A reusable Thermal History Sensor based on the Oxidation of a Divalent Rare Earth Ion based Phosphor Synthesized by the Sol-Gel Process

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Abstract

Reversible changes in thermographic phosphors have been used for the last 20 years to perform on-line surface temperature measurements in harsh environments such as in gas turbines. However, when on-line measurements cannot be performed, thermal history sensors are used and the temperatures are recorded during operation and read later off-line. Thermal paints have been used for many years as thermal history sensors, but they present some disadvantages. Recently, a new method based in irreversible changes in phosphor materials has been proposed and, in particular, oxidation of Eu^{2+} to Eu^{3+} in $BaMgAl_{10}O_{17}$:Eu (BAM:Eu) proved to be temperature sensitive up to 1400 °C. In this work, BAM:Eu powder was manufactured using the sol-gel process. This process can be adapted to create a coating without using any binder via the sol-gel dip coating process. Optical properties of the powder after treatment in air and argon atmospheres are reported, which proved that after treatment in argon the oxidation process Eu^{2+} to Eu^{3+} can be reversed and therefore a possible reusability of the thermal history phosphor. The change of optical properties with temperature and time has also been investigated for BAM, and a measurand based on the intensity ratio of the emission lines from Eu^{2+} and Eu^{3+} has been defined, with a temperature range from 700 °C to 1100 °C.

1 Introduction

In the gas turbine industry, where temperatures above 1200 °C may exceed material limits, accurate measurement of the temperature is of vital importance. When on-line measurements are not possible to perform, thermal history sensors can be used instead. These thermal history sensors can record the temperatures to which they are exposed during operation and these temperatures can be determined later off-line. Temperature indicating paints, or thermal paints, are widely used as thermal history sensors in gas turbine development [1-5]. However, they present some drawbacks such as subtle colour changes with temperature that lead to poor resolution, great dependence on local conditions such as ambient illumination and their chemical composition, which includes components hazardous to health (chromium, lead and nickel cobalt).

Recently, Feist et al. [6] proposed an alternative technique based on irreversible changes in the luminescent properties of phosphor materials. Phosphors consist of a ceramic host doped with rare-earth or transition metal ions which act as luminescent centres. When these materials are illuminated with UV light they exhibit phosphorescence which is dependent on temperature. Reversible changes in these phosphors have been used for many years to measure surface temperatures [7-9], evaluate the condition of coatings [10-12] and as tracers for combined fluid flow and temperature measurements [13, 14]. One of the first studies to consider the use of irreversible changes in phosphors for thermal history sensing, reported in [15], proved the amorphous-to-crystalline transformation to be temperature sensitive. However, manufacturers do not sell amorphous phosphors and the method required a custom manufacturing process. Later, oxidation of Eu^{2+} to Eu^{3+} in different host materials such as $BaMgAl_{10}O_{17}$ (BAM) and $SrAl_{14}O_{25}$ (SAE), proved to be suitable for temperature sensing up to 1400 °C [16]. The sensing abilities were related to the relative change in the optical emission properties when Eu^{2+} is oxidised to Eu^{3+} at different temperatures. Calibration curves were provided for the different phosphors over a temperature range from about 700 °C to 1400 °C, and BAM:Eu proved to be especially promising for thermal history sensing.

This phosphor is often reported in the literature in relation to its use in Plasma Display Panels (PDP), where thermal damage is undesirable and efforts mainly focused in avoiding oxidation of Eu^{2+} [17-23]. Conclusions derived from these studies have to be carefully considered, since the exposure of the phosphor to high temperatures, usually 1 h or above, is longer than might be needed for thermal history sensing, and the wavelength of the light used to excite the phosphor is normally different, typically the 147 nm of a Xenon lamp. In addition, the reported studies show lack of agreement as to what is the exact degradation mechanism of the phosphor, although they seem to agree that it may be related to oxidation of Eu^{2+} to Eu^{3+} when the phosphor is heated in an atmosphere that contains oxygen. Therefore more work is needed if BAM:Eu is to be used as a thermal history sensor, and the change of its optical properties with temperature characterised in order to obtain reliable and repeatable

measurements. It is also necessary to investigate the manufacture of a phosphor coating. This involves selection of a suitable binder that does not affect the luminescence properties of the phosphor and/or the consideration of a technique for manufacturing coatings without any binder. An additional desirable feature of a thermal history sensor would be the possibility of reuse, since current paints can only be used once. This means that, when the sensor is exposed to high temperature and the temperature read off-line, it would then be possible to reset the sensor to its initial condition. It is essential that consecutive measurements are repeatable and consistent.

In the present work, the manufacture of BAM:Eu via a sol-gel process is explored. Manufacture of BAM:Eu using this process may permit to create a coating without any binder using the sol-gel dip coating method [24, 25]. The possibility of resetting the sensor was also investigated, and the manufactured BAM:Eu was heat treated in air and argon atmospheres. Investigation of optical properties before and after these heat treatments permitted identification of the oxidation state of the phosphor and study of the possibility of reuse after oxidation. Optical properties have also been investigated related to degradation of the phosphor in air at different temperatures to analyse its sensing capabilities. Similarly to previous studies [16], a measurand based on the intensity ratio between two emission lines of the phosphor has been defined and calibrated for a dynamic range from 700 °C to 1100 °C. The evolution of this ratio has also been investigated with regards to exposure time at a constant temperature.

2 Experimental

2.1 Sample preparation

BAM:Eu powder samples were prepared via a sol-gel method following the same procedure reported previously in the literature [26, 27]. Initial precursor materials were aluminium nitrate nonahydrate (Alfa Aesar; 98 %), barium nitrate (Alfa Aesar; 99.95 %), magnesium nitrate hydrate (Alfa Aesar, 99.999 %) and europium (III) nitrate hydrate (Alfa Aesar, 99.99 %). As shown in Figure 1, precursor materials were first dissolved in deionized water and then, a mass of citric acid equal to the weight of all metal precursors was added. Citric acid acted as the chelating agent. After stirring for 90 minutes, 5 ml of ethylene glycol (Alfa Aesar) was added to the solution as the polymerizing agent. After that, the solution was heated on a hot plate at 100 °C and stirred for 3 h. The obtained product was a dried gel which was then heated in a furnace at 300 °C for 90 minutes. The brown product obtained was then ground thoroughly and the resulting powder heated in air at 1200 °C for 4 h. A white powder sample was obtained as a result of this process and its structure was analysed using X-ray diffraction (XRD). Its optical properties were also investigated at this point. Following this, the powder was heated in an argon atmosphere at 1400 °C for 4 h. The optical properties of the sample were again interrogated after this step.

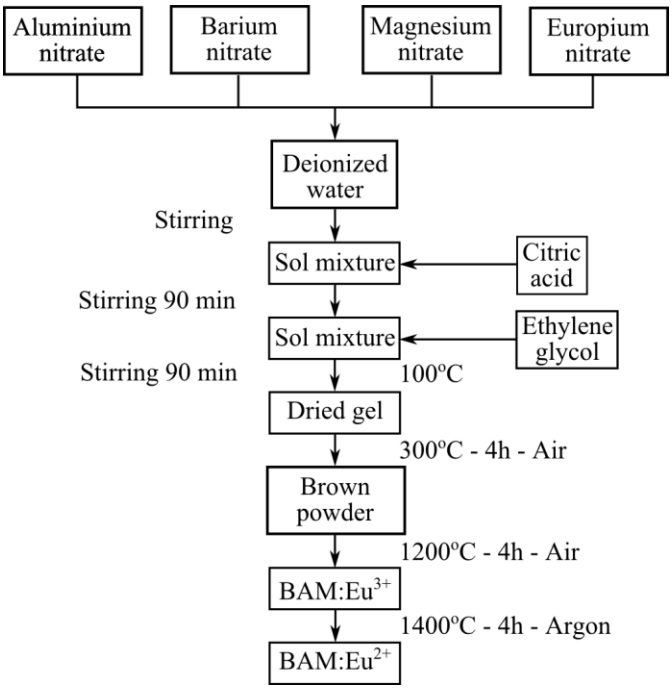


Figure 1: Sol-gel process to prepare BAM:Eu

The investigation of the use of BAM:Eu degradation in an air atmosphere for sensing temperature was performed using a commercial BAM:Eu (Phosphor Technology, KEMK63/UF-P1). As will be shown later, this powder shows the same photoluminescence properties as the sample prepared by the sol-gel method. The powder samples were heated in air for 20 minutes at constant temperatures ranging from 700 °C to 1100 °C to study the effect of the temperature in the optical properties of the phosphor. On the other hand, a series of samples were treated in air at a constant temperature of 1000 °C with treatment durations from 5 minutes to 60 minutes to investigate the effect of time on the degradation of the phosphor.

2.2 Characterization

The sample manufactured by the sol-gel process was analysed after heat treatment in air atmosphere using XRD. The analysis was performed using Cu Kα radiation (Bruker D2, Phaser) with the angle increasing in steps of 0.0322 ° increments every 0.4 s.

The photoluminescence properties of the sol-gel and the commercial BAM:Eu samples were examined at room temperature after annealing. The phosphor was excited by the fourth harmonic (266 nm) of a pulsed Nd:YAG laser (Quanta-Ray LAB-150, Spectra Physics). Repetition rate was 10 Hz, pulse width 5-7 ns and the maximum energy used was 5 mJ. The beam was unfocused to avoid heating of the sample or other non-linear effects resulting in a spot size of approximately 4 mm. Emission spectra of BAM were recorded using a Czerny-Turner spectrometer (Acton SP-2300i, Princeton Instruments), with a 300 mm focal length

and grating groove density of 300 g/mm. The light was focused by a standard 50 mm Nikon lens onto the entrance slit (100 μm) of the spectrometer. At the exit slit, the emission spectra were recorded by a CCD camera (LaVision Imager Intense) with an exposure time of 0.1 ms. The CCD was wavelength calibrated using the narrow emission lines of a mercury lamp, and the measured resolution was better than 1 nm. The CCD was also intensity calibrated using a Tungsten lamp as a light source with a known spectrum.

3 Results and discussion

3.1 BAM:Eu prepared via sol-gel process

Results for the XRD analysis of the sol-gel manufactured BAM:Eu after annealing in air at 1200 °C are shown in Figure 2. Two phases, $BaAl_2O_4$ (BAL) and $BaMgAl_{10}O_{17}$ (BAM), are present as previously reported in [26], due to the relatively low temperature of annealing. The patterns agree with the standard patterns from the Joint Committee on Powder Diffraction Standard for BAM (ICDD Card No. 026-0163) and BAL (ICCD Card No. 017-0306), whose peaks are also shown in Figure 2 for comparison.

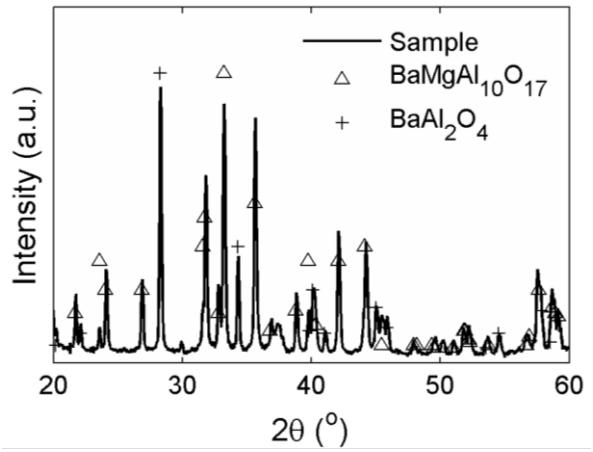


Figure 2: XRD patterns for the powder sample after annealing in air at 1200 °C for 4 h. Main peaks of BAM and BAL are also shown for comparison.

Photoluminescence properties of the manufactured powder were examined at room temperature after treatment in air and argon atmospheres. After treatment in air at 1200 °C, no observable emission around 445 nm corresponding to Eu in the divalent state ($4f^65d \rightarrow 4f^7$ transitions) was observable. However, spectral features between 550 nm and 750 nm due to Eu in the trivalent state (transitions from the $^5D_0$ to ^7F_J - J=0, 1, 2, 3, 4- levels) were evident, with the brightest peak at 611 nm. After annealing in argon at 1400 °C, the emission due to trivalent europium almost completely disappeared, while a broad band emission around 445 nm was now observable. This confirmed the reduction of the trivalent europium to the divalent state by means of heat treatment under argon atmosphere.

The optical properties of the manufactured BAM:Eu after treatment in argon were compared with commercial BAM powder before and after resetting. Results are shown in Figure 3, where it is clear that after treatment in argon there is a blue shift of about 3 nm of the broadband emission peak. This blue shift has been reported previously when BAM:Eu is annealed in a reducing atmosphere (N_2 or H_2/N_2) [22], and it is thought to be related to the different sites occupied by Eu in the crystal lattice. The potential effect of this peak shift in temperature measurements is studied later in this paper.

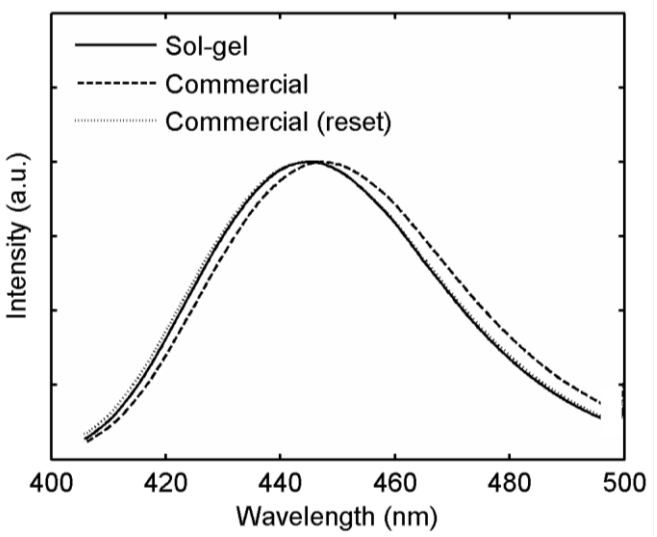


Figure 3: Normalised Eu^{2+} emission spectra from BAM:Eu manufactured using the sol-gel process, commercial BAM and commercial BAM after resetting.

Since the optical properties of the sol-gel manufactured BAM:Eu are the same as for the commercial BAM:Eu, the commercial powder was subsequently used in this work to study the sensing capabilities of BAM:Eu as a thermal history sensor.

3.2 Sensing capabilities of commercial BAM:Eu

Sensing capabilities depend on the possibility to define a measurand that changes continuously and monotonically with temperature. The proposed measurand in this work is based on the intensity ratio between the two emission lines of Eu^{2+} and Eu^{3+}.

Emission spectra of BAM:Eu samples annealed in air for 20 minutes at different temperatures were recorded at room temperature and are shown in Figure 4. It can be observed that the intensity of the broadband emission at around 445 nm due to Eu^{2+} decreases with treatment temperature for temperatures above 700 °C, whereas the peak intensity at 611 nm due to Eu^{3+} emission increases with temperature. This trend suggests the definition of an intensity ratio. The emission of the two peaks was integrated over a 10 nm range under the curve and the ratio calculated for each temperature in a similar manner as it would be calculated using optical spectral bandpass filters at the selected wavelengths and a

FWHM of 10 nm, as this is how a temperature history mapping would be ultimately obtained.

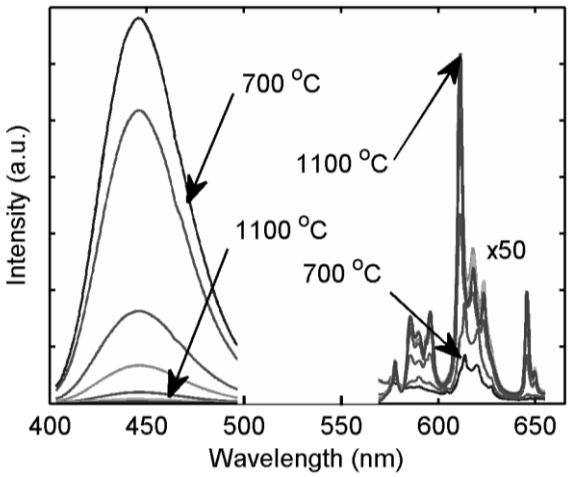


Figure 4: Spectra of BAM:Eu samples treated at different temperatures for 20 minutes. Spectra corresponding to the Eu^{3+} emission is multiplied by a factor of 50 for better visualization. Curves at: 700 °C, 800 °C, 900 °C, 950 °C, 1000 °C, 1050 °C and 1100 °C.

Results for the evolution of the calculated ratio with temperature treatment are shown in Figure 5. The ratio, as defined previously, follows an almost exponential behaviour with temperature and increases continuously over three orders of magnitude for the temperature range of interest, offering a dynamic range from 700 °C to 1100 °C. In the semi-logarithmic graph in Figure 5, the slope of the ratio increases at around 900 °C, which is thought to be related to the appearance of a second phase [20]. The sensitivity of the ratio would be therefore greater in the temperature range between 900 °C and 1100 °C.

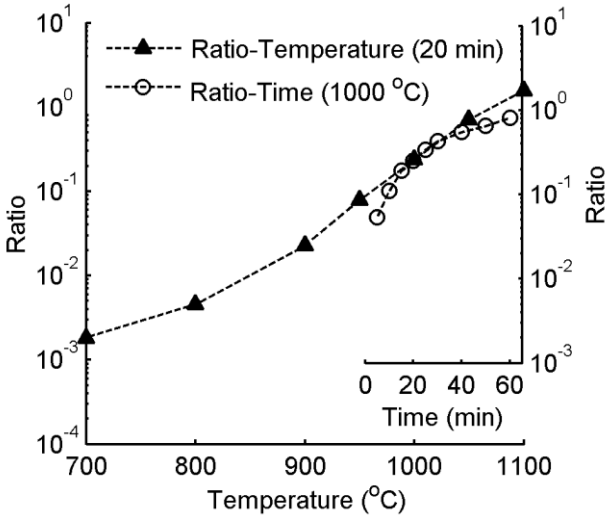


Figure 5: Intensity ratio variation with heat treatment temperature for a treatment time of 20 minutes. In the right insert, the variation of the intensity ratio with treatment time at 1000 °C is shown.

In the right plot in Figure 5, the evolution of the ratio with treatment time for samples treated at a constant temperature of 1000 °C is shown. The ratio increases continuously and almost linearly with treatment time by more than one order of magnitude from duration of 5 to 60 minutes. The linear trend can be more easily observed in Figure 6. The intensity ratio is clearly very sensitive to the annealing time and therefore careful consideration of the treatment duration is necessary when providing a calibration curve for the ratio.

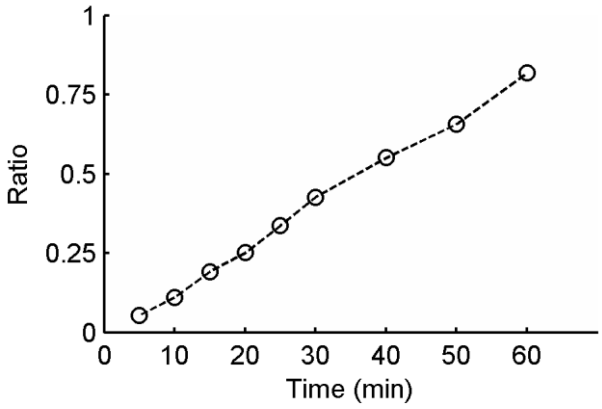


Figure 6: Intensity ratio variation with heat treatment time at a constant temperature of 1000 °C.

It is also interesting to note that results from samples used to calculate time dependent and temperature dependent ratio are consistent. In particular, the two samples treated at 1000 °C for 20 minutes reflect calculated ratios of 0.2388 and 0.2511, which in terms of temperature sensing correspond to a difference of less than 2 °C.

As explained in the previous section, there is a 3 nm blue shift in the peak of the Eu^{2+} emission after the resetting treatment under argon. To check the effect of this shift in the temperature measurements, the ratio has been re-calculated for all the samples considering a 3 nm shift in the integration range under the 445 nm emission curve. The error induced in the temperature value measured by this shift is in all cases less than 1 °C.

4 Conclusions

The concept of thermal history phosphor has been further investigated for the phosphor BAM:Eu. This method offers some advantages over conventional thermal paints, and is a potential substitute for use in gas turbines. Therefore, sensing capabilities and manufacture of the phosphor have been explored.

BAM:Eu powder has been manufactured using a sol-gel process. This method is expected to permit the manufacture of a phosphor coating via the sol-gel dip coating method. The structure of the manufactured powder was analysed using XRD, confirming that the powder obtained was BAM. Optical properties of the powder were compared with

commercial BAM:Eu showing good agreement in the emission spectrum.

The possibility to reuse the sensor was explored, and BAM:Eu was degraded in air and then treated under argon atmosphere. Optical properties after treatment in different atmospheres were interrogated, and it was observed that after treatment in argon emission corresponding to Eu in the trivalent state was negligible. This proved the possibility to reset the sensor after exposure to high temperatures.

A measurand based on the intensity ratio of two emission lines was defined with a dynamic range from 700 °C to 1100 °C. The ratio expands over three orders of magnitude for the mentioned dynamic range. This ratio also shows sensitivity to the duration of the exposure, and increases over one order of magnitude for annealing times ranging from 5 minutes to 60 minutes at a constant temperature of 1000 °C.

Further work is being carried on with respect to the understanding of the resetting process and calibration of the sensor after successive implementations.

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