

On the kinetics of thermal oxidation of the thermographic phosphor BaMgAL₁₀O₁₇:Eu

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Abstract

Decreased photoluminescence of the phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ due to oxidation of the europium dopant at high temperatures has been a subject of study for many years in relation to its use in lighting applications. However, understanding of the underlying effects that cause this reduction in photoluminescence remains incomplete and some of the mechanisms proposed in the literature are contradictory. Recent use of this phosphor as a thermal history sensor has extended the range of exposure conditions normally investigated in lighting applications to higher temperatures and multiple exposure times. The kinetics of the process were investigated by means of spectroscopy and material characterisation techniques. It was found that changes in the luminescence are the result of two simultaneous processes: the oxidation of Eu^{2+} ions (through a process of diffusion) and a phase transition. The level of degradation of the phosphor is suggested to follow the Kolmogorov-Johnson-Mehl-Avrami (KJMA) model above 900 °C and thus can be predicted with knowledge of the exposure time and temperature. This is useful in applications of the phosphor as a temperature sensor.

Keywords

Phosphorescence; Temperature sensor; Thermographic phosphor; Thermal paint; Oxidation; BAM:Eu

Introduction

The phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ (BAM:Eu) is normally used as the blue component in lighting applications, such as plasma display panels (PDPs), fluorescent lamps (FL) and LEDs [1-4]. This is due to its high quantum efficiency and ideal chromaticity. However, the manufacture of these devices usually involves heat treatment in air at a relatively high temperature (about 600 °C), and the photoluminescence of the phosphor is then decreased due to thermal degradation that results in oxidation of the dopant ion from Eu^{2+} to Eu^{3+} and a substantial reduction in blue emission. This thermal degradation has been a common subject of study in recent years with the objective of understanding the mechanisms by which the phosphor degrades and thereby being able to fabricate a more resistant phosphor that remains efficient even after the necessary heat treatment [4-10]. The literature in the field, however, suggests that understanding remains incomplete and some of the mechanisms suggested are contradictory. The current authors have conducted a study of the thermal degradation of BAM:Eu with a view to using it as a sensor rather than merely a source of blue emission [11]. This previous work revealed both temperature and time dependent variation in the luminescence of the phosphor as shown on figure 5. The current study has extended the range of exposure conditions considered and included the kinetics of the process so that we provide new data and insights concerning the degradation mechanisms and a more complete explanation of the behaviour previously observed.

Oshio et al. [4] suggested that oxidation of Eu^{2+} results in the formation of a new magnetoplumbite phase ($\text{Eu}^{3+}\text{MgAl}_{11}\text{O}_{19}$), and Kim et al. [6] used Rietveld refinement analysis to calculate the concentration of this secondary phase to be 2.5 %, 3.7 % and 12 % by weight after exposure for 1 hour at 700 °C, 900 °C and 1400 °C respectively. On the other hand, using x-ray diffraction (XRD), Yamada et al. [7] could only identify the new phase after exposures to temperature in excess of 900 °C. They concluded that the second phase is only present after exposures to temperatures higher than 900 °C and further supported this by observing the fact that the unit cell volume, estimated by Rietveld refinement, only changed significantly above this temperature. Boolchand et al. [8] used Mössbauer spectroscopy to find Eu^{3+} ions even in fresh samples, with the ions moving to new previously unoccupied sites after thermal degradation in air. However, the nature of this new site and the possibility that it is created as a consequence of the appearance of a new phase is not discussed by these authors. Bizarri and Moine [9] proposed a mechanism for the degradation of the phosphor based on luminescence, thermoluminescence and electron spin resonance (ESR) measurements. The mechanism involves three consecutive steps: the adsorption of gaseous oxygen into oxygen vacancies at the surface of the phosphor, the diffusion of europium ions through bulk material triggered by high temperatures, and electronic transfer from Eu^{2+} ions to the adsorbed oxygen when the two elements are in close proximity. They simulated these three steps to account for the loss of luminescence and numerical results agreed well with the values of luminescence intensity obtained experimentally. The

maximum temperature achieved in this study was only 1000 °C and the appearance of a second phase was not investigated. In a later paper, Lacanilao et al. [10] used x-ray photoelectron spectroscopy (XPS) to study the concentration gradient of ions from the surface towards the bulk material in samples heat treated at 600 °C in air. Their results indicated that the maximum concentration of Eu^{3+} is found at the surface, where Eu^{2+} is depleted. The concentration gradient of species strongly supports the idea that Eu diffusion plays an important role in the degradation process and that oxidation of the ion occurs at the surface, where the gaseous oxygen was adsorbed.

Recently, the possibility of using phosphors as thermal history sensors has been suggested [12], and the use of BAM:Eu shown to be particularly promising [11, 13, 14]. A thermal history sensor is one that records a measure of its exposure to a particular thermal environment and that is affected by both the temperature and the duration of exposure. If the latter is known the temperature, usually the desired measurand, can be determined. The concept has existed for quite some time and there are several different embodiments of the thermal history sensor concept that were reviewed by the authors in an earlier paper [15]. Arguably the best known examples are temperature indicating paints which change colour with exposure and are widely used in the aerospace industry [16-19]. BAM:Eu has also previously been used as a temperature sensor by the current authors and others. However, here, reversible temperature driven changes in luminescence were used to develop on-line sensors [20-22].

In the context of a thermal history sensor, the thermal degradation of the luminescence of BAM:Eu is not regarded as a negative feature that needs to be minimised or eliminated but rather a desirable effect that allows permanent changes in the luminescent emission of BAM:Eu to be related to the temperature of exposure. As such, in this context, the process is not considered to be degradation but merely oxidation. Changes in the emission of BAM:Eu due to oxidation are not only related to the temperature experienced, but also to the duration of the exposure and potentially to the composition of the local atmosphere. Characterising the phosphor in the context of its use as a sensor, which is the main motivation of the work conducted by the authors, requires the oxidation/thermal damage process to be characterised over a wider range of temperatures, exposure periods and atmospheres than has been the case for any of the work conducted to date. In particular, temperatures reported in previous studies are normally lower than those of interest in sensing applications, and the effect of exposure time has only been briefly considered at 600 °C in Ref. [10]. As such, the characterisation of BAM:Eu conducted by the authors provides new data concerning the behaviour of the phosphor and new insights into the nature of the oxidation/thermal degradation process.

In this paper emphasis is placed on the kinetics of the process in a relatively high temperature range (800 °C -1200 °C) and for exposure times in the range 5 - 120 minutes. The level of degradation has been measured using photoluminescence by defining an intensity ratio (ρ) between the main emission lines of Eu^{3+} and Eu^{2+} ions. The degradation was then modelled using the Avrami equation, which is

commonly used to describe transformations dependent on both time and temperature, such as crystallisation or phase transformation [23-26]. This indicates that the oxidation process is similar to that of a phase transformation in which the growth rate shows Arrhenius dependency.

Materials and methods

In this study, powder samples of commercially available BAM:Eu phosphor (KEMK63 UF-P1, Phosphor Technology) were used. This phosphor was manufactured by a solid state reaction method which heats the phosphor to excess of 1600 °C in a reducing atmosphere, and results in a fully crystalline material in which all the dopant ions are in the divalent state.

Powder samples were placed inside an alumina crucible and then placed in a box furnace pre-heated to the selected temperature. An N-type thermocouple in contact with the powder was used to continuously monitor the temperature of the sample. In order to ensure that the phosphor was exposed for the desired time at the selected temperature, the timing of the heat treatment was started when the sample reached 98% of the set temperature. Heating and cooling times were normally below 5 minutes. When the heat treatment was finished the sample was removed from the furnace and cooled down in ambient air.

In order to investigate the mechanism of oxidation of BAM:Eu, samples of BAM:Eu powder were heat treated in air in the temperature range 800 °C - 1200 °C at 100 °C intervals. The duration of the exposure was varied with values of 5, 10, 20, 40, 60 and 120 minutes.

Luminescence from the samples was measured at room temperature after the samples were heat treated. Samples were excited by using the fourth harmonic (266 nm) of a Nd:YAG laser (Quanta-Ray LAB-150, Spectra Physics) Q-switched with a repetition rate of 10 Hz. The laser spot size was kept constant at approximately 4 mm and the energy used was 1 ± 0.1 mJ, as measured by an energy meter (PEM-45K, Radiant Dyes). Effects of the energy fluence on the phosphor emission were investigated in Ref [11] and found to be insignificant.

Emission spectra were measured by a Czerny-Turner spectrometer (Acton SP-2300i, Princeton Instruments) attached to a CCD array camera (Imager Intense, LaVision) with an exposure time of 1 ms. The spectrometer had a focal length of 300 mm and a grating with 300 g/mm. Light was directed onto the 100 μ m entrance slit of the spectrometer by a 50 mm Nikon lens. The intensity of the spectra was corrected for instrument response by using a Tungsten lamp as a constant light source, and the wavelength corrected with the narrow emission lines of a mercury lamp. Recorded spectra were composed of 75 individually recorded single shot images thereby enabling statistical analysis.

XRD analysis was performed in a desktop instrument (D2 Phaser, Bruker) that used $\text{CuK}\alpha$ radiation ($1.5418 \text{ \AA}$) and permitted the scanning 2θ angles from 5° to 90° in steps of 0.032° . A simple search match was performed using the commercial software PANalytical X'Pert HighScore Plus.

Thermogravimetric and differential thermal analysis (TGA-DTA) were performed in a simultaneous TGA-DTA instrument (STA 449F1 Jupiter, Netzsch). Two different tests were performed under air and argon gas flows (60 ml/min) and a heating rate of 10°C/min . Samples were prepared by placing the powder inside an alumina crucible (67.2 mg and 94.5 mg for the air and argon tests respectively), which were then inserted into the TGA-DTA instrument. Maximum temperature achieved was 1600°C and data were corrected for systematic errors, including buoyancy effects, by measuring a calibration curve without any sample but under gas flow.

Results and discussion

Spectroscopy

The emission spectra of BAM:Eu after excitation at 266 nm consists of a broad band centred at 445 nm due to $4f^65d^1 \rightarrow 4f^7$ transitions of Eu^{2+} . It is well known that heat treatment of BAM:Eu in air results in a decrease in intensity of this line accompanied by the appearance of new emission lines from 575 nm to 720 nm due to $^5\text{D}_0 \rightarrow ^7\text{F}_N$ ($N=0,1,2,3,4$) transitions of Eu^{3+} [11, 13, 14]. The broad band remains invariant in shape with heat treatment, as shown in Figure 1. This suggests that Eu^{2+} ions remain in the same site within the crystal lattice. A blue-shift on the short-wavelength side of the spectra (with a maximum of 3 nm at 1200°C) can be discerned, which may be related to variation in the crystal field due to strain in the lattice following heat treatment, as reported in [7].

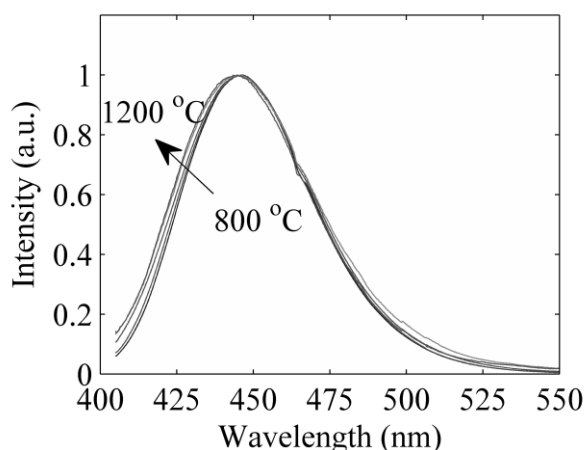


Figure 1. Normalised emission spectra of BAM:Eu samples after heat treatment in air for 20 minutes centred at the broad band at 445 nm .

In contrast to the relatively static emission from the Eu^{2+} ions, the emission spectra attributed to the Eu^{3+} ions changes considerably during oxidation as depicted in Figure 2. Herein the emission spectra

of Eu^{3+} ions is normalised to the most intense peak (data at 1000 °C is omitted for brevity). After exposure at 800 °C the peaks in the spectra are relatively broad and of low intensity. The low intensity is consistent with concentration quenching in the surface region as suggested in [5] whilst the indistinct peaks may indicate that the Eu^{3+} ions are subject to a range of local crystal fields as might be the case if they occupy different sites in the lattice. The peak with the highest intensity is located at 613.5 nm when the duration of the exposure is short but as the exposure time is increased, it moves to 611.5 nm. This is suggestive of a build-up of lattice strain as previously discussed with reference to the changes in the Eu^{2+} emission but given the spectral evolution that may be observed for exposures at higher temperatures, is more likely to be indicative of the emergence of a new phase. Emission from less intense transitions of Eu^{3+} , between 575-600 nm, 650 nm and in the range 675-710 nm, are also observed to progressively resolve into more intense and narrow peaks for long exposure times and high temperatures.

The overall evolution of the spectra with temperature and time is best illustrated by considering the spectra for exposure at 900 °C. After 5 minutes, the spectrum is very similar to that of the sample heat treated at 800 °C for 120 minutes suggesting that the rate of the evolutionary process has increased markedly at 900°C, a temperature at which Yamada et al. [7] suggested the appearance of a new magnetoplumbite phase. At 5 minutes the main peaks at 611.5 nm and 613.5 nm are of comparable intensity and the emission peaks around 611 nm are still broad. After 10 minutes of heat treatment, the peaks have resolved into a distinct pattern, a main peak and two secondary ones, which remain present for all longer exposure times. The diminishing relative intensity of the secondary peaks at 618 nm and 623.5 nm is the only feature that varies after 10 minutes of exposure. At temperatures of 1000 °C (not shown in the figure) and above, the changes in the emission spectra with the duration of the exposure are negligible, although oxidation of Eu is still occurring as indicated by the relative change of intensities of the Eu^{2+} and Eu^{3+} emissions. The crystal field experienced by Eu^{3+} ions is thus uniform at temperatures of 1000 °C and above, which might be indicative of the occupation of a particular and consistent site within the BAM lattice but equally may indicate the location of the Eu^{3+} within a new phase.

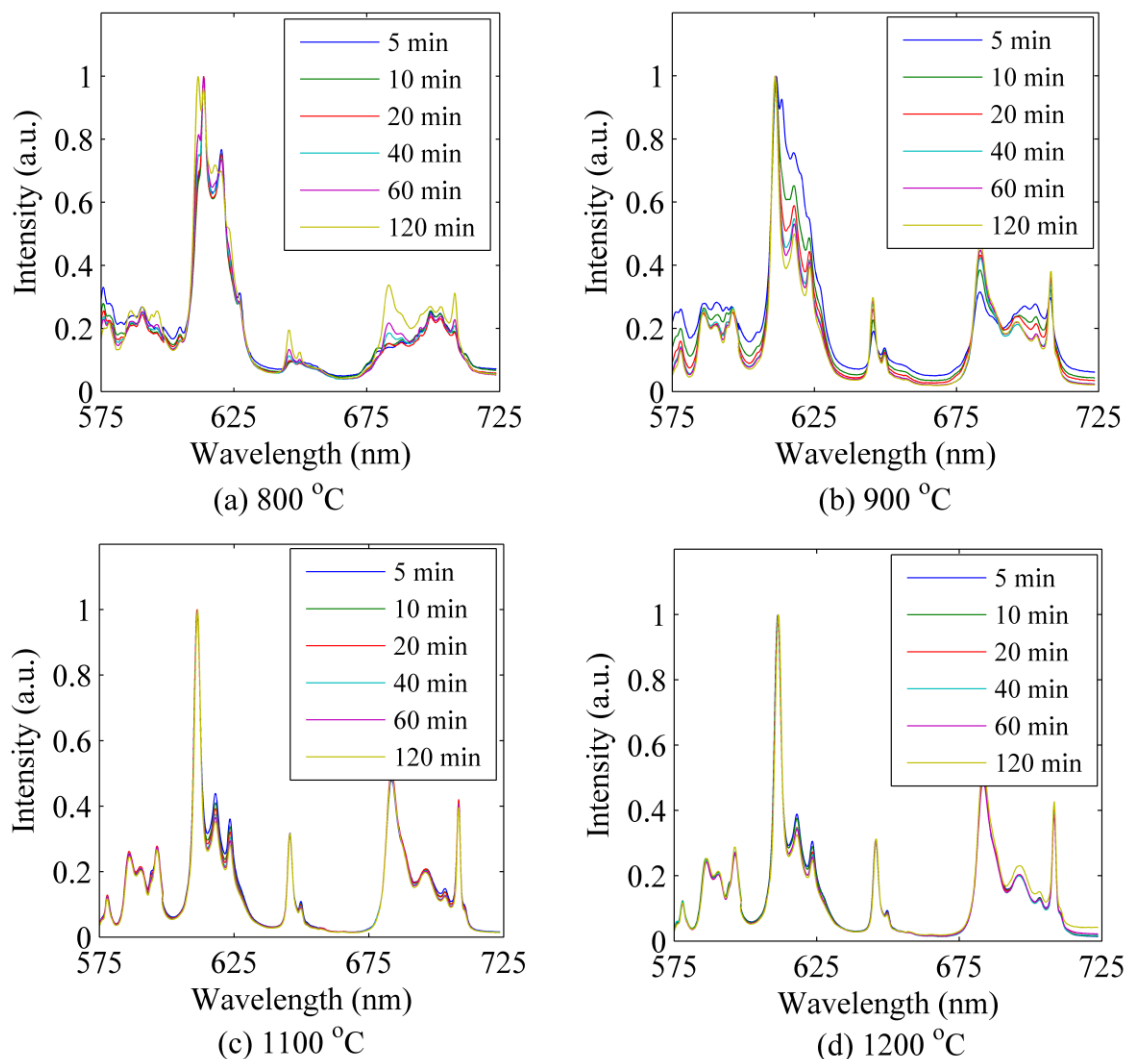


Figure 2. Emission spectra of BAM:Eu samples heat treated at the indicated temperatures and times.

Material characterisation

XRD analysis was performed to see if the presence of the magnetoplumbite phase could be confirmed. The resulting XRD patterns are presented in Figure 3 from which it can be seen that this phase was only detected in samples heat treated at the highest temperature of 1200 °C, and in such cases the intensity of peaks belonging to it were very low. The question then arises as to whether the magnetoplumbite phase only begins to form at 1200 °C or if it is present at lower temperatures in quantities below the resolving power of the instrumentation. The answer appears to be provided by the emission spectrum for exposure at 1200 °C which shows the same features that emerged at 900 °C and no indication of a change in the site characteristics of the Eu^{3+} ions as would be the case if they were transferred to a new phase. Taken together the emission spectra and the XRD patterns suggest that the magnetoplumbite phase begins to form at temperatures as low as 800 °C but that once thermally triggered its formation is dependent on the availability of Eu^{3+} ions around which it forms

so that the formation rate is limited by processes associated with the formation of Eu^{3+} namely diffusion and oxidation.

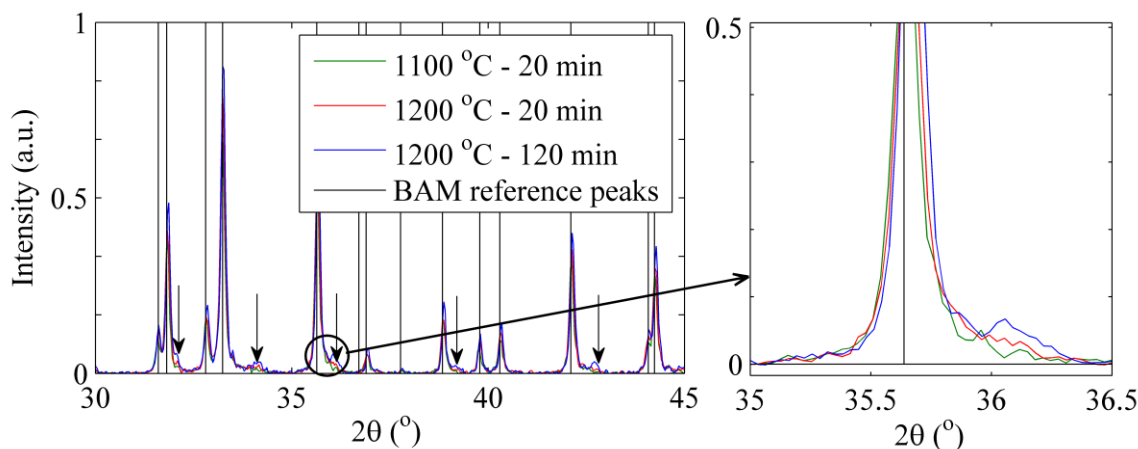


Figure 3. XRD patterns of BAM:Eu samples heat treated at 1100 °C – 20 minutes, 1200 °C – 20 and 120 minutes.

Further investigation of structural and compositional changes undergone during heat treatment was performed by simultaneous thermogravimetric analysis and differential thermal analysis (TGA-DTA). This analysis was performed under air and argon atmospheres since there is previous evidence that the oxidation of the phosphor is highly dependent on the oxidising characteristics of the surrounding gas. Kim and Kang (2010) and Liu et al. (2010) suggested that little degradation of the phosphor was observed under neutral or reducing atmospheres. Further studies in Ref [11] indicate a relationship between the oxidation of the phosphor and the partial pressure of oxygen in the surrounding atmosphere. The results of the TGA-DTA in air and argon are shown in Figure 4. The TGA in air (dashed-blue) presents a significant mass gain at the beginning of the curve, which might be related to adsorption of oxygen on vacancies at the surface of the phosphor [9]. Later, the mass reduces due to water evaporation and does not present any further changes above 250 °C. In the inert atmosphere (dashed-green), only a mass loss due to evaporation of water is evident, which supports the previous observations. DTA shows an endothermic reaction in both gas atmospheres with the peak maximum at 220 °C which is related to this evaporation process. DTA also shows a broad exothermic peak in the samples heated in air (solid-blue) that extends up to approximately 1100 °C. This is ascribed to the continuous oxidation of the europium dopant upon heating. This reaction is still present under argon (solid-green), but to a lesser extent. An explanation for this might be that air is trapped in the voids within the powder inside the crucible that leads to limited oxidation.

The DTA plot shows two additional features worthy of note. At around 900 °C there is an exothermic dip in the curve. This may indicate the onset of the formation of the magnetoplumbite phase and would be consistent with the observations made using the emission spectra and previous studies that suggest the formation of this phase at this temperature [7]. In addition, at around 1300 °C, another exothermic reaction is observed to be initiated. This could be another phase change but the hypothesis

cannot be corroborated by any of the other data recorded since these were limited to a maximum temperature of 1200 °C.

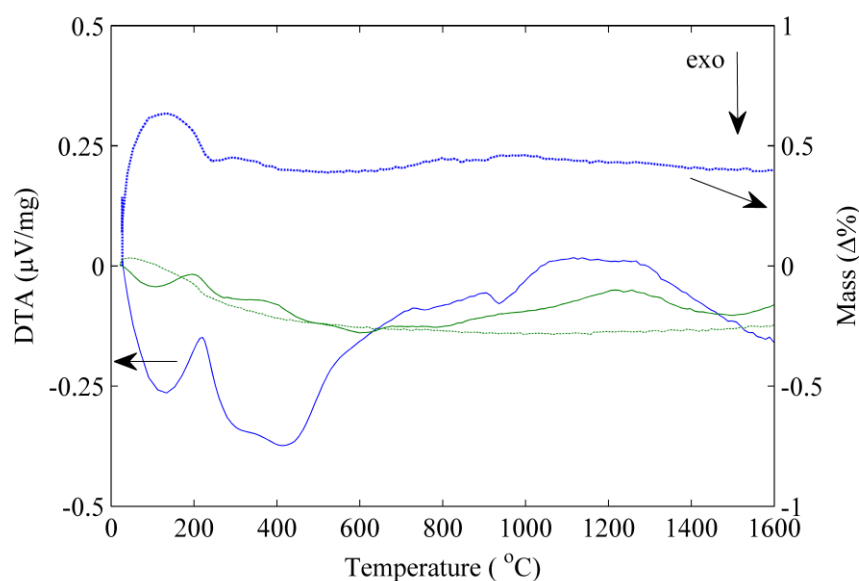


Figure 4. TGA-DTA curves of the BAM:Eu sample under air (blue) and argon (green) atmospheres. Dashed and solid lines represent TGA and DTA curves, respectively.

Kinetics

Spectroscopy and material characterisation techniques suggest that the changes undergone in BAM:Eu during heat treatment in air are a continuous process in which europium progressively diffuses (high cation mobility in β -alumina [10]) and oxidises within the BAM lattice as a result of exposure to high temperatures with the formation of a magnetoplumbite phase containing the Eu^{3+} for temperatures of 900 °C and above. The normalised intensity ratio (ρ) between the two main peaks of the emissions of Eu^{3+} (611 nm) and Eu^{2+} (445 nm), presented by the authors in an earlier work [11] and which is plotted in Figure 5 for samples heat treated for the indicated times and at the indicated temperatures, is a measure of the level of transformation achieved. This ratio generally presents a continuous and monotonic increase with temperature and exposure time. However, it shows a slight decrease for samples heat treated at 1200 °C for more than 40 minutes which may be the onset of the process indicated in the DTA analysis at 1300 °C evident in the spectra due to the longer exposure time relative to DTA. A maximum level of oxidation/degradation is evident as the normalised intensity ratio tends to 1 as time increases.

The mechanism of oxidation, as suggested by Bizarri and Moine [9], involves three steps in which adsorption of oxygen and diffusion of europium control the rate of oxidation. Oxygen is mainly adsorbed at relatively low temperatures according to the TGA data and the number of Eu^{3+} that can be generated is thus limited. As Eu^{3+} is formed the rate of transformation can therefore be expected to

diminish as the oxygen is consumed. Herein, we have additionally proposed that a magnetoplumbite phase forms around the Eu^{3+} ions wherein emission from them increases and becomes more distinct. Intensity ratio data should, therefore, reflect this additional process also.

To test this, an attempt has been made to fit the intensity ratio data to the well-known Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory of transformation kinetics, which describes the process as being composed of three phases. An initiation phase wherein the new phase appears, to create nucleation sites, in an essentially random fashion, followed by a growth phase from the nucleation sites and finally a saturation phase as the amount of untransformed material diminishes. Given that the transformation in BAM:Eu includes the emergence of a new phases, it was thought likely that the transformation would follow such as process, at least in parts, and indeed the theory is widely and successfully used to describe transformations such as crystallisation, chemical reactions, phase changes and oxidation [23-26]. Herein, the transformation has additional features, associated with diffusion for example, so that the actual transformation is more complex than the basic theory suggests. Nevertheless, growth and saturation were thought to remain as key features and, as such, it was thought that the KJMA theory remains a good candidate for a reliable mathematical representation of the process. This model is expressed by the following equation:

$$y = 1 - \exp(-kt^n) \quad (1)$$

where y is the ratio of transformed to untransformed material, k is the growth rate, t is the time and n is the Avrami exponent. The growth rate is generally dependent on the absolute temperature following an Arrhenius expression:

$$k(T) = A \exp\left(-\frac{E_a}{k_b T}\right) \quad (2)$$

A is a pre-exponential constant, E_a is the activation energy, k_b is the Boltzmann constant and T the absolute temperature.

The experimental data from the authors' previous work [11] are shown in Figure 5 fitted with only two parameters A and E_a , and an Avrami exponent of 1. This value was chosen since it corresponds to a process in which no initiation phase exists i.e. it describes growth and saturation in a pre-nucleated material. This was done because it was earlier hypothesised by the authors that the rate of formation of the magnetoplumbite phase is controlled by diffusion of Eu ions rather than a probabilistic initiation process. Nevertheless, in order to test this hypothesis a fit was calculated with the exponent as one of the fitting variables and a value close to 1 (0.98) was determined. The fit agrees quite well with the experimental data, thereby supporting the hypothesis, at all except the lowest temperature of

800 °C. This observation is, however, consistent with the changes in the emission spectra at this temperature, which suggests that at 800 °C diffusion and oxidation occur but that the phase change has not begun.

In the temperature range from 900 °C to 1200 °C, the intensity ratio predicted by the KJMA model can be used as a measure of temperature if the temperature is held constant for a known period of time. Thus, in this range the BAM:Eu phosphor could be used as a temperature sensor with a calibration curve in the form of Equation (1) above. In industrial applications of the sensor, the time at temperature can be controlled or at least recorded so that only temperature is an unknown. At lower temperatures measurements can still be made using customised calibration data in the form of look-up tables and further research would be necessary to find a model that can explain the variation of the intensity ratio with temperature and time at these levels.

Data presented in Figure 5 and analysis of Equation (1) suggest that the temperature sensitivity of the sensor diminishes for long exposure times, especially at temperatures above 1100 °C and after approximately 60 min exposure. It would therefore be essential to keep exposure times below 1 h in order to perform reliable temperature measurements above 1100 °C. However, the possibility to tune the response of the phosphor by manipulating the dopant concentration has been presented by the authors in [11]. This would maintain sensitivity at higher temperatures even for long exposure times.

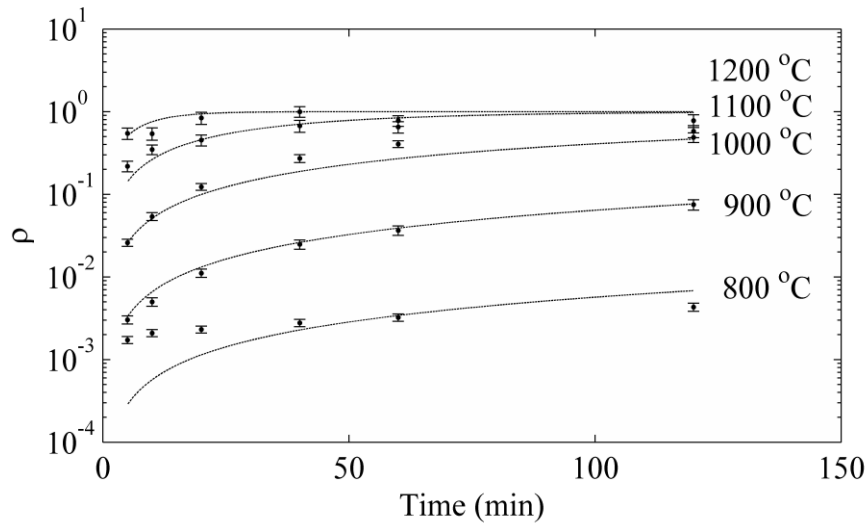


Figure 5. Intensity ratio versus heat treatment time of samples heat treated at the indicated temperatures from 800 °C to 1200 °C. The experimental data is fitted to the KJMA model.

Conclusions and future work

The oxidation mechanism of BAM:Eu has been studied related to its potential application as a thermal history sensor at temperatures of 800 °C - 1200 °C. Despite the complex processes that occur during oxidation of BAM:Eu, the optical properties of the phosphor evolve continuously and do not seem to

be affected by the formation of a second phase as suggested in previous studies. In contrast to previous investigations, XRD in this work indicates the presence of this second phase only in samples heat treated at 1200 °C, although no effect on the emission spectra of the phosphor is observed. Furthermore, TGA-DTA does not show any evidence of structural changes occurring up to 1600 °C. Future work should clarify if this phase is already present at lower temperatures and determine if Eu^{3+} only occupies sites within that phase, which would explain why the emission spectra remains constant. Furthermore, the findings presented in this work are in line with previous models that suggest that adsorption of oxygen, diffusion and oxidation of Eu play an important role in the degradation of the phosphor.

The continuous oxidation of Eu^{2+} into Eu^{3+} can be measured by defining an intensity ratio between the main emission lines of these two ions, which is dependent on both the time of exposure and the temperature. Experimental data agrees well to the KJMA theory of transformation kinetics at temperatures of 900 °C and above. The Avrami exponent employed, with a value of 1, suggests that the initiation phase is negligible in this process and the kinetics are thus only limited by diffusion of europium ions. The possibility to simultaneously relate the intensity ratio to temperature and time makes this phosphor a promising candidate to perform temperature measurements in this temperature range if the time of the exposure can be controlled. At the lower temperatures of 800 °C further research is necessary to clarify the mechanisms that govern the oxidation of BAM:Eu and a suitable model should be defined to relate the intensity ratio to the other two variables.

Acknowledgements

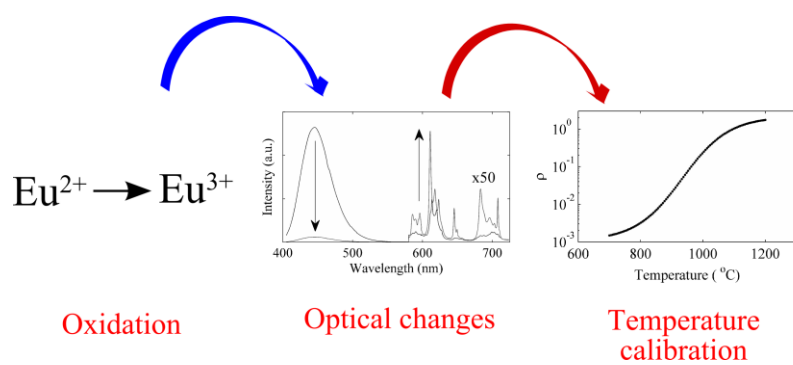
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References

- [1] J. Verstegen, A survey of a group of phosphors, based on hexagonal aluminate and gallate host lattices, *J Electrochem Soc*, 121(1974) 1623-7.
- [2] J. Verstegen, D. Radielović, L.E. Vrenken, A new generation of “deluxe” fluorescent lamps, combining an efficacy of 80 lumens/W or more with a color rendering index of approximately 85, *J Electrochem Soc*, 121(1974) 1627-31.
- [3] B. Smets, J. Verlijsdonk, The luminescence properties of Eu^{2+} -and Mn^{2+} -doped barium hexaaluminates, *Materials Research Bulletin*, 21(1986) 1305-10.
- [4] S. Oshio, B. Matsuoka, S. Tanaka, H. Kobayashi, Mechanism of luminance decrease in $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor by oxidation, *J Electrochem Soc*, 145(1998) 3903-7.

- [5] K. Mishra, M. Raukas, G. Marking, P. Chen, P. Boolchand, Investigation of fluorescence degradation mechanism of hydrated $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor, *J Electrochem Soc*, 152(2005) H183-H90.
- [6] K.B. Kim, K.W. Koo, T.Y. Cho, H.G. Chun, Effect of heat treatment on photoluminescence behavior of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ phosphors, *Mater Chem Phys*, 80(2003) 682-9.
- [7] H. Yamada, W.S. Shi, C.N. Xu, Lattice deformation in thermally degraded barium magnesium aluminate phosphor, *J Electrochem Soc*, 151(2004) E349-E51.
- [8] P. Boolchand, K. Mishra, M. Raukas, A. Ellens, P. Schmidt, Occupancy and site distribution of europium in barium magnesium aluminate by ^{151}Eu Mössbauer spectroscopy, *Physical Review B*, 66(2002) 134429.
- [9] G. Bizarri, B. Moine, On $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor degradation mechanism: thermal treatment effects, *J Lumines*, 113(2005) 199-213.
- [10] A. Lacanilao, G. Wallez, L. Mazerolles, P. Dubot, L. Binet, B. Pavageau, et al., Structural analysis of thermal degradation and regeneration in blue phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ based upon cation diffusion, *Solid State Ionics*, 253(2013) 32-8.
- [11] A. Yañez Gonzalez, E. Ruiz-Trejo, B. Van Wachem, S. Skinner, F. Beyrau, A. Heyes, A detailed characterization of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ phosphor as a thermal history sensor for harsh environments, *Sensors and Actuators A: Physical*, 234(2015) 339-45.
- [12] J. Feist, J. Nicholls, A. Heyes, Determining thermal history of components, 2007.
- [13] A. Rabhiou, A. Kempf, A. Heyes, Oxidation of divalent rare earth phosphors for thermal history sensing, *Sens Actuator B-Chem*, 177(2013) 124-30.
- [14] A. Yañez Gonzalez, S. Skinner, F. Beyrau, A. Heyes, Reusable Thermal History Sensing via Oxidation of a Divalent Rare Earth Ion Based Phosphor Synthesized by the Sol-Gel Process, *Heat Transfer Engineering*, 36(2015) 1275-81.
- [15] A. Rabhiou, J. Feist, A. Kempf, S. Skinner, A. Heyes, Phosphorescent thermal history sensors, *Sens Actuator A-Phys*, 169(2011) 18-26.
- [16] J. Cowling, P. King, A.L. Alexander, Temperature-indicating paints, *Industrial & Engineering Chemistry*, 45(1953) 2317-20.
- [17] H. Watson, E. Hodgkinson, Temperature indicating paint, 2002.

- [18] C. Lempereur, R. Andral, J.Y. Prudhomme, Surface temperature measurement on engine components by means of irreversible thermal coatings, *Meas Sci Technol*, 19(2008).
- [19] C. Bird, J. Mutton, R. Shepherd, M. Smith, H. Watson, Surface temperature measurements in turbines, *AGARD Conference Proceedings* 1998, pp. 21.4-10.
- [20] G. Sarner, M. Richter, M. Alden, Investigations of blue emitting phosphors for thermometry, *Meas Sci Technol*, 19(2008).
- [21] J. Linden, C. Knappe, M. Richter, M. Alden, Precision in 2D temperature measurements using the thermographic phosphor BAM, *Meas Sci Technol*, 23(2012).
- [22] C. Knappe, J. Lindén, M. Richter, M. Aldén, Enhanced color ratio calibration for two-dimensional surface thermometry using laser-induced phosphorescence, *Measurement Science and Technology*, 24(2013) 085202.
- [23] M.C. Weinberg, D.P. Birnie, V.A. Shneidman, Crystallization kinetics and the JMAK equation, *Journal of Non-Crystalline Solids*, 219(1997) 89-99.
- [24] G. Ruitenberg, E. Woldt, A. Petford-Long, Comparing the Johnson–Mehl–Avrami–Kolmogorov equations for isothermal and linear heating conditions, *Thermochimica Acta*, 378(2001) 97-105.
- [25] J.W. Christian, *The theory of transformations in metals and alloys*: Newnes; 2002.
- [26] J. Kohout, An alternative to the JMAK equation for a better description of phase transformation kinetics, *Journal of Materials Science*, 43(2008) 1334-9.



Graphical abstract

Highlights

- Oxidation of BAM:Eu is investigated for a new temperature sensing application.
- The oxidation follows the KJMA model above 900 °C.
- Optical spectroscopy and materials characterisation techniques are employed.
- Temperature can be sensed with knowledge of the exposure time.