. From the measured temperature difference, measured heating rate, heat capacity of the reference and equipment related calibration constant, the heat capacity of the sample is obtained⁵⁶. Similarly to drop calorimetry, this technique provides accurate results for heat capacity in the temperature range 300 K to 1550 K⁵⁷. This method's main disadvantages are the need for precise calibration (e.g. to remove effects due to resistance and capacitance differences between sample and reference instrumentation)⁵⁸ and limited measurement temperature below 1900 K^{59,60}.

The direct electrical heating (DEH) method involves resistive heating of a wire shaped sample produced by a current supplied through the sample⁴⁵. By measuring the temperature of the sample, as well as the potential and current across the sample, one can determine the energy input and thus the heat capacity of the material. The high temperature capability and short measurement times are among the strengths

of this technique. The method is limited to conductive or semi-conductive materials (for materials with semi-conductive properties, a furnace pre- heating can be used to increase the sample's electrical resistivity. Then, the DEH method can be applied⁶¹). Furthermore, this method is based on the assumption of uniform heating and crudely approximates the effect of dominant radiative heat losses at high temperatures⁶².

2.1.3 Thermal diffusivity

Thermal diffusivity is linked to specific heat capacity and thermal conductivity. It represents the ratio between heat flowing out of a unit volume of a material and the heat per unit mass stored within this unit volume. Among the most common measurement techniques are the laser flash method⁶³ and wave methods⁶⁴.

The laser flash (LF) technique involves performing a laser pulse on one side of a sample and measuring the thermal response on the other side⁶³. Initially, the diffusivity was calculated from the half-time to maximum of the measured transient and the sample thickness. With the advancement of research in this field, models have been developed, improving the description of the physics of LF experiments. As a result of the increasing complexity of these models, an inverse problem needs to be solved – model data fitted to experimental data in order to obtain the optimal thermal diffusivity. The main advantages of the LF method are a relatively small sample size^{40,41}, high temperature capability (i.e. temperatures beyond the melting point of the material)⁴¹, absence of physical contact with heat source and short

measurement times⁴². The method can also be used to determine specific heat capacity from the pulse energy and thermal conductivity, based on the diffusivity, specific heat capacity and density of the sample. Amongst the technique's drawbacks is the difficulty in the quantitative determination of the heat losses due to radiation and convection^{40,43}. In particular, radiation becomes more important at higher temperatures⁴⁴. Other problems arise from finite pulse effects, whereby the pulse is too long in comparison to the characteristic time needed for the pulse to propagate through the thickness of the sample⁴³. Another issue can arise from non-uniform sample heating, whereby the spatial profile of the pulse energy is not homogeneous⁴⁵. The latter two errors can be overcome by introducing an optical fiber, which facilitates a nearly square shaped spatial laser beam power profile^{41,43}.

The wave method (WM) involves submitting a specimen to a sinusoidal heat flux on one side and measuring the temperature-time variation on the opposite side. The thermal diffusivity can be calculated either from the phase shift⁶⁴ between the temperature sinusoids on each side of the sample, or from the ratio of their amplitudes⁷⁰. The strengths of the method are in-situ reference for the measured diffusivity (due to multiple calculation paths using the same dataset), high temperature capability and contactless heating via electron⁷¹ or laser beams⁷². Furthermore, the method has been extended for evaluating thermal conductivity and specific heat capacity⁷³. The main limitations of the wave method are its sensitivity to the frequency of the modulated heat flux, sensitivity to heat losses and necessity

for well calibrated temperature measurement equipment⁷⁴, as well as a sensitivity to noise⁷².

2.1.4 Emissivity (spectral and total)

The emissivity of a material governs the radiant power that is radiated away from an object at a certain temperature, angle, wavelength and surface roughness. The spectral emissivity is of immense importance for precise calibrations of optical temperature measurement equipment (e.g. pyrometers), while knowledge of the total hemispherical emissivity is critical for determining radiative heat losses at high temperatures. The most common measurement techniques include laser polarimetry⁷⁵, black-body cavity⁷⁶, integrating sphere reflectometry⁷⁷, multi-wavelength pyrometry⁷⁸ and the comparative method⁷⁹.

Laser polarimetry (LP) involves measuring the polarization of light reflected off a materials surface. From the polarization state of incident and reflected light the refractive index and extinction coefficient, spectral emissivity can be calculated⁷⁵. The advantage of laser polarimetry is in not requiring a reference sample. The major drawbacks of this technique are the high sensitivity to surface topology and sample alignment^{76,80}.

The trough-hole or black-body cavity (BBC) technique relies on a thin and relatively deep hole machined in a material, which approximates the conditions within a black body cavity. The specimen is heated and two pyrometers measure the radiation

intensity in the hole as well as the intensity on the opposite side of the cavity. In theory the two measurement points have to correspond to approximately the same temperature in the sample and thus from the ratio of the intensities, at these two points, the emissivity at the pyrometer wavelength can be obtained⁷⁶. The method's main limitation is its sensitivity to temperature gradients in the sample along the displacement between the two measurement points. This could be particularly important for thermally insulating materials.

Integrating sphere reflectometry (ISR) employs an integrating sphere to measure the light reflected from a sample in all directions. This technique can be absolute or relative. The relative method relies on precisely characterised reference specimen so that, based on the ratio of the radiances of the reference and target samples, as well as the reflectivity of the reference, one can calculate the reflectivity of the sample. Furthermore, by assuming opacity, the emissivity can be obtained⁷⁷. The absolute method measures the radiant flux arising from the reflections in the presence of a sample and in the case when the sample is removed. Based on the ratio of these fluxes the sample reflectivity can be obtained. The strength of ISR is that the effect of surface roughness can be measured and hence the surface condition is not a prerequisite for the reliability of the method⁸¹. Problems may arise from the directional dependence of scattered light off the sample surface⁸², imperfect reflections off the sphere walls⁸¹, as well as the inequality between sample and reference test conditions

^{81,83}.

Multi-wavelength pyrometry (MWP) utilises radiance measurements from pyrometer channels at different wavelengths. Based on these measurements and an assumption about the functional dependence of emissivity with wavelength, the spectral emissivity can be calculated⁷⁸. This technique has been shown to give accurate results for certain metals⁸⁴. However, the main criticism towards this approach is the lack of physical basis for most functional forms, leading to non-uniqueness of the solution and thus large uncertainties in the emissivity results⁷⁸.

The comparative method (CM) compares the radiance of a sample to that of a blackbody at the same temperature. The ratio of those radiances, at a given wavelength, yields the spectral emissivity. The sample temperature is monitored via a thermocouple⁷⁹ and the radiance from the sample is measured via a multi-wavelength pyrometer. The advantage of this method is that it is exact and does not share most of the weaknesses of the previous methods. However, errors can arise from the inaccurate measurement of the specimen temperature⁸⁵. Furthermore, this technique has not been designed for temperatures higher than 1800 K.

2.1.5 Melting Point

The melting point marks a first order phase transition at a temperature where the solid material turns into liquid. The two main techniques for measuring high melting point materials are inductive furnace heating⁸⁶ and laser heating⁸⁷.

Inductive furnace heating (IFH) involves an encapsulated sample heated via induction until melting. The temperature is measured via a pyrometer along a black-body hole in the centre of the capsule. The method has shown to yield good results, however reactions between the studied material and the capsule material often occur which could compromise the accuracy and reliability of the results^{86,88}.

Laser heating (LH), as the name suggest, employs a laser in order to heat up the sample and measures the temperature via a pyrometer⁸⁹. The method has been improved by applying reflected signal analysis⁹⁰. The main strength of this approach is in-situ encapsulation limiting migration of material from or to the melting zone. Problems arise from the accurate determination of the emissivity, which could lead to uncertainties in the measured melting point⁹¹, which also scale with increasing measurement temperatures.

A comparative summary of all techniques and their practical limits is provided in Table 2-1. It is evident that few techniques are applicable at temperatures above 2000 K and even fewer exceed 3000 K. Table 2-1 suggests that the LF technique is a strong candidate for the measurement of high temperature thermo-physical properties. In addition LF also offers other significant benefits: 1) very short measurement time and thus limits possible sample instability – mass loss due to prolonged vapourisation, significant oxidation or reduction; 2) relatively small sample size; 3) wide applicability to conductive and non-conductive solids. The current study will also utilise another advantage of the LF technique: the possibility of

simultaneously determining specific heat, thermal diffusivity and thermal conductivity. These make the LF method well suited for testing nuclear fuel materials at temperatures representative of reactor accident conditions⁹². In particular the LF method can be used on a single specimen to obtain multiple thermo-physical properties, which can be very beneficial in the case of limited availability and quantity of irradiated nuclear materials.

2.2 Brief review of advancements in the laser flash method

The original method was developed by Parker⁶³, in which he used a flash lamp to produce a heat pulse traveling from the front to the rear surface of a specimen. By modelling the heat transfer conditions of the experiment, he was able to obtain an expression for thermal diffusivity. Parker's solution assumes: a) an instantaneous surface heat source; b) opaque sample; c) no heat losses and d) purely axial heat flow. Cowan's solution⁶⁸ introduced radiative heat losses, while Ronchi et al.¹⁸ and Baba et al.⁶⁹ introduced an optical fiber in order to homogenise the spatial profile of the laser beam. Ronchi et al.¹⁸ also considered the radial conduction of heat⁶⁵ and determined simultaneously thermal diffusivity, specific heat capacity and hence thermal conductivity by least squares fitting between model and experimental data. However, Ronchi et al.¹⁸ used the heat transfer coefficient, total emissivity and laser beam radius as possible fitting parameters, which they showed could lead to overfitting¹⁸. Furthermore, it was assumed that the spatial profile of the laser can be

represented by a top hat function, and whilst this is a good approximation and can be very representative in some more high quality LF units^{69,93}, it is not exact and can lead to significant uncertainties in lower quality LF setups. Finally, in their recent work, Salzar et al.⁹⁴ presented a model incorporating the volumetric heating effect present in semi-transparent materials.

In the context of high temperature measurements of thermal conductivity, heat capacity, thermal diffusivity, emissivity and melting point, the present study will introduce an improved LF set-up coupled with a novel numerical inverse method for the determination of these properties. The set-up offers the adoption of a spectropyrrometer for the estimation of spectral emissivity. The numerical model incorporates radial heat transfer, the heat losses due to convection, radiation and vapourisation. The inverse method allows simultaneous determination of the thermal conductivity and specific heat capacity at the measured temperature (measured via a pyrometer). Furthermore, an additional extension of model and inverse method is presented in this work. This involves determining an entire space dependent (along the radius of a pellet) and, hence, temperature dependent profile of a single property with a single measurement (via an infrared camera). The latter methodology could prove extremely valuable for examining the radial variation of thermal conductivity or specific heat along the radius of an irradiated fuel pellet. As a result of irradiation, the aforementioned properties could vary strongly along the radius of the fuel, due to compositional and microstructural changes – radiation damage⁹⁵, fission product

concentration⁹⁶, high burnup structure^{97,98}, formation of a pellet cladding interaction layer⁹⁹.

Chapter 2: Techniques for measuring material thermo-physical properties

Table 2-1: Summary of techniques for measuring thermo-physical properties. GHP – guarded hot plate; HW – hot wire; RM – radial method; DEH – direct electrical heating; AC – adiabatic calorimetry; DC – drop calorimetry; DSC – differential scanning calorimetry; LF – laser flash; WM – wave method; LP – laser polarimetry; BBC – black body cavity; ISR – integrating sphere reflectometry; MWP – multi-wavelength pyrometry; CM – comparative method; LH – laser heating; IFH – inductive furnace heating. N/L – no limit.

	Technique	Application limits								
		insulators	metals	gases	liquids	max. measurement temperature (K)	min. measurement time (s)	min. specimen size (m ³)	error range (%)	reference
thermal conductivity	GHP	✓	✓	X	X	1000	5e+03	4e-02	0.2 - 4	26-28
	HW	✓	X	✓	✓	2300	3e+02	1e-03	1 - 8	24,29-31
	RM	✓	✓	X	X	2300	1e+03	1e-03	2 - 12	24,34,36
	DEH	X	✓	X	X	4000	1e-01	2e-06	4 - 14	25,40-42,75,100
specific heat	AC	✓	✓	✓	✓	1900	2e+03	7e-05	0.1 - 2	46-49
	DC	✓	✓	X	✓	3500	1e+03	7e-08	2 - 14	43,50-54
	DSC	✓	✓	X	✓	1900	1e+03	7e-08	2 - 10	55-58,85
	DEH	X	✓	X	✓	4000	1e-01	2e-06	5 - 10	45,61,62,100
thermal diffusivity	LF	✓	✓	X	✓	N/L	1e-01	2e-08	2 - 10	18,66-68,101,102
	WM	✓	✓	✓	✓	N/L	2e-01	2e-08	2 - 10	64,70,72,73,103
emissivity	LP	✓	✓	X	✓	N/L	1e-08	1e-08	2 - 8	75,76,80
	BBC	X	✓	X	X	N/L	1e-08	1e-08	1 - 2	76
	ISR	✓	✓	X	✓	N/L	1e-08	1e-08	1 - 5	77,81-83
	MWP	✓	✓	X	✓	N/L	1e-08	1e-08	5 - 15	78,84
	CM	✓	✓	✓	✓	2000	1e-08	1e-08	1 - 2	79,85
melting point	LH	✓	✓	N/A	N/A	N/L	1e+00	2e-08	1 - 5	87-90
	IFH	✓	✓	N/A	N/A	4000	2e+02	1e-05	1 - 5	86

Chapter 3 : Theory of condensed matter

– “I am drawn to condensed matter physics because it is simultaneously useful and fundamental, simultaneously mundane and fantastical, simultaneously large and small, and most of all, some of the phenomena that are observed in condensed matter systems are just flipping cool. “ –

Inna Vishik, physicist

In this chapter most of the solid state theory, which is used throughout the rest of this work, is introduced. Existing theory based on the works of Boltzmann, Debye, Kelemens and Einstein is outlined. Furthermore, new models are derived quantifying the effect of high defect concentrations on the thermo-physical properties of materials. The considered properties are thermal conductivity, specific heat, thermal expansion coefficient (and hence density), thermal diffusivity, electrical conductivity, spectral and total hemispherical emissivity.

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3.1 Specific heat

In order to understand the evolution of specific heat capacity as a function of temperature, it is necessary to de-convolute the various contributing mechanisms. Specific heat can be expressed in the following way:

$$c_P^{tot} = c_V^h + c_V^{el} + c_V^d + c_V^m + \Delta c_{V \rightarrow P} \quad (3-1)$$

where the superscripts “*h*”, “*el*”, “*d*” and “*m*” stand for harmonic, electronic, defect and magnetic contributions, while the subscripts “*V*” and “*P*” stand for constant volume and pressure, respectively. For all considered systems above room temperature $c_V^m \approx 0$. UO_2 has a Neel temperature of around 30 K and is paramagnetic above that temperature^{104,105}. Graphite and ThO_2 are diamagnetic^{106,107} and similarly to paramagnetic UO_2 exhibit no local ordering of the magnetic spin.

3.1.1 Harmonic specific heat

The harmonic contribution to specific heat capacity was calculated using a Debye-Einstein approach. All acoustic modes are treated as coupled phonon vibrations using the Debye formalism, while all optical modes are approximated as mono-frequency phonons via the Einstein model. For a compound made up of *N*-atomic molecules there are three acoustic modes and $3N-3$ optical modes.

In order to simulate the phonon density of states, the acoustic modes have been approximated by linearly varying dispersion curves, which yield the Debye phonon density of states function (PDOS):

$$PDOS_{Debye}(\omega_j) = \frac{\omega_j^2}{(2V_j^3\pi^2)} \quad (3-2)$$

$$V_j = \frac{C_B\vartheta_j}{\hbar} \left(\frac{\Omega}{6\pi^2} \right)^{1/3} \quad (3-3)$$

where V_j is the velocity of the j -th vibrational mode, Ω is the atomic volume (m^3), C_B is Boltzmann's constant ($\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$), ω is the phonon frequency (Hz), T is temperature (K) and $\hbar$ is the reduced Planck constant ($\text{kg m}^2 \text{ s}^{-1} \text{ K}^{-1}$). The optical modes have been approximated by Dirac delta functions under the Einstein approximation.

$$c_V^h = \sum_{i=1}^3 \frac{w_i}{N_{atoms}} \Delta(\vartheta_i) + \sum_{j=1}^{3N_{atoms}-3} \frac{w_j}{N_{atoms}} \Xi(E_j) \quad (3-4)$$

where

$$\Delta(\vartheta_i) = 3N_{atoms}C_B \left(\frac{T}{\vartheta_i} \right)^3 \int_0^{\frac{\vartheta_i}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (3-5)$$

and $x = \frac{\hbar\omega}{C_B T}$. The evaluation of this integral was performed numerically using the trapezium rule.

$$\Xi(E_j) = N_{atoms}C_B \left(\frac{T}{E_j} \right)^2 \frac{x^2}{(e^x - 1)^2} \quad (3-6)$$

where θ is the Debye temperature (K), N_{atoms} is the number of atoms per mole (mol^{-1}) and E_j is the Einstein temperature (K) and w_i is the relative weight assigned to a particular vibrational mode.

3.1.2 Electronic specific heat due to localised electrons

Compounds bearing elements with localised f-electrons in the most outer shell (e.g. certain actinides) can undergo splitting of the ground state of the f-orbital. This occurs as a result of the geometric proximity of certain f-orbitals of an ion to the outer orbitals of different neighbouring ions. This type of electronic contribution to specific heat can be estimated using the following approach:

$$F = -C_B T \ln(Z^N) \quad (3-7)$$

where F is the Helmholtz free energy and Z is the grand canonical partition function of an atomic orbital.

$$C_V = -T \left(\frac{d^2 F}{dT^2} \right) \quad (3-8)$$

$$C_V = \frac{C_B T N}{Z} \left[2 \frac{dZ}{dT} + T \left(\frac{d^2 Z}{dT^2} - \left(\frac{dZ}{dT} \right)^2 \frac{1}{Z} \right) \right] \quad (3-9)$$

The partition function has been approximated using the following formulation:

$$Z = \sum_{i=1}^{\mathfrak{L}} g_i e^{\left(-\frac{E_i}{C_B T} \right)} \quad (3-10)$$

where “ i ” is the excitation level of the localised outer electrons (e.g. 5f in UO_2), $\mathfrak{L}$ is the number of different energy states, g_i is the degeneracy and E_i is the respective energy of the excited state (crystal field levels). The degeneracy factor is assumed equal to the number of available orbitals at a particular energy and an approximate microstate of one electron per atomic orbital has been used. This approximation does not take into account degenerate states occurring from electrons in orbitals of

different energy. Interactions between electrons are not included, while possible empty and filled atomic orbitals are also not considered.

$$\frac{dZ}{dT} = \sum_{i=1}^{\mathfrak{N}} \frac{g(i)E(i)}{C_B T^2} e^{\left(-\frac{E(i)}{C_B T}\right)} \quad (3-11)$$

$$\frac{d^2 Z}{dT^2} = \sum_{i=1}^{\mathfrak{N}} g(i) e^{\left(-\frac{E(i)}{C_B T}\right)} \left[\left(\frac{E(i)}{C_B T^2} \right)^2 - 2 \frac{E(i)}{C_B T^3} \right] \quad (3-12)$$

3.1.3 Electronic specific heat due to free electrons

In metals and semi-metals the contribution of free electrons to specific heat can be approximated semi-empirically using the Sommerfield relationship¹⁰⁸:

$$c_V^{el} = \gamma_e T \quad (3-13)$$

where γ_e is the Sommerfield coefficient.

3.1.4 Specific heat due to defect formation

Frenkel pairs are assumed to be the dominant defect species in the materials considered throughout this work and hence are used as the example for the following mathematical derivation. Prior to deriving the governing defect equation for the concentration of Frenkel pairs, the interaction of oppositely charged defects will be derived. The Poisson equation integrated over all solid angles with respect to a spherical surface yields:

$$\nabla \cdot (\nabla \psi) = -\frac{4\pi \mathfrak{K}}{D} \quad (3-14)$$

Where ψ is the electrostatic potential (V), $\mathfrak{N}$ is the charge number density (C m^{-3}) and D is the dielectric constant of the dielectric medium ($\text{C V}^{-1} \text{ m}^{-1}$). Furthermore, assuming charged species adopt a Boltzmann distribution, $\mathfrak{N}$ can be expanded:

$$\mathfrak{N} = \sum_i z_i e n_{i,o} \exp \left[-\frac{z_i e \psi_i}{C_B T} \right] \quad (3-15)$$

Where i stands for the oppositely charged defect types (e.g. vacancy, interstitial, etc.) z stands for the charge multiple, e represents the elementary charge, $n_{i,o}$ is the defect number density at 0 V electrostatic potential or at a temperature of 0 K, ψ is the electrostatic potential and i is the defect species. If we assume $\exp \left[-\frac{z_i e \psi_i}{C_B T} \right] \ll 1$, then $\mathfrak{N}$ can be linearized:

$$\mathfrak{N} = \sum_i z_i e n_{i,o} \left[1 - \frac{z_i e \psi_i}{C_B T} \right] \quad (3-16)$$

Due to charge neutrality $\sum z_i e n_{i,o} = 0$ and hence:

$$\mathfrak{N} = - \sum_i n_{i,o} \frac{z_i^2 e^2 \psi_i}{C_B T} \quad (3-17)$$

By substituting equation (3-17) in equation (3-14):

$$\nabla \cdot (\nabla \psi) = \frac{4\pi}{D} \sum_i n_{i,o} \frac{z_i^2 e^2 \psi_i}{C_B T} \quad (3-18)$$

In 1-D spherical coordinates equation (3-18) can be rewritten in the following form:

$$\frac{d^2 \psi_i}{dr^2} + \frac{2}{r} \frac{d\psi_i}{dr} = \left\{ \frac{4\pi}{D} \sum_i n_{i,o} \frac{z_i^2 e^2}{C_B T} \right\} \psi_i \quad (3-19)$$

Let a constant ς be introduced independent of ψ :

$$\varsigma_i^2 = \left\{ \frac{4\pi}{D} \sum_i n_{i,o} \frac{z_i^2 e^2}{C_B T} \right\} \quad (3-20)$$

$$\frac{d^2 \psi_i}{dr^2} + \frac{2}{r} \frac{d\psi_i}{dr} = \varsigma_i^2 \psi \quad (3-21)$$

where r is the radius. This ordinary differential equation has a solution of the following type:

$$\psi_i(r) = \frac{A}{r} \exp[-\varsigma_i r] + \frac{B}{r} \exp[\varsigma_i r] \quad (3-22)$$

where A and B are constants. Applying the boundary condition $|\psi_i(r)|_{r \rightarrow \infty} < \infty$, yields $B = 0$, and hence:

$$\psi_i(r) = \frac{A}{r} \exp[-\varsigma_i r] \quad (3-23)$$

Furthermore, when the defect concentration tends to zero:

$$\psi_i(r)|_{\varsigma \rightarrow 0} = \frac{A}{r} = \frac{e z_i}{D r} \quad (3-24)$$

and hence:

$$\psi_i(r) = \frac{e z_i}{D r} \exp[-\varsigma_i r] \quad (3-25)$$

This is the expression for the electrostatic potential experienced by an ion immersed in a charge field. This can be further decomposed in:

$$\psi_i(r) = \psi_i(r)_{ion} + \psi_i(r)_{charge\ field} \quad (3-26)$$

$$\psi_i(r)_{charge\ field} = \psi_i(r) - \psi_i(r)_{ion} \quad (3-27)$$

Substituting equations (3-24) and (3-25) in equation (3-27) leads into:

$$\psi_i(r)_{charge\ field} = \frac{e z_i}{D r} \exp[-\varsigma_i r] - \frac{e z_i}{D r} \quad (3-28)$$

Once again the exponential term is linearized yielding:

$$\psi_i(r)_{charge\ field} = \frac{ez_i}{Dr}(1 - \varsigma_i r - 1) \quad (3-29)$$

$$\psi_i(r)_{charge\ field} = -\frac{ez_i}{D}\varsigma_i \quad (3-30)$$

And hence the electric potential energy is the work necessary to introduce a charge (from 0 to z_i) into a potential field $\psi_i(r)_{charge\ field}$:

$$\Delta H_i = \int_0^1 \{ez_i\psi_i(r)_{charge\ field}\} dz_i = -\frac{e^2 z_i^2}{2D}\varsigma_i \quad (3-31)$$

where z' is the relative weight of the charge z_i and ΔH_i is the interaction energy per atom. In order to devise the governing equations for the defect concentrations it will be necessary to revisit the Gibbs free energy of formation for a given defect number density:

$$n'\Delta G_F = n'\Delta H_F - T\Delta S_{F,tot} \quad (3-32)$$

where ΔG_F , ΔH_F and ΔS_F are the Gibbs free energy per defect, the enthalpy per defect and the total entropy of formation, respectively. The entropy term can be expanded in the following manner:

$$\Delta S_{F,tot} = \Delta S_C + n'\Delta S_{NC} \quad (3-33)$$

where ΔS_C , ΔS_{NC} and n' are the configurational entropy term, the non-configurational or vibrational entropy term and the defect number density, respectively. From statistical thermodynamics:

$$\Delta S_C = C_B \ln(\Omega) \quad (3-34)$$

where Ω is the number of different ways defects can be accommodated on the available lattice sites and C_B is Boltzmann's constant. For Frenkel pairs Ω can be decomposed into:

$$\Omega = W_i W_v \quad (3-35)$$

where W_i and W_v are the number of combinations of interstitial and vacancy sites.

Hence, the total number of combinations is:

$$\Omega = \frac{(\varpi N)!}{(\varpi N - n')! n'!} \times \frac{(\kappa N)!}{(\kappa N - n')! n'!} \quad (3-36)$$

where, N is the total number of lattice sites per mole, n' is the number of vacancies per mole, ϖ is the fraction of sites available for vacancies to form and κ is the fraction of sites available for interstitial formation. Using Stirling's approximation for high values of N :

$$\ln(N!) \sim N \ln(N) - N \quad (3-37)$$

Substituting equation (3-36) into equation (3-35) and applying equation (3-37) yields:

$$\begin{aligned} \ln(\Omega) = & \varpi N \ln(\varpi N) - \varpi N - [(\varpi N - n') \ln(\varpi N - n') - (\varpi N - n')] \\ & - [n' \ln(n') - n'] + \kappa N \ln(\kappa N) - \kappa N \\ & - [(\kappa N - n') \ln(\kappa N - n') - (\kappa N - n')] - [n' \ln(n') - n'] \end{aligned} \quad (3-38)$$

Simplifying equation (3-38) leads to:

$$\begin{aligned} \ln(\Omega) = & \varpi N \ln(\varpi N) + \kappa N \ln(\kappa N) - [(\varpi N - n') \ln(\varpi N - n')] - 2[n' \ln(n')] \\ & - [(\kappa N - n') \ln(\kappa N - n')] \end{aligned} \quad (3-39)$$

Assuming the defect concentration is subjected to equilibrium conditions:

$$\frac{d(n' \Delta G_F)}{dn'} = 0 \quad (3-40)$$

Expanding the Gibbs free energy terms yields:

$$\frac{d(n'\Delta H_F)}{dn'} - T \frac{d(\Delta S_{F,tot})}{dn'} = 0 \quad (3-41)$$

Assuming non-configurational entropy is constant:

$$\frac{d(n'\Delta H_F)}{dn'} = T \left[\frac{d(\Delta S_C)}{dn'} + \Delta S_{NC} \right] \quad (3-42)$$

Furthermore, the configurational entropy term can be expanded in the following manner:

$$\frac{d(\Delta S_C)}{dn'} = C_B \frac{d\ln(\Omega)}{dn'} \quad (3-43)$$

By using equation (3-39) one can expand the right hand side of equation (3-43):

$$\frac{d\ln(\Omega)}{dn'} = \ln(\varpi N - n') + 1 - 2 - 2\ln(n') + 1 + \ln(\kappa N - n') \quad (3-44)$$

$$\frac{d\ln(\Omega)}{dn'} = \ln(\varpi N - n') - 2\ln(n') + \ln(\kappa N - n') \quad (3-45)$$

A substitution can be introduced by relating the number density with the fractional defect concentration:

$$n = \frac{n'}{N} \quad (3-46)$$

Substituting equation (3-46) in equation (3-45) and simplifying, leads to the following expression:

$$\frac{d\ln(\Omega)}{dn} = \ln \left\{ \frac{(\varpi - n)(\kappa - n)}{n^2} \right\} \quad (3-47)$$

Furthermore, equation (3-47) can be substituted in equation (3-42) leading to:

$$\frac{d(n\Delta H_{F,Fr})}{dn} = T \left[C_B \ln \left\{ \frac{(\varpi - n)(\kappa - n)}{n^2} \right\} + \Delta S_{NC_0,Fr} \right] \quad (3-48)$$

where the subscript Fr stands for Frenkel pairs. Equation (3-48) is expanded using the product rule:

$$\Delta H_{F,Fr} + n \frac{d(\Delta H_{F,Fr})}{dn} - T \Delta S_{NC_0,Fr} = T C_B \ln \left\{ \frac{(\varpi - n)(\varsigma - n)}{n^2} \right\} \quad (3-49)$$

Equation (3-49) is rearranged leading to the non-linear relationship for the concentration of Frenkel pairs:

$$(\varpi - n)(\varsigma - n) \exp \left[-\frac{1}{C_B T} \left\{ \Delta H_{F,Fr} + n \frac{d(\Delta H_{F,Fr})}{dn} - T \Delta S_{NC_0,Fr} \right\} \right] = n^2 \quad (3-50)$$

The enthalpy terms can further expanded leading to:

$$\left\{ \Delta H_{F,Fr} + n \frac{d(\Delta H_{F,Fr})}{dn} \right\} = \Delta H_{F_0,Fr} + \frac{1}{3} \Delta H_{I_{tot},Fr} + \frac{1}{3} n \frac{d(\Delta H_{I_{tot},Fr})}{dn} \quad (3-51)$$

where $\Delta H_{F_0,Fr}$ stands for formation enthalpy at 0 K and $\Delta H_{I_{tot},Fr}$ stands for the total interaction enthalpy for Frenkel pairs. The factor of one third is needed to convert the interaction energy per atomic or elemental mole (as it has been calculated via equations (3-14) to (3-31)) to interaction energy per mole of UO_2 . By revisiting equations (3-31) and (3-20), it can be shown that:

$$\frac{d(\Delta H_{I_{tot},i})}{dn} = \frac{1}{2n} \Delta H_{I_{tot},i} \quad (3-52)$$

Substituting equation (3-52) in equation (3-51) yields:

$$\left\{ \Delta H_{F,Fr} + n \frac{d(\Delta H_{F,Fr})}{dn} \right\} = \Delta H_{F_0,Fr} + \frac{1}{2} \Delta H_{I_{tot},Fr} \quad (3-53)$$

Furthermore, the interaction enthalpy for a defect type is a sum of the interaction enthalpies of its constituent point defects and hence:

$$\Delta H_{I_{tot},i} = \sum_j \Delta H_{I,i,j} \quad (3-54)$$

Where i stands for the defect type (i.e. Frenkel, Schottky, etc.), while j stands for the constituent point defect type (e.g. vacancy, interstitial). For Frenkel pairs this becomes:

$$\Delta H_{I_{tot},Fr} = \left(-\frac{e^2 z^2}{2D} \varsigma \right) + \left(-\frac{e^2 z^2}{2D} \varsigma \right) = 2 \left(-\frac{e^2 z^2}{2D} \varsigma \right) \quad (3-55)$$

Finally, by substituting equation (3-53) in equation (3-50) the governing defect equation for Frenkel pairs can be expressed in the following manner:

$$n^2 = (\varpi - n)(\kappa - n) \exp \left[-\frac{\Delta H_{F_0,Fr} - \frac{1}{2} \Delta H_{I_{tot},Fr}}{C_B T} + \frac{\Delta S_{NC,Fr}}{C_B} \right] \quad (3-56)$$

For small defect concentrations equation (3-56) can be simplified to:

$$n = \sqrt{(\varpi)(\kappa)} \exp \left[-\frac{\Delta H_{F_0,Fr}}{2C_B T} + \frac{\Delta S_{NC,Fr}}{2C_B} \right] \quad (3-57)$$

A similar approach can be applied to other defect species, such as Schottky defects and other defect types. Equation (3-56) becomes particularly important for high defect concentrations and will be solved numerically within this work.

3.1.5 Conversion from c_V to c_P

So far relationships were derived for the evolution of specific heat at constant volume (c_V), however experimentally one is closer to constant pressure conditions when measuring specific heat (c_P). Hence, a relationship for these two quantities will be

presented, in order to make valid comparisons between theory and experiment. The full derivation is given in the Appendix.

$$c_P - c_V = VTK_T\beta^2 \quad (3-58)$$

where V is the molar volume (m^3), β is the volumetric thermal expansion (K^{-1}) coefficient and K_T is the isothermal bulk modulus (Pa).

3.2 Thermal and electrical conductivity theory

The thermal conductivity of the materials examined in this work can be deconvoluted into a maximum of four components, which are expressed as follows:

$$k_{tot} = k_l + k_p + k_{ion} + k_e \quad (3-59)$$

where k_{tot} is the total thermal conductivity, while k_l , k_p , k_{ion} and k_e stand for the lattice, polaron, ionic and free electron contributions.

3.2.1 Thermal conductivity due to free electrons

In metals and semi-metals, the Fermi energy lies within the conduction band, which means electrons contribute to thermal conductivity as well as phonons and their contribution can be quantified via the Wiedmann-Franz Law:

$$k_e = \sigma L_0 T \quad (3-60)$$

where σ is the electrical conductivity (Sm^{-1}) and L_0 is the theoretical Lorentz number ($L_0 = 2.445 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$).

3.2.2 Lattice thermal conductivity

The lattice contribution can be expressed via a Debye-Klemens approach:

$$k_l = \frac{1}{9} \sum_j \left(\frac{C_B}{\hbar} \right)^3 \frac{C_B}{2\pi^2 V_j} T^3 \int_0^{\frac{\vartheta_j}{T}} \frac{\tau_{tot} x_j^4 e^{x_j}}{(e^{x_j} - 1)^2} dx_j \quad (3-61)$$

where j represents the different vibrational modes, τ_{tot} is total or effective relaxation time between phonon scattering events, V_j is the effective group velocity of phonons, which is calculated using the Debye formalism described by equation (3-3). It is also assumed that only the three acoustic modes contribute to the thermal conductivity, while the optical modes are neglected. Furthermore, the total relaxation time is approximated via the Mathesius rule:

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_u} + \frac{1}{\tau_{im}} + \frac{1}{\tau_{gb}} + \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_{SP}} \quad (3-62)$$

where τ_u , τ_{im} , τ_{gb} , τ_{e-ph} and τ_{SP} are the Umklapp, impurity, grain boundary, electron-phonon and spin-phonon scattering relaxation times. The umklapp relaxation time can be modelled using the approach of Klemens¹⁰⁹:

$$\frac{1}{\tau_u} = \frac{2\gamma^2 C_B T \omega^2}{m^{at} V_j \omega_j^d} \quad (3-63)$$

where m^{at} is the atomic mass (kg) and γ is the Grüneisen parameter (-). Phonon scattering by impurities is represented by the following relaxation time¹¹⁰:

$$\frac{1}{\tau_{im}} = \left(\frac{\Delta m}{\bar{m}} \right)^2 \frac{n_d C_B^4 \Omega \omega^4}{4\pi \hbar^4 V_j} \quad (3-64)$$

where $\bar{m}$ is the average atomic mass (kg), n_{im} is the defect or impurity molar concentration (-) and Δm is the mass difference due to the defect or impurity (kg),

while Ω is the atomic volume (m^3). Grain boundary scattering of phonons is modelled via¹¹⁰:

$$\frac{1}{\tau_{gb}} = \frac{V_j}{L_g} \quad (3-65)$$

where L_g is the grain size (m). The electron-phonon relaxation time is estimated based on the work of Zou et al.¹¹¹:

$$\frac{1}{\tau_{e-ph}} = \frac{n_e \epsilon_1^2 \omega}{\rho_{TD} V_i^2 C_B T} \sqrt{\frac{\pi m^* V_i}{2 C_B T}} \exp\left(-\frac{m^* V_i^2}{2 C_B T}\right) \quad (3-66)$$

where n_e is the free electron number density (m^{-3}), ϵ_1 is the deformation potential, m^* is the effective electron mass (kg) and ρ_{TD} is the material theoretical density (kg m^{-3}).

$$\frac{1}{\tau_{SP}} = C_{SP} \frac{\omega^4}{(\omega^2 - \omega_o^2)^2} \frac{1 - \exp\left[-\frac{\hbar\omega_o}{k_b T}\right]}{1 + \exp\left[-\frac{\hbar\omega_o}{k_b T}\right]} \quad (3-67)$$

where τ_{SP} is the spin-phonon scattering relaxation time (equation adopted from the work of Verma¹¹²), C_{SP} is the coupling constant and ω_o is the coupling frequency. Equation (3-67) is relevant for materials with magnetic ordering, due to preferential spin alignment of free outer shell electrons (e.g. 5f in UO_2). For diamagnetic materials, which have no unpaired outer shell electrons, the contribution of spin-phonon scattering can be neglected (i.e. for graphite, ThO_2 and UO_2 at high temperatures)^{113,114}.

3.2.3 Ionic thermal and electrical conductivity

For ionic conductivity the Nernst- Einstein relationship was used¹¹⁵:

$$\sigma = \frac{n_i z_i^2 q^2}{C_B T} D_i \quad (3-68)$$

where σ is the electrical conductivity (S m^{-1}), z_i is the valence (-), q is the elementary charge (C) and D_i is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) of species i . Using Einstein's relation for random diffusion, the diffusion coefficient can be expressed by¹¹⁵:

$$D_i = \frac{s_i^2}{6} F_i \nu_i \quad (3-69)$$

where s_i is the hopping distance (m), F_i is the coordination number (-) and ν_i is the mobility of species (Hz) i . Furthermore, ν_i can be expanded in an Arrhenius form:

$$\nu_i = \nu_{i,0} \exp \left[\frac{-M_i}{C_B T} \right] \quad (3-70)$$

where $\nu_{i,0}$ is the hopping frequency (Hz) and M_i is the migration energy (eV) of species i . Hence the electrical conductivities due to oxygen defect species can be calculated via:

$$\sigma_{V,O} = \frac{\nu_0 (1 - n_{V,O}) n_{V,O} Z_{V,O}^2}{a_0 C_B T} \exp \left[\frac{-M_{V,O}}{C_B T} \right] \quad (3-71)$$

$$\sigma_{I,O} = \frac{\nu_0 (1 - n_{I,O}) n_{I,O} Z_{I,O}^2}{a_0 C_B T} \exp \left[\frac{-M_{I,O}}{C_B T} \right] \quad (3-72)$$

where $\sigma_{V,O}$ and $\sigma_{I,O}$ are the oxygen vacancy and oxygen interstitial contributions to electrical conductivity.

$$k = \sigma L_i T \quad (3-73)$$

Using the modified “Wiedemann-Franz” law¹¹⁶ for ionic conductors (equation (3-73)), the thermal conductivities due to oxygen vacancy and oxygen interstitial migration are:

$$k_{V,O} = \frac{\nu_0(1 - n_{V,O})n_{V,O}Z_{V,O}^2 L_I}{a_0 C_B} \exp \left[\frac{-M_{V,O}}{C_B T} \right] \quad (3-74)$$

$$k_{I,O} = \frac{\nu_0(1 - n_{I,O})n_{I,O}Z_{I,O}^2 L_I}{a_0 C_B} \exp \left[\frac{-M_{I,O}}{C_B T} \right] \quad (3-75)$$

where $_{V,O}$ stands for oxygen vacancy and $_{I,O}$ stands for oxygen interstitial, L_I is the ionic Lorentz number ($\text{W } \Omega \text{ K}^{-2}$) as derived by Rice and Roth¹¹⁶ ($L_I = \left[\frac{9L_0}{2\pi^2 Z^2} \right] \left[\frac{M_I}{C_B T} \right]$), L_0 is the theoretical Lorentz number ($2.445 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$), while a_0 is the lattice parameter of UO_2 (m).

3.2.4 Polaron thermal and electrical conductivity

Using the same approach as in equations (3-68) to (3-75) the electronic contribution to electrical conductivity can be expressed as:

$$\sigma_P = \frac{2\Gamma q^2}{C_B T} n_p (1 - 2n_p) \exp \left[\frac{-M_{Pol}}{C_B T} \right] \quad (3-76)$$

where σ_P is the polaron contribution to electric conductivity (S m^{-1}), n_p is the molar concentration of polarons (-), M_{Pol} is the polaron migration enthalpy (eV), Γ is a pre-exponential factor, which according to Casado et al.¹¹⁷ can be expressed as $\Gamma =$

$$\frac{J^2}{\hbar} \sqrt{\frac{\pi}{C_B M_{Pol}}} \text{ and } J \text{ is the electron overlap integral (eV).}$$

The expression adopted by Winter¹¹⁵ and Hyland¹¹⁸ relates electrical and thermal conductivity for small polaron hopping, assuming electrons and holes exhibit the same concentrations and mobilities:

$$k_P = \frac{1}{4} \left(\frac{U}{C_B} \right)^2 \frac{\sigma_P}{T} \quad (3-77)$$

$$k_P = \Gamma \left(\frac{U}{C_B} \right)^2 \left(\frac{1}{T} \right)^{5/2} \left(\frac{n_p}{2} \right) (1 - 2n_p) \exp \left[\frac{-M_{Pol}}{C_B T} \right] \quad (3-78)$$

where U is the polaron formation energy (eV).

3.3 Thermal expansion

The volumetric thermal expansion coefficient will be approximated as the sum of a lattice (β^l) and defect contribution (β^d):

$$\beta^{tot} = \beta^l + \beta^d \quad (3-79)$$

3.3.1 Lattice contribution

The lattice contribution to the volumetric thermal expansion coefficient can be evaluated using the Mie-Grüneisen approach, which is described in detail in Appendix B.2. The derivation presented in Appendix B.2. leads to the following expression:

$$\beta^l = \frac{\gamma C_V}{K_T V} \quad (3-80)$$

3.3.2 Defect contribution

The enthalpy of a system H can be expressed in terms of its internal energy U , its pressure P and its volume V :

$$H = U + PV \quad (3-81)$$

By taking the partial derivatives of each of the above quantities one finds:

$$dH = dU + VdP + PdV \quad (3-82)$$

By referring to the first law of thermodynamics the change in internal energy can be expanded $dU = TdS - PdV$, leading to:

$$dH = TdS - PdV + VdP + PdV \quad (3-83)$$

By simplifying and rearranging equation (3-83) under constant entropy conditions

$$\left. \frac{dH}{dP} \right|_S = V \quad (3-84)$$

where V is the volume per mole, P is the pressure and S is the entropy.

$$\frac{dH}{dT} \frac{dT}{dV} \frac{dV}{dP} = V \quad (3-85)$$

$$\frac{1}{K} \sum_i \left[\Delta H_i \frac{dn}{dT} + n_i \frac{d\Delta H_i}{dT} \right] = \frac{dV}{dT} \quad (3-86)$$

where K is the temperature dependent adiabatic bulk modulus. Equation (3-86) is

solved with a forward Euler scheme:

$${}_{z-1}V_i^d + \left\{ \frac{1}{K} \sum_i [\Delta H_i dn + n_i d\Delta H_i] \right\} = {}_zV_i^d \quad (3-87)$$

where z is the iteration. Every iteration corresponds to a particular temperature.

$$\beta^d = \frac{1}{V} \frac{dV}{dT} = \sum_i \frac{1}{y_{-1} V_i^d} \frac{y V_i^d - y_{-1} V_i^d}{\Delta T} \quad (3-88)$$

where β is the volumetric thermal expansion coefficient and ΔT is the numerical temperature increment ($\Delta T = 10K$). Hence, the defect contribution to the total volumetric thermal expansion coefficient is calculated using equation (3-88).

3.4 Thermal diffusivity

Thermal diffusivity will be evaluated from the temperature dependent properties described previously - specific heat, thermal conductivity and density (from thermal expansion coefficients). These are linked via the following relationship

$$\alpha = \frac{k}{\rho c_p} \quad (3-89)$$

3.5 Emissivity

Emissivity is a material property, which expresses the radiation emitted by a material relative to a perfect black-body. Hence, by referring to Planck's law¹¹⁹ of radiation this property can be expressed as follows:

$$\varepsilon(\theta, T, \lambda) = \frac{L(\theta, T, \lambda)}{B(\theta, T, \lambda)} = \frac{c_1 \lambda^{-5} \left(\exp\left(\frac{c_2}{\lambda T_L}\right) - 1 \right)^{-1}}{c_1 \lambda^{-5} \left(\exp\left(\frac{c_2}{\lambda T_B}\right) - 1 \right)^{-1}} = \frac{\left(\exp\left(\frac{c_2}{\lambda T_L}\right) - 1 \right)^{-1}}{\left(\exp\left(\frac{c_2}{\lambda T_B}\right) - 1 \right)^{-1}} \quad (3-90)$$

where ε is the spectral emissivity, T_L is the radiance temperature, T_B is the blackbody temperature λ is the wavelength, L is the radiance of the material, B is the radiance of a perfect black body, c_1 and c_2 are the first and second radiation constants, respectively. Throughout this work spectral emissivity will be assumed

independent of angle. Furthermore, by assuming that $\left\{\exp\left(\frac{c_2}{\lambda T_B}\right)\right\} \gg 1$, equation

(3-90) can be simplified, yielding Wien's approximation:

$$\frac{1}{T_B} = \lambda \frac{\ln[\varepsilon(T_B, \lambda)]}{c_2} + \frac{1}{T_L} \quad (3-91)$$

Furthermore, a useful method of assessing the effect of relative changes in emissivity on the black body temperature is to take the first order derivative of temperature with respect to emissivity in equation (3-91), the following expression is obtained:

$$dT_B = -\lambda \frac{d\varepsilon}{\varepsilon(T_B, \lambda)} \frac{T_B^2}{c_2} \quad (3-92)$$

Finally, if spectral emissivity is integrated over all wavelengths and solid angles (assuming no angular dependence of spectral emissivity) an expression for total hemispherical emissivity can be obtained:

$$\varepsilon_{tot}(T_B) = \int_0^\infty \frac{\varepsilon(T_B, \lambda) \lambda^{-5} \left(\exp\left(\frac{c_2}{\lambda T_L}\right) - 1\right)^{-1}}{\lambda^{-5} \left(\exp\left(\frac{c_2}{\lambda T_B}\right) - 1\right)^{-1}} d\lambda \quad (3-93)$$

Chapter 4 : Experimental methods

- *“You make experiments and I make theories. Do you know the difference? A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it.”* -

Albert Einstein, physicist

Previously, all solid state physics theory applied and developed in this work was introduced. The following chapter deals with all the experimental methods that are used throughout this work. A major part of this chapter is concerned with the newly developed laser flash methodologies using both pyrometer and infrared camera devices. Finally, other applied experimental techniques are described – multi-wavelength pyrometry, x-ray diffraction and scanning electron microscopy.

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Parts published in: **Pavlov, et al. *Acta Mater.* 139, 138 - 154 (2017).**

4.1 New inverse method (based on the laser-flash technique)

The newly developed inverse method uses experimental data obtained via a custom made laser flash set-up¹⁸. The measurements are then treated using noise filtering and base-line subtraction algorithms. Finally, model generated data is fit to the experimental results using the least square difference (between experimental and theoretical data) as the cost-function to be minimised and key thermo-physical properties as optimisation parameters.

4.1.1 Laser flash equipment and measurement procedure

A schematic of the laser flash experiment and related equipment is shown in Figure 4-1. The apparatus includes a disc shaped sample, held by three or four zirconia pins to a graphite sample holder, all of which are sealed within a chamber. The sample can have a diameter between 5 and 12 mm and the thickness is in the range 0.5 - 3 mm. The dimensions of the samples are measured using a thickness gauge and Vernier Calipers. The weight of the samples is measured using an analytical balance. From the measured dimensions and respective weights of the cylindrical samples, the room temperature density is calculated. The specimens are kept under a controlled atmosphere. The pressure in the chamber can be varied between 5 μ bar and 4 bar (possible buffer gases include: argon, oxygen, argon/hydrogen, air, carbon dioxide)¹.

¹ During the measurements performed on isostatically pressed graphite and UO₂, argon was the buffer gas, while for all ThO₂ measurements pure oxygen was used as a buffer gas.

There are transparent sapphire windows on both sides of the stainless steel chamber, which allow for two continuous-wave lasers (Nd-YAG with $\lambda = 1064$ nm), to pre-heat each side of the specimen from around 300 K to a chosen equilibrium temperature. The equilibrium temperatures can be varied from around 1000 K to above 3000 K. The temperatures are continuously monitored by high speed pyrometers on the front and rear sides. Furthermore, a spectropyrometer measures the radiance on the front side at 256 wavelengths in the range 500 nm to 1000 nm.

Once the desired steady-state temperature has been reached (the temperature measured by the pyrometer becomes stable over time) a short pulse is applied (generally around 10 ms) using the front Nd-YAG laser. On the rear side, the rise in temperature is measured as a function of time via a pyrometer, which is automatically triggered upon the initiation of the laser pulse. The pyrometer measurements are transferred to a 14-bit digitiser (Nicolet Pro 34) and subsequently the radiance signal is converted into temperature. The triggering sequence involving the various devices is discussed in further detail in section 4.1.2.5.

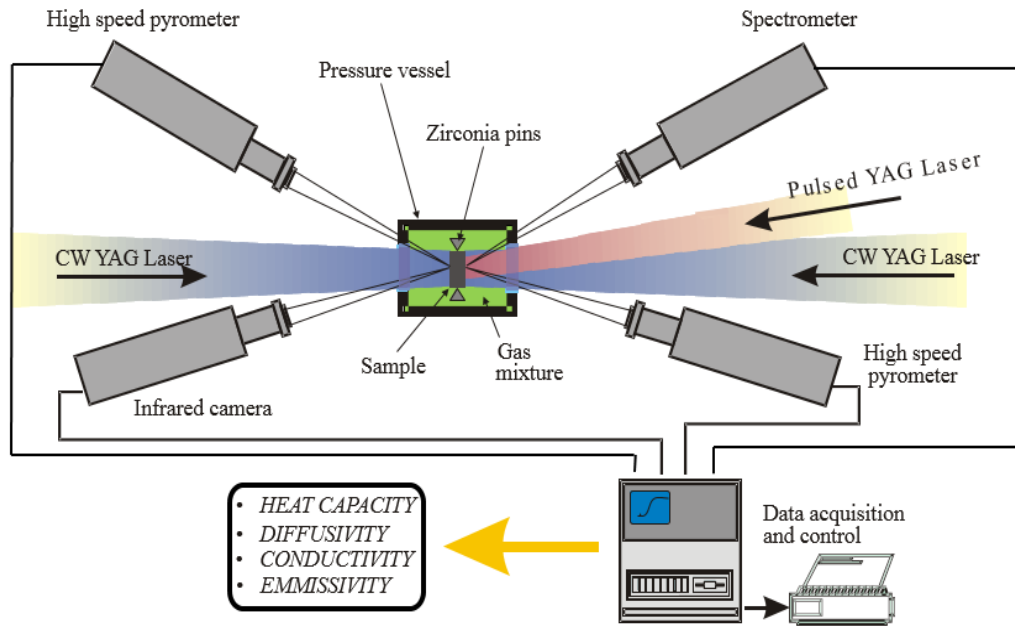


Figure 4-1: Schematic of the laser flash experimental set-up.

4.1.2 Devices and calibrations

A basic description of all devices mentioned in section 4.1.1 is provided. Furthermore, all calibrations, which were performed and were necessary for the analysis of all data, are provided.

4.1.2.1 Lasers

Two lasers have been used throughout this work, manufactured by TRUMPF Group and Haas Laser Technologies, Inc. Both of these are 4-level lasers and use Nd:YAG (neodymium-doped yttrium aluminium garnet $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$) as a pumping medium. The HAAS laser uses a krypton lamp as the laser source, while the TRUMPF laser uses a diode. The HAAS laser was used for preheating the sample on the rear side, while the TRUMPF laser is used both for preheating the front sample surface and

subjecting the front surface to a pulse. Hence, the power of the TRUMPF laser was calibrated using an OPHIR Photonics power meter. The power vs. voltage curve is shown in Figure 4-2. The presence of a sapphire window was also taken into account and this calibration curve was used for converting the measured voltage into power.

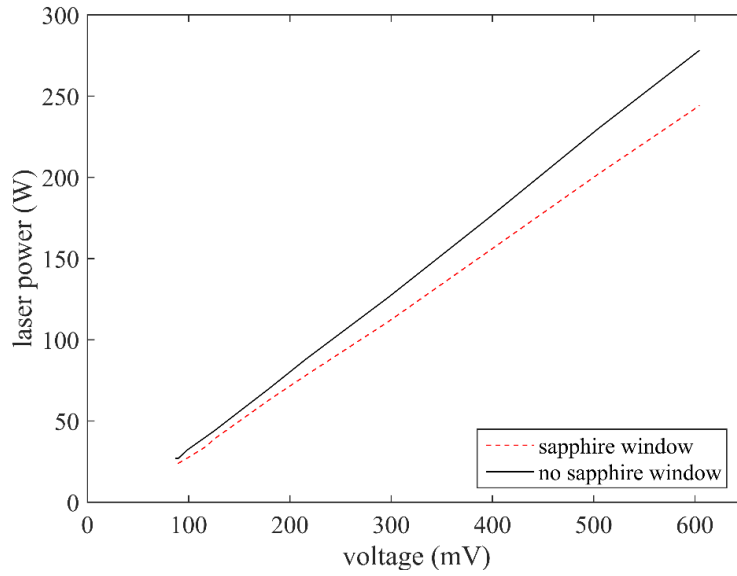


Figure 4-2: TRUMPF laser power vs. measured voltage. The black solid line represents the calibration curve when a sapphire window was absent, while the red dotted line takes into account the effect of the sapphire window.

The spatial profile of the laser was also characterised with respect to the absolute power and nominal beam spot radius (see Figure 4-3A). The nominal beam spot radius is determined based on the optical fiber diameter and the ratio of the focal lengths (i.e. the magnification) of the optical lenses used. In the configuration used for these experiments, the diameter of the optical fiber was 0.6 mm while the two lenses (i.e. collimating and focusing) have focal lengths of 100 mm and 500 mm,

respectively, resulting in a magnification of 5. The profile has been calibrated via a cmos camera (USBeam Pro PS-2323 by Photon Inc). The calibration has been performed for a beam spot of 3 mm in diameter for laser powers of 50 W and 100 W. No differences were measured between the two powers. The measurement was performed at best focus (shown in Figure 4-3A) and the depth of focus was determined to be about 14 mm (i.e. +/- 7 mm from best focus). Furthermore, the spatial profile was measured at distances up to 60 mm away from best focus (defocused). The spatial profile, defocused by 50 mm was used as a conservative uncertainty limit, which was used for the error analysis (the $P(r)$ parameter introduced in section 5.1 and used in section 5.4.1 for estimating the propagation of errors in certain input parameters).

A typical time profile of the laser power during a pulse is shown in Figure 4-3B. The representative functional approximations of space and time power variations are also plotted in Figure 4-3A and Figure 4-3B. These are used as input for the FEA model used (description to follow in section 4.1.5). Finally, the top-hat approximation shown in Figure 4-3B is automatically scaled for every measurement, in order to match the energy calculated from the experimentally recorded power vs. time profile. Finally, it is important to note that the spatial profile and time profile of the laser are critical for the accuracy of new inverse method proposed in this work.

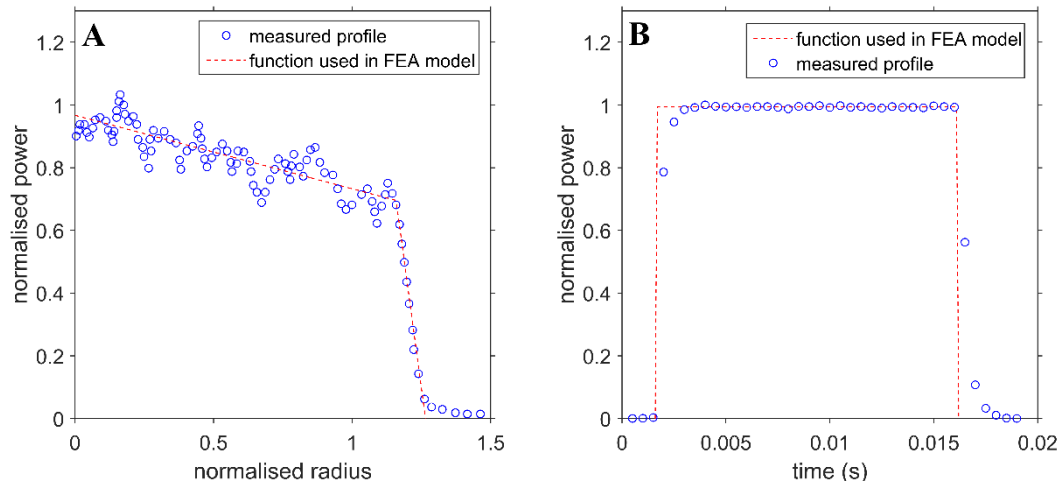


Figure 4-3: The space-time variation of the laser power: A) Normalised power as a function of normalized beam spot radius (nominal); B) Normalised power as a function of time. The blue dots represent the measured profiles, while the red dotted lines represent the functional approximation of the measured profiles.

4.1.2.2 Pyrometers

Two pyrometers are used for recording the temperature as a function of time on each side of the sample surface. Throughout this work these pyrometers will be referred to as “Russpyro” and “HS01”. Both of these operate in the visible wavelength range with a silicon detector. Russpyro has a nominal spot size (radius) of 0.4 mm, while HS01 has a spot size (radius) of 0.3 mm. The pyrometers were calibrated with a vacuum lamp (1400 to 1800 °C) and a gas lamp (1800 to 2500 °C). The calibration curves of each of these are shown in Figure 4-4A and Figure 4-4B. The effect of the sapphire window has been examined as well and the transmissivity of the window has been determined to be 0.86 at 645 nm.

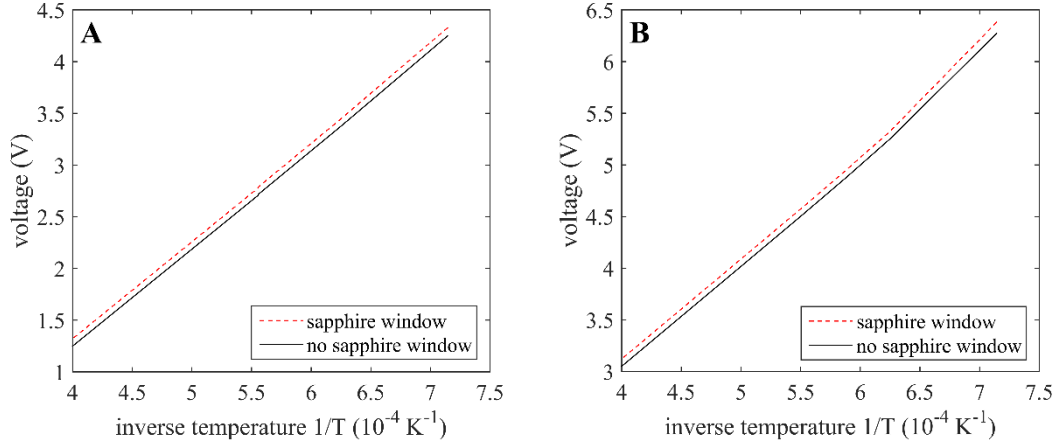


Figure 4-4: Voltage vs. inverse temperature obtained via tungsten ribbon lamp calibration: A) Russpyro; B) HS01. Black line represent absence of sapphire window during calibration, while red dotted lines represent the calibration with a sapphire window (between tungsten lamp and pyrometers).

4.1.2.3 Infrared camera

The infrared camera has been manufactured by PHOENIX and operates in a wide infrared wavelength band ($0.9\mu\text{m} - 1.7\mu\text{m}$). However, for temperatures above 1400°C , a narrow band pass filter is used centred at $1.5 \mu\text{m}$. Two point non-uniformity corrections (NUC) have been performed on all pixels and bad pixel recognition has been adopted. The two point NUC consists of an offset correction (pixel response functions translated by individually assigned constants to the same reference value) followed by a gain correction (response functions' slopes scaled by individually assigned constants). The result is that the linear (nearly linear) segments of every pixel's response function overlap (nearly overlap). Using the NUCs created, the PHOENIX camera was calibrated via a high temperature black body from 700°C to

2900°C at Laboratoire national de métrologie et d'essais (LNE). The calibration curves for “NUC D” and “NUC F” are shown in Figure 4-5A and Figure 4-5B, respectively. Each of these have been calibrated using 35 μ s acquisition time. Since, the calibration was performed without the sapphire window of the chamber, all radiance measurements were corrected by the material’s spectral emissivity scaled by a factor of 0.86 (the estimated transmissivity of sapphire via the pyrometer calibration).

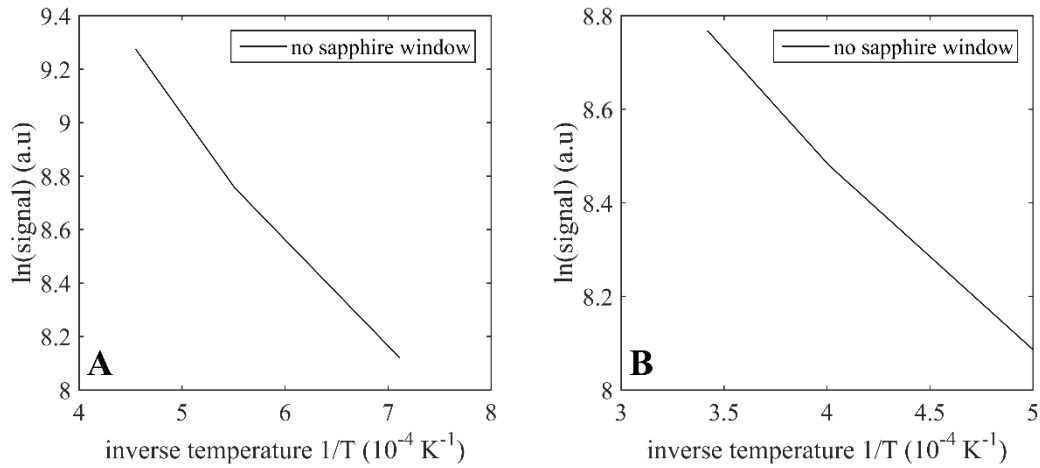


Figure 4-5: Ln(signal) vs. inverse temperature obtained via high temperature black body calibration: A) NUC D; B) NUC F.

4.1.2.4 Spectropyrometer

A spectropyrometer measures the radiance on the front side at 256 wavelengths in the range 500 nm to 1000 nm. The spectropyrometer has a nominal spot diameter of 0.4 mm and a maximum deviation from linearity of 0.003 (0.3%) of end point (the maximum deviation divided by the maximum output of the transducer, i.e. the

detector). At the central wavelength (at 648 nm) the spectropyrometer was calibrated using the same tungsten ribbon lamps also used for the Russpyro and HS01 pyrometers in addition to low temperature (up to 1473 K) black-body.

4.1.2.5 Triggering procedure

As it has become clear by now, the set-up and measurement procedure is not trivial. In order for all information to be recorded on time and correctly, a triggering procedure has been devised (see Figure 4-6) and implemented via a LabVIEW program. The trigger is a signal which instructs the oscilloscope to record a certain portion of the data passing through it. The trigger used throughout this work has been the laser power (i.e. via voltage). Once the laser pulse is initiated, the oscilloscope obtains a reference point in time to create a transient record of the voltage values measured by the pyrometers. The recorded data is then transferred to a personal computer (PC) via General Purpose Interface Bus (GPIB) controller. The infrared camera is also triggered via the laser, however it requires a trigger voltage variation in the range 0 to 1.6 V. Since, the trigger voltage ramp provided by the laser is too high (2 to 20 V), a transformer box is used to downscale this ramp to 0.4 to 5V. The infrared camera does not communicate to the oscilloscope, as it has its own computer where the data is initially recorded. This data is then manually transferred to the common PC used for storage of all acquired data shown in Figure 4-6. The spectropyrometer is a standalone device, which needs to be triggered

manually. It also has its own computer for storing the recorded data and, similarly to the infrared camera, this data is then manually transferred to a common PC.

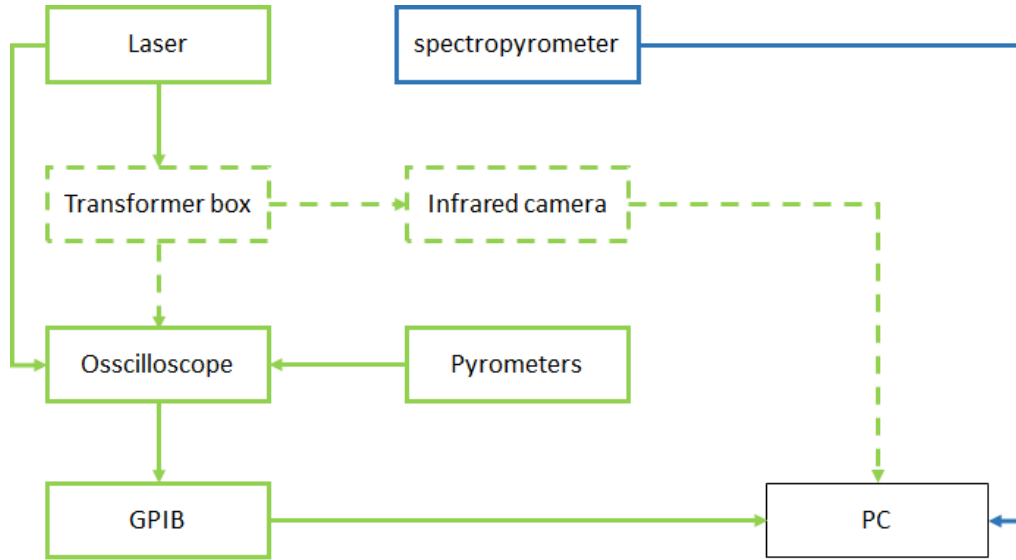


Figure 4-6: Logic diagram of triggering procedure. Solid green lines represent the standard devices used and standard information transfer sequence. Dotted green lines represent the devices used and the sequence of information transfer when using the infrared camera. The blue lines represents the spectropyrometer as a stand-alone device, where data is transferred directly to the PC.

4.1.3 Computational methodology

A logic diagram of the method is shown in Figure 4-7. The experimental thermograms are converted from a signal or voltage reading to a temperature reading. Prior to the onset of the pulse, the quasi steady-state temperature is recorded as a function of time. The name quasi steady-state is given, as the temperature fluctuates slightly, due to high frequency noise in the laser power. This pre-trigger temperature record provides the information necessary for a base line correction. Furthermore, Fast

Fourier transforms are employed to filter high frequency noise in the thermograms recorded by the pyrometers or infrared camera. As shown in Figure 4-7, one of these methodologies involves using one of the pyrometer devices (pyrometer method), whereby only the thermogram at the central radial location on the rear side of the sample is analysed to obtain a set of thermo-physical properties (e.g. specific heat, thermal and total hemispherical emissivity). The camera method is similar, however it uses an infrared camera, which measures the transient temperature response on the whole rear surface of the sample (i.e. not only at the centre as it is the case for the pyrometer method). The camera measures a 2-D thermal map obtained from a grid of pixels, each of which corresponds to the radial location of a temperature measurement on the sample surface. The two methods are described in further detail in the following sections and in Chapter 5.

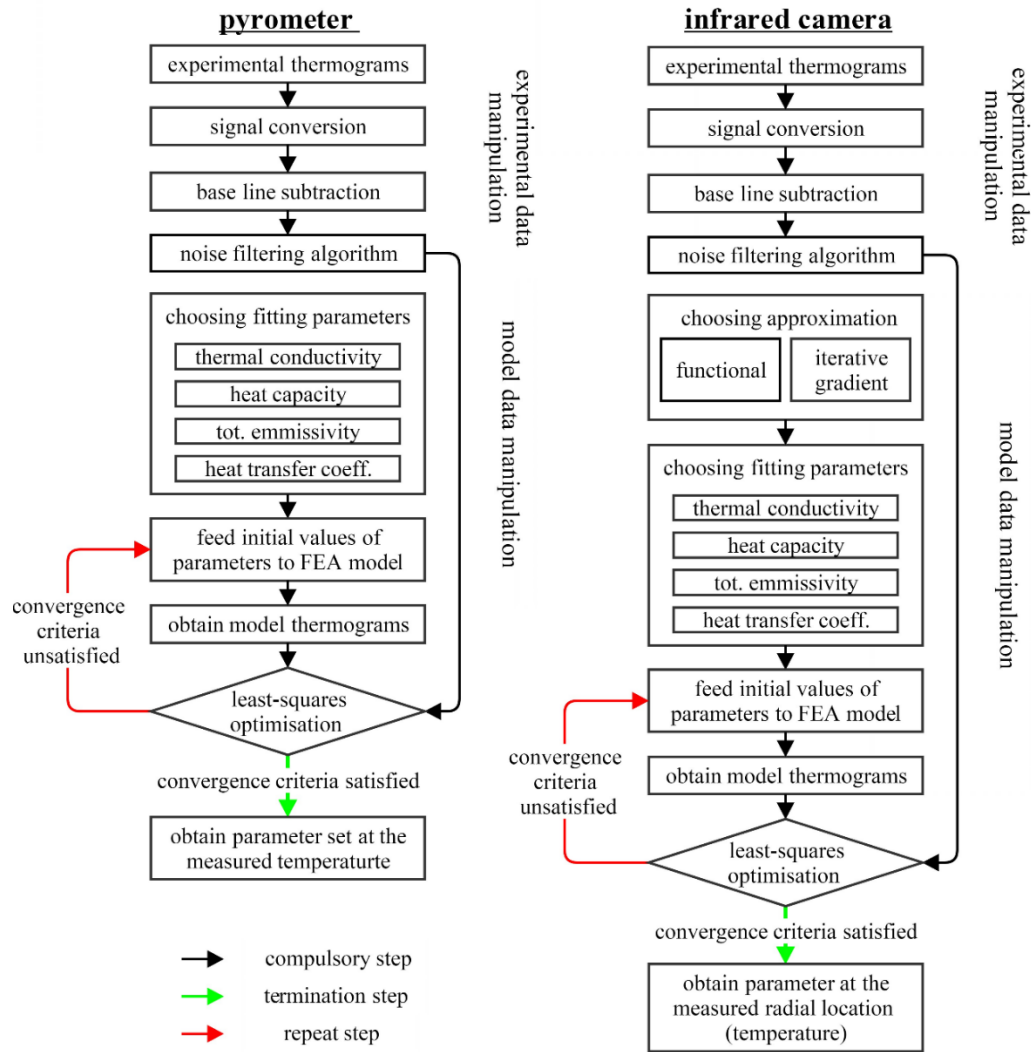


Figure 4-7: Logic scheme of the computer programs developed for the infrared camera and pyrometer measurements.

4.1.4 Noise filtering

In order to filter the inherent data noise, fast Fourier transforms (FFT) were employed. A low frequency band pass filter was used, cutting off high frequency noise. The cut-off frequency was chosen such that the accuracy of the fitted parameters was not affected. This cut-off frequency was established based on

synthetic thermograms, which were computed via the FEA model (described in section 4.1.5) based on known (exact) input parameters. Subsequently, these were filtered using a top-hat low frequency FFT band pass filter of a particular band pass width. The new filtered thermograms were used in the same respect as experimental thermograms, whereby the inverse methodology shown in Figure 4-7 was followed. Thermal conductivity and specific heat were optimised and a conservative band pass width was determined (expressed as a fraction of the highest frequency). This is shown in Figure 4-8. The narrowest band width, which did not alter the accuracy of the results, was chosen and corresponds to 2% of the highest frequency. Hence 98% of the high frequencies are filtered.

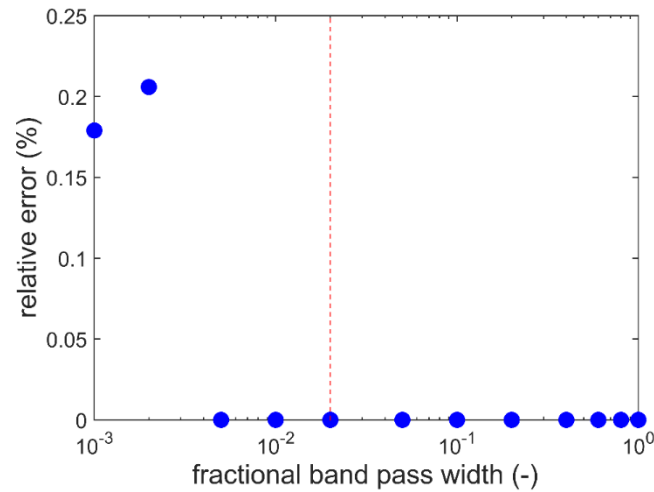


Figure 4-8: Relative error vs. fractional band width of the FFT filter obtained from least square optimisation of filtered synthetic thermograms. Red line shows the band width chosen for filtering all experimental results.

4.1.5 Finite Element Analysis (FEA)

The FEA model, which has been created with the FlexPDE¹²⁰ software, is axisymmetric (shown in Figure 4-9). The model describes the onset of the transient conditions in the sample immediately after the application of the laser pulse.

The governing equation is the transient heat equation:

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + q \quad (4-1)$$

where q is the volumetric heat source (W m^{-3}), ρ is the density (kg m^{-3}), c_p is the specific heat capacity at constant pressure ($\text{J kg}^{-1} \text{K}^{-1}$), k is thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), T is temperature (K) and t is time (s). Throughout this work the heat sources are assumed to be confined to the boundaries only (i.e. $q = 0$). Furthermore, a reduced variable is introduced such that:

$$T(t, r, z) = T(0, r, z) + \Psi(t, r, z) = T_0 + \Psi \quad (4-2)$$

where T_0 is the steady state temperature (K) and Ψ is the reduced variable temperature (K). Hence, the reduced boundary conditions are:

$$\begin{aligned} -k \frac{\partial \Psi}{\partial z} \Big|_{z=0} &= \theta(r, t) \times \varepsilon_{1064} - h(T) \times [T - T_0] - \varepsilon_{tot}(T) \times \sigma_{SB} \\ &\quad \times [T^4 - T_0^4] - [q_{vap}(T, P_0) - q_{vap}(T_0, P_0)] \end{aligned} \quad (4-3)$$

$$\begin{aligned} -k \frac{\partial \Psi}{\partial z} \Big|_{z=z_s} &= -h(T) \times [T - T_0] - \varepsilon_{tot}(T) \times \sigma_{SB} \times [T^4 - T_0^4] \\ &\quad - [q_{vap}(T, P_0) - q_{vap}(T_0, P_0)] \end{aligned} \quad (4-4)$$

$$\begin{aligned}
 -k \frac{\partial \Psi}{\partial r} \Big|_{r=r_s} &= -h(T) \times [T - T_0] - \varepsilon_{tot}(T) \times \sigma_{SB} \times [T^4 - T_0^4] \\
 &\quad - [q_{vap}(T, P_0) - q_{vap}(T_0, P_0)]
 \end{aligned} \tag{4-5}$$

where $h(T)$ is the temperature dependent convective heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$) and is discussed in section 4.1.11, ε_{tot} is the total hemispherical emissivity, σ_{SB} is the Stefan-Boltzmann constant ($\text{W m}^{-2} \text{K}^{-4}$), $\varepsilon_{(1064 \text{ nm})}$ is the emissivity at the laser wavelength (absorptivity), q_{vap} is the vapourisation heat flux (W m^{-2}) and is described in section 4.1.10, P_0 is the ambient pressure (-), z_s is the sample thickness (m) and r_s is the sample radius (m). The initial condition is:

$$\Psi_{t=0} = 0 \tag{4-6}$$

Quadratic triangular elements (6 nodes per element) have been used together with adaptive re-meshing. Further details on the convergence criteria are given in section 4.1.6. The model is based on the approximation of an isothermal steady state, which is tested and validated in section 5.2. Furthermore, the effect of the zirconia pins was examined (via a full 3-D FEA model) and found negligible due to the low thermal conductivity of zirconia and the small contact area with the sample.

The power profile of the laser is time and space dependent as was shown in Figure 4-3. The spatial profile of the laser can be described via two intersecting linear functions (shown already in Figure 4-3 and is further discussed in section 4.1.8), while the time dependence can be approximated via a top hat function. The space-

time profile, described by the $\theta(r, t)$ function in equation (4-3), can be expanded in the following manner:

$$\theta(r, t) = \frac{P(r, t)}{\pi r_b^2} = \frac{P(r) \times P(t)}{\pi r_b^2} \quad (4-7)$$

where P (J s^{-1}) is the power of the laser pulse, θ is the energy density (J m^{-2}) deposited by the beam, r_b is the nominal beam spot radius (m).

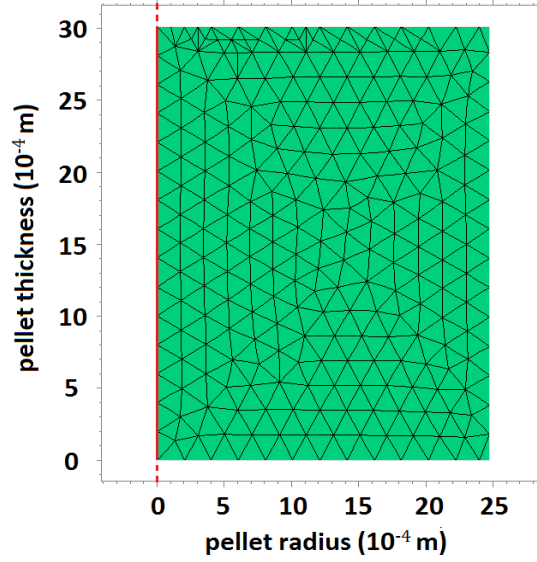


Figure 4-9: Example geometry of the axisymmetric model and the mesh used in FlexPDE. The red dashed line denotes the axis of symmetry at $r = 0$.

4.1.6 FEA convergence criteria

An adaptive convergence criterion is used within FlexPDE for both time and space. The relative convergence criteria on the dependent variable (temperature) is set to 0.002 (0.2%). This means that both the initial time step and mesh size are automatically adjusted and if needed, reduced to meet this criteria. FlexPDE uses a

variable-order implicit backward difference method in time. The time step is automatically adjusted by FlexPDE, as for the cubic term in a Taylor expansion of the variables in time to be lower than the convergence criteria applied (0.2%)¹²⁰. However, the adaptive mesh density controls are not sufficient to satisfy the aforementioned convergence criterion. Hence, additionally the larger dimension of the axisymmetric geometry is mapped by a finer user specified mesh grid. The grid mapped on the smaller dimension of the axisymmetric geometry is automatically adjusted to produce mesh elements of approximately equal size (compared to the elements along the larger dimension). The number of grid points at the boundary has been determined such that a minimum number of grid points is used to achieve a relative accuracy of approximately 0.2% on the dependent variable. The relative error has been calculated in two ways. The first of these is with respect to the maximum value of the thermogram with highest accuracy:

$$RE(t) = \left| \frac{f(t) - f_{ac}(t)}{f_{ac}(t_{max})} \right| \quad (4-8)$$

where RE is the time dependent relative error, f is the time dependent temperature (thermogram) f_{ac} is the time dependent temperature of the most accurate thermogram (50 grid points along the larger dimension) and $f_{ac}(t_{max})$ is the maximum value (constant) of the most accurate thermogram. The results from equation (4-8) for various numbers of grid points (g.p.) are plotted in Figure 4-10. It can be observed that 30 g.p. offer a sufficiently low relative error (0.2%). Finer

meshing leads to longer simulation times and increases the time needed for evaluating the fitting parameters. The variation of the relative error at both radial locations is comparable and shows nearly identical trends.

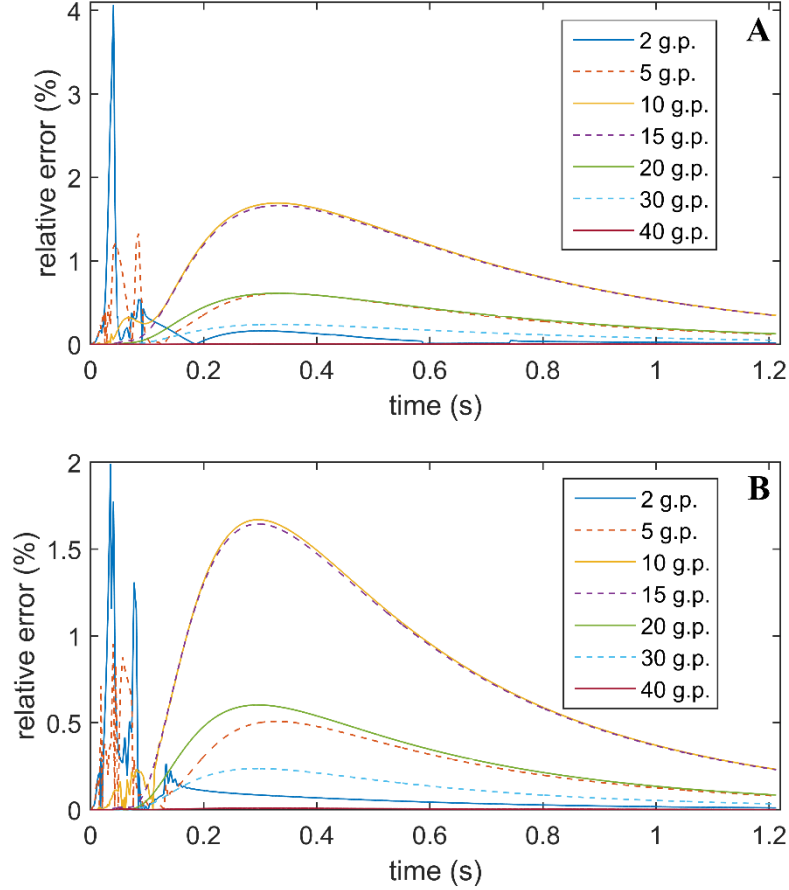


Figure 4-10: Relative error (RE) vs. time (duration of simulation, i.e computed thermogram) calculated via equation (4-8) for various numbers of grid points. A) Calculations of RE performed on the rear side of the axisymmetric geometry at the central radial location ($r/r_p=0$); B) Calculations of RE were performed on the rear side of the axisymmetric geometry at the central radial location ($r/r_p=0.5$).

The second method of evaluating the relative error is similar to its predecessor:

$$RE(t) = \left| \frac{f(t) - f_{ac}(t)}{f_{ac}(t)} \right| \quad (4-9)$$

where the constant denominator of equation (4-8) is substituted by the variable function $f_{ac}(t)$. The results from equation (4-9) are shown in Figure 4-11. Once again it is evident that 30 g.p. offer a sufficiently low relative error.

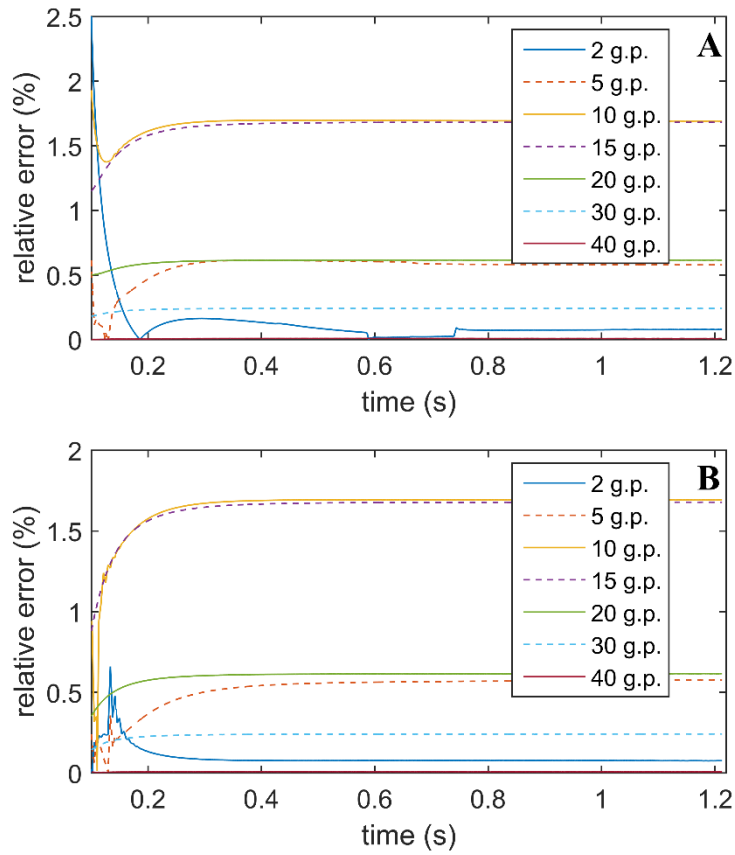


Figure 4-11: Relative error (RE) vs. time (duration of simulation, i.e. computed thermogram) calculated via equation (4-9) for various numbers of grid points.; A) Calculations of RE performed on the rear side of the axisymmetric geometry at the central radial location ($r/r_p=0$); B) Calculations of RE were performed on the rear side of the axisymmetric geometry at the central radial location ($r/r_p=0.5$).

4.1.7 Optimisation algorithm

The Levenberg-Marquardt method^{121,122} was used to find the least squares minimum between the experimental thermograms and the model thermograms. The convergence criteria used is the relative difference in the parameter vector between two consecutive iterations. One of the convergence criteria is the absolute relative difference in all individual parameters. If this absolute relative difference is lower than 10^{-4} after two consecutive parameter updates, the code terminates. The other convergence criterion is related to the gradient of the least square difference between model and experimental thermograms (see equation (4-12)) and is discussed below. The possible fitting parameters are thermal conductivity (k), specific heat capacity (c_p) total hemispherical emissivity (ϵ_{tot}) and heat transfer coefficient (h) and hence the parameter vector $\mathbf{p}$ is:

$$\mathbf{p} = \begin{pmatrix} k \\ c_p \\ \epsilon_{tot} \\ h \end{pmatrix} \quad (4-10)$$

The computer code, however, has been designed in a flexible manner, whereby any combination of the 4 fitting parameters (thermal conductivity (k), specific heat capacity (c_p), total hemispherical (ϵ_{tot}) and heat transfer coefficient (h)) can be chosen, while providing the other unselected parameters as input. In Figure 4-1 thermal diffusivity is also identified as a property, which can be evaluated, however thermal diffusivity would be indirectly estimated from two of the fitted properties.

This means that if for instance the code is used to evaluate thermal conductivity and specific heat, then by using the obtained results in addition to literature values for density one can calculate thermal diffusivity.

The cost function (f_c) for the least square minimisation is shown via equation (4-11), while the convergence criterion for the minimum least square difference is given by equation (4-12).

$$f_c(p) = \sum_{i=1}^N (f_M(p, t_i) - f_E(t_i))^2 \quad (4-11)$$

$$\frac{df_c}{dp} < 10^{-4} \quad (4-12)$$

where f_M is the time dependent temperature profile calculated by the model, f_E is the time dependent temperature profile measured by the infrared camera or pyrometer, t_i is the time at which a temperature reading was recorded by the camera or pyrometer after initiation of the laser pulse, p is the parameter vector, i is the index of the temperature measurement at a particular time and N is the total number of temperature records acquired at different times t_i .

An example thermogram is shown in Figure 4-12, which has been used in the evaluation of thermo-physical properties via the pyrometer method. This thermogram has been recorded via one of the high speed pyrometers, which provides a transient temperature measurement at the central radial location ($r=0$) on the rear surface of the sample. The FEA solution represents the calculated thermogram via the finite element model, which corresponds to the optimal set of fitting parameters.

In Figure 4-12 the thermogram's ascend is dominated by the thermal diffusivity and conductivity, the amplitude of the thermogram is predominantly dependent on the specific heat capacity and density of the material, while the descent is due to heat losses such as convective and radiative heat transfer. This will be quantitatively shown in Chapter 5.

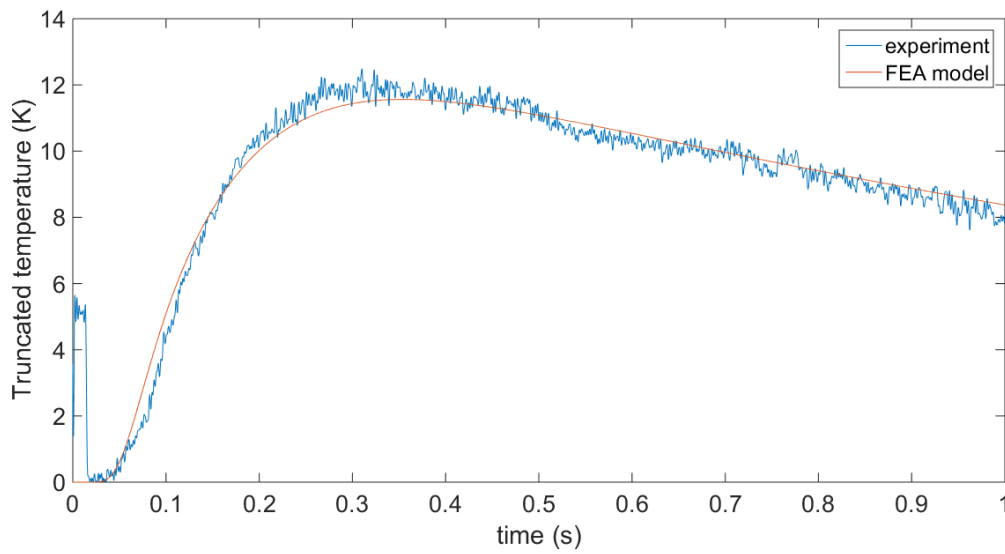


Figure 4-12: Example of a thermogram (temperature vs. time graph) obtained from experiment compared to the model thermogram obtained via least squares minimisation.

Figure 4-13A, Figure 4-13B and Figure 4-13C show the measurements, which can be obtained using the infrared camera described previously. Figure 4-13A shows an example of a 2-D steady state profile for a cylindrical sample. The profile is recorded prior to the onset of the laser pulse. Due to axial symmetry, Figure 4-13A can be described by the axi-symmetric profile presented in Figure 4-13B. Figure 4-13C shows the transient measurements performed by the camera corresponding to each of the

radial locations in Figure 4-13B. These range from $r=0$ (centre) to $r=r_p$ (edge). The FEA model results correspond to the optimal values describing the radial profile (and hence temperature profile) of one thermo-physical property (in this example thermal conductivity). Figure 4-13D shows the optimal FEA solution compared to computer generated data (synthetic data). The principle of the camera method is described in further detail in in section 4.1.12.2 and Chapter 5.

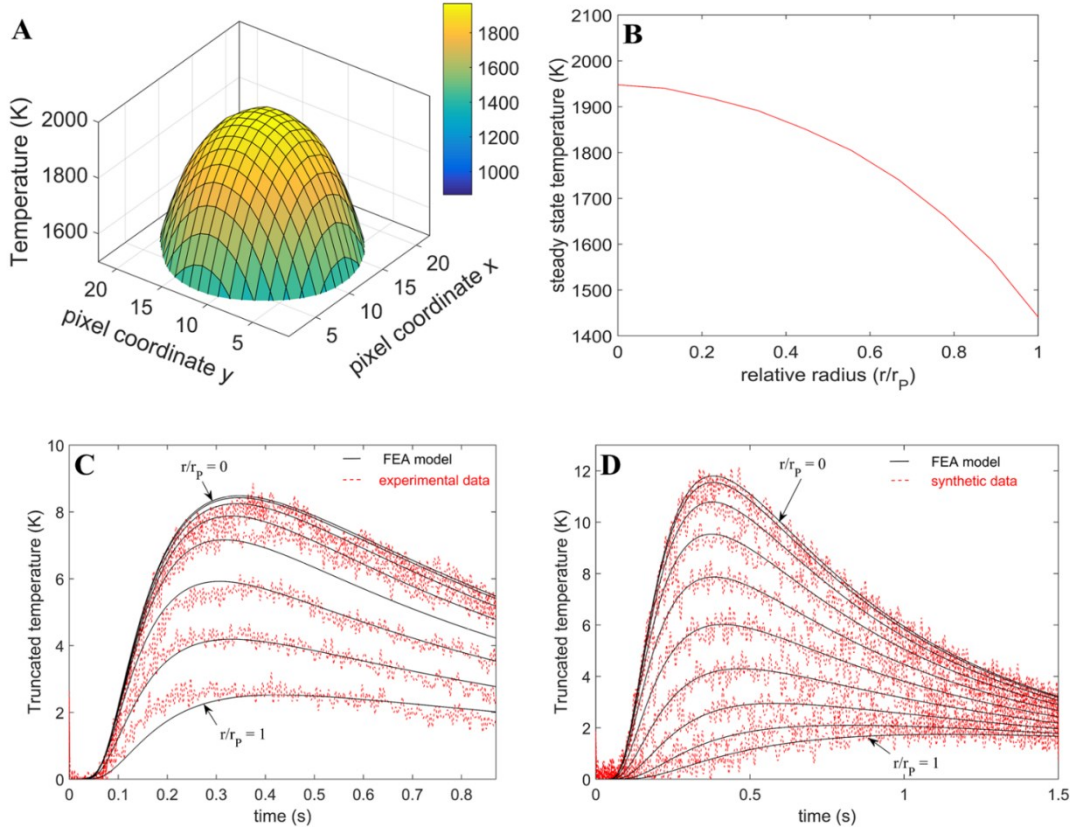


Figure 4-13: Steady state and transient measurements recorded using an infrared camera. (A) Example of a 3-D steady state temperature profile of a UO₂ sample. The magnitudes of the x and y axes are indices and not metric quantities.; (B) the axisymmetric steady state temperature distribution deduced from (A); (C) example of radially distributed thermograms for a UO₂ sample measured by the infrared camera compared to the optimised finite element (FEA) solution. (D) Radially distributed synthetic thermograms (produced via the FEA model with perturbed input parameters and added artificial noise) compared to the optimised finite element solution.

4.1.8 Impact of the laser beam's spatial profile

Some of the most influential input parameters are the set of parameters describing the spatial profile of the laser (this is shown via the sensitivity study in section 5.1.1).

In Figure 4-14 the spatial profile of the laser (calibrated for the optical arrangement) is compared to a top hat function. The integral of the power with respect to the normalized radius is the same for both profiles. This implies that the total laser energy density was the same in each case, only its spatial distribution differs. It is evident that the actual characteristics of the laser beam are significantly different from the assumed top hat characteristics. Previous studies that developed similar methods have used the approximate top hat form in their analytical model (a sufficiently accurate approximation in their case considering they had measured a relatively flat near square shaped spatial power profile) and also fitted parameters such as r_0 (beam spot or waist radius)⁶⁵. The latter may be problematic due to a high degree of correlation between the beam spot radius and specific heat. In this work the more representative spatial laser profile (for the presented optical configuration in Figure 4-12) will be implemented in the finite element model. In order to evaluate the effect of the spatial profile on the fitted properties (thermal conductivity (k) and specific heat (c_F)), two cases are examined for a single experimental thermogram at 1536 K. The first case determines k and c_P using the top-hat approximation as input, while in the second case the calibrated or measured spatial laser profile is used. The top hat function has been implemented in the finite element model as follows:

$$P(r) \begin{cases} P_{max} & r \in (0, r_B) \\ 0 & r \in (r_B, \infty) \end{cases} \quad (4-13)$$

The calibrated profile is expressed in the following manner:

$$P(r) \begin{cases} P_{\max} (0.967 - 0.2342 \times r) & r \in (0, 1.1587 r_B) \\ P_{\max} (8.2923 - 6.5561 \times r) & r \in (1.1587 r_B, 1.2648 r_B) \\ 0 & r \in (1.2648 r_B, \infty) \end{cases} \quad (4-14)$$

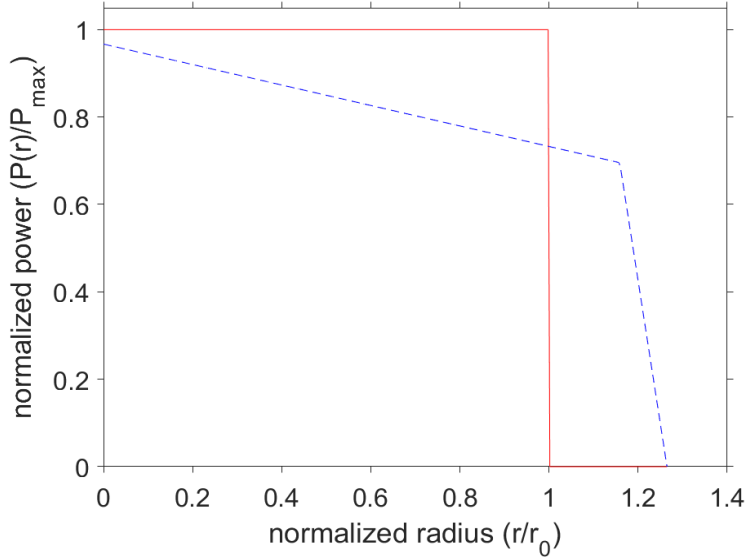


Figure 4-14: The calibrated spatial profile (blue dashed line) of the laser compared to a top hat approximation of the spatial laser profile (red line). $P(r)$ represents the calibrated or measured power as a function of radius, while $P_{\max}$ represents the integral power.

The impact of the different spatial laser profiles is presented in Table 4-1. It is evident that the effect on thermal conductivity and specific heat capacity is around 15% and 20% respectively. Furthermore, the values obtained via calorimetry measurements combined with conventional LF diffusivity measurements at JRC-Karlsruhe⁸⁵ are in very good agreement with the output from the new method using the calibrated power profile. However, this finding does not discard the accuracy of studies where the laser spatial profile was square shaped, it just serves to show the numerical model

can be used to harness the full potential of the LF method when using lasers with spatial power profiles deviating from the ideal top hat shape.

Table 4-1: A comparison between the calculated properties (thermal conductivity (k) and specific heat (c_p)) using the calibrated and top hat laser profiles at pressure $p = 0.4$ MPa. Furthermore, results are compared to the values obtained by Hay et al.⁸⁵.

	T (K)	k (W m ⁻¹ K ⁻¹)	c_p (J kg ⁻¹ K ⁻¹)
Top hat approximation	1536	46.93	2327
Calibrated profile	1536	40.87	1938
Hay et al. (JRC-Karlsruhe) ⁸⁵	1523	42.04	1976

4.1.9 Impact of noise filtering

The signal to noise ratio can be improved either by post-processing the experimental data via noise filtering or by increasing the laser pulse power and hence increasing the signal gain. The second is appropriate only to the extent, whereby the fitted properties are not significantly impacted by the temperature variation of the sample (e.g. large temperature amplitude on the front side leading to deviation from the isothermal assumption or inducing phase changes, such as melting). Hence, a combination of sufficient signal gain and adoption of noise filtering has been used. In Table 4-2 the results for thermal conductivity and specific heat capacity of isostatically pressed graphite are compared for two cases: 1) a noisy (unfiltered)

thermogram; 2) the same thermogram passed through the low pass filter (filtered).

The values of these two properties are exactly the same in both cases. However, the signal to noise ratio and the computation time are significantly improved when using the FFT low pass filter.

Table 4-2: Comparison of the effect of noise filtering for a thermogram at temperature $T = 2219$ K and pressure $p = 0.4$ MPa. The examined parameters include: the fitted properties (thermal conductivity and specific heat capacity); signal to noise ratio (SNR); computational time (t_{comp}) for a single core processor of 2.6 GHz frequency and RAM (random-access memory) 8 GB.

	T	k	c_p	SNR	t_{comp}
	(K)	(W m ⁻¹ K ⁻¹)	(J kg ⁻¹ K ⁻¹)	(10 ³)	(10 ³ s)
Unfiltered	2219	35.64	1895	1.406	2.789
Filtered	2219	35.64	1895	2.443	1.834

4.1.10 Heat losses due to vapourisation

The vapourisation heat flux can be expressed using the Hertz-Langmuir formulation^{123,124}:

$$q_{\text{vap}}(T, P) = \sum m_{\text{mol},i} \varphi_i(T, P) \Delta H^v_i \quad (4-15)$$

where $m_{\text{mol},i}$ is the molar mass (kg mol⁻¹), φ_i is the vapour flux (mol m⁻² s⁻¹) and ΔH^v_i is the enthalpy of vapourisation (J kg⁻¹) of the respective gaseous species i . The flux can be expressed as:

$$\varphi_i(T, P) = (1 - u) \frac{p_i(T) \times 10^5}{P_0 \sqrt{2\pi m_{mol,i} RT}} \quad (4-16)$$

where u is a backscattering coefficient ($u = 0.18$)¹²³, p_i is the equilibrium partial pressure of species i with respect to 1 bar ambient pressure (bar), R is the universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and P_0 is the ambient pressure factor (-). Vapourisation has only been considered for UO_2 and ThO_2 and the methodology for the calculation of the partial pressures of the respective gas species is outlined in Chapter 7 and Chapter 8. It must be noted, that for all measured samples, the reduction in mass and thickness was measured to be less than 1 % after the experiment. Hence, mass loss and sample geometry changes (due to vaporisation) have been neglected in the FEA model.

4.1.11 Convective heat transfer coefficient

One of the heat loss mechanisms is natural convection and is described by a convective heat transfer coefficient. Previously values for this property have been either fitted⁶⁵, arbitrarily chosen⁹⁴ or approximated as constant over a broad temperature range¹²⁵. In this work the convective heat transfer coefficient is semi-empirically evaluated based on the sample geometry and the properties of the gaseous atmosphere. Equations (4-17) to (4-20) have been used to derive the convective heat transfer coefficient ($\bar{h}_D$) as a function of temperature.

$$\bar{h}_D = \frac{\overline{Nu}_D k_g}{D} \quad (4-17)$$

where k_g represents the thermal conductivity of the gas ($\text{W m}^{-1} \text{K}^{-1}$), D is the sample diameter (m) and $\overline{Nu}_D$ represents the Nusselt number. Churchill and Chu¹²⁶ suggested the following expression for the Nusselt number during laminar flow for a vertical plate:

$$\overline{Nu}_D = 0.68 + 0.67 \times Ra_D^{1/4} \left\{ 1 + \left[\frac{0.492}{Pr} \right]^{9/16} \right\}^{-4/9} \quad (4-18)$$

where Ra_D and Pr are the Rayleigh and Prandtl numbers. Furthermore these dimensionless numbers can be related to the gas properties in the following way:

$$Ra_D = \frac{g\beta\Delta TD^3}{\alpha\nu} \quad (4-19)$$

$$Pr = \frac{\alpha}{\nu} \quad (4-20)$$

where g is the gravitational acceleration (m s^{-2}), β is the gas compressibility, α is the gas thermal diffusivity ($\text{m}^2 \text{s}^{-1}$) and ν is the kinematic viscosity of the gas ($\text{m}^2 \text{s}^{-1}$).

The properties of argon have been taken from Little¹²⁷ and Stewart et al.¹²⁸.

The results for the convective heat transfer coefficient calculated via equations (4-17) to (4-20) are shown in Figure 4-15. These are then used as input in the finite element model. The results presented in Figure 4-15 were not experimentally validated, as the model sensitivity to this parameter (see section 5.1) was shown to be negligible.

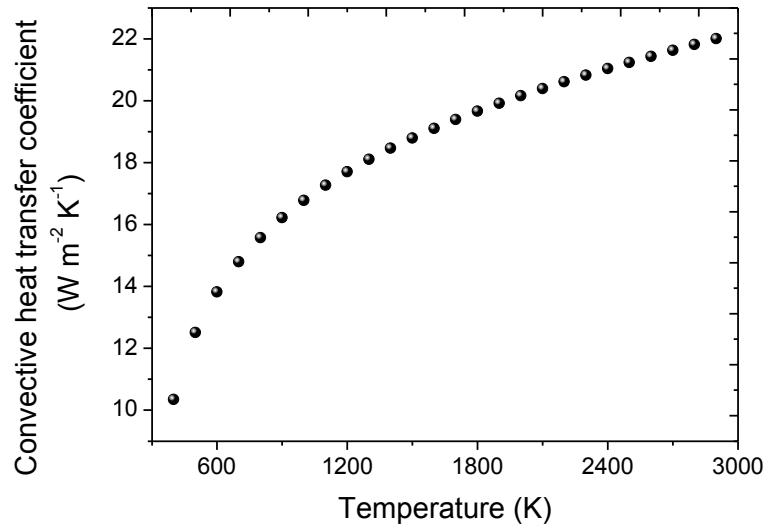


Figure 4-15: Calculated heat transfer coefficient for a cylindrical pellet of graphite in Argon as a function of temperature at a pressure of 1 bar.

4.1.12 Fitting approximations

Three different approximations have been adopted regarding the variation of the thermo-physical properties radially across the cylindrical geometry of the examined samples (pellets). One of these approximations is applied when using the pyrometer method. Two additional approximations are implemented for the radial variation of the properties, when evaluated via the infrared camera method.

4.1.12.1 Pyrometer method

The approximation used, as part of the pyrometer method, is to assume invariant fitting parameters (i.e. the properties of interest – specific heat, thermal conductivity, total hemispherical emissivity). Hence, the properties are assumed constant across the radius of the sample, which is shown in Figure 4-16.

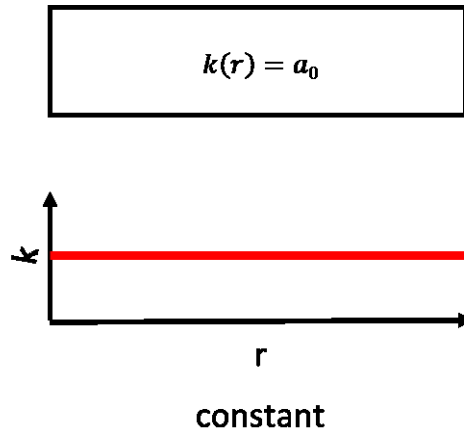


Figure 4-16: Approximation of thermal conductivity (k) as a function of radius for the pyrometer method. The box on top represents the axisymmetric geometry of the sample with the axis of symmetry at $r = 0$. A constant value (a_0) is used to describe the radial dependence of the evaluated property (e.g. k – thermal conductivity).

4.1.12.2 Infrared camera method

Two approximations are used to model the radially distributed thermograms obtained experimentally from the infrared camera – a functional approximation (polynomial function or PNOM) and an iterative gradient (IG) approximation. The functional approximation pre-sets an equation based radial dependence (and hence temperature dependence) on the calculated properties. The parameters describing the property's function are then optimised. A schematic of the functional

approximation is shown in Figure 4-17 where thermal conductivity is represented as a function of radius by a (N-1)th order polynomial.

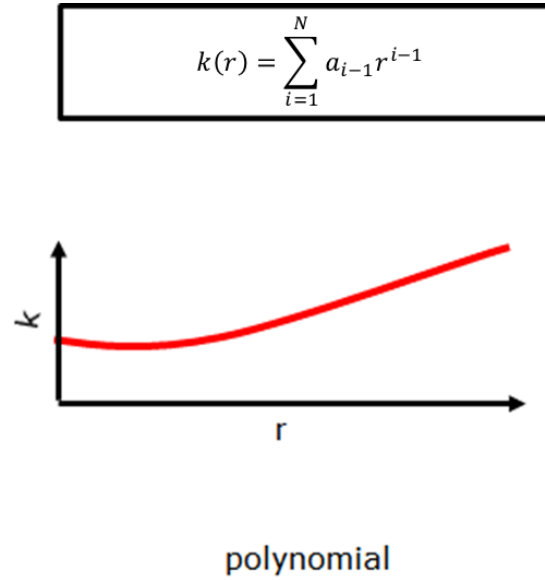


Figure 4-17: Approximation of thermal conductivity (k) as a function of radius (infrared camera method). The box on top represents the axisymmetric geometry of the sample with the axis of symmetry at $r = 0$ on the graph below. In this case an (N-1)th order polynomial is used to describe the radial dependence of the evaluated property. The respective fitting parameters are N constants a_{i-1} .

In Figure 4-17 thermal conductivity serves as an example property; the method can be applied to other properties such as specific heat capacity and, possibly, total hemispherical emissivity. The last of the three will be estimated in this work only by using the pyrometer method.

The IG approach does not assume a global functional form for the radial dependence (and hence temperature dependence) of the calculated property. Using this approach the central thermal conductivity is calculated first and stored at its respective

position, while the neighbouring value is allowed to fluctuate and thus establish a linear gradient between the two radial positions. The calculated properties are stored and the iteration process moves in a radial direction from the centre towards the outer edge.

Figure 4-18 shows a schematic of the IG method. The first iteration assumes constant properties along the sample radius, which is a sufficiently good approximation for a relatively large (in terms of surface area) and homogenous surface heat source. The values obtained (e.g. $k(r_1)$) in the first iteration are stored and are invariant within the first radial segment (first small section of the rectangular box in Figure 4-18) during iteration 2. It must be noted that the first radial segment is made infinitesimally small, confining the converged property value to $r_1=0$ (e.g. $k(r=0)$). During iteration 2 a linear gradient is established to describe the local property variation as a function of radius. By using the stored properties from the previous iteration ($k(r_{stored})$ in equation (4-21)) only one parameter is varied, namely the gradient of the line (e.g. m_2 or equivalently $\left.\frac{dk}{dr}\right|_{r=r_2}$ in equation (4-21)). At a critical radius (r_c) the linearly varying property becomes radially invariant. Hence, a step function is achieved with a cut-off radius at r_c . Upon convergence, the linear variation of the properties is stored within the second radial segment and the process moves on towards the edge of the axisymmetric geometry. Another way to imagine this procedure is via a first order Taylor expansion:

$$k(r)_i \approx \begin{cases} k(r_{stored}) & r \in \{0, r_{i-1}\} \\ \left\{ k(r_{i-1}) - r_{i-1} \frac{dk}{dr} \Big|_{r=r_i} \right\} + r \frac{dk}{dr} \Big|_{r=r_i} & r \in \{r_{i-1}, r_C\} \\ \left\{ k(r_{i-1}) - r_{i-1} \frac{dk}{dr} \Big|_{r=r_i} \right\} + r_C \frac{dk}{dr} \Big|_{r=r_i} & r \in \{r_C, r_P\} \end{cases} \quad (4-21)$$

where i represents the respective iteration and also coincides with the radial segment identifier (e.g. $\mathbf{r}_1, \mathbf{r}_2$, etc.).

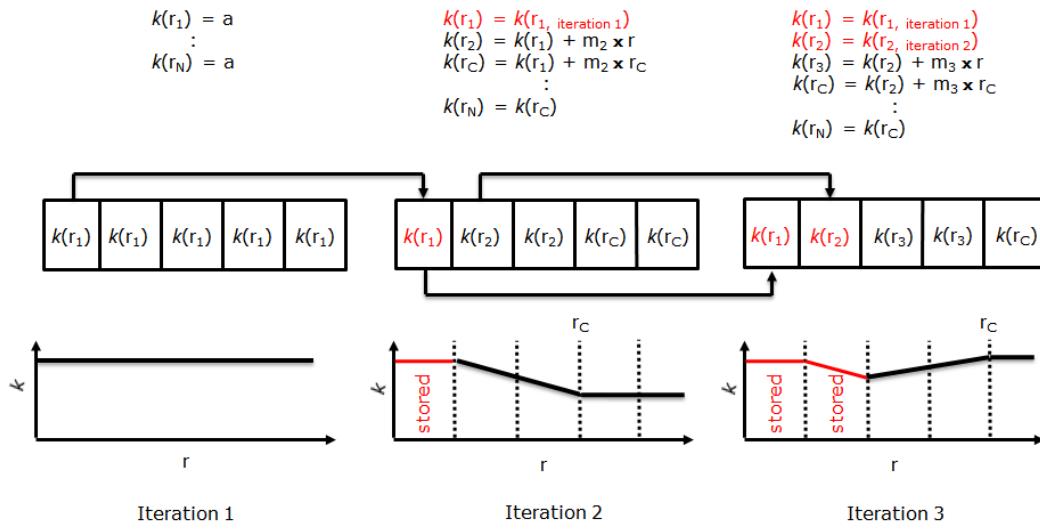


Figure 4-18: Schematic of the first three iterations of the iterative gradient (IG) method. In black are all the values, which are allowed to vary during the optimisation procedure of the respective iteration, while in red are the values which have been stored and fixed as a result of prior iterations.

4.2 Spectral emissivity (640 nm)

At higher temperatures (> 2000 K) the uncertainty in normal spectral emissivity can lead to significant temperature measurement uncertainties (this is further discussed and quantified in section 5.4.2 of Chapter 5). Wien's approximation¹²⁹ (equation (3-91)) can be used to estimate the true temperature and emissivity from multi-

wavelength pyrometry. Assuming that this property does not vary within a given wavelength range (e.g. 600 - 800 nm) and from the measured radiances (and hence temperatures) at different wavelengths (via a multi-wavelength spectropyrometer) the spectral emissivity can be retrieved from the slope of the linear fit shown in Figure 4-19. Furthermore, the y-intercept in Figure 4-19 corresponds to the inverse of the true (black-body) temperature. Once, the spectral emissivity at the pyrometer wavelength (shown in Figure 4-19) has been determined, the pyrometer radiance temperatures (T_R) can be converted into true temperatures (T_B) again using equation (3-91).

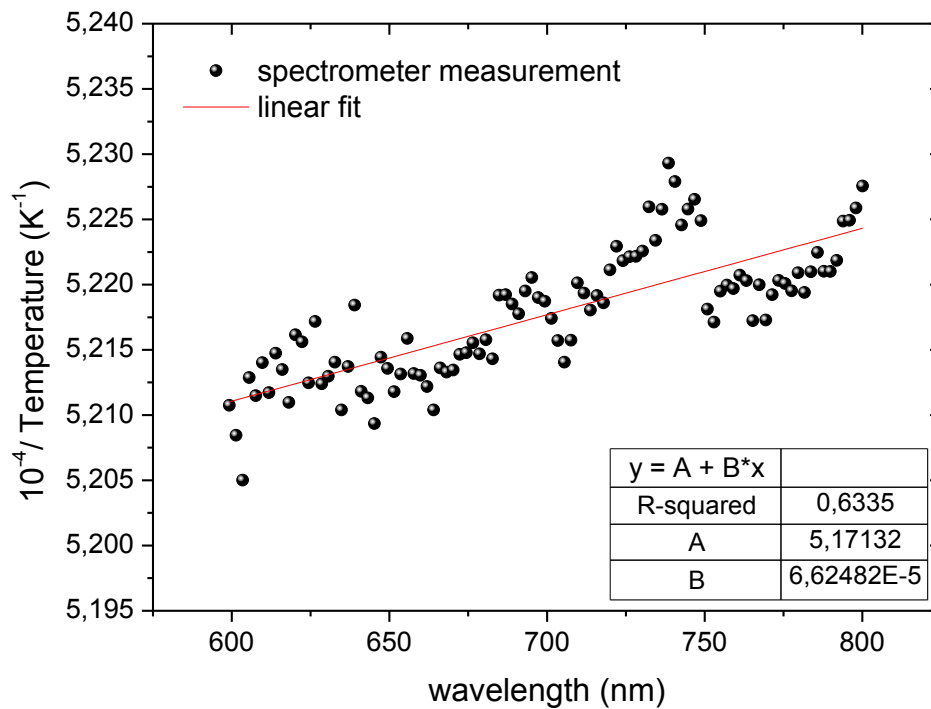


Figure 4-19: Inverse temperature as a function of wavelength measured by a 256 channel spectropyrometer (example from a measurement on isostatically pressed graphite at 1933 K).

4.3 X-ray diffraction (XRD)

X-ray diffraction patterns are obtained from powder produced by mechanically milling the specimen. The main components of the XRD set-up are a tungsten filament, a ceramic copper tube target, a Ge monochromator (allowing for purely Cu $K\alpha_1$ X-ray radiation to be recorded) and a Bruker D8 X-ray diffractometer. All recorded spectra are refined using the Rietveld method via the JANA 2006 software¹³⁰.

4.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is performed via a FEI (Philips) XL 40 microscope using a tungsten filament (200 V – 30 keV). Both secondary electrons and backscattered electrons were used for acquiring high resolution images.

Chapter 5 : Testing and validation of the new inverse method

– “*There can be theory but, you know, the problem is you've got to be able to test it. So theories are one thing, testing is another.*” –

Brian Schmidt, astrophysicist

In Chapter 4 all experimental methods were outlined. Among these, a new methodology was proposed in the form of an inverse method using experimental data from a laser flash set-up. In this chapter this new methodology will be analysed using the concepts of sensitivity and correlation. Furthermore, both synthetic and experimental data will be used to test and validate the novel numerical inverse method and all associated approximations. Finally, the errors of the evaluated thermo-physical properties will be estimated.

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Parts published in: Pavlov, et al. *Int. J. Therm. Sci.* under review (2017).

5.1 Sensitivity analysis and correlation between parameters

Sensitivity and dependence studies have been performed for both methods – the pyrometer and infrared camera methods. The sensitivity study is particularly important in selecting uncertain input parameters, which strongly affect the propagated output error. The correlation study is useful when examining possible parameter pairs, which can be fitted simultaneously.

In order to examine the relative importance of the different model parameters a sensitivity analysis was performed. The sensitivity analysis, presented in Figure 5-1 and Figure 5-2, is based on the following numerical derivative:

$$S = p \frac{df}{dp} \tag{5-1}$$

where S is the sensitivity coefficient (K), p is the respective parameter (e.g. thermal conductivity, specific heat, sample thickness, spatial profile of laser beam, etc.), f is the temperature output of the finite element analysis (FEA) model or model thermogram (K). The parameters with the highest absolute sensitivity coefficients (positive or negative) have the strongest effect per change in parameter on the model output thermogram. Hence, small changes in these sensitive parameters lead to relatively big differences in the model output. Furthermore, parameters with sensitivity coefficients close to zero have a much lower relative effect on the

calculated output. In order to examine the integral sensitivity with respect to the whole duration of a thermogram the following integral is written:

$$\int S_i(t) = \int_0^{t_D} \left| \frac{df(t)}{dp_i} p_i \right| dt \quad (5-2)$$

where t_D ($t_D = 1.5$ s) is the duration of the transient (thermogram). All derivatives and integrals have been performed numerically using the forward difference method and trapezium rule, respectively. The $\int S_i(t)$ results facilitate a comparison over the whole duration of a thermogram and are complimentary to the time dependent sensitivity coefficients $S_i(t)$. Parameters with larger integral sensitivity coefficients have relatively larger influence on the output compared to parameters with lower values.

Finally, in order to further analyse the potential and limitations of an inverse method one must consider the interdependence of parameters and in particular the Pearson correlation coefficient. This parameter can be calculated in the following manner:

$$\rho_{ij} = \frac{\int_0^{t_D} \left(\frac{df(t)}{dp_i} \cdot \frac{df(t)}{dp_j} \right) dt}{\left[\left(\int_0^{t_D} \left(\frac{df(t)}{dp_i} \right)^2 dt \right) \cdot \left(\int_0^{t_D} \left(\frac{df(t)}{dp_j} \right)^2 dt \right) \right]^{1/2}} \quad (5-3)$$

Where ρ_{ij} is the correlation coefficient between parameters i and j . By calculating the coefficient for each pair in the parameter vector (see equation (4-10) in Chapter 4), it can be determined which pairs of parameters may be suitable for simultaneous determination. Highly correlated parameters, with their absolute correlation

coefficients (positive or negative) approaching unity, are not suitable for simultaneous fitting, as it is easy to obtain good fits (low least squares difference between model and experimental data) with a set of physically unsound parameter values. Hence, the inverse problem becomes highly ill-posed.

5.1.1 Pyrometer method

The sensitivity analysis in Figure 5-1 shows that the highest absolute sensitivity was exhibited by sample thickness (t_s) at 0.25 s. However, the spatial profile of the laser beam shows the greatest integral sensitivity over the first 1.5 s. The spatial profile sensitivity has been obtained by changing the parameters describing the radial dependence of the power (see section 4.1.8 in Chapter 4). These are incrementally changed from values corresponding to the most focused state of the laser beam to values of a more defocused state. Furthermore from Figure 5-1, it can be concluded that the thermogram is sensitive to thermal conductivity and specific heat capacity. This is important as it shows that relatively small changes in these properties will have a measurable effect on the thermogram. Additionally, since the peaks and shapes of the curves are noticeably different, this means the two are not highly correlated. This is also quantitatively confirmed in Table 5-1 by the calculated correlation coefficient between specific heat and thermal conductivity. Hence, the method is suitable for the determination of these two properties by simultaneous fitting. It must be noted that the sensitivity coefficient of density (ρ) follows exactly

the one of specific heat capacity (c_P) and has not been plotted in Figure 5-1 for better clarity. This means that these two properties are completely correlated – a result of the formulation of the heat equation (equation (4-1) in Chapter 4) where specific heat capacity and density are the two multiples composing the energy stored per unit temperature. Furthermore, it is evident that the sensitivity coefficients of total hemispherical emissivity, spatial laser profile, absorptivity, density (equivalent to c_F) and thickness are all significant. Hence, uncertainties in these input parameters can propagate and lead to an appreciable uncertainty in the calculated output (specific heat capacity and thermal conductivity). Therefore, these will be examined carefully and, based upon their measurement uncertainty, it will be possible to estimate the model output error (described in section 5.4.1).

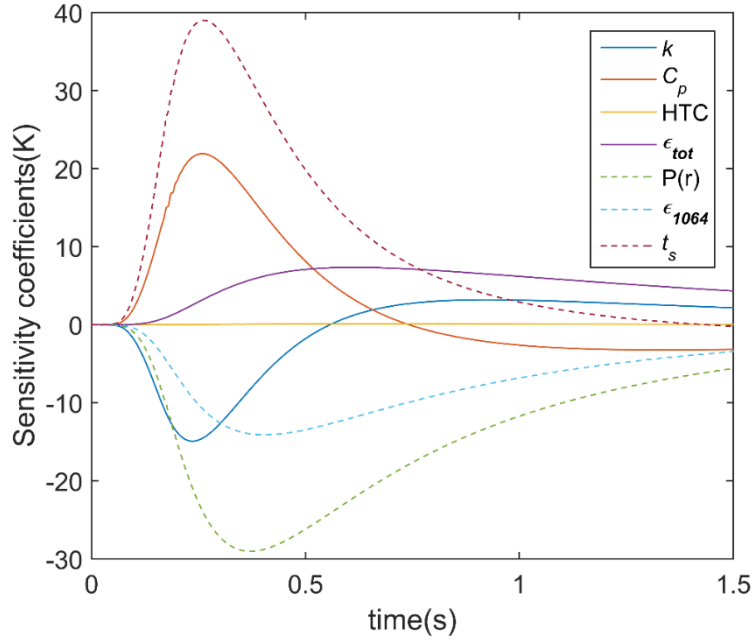


Figure 5-1: Sensitivity coefficients (K) vs. time at the central rear location of the axisymmetric geometry. Examined parameters include thermal conductivity (k), specific heat capacity (c_p), convective heat transfer coefficient (HTC), the total hemispherical emissivity (ϵ_{tot}), spatial laser beam profile ($P(r)$), absorptivity (ϵ_{1064}) and thickness (t_s).

The correlation matrix for the four possible fitting parameters for a thermogram at the central radial location on the rear boundary of the cylindrical sample geometry is shown in Table 5-1. The most correlated pair is the one of the convective heat transfer coefficient (h) and the total hemispherical emissivity (ϵ_{tot}) with a correlation coefficient of unity. This makes the reliable simultaneous determination of these two parameters impossible. All other parameter pairs are significantly less correlated and can be determined simultaneously.

Table 5-1: Correlation matrix for the possible fitting parameters for the rear central thermogram.

	k	c_p	h	ε
k	1.00	-0.74	0.11	0.11
c_p	-0.74	1.00	0.56	0.56
h	0.11	0.56	1.00	1.00
ε	0.11	0.56	1.00	1.00

5.1.2 Camera method

Figure 5-2 shows the sensitivity coefficients at different radial locations on the rear boundary according to equation (5-1), while Figure 5-3 compares the integral sensitivity coefficients using equation (5-2). It is evident that there is a general nonlinear drop in the sensitivity of all parameters towards the edge of the sample. This follows the radial drop in the deposited laser energy density from the centre of the sample towards the outer periphery. This could lead to experimental variances (e.g. noise) having an increasingly stronger adverse effect on the accuracy of the fitted property values towards the sample periphery. However, this negative effect could be partially offset by the increase in the relative integral sensitivity of the parameters of interest, namely thermal conductivity and specific heat capacity. Figure 5-3B and Figure 5-2E shows thermal conductivity and specific heat capacity become the most sensitive parameters at $r/r_p=1$.

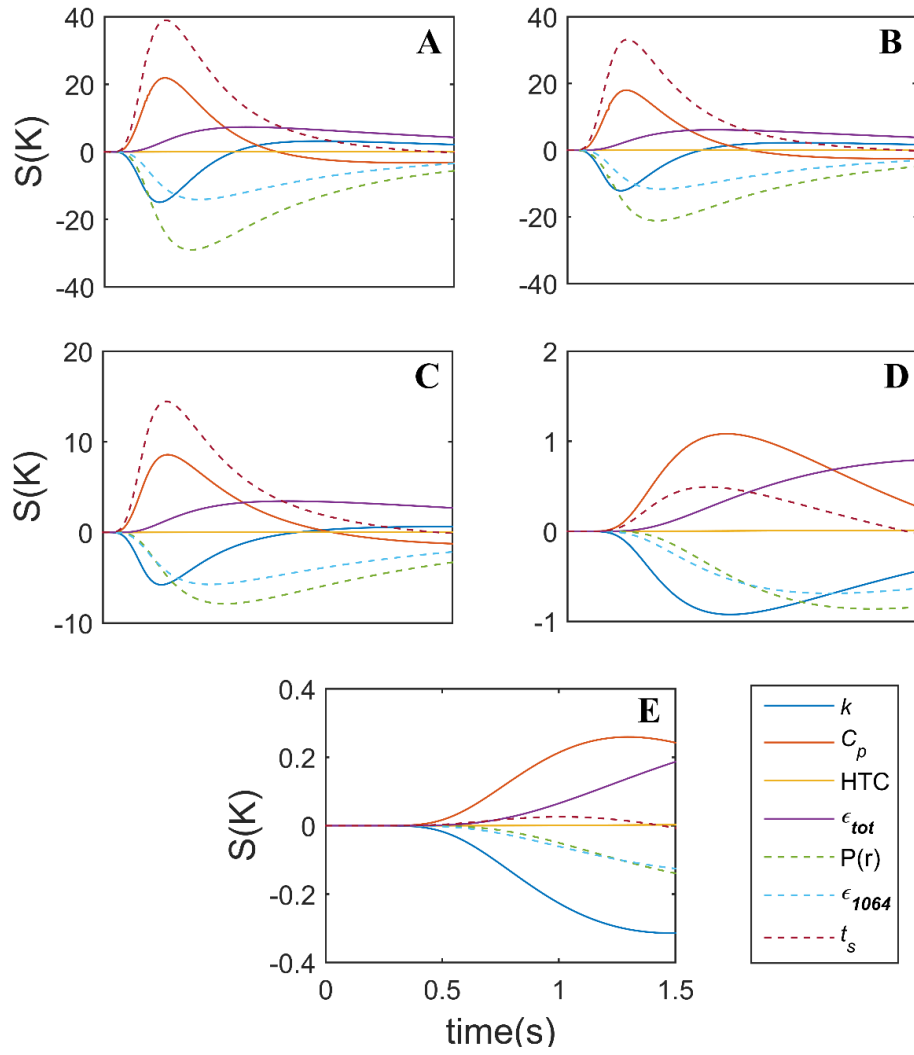


Figure 5-2: Sensitivity coefficients $S(K)$ on the rear boundary as a function of time computed using the thermo-physical properties of UO_2 for various parameters (thermal conductivity (k), specific heat (c_p), convective heat transfer coefficient (HTC), the total hemispherical emissivity (ϵ_{tot}), spatial laser beam profile ($P(r)$), absorptivity (ϵ_{1064}) and thickness (t_s)). A) radial location $r=0$; B) radial location $r=r_B/2$; C) radial location $r=r_B$; D) radial location $r=r_B + (r_P - r_B)/2$; E) radial location $r=r_P$; (r_B – beam spot radius (m), r_P – sample radius (m)). The range of each x-axis in each subplot is identical to the one shown in E).

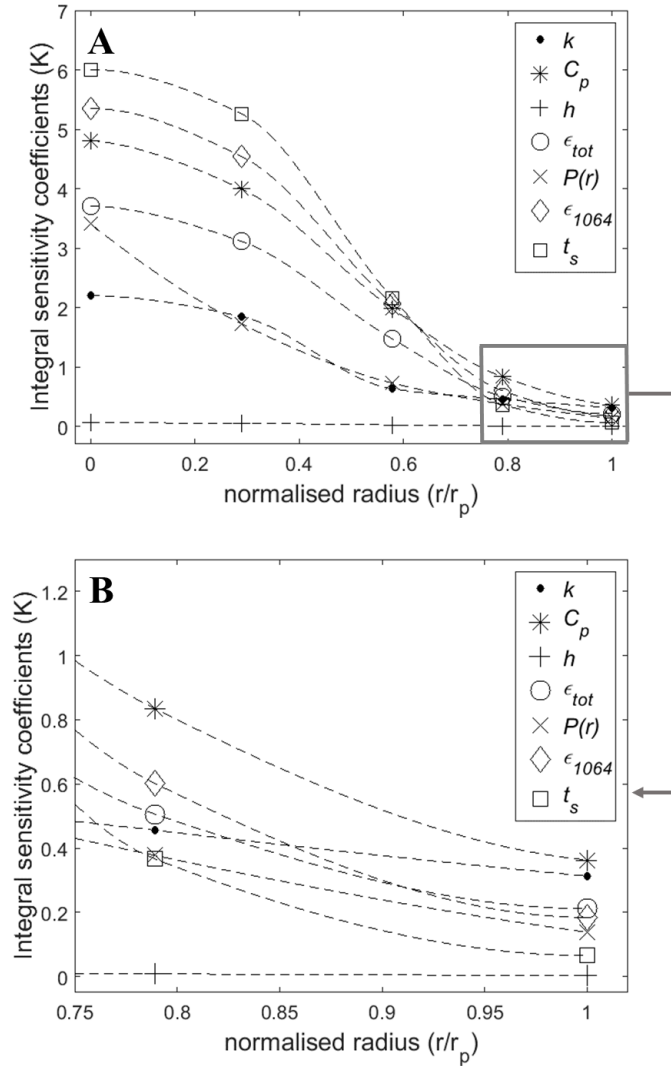


Figure 5-3: (A) Integral sensitivity coefficients as a function of the relative radial location (r/r_p). Examined parameters include thermal conductivity (k), specific heat capacity (c_p), convective heat transfer coefficient (h), the total hemispherical emissivity (ϵ_{tot}), spatial laser beam profile ($P(r)$), absorptivity (ϵ_{1064}) and sample thickness (t_s); (B) zoom-in of the lower right corner of (A).

In Figure 5-4 the correlation curves for 6 unique pairs of fitting parameters are shown (based on the parameters in equation (4-10) in Chapter 4 and calculated via equation (5-3)). The correlation coefficients have been plotted as a function of radius in order

to examine the radial dependence between parameters. This carried out, in order to understand if simultaneous property determination is possible for all radially distributed thermograms. From Figure 5-4 it becomes evident that the heat loss parameters (convective heat transfer coefficient (h) and total hemispherical emissivity (ϵ_{tot})) are very strongly positively correlated and hence cannot be fitted simultaneously. Furthermore, all parameter pairs tend to become strongly correlated towards the edge of the sample, making simultaneous fitting unadvisable. However, simultaneous fitting of thermal conductivity, specific heat capacity and one of the heat loss parameters (preferably total hemispherical emissivity, due to the significantly larger sensitivity) is possible for the central thermogram. This corresponds to the approach applied as part of the pyrometer method and has been investigated already by Pavlov, et al.¹³¹ and Ronchi et al.¹⁸. Hence, using the infrared camera methodology one should investigate the radial profile of one property at a time, in order for the converged parameter set to be physically correct.

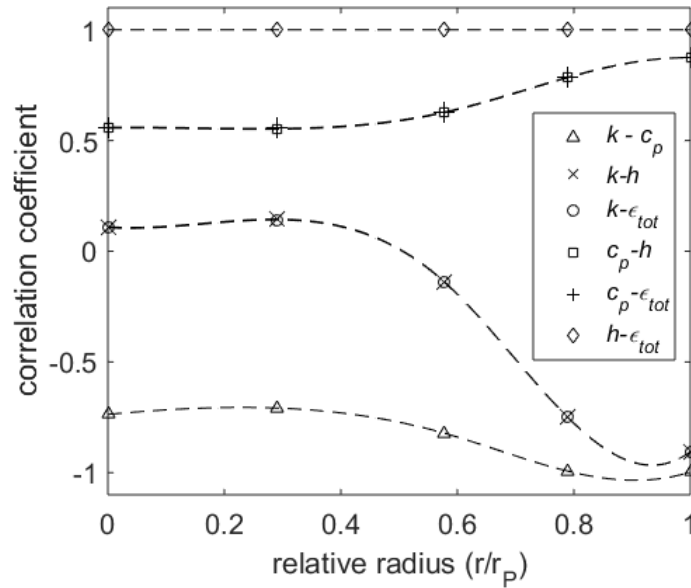


Figure 5-4: The correlation (Pearson coefficient) of parameter pairs vs. relative radial position. The chosen parameters are based on equation (5-3) and are thermal conductivity (k), specific heat (c_p), convective heat transfer coefficient (h) and total hemispherical emissivity (ϵ_{tot}).

5.2 Synthetic data tests

The purpose of the synthetic data tests is to ensure that from a theoretical perspective the proposed methodologies work with a high degree of accuracy and reliability. Such tests must be completed prior to experimentally validating the new methodologies. In this way, one can be confident about the fundamental robustness of the methods before being confronted by the vast spectrum of experimental related issues and uncertainties. All synthetic data was produced using the properties of 95% dense UO_2 reported by Fink¹³².

5.2.1 Pyrometer method

The synthetic data tests performed on the pyrometer method examine the theoretical capability of the method to evaluate thermal conductivity, specific heat and total hemispherical emissivity. Thermal conductivity and specific heat are evaluated with an accuracy of less than 0.5% and around 1%, respectively (see Table 5-2). Total hemispherical emissivity has been evaluated with an accuracy of around 1.5% (see Table 5-2). Hence, the pyrometer method can be used to determine these properties simultaneously.

Table 5-2: Comparison of the evaluated and exact properties using synthetic thermograms (computed using the properties of 95% dense UO_2 reported by Fink¹³²) and the isothermal approximation for the central radial location.

	k ($\text{W m}^{-1} \text{K}^{-1}$)	c_p ($\text{J kg}^{-1} \text{K}^{-1}$)	ϵ (-)
calculated	2.073	361.9	0.837
exact	2.068	365.7	0.85
error (%)	0.24	1.04	1.53

5.2.2 Camera method

In order to assess the two approximations (iterative gradient or IG approximation and polynomial or PNOM approximation), a set of synthetic radially distributed thermograms were computed. These were also based on the thermo-physical properties of UO_2 ¹³². The input parameters (steady state radial temperature profile of the sample, sample dimensions and laser beam spot characteristics) are obtained

experimentally. The steady state radial temperature profile is obtained via laser heating (described in this work and shown in Figure 4-1) of a UO_2 specimen. The reference thermal conductivity used was taken from Ronchi et al.⁶⁵, while the reference specific heat correlation was taken from Fink et al.¹³².

Once the synthetic thermograms are calculated, each approximation is initiated in close proximity to the reference values of one property – either specific heat capacity or thermal conductivity. As shown in the previous section, it is important to fit only one property and its associated parameters at a time. Figure 5-5 compares the two approximations and their results to the exact solution (i.e. the input property used for producing the synthetic data). Separate evaluations were completed for thermal conductivity and specific heat.

Figure 5-5 shows that both approximations give good estimates to the exact solutions. The IG approach outperforms the PNOM approximation in the case of thermal conductivity, while the PNOM approach gives a slightly better estimate of the specific heat profile. This can also be shown by comparing the relative standard deviation (RSD) and R^2 values (calculated via equations (5-4) to (5-6)) of each approximation for the two properties (see Table 5-3).

$$R^2 = 1 - \sum_i^N \frac{(f_{exact}(r_i) - f_{evaluated}(r_i))^2}{(f_{exact}(r_i) - \bar{f}_{evaluated})^2} \quad (5-4)$$

$$RSD = \frac{1}{\bar{f}_{exact}} \sum_i^N \frac{\sqrt{(f_{exact}(r_i) - f_{evaluated}(r_i))^2}}{N - 1} \quad (5-5)$$

$$\bar{f}_{exact} = \sum_i^N \frac{f_{evaluated}(r_i)}{N} \quad (5-6)$$

where f_{exact} is the exact profile of the property, $f_{evaluated}$ is the evaluated profile of the property using either the PNOM or IG approximation, $\bar{f}_{exact}$ is the mean of the exact property profile. In the case of specific heat capacity the PNOM output exhibits both a lower RSD, as well as higher coefficient of dependence (R^2), while for thermal conductivity the output of the IG approach is associated with both a lower RSD and higher R^2 .

Table 5-3: Comparison of the relative standard deviation (RSD) and the coefficient of determination (R^2) for the output of each approximation.

Statistical parameter	IG	PNOM
RSD of c_p (%)	0.23	0.07
RSD of k (%)	0.15	0.34
R^2 of c_p	0.967	0.997
R^2 of k	0.993	0.971

The radial profile of thermal conductivity cannot be very exactly reproduced by a 2nd order polynomial and hence the PNOM approximation performs worse. Furthermore, the polynomial approximation can lead to results exhibiting unphysical features such as pronounced minima or maxima, while in reality this is just a

functional-fitting artefact. This can be observed in Figure 5-5B and Figure 5-5D where the PNOM approach erroneously predicts a minimum in thermal conductivity at $r/r_p \approx 0.25$ at around 1925 K. In terms of computation time the IG approximation is more expensive and scales linearly with the number of radially distributed thermograms. The IG approximation was initialised around 64% away from the exact profile (for thermal conductivity at $3.4 \text{ W m}^{-1} \text{ K}^{-1}$ while for specific heat at around $600 \text{ J kg}^{-1} \text{ K}^{-1}$). The PNOM approximation was initialised with parameter values only 15% away from the values representing the optimal fit to the exact profile as the PNOM approximation is much more sensitive to the initial values of its parameter vector. Hence, in cases where the temperature dependence of the evaluated property is completely unknown, the converged parameter set may not accurately reflect the true underlying property profile. The IG approach is less sensitive to the initial values as it fits a single parameter per property at a time. This makes the IG approximation very attractive when there is no prior knowledge of the temperature dependence of a property. Hence, the IG approach is more general and non-parametric in nature.

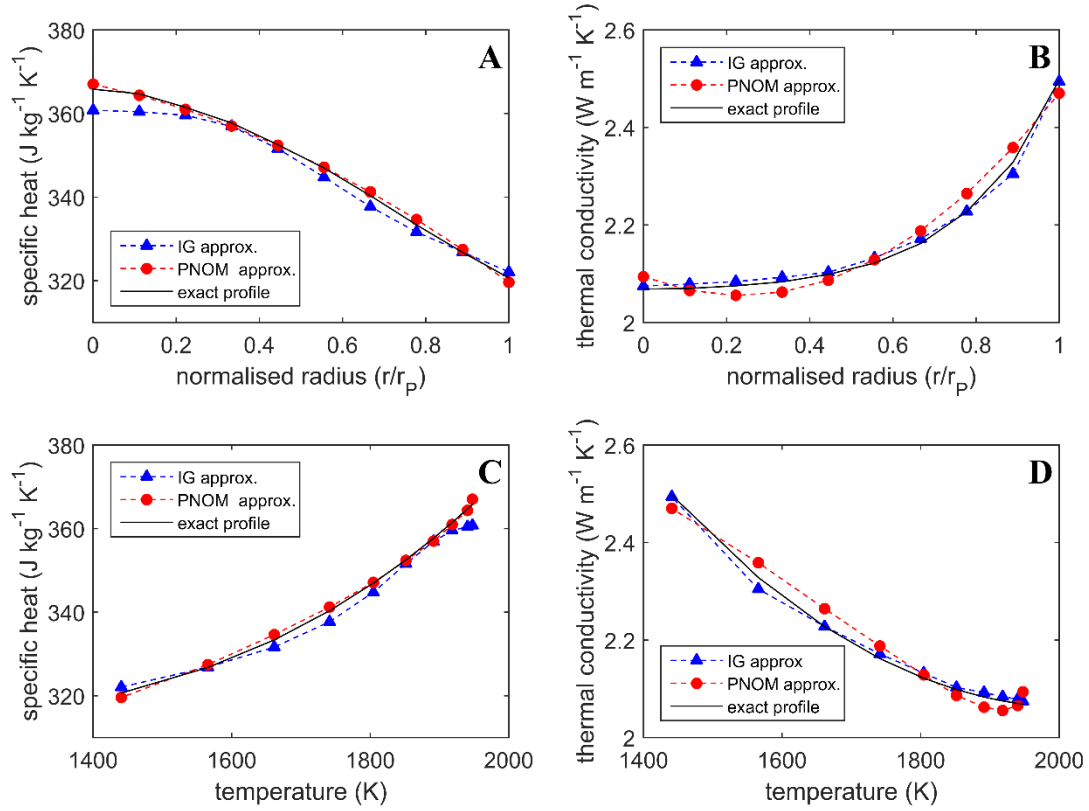


Figure 5-5: Summary of synthetic data tests. A) specific heat vs. normalised radius; B) thermal conductivity vs. normalised radius. Both plots compare the output of the two approximations (Iterative gradient (IG) approximation vs. polynomial (PNOM) approximation) to the exact solution (the exact solutions are the property profiles used to generate the synthetic thermograms, which were then used to test the approximations). The two property profiles were obtained from independent runs of the IG and PNOM approximations (i.e. the two properties were not fitted simultaneously); C) specific heat vs. temperature; D) thermal conductivity vs. temperature. Graphs C and D were obtained by assigning the known temperature at each radial position to the corresponding property value at the same radial coordinate.

5.3 Experimental data tests

After exploring their theoretical limits, the new inverse methodologies have to be tested experimentally. This has been accomplished by comparing the results of the two methods to the recommended literature values at temperatures below 2000 K for two different materials – UO_2 and isostatically pressed graphite. These materials are described in further detail in Chapter 6 and Chapter 7. The results presented in this section have been obtained by following the methodology described in section 4.1.

5.3.1 Pyrometer method

The pyrometer method performs well for two materials with significantly different thermo-physical properties - isostatically pressed graphite (samples described in Chapter 6) and UO_2 (samples described in Chapter 7). Thermal conductivity was evaluated within 3%, while specific heat was within 2% of the reference values. The estimated total hemispherical emissivity for UO_2 is close to the recommended value by Fink¹³², however in the case of isostatically pressed graphite a deviation of 10% is observed between the current and literature values.

Table 5-4: Comparison of evaluated and reference properties for UO_2 at 1562 K and isostatically pressed graphite at 1536 K.

	property	calculated	literature	reference	deviation (%)
UO_2	k ($\text{W m}^{-1} \text{K}^{-1}$)	2.27*	2.33	¹³²	2.6
	c_p ($\text{J kg}^{-1} \text{K}^{-1}$)	326	327	¹³²	0.3
	ε (-)	0.86	0.85	¹³²	1.2
graphite	k ($\text{W m}^{-1} \text{K}^{-1}$)	40.87	42.04	⁸⁵	2.8
	c_p ($\text{J kg}^{-1} \text{K}^{-1}$)	1938	1976	⁸⁵	1.9
	ε (-)	0.75	0.84	¹³³	10.6

*corrected to 95% porosity

5.3.2 Camera method

Ultimately, the practical capabilities of the infrared camera methodology were tested.

The two materials investigated were UO_2 and isostatically pressed polycrystalline graphite, and their thermal conductivities were evaluated. The results of their thermal conductivities are presented in Figure 5-6. It is clear that the PNOM approximation and the IG approximation yield very good results for both materials.

The UO_2 results were corrected to 95% porosity using the Brand and Neuer¹³⁴ correction. The model curve in Figure 5-6B is representative of the experimental data in this temperature range, as has been shown previously by Pavlov et al¹³¹. The error on thermal conductivity is 19.6%, based on the same work¹³¹ and will be discussed in section 5.4.1.

Figure 5-6 shows rather flat thermal conductivity profiles with respect to temperature for both materials. In the case of graphite, this is due to its high thermal conductivity.

Uranium dioxide, on the other hand, exhibits a minimum in thermal conductivity at around 2000 K. In the vicinity of this stationary point the thermal conductivity of UO_2 does not vary significantly. Future experimental investigations will test the inverse method on systems with more significant property variations with respect to temperature. Furthermore, the future advance to more precise, higher resolution thermal cameras and lasers with more stable power outputs will enable the method to be even more sensitive to property variations.

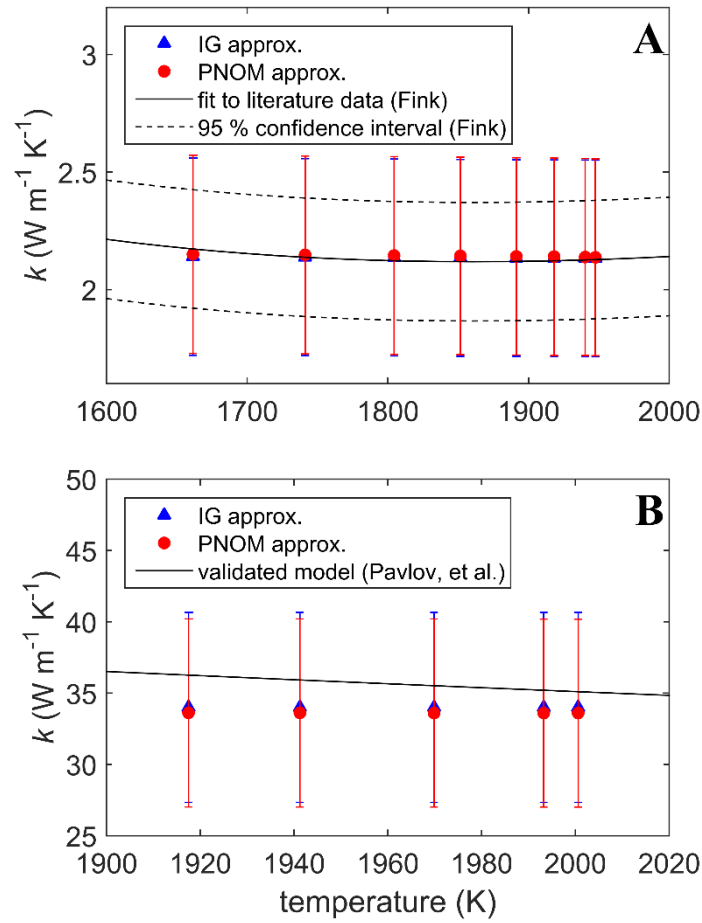


Figure 5-6: Experimental evaluation of thermal conductivity (k) vs. temperature using the camera method. A) Results for UO_2 using PNOM and IG approximations compared to recommendation of Fink; B) Results for isostatically pressed graphite using PNOM and IG approximations compared to recommendation of Pavlov, et al.¹³¹

5.4 Error analysis

The error in the fitted properties (thermal conductivity, specific heat and thermal diffusivity) is discussed. Furthermore, errors in the measured temperatures are discussed, due to uncertainties in spectral emissivity and due to the limiting nature of Wien's approximation.

5.4.1 Specific heat, thermal conductivity and thermal diffusivity

Previously little effort has been made to accurately estimate the error of equivalent methods (arising from uncertainty in input parameters)^{18,65}. The sensitivity analysis performed (shown in Figure 5-1) has demonstrated that the five input parameters - total hemispherical emissivity (could also be used as a fitting parameter), spatial laser profile, absorptivity thickness and density, have a significant impact on the calculated thermogram. These parameters are then used as factors in a 3-level full factorial design.

The five parameters selected, based on the sensitivity study (see Figure 5-1), have been split into three levels corresponding to a best estimate, minimum and maximum value, both at two standard deviations away from the mean estimated value. The corresponding histograms of the output are presented in Figure 5-7. From the quantile-quantile plots it can be seen that a normal distribution is a reasonable approximation of the output distributions of thermal conductivity, specific heat capacity and thermal diffusivity.

Assuming the input parameters are randomly distributed and treating them as independent events, the total uncertainty can be represented in the following way:

$$\mathfrak{d}_{total} = \mathfrak{d}_{model} + \mathfrak{d}_{exp}. \quad (5-7)$$

where $\mathfrak{d}_{exp}$ is the uncertainty associated with experimental scatter based on a variation in the recorded thermograms for the same measurement temperature, while

$\mathfrak{d}_{model}$ is the propagated error resulting from uncertainties in the five model input parameters - total hemispherical emissivity, spatial laser profile, absorptivity (spectral emissivity at 1064 nm), density and thickness. The number of different ways to combine the 5 input parameters, each consisting of 3 levels, is 243. One can weight the output of each combination of input parameters assuming a Gaussian probability density function for each input parameter.

$$\mathfrak{d}_{model} = \sqrt{\sum_{k=1}^{243} \frac{w_k (y_k - \overline{y_w})^2}{\left(\frac{N}{N-1} \sum w_k\right)}} \quad (5-8)$$

where k is the combination index, y_k is the output value (α, C_p, k) of that particular combination and the weighted mean $(\overline{y_w})$ is:

$$\overline{y_w} = \sum_{k=1}^{243} y_k w_k \left[\sum_{k=1}^{243} w_k \right]^{-1} \quad (5-9)$$

where the weight (w_k) is expressed as follows:

$$w_k = \prod_{i=1}^5 \left[\exp \frac{-(x_{ij} - \mu_i)^2}{2\sigma_i^2} \right] \quad (5-10)$$

where the value of a certain parameter of certain level is:

$$x_{ij} = \begin{cases} \mu_i + 2\sigma_i & \text{for } j = 1 \\ \mu_i & \text{for } j = 2 \\ \mu_i - 2\sigma_i & \text{for } j = 3 \end{cases} \quad (5-11)$$

where μ represents the arithmetic mean, σ stands for one standard deviation, i represents the input parameter and j is the level.

The results from the error analysis are summarized in Table 5-5. Thermal conductivity has the largest associated error of 20% while specific heat capacity and thermal diffusivity have an error of around 15%. The reason for thermal diffusivity having a smaller associated error is due to the negative correlation between thermal conductivity and specific heat capacity, whereby the increase in the fitted value of one of these properties is generally compensated by an increase in the other. This implies that thermal diffusivity, representing the ratio of the two prior properties, would not necessarily follow the error propagation law, as seen from Table 5-5.

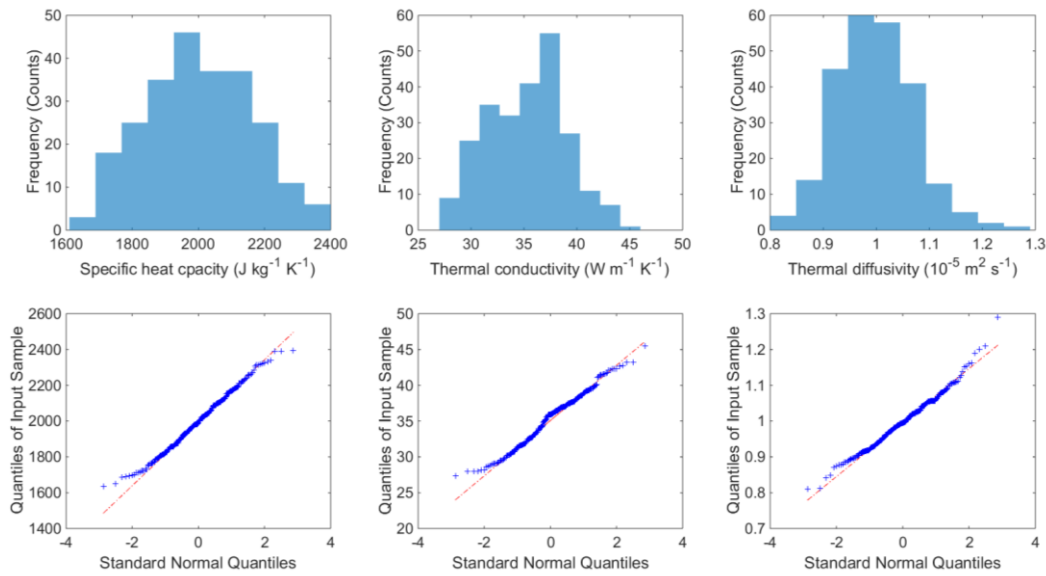


Figure 5-7: Histogram of specific heat values (top left) with its respective quantile – quantile plot (bottom left), thermal conductivity values (top middle) with its respective quantile – quantile plot (bottom middle) and thermal diffusivity values (top right) with its respective quantile – quantile plot (bottom right).

Table 5-5: Summary of the output uncertainty of specific heat (Δc_P), thermal conductivity (Δk) and thermal diffusivity ($\Delta \alpha$) for a thermogram at temperature $T = 2050$ K and at a pressure $p = 0.4$ MPa.

uncertainty type	Δc_P (J kg ⁻¹ K ⁻¹)	Δk (W m ⁻¹ K ⁻¹)	$\Delta \alpha$ (10 ⁻⁶ m ² s ⁻¹)
$2\mathfrak{J}_{model}/\overline{y_w}$	0.095	0.123	0.085
$2\mathfrak{J}_{exp.}/\overline{y_w}$	0.047	0.071	0.065
$2\mathfrak{J}_{total}/\overline{y_w}$	0.152	0.194	0.150

5.4.2 Measured temperature and spectral emissivity

The accuracy of the measured temperature can be adversely affected by two phenomena: i) uncertainty in the measured spectral emissivity (shown in Figure 5-8); ii) deviation of the black-body temperature calculated using Wien's approximation from the correct black-body temperature (shown in Figure 5-9). The first (i) is estimated via equation (3-92) and from Figure 5-8 it can be seen that large emissivity uncertainties could lead to several hundred or, in extreme cases, thousands of degrees Kelvin error in the measured temperatures. Furthermore, it is evident that the less emissive the material is, the greater is the uncertainty in the estimated temperature. The limitations of Wien's law are shown in Figure 5-9. The absolute error plotted in Figure 5-9 represents the difference between the numerically calculated temperature, based on Planck's law, and the temperature calculated via Wien's approximation. It is clear that for devices measuring the material's temperature in the visible wavelength range (e.g. 645 nm) the error is not significant (with the exception of

materials with extremely low emissivities - below 0.1). Such devices are the pyrometers used in this work. However, in the case of devices operating at longer wavelengths (e.g. the infrared camera used in this work operates at 1500 nm) the error at higher temperatures (above 3000 K) could become significant as can be seen in Figure 5-9. However, all materials, which were examined via the infrared camera method in this work, exhibited relatively high spectral emissivities and were subjected to low enough temperatures (up to 2000 K).

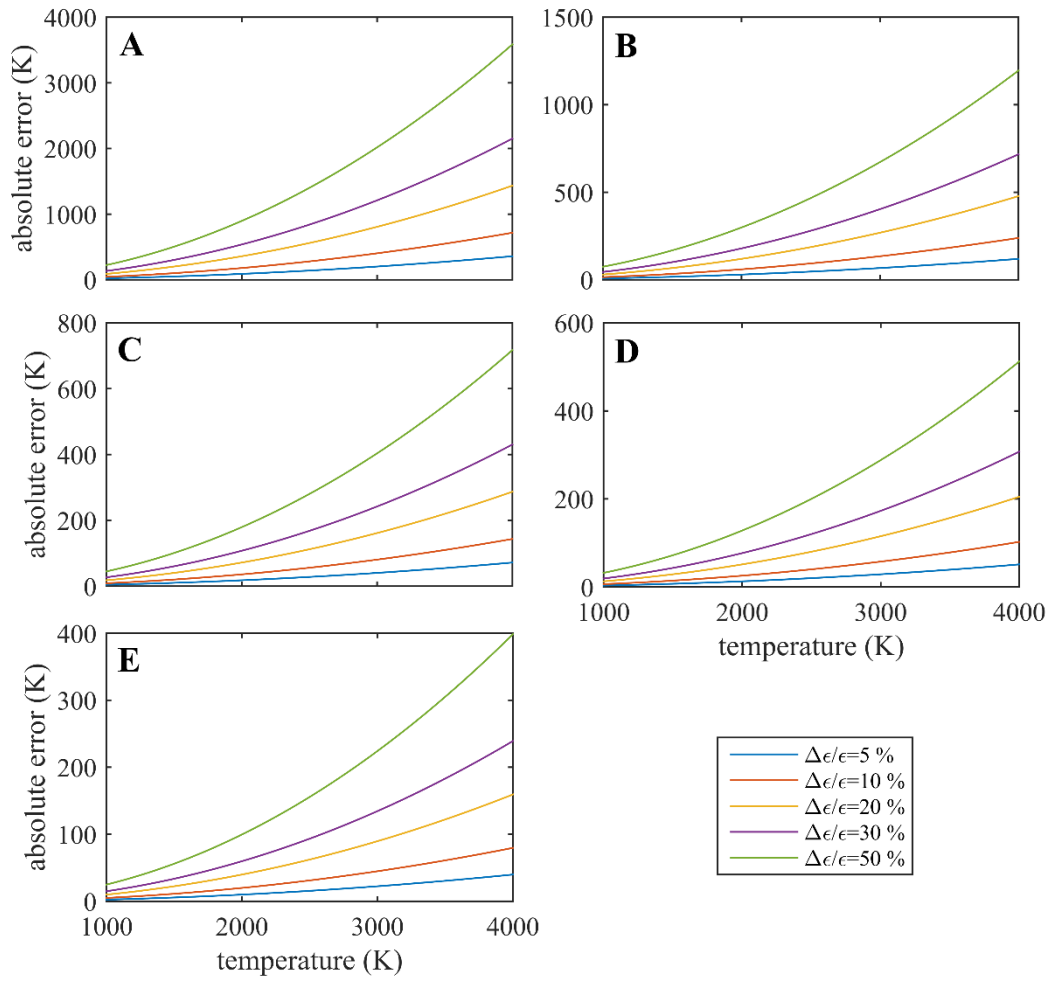


Figure 5-8: Absolute measurement error (K) vs. temperature (K) for different spectral emissivities at 645 nm. A) spectral emissivity (ϵ) = 0.1; B) spectral emissivity (ϵ) = 0.3; C) spectral emissivity (ϵ) = 0.5; D) spectral emissivity (ϵ) = 0.7; E) spectral emissivity (ϵ) = 0.9. Various deviations from the correct spectral emissivity are represented by the different colored lines. The range of each x-axis in each plot is identical to the ones shown in D) and E).

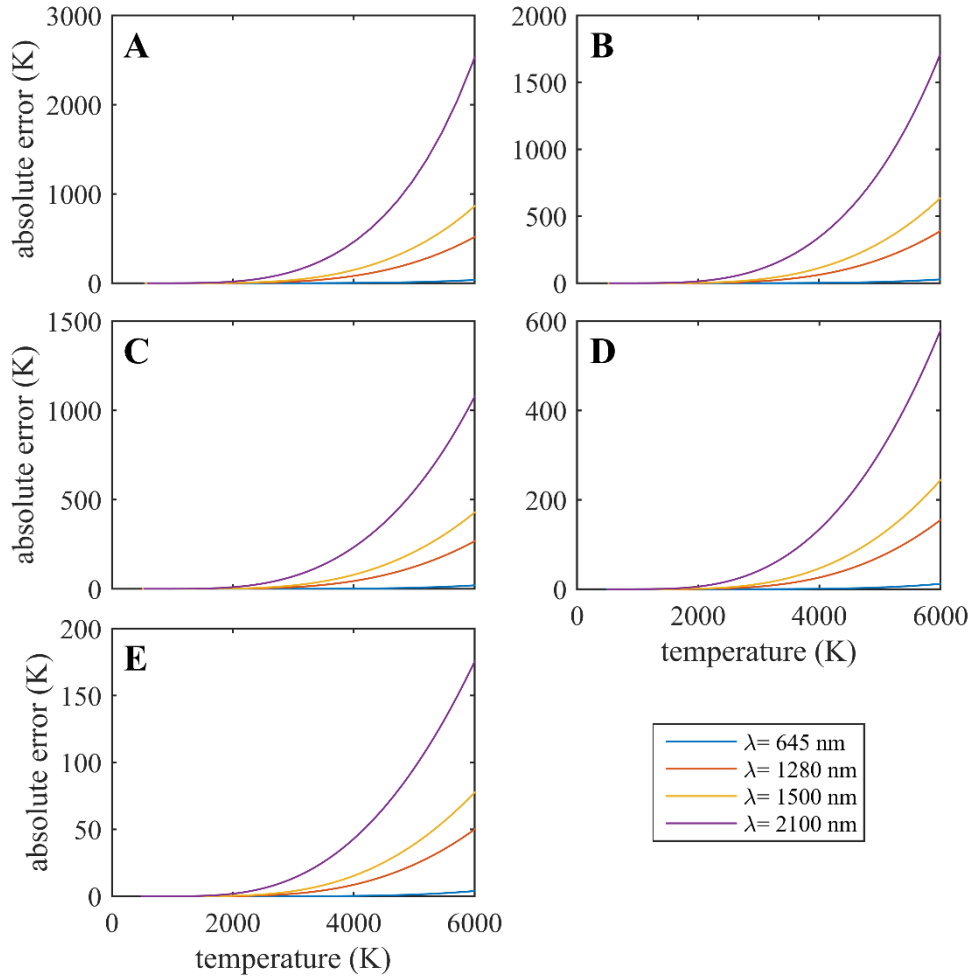


Figure 5-9: Absolute measurement error (K) vs. temperature (K) for different values of spectral emissivity: A) spectral emissivity (ϵ) = 0.1; B) spectral emissivity (ϵ) = 0.3; C) spectral emissivity (ϵ) = 0.5; D) spectral emissivity (ϵ) = 0.7; E) spectral emissivity (ϵ) = 0.9. The different colored lines represent different wavelengths. The measurement error represents the difference between the implicit numerical solution to Planck's law and Wien's approximation. The range of each x-axis in each plot is identical to the ones shown in D) and E).

5.5 Summary

The two new approaches – infrared camera and pyrometer methods, were successfully tested using both synthetic and experimental data. The correlation analysis showed that by using the pyrometer method specific heat and thermal conductivity can be evaluated simultaneously alongside one heat loss parameter (preferably total hemispherical emissivity, due to higher sensitivity). The increase in the correlation between these parameters as a function of radius indicated that the camera method is only suitable for the evaluation of a single property as a function of radius and hence temperature. The sensitivity analysis identified input parameters, which significantly contribute to the error of the evaluated properties. These were then introduced in a 3-level full factorial design in order to estimate the combined experimental and theoretical error on the evaluated properties (relative errors of: 19.4% for k ; 15.2% for c_P ; and 15% for α). The uncertainty of the measured temperature was estimated based on the range of error in the measured spectral emissivity. Finally, the validity of the Planck approximation was examined and it was shown that it can be applied within the scope of the current study (i.e. for the wavelengths and temperatures at which measurements have been taken).

Chapter 6 : Isostatic graphite

– “A #2 pencil and a dream can take you anywhere. “–

Joyce Meyer, author

This chapter reports experimental thermo-physical property values of isotropic, isostatically pressed graphite (specific heat, thermal conductivity, thermal diffusivity and spectral emissivity). These are compared to previous literature values but extend the available data from 1500 K up to 2800 K. Additionally, a model based on the theory described in Chapter 3, has been used to predict, for isotropic graphite, the temperature dependence of thermal conductivity, specific heat and thermal diffusivity.

Majority published in: Pavlov, et al. *Thermochim. Acta* 652, 39–52 (2017).

6.1 Introduction

Graphite is a rather complex material, which consists of strongly covalently bonded carbon atoms (sigma bonds) arranged in hexagonal planes. In between these planes of carbon atoms weaker covalent bonds exist (pi bonds). The relative strength of these sigma and pi results in a highly anisotropic crystal structure. The perfect hexagonal unit cell of graphite is shown in Figure 6-1A. Figure 6-1B shows an example of a carbon Frenkel pair, while Figure 6-1C indicates the available positions for interstitial carbon atoms (in the empty plane between the hexagonal layers), which are assumed in this work.

Graphite has a vast number of applications, due to its favourable high-temperature thermo-physical properties. In nuclear reactors, graphite is used as a moderator material to thermalise fast neutrons but also as a barrier to fission gas release in TRISO particles¹³⁵. For nuclear applications isotropic graphite is preferred and hence in this study a quasi-isotropic polycrystalline graphite is examined.

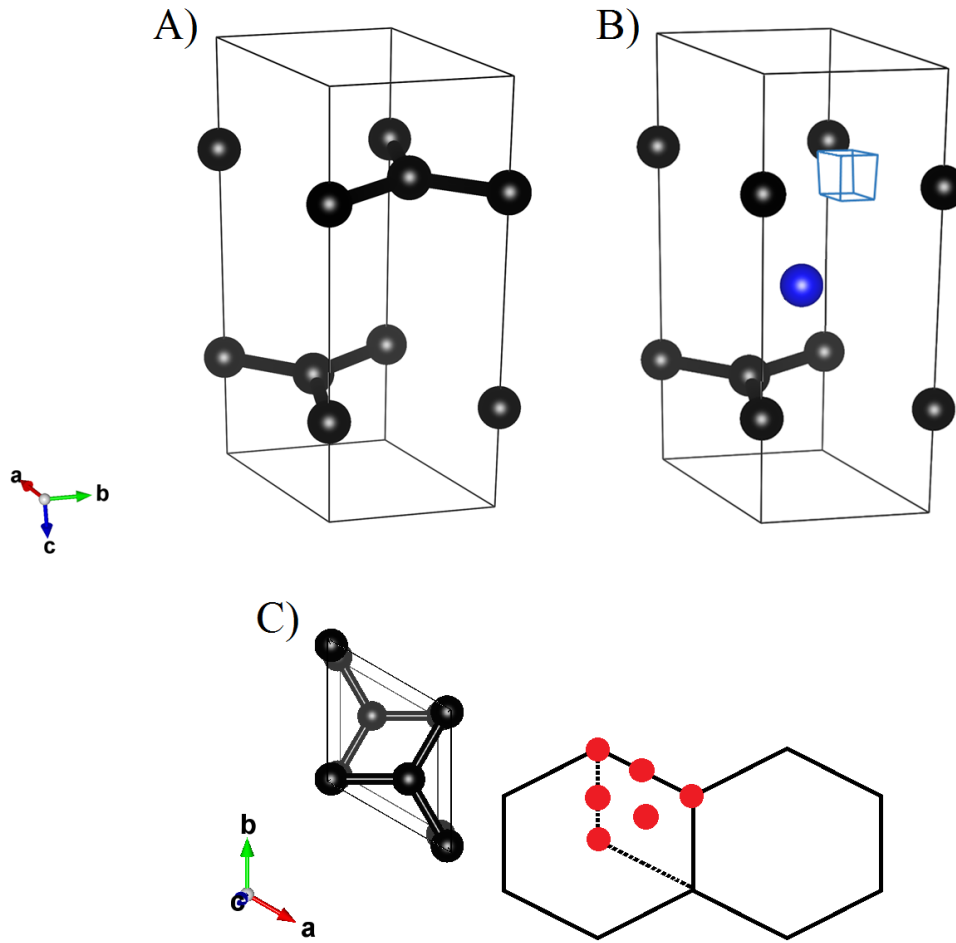


Figure 6-1: Crystal structure of graphite. A) primitive unit cell; B) carbon Frenkel pair introduced in unit cell; C) Left: top down view of a defect free primitive (perfect) unit cell (c direction points out of the viewing plane); C) Right: possible interstitial positions (marked by solid red circles) in close proximity to the empty plane at $c = 0.5c_0$ shown via the 2-D hexagonal lattice (the dotted lines mark the primitive unit cell in 2-D). The interstitial positions have been assigned based on the work of Li et al.¹³⁶

6.2 Samples

Samples were manufactured out of polycrystalline graphite produced by cold isostatic pressing. The specimens were produced by SLG carbon group and are grade R6650P5

with purity above 99.9998%. The sample properties, dimensions and laser beam specifications are tabulated in Table 6-1 and Table 6-2 and are used as input for the FEA model described in Chapter 4.

Table 6-1: Material properties of isostatically pressed graphite (measured at 0.1 MPa).

Property	Value	Ref.
$\rho(T)^+$	$\rho_{298} \times \left(\frac{-1.174 \times 10^{-12}T^3 + 1.677 \times 10^{-5}T^2 -}{-1.676 \times 10^{-5}T + 1.005} \right)$	137
$\epsilon(1064 \text{ nm})^+$	$4.053 \times 10^{-5}T + 0.874$	137
$\epsilon(640 \text{ nm})$	0.87	this work*
ϵ_{tot}^+	$0.92 - 5.33 \times 10^{-5}T$	133

⁺ polynomial fits to experimental data obtained from the respective reference

* experimentally measured

Table 6-2: Summary of the measured graphite sample characteristics and laser beam parameters.

Parameter (units)	Value
room temperature density ρ_{298} (kg m ⁻³)	1810
porosity (%)	20
thickness (mm)	3.05
radius (mm)	2.495
beam spot radius (mm)	1.5
pulse duration (ms)	10

6.3 Spectral emissivity

Figure 6-2 shows the spectral emissivity of the graphite samples at 640 nm. The low R-squared value of the linear fit in Figure 6-2 is due to the residual sum of squares (difference between data and fit) being comparable to the total sum of squares

(difference between data and data mean). This indicates that the mean of the data is almost identical to the fitted line. Hence, the spectral emissivity at 640 nm can be considered temperature invariant in the range 1700 K to 2400 K. The mean value of 0.87, also shown in Table 6-1, will be used to convert the radiance temperature to true temperature.

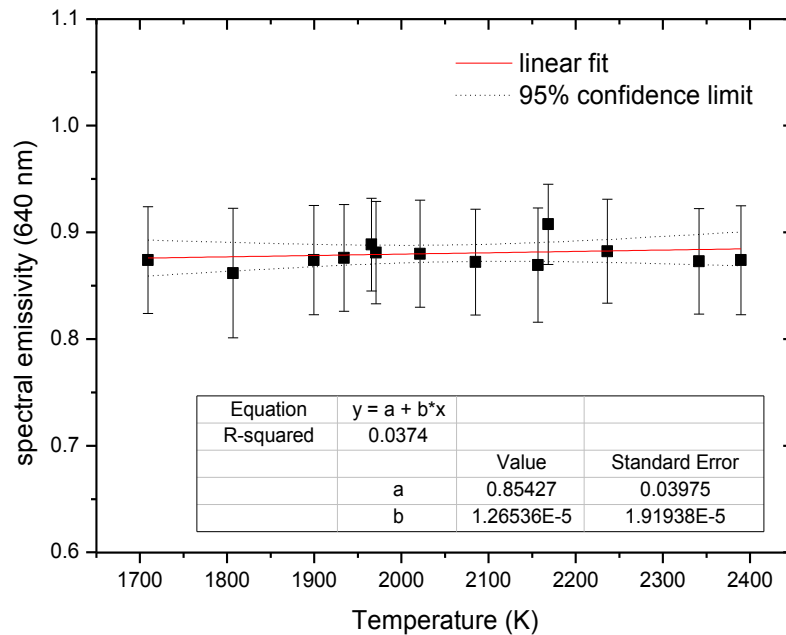


Figure 6-2: Spectral emissivity at a wavelength of 640 nm for fine grained polycrystalline graphite.

6.4 Specific heat capacity

Measurements of specific heat capacity, thermal conductivity and thermal diffusivity are presented in Figure 6-3, Figure 6-4 and Figure 6-5, respectively, where they are

compared to literature data obtained previously from the same batch of isostatically pressed graphite¹³⁷.

The specific heat capacity results obtained from the inverse method, described in this work, are shown in Figure 6-3. It is evident that there is good agreement between the measured heat capacities and previously reported values at temperatures close to 1500 K. Around 1800 K, the results obtained in the National Physical Laboratory (NPL) by Hay et al.¹³⁷ show a steeper increase in specific heat capacity relative to the measurements in this work. In view of this discrepancy and in order to gain a physical understanding of the phenomena that govern the temperature dependent changes of this property, a physical model was developed. It is based on solid state theory and will be extended to predict thermal conductivity and hence thermal diffusivity as a function of temperature. The fundamental concepts of the models have been described in Chapter 3.

The specific heat of graphite can be expressed as the sum of harmonic, electronic, and defect contributions. The electronic term has been evaluated via equation (3-13). The hexagonal crystal structure of graphite imposes a degree of anisotropy on the thermal transport. The macroscopic isotropy is achieved by small, randomly oriented grains. Nevertheless, on the meso-scale there are two major contributions – from in-plane and out-of plane vibrations. Hence, the harmonic term of the specific heat capacity (c_V^h) can be described in the following way¹³⁸:

$$c_V^h = \frac{2}{3}\Delta(\vartheta_a) + \frac{1}{3}\Delta(\vartheta_c) \quad (6-1)$$

where ϑ_a is the Debye temperature corresponding to acoustic mode vibrations along the a or b crystal directions, while ϑ_c is the Debye temperature related to acoustic mode vibrations along the c crystal direction. The specific heat capacity contribution, due to defect formation can be derived from statistical thermodynamics (see section 3.1.4). Assuming that the dominant defect species are Frenkel pairs and based on the work by Reich et al.¹³⁶ it is estimated that there are 2 interstitial sites per carbon atom (see Figure 6-1C). By using the approach described in section 3.1.4 the following equation can be derived for the defect concentration n :

$$n = \sqrt{(1-n)(2-n)} \exp\left(-\frac{\Delta H_{C,F}}{2RT}\right) \quad (6-2)$$

where $\Delta H_{C,F}$ is the formation energy (kJ mol^{-1}) of a carbon Frenkel pair (the subscripts stand for carbon and Frenkel respectively), R is the universal gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is temperature (K) and n is the defect concentration (mol).

Assuming small defect concentrations (n):

$$n \approx \sqrt{2} \exp\left(-\frac{\Delta H_{C,F}}{2RT}\right) \quad (6-3)$$

By referring back to Chapter 3:

$$c_V^d = \frac{d(n\Delta H_{C,F})}{dT} = \frac{\sqrt{2}\Delta H_{C,F}^2}{2RT^2} \exp\left(-\frac{\Delta H_{C,F}}{2RT}\right) \quad (6-4)$$

Finally, the specific heat at constant volume has been converted to specific heat at constant pressure via equation (3-58). All these considerations lead to equation (6-5):

$$c_p^{tot} = \frac{2}{3}\Delta(\vartheta_a) + \frac{1}{3}\Delta(\vartheta_c) + \gamma_e T + \frac{\sqrt{2}\Delta H_{C,F}^2}{2RT^2} \exp\left(-\frac{\Delta H_{C,F}}{2RT}\right) + \frac{\beta^2 T K_T}{V_{mol}(T)} \quad (6-5)$$

where γ_e is the Sommerfeld coefficient (J kg^{-1}), K_T is the isothermal bulk modulus (Pa), β is the volumetric thermal expansion coefficient (K^{-1}), V_{mol} is the molar volume (m^3). From Figure 6-3 it is evident that there is excellent agreement between the model and both the current and previous experimental data. The model therefore demonstrates the current experimental results can be understood in terms of established physics. The underlying physical processes are discussed in Chapter 9.

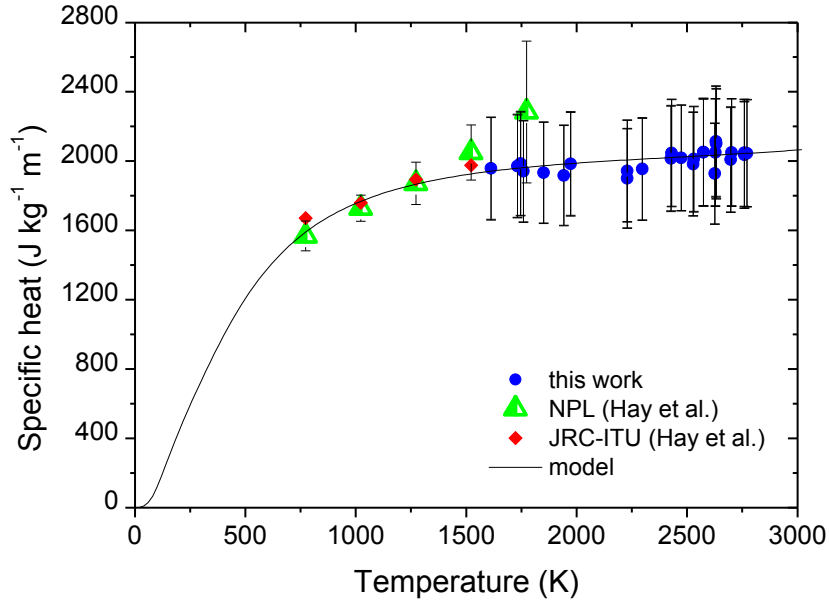


Figure 6-3: Measured specific heat capacity as a function of temperature for polycrystalline graphite, compared to the calculated specific heat capacity using equation (6-5). The literature data (green triangles and red rhombohedra) has been taken from Hay, et al.¹³⁷. The error bars on the blue data points correspond to two standard deviations and are equivalent to 15.2% relative error (for details on error analysis refer to Section 5.4).

6.5 Thermal conductivity

Graphite is a semi-metal, meaning its Fermi level lies in the conduction band, just above the band edge. Hence, conduction electrons, as well as phonons, contribute to thermal transport. Thus, the thermal conductivity can be written as¹³⁹:

$$k_{tot} = k_{el} + k_l \quad (6-6)$$

where k_{el} and k_l stand for the electronic and lattice contribution respectively. The electronic term (k_{el}) is calculated according to the Wiedmann-Franz law (see equation (3-60)) and the electrical resistivity ($\Upsilon = 1/\sigma$) is taken from literature data on isotropic polycrystalline graphite with very similar density¹⁴⁰. The following expression has been fit to the electrical resistivity data:

$$\Upsilon(T) = \begin{cases} \left(-3.91 \times 10^{-7} T^3 + 1.65 \times 10^{-3} T^2 - 2.15 \times T + 1.75 \times 10^3 \right) \times 10^{-8} & \in T < 1700 \text{ K} \\ (2.15 \times 10^{-1} T + 5.56 \times 10^2) \times 10^{-8} & \in T > 1700 \text{ K} \end{cases} \quad (6-7)$$

where 10^{-8} is a unit conversion factor from $\mu\Omega \text{ cm}$ (units used by Taylor and Groot¹⁴⁰) to $\Omega \text{ m}$. The theoretical Lorenz number is $2.443 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, however, lower values have been determined experimentally^{141,142}. In this work the value of $2.0 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ was used based on the work by Bapat et al.¹⁴².

With the effective medium approach of Bruggeman¹⁴³, the lattice thermal conductivity of a polycrystalline material with polyhedral grains can be expressed as follows:

$$k_l = \frac{1}{2} \left(-k_c + (k_a^2 + 8k_c k_a)^{\frac{1}{2}} \right) \quad (6-8)$$

where the subscripts "a" and "c" stand for the respective crystallographic directions.

The components in each direction have an associated Debye temperature and frequency, respectively. These terms have been calculated using the Debye-Klemens formalism described in section 3.2 via equations (3-61) to (3-66).

The model alongside experimental data is presented in Figure 6-4 and all input parameters for the model are listed in Table 6-3. Figure 6-4 shows that at temperatures close to 1500 K the thermal conductivity results are in excellent agreement with the ones measured by Hay et al.¹³⁷. At around 1800 K, there was some disagreement between the current results and the ones obtained at the NPL¹³⁷. This work suggests a continued degradation of thermal conductivity with respect to temperature in the range 1500 K – 1800 K, while the NPL results show that the rate of decrease in thermal conductivity with respect to temperature is more gradual.

Table 6-3: Summary of parameters used in the specific heat capacity and thermal conductivity models.

Parameter description	Units	Symbol	Value	Reference
Debye temperature in "a" direction	K	ϑ_a	2280	138
Debye temperature in "c" direction	K	ϑ_c	760	138
Sommerfeld constant	mJ mol ⁻¹ K ⁻²	γ_e	0.014	144
formation enthalpy of Frenkel pair	kJ	ΔH_F	467.94	136
bulk modulus	GPa	K_T	8.82	145
Lorenz number	nW Ω K ⁻²	L	20	142
Grüneisen parameter	-	γ	2.0	110
atomic mass	u	M_{at}	12.01	146
free electrons per carbon atom	-	n_e	1.0	147
deformation potential	ev	ϵ_1	6.13	148
grain size	μm	L_g	7.0	149
thermal conductivity of pore gas	W m ⁻¹ K ⁻¹	k_p	0.07	128
pore fraction (at 298 K)	-	v_p	0.202	*
molar mass	kg mol ⁻¹	M_{mol}	0.012	-
atomic volume	$\text{\AA}^3$	Ω	8.813	-
density (theoretical)	kg m ⁻³	ρ_{TD}	2260	150

* experimentally determined from the measured density (ρ_{298}) and theoretical density (ρ_{TD}).

^a Standard uncertainty $u(v_p) = 0.002$.

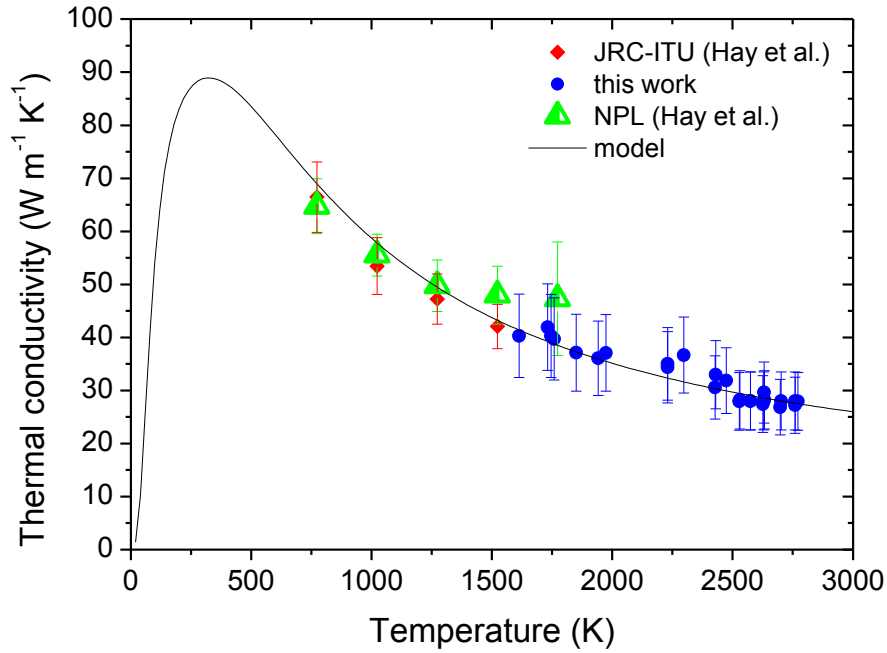


Figure 6-4: Thermal conductivity of isotropic graphite as a function of temperature. Experimental data is compared to the model described in this work. The error bars on the blue data points correspond to two standard deviations and are equivalent to 19.4% relative error (for details on error analysis refer to Section 5.4).

6.6 Thermal diffusivity

Thermal diffusivity is evaluated according to equation (3-89) in section 3.4. Figure 6-5 shows excellent agreement between the diffusivity obtained in this work and the results of Hay et al.¹³⁷ The model for thermal diffusivity is based on the models for specific heat capacity and thermal conductivity linked via equation (3-89) (using the measured density in this work, corrected for thermal expansion based on the work of Hay et al.¹³⁷). Furthermore, the model describes the temperature evolution of diffusivity almost exactly.

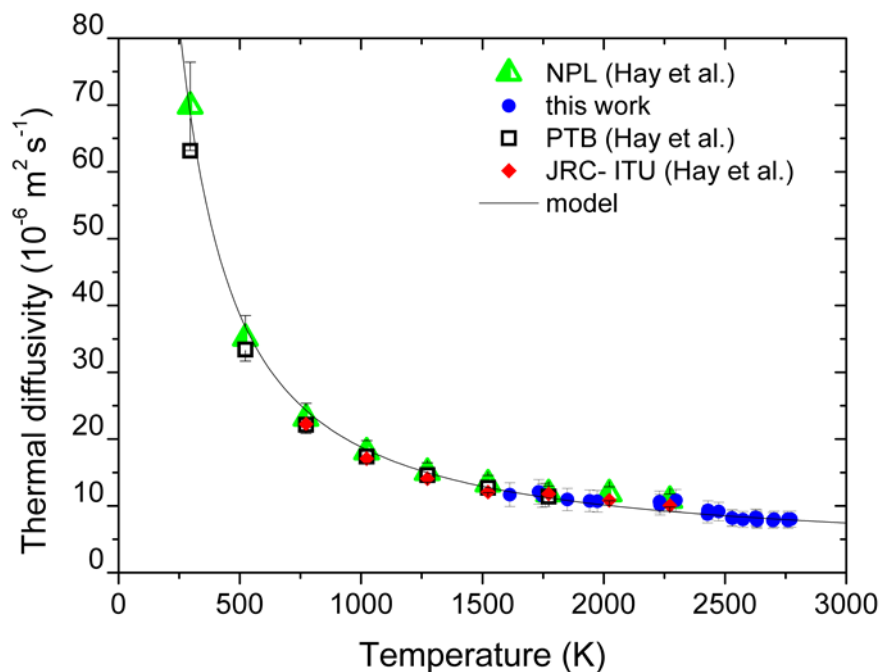


Figure 6-5: Thermal diffusivity of isotropic graphite as a function of temperature. The error bars on the blue data points correspond to two standard deviations and are equivalent to 15% relative error (for details on error analysis refer to Section 5.4).

6.7 Summary

The specific heat, thermal conductivity, thermal diffusivity and spectral emissivity of isostatically pressed graphite have been measured between 1500 K and 2800 K. These measurements extend the range of available literature values and can be considered indicative of the properties of isostatically pressed nuclear grade graphite, although to be definitive samples specifically produced for in-reactor use should be considered. Furthermore, the governing mechanisms involved have been deconvoluted via a solid state physics model, which is in very good agreement with the literature results. The underlying physical mechanisms are further discussed in Chapter 9.

Chapter 7 : Uranium dioxide

– “*Nuclear energy, in terms of an overall safety record, is better than other energy.*” –

Bill Gates, entrepreneur

In this chapter experimental values of the thermo-physical properties of UO_2 are reported (specific heat, thermal conductivity, thermal diffusivity and spectral emissivity). These have been measured in the temperature range 1500K to 2900K and are compared to existing literature results. The solid state physics model, which is presented, is based on the theory described in Chapter 3 and is in good agreement with experiment.

Parts published in: Pavlov, et al. *TopFuel* 1227–1235 (2016).

Majority published in: Pavlov, et al. *Acta Mater.* 139, 138 - 154 (2017).

7.1 Introduction

Uranium dioxide exhibits cubic symmetry and adopts the fluorite structure. The perfect unit cell is shown in Figure 7-1A. UO_2 exhibits both Schottky (see Figure 7-1C) and Frenkel defects (see Figure 7-1B and Figure 7-1D). These defects have a significant impact on the thermo-physical properties and are of key importance for bulk diffusion processes.

Uranium dioxide is the most common fuel material used in current nuclear reactors. Even though UO_2 has a relatively low thermal conductivity (leading to relatively high fuel centre temperature), it has a number of other physical and chemical properties, which make it particularly suitable for the purpose of a nuclear fuel material. It does not corrode as quickly as metallic fuels when exposed to water in the case of coolant ingress through a cladding breach^{151,152}. Alongside chemical stability UO_2 also exhibits good dimensional stability under irradiation in comparison to metallic fuels^{153,154}. Uranium dioxide also has a high melting point ($3118 \pm 55 \text{ K}$)¹⁵⁵, which favors a larger margin to melting in an accident.

The properties of UO_2 have been extensively studied, however not all aspects of the fuel's behaviour have been thoroughly examined and are not fully understood. In particular, having access to experimental data for thermal conductivity and specific heat, as well as understanding the governing physical processes, are pre-requisites for reliably predicting the fuel centre temperature, both during reactor operation and

accident conditions. There have been extensive studies of these properties up to 1500 K¹³², however, significantly fewer measurements are available at higher temperatures. Thermal conductivity has been studied by Weilbacher¹⁵⁶, Stora¹⁵⁷ and Ronchi⁶⁵ at temperatures above 1900 K. These have indicated the presence of a thermally activated small polaron contribution. The work of Casado¹¹⁷ has shown small polarons are not strongly coupled with their associated optical phonons, resulting in a non-adiabatic character. The high temperature specific heat capacity of UO₂ has been studied via indirect methods such as the enthalpy increment measurements by Fink et al.¹⁵⁸ and Leibowitz et al.⁵³. Affroiti⁶¹ measured the specific heat capacity of UO₂ via the electrical pulse method. Ronchi et al.¹⁵⁹ measured specific heat via a laser pulse method and have identified an order-disorder transition in the temperature range 2600-2700 K. This was attributed to the rapid formation of oxygen Frenkel pairs and their subsequent saturation, yielding an abrupt increase in specific heat, followed by a decrease. However, this phenomenon was not confirmed by any of the enthalpy measurements.

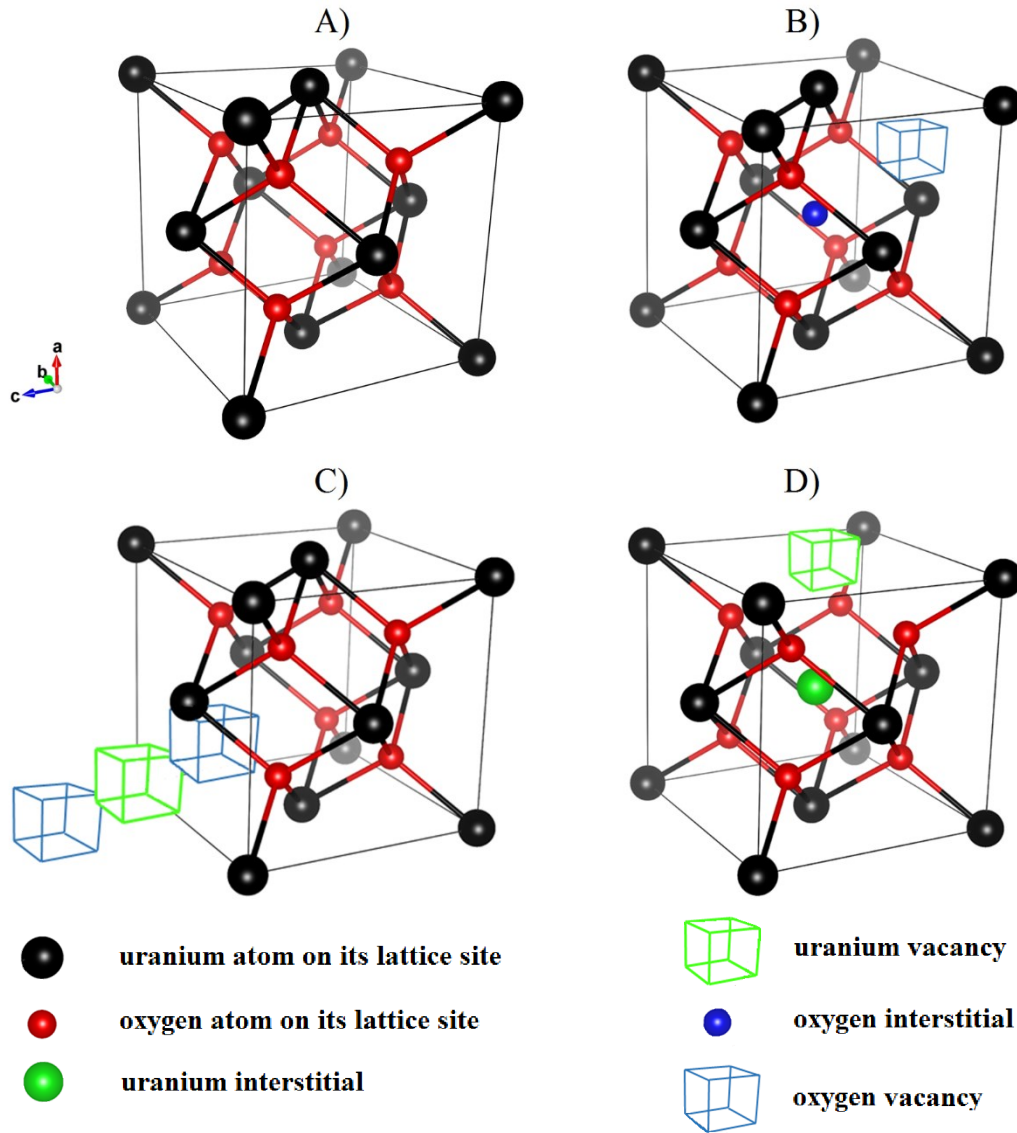


Figure 7-1: Crystal structure of UO_2 : A) Perfect unit cell; B) Unit cell containing an oxygen Frenkel pair; C) Unit cell containing a Schottky trio (tri-vacancy defect); D) Unit cell containing a uranium Frenkel pair.

7.2 Samples

The UO_2 specimen were produced and provided by Siemens AG. These were sintered pellets with average grain size ranging from $10\ \mu\text{m}$ to $14\ \mu\text{m}$ and an impurity content

of less than 0.05 %. The powder was produced via dissolution, precipitation and calcination¹⁶⁰. The powder was compacted in green pellets and then further pressed to achieve higher densities¹⁶¹ (above 93 % TD).²

The material properties and dimensions of the UO₂ samples, as well as laser beam specifications, are summarized in Table 7-1 and Table 7-2. These are used as input for the FEA model described in section 4.1.5. The emissivity at 645 nm is used for converting measured radiance temperature to true temperature, while the emissivity at 1064 nm governs the portion of laser radiation absorbed by the sample. It is worth noting that the temperature dependence of the emissivity at 645 nm and at 1064 nm is very weak and a constant value would also be a sufficiently accurate approximation. Finally, all thermal conductivity values are corrected to 95% porosity using the Brandt and Neuter correction^{132,134}.

Table 7-1: Summary of UO₂ sample characteristics and laser beam parameters.

Parameter (units)	Value range
room temperature density ρ_{298} (kg m ⁻³)	10300 - 10100
porosity (%)	6 - 8
thickness (mm)	0.7- 0.9
radius (mm)	4.175
beam spot radius (mm)	2.5
pulse duration (ms)	1-10

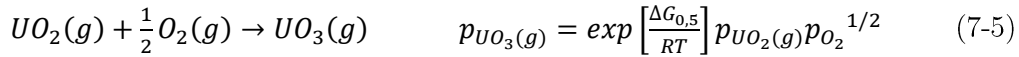
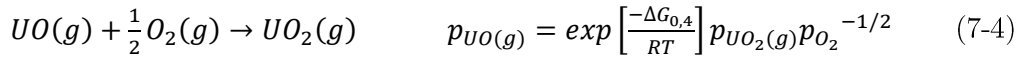
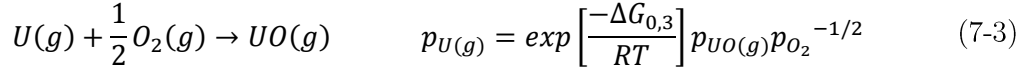
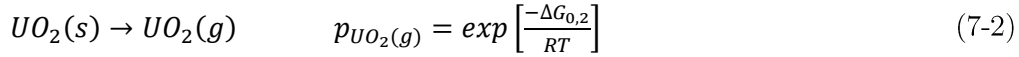
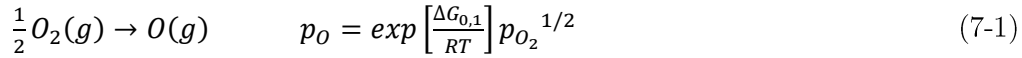
² The information regarding the UO₂ powder preparation and fabrication processes has been derived from the publically available patents of Siemens AG^{160,161}.

Table 7-2: Material properties of UO_2 used as input in the FEA model.

Property	Expression	Ref.
$\rho(T)$	$\rho_{298}\{9.973 \times 10^{-1} + 9.08 \times 10^{-6}T - 2.705 \times 10^{-6}T^2 + 4.391 \times 10^{-13}T^3\}$	132
$\epsilon_{(1064 \text{ nm})}$	0.9	162
$\epsilon_{(645 \text{ nm})}$	$0.836 + 4.321 \times 10^{-6}(T - 3120)$	163
ϵ_{tot}	0.85	164

7.3 Vapourisation heat losses

In section 4.1.10 it was shown that the heat lost due to vapourisation depends on all material related vapour species and their respective partial pressures. Hence, these will be expressed via the Rand-Markin approach^{165,166}. Their model is expressed by the following reactions and respective equilibrium partial pressure equations:



The standard Gibbs free energies of formation have been refitted based on the most recent updated information available in the FactSage database¹⁶⁷. These are summarized below in Table 7-3. The Rand-Markin approach is validated by comparing the results for calculated vapour pressures with the ones obtained from FactSage¹⁶⁷ (see Figure 7-2). The maximum relative difference between the two

calculations is around 4% above 1500 K. This is likely due to differences in the Gibbs free energy fits (see Table 7-3) used in this work compared to the ones used in FactSage. The vapourisation enthalpies of all gaseous species have been assumed equal to the one of UO_2 . Based on this and the total vapour pressure of all species the vapourisation heat flux is determined (see section 4.1.10).

Table 7-3: Summary of standard formation enthalpies and entropies. The subscript corresponds to the respective reaction number in equations (7-1) to (7-5).

ΔH_0	Value (kJ mol ⁻¹)	$\Delta S_0(T)$	Function (kJ mol ⁻¹)
$\Delta H_{0,1}$	250.5	$\Delta S_{0,1}$	$1.65 \times 10^{-3} \times T + 61.6$
$\Delta H_{0,2}$	621.7	$\Delta S_{0,2}$	$9.76 \times 10^{-3} \times T + 199.6$
$\Delta H_{0,3}$	-509.7	$\Delta S_{0,3}$	-45.5
$\Delta H_{0,4}$	-483.5	$\Delta S_{0,4}$	-78.4
$\Delta H_{0,5}$	-332.3	$\Delta S_{0,5}$	$-1.25 \times 10^{-3} \times T - 67.3$

A comparison between the different heat loss mechanisms has been presented via Figure 7-3 in the form of a dominance diagram. The black borders represent the temperature and pressure at which the heat fluxes of neighbouring regions are equal (or approximately 50 % of the total heat flux). It is evident that at high temperatures and low pressures vapourisation is the dominant heat loss mechanism. At low pressure and high temperature or high temperature and intermediate pressure, most of the heat lost by UO_2 is via radiation. Finally, at high pressure or at low

temperature and intermediate pressure natural convection is the most significant heat loss mechanism.

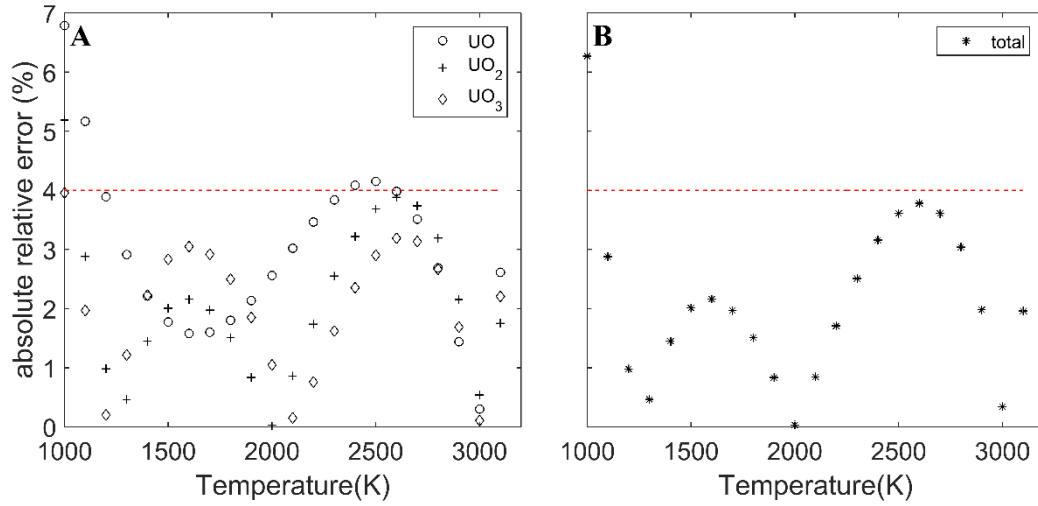


Figure 7-2: Comparison of the partial pressures calculated via the Rand-Markin model and those predicted by FactSage¹⁶⁷ at 1 bar ambient pressure. (A) Comparison of the relative errors of the 3 dominant vapour species; (B) Relative error of the total vapour pressure. The dotted red line represents 4% relative error and is intended for visual guidance.

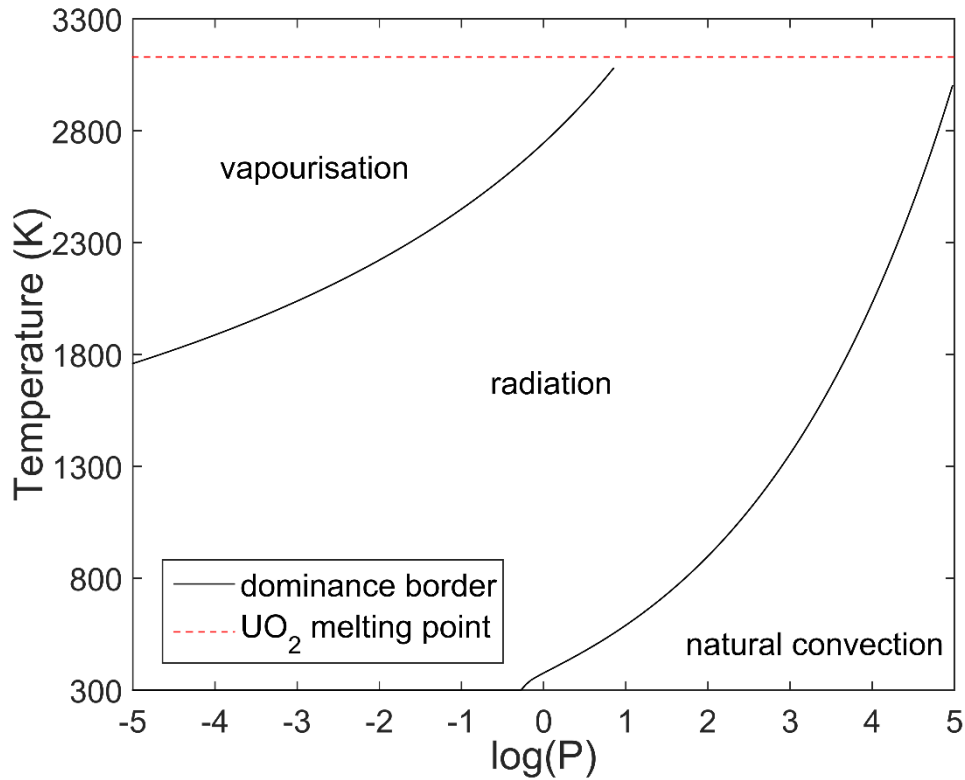


Figure 7-3: The heat loss dominance diagram for UO_2 calculated according to the equations described in sections 4.1.5, 4.1.10 and 4.1.11 of Chapter 4. The solid black lines indicate where the dominant heat flux loss transitions from one mechanism to another. The dotted red line indicates the melting point of the UO_2 .

7.4 Experimental measurements

The UO_2 samples and their respective lattice parameters were characterised via Rietveld refinement of the recorded XRD spectra shown in Figure 7-4. The calculated lattice parameters are shown Table 7-4. The samples were exposed to different maximum temperatures prior to being quenched (under argon atmosphere) to room temperature. By comparing these to the theoretical lattice parameter of stoichiometric UO_2 ^{168,169}($5.4707 \pm 0.0008 \text{ \AA}$), it seems there has been no significant

departure from stoichiometry during the experiments. Based on this evidence the O/U ratio during the experiments is assumed to be 2.000 ± 0.005 .

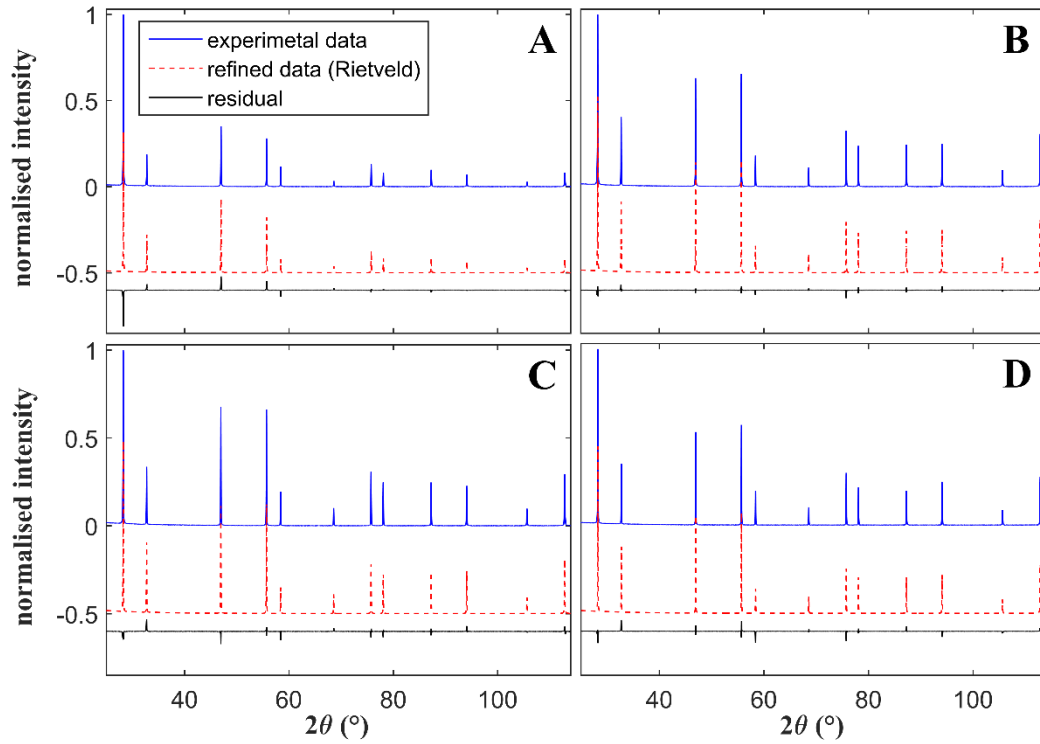


Figure 7-4: X-ray diffraction spectra of four different UO_2 samples compared with the Rietveld refinement used for determining the respective lattice parameters. (A) UO_2 specimen subjected to a maximum temperature of 2780 K; (B) UO_2 specimen subjected to a maximum temperature of 2450 K; (C) UO_2 subjected to a maximum temperature of 2340 K; (D) UO_2 specimen held at room temperature (300 K).

Table 7-4: Lattice parameter of UO_2 (derived from refined XRD spectra in Figure 7-4) for different exposure temperatures. The uncertainty on the lattice parameter has been approximated to be of the order of $\pm 0.001 \text{ \AA}$ (95% confidence interval).

Exposure temperature (K)	Lattice parameter ($\text{\AA}$)
2780 K	5.4705
2450 K	5.4711
2340 K	5.4707
300 K	5.4709

Finally, a series of cooling curves were recorded to determine the melting point and examine the presence of pre-melting arrests in UO_2 . The melting point was determined from the detected thermal arrest upon cooling the partially molten UO_2 specimen (see Figure 7-5). This first order phase transition was measured at $3118 \text{ K} \pm 55 \text{ K}$, which is consistent with various experimental studies^{86,155,170,171}. The melting pool was observed and an example of such a melting pool can be seen via the SEM image in Figure 7-6. Furthermore, Figure 7-6 is evidence for erroneously measured melting of UO_2 at a temperature, which is around 160 K lower than the correct one^{155,172}. Both measurements were obtained under the same atmospheric conditions (using an argon atmosphere). The latter lower melting arrest was obtained with a chamber with smaller sapphire windows and hence a smaller pyrometer acceptance angle. If not analysed with care, this measurement could be falsely used as evidence for the presence of a pre-melting transition. This is further discussed in section 9.3.2 of Chapter 9.

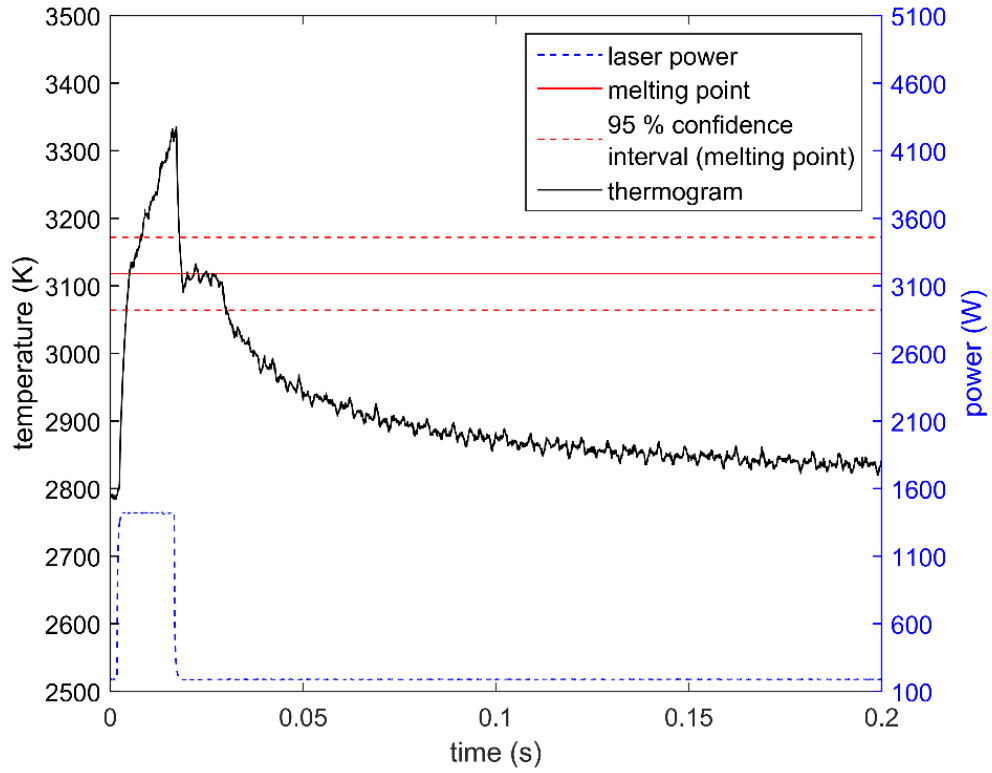


Figure 7-5: Temperature (left) vs. time and laser power (right) vs. time after subjecting a UO_2 sample to a laser pulse. Melting point has been identified from the thermal arrest observed upon cooling.

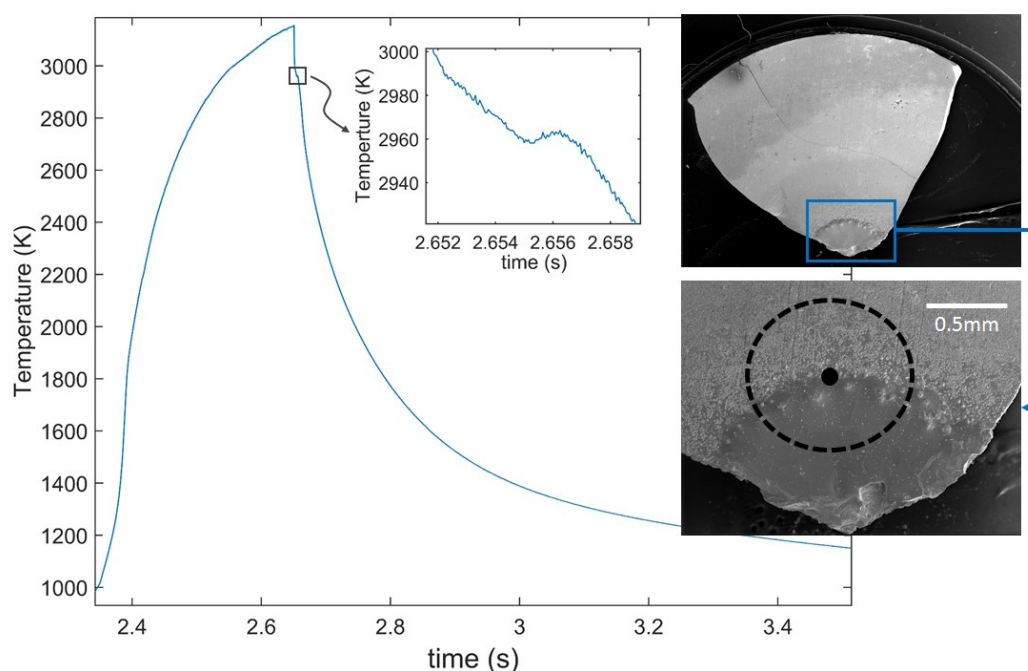


Figure 7-6: Temperature vs. time graph (thermogram) recorded after applying a laser pulse to both sides of a UO_2 sample simultaneously (with optical fiber splitting of 50%) under 100 bar He. The small temperature vs. time graph (upper centre) shows a zoom-in of the thermogram indicating a plateau at 2960 K. The two SEM images (right) show the melting pool (the darker central region). The black dot surrounded by a black dotted circle (lower right) indicate the approximate pyrometer spot location and nominal spot size, respectively.

Furthermore, in the current study a number of other cooling curves were recorded by holding a UO_2 sample (sample thickness - 2 mm; sample diameter - 10.5 mm; nominal laser beam spot diameter - 8.9 mm) at temperatures 2800-3000 K for 2-8 s prior to cooling (an example is shown in Figure 7-7). These measurements were carried out at pressures between 40 and 100 bar of He with two sided laser heating (using optical fiber paths with 50% splitting). Multiple experiments were performed, however no pre-melting arrest was observed. Once again the importance of these results are discussed in further detail in section 9.3.2.

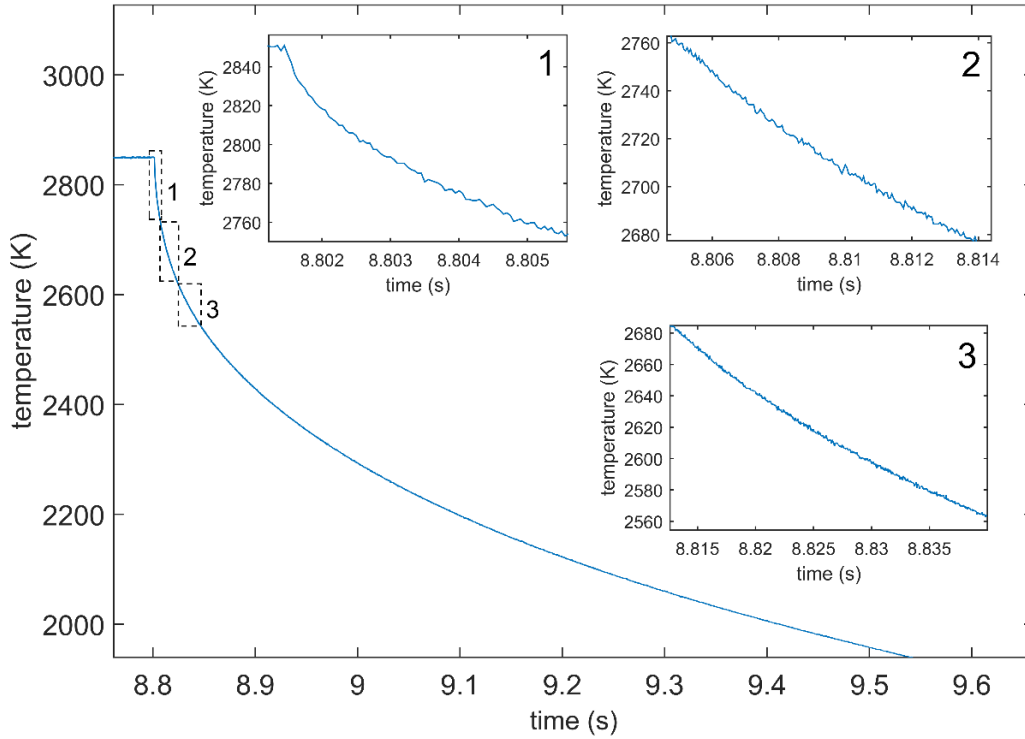


Figure 7-7: An example cooling curve for a 2mm thick UO_2 sample under He at 100 bar (recorded by switching off the laser, which was heating both sides of the disc shaped sample). Each number corresponds to a zoom-in of the respective region on the cooling curve indicated by black dotted lines. No observable arrest in temperature drop can be seen.

The measured values of specific heat, thermal conductivity and thermal diffusivity of UO_2 are presented in Figure 7-8. These new measurements are also compared to some of the few open literature data sets measured above 2000 K, which have been reported in the open literature. The specific heat measurements in the current study indicate a maximum at around 2700 K, similar to the transition temperature reported by Hiernaut et al.¹⁷³ using a laser heating technique in which a sphere, held by a tungsten pin was heated by four beams in a tetrahedral configuration. However, their

study showed a much more abrupt increase in specific heat, followed by a sharp decrease. In the current work, a more gradual transition was observed. The measurements of thermal diffusivity reported here suggest a minimum between 2600 and 2700 K, which has not been previously measured, although it was suggested by Ronchi¹⁷⁴. This phenomenon will be explained and quantified by a solid state physics approach in the following sections. The measured thermal conductivity values are consistent with the experimental study of Ronchi et al.⁶⁵. The measured normal spectral emissivity agrees with the experimental data fit suggested by Bober et al.¹⁶², which, for the purpose of simplicity, will be used when converting the measured radiance (apparent) temperature to black body (true) temperature. The small deviation between the current measurements and the fit of emissivity could be expected to yield errors lower than 0.5% in temperature (respective contribution towards the error of the fitted parameters can be assumed to be of similar low magnitude).

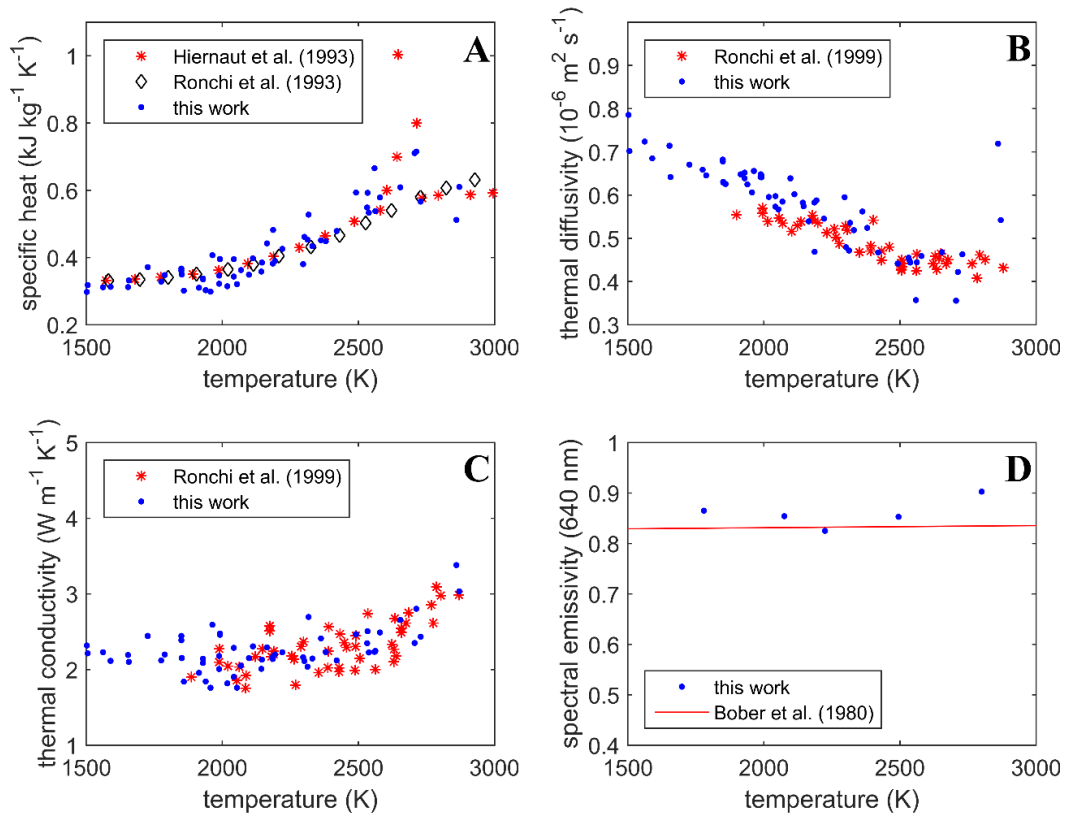


Figure 7-8: (A) Specific heat vs. temperature measured in this work compared to Hiernaut et al.¹⁷³ and Ronchi et al.¹⁵⁹; (B) Thermal diffusivity vs. temperature measured in this work compared to Ronchi et al.⁶⁵; (C) Thermal conductivity vs. temperature measured in this work compared to Ronchi et al.⁶⁵; and (D) Spectral emissivity at 640 nm vs. temperature measured in this work compared to Bober et al.¹⁶².

7.5 Phonon density of states

The phonon density of states (PDOS) for UO_2 have been approximated using a Debye-Einstein approach. The PDOS model is presented in Figure 7-9 and the model results are compared to the measurements of Dolling et al.¹⁷⁵. UO_2 has three atoms or ions per molecule and hence 3 acoustic branches (1 longitudinal and 2 transverse) and 6 optical branches (2 longitudinal and 4 transverse). The acoustic branches have been treated via a Debye approach whereby phonons can have a range of frequencies or energies and their respective number follows Bose statistics. Optical modes are approximated by single frequency particles and were represented using the Einstein model. The parameters for this model are summarised in Table 7-5 and the approach has been described in section 3.1.1. The relative weights can be understood as the fraction of vibration modes characterised by the respective model parameter. From Figure 7-9 it is evident that the model is in acceptable agreement with experimental data. Even though approximate, the model captures sufficiently well the features of the acoustic and optical branches.

Table 7-5: Summary of input parameters for PDOS model.

Parameter description	units	symbol	value	indicative range	relative weight	Ref
Debye temperatures (acoustic modes)	K	ϑ_{TA1}	180	160-216	1/9	176,177
	K	ϑ_{TA2}	250	-	1/9	**
	K	ϑ_{LA}	385	-	1/9	178
Einstein temperatures (optical modes)	K	E_{LO}	390	-	2/9	179
	K	E_{TO1}	630	-	2/9	179
	K	E_{TO2}	840	-	2/9	179

** recommended in this work

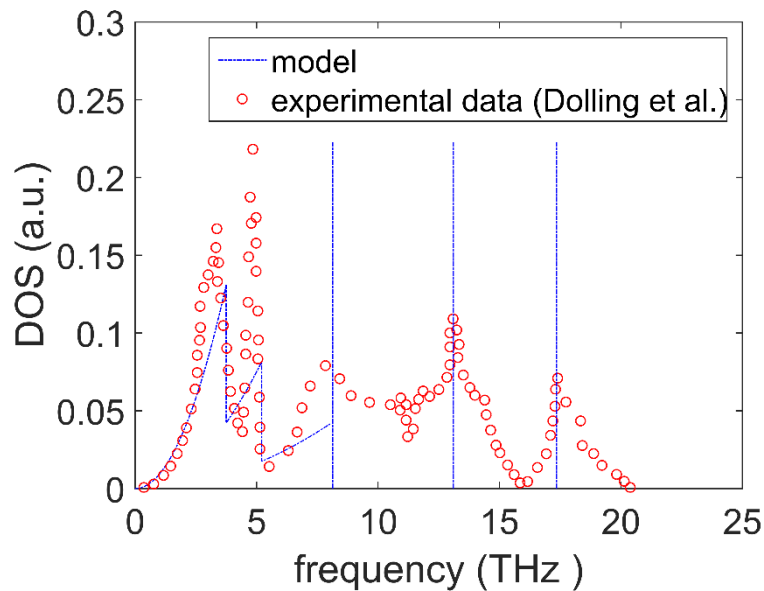
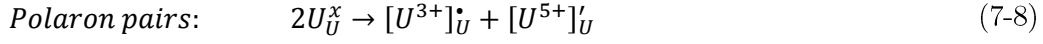
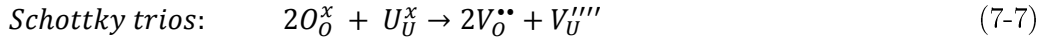
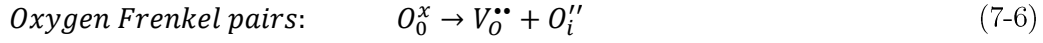


Figure 7-9: Phonon density of states (PDOS or DOS) vs. frequency - comparison between the proposed model for the phonon density of states and the experimental data of Dolling et al.¹⁷⁵

7.6 Defect concentrations

A statistical thermodynamics approach is proposed for calculating the equilibrium defect concentrations. We assume the dominant defects and their corresponding reactions are the following using Kröger-Vink notation:



Using statistical thermodynamics for configurational entropy and Sterling's approximation we obtain the following system of non-linear equations to be solved:

$$n_F^2 = \left(\frac{2}{3} - n_F - 2n_S\right) \left(\frac{1}{3} - n_F\right) \exp\left(-\frac{\Delta H_{F,Fr}}{C_B T} + \frac{\Delta S_{NC,Fr}}{C_B}\right) \quad (7-9)$$

$$n_S^3 = \left(\frac{2}{3} - n_F - 2n_S\right)^2 \left(\frac{1}{3} - n_S - n_P\right) \exp\left(-\frac{\Delta H_{F,Sch}}{C_B T} + \frac{\Delta S_{NC,Sch}}{C_B}\right) \quad (7-10)$$

$$n_P^2 = \left(\frac{1}{3} - n_P - n_S\right)^2 \exp\left(-\frac{\Delta H_{F,Pol}}{C_B T} + \frac{\Delta S_{NC,Pol}}{C_B}\right) \quad (7-11)$$

where n_F, n_S and n_P are the concentrations (fraction per mole of UO_2) of Frenkel pairs, Schottky defects and polarons, respectively. Furthermore, oppositely charged oxygen defects (i.e. vacancies and interstitials) experience a net attractive force. This interaction is treated using Debye-Hückel theory¹⁸⁰ and has been described in section 3.1.4. The coupled system described by equations (7-9) to (7-11), can be solved using the root finding sequence shown in Figure 7-10. All equation roots were calculated using Newton-Raphson and bisection methods (see Appendix A), the combination of which were devised in this work and implemented in MATLAB. The convergence criteria for the final set of defect concentrations has to satisfy:

$$\left| \frac{n_i^y - n_i^{y+1}}{n_i^{y+1}} \right| < 10^{-7} \quad (7-12)$$

where n is the defect concentration of species i and y is the calculation iteration.

The convergence criteria is generally met in less than 10 iterations.

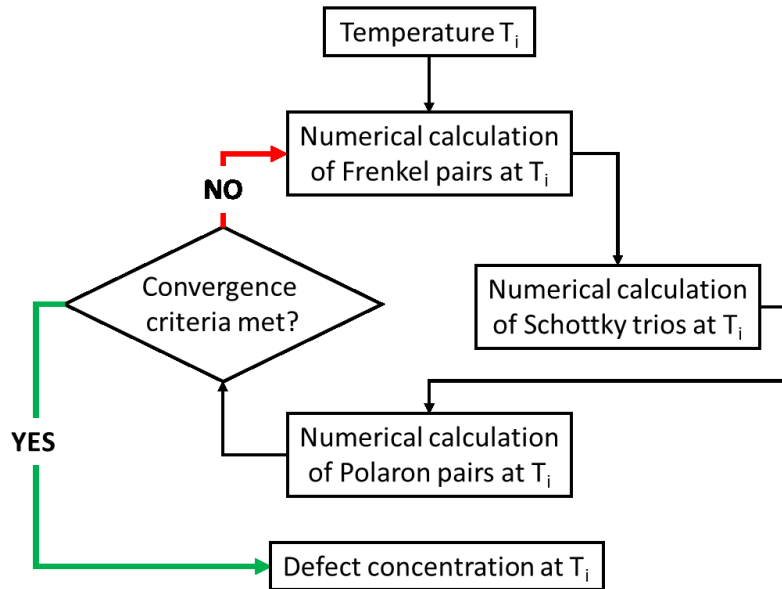


Figure 7-10: Convergence scheme for defect concentration calculations following from equations (7-9) to (7-12).

Table 7-6 summarizes the input parameters used in the defect model. The recommended set of input parameters relies on the assumption that oxygen Frenkel pairs are the dominant defect mechanism at high temperatures, which has been demonstrated experimentally by Hutchings¹⁸¹. Furthermore, variations in the parameters representing the Schottky and polaron formation energies have been examined. These have a limited quantitative impact on the calculated properties (e.g. specific heat and enthalpy) and exhibit no qualitative impact.

Table 7-6: Summary of input parameters for the defect concentration calculation. All parameters are expressed per molecule of UO_2 .

Parameter description	Units	Symbol	Value	Indicative range	Ref
Frenkel pair formation enthalpy	eV	$\Delta H_{F,Fr}$	3	3-4	182,183
Schottky trio formation enthalpy	eV	$\Delta H_{F,Sch}$	6.5	6.0-8.0	184,185
polaron pair formation enthalpy	eV	$\Delta H_{F,Pol}$	2.3	1.9-2.3	65,115,186
Frenkel pair formation entropy	meV K ⁻¹	$\Delta S_{NC,Fr}$	0.73	-	182,183
Schottky trio formation entropy	meV K ⁻¹	$\Delta S_{NC,Sch}$	0.37	-	184
polaron pair formation entropy	meV K ⁻¹	$\Delta S_{NC,Pol}$	0.27	-	115

The results of the defect model are shown in Figure 7-11. Two solutions are presented – an implicit solution and an explicit approximation. The implicit method is solved according to the numerical procedure presented in Figure 7-10 and by equations (7-9) to (7-11). The explicit approximation does not consider defect interactions and assumes defect concentrations can be neglected in the pre-exponential terms of equations (7-9) to (7-11). The explicit approximation has, consequently, a linear functional form and is generally accepted to hold for low concentrations of defects. Figure 7-11 shows oxygen Frenkel pairs are the dominant defect type, followed by polaron pairs, while Schottky trios exhibit the lowest concentration amongst the examined defects. The implicit solution differs significantly from the explicit solution in the case of oxygen Frenkel pair and Schottky trio concentrations, while less of a discrepancy between the two solutions is observed for polarons. Furthermore, defect species of higher effective charge show higher relative difference between the two solutions. The implicit solution for Frenkel pairs leads to a maximum in specific heat

(see Figure 7-11D). This is consistent with an inflection point in the concentration of Frenkel pairs as a function of temperature. Excess specific heat is dominated by the derivative of defect concentration with respect to temperature. Furthermore, from Figure 7-11G, Figure 7-11H and Figure 7-11I it is evident that the formation enthalpy diminishes with increasing defect concentration and hence temperature. The most pronounced decrease in formation enthalpy is exhibited by Schottky defects followed by Frenkel pairs and Polarons. Figure 7-12 compares the defect concentrations calculated in this work with those measured by Hutchings et al. using high temperature neutron diffraction¹⁸¹. There is good agreement between the measured and calculated values.

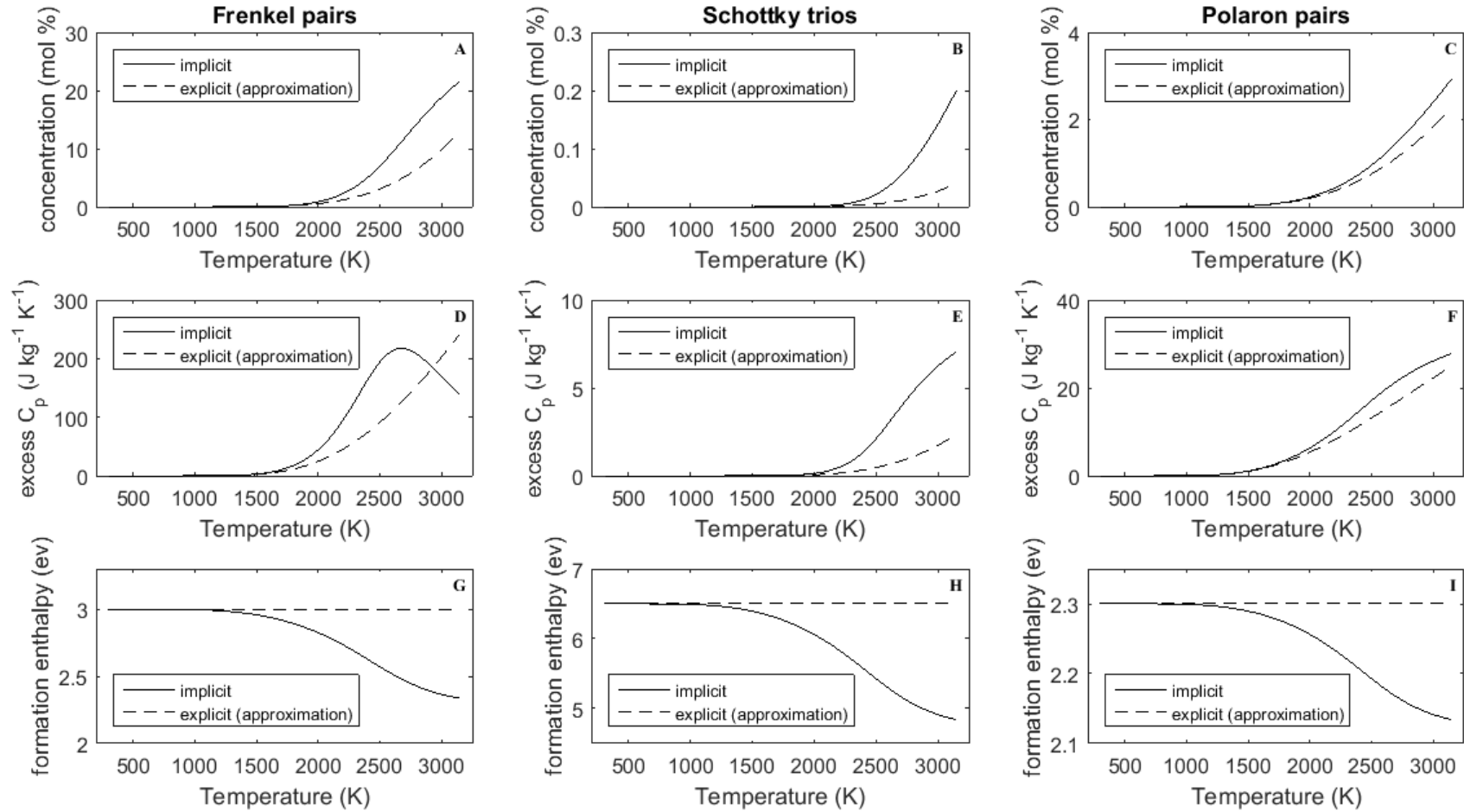


Figure 7-11: Matrix plot of defect type vs. concentration, specific heat contribution and enthalpies of formation as a function of temperature. Each column of the matrix plot represents a defect type (graphs A, D, G – Frenkel pairs; graphs B, E, H – Schottky trios, graphs C, F, I – polaron pairs). The implicit solution is compared to the explicit approximation of equations (7-9) to (7-11).

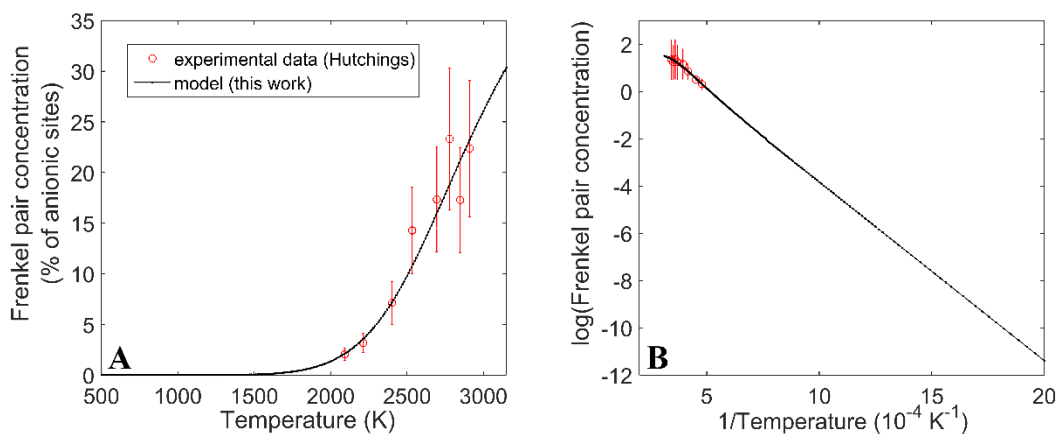


Figure 7-12: (A) Oxygen Frenkel pair concentration vs. temperature. The model output is compared to the measured data of Hutchings et al.¹⁸¹; (B) Arrhenius plot of A.

7.7 Specific heat

The specific heat of UO_2 can be expressed as a sum of its constituent contributions:

i) harmonic; ii) electronic; iii) defect; iv) conversion from constant volume to constant pressure. The harmonic, electronic and conversion terms are described in sections 3.1.1, 3.1.2 and 3.1.5, respectively. The defect term consists of applying the methodology in section 3.1.4 to equations (7-9) to (7-11) .

Figure 7-13 compares the specific heat measured and calculated in this work with the relationship suggested by Fink et al.¹³²; below 2500 K there is very good agreement. The experimental results presented here, however, suggest a maximum in specific heat at $2715 \text{ K} \pm 100 \text{ K}$ (~ 0.87 of the melting point), which is consistent with the model prediction of a maximum. Figure 7-13B compares the model enthalpy increment prediction to the literature data collected by Fink¹⁵⁸. It is evident that

there is very good agreement between the current model prediction and the independent experimental data provided by various authors.

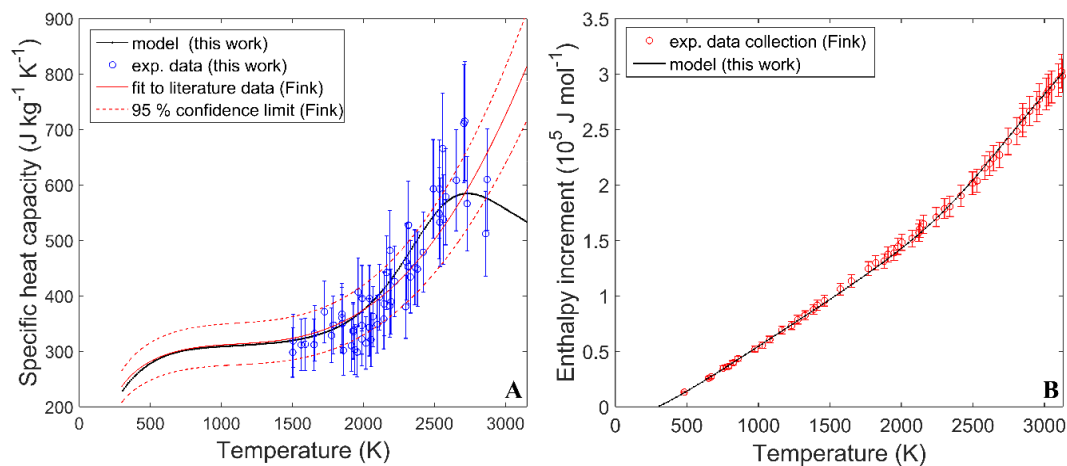


Figure 7-13: (A) Specific heat capacity vs. temperature comparing the experimental results obtained in this work with the model output and fit to literature data. Red dashed lines denote a 95% confidence range based on Fink's function. (B) Enthalpy increment vs. temperature comparing the model output to the experimental data collected by Fink¹⁵⁸.

7.8 Thermal expansion

The volumetric thermal expansion coefficient can be expressed as the sum of defect and lattice terms, respectively. This has been previously established in section 3.3. Figure 7-14 shows the effect of the vibrational (lattice) and defect terms on the material dimensions in UO_2 as a function of temperature. Figure 7-14A shows significant defect contributions to the thermal expansion coefficient with a diffuse maxima at around 2850 K. The lattice parameter (Figure 7-14C) and relative thermal expansion (Figure 7-14D) calculated by the model agree very well with existing

experimental data. According to the model prediction (see Figure 7-14) at temperatures above 2000 K defects contribute significantly to the thermal expansion coefficient of UO_2 and hence to changes in density, lattice parameter and relative thermal expansion.

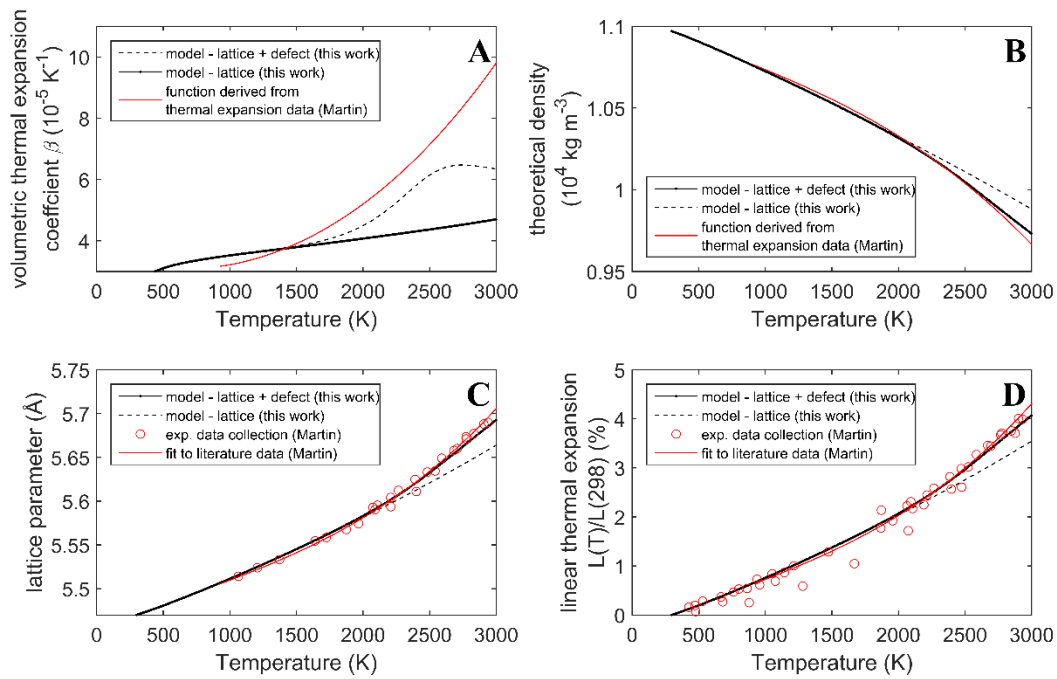


Figure 7-14: Model prediction for certain dimensional properties of UO_2 as a function of temperature. Each graph shows the lattice contribution to the particular property as well as the combined contributions of the lattice and defect terms: (A) Volumetric thermal expansion coefficient as a function of temperature; (B) Theoretical density as a function of temperature; (C) Lattice parameter as a function of temperature; (D) Thermal expansion vs. temperature. The model results are compared to available experimental data^{187,188}.

7.9 Electrical conductivity

Electrical conductivity is associated with the motion of charged species through the crystal lattice and can be understood in terms of polaron and ionic (i.e. vacancy/interstitial) electrical conductivities. The methodology for modelling electrical conductivity can be found in sections 3.2.3 and 3.2.4. Figure 7-15A shows good agreement between the model calculation of electrical conductivity vs. temperature with independent experimental results and established relationships by various authors. From Figure 7-15B it is clear that polarons are the dominant defect governing the evolution of electrical conductivity, followed by oxygen vacancies and finally oxygen interstitials (this is consistent with the differences in transport activation energies for these defects¹⁸⁹).

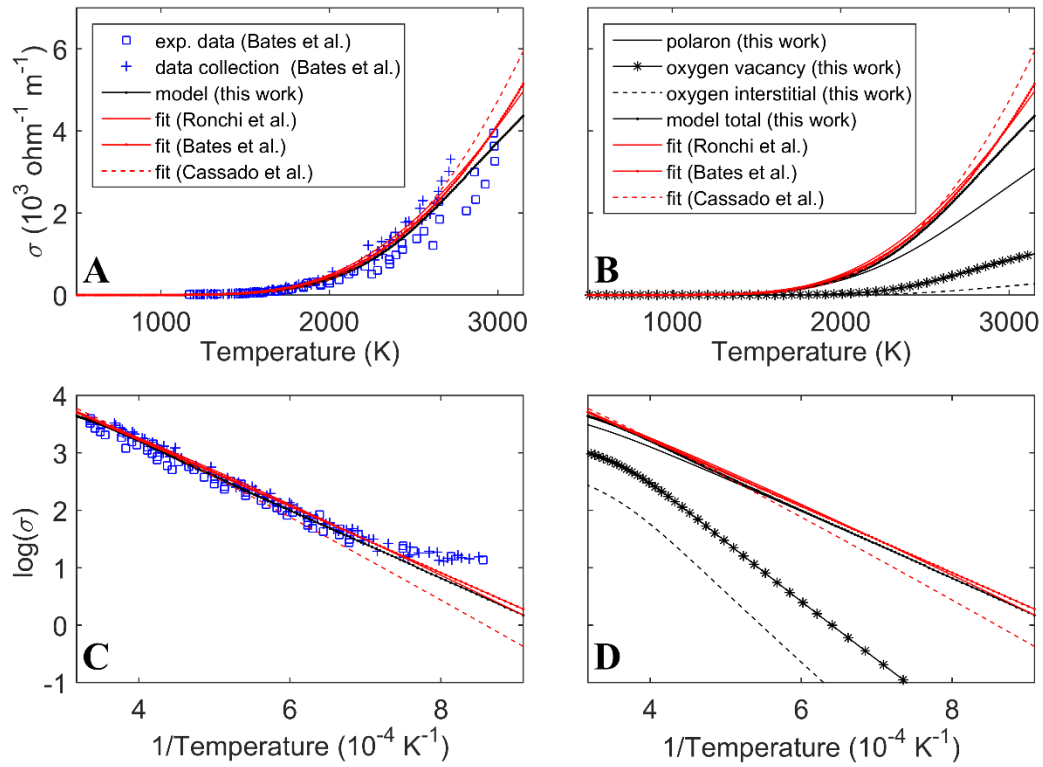


Figure 7-15: Plot of electrical conductivity vs. temperature. (A) the model proposed in this work compared to experimental data^{190,191} and various fits to the respective literature data^{65,117,190}; (B) the contributions to electrical conductivity based on the dominant defect species and their concentrations estimated in this work; (C) Arrhenius plot of A; (D) Arrhenius plot of B.

7.10 Thermal conductivity

The thermal conductivity of UO_2 can be expressed as the sum of lattice, polaron and ionic contributions. Detailed descriptions of each term are given in section 3.2.

Figure 7-16A shows that there is good agreement between the model and data reported in this study and the recommendations of Fink¹³² and Ronchi et al.⁶⁵ (based on several independent measurements). Figure 7-16B shows a deconvolution of thermal conductivity into the two operating mechanisms – lattice and electronic (i.e.

polaron) terms. The model established in this work suggests the two terms lie between the fits of Fink¹³² and Ronchi et al.⁶⁵ Both model terms are close to the fitted terms of Ronchi et al.⁶⁵ at temperatures below 2000 K and approach the fitted terms obtained by Fink¹³² at higher temperatures. The model predicts a significant contribution by spin-phonon scattering at lower temperatures.

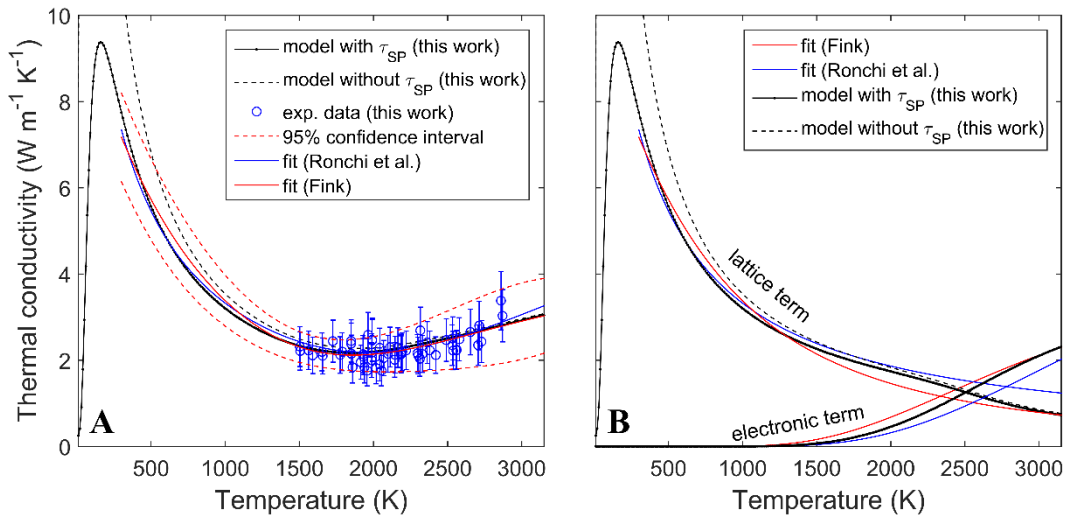


Figure 7-16: Thermal conductivity vs. temperature. (A) the experimental data measured in this work compared with the proposed model and established literature fits^{65,132}. (B) lattice and electronic contributions to thermal conductivity estimated via the model proposed in this work compared with the estimates from fits reported in the literature^{65,132}. The 95% confidence interval is obtained from a polynomial fit to the absolute residual difference between all reported data by Fink¹³² and the suggested fit by the same author. The acronym τ_{SP} stands for the spin – phonon scattering relaxation time.

7.11 Thermal diffusivity

Thermal diffusivity has been derived from the measured and calculated quantities of thermal conductivity, specific heat and density via equation (3-89) (see section 3.4). Figure 7-17 compares thermal diffusivity data measured in this work with the results of the current model and the fit recommended by Ronchi et al.⁶⁵ Again, below 2700 K the current experimental data agrees well with the fit recommended by Ronchi et al.⁶⁵ and the model calculation. The model and experimental data in this work, however, suggest a minima in thermal diffusivity at $2600 \text{ K} \pm 100 \text{ K}$, which is not apparent in the function suggested by Ronchi et al.⁶⁵. Some of the measured data above 2700 K shown in Figure 7-17 suggests a steeper increase in thermal diffusivity compared to the model prediction. Hence, the model could be underestimating thermal conductivity, as there is good agreement between the model predictions and experimental data for specific heat and thermal expansion. A possible reason for this underestimation could be a lower polaron activation energy.

Finally, all parameters used as input for the models describing the various thermo-physical properties of UO_2 are provided in Table 7-7. It is important to state that only a single coupling constant (see C_{SP} in Table 7-7) and energy (see $\hbar\omega_0$ in Table 7-7) are employed, as the coupling frequencies provided by Liu et al.¹¹³ are very close in magnitude (3% difference). Finally, the coupling constant has been determined empirically in this work, in order for the model to accurately represent the low temperature thermal conductivity data (see Figure 7-16).

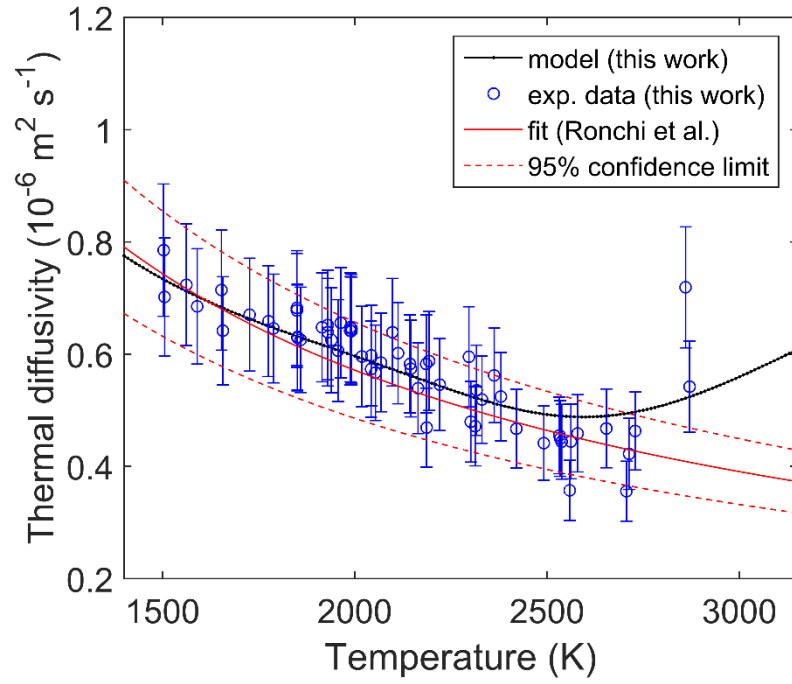


Figure 7-17: A plot of thermal diffusivity vs. temperature, comparing experimental data from this work with the model output and the literature fit proposed by Ronchi et al.⁶⁵

Table 7-7: Summary of input parameters for the calculation of thermal and electrical conductivity.

Parameter description	Units	Symbol	Value	Indicative Range	Ref
oxygen vacancy migration energy	eV	$\mathbf{M}_{V,O}$	0.55	0.5 - 0.6	185
oxygen interstitial migration energy	eV	$\mathbf{M}_{I,O}$	0.9	0.6 - 1.0	184,185
polaron migration energy	eV	$\mathbf{M}_{Pol}$	0.18	0.14 - 0.3	65,115,189,192
Grüneisen parameter	-	γ	1.9	1.7 - 2.2	178
atomic mass	u	$\mathbf{M}_{at}$	270	-	-
grain size	μm	$\mathbf{L}_g$	10.0	8 - 12	*
pore fraction	(%)	$\mathbf{v}_p$	5	4.5 - 5.5	*
electron overlap integral	eV	$\mathbf{J}$	0.07	0.04 - 0.07	117
ion hopping frequency	THz	$\mathbf{v}_0$	10.5	-	**
molar mass	kg mol^{-1}	$\mathbf{M}_{mol}$	0.27	-	-
lattice parameter (298 K)	$\text{\AA}$	$\mathbf{a}_0$	5.47	-	168
density (theoretical)	kg m^{-3}	ρ	10970	-	-
spin-phonon coupling energy	ev	$\hbar\omega_0$	0.003529	-	113
spin-phonon coupling constant**	GHz	$\mathbf{C}_{SP}$	250	-	113

* determined experimentally in this work

** recommended in this work

7.12 Summary

In this chapter measurements of the specific heat, thermal conductivity, thermal diffusivity, spectral emissivity and melting point of UO_2 have been presented. The melting arrest was measured at $3118 \text{ K} \pm 55 \text{ K}$, which is in good agreement with literature values and hence provides further evidence for the reliability of the new method and equipment. A specific heat maximum has been identified at around $2715 \pm 100 \text{ K}$. For the first time a diffuse maximum has been measured, which is in agreement with various enthalpy data sets in the literature. Minima have been identified in thermal diffusivity at $2600 \text{ K} \pm 100 \text{ K}$ and thermal conductivity at 2000

$K \pm 100$ K. The solid state physics model presented has successfully reproduced the properties measured in this work. Furthermore, the model has also been used to evaluate other thermo-physical properties – electrical conductivity and thermal expansion. The model has helped identify the underlying mechanisms, which will be discussed in Chapter 9.

Chapter 8 : Thorium dioxide

– *“For a successful technology, reality must take precedence over public relations, for nature cannot be fooled.”* –

Richard Feynman, physicist

In this chapter the results of the thermo-physical properties of ThO₂ are reported (specific heat, thermal conductivity, thermal diffusivity, spectral emissivity and total hemispherical emissivity). These have been measured in the temperature range 1500 K to 2900 K and are compared to existing literature results. The experimental data are complemented by the same condensed matter models applied in the previous chapter and described in Chapter 3.

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8.1 Introduction

ThO₂ has a fluorite structure with the same type of unit cell as UO₂ and exhibits the same point defects (see Figure 7-1). Furthermore, it is an alternative nuclear fuel to UO₂, however the naturally occurring ²³²Th is fertile. ²³²Th undergoes neutron capture, in order to form the fissile ²³³U. Hence, in order to sustain a fission reaction, in the beginning of its life inside a nuclear reactor, the ThO₂ based fuel material has to be mixed with small amounts (e.g. 6% ²³³U) of fissile isotopes, such as ²³³U, ²³⁵U or ²³⁹Pu (i.e. (Th_{1-x},U_x)O₂ or (Th_{1-x},Pu_x)O₂ mixed oxides). There are a number of reasons for exploring a thorium fuel cycle. ThO₂ is 3 to 4 times more abundant than urania¹⁹³ and can be relatively easily extracted from monazite. The overburden during extraction is significantly lower compared to UO₂, leading to less radiotoxic spoil¹⁹⁴. Furthermore, thoron (²²⁰Rn) produced in the decay chain of ²³²Th is much shorter lived than the corresponding radon (²²²Rn)¹⁹⁵ - decay product of ²³⁸U. Another advantage of ²³²Th is the high absorption cross section of thermal neutrons, which makes it suitable for thermal reactors. Furthermore, ²³²Th is more efficient for breeding ²³³U compared to ²³⁹Pu bred from ²³⁸U in fast reactors¹⁹⁶. The low capture cross section of ²³³U leads to a slower buildup of neutron poisons¹⁹⁷, while the high neutron multiplier coefficient over a large range of neutron energies makes thorium applicable to both thermal and fast reactors. Furthermore, the release of fission gas may be lower^{198,199}, possibly due to slower diffusion of xenon through the ThO₂

lattice²⁰⁰. However, the measured fission gas release for ThO₂^{198,199} was for fuel irradiated at lower temperature and hence may not be representative of in-reactor conditions, that is with a higher average irradiation temperature (note: during operation conditions fission gases may more readily migrate to grain boundaries due to higher diffusion coefficients at higher temperatures leading to higher rod internal pressure). Furthermore, ThO₂ can be used as a means of incinerating and hence utilising weapon grade plutonium. ThO₂ is considered more proliferation resistant due to certain highly active decay products of ²³²U, which require special handling facilities. However, recent studies have indicated that thoria does pose proliferation risks²⁰¹. A decay product of ²³²Th, known as protactinium has a significant fission yield and could be separated early-on in the fuel life before significant amounts of ²³²U are formed. ²³³Pa then decays into ²³³U, which can be used to make a nuclear weapon. The problem arises from the ease with which ²³³Pa can be extracted using established industrial processes such as acid based techniques, with no need for special handling facilities. Finally, ThO₂ has superior thermo-physical properties compared to UO₂, such as a higher melting point²⁰², a higher thermal conductivity up to 2000 K^{203,204} and is resistant to oxidation (i.e. Th ions are not stable in valance states higher than 4+).

Even though ThO₂ offers various benefits it also has shortcomings. One of the challenges is the lower sinterability of ThO₂ compared to UO₂²⁰⁵. This results in the need for high sintering temperatures, in order to produce high density pellets. The

high chemical stability of thorium makes it difficult to dissolve²⁰⁶ and reprocess in a closed fuel cycle. Furthermore, the fission product decays into Th^{228} , which has highly active daughter products – Bi, Tl, Pb and Po. These require special handling of the fuel during reprocessing. Furthermore, since U^{232} and Th^{228} cannot be separated from their original isotopes, the re-sintering of U, Th powder also requires specialized and, hence, costly handling facilities. Finally, our knowledge of the material properties of ThO_2 is limited, which constrains our understanding of fuel fabrication, fuel reprocessing and fuel behaviour during reactor operation, as well as during reactor accident conditions. Hence, this chapter is focused on the high-temperature thermo-physical properties of ThO_2 as measurements at extreme temperatures are scarce.

Up to 2000 K specific heat has been measured by a number of authors^{207,208}, while above 2000 K few studies exist. Amongst these works are the experimental investigations of Ronchi et al.²⁰⁹ and Ralph et al.²¹⁰ Their work has provided evidence for a significant increase in specific heat above 2000 K, most likely due to the formation of oxygen defects. Furthermore, Ronchi et al. measured a steep increase in specific heat followed by a decrease, marking a maximum at around 3100 K. Thermal conductivity has also been investigated by various authors at temperatures up to 2000 K^{211,212}. At higher temperatures, Weilbacher²¹³ and Faucher²¹⁴ have measured thermal diffusivity and from the density and specific heat one could estimate the thermal conductivity. However, as previously mentioned, there are few high temperature specific heat values and they differ significantly. This introduces a

degree of uncertainty when calculating thermal conductivity based on an indirect approach (i.e. by using literature values for specific heat and density). Thus, the aim of this work is to establish experimental values of thermal conductivity, and specific heat in the temperature range 2000 K to 3050 K via the newly developed semi-direct method^{131,215} (i.e. the laser-flash based pyrometer method described in Chapter 4). It is described as semi-direct, meaning specific heat and thermal conductivity are determined simultaneously, but the method requires density as input. The method and apparatus have also been used to determine also thermal diffusivity, spectral emissivity and the total hemispherical emissivity of ThO₂, in the temperature range 2000 K to 3050 K. Furthermore, the temperature dependence of the experimental results is described using a solid state physics model²¹⁵, which is based on the governing physical processes. All new results are important for the reliable prediction of ThO₂ bearing fuel behaviour during off-normal, accidental conditions via fuel performance or fuel safety codes.

8.2 Samples

The ThO₂ samples were provided by Tadeas Wangle and produced at SCK-CEN. Green pellets were prepared according to the process proposed by Wangle et al.²¹⁶. A solution of 1 mol/l Th(NO₃)₄ in HNO₃ (Solvay) was added to a 0.75 mol/l oxalic acid (Sigma-Aldrich) solution (5% excess), which was cooled to 10 °C. After precipitation, the solution was digested for 15 minutes, filtered and dried at 70 °C overnight. The

filter cake was finally forced through a 300 μm sieve. The sieved $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$ precursor was calcined to ThO_2 in a Nabertherm LT 9/13/P330 muffle furnace at $1^\circ\text{C}/\text{min}$ at 350°C and held for 12 h, then heated at $1^\circ\text{C}/\text{min}$ to 700°C and held for 1 h. The powder was loaded without further manipulation into a stearic acid coated 6.9 mm diameter steel die. The green pellets were pressed in a uniaxial Atlas Auto 8T press at 300 MPa. Sintering was performed in a Linn HT 1800 Moly high temperature furnace, by heating to 1700°C at $5^\circ\text{C}/\text{min}$ with a dwell time of 8 h. An atmosphere of $\text{Ar} + 5\% \text{H}_2$ with a small admixture of $\text{Ar} + 0.5\% \text{O}_2$ was used to give an oxygen potential of -420 kJ/mol at 1700°C .

The material properties and dimensions of ThO_2 alongside laser beam characteristics are summarized in Table 8-1 and Table 8-2. This data is then used as input for the FEA model described in section 4.1.5. The emissivity at 645 nm is used for converting measured radiance temperature to true temperature, while the emissivity at 1064 nm governs the portion of laser radiation absorbed by the sample. The emissivities at these two wavelengths have been assumed identical. This assumption is confirmed by the results of Ronchi, et al.²⁰⁹ These authors report temperature dependent emissivity values for ThO_2 at 960 nm (i.e. close to 1064 nm) and their results are in very good agreement with the current reported values at 645 nm (see Figure 8-6). Equation (8-1) is based on the data shown in Figure 8-6 and represents the spectral emissivity of ThO_2 in the measured temperature range. All thermal conductivity values are corrected to 95% theoretical density using the Brandt and Neuer

relation^{132,134}. The sample stoichiometry was characterised, via X-ray diffraction, for two samples before and after the laser flash experiments; the O/Th ratio was consistently determined to be 2.000 ± 0.001 .

Table 8-1: Summary of ThO₂ sample characteristics and laser beam parameters.

Parameter (units)	Value
room temperature density ρ_{298} (kg m ⁻³)	9300
porosity (%)	7
thickness (mm)	1.56
radius (mm)	2.825
beam spot radius (mm)	1.5
pulse duration (ms)	10

Table 8-2: Material properties of ThO₂ used as input in the FEA model.

Property	Expression	Ref.
thermal expansion $E(T)$ ⁺	$9.9729 \times 10^{-10} T^2 + 7.8410 \times 10^{-6} T$	217
density $\rho(T)$	$\rho_{298} \{1 + E\}^{-3}$	217
$\epsilon_{(1064 \text{ nm})}^{**}$	$f(T)$	this work
$\epsilon_{(645 \text{ nm})}^{**}$	$f(T)$	this work

⁺ fitted to reference experimental data.

^{**} see equation (8-1).

The function $f(T)$ in Table 8-2 defines the evolution of the spectral emissivities at 645 nm and 1064 nm as a function of temperature and is expressed by the following equation:

$$f(T) = \begin{cases} 0.1 & \in T < 1545K \\ 3.67 \times 10^{-11} T^3 - 6.09 \times 10^{-7} T^2 + 2.72 \times 10^{-3} T - 2.78 & \in 1545K < T < 3000K \\ 0.9 & \in T > 3000K \end{cases} \quad (8-1)$$

where T is temperature.

8.3 Vapourisation heat losses

As discussed in the previous chapter the partial pressures of the material heavily influence the vapourisation heat flux. Hence, a modification of the Rand-Markin model^{165,166} is used for the calculation of the partial pressures of the vapour species of ThO₂:

$$\frac{1}{2}O_2(g) \rightarrow O(g) \quad p_O = \exp\left[\frac{\Delta G_{0,1}}{RT}\right] p_{O_2}^{1/2} \quad (8-2)$$

$$ThO_2(s) \rightarrow ThO_2(g) \quad p_{ThO_2(g)} = \exp\left[\frac{-\Delta G_{0,2}}{RT}\right] \quad (8-3)$$

$$Th(g) + \frac{1}{2}O_2(g) \rightarrow ThO(g) \quad p_{Th(g)} = \exp\left[\frac{-\Delta G_{0,3}}{RT}\right] p_{ThO(g)} p_{O_2}^{-1/2} \quad (8-4)$$

$$ThO(g) + \frac{1}{2}O_2(g) \rightarrow ThO_2(g) \quad p_{ThO(g)} = \exp\left[\frac{-\Delta G_{0,4}}{RT}\right] p_{ThO_2(g)} p_{O_2}^{-1/2} \quad (8-5)$$

$$p_{O_2} = \exp\left[\frac{\Delta G_{0,5}}{RT}\right] \quad (8-6)$$

The standard Gibbs free energies of formation have been refitted, based on the most recent updated information available in the FactSage database¹⁶⁷. These are summarized below in Table 8-3. Figure 8-1 compares the relative error between the calculated partial pressures based on equations (8-2) to (8-6) and the values obtained from FactSage. The small discrepancy between FactSage and the current vapour pressure results are possibly due to the use of slightly different Gibbs free energy fits. It should be noted that, due to the use of a very pure oxygen atmosphere during the laser flash experiments, equation (8-6) is modified to $p_{O_2} = 1$ when calculating the vapourisation heat losses.

Table 8-3: Summary of standard formation enthalpies and entropies. The subscript corresponds to the respective reaction number in equations (8-2) to (8-6).

ΔH_0	Value (kJ mol ⁻¹)	$\Delta S_0(T)$	Function (kJ mol ⁻¹)
$\Delta H_{0,1}$	250.5	$\Delta S_{0,1}$	$1.649 \times 10^{-3} \times T + 61.6$
$\Delta H_{0,2}$	785.84	$\Delta S_{0,2}$	$8.423 \times 10^{-3} \times T - 213.7$
$\Delta H_{0,3}$	-149.9	$\Delta S_{0,3}$	$4.748 \times 10^{-4} \times T + 13.21$
$\Delta H_{0,4}$	-406.5	$\Delta S_{0,4}$	$2.446 \times 10^{-3} \times T + 46.68$
$\Delta H_{0,5}$	-938.4	$\Delta S_{0,5}$	$-6.743 \times 10^{-3} \times T + 295.1$

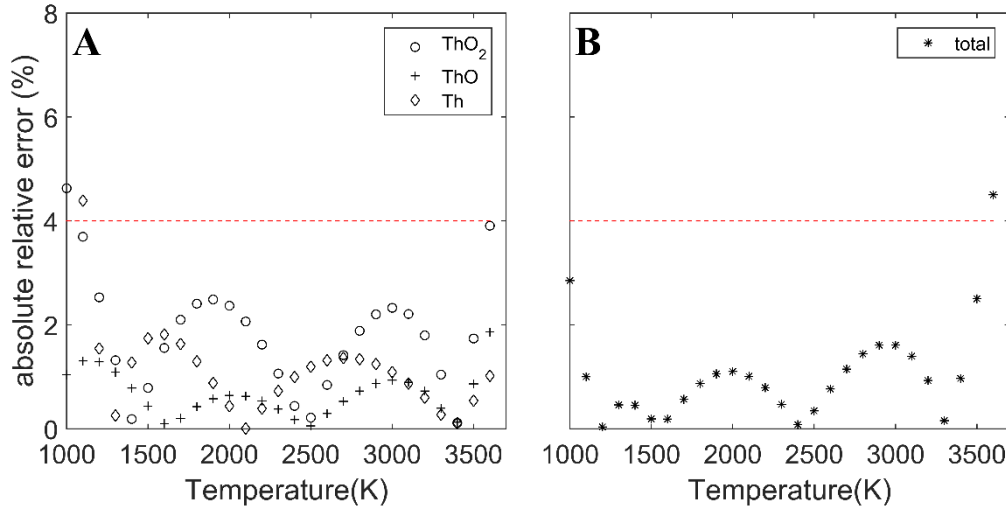


Figure 8-1: Comparison of the partial pressures calculated via the Rand-Markin model and those predicted by FactSage¹⁶⁷ at 1 bar ambient pressure. (A) comparison of the relative errors of the 3 dominant vapour species (B) the relative error of the total vapour pressure.

The heat loss dominance diagram for ThO₂ is shown in Figure 8-2. The black borders represent the temperature and pressure at which the heat fluxes of neighbouring regions are equal (or approximately 50 % of the total heat flux). The trends are very similar to those observed for UO₂ in Figure 7-3. At high temperatures and low

pressures vapourisation dominates. At low pressure and high temperature or high temperature and intermediate pressure radiation is the most significant heat loss process. It is important to note that total hemispherical emissivity is based on the numerical solution of equations (3-93) and (8-20). Finally, at high pressure or at low temperature and intermediate pressure natural convection is the main heat loss mechanism. The kink observed in Figure 8-2 (between the radiation and natural convection regions) is due to a minimum in total hemispherical emissivity (see section 8.10)

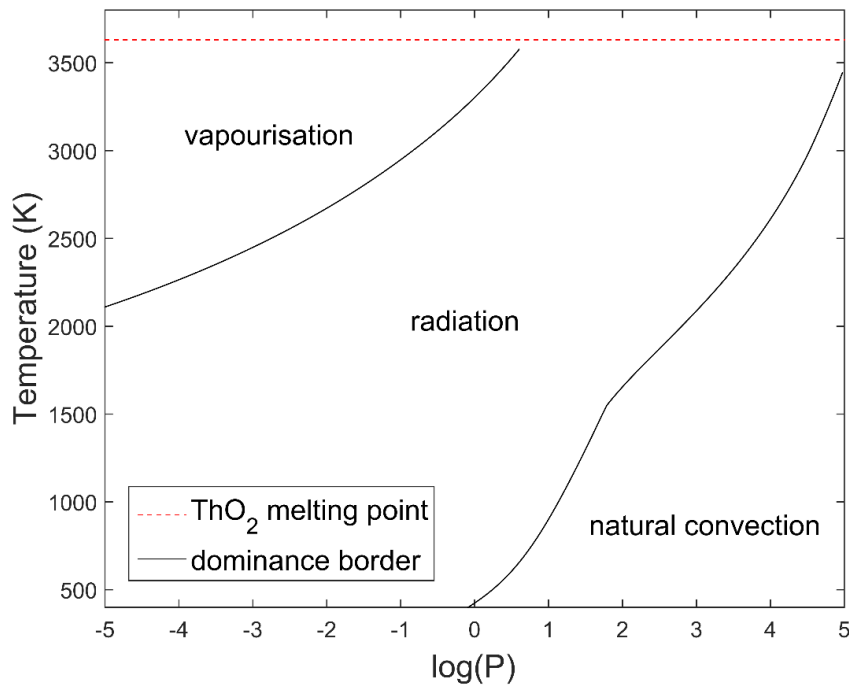


Figure 8-2: The heat loss dominance diagram for ThO_2 calculated according to the methodology in sections 4.1.5, 4.1.10 and 4.1.11 of Chapter 4. The solid black lines indicate where the dominant heat flux loss transitions from one mechanism to another. The dotted red line represents the melting point of the material.

8.4 Experimental results

The lattice parameters of three ThO₂ samples were determined via Rietveld refinement of the recorded XRD spectra shown in Figure 8-3. The calculated lattice parameters are shown in Table 8-4. The three samples were exposed to different maximum temperatures prior to being quenched (under pure oxygen atmosphere) to room temperature. Comparing these to the theoretical lattice parameter of stoichiometric ThO₂²¹⁸⁻²²⁰ (5.5975 ± 0.0005 Å), it is evident that no significant departure from stoichiometry has been measured. Hence, the O/Th ratio during the experiments is consistent with a value of 2.000 ± 0.005 .

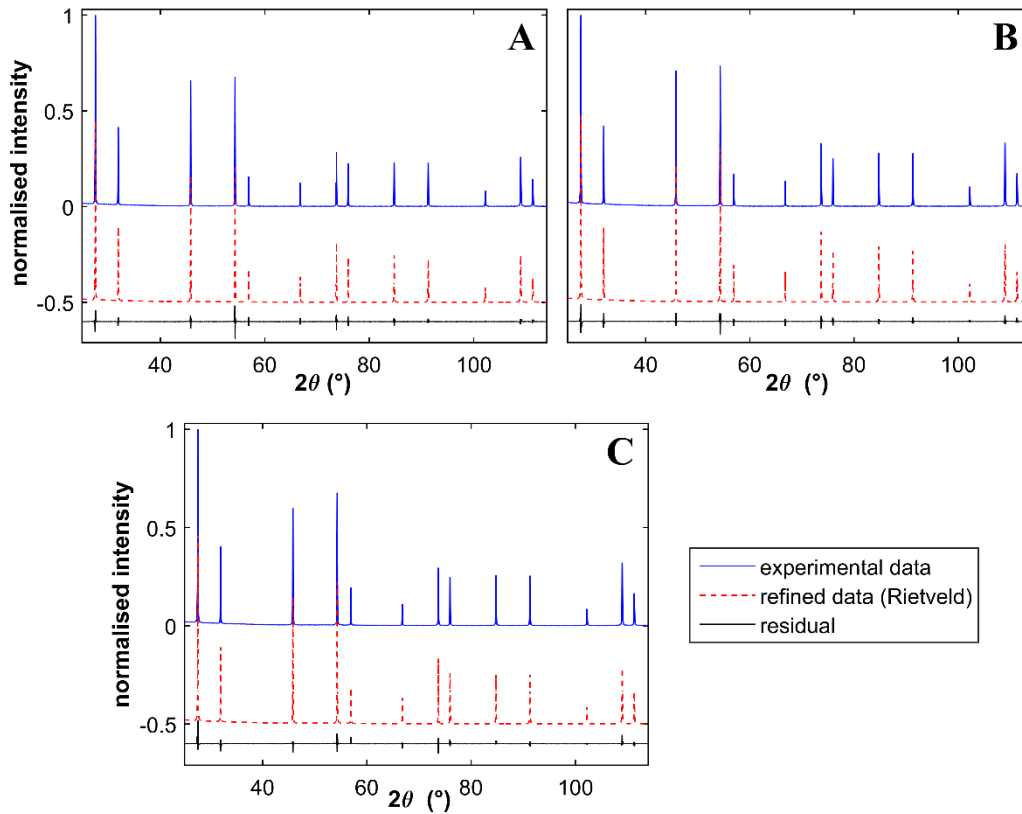


Figure 8-3: X-ray diffraction spectra of three different ThO_2 samples compared with the Rietveld refinement used for determining the respective lattice parameters. (A) ThO_2 specimen subjected to a maximum temperature of 2500 K; (B) ThO_2 specimen held at room temperature (300 K); (C) ThO_2 specimen subjected to a maximum temperature of 3000 K.

Table 8-4: Lattice parameter of ThO_2 (derived from refined XRD spectra in Figure 8-3) for different exposure temperatures. The uncertainty on the lattice parameter has been approximated to be of the order of $\pm 0.001 \text{ \AA}$ (95% confidence interval).

Exposure temperature (K)	Lattice parameter ($\text{\AA}$)
2500 K	5.5976
300 K	5.5975
3000 K	5.5973

The melting point of ThO_2 was identified at $3665 \text{ K} \pm 70$ in this work. This result is based on the measured cooling curve in Figure 8-4A. The maximum temperature reached was around 4400 K (not shown in Figure 8-4A). Two different cooling curves were recorded without melting the material (maximum temperatures reached were just below 3600 K). These are compared to the thermogram reported by Ronchi et al.²⁰⁹ in Figure 8-4B. The study of Ronchi et al.²⁰⁹ indicates both a melting plateau (at around 3650 K) as well as a pre-melting transition around 3100 K. The cooling curves recorded in this work do not indicate the presence of a pre-melting transition.

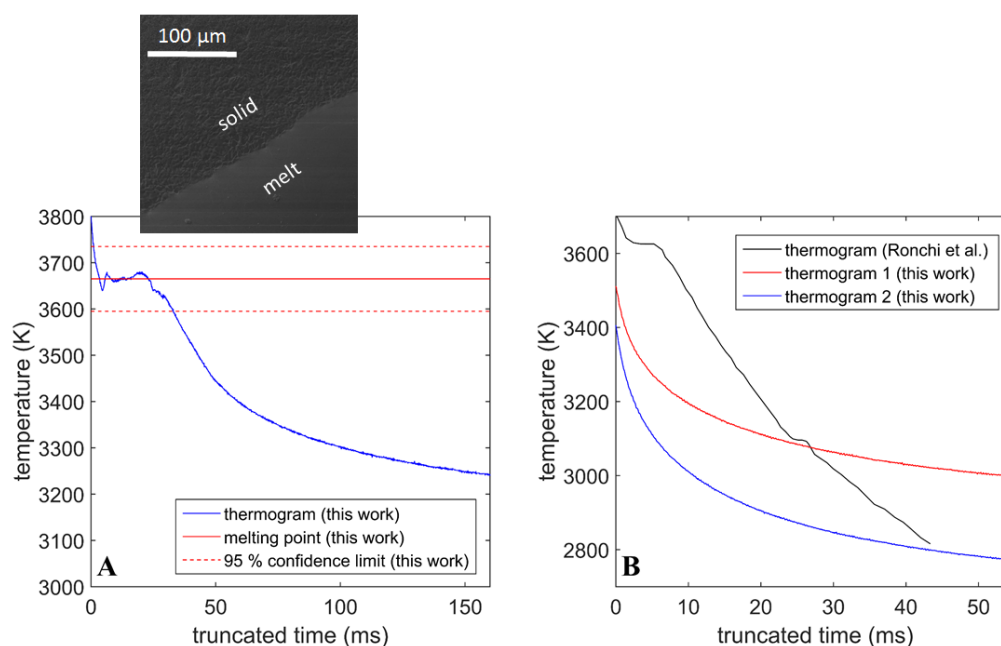


Figure 8-4: (A) Temperature vs. truncated time showing the melting plateau of ThO_2 ; the melting point is indicated via a solid red line; SEM image of the melting pool presented above the red dashed line. Red dashed lines indicate the confidence limits of the measured melting point. (B) Temperature vs. truncated time plots for two thermograms measured in this work compared to the thermogram reported by Ronchi et al.²⁰⁹.

Figure 8-5 shows the current measurements of specific heat compared to the experimental data of various authors²⁰⁹ and the function describing $c_p(T)$ recommended by Konings, et al.²²¹. There is generally good agreement between the new results, previous experimental studies and the recommended function up to 3000 K.

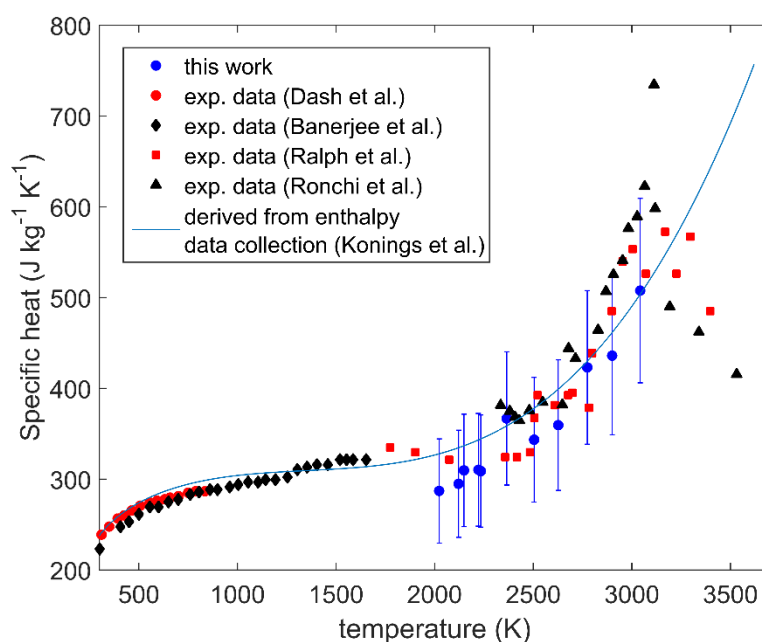


Figure 8-5: Specific heat evaluated in this work compared to the measurements of Dash, et al.²⁰⁷, Banerjee, et al.²⁰⁸, Ralph, et al.²¹⁰ and Ronchi, et al.²⁰⁹. The blue line is the recommended curve by Konings, et al.²²¹, based on the derivative of a fit to enthalpy data collected from literature.

Figure 8-6 presents the spectral and total hemispherical emissivity of ThO_2 . Furthermore, the spectral emissivity values were determined via the two different techniques (the ratio pyrometer (RP) and spectropyrometer (SP) methods), which are shown to be consistent with each other. Values for spectral emissivity measured

by Ronchi et al.²⁰⁹, in the near infrared wavelength range, are close to the measurements presented in the current study, which are in the visible wavelength spectrum. This suggests either a small or no variation of the spectral emissivity of ThO₂ with respect to wavelength in the range 600 – 1000 nm. Furthermore, both spectral and total hemispherical emissivity values increase as a function of temperature. The spectral emissivity at 645 and 960 nm is systematically higher compared to the total hemispherical emissivity at all measured temperatures.

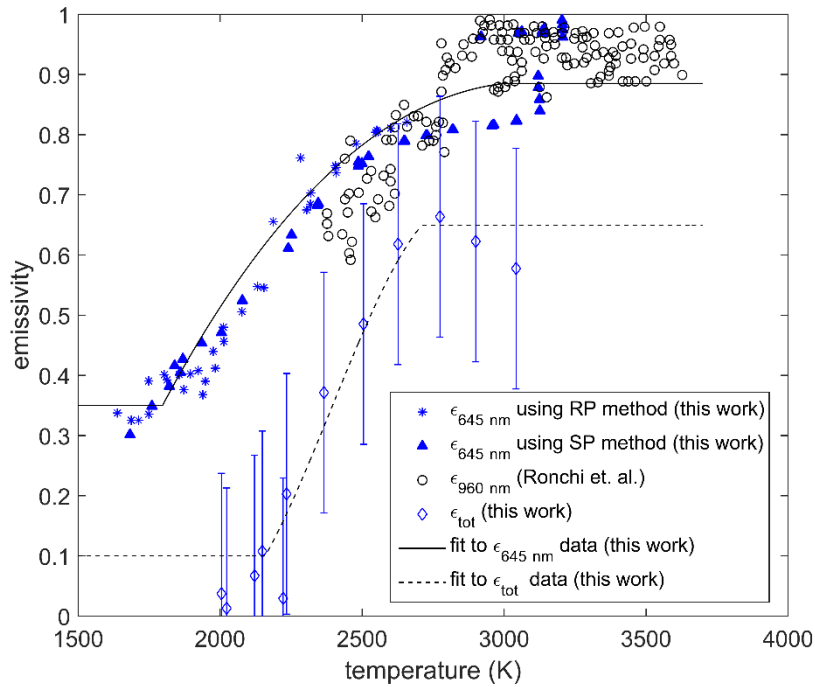


Figure 8-6: Spectral emissivity at 645 nm and total hemispherical emissivity as a function of temperature measured in this work. Spectral emissivity is compared to the measurements by Ronchi, et al.²⁰⁹ at 960 nm. The solid and dashed lines are fitted to the data in this work for guidance.

Figure 8-7 shows the thermal conductivity measurements for 95% dense ThO_2 (corrected from 93% TD to 95% TD using the relationship of Brandt and Neuer¹³⁴) as shown in Figure 8-7 compared to previous values reported by various authors^{211-213,222-224}. Most of the literature thermal conductivity values have been indirectly calculated from the thermal diffusivity measurements of the respective authors, the density (based on the thermal expansion recommendation of Hoch and Momin²¹⁷) and the specific heat recommendation of Konings et al.²²¹ Only the current measurements and data reported by Pillai et al.²²² can be referred to as direct measurements (this is further discussed in section 9.4). All values have been amended using the correction due to Brandt and Neuer^{132,134} to 95% dense ThO_2 . There is good agreement between the existing experimental literature values and the new results. Thermal conductivity decreases from around $9 \text{ W m}^{-1} \text{ K}^{-1}$ at 500 K to approximately $3 \text{ W m}^{-1} \text{ K}^{-1}$ at 2000 K. Beyond 2000 K, the property appears to remain invariant.

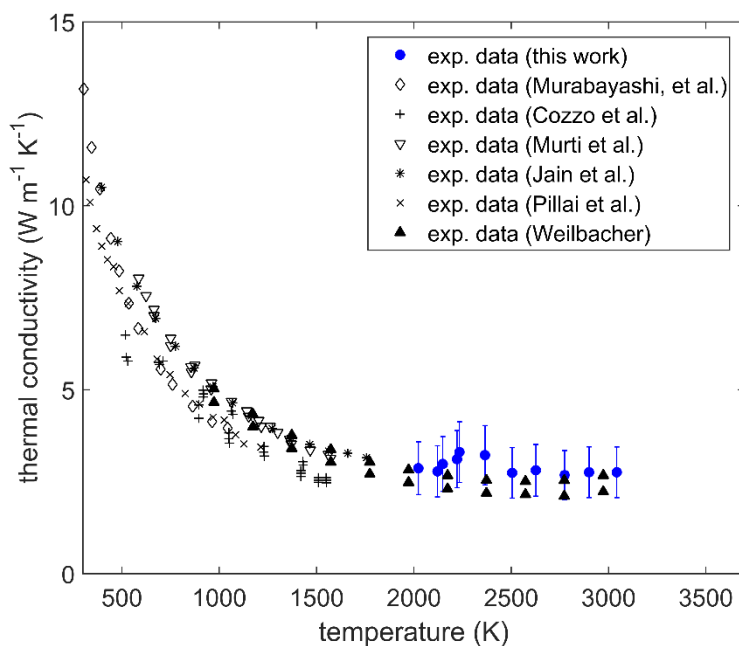


Figure 8-7: Thermal conductivity as a function of temperature for ThO_2 corrected to 95% TD. Measurements in this work compared to the data of Murabayashi²¹², Cozzo et al.²¹¹, Murti et al.²²³, Jain et al.²²⁴, Pillai et al.²²² and Weilbacher²¹³.

Thermal diffusivity as a function of temperature is shown in Figure 8-8. The current results are in good agreement with previous values at around 2000 K. In the temperature range 2000-2600 K the new measurements are around 10-15% higher compared to Weilbacher's results²¹³.

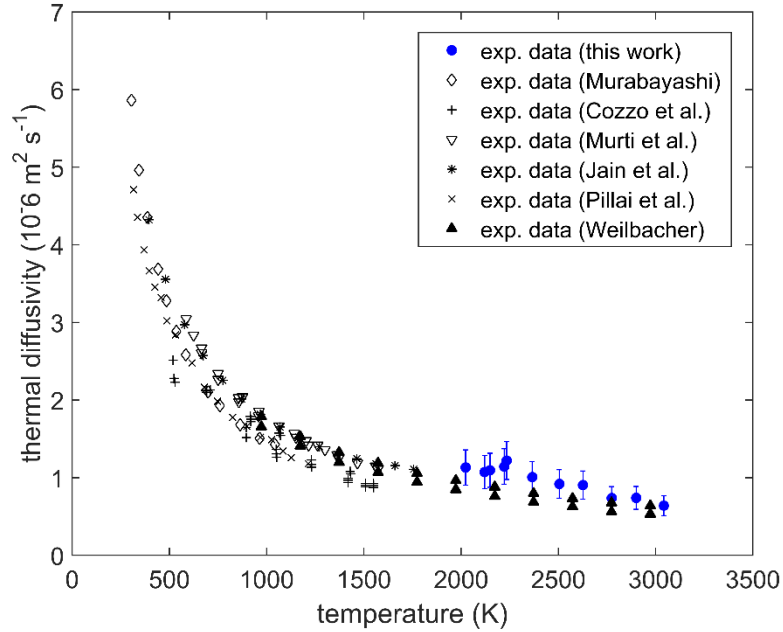


Figure 8-8: Thermal diffusivity as a function of temperature measured in this work compared to the experimental measurements of Murabayashi²¹², Cozzo et al.²¹¹, Murti et al.²²³, Jain et al.²²⁴, Pillai et al. and, Weilbacher²¹³.

8.5 Phonon density of states

The phonon density of states for ThO_2 have been approximated using a Debye-Einstein approach and are compared to DFT calculations (Wang et al.²²⁵) in Figure 8-9. ThO_2 has three atoms or ions per molecule and hence 3 acoustic branches (1 longitudinal and 2 transverse) and 6 optical branches (2 longitudinal and 4 transverse). The acoustic branches have been treated via a Debye approach whereby phonons can have a range of frequencies or energies and their respective number follows Bose statistics. Optical modes are approximated by single frequency particles and were represented using the Einstein model. The parameters for this model are summarised in Table 8-5 and the approach has been described previously²¹⁵. The

relative weights can be understood as the fraction of vibration modes characterised by the respective model parameter. From Figure 8-9 it is evident that in the lower frequency range there is good agreement between the density functional theory (DFT) results of Wang et al.²²⁵ and the model proposed in this work. At higher frequency (representative of the optical modes of vibration in ThO₂) the current model, even though simplified, captures the correct features of the phonon density of states of ThO₂.

Table 8-5: Summary of input parameters for the phonon density of states model.

Parameter description	units	symbol	value	indicative range	relative weight	Ref**
Debye temperatures (acoustic modes)	K	ϑ_{TA1}	170	160-216	1/9	225,226
	K	ϑ_{TA2}	260	-	1/9	225,226
	K	ϑ_{LA}	430	-	1/9	225,226
Einstein temperatures (optical modes)	K	E_{LO}	800	-	2/9	225,226
	K	E_{TO1}	630	-	2/9	225,226
	K	E_{TO2}	630	-	2/9	225,226

**the Debye and Einstein temperatures have been assigned in this work based on the phonon density of states data reported in the listed references.

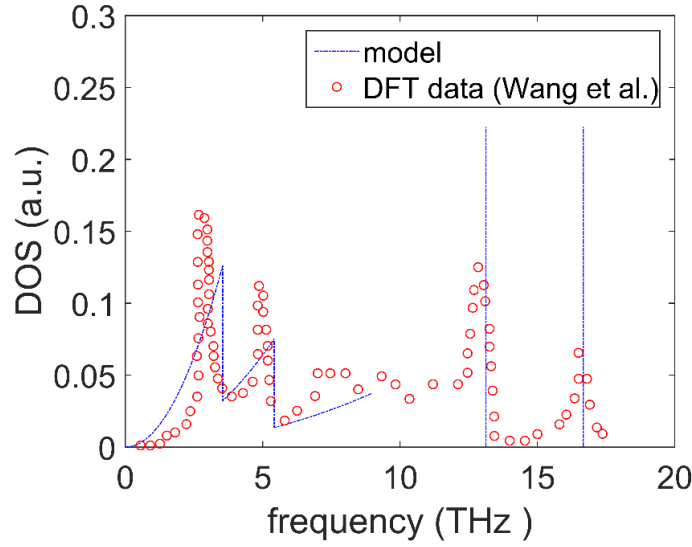
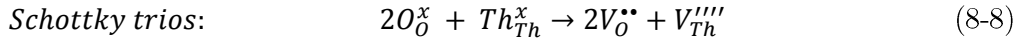
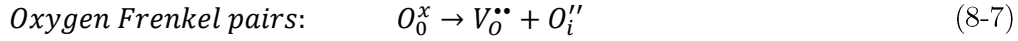


Figure 8-9: Phonon density of states (PDOS) vs. frequency - comparison between the proposed model for the phonon density of states and the DFT data of Wang et al.²²⁵

8.6 Defect concentrations

Defect concentrations are calculated based on the following reactions:



From statistical thermodynamics the following non-linear equations are obtained:

$$n_F^2 = \left(\frac{2}{3} - n_F - 2n_S\right) \left(\frac{1}{3} - n_F\right) \exp\left(-\frac{\Delta H_{F,Fr}}{C_B T} + \frac{\Delta S_{NC,Fr}}{C_B}\right) \quad (8-9)$$

$$n_S^3 = \left(\frac{2}{3} - n_F - 2n_S\right)^2 \left(\frac{1}{3} - n_S\right) \exp\left(-\frac{\Delta H_{F,Sch}}{C_B T} + \frac{\Delta S_{NC,Sch}}{C_B}\right) \quad (8-10)$$

where n_F and n_{Sch} are the Frenkel pair and Schottky trio concentrations per mole of ThO_2 , $\Delta H_{F,Fr}$ and $\Delta H_{F,Sch}$ are the formation enthalpies of Frenkel and Schottky defects respectively, while $\Delta S_{NC,Fr}$ and $\Delta S_{NC,Sch}$ are the non-configurational entropies

associated with the same Frenkel and Schottky defect species. The details of the calculation methods are described in section 3.1.4. However, it should be noted that the formation enthalpy is concentration dependent, due to the net attraction between oppositely charged defect species, leading to the implicit solution. The (approximate) explicit form of this equation is obtained by neglecting defect concentrations in the pre-exponential terms of equations (8-9) and (8-10) and also by assuming no columbic defect interactions. The results of these two approaches are presented in Figure 8-10 and the defect parameters used are given in Table 8-6. At temperatures below 2300 K the two methods yield similar results, however, at higher temperatures the implicit solution calculates higher defect concentrations compared to the explicit approximation. Furthermore, the implicit results show a maximum in the excess specific heat due to Frenkel pairs and a reduction in enthalpy. Schottky trios exhibit more significant relative differences between the two solutions compared to Frenkel pairs.

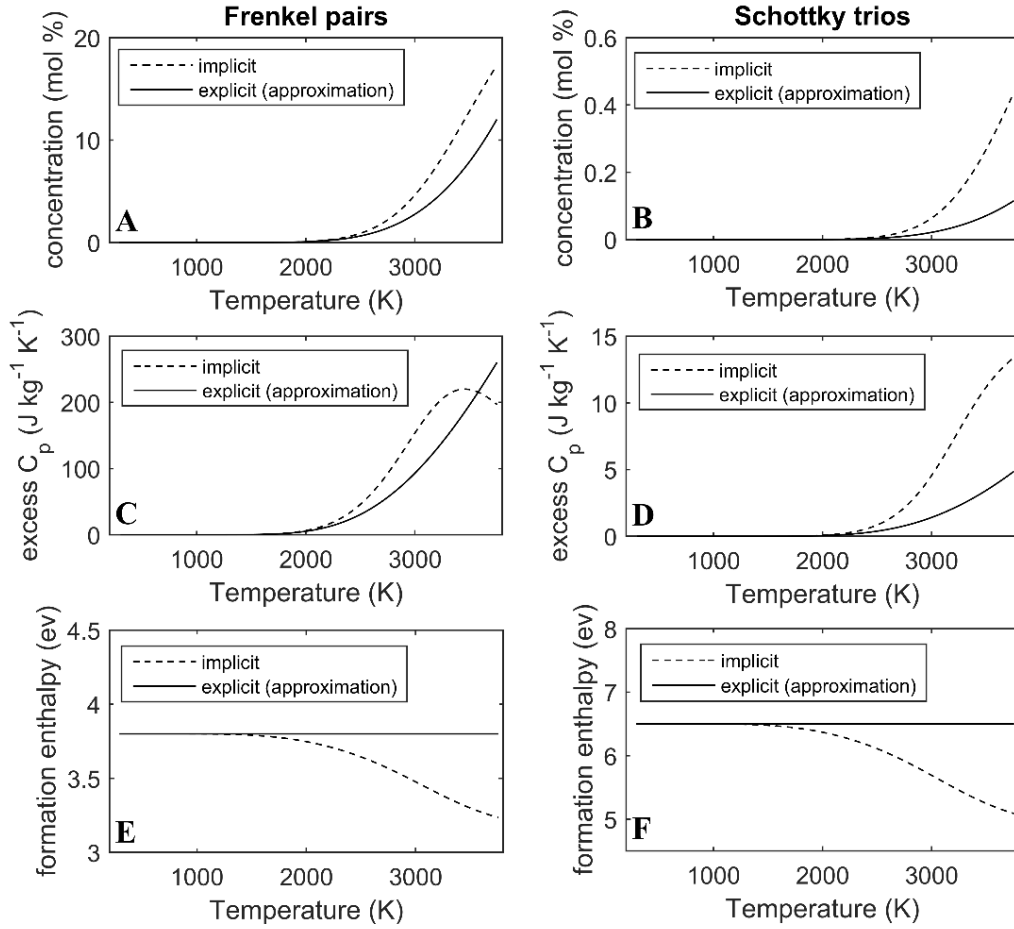


Figure 8-10: Plot of defect type (the title of each column) vs. the respective concentrations, excess specific heat and formation enthalpies. (A), (C), (E) represent the temperature dependent concentration, excess specific heat and formation enthalpy of oxygen Frenkel pairs respectively, while (B), (D), (F) show the temperature dependent concentration, excess specific heat and formation enthalpy of Schottky trios.

Table 8-6: Summary of input parameters for the defect concentration calculation.

Parameter description	Units	Symbol	Value	Indicative range	Ref.
Frenkel pair formation enthalpy	eV	$\Delta H_{F,Fr}$	3.8	3.0-4.5	183,226-228
Schottky trio formation enthalpy	eV	$\Delta H_{F,Sch}$	6.5	6.0-8.0	226,227
Frenkel pair formation entropy	meV K^{-1}	$\Delta S_{NC,Fr}$	0.78	-	183
Schottky trio formation entropy	meV K^{-1}	$\Delta S_{NC,Sch}$	0.17	-	**

** recommended in this work

8.7 Specific heat

The specific heat of ThO_2 can be understood in terms of an harmonic contribution, a defect contribution and a conversion term from constant volume to constant pressure (see section 3.1). The methodology for modelling specific heat has been described in section 3.1. Figure 8-11A compares the experimental data measured in this work with the model results and the function recommended by Konings et al.²²¹. It shows that both the model and the recommended function agree with the current measurement³. The differences between the model and the recommended relationship for specific heat are significant prior to melting, where the model predicts lower specific heat values compared to the results obtained by extrapolating the recommended empirical function. Even though not plotted in Figure 8-11A, the model also predicts the specific heat of ThO_2 at lower temperatures to be increasing from 0 at 0 K to $\approx 210 \text{ J kg}^{-1} \text{ K}^{-1}$ at 300 K. Figure 8-11B compares the model results for enthalpy increment to the experimental data set collected by Fink²²⁹. The model results are in excellent agreement with experiment.

³ Measurements above 3000 K were not performed due to transient instabilities in the rear laser.

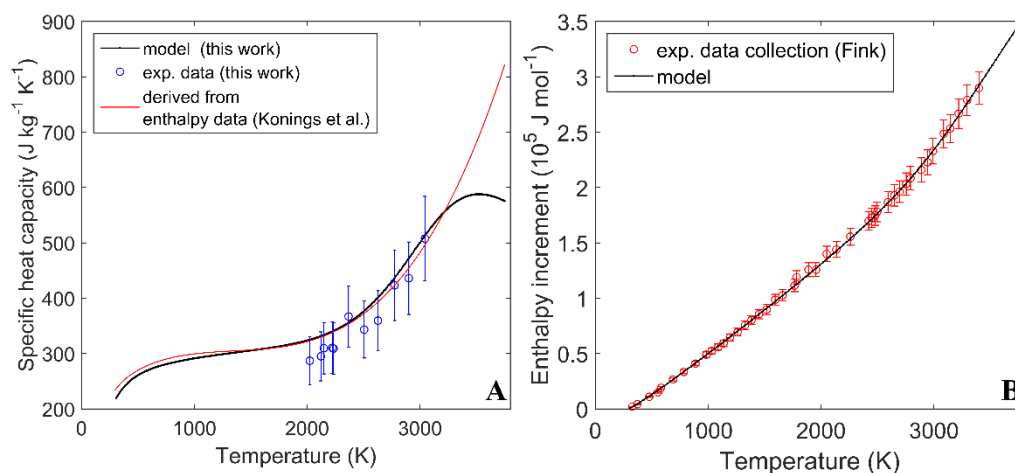


Figure 8-11: (A) Measurements of specific heat as a function of temperature compared to the model results and the fit recommended by Konings et al.²²¹ (B) Enthalpy increment data collected by Fink²²⁹ compared to the model output.

8.8 Thermal expansion

The coefficient of volumetric thermal expansion can be separated into a lattice and a defect contribution. These two terms are modelled using the methodology described in section 3.3. The defect term is based on the formation enthalpy of the defect species, while the lattice term utilises the specific heat at constant volume computed from the phonon density of states model (see Figure 8-9). Both defect and lattice terms use experimental values for the temperature dependent bulk modulus. Figure 8-12B, Figure 8-12C and Figure 8-12D show that the model results agree well with available experimental data. Furthermore, Figure 8-12A shows that above 2300K the coefficient of volumetric thermal expansion calculated by the model increases significantly faster with respect to temperature compared to the recommended function by Belle and Berman¹⁹⁶. Figure 8-12B shows that the calculated density in

this work is higher compared to the proposed correlation by Belle and Berman¹⁹⁶ above 1500 K. In Figure 8-12D the model prediction exceeds the correlation proposed by Belle and Berman at temperatures above 2500 K. Finally, all subplots in Figure 8-12 show that between 2000 K and the melting point of ThO₂ (approximately 3665 K), the defect contribution becomes increasingly more significant, which is similar to previously reported results for UO₂²¹⁵.

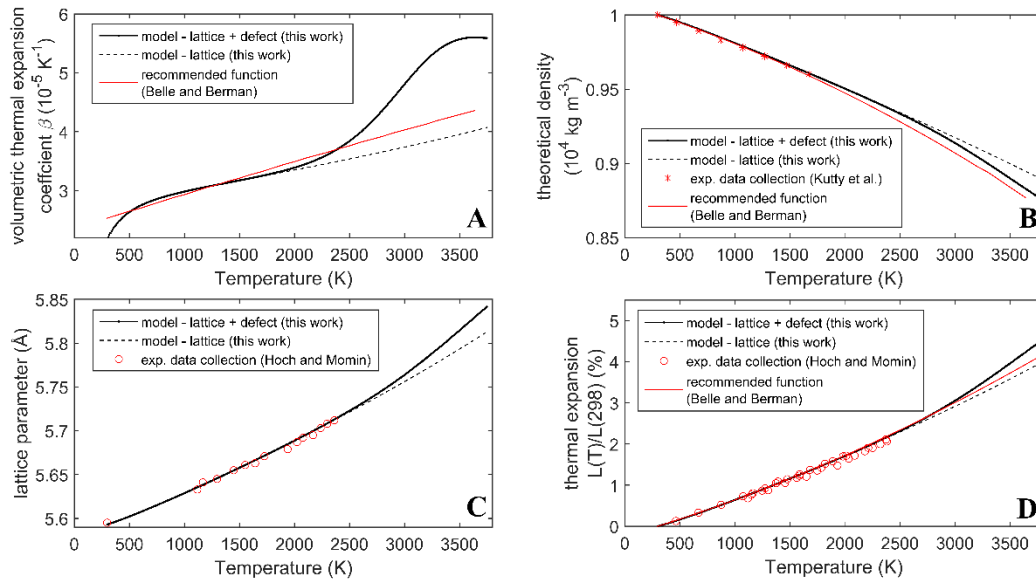


Figure 8-12: Experimental and model results for dimensional property parameters of ThO₂ as a function of temperature. (A) Volumetric thermal expansion coefficient as a function of temperature; (B) Theoretical density as a function of temperature; (C) Lattice parameter as a function of temperature and (D) Thermal expansion vs. temperature. The model results have been compared to available experimental data¹⁹⁶ and the recommended correlation²¹⁷. The dashed black lines show only the lattice contribution to thermal expansion, while the solid black lines represent the combined contributions of lattice and defects.

8.9 Thermal conductivity

In this section an expression is proposed for the temperature dependence of the thermal conductivity of ThO₂. Firstly, the total thermal conductivity k_{tot} is expressed as:

$$k_{tot} = k_l + k_{el} \quad (8-11)$$

where k_l is the lattice contribution and k_{el} is the electronic contribution. The lattice contribution has been determined empirically and mechanistically. The mechanistic approach has been described previously²¹⁵ (see also Chapter 3). It is worth noting, however, that, in the case of ThO₂ no spin-phonon scattering is considered. This is consistent with the diamagnetic nature of the material, i.e. no ordering of magnetic moments is exhibited.

The electronic term in equation (8-11) has been determined empirically based on the following assumptions: i) significant defect concentrations are generated at high temperatures, which lead to the formation of isolated energy states inside the band gap of ThO₂ (see Figure 8-13); ii) these defect states lead to a shift in the Fermi energy towards either the conduction or valence bands; iii) hybridization exists between Th-f and O-p orbitals (i.e. excited charge carriers are free and not localised as they are for UO₂).

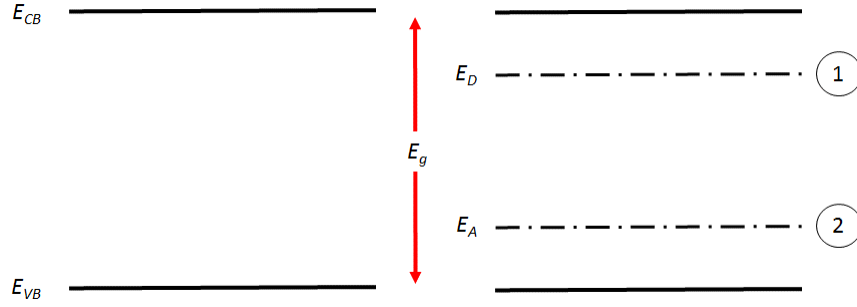


Figure 8-13: Schematic of the ThO₂ band gap free of defects (left) and the possible donor (1) or acceptor energy levels (2) (right). E_{CB} is the energy of the conduction band edge, E_{VB} is the valence band edge energy, while E_A and E_D are the possible acceptor and donor energy levels, respectively.

According to Yang²³⁰, the thermal conductivity due to the excitation of an electron or hole in a semi-conductor can be expressed by:

$$k_{el} = \sigma T \left(\frac{C_B}{e} \right)^2 \left(2 + \left[4 + \frac{E_{DF}}{C_B T} \right]^2 \frac{\mu_e}{\mu_h} \left(1 + \frac{\mu_e}{\mu_h} \right)^{-2} \right) \quad (8-12)$$

where σ is electrical conductivity, T is temperature (K), C_B is Boltzman's constant (J K⁻¹), e is the elementary charge (C), E_{DF} is the electron fromation energy (eV), due to defect donor or acceptor levels, μ_e is the electron mobility, μ_h is the hole mobility. Furthermore, in the case of electron carriers, $E_{DF} = E_{CB} - E_F$, while for holes $E_{DF} = E_F - E_{VB}$, where E_F , E_{CB} , E_{VB} are the Fermi energy, conduction band energy and valence band energy, respectively. Here, it is assumed that electron and hole mobilities are equal, so that:

$$k_{el} = \sigma T \left(\frac{C_B}{e} \right)^2 \left(2 + 4 \left[1 + \frac{E_{DF}}{4 C_B T} \right]^2 \right) \quad (8-13)$$

$$k_{el} = \sigma T \left(\frac{C_B}{e} \right)^2 \left(6 + 2 \left[\frac{E_{DF}}{C_B T} \right] + \frac{1}{4} \left[\frac{E_{DF}}{C_B T} \right]^2 \right) \quad (8-14)$$

$$\sigma = nq\mu \quad (8-15)$$

$$n \propto \exp\left(-\frac{E_{DF}}{C_B T}\right) \quad (8-16)$$

Assuming that free carrier scattering is dominated by impurities^{231,232}, since at high temperatures the concentration of charged defects (oxygen Frenkel pairs) is significant, the mobility can be approximated via:

$$\mu \propto T^{3/2} \quad (8-17)$$

$$\sigma_{el} = CT^{3/2} \exp\left(-\frac{E_{DF}}{C_B T}\right) \quad (8-18)$$

where C is a constant of proportionality. Therefore, thermal conductivity will be expressed by the following expression:

$$k_{tot} = \frac{1}{A + BT} + CT^{5/2} \left(\frac{C_B}{e}\right)^2 \left(6 + 2 \left[\frac{E_{DF}}{C_B T}\right] + \frac{1}{4} \left[\frac{E_{DF}}{C_B T}\right]^2\right) \exp\left(-\frac{E_{DF}}{C_B T}\right) \quad (8-19)$$

where A and B are constants associated with the lattice term of thermal conductivity.

The constants C and E_{DF} are associated with the electronic term of thermal conductivity. This expression has been fitted to the experimental data measured in this work as well as to literature data. The fitting results suggest that: $A = 2.31692 \times 10^{-2} \text{ W}^{-1} \text{ m K}$; $B = 1.97516 \times 10^{-4} \text{ W}^{-1} \text{ m}$; $C = 7.4086227 \times 10^{-2} \text{ C}^2 \text{ J}^{-1} \text{ s}^{-1} \text{ m}^{-1} \text{ K}^{-3/2}$; $E_{DF} = 0.173227 \text{ eV}$. The value of E_{DF} is lower compared to the activation energies recommended by Bates²³³ (1.3 - 2.6 eV). Figure 8-14 summarises and compares the resulting fit, the new experimental results presented in this work, existing literature data and the model prediction of the lattice

thermal conductivity of ThO_2 (according to the solid state theory described in section 3.2.2 of Chapter 3.

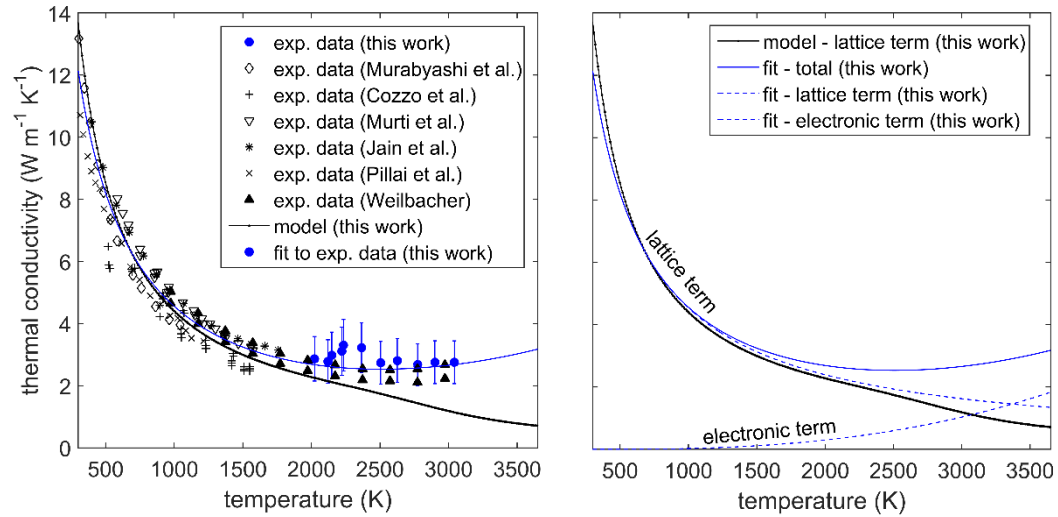


Figure 8-14: (A) Thermal conductivity as a function of temperature measured in this work compared to: the experimental data of Murabayashi²¹², Cozzo et al.²¹¹, Murti et al.²²³, Jain et al.²²⁴, Pillai et al.²²², Weilbacher²¹³, the current model results and the fit proposed in this work; (B) The lattice term of thermal conductivity calculated by the model compared to the lattice and electronic terms obtained from the fit.

Table 8-7: Summary of input parameters for the calculation of thermal conductivity of ThO₂.

Parameter description	Units	Symbol	Value	Indicative Range	Ref.
Grüneisen parameter	-	γ	1.9	-	**
atomic mass	u	M_{at}	264	-	-
grain size	μm	L_g	10.0	8 - 12	*
pore fraction	(%)	v_p	7	-	*
molar mass	kg mol ⁻¹	M_{mol}	0.264	-	-
lattice parameter (298 K)	Å	a_0	5.597	-	-
density (theoretical)	kg m ⁻³	ρ	10000	-	-
Bulk modulus (298 K)	GPa	K_0	200	175 - 230	234,235

* determined experimentally in this work

** recommended in this work

8.10 Total hemispherical emissivity

Based on the work of Mason²³⁶ and Flügge²³⁷, the spectral emissivity of ThO₂ transitions from a transparent state (0-0.2) to an opaque state (0.85-0.95) above a wavelength of approximately 7 μm (measurements by Mason were performed at 1273 K). At longer wavelengths (above 7 μm) or alternatively lower photon energies, absorption and emission can be understood in terms of the interaction of photons with phonons. In this work it will be assumed that below a critical wavelength of 2 μm the emissivity is temperature dependent. This is consistent with equation (8-1) and can be explained by the formation of intrinsic donor states (represented by E_D in Figure 8-13) or acceptor states (represented by E_A in Figure 8-13), in the band gap of ThO₂. Based on the work of Lu et al.²²⁶, it is likely that these defect energy levels are indeed donor states formed via the creation of oxygen interstitials, as their respective energy level is in relative proximity to the conduction band edge of ThO₂.

Furthermore, oxygen Frenkel pairs are also the dominant defect species at elevated temperatures. In an intermediate wavelength range $2 - 7 \mu m$, it will be assumed that the material remains transparent with a spectral emissivity of 0.1, where the photon energy is too high for any interaction with lattice vibrations to be possible and too low for an electron to be excited from the donor states to the conduction band. Finally, if photons have an energy higher than 6 eV (approx. $0.2 \mu m$) it is considered that electrons can be excited directly from the valence to the conduction band in ThO_2 . These considerations yield the following dependence of emissivity on wavelength and temperature:

$$\epsilon(\lambda, T) \begin{cases} 0.95 & \text{for } \lambda > 7 \mu m \\ 0.05 & \text{for } 2 \mu m < \lambda < 7 \mu m \\ f(T) & \text{for } 0.2 \mu m < \lambda < 2 \mu m \\ 0.95 & \text{for } \lambda < 0.2 \mu m \end{cases} \quad (8-20)$$

An expression for total hemispherical emissivity has been derived from Planck's law in section 3.5 (see equation (3-93)). Equation (8-20) is substituted in equation (3-93) and solved numerically. Figure 8-15 shows the measured total hemispherical emissivity in this work plotted together with the few existing data sets for this property at lower temperatures (500 – 1300 K), all of which are compared to the numerical calculation. There is good agreement between the model and the experimental data of Sully et al.²³⁸ as well as the measurements in this work above 2400 K. There is also qualitative agreement between the trends observed experimentally and the ones appearing from the model prediction. Total hemispherical emissivity shows a decrease between 500 K and 1400 K. At

approximately 1500 K a minimum is reached, followed by an accelerated increase with respect to temperature up to ~2800 K. Above 2800 K total hemispherical emissivity increases at a slower rate with respect to temperature. When compared with the new experimental results at around 2000 K, the model seems to over predict total hemispherical emissivity. This could be due to the fact that spectral emissivity varies as a function of wavelength in the range $0.2 - 2 \mu\text{m}$, while the model assumes constant values. Furthermore, some of the experimental data for total hemispherical emissivity close to 2000 K is approaching 0. This is unlikely as a significant amount of radiation should still be emitted at wavelengths in the infrared range.

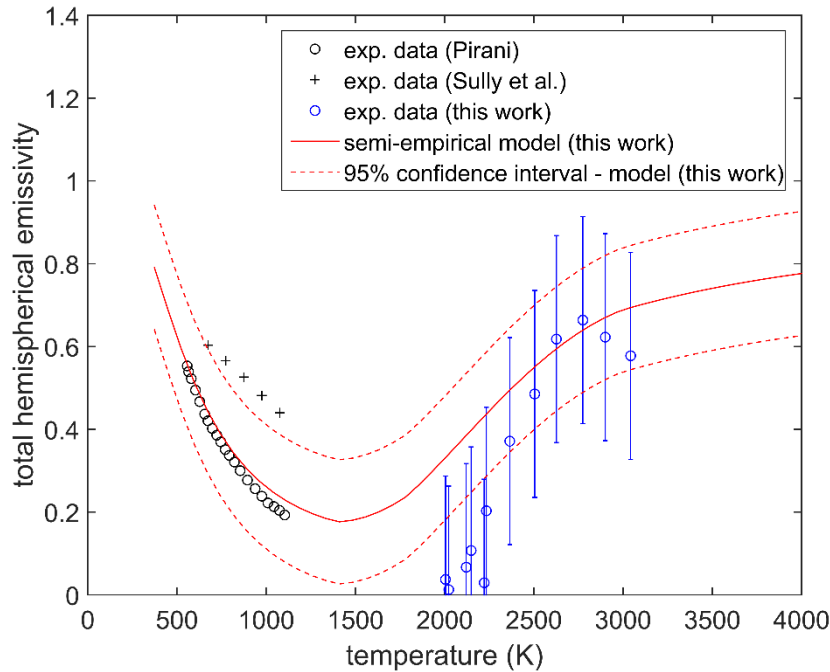


Figure 8-15: Total hemispherical emissivity measured in this work plotted together with the experimental results of Pirani²³⁹, the measurements by Sully et al.²³⁸ and the semi-empirical model proposed in this work. The red dashed lines represent the indicative 95% confidence intervals of the model calculation.

8.11 Summary

In this chapter measurements of the specific heat, thermal conductivity, thermal diffusivity, spectral emissivity, total hemispherical emissivity and melting point of ThO₂ have been presented. The melting arrest was measured at $3665\text{ K} \pm 70\text{ K}$. For the first time direct measurements of thermal conductivity have been performed above 2000 K showing the thermal conductivity of ThO₂ (corrected to 95% TD) stabilises at around $3\text{ W m}^{-1}\text{ K}^{-1}$. The solid state physics model suggests the presence of a diffuse maximum in specific heat prior to melting at $3520\text{ K} \pm 100\text{ K}$. The solid state physics model has also been used to predict the evolution of thermal expansion with respect to temperature. The measurements of total hemispherical emissivity show that this property increases above 2000 K, while the semi-empirical model for total hemispherical emissivity shows that this property exhibits a minimum at around 1450 K. A discussion of the physical process governing the evolution of these properties is to follow in Chapter 9.

Chapter 9 : Discussion

– “*The aim of argument, or of discussion, should not be victory, but progress.*” –

Joseph Joubert, writer

This chapter provides a critical analysis of all new developments and experimental results. The two new methodologies are compared – the pyrometer and infrared camera methods. The experimental results for the various properties of graphite, UO_2 and ThO_2 are discussed in terms of the newly developed solid state physics models. Finally, the relevance of the new findings for fuel safety and fuel performance codes is addressed.

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Parts published in: Pavlov, et al. *Int. J. Therm. Sci.* under review (2017).

Parts published in: Pavlov, et al. *Acta Mater.* **139**, 138 - 154 (2017).

Parts published in: Pavlov, et al. *Sci. Rep.* under review (2017).

9.1 New methodology

The newly developed methodologies are discussed in terms of their applicability and limitations. The two approaches are described in Chapter 4 and Chapter 5 and were named the pyrometer method and the infrared camera method. Both of these are based on an axi-symmetric FEA model. The FEA model offers the benefits of treating more complex boundary conditions, such as a nontrivial distribution of the surface heat source and complex heat loss mechanisms (e.g. vapourisation). The downside of using a numerical solution to the heat transfer problem compared to an analytical one, is the significant computation time. Furthermore, both methodologies benefit from the use of a spectropyrometer for the determination of the spectral emissivity. This is needed to reduce the uncertainty in the measured temperature.

9.1.1 Pyrometer method

The pyrometer method was the method mostly used throughout this work. It is capable of simultaneously determining up to three material properties at a particular temperature with a single measurement – thermal conductivity, specific heat and total hemispherical emissivity. This benefit, however, is partially offset by the significant number of measurements needed for each sample, in order to obtain the full temperature dependent profile of the respective properties. Even though, the measurement itself is quick (second or sub-second duration), the prompt and repetitive thermal cycling (due to many short intense power pulses) to which samples

are exposed often causes the ceramic samples to crack, fragment and fall apart. Hence, multiple samples are often required to complete the measurement campaign.

9.1.2 Infrared camera

The infrared camera could partially solve the previously stated problem of the pyrometer method, avoiding the use of multiple samples. This is due to the ability to extract a full temperature profile of the properties (via radially distributed thermograms) with a single measurement. However, two limitations are present: i) due to a high degree of parameter correlation only one property profile can be extracted; ii) the drop in sensitivity towards the edge of the axisymmetric geometry leads to experimental uncertainties (e.g. noise, presence of a slightly non-linear base line) deteriorating the accuracy of the results. The latter can be improved by using a laser beam spot radius comparable to the sample radius. Furthermore, the applicability of the spectropyrometer results to the infrared camera measurements must be treated with caution, as the measurement wavelength of the infrared camera is 1500 nm, which is outside the range of operation of the spectropyrometer (500 nm – 900 nm).

9.2 Graphite

In this section two of the measured properties of isostatically pressed polycrystalline graphite are discussed in terms of condensed matter theory. These properties are specific heat and thermal conductivity.

9.2.1 Specific heat

Figure 6-3 shows the specific heat of graphite to initially increase and then saturate just above $2000 \text{ J kg}^{-1} \text{ K}^{-1}$. At high temperatures the specific heat capacity approaches the Dulong-Petit limit. This occurs as a result of a decrease in the number of new, higher energy, unoccupied phonon states. The slight linear ascent noticeable above 2300 K results from the small electronic contribution to c_p . A significant defect contribution towards specific heat capacity would only be expected at temperatures above 3500 K due to the large formation energies associated with the creation of Frenkel pairs.

9.2.2 Thermal conductivity

From Figure 6-4 it is clear that the model is in very good agreement with experimental data. The observed maximum, which occurs close to 300 K, is due to the competition between two main mechanisms: 1) phonon heat capacity appreciation and 2) phonon life-time reduction. From 0 K to 300 K the thermal conductivity increases as it is dominated by the increase in the phonon specific heat. Above 300 K this increase is overcome by degradation of thermal conductivity due to an increase in the frequency of phonon scattering events. This diminishes the average phonon life-time. At temperatures below 300 K phonon scattering is dominated by electron-phonon interactions, grain boundary scattering and impurity

scattering, while at higher temperatures phonon-phonon (Umklapp) interactions become the dominant scattering mechanism.

9.3 Uranium dioxide

The measured properties of UO_2 are discussed in terms of solid state physics theory. These properties include specific heat and thermal conductivity. Furthermore, the model predictions of defect concentrations, electrical conductivity and thermal expansion are also explained.

9.3.1 Defects

Two solutions to the defect model were presented – implicit and explicit. At temperatures above 1500 K the implicit solution (including terms due to defect interactions and the lattice site constraint) deviated from the linear explicit approximation commonly used in the literature. The reduction in formation enthalpy at elevated temperatures (shown in Figure 7-11G, Figure 7-11H and Figure 7-11I) is due to the net attractive force experienced by oppositely charged species. Initially, this leads to the more abrupt increase in concentration. However, the number of lattice atoms and sites from which defects can be formed is finite and hence sets a maximum constraint on the concentration of each defect type. The magnitude of this constraint is set by the concentration dependent pre-exponential factor. As a result, at a certain temperature, or more specifically at a certain concentration, a saturation of the defect concentration begins. This phenomenon is characterised by an inflection

point in the defect concentration and a maximum in specific heat, which is shown by the implicit solution in Figure 7-11A and Figure 7-11D.

9.3.2 Specific heat

In the current study it was shown experimentally that: 1) a specific heat maximum exists; 2) this transition is gradual and not abrupt. The current study is the first LF experiment on UO_2 , which detects such a specific heat transition, which is likely due to the capability of the current method to take into account vapourisation. This heat loss mechanism is dominant at temperatures above ≈ 2700 K at atmospheric pressure. Furthermore, if vapourisation is not taken into account specific heat increases artificially to obtain a similarly good least square fit between the experimental and model thermogram.

The abrupt transition in specific heat has been previously derived from the cooling curves of spherical UO_2 samples of the order of 1mm in diameter, held by a tungsten pin¹⁷³. Pre-melting thermal arrests were detected and the temperature-time derivative of the cooling curves was used to evaluate specific heat. One possible explanation for the appearance of a pre-melting arrest and the observed undercooling effects is partial/local melting of the samples. In combination with the finite nominal spot size of pyrometers (generally a diameter of the order of 0.8 - 1mm) and thus possible contributions from the cooler gaseous surroundings, this could have led to the measurement of a lower effective temperature on the surface of the sphere.

In the current study cooling curves were also measured at high pressure (up to 100 bar). One of these experiments is used as a supporting example for the current discussion and is shown in section 7.4 (see Figure 7-6). During this experiment a pre-melting (similar to the ones measured by Hiernaut et al. ¹⁷³) was observed. Subsequent scanning electron microscope (SEM) analysis, however, showed partial melting on the sample surface, characterised by large coarse grains, which were free of porosity. After the experiment, it was also observed that the angle of acceptance of the pyrometer recording the temperature could have been partially blocked by the pressure vessel walls (possibly a fraction of the radiance signal was not detected by the pyrometer, as the pyrometer was positioned at a very wide angle to the direction normal to the sample surface). Furthermore, the pyrometer spot was centred at the border of the melting pool, which is shown in the SEM image (lower right) in Figure 7-6. The offset, together with the restricted angle of acceptance, are the most likely reasons for the erroneous pre-melting arrest shown in Figure 7-6.

No pre-melting arrest was measured after recording several other cooling curves (an example is presented in Figure 7-7; it is worth noting that for these measurements the pyrometer was carefully positioned normal to the sample surface to assure a completely free angle of acceptance). Finally, it is important to stress that the arguments presented in this section do not aim to discard or undermine previous studies, but to offer an explanation satisfying all existing measurements.

Specific heat at lower temperatures is dominated by harmonic phonon vibrations with contributions from thermal excitation of f-electrons localised on uranium ions. At higher temperatures the defect term of specific heat becomes dominant, complemented by a smaller but significant anharmonic contribution due to thermal expansion. As noted in the previous section the specific heat anomaly is due to the onset of saturation in oxygen defect concentrations and in particular the onset of saturation in the oxygen interstitial concentration. The measured and calculated maximum in specific heat is in qualitative agreement with molecular dynamics simulations^{240,241}. However, the present work demonstrates both experimentally and theoretically a more gradual transition should exist. This explains the absence of a clear indication of a second order transition (e.g. a kink) in the enthalpy data for UO_2 and the recorded cooling curves presented in this work (see Figure 7-7).

9.3.3 Thermal conductivity

The measurements of thermal conductivity presented in the current study showed a minimum at around 2000 K. This can be explained by the competition between two processes – polaron mobilisation and degradation of lattice thermal conductivity. The first term is due to the combined effect of increasing polaron concentration and, more significantly, an increase in the high temperature polaron mobility due to a low migration energy (0.14-0.3 eV)^{65,115,189,192}. The lattice term is dominated by two main phenomena at high temperatures – phonon-phonon scattering and phonon-defect

scattering. Phonon-defect scattering scales with the increase in concentration of oxygen defects. Comparing the model prediction of this work to the established literature data fits of Ronchi et al.⁴ and Fink¹ (Figure 7-16B), it is suggested that at higher temperatures the model diverges from Ronchi's fit towards that of Fink. This can be explained by the fact that Ronchi et al. obtained the lattice term of thermal conductivity by fitting to experimental data at lower temperatures (in the range 500 to 1100 K). In this temperature range the oxygen defect concentration is low ($\approx 10^{-14}$ Frenkel pairs per mole of UO_2 at 500 K, increasing up to $\approx 10^{-6}$ Frenkel pairs per mole of UO_2 at 1100 K) and hence the phonon-defect scattering term is not significant. Finally, the maximum in thermal conductivity, at around 200 K, is due to a competition between: 1) phonon specific heat appreciation and 2) phonon mean free path reduction due to more frequent scattering events. The spin-phonon term arises due to the interaction of phonons with the localised f electrons and has previously been discussed by various authors^{113,114}. This process is one of the dominant thermal degradation mechanisms up to around 500 K.

9.3.4 Model analysis of other thermo-physical properties (not measured in this work)

The solid state physics approach described in this paper was also used to analyse and explain experimental results of thermal expansion^{187,188} and electrical conductivity^{190,191}.

9.3.4.1 Thermal expansion

At temperatures below 1500 K, thermal expansion is dominated by lattice vibrations or phonon-phonon interactions. As temperature increases (above 1500 K) defect concentrations increase rapidly (oxygen Frenkel pair concentrations in particular). As a result, the material begins to experience an additional volumetric term associated with the displacement of atoms. This leads to a defect assisted thermal expansion contribution, shown in Figure 7-14. The volumetric thermal expansion coefficient exhibits a maximum which, similarly to specific heat, is related to the onset of defect saturation. The stationary point is preceded and followed by a gradual variation in the coefficient of thermal expansion. Hence, the transition is difficult to identify on a lattice parameter graph (Figure 7-14C) or a relative thermal expansion plot (Figure 7-14D). This maximum, similarly to specific heat, is related to the onset of saturation of oxygen defects.

9.3.4.2 Electrical conductivity

In Figure 7-15B it was shown that not only do the polarons contribute to electrical conductivity, but also oxygen interstitials and oxygen vacancies. The polaron contribution is dominated by the increasing mobility of localised electron-hole pairs at high temperatures. In comparison, the much lower mobility of oxygen defects (e.g. oxygen vacancy migration energy is around 0.5-0.6 eV¹⁸⁵ compared to 0.14-0.3 for polarons) is partly overcome by their high concentrations (≈ 0.2 oxygen Frenkel pairs

per mole of UO_2 at around 3100 K). Furthermore, oxygen vacancies have a larger impact on electrical conductivity compared to oxygen interstitials, due to their lower migration energy^{184,185}.

9.3.5 Relevance for fuel performance and safety

Finally, it is important to stress the significance of the new high temperature results for modelling fuel performance during off-normal (accidental) conditions. The current results suggest that specific heat is higher than the widely accepted correlation of Fink in the range 2100 to 2600 K and lower compared to the same correlation above 2700 K. In the case of a prolonged loss of coolant accident, such differences would result in a slower heating up of the material in the range 2100 to 2600 K and accelerated temperature increase with respect to time above 2700 K (assuming the correlation for thermal conductivity remains unchanged). Similarly, based on the model developed in this work, the fuel may be expected to expand at a significantly slower rate with respect to temperature above 2700 K compared to the results from extrapolated empirical correlations. Furthermore, the same empirical correlations may be over predicting the thermal expansion coefficient of UO_2 prior to melting.

9.4 Thorium dioxide

The measurements of specific heat, thermal conductivity and total hemispherical emissivity of ThO_2 are explained based on the condensed matter models introduced

in this work. Furthermore, the evolution of defect concentrations and thermal expansion are also discussed.

9.4.1 Defects

Figure 8-10 shows significant differences at high temperatures between the two approaches for calculating defect concentrations – the implicit solution and explicit approximation. The implicit method calculates higher defect concentrations compared to the explicit one, as the prior includes the net attractive coulombic potential between oppositely charged species. Frenkel pairs dominate over Schottky trios due to their lower formation enthalpy and high non-configurational entropy. The maximum in the excess specific heat is thus due to oxygen Frenkel pair formation and can be understood in terms of the onset of saturation of oxygen interstitial sites (also discussed previously²¹⁵).

9.4.2 Specific heat, melting and pre-melting transition

The new measurements of specific heat are generally in good agreement with the works of Ralph²¹⁰ and Ronchi et al.²⁰⁹. They do not, however, indicate the abrupt increase in this property at around 3100 K as measured by Ronchi et al.¹². This is further supported by the measured cooling curves (see Figure 8-4B), which do not show a pre-melting transition. This could be due to the nature of the set-up used by Ronchi et al.²⁰⁹. In their work, a spherical ThO₂ sample of 1 mm diameter was held in place by a tungsten pin and was melted via pulsed laser heating. The maximum

temperature recorded during heating was reported to be 4500 K. This means that the temperature reached on the surface of the sample was approximately 800 K above the melting point of tungsten (around 3700 K). It is thus possible that not only the ThO₂ sample was melted but also the tungsten pin. This means that the two molten materials could have interdiffused leading to the formation of a ThO₂-W mixture. Upon cooling, this mixture could have undergone an eutectic transition, which was at a lower temperature. This would explain the pre-melting plateau measured by Ronchi et al.²⁰⁹ at ~3100 K.

As discussed in section Chapter 8, the model predicts that the specific heat of ThO₂ increases rapidly up to 500 K (see also Figure 8-11A). This is due to lattice vibrations, in particular, due to phonons accessing new higher energy (or frequency) modes of vibration, as well as due to the increase of the population of existing high frequency phonon states. In the temperature interval of 1000 K to 2000 K the steady increase in specific heat is predominantly governed by the thermal expansion of the material. Above around 2300 K specific heat begins to increase again at a higher rate with respect to temperature. This phenomenon can be explained by defect production, in particular the creation of oxygen Frenkel pairs with a limited contribution from Schottky trios. The faint maximum predicted by the model prior to melting is a result of the constraint the lattice imposes on the formation of oxygen interstitials²¹⁵.

9.4.3 Thermal conductivity

The work of Pillai et al.²²² is the only previous literature study providing direct measurements of the thermal conductivity of ThO₂. The new measurements of thermal conductivity above 2000 K are the first direct laser flash measurements of this property at such high temperatures. The current measurements are characterised as direct, since specific heat values are not taken from literature, but simultaneously measured. However, it must be noted that in this work, density is still a necessary input. However, since density and specific heat are completely correlated (correlation coefficient of unity), any small or moderate uncertainty in density would not impact the results of thermal conductivity as significantly as the values of specific heat. Thus, the experimental technique used here can still be considered a predominantly direct method of measuring thermal conductivity. In comparison, the measurements of Weilbacher²¹³ can be referred to as indirect, as they utilise the measured thermal diffusivity, together with literature values of specific heat²²¹ and density²¹⁷, in order to obtain thermal conductivity. Nevertheless, the new results are in good agreement with Weilbacher's results. There is, however, no evidence in the new measurements for a sudden increase in thermal conductivity around 3000 K as was discussed by Kutty et al.²⁰³.

Figure 8-14A shows a decrease in thermal conductivity in the temperature range 300 K to 2000 K. This occurs as a result of various phonon scattering mechanisms: grain boundary scattering, phonon-phonon scattering and defect scattering. Among these,

the phonon-phonon interaction dominates within this temperature range. At temperatures above 2000 K the model predicts an accelerated thermal conductivity degradation (see Figure 8-14A), due to the significant increase in the concentration of defects. This decrease is, however, compensated by the mobilisation of free charge carriers from intra-band, intrinsic donor or acceptor states. These are assumed to be associated with charged defects and in particular oxygen Frenkel pairs, due to their significant concentration at elevated temperatures. The competition between the decreasing lattice thermal conductivity and the growing electronic term leads to the minimum at around 2500 K. A function is suggested in this study for the variation of thermal conductivity with respect to temperature. This function provides a good fit to all new and existing data. However, it should be noted that further work is necessary in order to quantify and understand activated thermo-electronic transport.

9.4.4 Total hemispherical emissivity

The new results of total hemispherical emissivity (see Figure 8-15), even though approximate, are the first results of this property at high temperatures. It has been shown by both Sully et al.²³⁸ and Pirani²³⁹ that total hemispherical emissivity decreases between 300 K and 1300 K. This can be understood in terms of a shift of the Planck curve to shorter wavelengths (or higher energies) with increasing temperature. At temperatures up to 1500 K, ThO₂ is transparent to higher energy photons (i.e. photons in the visible and near infrared wavelength range). Thus,

increasing the temperature between 300 K and 1500 K leads to a greater contribution to total hemispherical emissivity from the shorter wavelengths ($0.2\mu m < \lambda < 7\mu m$), at which point the material is nearly transparent to radiation. As the temperature increases, the concentration of defects, in particular oxygen Frenkel pairs, rapidly increases. These defects lead to the formation of “intra-band gap” states, which provide a path for radiation absorption and emission. In particular, electrons could be promoted either from donor levels to the conduction band or excited from the valence band edge to acceptor states. This mechanism can proceed at energies significantly lower compared to the band gap of ThO_2 , leading to absorption and emission within the visible and very near-infrared wavelength range ($0.2\mu m < \lambda < 2\mu m$). The creation of more defect species leads to an increase in the density of states in these “intra-band gap” states, which then increases the probability of defect assisted photon absorption/emission. This explains the increase in spectral emissivity in the visible wavelength range above 1500 K, which was measured in this work. Moreover, the proposed mechanism is also consistent with the increase in spectral emissivity at 960 nm previously reported by Ronchi et al.²⁰⁹. Thus, at temperatures above 1500 K there are two competing phenomena, which yield the minimum predicted by the semi-empirical model (shown in Figure 8-15): i) the shift of the Planck curve towards a lower transparent wavelength region with increasing temperature; ii) defect-assisted absorption at these shorter wavelengths, which increases with temperature and leads to a shift from transparency to opacity.

9.4.5 Thermal expansion

The model for the volumetric thermal expansion coefficient of ThO_2 (see Figure 8-12) predicts a significantly different variation of volumetric thermal expansion compared to the empirical correlation by Belle and Bermann¹⁹⁶. In this work, it has been demonstrated theoretically that this property is predominantly governed by lattice vibrations up to 2300 K. Beyond this temperature, the formation of defects contributes to the dimensional changes in ThO_2 . Displacement of atoms from their perfect lattice sites leads to an additional increase in the rate of volume change with respect to temperature. This results in an increase in thermal expansion and a decrease in the density of ThO_2 .

9.4.6 Relevance of new results for fuel performance

The new experimental and model results have several implications for the performance of ThO_2 containing fuels under accident conditions. The thermal conductivity of ThO_2 has been shown to be relatively high compared to UO_2 up to 3000 K. This suggests that ThO_2 bearing fuel will have a greater margin to melting and could help in achieving a higher coping time compared to UO_2 (note: this analysis does not take into account impurity scattering, due to solid solution atoms and fission products, which will degrade the lattice thermal conductivity). The measurements of total hemispherical emissivity show an increase with temperature, which is also a favourable feature of the material when subject to accident conditions. The increasing

total hemispherical emissivity would retard the heating-up of the material. Specific heat has been shown to increase significantly with temperature, which would lead to a beneficial slower heating up of the fuel. However, it has been predicted (via the defect model), that specific heat would cease to increase prior to melting, reaching a maximum followed by a decrease. This prediction is markedly different from the predictions of extrapolated empirical functions at temperatures above 3000 K. The lower specific heat above 3000 K would lead to quicker heating up of ThO₂ bearing fuels. Finally, the coefficient of volumetric thermal expansion above 2500 K, calculated here, is significantly higher compared to the empirically extrapolated values. This implies the fuel would expand more quickly with respect to temperature during extreme off-normal scenarios. This could result in higher tensile stresses exerted by the fuel on the cladding. Nevertheless, other phenomena, such as the possible presence of ductility at high temperatures (observed in UO₂^{242,243}), must also be considered in such analyses. The compound effect of these differences in property values should be realized through their use in a fuel performance code.

Chapter 10: Conclusions and future work

– “*Now this is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning.*” –

Winston Churchill

This chapter summarises the main outcomes of the current work. The three main goals of the project are addressed (as outlined in Chapter 1). These comprise: i) development of a new inverse method for the measurement of thermo-physical properties above 1500 K; ii) application of the method to three nuclear materials - graphite, UO_2 and ThO_2 and iii) identification of underlying physical process governing the properties' dependence on temperature. Finally, possible directions for future work are proposed.

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Parts published in: Pavlov, et al. *Int. J. Therm. Sci.* under review (2017).

Parts published in: Pavlov, et al. *Acta Mater.* 139, 138 - 154 (2017).

Parts published in: Pavlov, et al. *Sci. Rep.* under review (2017).

10.1 New methods

The new method has been developed in two variations, in order to be coupled with two different devices – pyrometer and infrared camera. Both methods rely on the same numerical (FEA) model and make use of a laser flash apparatus. The apparatus has been modified for the simultaneous measurement of spectral emissivity, reducing the uncertainty in the measured temperature to $0.3 - 0.7\%$ between 1500 and 3000 K. Other strengths include high temperature capability, simultaneous property evaluation and semi-empirical determination of the convective heat transfer coefficient instead of fitting.

10.1.1 Pyrometer method

This method is used for the simultaneous determination of up to three parameters – thermal conductivity, specific heat and total hemispherical emissivity. A significant improvement in the accuracy of the approach is made by how the laser spatial profile is implemented in the FEA model. The representative profile is shown to improve the evaluation of thermal conductivity and specific heat capacity by 15% and 20%, respectively. The method has been tested with synthetic data, as well as on isotropic graphite and UO_2 by comparing to existing literature data. Specific heat capacity, thermal conductivity and thermal diffusivity are in good agreement with literature values. The errors in specific heat capacity and thermal diffusivity values have been estimated to be 15%, while the error in thermal conductivity approaches 20%.

10.1.2 Infrared camera method

This method can evaluate thermal conductivity and specific heat capacity as a function of radius and temperature with a single measurement. Two approximations were used for the dependence of each property as a function of radius – a polynomial (PNOM) approximation and an iterative gradient (IG) approximation.

The high correlation between fitting parameter pairs does not make simultaneous parameter determination favourable. The synthetic data tests show that both approximations were capable of yielding very good results. The IG approximation is more universal and less sensitive to the fitting initialisation, while the PNOM approximation is less computationally expensive, though, prone to functional artefacts (such as un-physical minima or maxima) and more dependent on the initial fitting parameters.

The experimental results for thermal conductivity of UO_2 and isostatically pressed graphite are in very good agreement with literature correlations. This provides further confidence in the proposed methodology and its application to other systems.

10.2 Measurements and interpretation

The thermo-physical properties of polycrystalline isostatically pressed graphite, UO_2 and ThO_2 have been measured via the new methodology (mainly using the pyrometer method). Furthermore, the evolution of these properties has been analysed using both established and newly developed solid state physics models.

10.2.1 Graphite

The specific heat of graphite appears to saturate above 2000 K, while the thermal conductivity of the material progressively decreases throughout the whole measured range (1500 K – 2800 K). A condensed matter model was developed for the prediction of these two properties. The theoretical results are in very good agreement with previous experimental data and the new experimental data up to 2800 K. The model identifies that: i) the harmonic contribution to specific heat saturates, due to a lack of availability of new phonon energy states at high temperatures (Dulong-Petit limit), while other contributions are minimal in the measured range; ii) thermal conductivity decreases mainly due to phonon-phonon scattering.

10.2.2 UO₂

A new set of measurements of specific heat, thermal conductivity and thermal diffusivity of UO₂ have been presented in the temperature range 1500 K to 2900 K. The measurements have been complemented by solid state physics models with novel numerical solutions.

A specific heat maximum is observed at $2715 \text{ K} \pm 100 \text{ K}$. The proposed defect model has shown that this transition can be understood in terms of a competition between oxygen defect interactions (attraction of oppositely charged defects) and the saturation of oxygen interstitial sites. The new defect model shows that a diffuse transition in specific heat is compatible with the measurements presented in this

work, but that it is very difficult to identify from enthalpy data alone. It has also been shown that the same gradual transition is to be expected in the volumetric thermal expansion coefficient. Hence, for the first time, an explanation is presented (via the defect model) satisfying both theory and various independent experiments of specific heat, enthalpy and defect concentrations.

The measurements of thermal conductivity showed the presence of a minimum at $2000\text{ K} \pm 100\text{ K}$ as a result of competing lattice and electronic mechanisms. Phonon-phonon interactions are the dominant process, by which thermal conductivity diminishes above room temperature. Furthermore, the significant concentration of oxygen defects at temperatures above 1500 K results in phonon-defect scattering assisted degradation of lattice thermal conductivity. At around 2000 K these mechanisms are overcome by mobile thermally activated hopping of localised electrons (polarons), leading to a minimum in thermal conductivity.

It has been demonstrated theoretically that at temperatures above 2000 K oxygen defects contribute to electrical conductivity. Polaron mobility, however, remains the dominant mechanism for electrical charge transport due to their significantly lower activation energy compared to oxygen vacancies and interstitials.

10.2.3 ThO_2

Measurements of thermal conductivity, specific heat, and thermal diffusivity, spectral and total hemispherical emissivity of ThO_2 have been presented in the temperature

range 2000 K to 3050 K. Furthermore, the solid state physics models (developed for UO_2) have been used to interpret the results. Measurements show that the specific heat of ThO_2 increases with temperature up to 3500 K, which can be attributed predominantly to the formation of oxygen Frenkel pairs. The defect model shows that a maximum in specific heat exists around 3500 K, due the onset of saturation of oxygen interstitial sites.

The experimental results for thermal conductivity show that, while this property initially decreases with increasing temperature, it levels out above 2000 K. Nevertheless, the solid state physics model shows continuous degradation of lattice thermal conductivity above 2000 K. This is, however, compensated by an electronic contribution, most likely due to the thermal delocalization of electrons from donor or acceptor levels. The population of these levels is associated with the rapidly increasing concentration of oxygen defects as a function temperature. The model for thermal expansion shows significant defect assisted swelling of ThO_2 above 2500 K. A maximum in the coefficient of volumetric thermal expansion is predicted prior to melting, due to the onset of saturation of oxygen interstitials.

Spectral emissivity (in the visible and near infra-red wavelength range) and total hemispherical emissivity were shown to increase above 1500 K. This can be understood in terms of: i) an increase of the population of the electronic density of states of donor/acceptor levels, due to the increasing defect concentration and ii) a

simultaneous shift of the Planck curve to lower wavelengths (at which donor/acceptor level assisted absorption takes place).

10.2.4 Comparing UO_2 and ThO_2

Considering ThO_2 is a potential nuclear fuel material and UO_2 is the most widespread, currently used nuclear fuel, it is important to compare the new results for these two compounds. Both materials exhibit the fluorite structure, however important differences exist: i) the 5f-electrons in UO_2 contribute to a higher specific heat at temperatures below 1000 K compared to ThO_2 , which has no free outer shell electrons (5f); ii) at temperatures above 2000 K, the higher Frenkel pair formation energy in ThO_2 leads to a slower increase in specific heat and thermal expansion with respect to temperature compared to UO_2 ; iii) the presence of localised 5f-electrons in UO_2 leads to significantly lower thermal conductivity values at temperatures below 300 K compared to ThO_2 (5f-electron induced spin-phonon scattering); iv) the Th ion is stable in a “4+” valence state and cannot exhibit higher valence states, while uranium ions in UO_2 can exhibit valence states ranging from “3+” to “6+”. Hence, in UO_2 small polaron hopping is present at high temperatures resulting in a thermal conductivity ascend, while in ThO_2 polarons are not formed. ThO_2 exhibits a thermal conductivity ascend as well, however the underlying mechanism is different and it is most likely associated with electron mobilisation from intrinsic donor levels at high temperatures (e.g. due to oxygen interstitials).

A comparison of the thermal conductivities of the two materials can be seen in Figure 10-1. ThO_2 exhibits a higher thermal conductivity throughout most of the temperature range. The integral thermal conductivity $\left(\int_{500}^{T_m} k(T) dT\right)$ of UO_2 has been calculated to be 7513 Wm^{-1} . This value compares with an integral thermal conductivity of 10878 Wm^{-1} for ThO_2 , which is nearly 45% higher than the one for UO_2 .

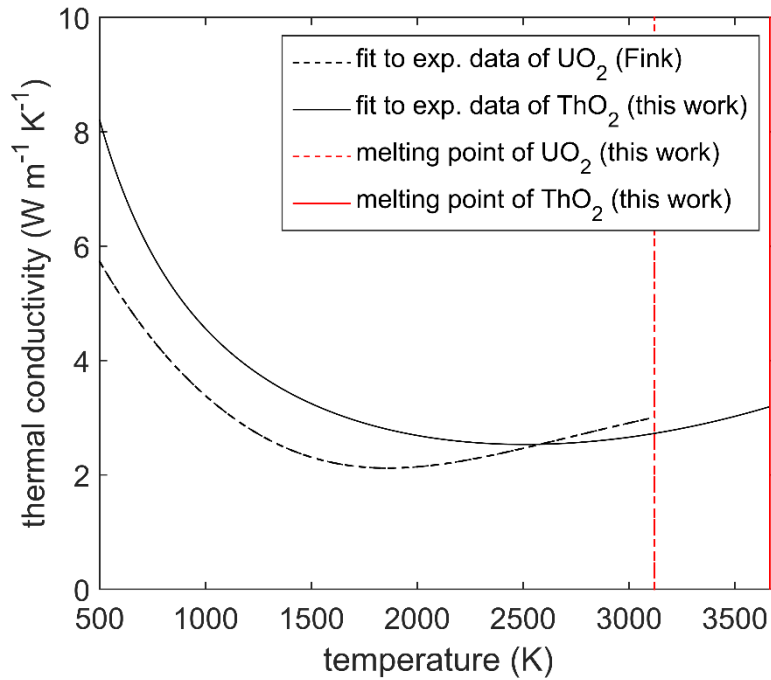


Figure 10-1: Comparison of the recommended fits of thermal conductivity of UO_2 and ThO_2 from 500 K up to melting point. The UO_2 curve is plotted based on the study of Fink¹³², while the ThO_2 curve as well as both melting points are recommended based on the current work.

10.3 Future work

The accuracy of the reported measurements can be improved by more accurately characterising some of the input data needed by the method. One such input parameter is the spectral emissivity at the laser wavelength. Accurate characterisation would require a second spectropyrometer operating in the infrared and near-infrared wavelength range, coupled with a laser operating in the visible or ultraviolet wavelength range. Such a spectropyrometer would also benefit the infrared camera method, for which radiance is detected at 1500 nm. At high temperatures the HAAS laser power stability with respect to time deteriorated. This made it difficult to use double sided laser heating and obtain a stable transient temperature response at temperatures above 3000 K. Hence, in order to extend the temperature range of the current apparatus, a new laser has been ordered.

The FEA model can be extended to deal with non-linear thermal expansion and semi-transparency (volumetric heating).

New measurements can now be carried out on PuO_2 , mixed oxide fuel (MOX – $(\text{U,Pu})\text{O}_2$ or TOX – $(\text{Th,U})\text{O}_2$) and simfuel up to their respective melting points. As stated previously the materials considered here are as they are at the beginning of deployment in a nuclear reactor, that is, unirradiated. It would be interesting to consider irradiated material that exhibit radiation damage and an inventory of fission products. Thus, the apparatus is planned to be moved in the future to a shielded glove box, where measurements would be performed on spent nuclear fuel samples.

For nuclear grade graphite it is important to consider possible anisotropy. Such graphite could differ from the isotropic graphite used in the current project due to a different manufacturing process (i.e. a moulding process rather than isostatic pressing). This work is currently ongoing and preliminary results of thermal conductivity have shown that the material exhibits anisotropy.

The condensed matter theory introduced in this work is subject to certain assumptions and simplifications. The defect interaction introduced in the defect model is based on Debye-Hückel theory, which simplifies the original governing equation (of a Poisson-Boltzmann form) via a first order Taylor expansion. This approximation yields the Helmholtz equation, which has an analytic solution and is well accepted for low defect concentrations. However, in fluorite structure materials, such as UO_2 , high defect concentrations are present at high temperatures. Hence, future work includes assessing the validity of the previous assumption for high defect concentrations. Furthermore, the model does not consider diffusion and hence variation of defect concentrations within the grains or alternatively across the bulk. These aspects will be also considered in a future study. Also, the effect of partial pressure on the defect concentrations and hence stoichiometry can be evaluated using the new defect model, employing similar analysis to the one set out by Dorado et al.²⁴⁴. This is highly relevant, since nuclear fuel becomes non-stoichiometric during irradiation. Finally, the effects of porosity will also be included in the future.

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Appendix A: Root finding algorithms

In this thesis two types of numerical root finding schemes are used – the bisection method and the Newton-Raphson method. The mathematical-computational framework of each of these is described in this Appendix.

A.1. Bisection method

Assume a continuous function $f(x)$ with a root bracketed in the interval $[a_0, b_0]$ and where the limits of this interval satisfy equation (A1-1) and (A1-2). For such a function the following iterative approach can be applied described by equation (A1-3) to equation (A1-6) and terminated when the convergence criteria of equation (A1-7) is satisfied.

$$f(a_0) > 0 \tag{A1-1}$$

$$f(b_0) < 0 \tag{A1-2}$$

$$c_i = \frac{a_i + b_i}{2} \tag{A1-3}$$

$$a_{i+1} \begin{cases} a_{i+1} = c_i & f(c_i) > 0 \\ a_{i+1} = a_i & f(c_i) < 0 \end{cases} \tag{A1-4}$$

$$b_{i+1} \begin{cases} b_{i+1} = c_i & f(c_i) < 0 \\ b_{i+1} = b_i & f(c_i) > 0 \end{cases} \tag{A1-5}$$

$$c_{i+1} = \frac{a_{i+1} + b_{i+1}}{2} \tag{A1-6}$$

$$\left| \frac{f(c_i)}{c_i} \right| < 10^{-7} \tag{A1-7}$$

A.2. Newton-Raphson method

One can expand the non-linear function $f(x)$ in proximity to x_i via a Taylor series (equation (A1-8)), where i is the iteration index. To a first order approximation, equation (A1-8) can be simplified to equation (A1-9). Hence, if x is substituted by x_{i+1} an approximate expression for $f(x_{i+1})$ can be obtained in the form of equation (A1-10). By applying $f(x_{i+1}) = 0$ and employing finite differences in order to determine $f'(x_i)$, equation (A1-12) is obtained. Based on the same equation, x_i is updated until it meets the convergence criteria postulated via (A1-13).

$$f(x) = f(x_i) + f'(x_i)(x - x_i) + \frac{1}{2!}f''(x)(x - x_i)^2 + \dots \quad (\text{A1-8})$$

$$f(x) = f(x_i) + f'(x_i)(x - x_i) \quad (\text{A1-9})$$

$$f(x_{i+1}) = f(x_i) + f'(x_i)(x_{i+1} - x_i) \quad (\text{A1-10})$$

$$x_{i+1} = \frac{f(x_i)}{f'(x_i)} + x_i \quad (\text{A1-11})$$

$$x_{i+1} = f(x_i) \frac{\Delta x}{f(x_i + \Delta x) - f(x_i)} + x_i \quad (\text{A1-12})$$

$$\left| \frac{f(x_i)}{x_i} \right| < 10^{-7} \quad (\text{A1-13})$$

Appendix B: Thermodynamic derivations

In this appendix thermodynamic derivations are presented for relationships, which are used in the current work. These derivations are focused on the following problems – conversion of specific heat at constant volume (c_V) to specific heat at constant pressure (c_P).

B.1. Conversion of c_V to c_P

Specific heat is often calculated from theory assuming constant volume conditions and hence when comparing to experiment, which is usually performed under constant pressure conditions, one has to apply a conversion factor in order to be physically consistent. By following through the derivation presented via equation (B1-1) to equation (B1-15) and keeping in mind the thermodynamic definitions of the isothermal bulk modulus ($K_T = V \frac{dP}{dV}$) and volumetric thermal expansion coefficient ($\beta = \frac{1}{V} \frac{dV}{dT}$), one obtains the conversion factor represented by equation (B1-15).

$$T \left(\frac{dS}{dT} \right)_P = c_P \tag{B1-1}$$

$$T \left(\frac{dS}{dT} \right)_V = c_V \tag{B1-2}$$

$$dS = dT \left(\frac{dS}{dT} \right)_V + dV \left(\frac{dS}{dV} \right)_T \tag{B1-3}$$

$$dV = dT \left(\frac{dV}{dT} \right)_P + dP \left(\frac{dV}{dP} \right)_T \tag{B1-4}$$

$$dS = dT \left(\frac{dS}{dT} \right)_V + \left[dT \left(\frac{dV}{dT} \right)_P + dP \left(\frac{dV}{dP} \right)_T \right] \left(\frac{dS}{dV} \right)_T \tag{B1-5}$$

$$dS = dT \left\{ \left(\frac{dV}{dT} \right)_P \left(\frac{dS}{dV} \right)_T + \left(\frac{dS}{dT} \right)_V \right\} + dP \left\{ \left(\frac{dV}{dP} \right)_T \left(\frac{dS}{dV} \right)_T \right\} \quad (\text{B1-6})$$

$$dS|_V = dT \left\{ \left(\frac{dV}{dT} \right)_P \left(\frac{dS}{dV} \right)_T + \left(\frac{dS}{dT} \right)_V \right\} + dP \left\{ \left(\frac{dV}{dP} \right)_T \left(\frac{dS}{dV} \right)_T \right\} \quad (\text{B1-7})$$

$$dS|_P = dT \left\{ \left(\frac{dV}{dT} \right)_P \left(\frac{dS}{dV} \right)_T + \left(\frac{dS}{dT} \right)_V \right\} \quad (\text{B1-8})$$

$$dS|_V - dS|_P = dP \left\{ \left(\frac{dV}{dP} \right)_T \left(\frac{dS}{dV} \right)_T \right\} \quad (\text{B1-9})$$

$$T \frac{dS}{dT} \Big|_V - T \frac{dS}{dT} \Big|_P = T \frac{dP}{dT} \left\{ \left(\frac{dV}{dP} \right)_T \left(\frac{dS}{dV} \right)_T \right\} \quad (\text{B1-10})$$

$$c_P - c_V = T \frac{dP}{dT} \left\{ \left(\frac{dV}{dP} \right)_T \left(\frac{dS}{dV} \right)_T \right\} \quad (\text{B1-11})$$

$$\left(\frac{dS}{dV} \right)_T = \left(\frac{dP}{dT} \right)_V \quad (\text{B1-12})$$

$$c_P - c_V = T \frac{dP}{dT} \left\{ \left(\frac{dV}{dP} \right)_T \left(\frac{dP}{dT} \right)_V \right\} \quad (\text{B1-13})$$

$$c_P - c_V = T \frac{dP}{dV} \frac{dV}{dT} \left\{ \frac{dV}{dT} \right\} \quad (\text{B1-14})$$

$$c_P - c_V = TVK_T\beta^2 \quad (\text{B1-15})$$

B.2. Lattice contribution to thermal expansion

The lattice contribution to the volumetric thermal expansion coefficient can be evaluated using the Mie-Grüneisen relationship. Assuming the pressure of the system is linearly proportional to the thermal energy and inversely proportional to the volume of the system leads to the following formulation:

$$P = P_0 + \gamma \frac{U}{V} \quad (\text{B1-16})$$

where γ is the Grüneisen parameter and P_0 is the pressure at 0 K. By taking the derivative of equation (B1-16) with respect to temperature:

$$\frac{dP}{dT} = \gamma \frac{dU}{dT} \frac{1}{V} - \frac{dV}{dT} \frac{1}{V^2} \quad (\text{B1-17})$$

By expanding the left hand side of equation (B1-17) one can show:

$$\frac{dP}{dV} \frac{dV}{dT} = \gamma V \frac{dU}{dT} \frac{1}{V^2} - \frac{dV}{dT} \frac{1}{V^2} \quad (\text{B1-18})$$

Finally by substituting for the volumetric thermal expansion coefficient $\frac{dV}{dT} \frac{1}{V} = \beta^l$

and the isothermal bulk modulus $\left(\frac{dP}{dV}\right)_T V = K_T$, one can show that

$$K_T \beta^l = (\gamma C_V - \beta^l) \frac{1}{V} \quad (\text{B1-19})$$

Finally the thermal expansion term is generally small compared to the product of the specific heat at constant volume and the Grüneisen parameter, meaning equation (B1-19) can be simplified and rearranged such that:

$$\beta^l = \frac{\gamma C_V}{K_T V} \quad (\text{B1-20})$$