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A detailed characterization of BaMgAl$_{10}$O$_{17}$:Eu phosphor as a thermal history sensor for harsh environments

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Abstract

Knowledge of component temperatures in gas turbines is essential for the design of thermal management systems and to maintain the lifetime of highly loaded parts as the firing temperature increases in pursuit of improved thermal efficiency. When on-line methods such as pyrometers and thermocouples are not suitable, a thermal history sensor can be used to record the maximum temperatures and read them out after operation. Currently, temperature sensitive paints are applied to obtain temperature profiles in gas turbine components but they present some limitations. A new method based on irreversible changes in the optical properties of thermographic phosphors can potentially overcome some of these difficulties. In particular, a sensor based on the oxidation of europium based phosphors has shown great potential. In this work the temperature sensing capabilities of the phosphor $BaMgAl_{10}O_{17}$:Eu are investigated in the temperature range from 700 °C to 1200 °C, and suitable measurands defined. The influence of practical factors comprising excitation fluence, exposure time, dopant concentration, cooling down time and atmosphere composition, on measurement accuracy and sensitivity are also reported.

1. Introduction

Increased thermal efficiency has been a main driver of gas turbine development since their inception in both their aerospace and land based forms and is set to remain so due to fuel costs and concerns about emissions. The firing temperature (analogous to turbine inlet temperature for jet engines) is the determining factor for thermal efficiency but is restricted by the material limits of the metallic components in the high-pressure turbine. This problem has been addressed by the development of new alloys, the implementation of complex air and steam cooling systems and the development of coatings that thermally insulate and protect against corrosion. Nevertheless, the lifetime of components remains dependent on their temperature and therefore it is essential to determine this as part of the engine development. It could also be of great value in service as part of the engine control system [1].

Temperature measurements can be performed in real time, using thermocouples or pyrometers for example, but all such conventional techniques are limited in the gas turbine environment. Thermocouples are intrusive, potentially affecting the conditions they are intended to measure, and giving erroneous temperature data. Furthermore, their installation is complicated (they cannot easily be installed on rotating components) and they provide only point measurements so that multiple sensors need to be set-up in order to acquire temperature maps. Pyrometers are passive optical devices and therefore are non-intrusive. However, their accuracy is compromised under conditions such as those present in the hot sections of gas turbines. The two main sources of error are the presence of secondary radiation reflected from other components of the turbine and the difficulty in correctly evaluating the emissivity of the surface whose temperature is being measured [2].

Off-line temperature measurements, performed after the operation of the system, are an alternative when on-line measurements are not possible. In this technique, sensors that *remember* the conditions to which they have been exposed are used and interrogated post exposure to determine them. Such sensors typically record a measure of the thermal exposure that is a function of temperature and exposure time so that steady state exposures of known duration are required if the temperature is to be accurately determined. Despite this apparent limitation such sensors, sometimes referred to as thermal history

sensors, are widely used with temperature sensitive paints (or thermal paints) the most common example. These incorporate a metallic pigment that permanently changes colour upon heating. This pigment is mixed with a binder and solvent to make a paint that can be applied on complex surfaces such as blades, nozzle guide vanes and combustor walls [3, 4]. Temperatures from 120 °C up to 1300 °C can be measured using different paints that are normally calibrated for exposure times from 3 to 60 minutes [5]. Despite their undoubted utility, these paints present some practical difficulties. Their application, normally via spray, needs to be carefully performed in order to obtain good surface finish that permits correct visual identification of the colour changes. The thickness of the deposited layer should be kept below a few microns to avoid interference with the heat flux of the component. However, this can result in spallation of the layer and loss of temperature information for long exposure times. Colour changes are sometimes subtle, limited to a fixed number (poor resolution) and require interpretation by an experienced operator typically under controlled conditions after dismantling of the engine, although the automation of the process is currently being investigated [6]. Finally, some of the substances present in thermal paints are now restricted by the EU REACH regulation [7].

An alternative off-line method based on the use of thermographic phosphors was has been devised by Feist et al. [8]. Thermographic phosphor materials usually consist of a ceramic host and a rare-earth dopant that emit luminescence upon excitation by a UV or visible light source. They have been studied for many years as on-line temperature sensors [9-13] with applications on surfaces [14-17] and for gas flow temperature measurements [18-21]. Off-line measurements using thermographic phosphors are based on irreversible changes in their optical properties caused by the exposure to high temperatures and oxidising environments. These optical properties can be measured using the same methods as on-line thermographic phosphors, such as the lifetime decay and intensity ratio methods widely described in the literature [9, 13]. Thermographic phosphors present some advantages when compared to thermal paints: the measurement is objective and unaffected by errors due to visual interpretation, temperature data is continuous and therefore resolution is improved, in-situ measurements can be made more easily which can remove the need to dismantle the engine and the chemicals used are not restricted by REACH regulations.

Two processes that cause permanent changes in phosphors have been the main focus of studies conducted to date: the amorphous to crystalline transformation [22] and oxidation [23]. The former requires an initially amorphous phosphor but normally manufacturers sell them fully crystallised so that custom-made materials are usually required. During crystallisation, the local environment of the dopant ions becomes more regular and luminescence becomes more intense and long lived. This concept has been investigated in several phosphors, for example Y_2SiO_5:Tb powder showed a dynamic range extending up to 1000 °C [22], a Eu based phosphor applied to a surface in paint form went up to 800 °C [24] and a YAG:Ln air plasma sprayed coating up to 900 °C [24].

The second mechanism makes use of the change in optical properties that results from oxidation of divalent rare-earth ions, such as europium, to a trivalent state. This has the advantage that well characterised commercially available, fully crystalline phosphors can be employed [23]. The concept has been investigated for a number of phosphors [23] sensitive to 1400 °C. $BaMgAl_{10}O_{17}$:Eu (BAM:Eu) phosphor shows great potential and an initial investigation of its sensing capabilities can be found in [23, 25]. In the literature thermally driven changes in BAM:Eu are usually regarded as a form of degradation due to the reduction in blue emission that the phosphor is commercially employed to provide in plasma display panels. In the context of thermal history sensing the process is desirable so that degradation seems an inappropriate term and is replaced herein by reference to oxidation notwithstanding the fact that this is not the only effect of heat treatment of the phosphor.

In this work, a detailed study of the temperature sensing capabilities of BAM:Eu from 700 °C to 1200 °C is presented. The influence of several factors that might affect the accuracy, sensitivity or practical utility of the phosphor is also discussed. These include excitation fluence, excitation wavelength, exposure time, dopant concentration, cooling down time and bath gas composition. The intensity ratio method was the focus of the investigation as it is better suited to 2-D surface temperature measurements. However, the lifetime decay method is also reported for the first time for this material.

2. Experiments

Samples of commercially available BAM:Eu phosphor powder (KEMK63 UF-P1, Phosphor Technology) were studied in this work. BAM:Eu samples were also manufactured by the sol-gel process reported previously [25] in order to study the effect of dopant concentration.

The luminescence properties of the samples were examined at room temperature and a diagram of the set-up   is   shown   in
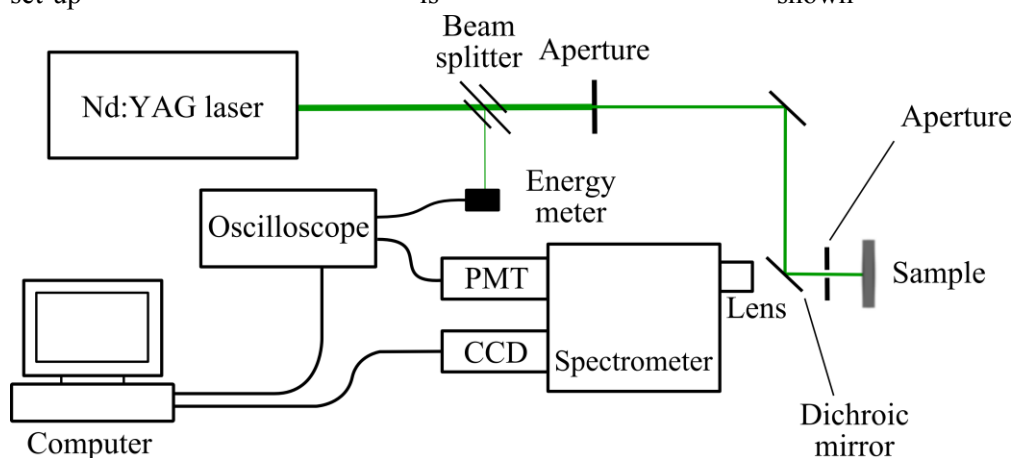

Figure 1. The samples were excited by using the third and fourth harmonics (355 nm and 266 nm respectively) of a pulsed Nd:YAG laser (Quanta-Ray LAB-150, Spectra Physics). The repetition rate was 10 Hz and the pulse width 5-7 ns. The laser spot diameter was approximately 4 mm in all measurements. The energy of a single pulse was kept constant at 1±0.1 mJ (so that fluence was approximately 8±0.8 mJ/cm^2) and it was calibrated using an energy meter (PEM-45K, Radiant Dyes). When the effect of the excitation energy was studied, energy was measured on a single shot basis using a previously calibrated energy monitor (LaVision).

The emission spectra were recorded by a Czerny-Turner spectrometer (Acton SP-2300i, Princeton Instruments) with a focal length of 300 mm and a grating with 300 g/mm. The collected light was focused by a 50 mm Nikon lens onto the entrance slit of the spectrometer, which was set to 100 μm so that the resolution was better than 1 nm. The spectra at the exit of the spectrometer were recorded by a CCD array camera (Imager Intense, LaVision) with an exposure time of 1 ms. This ensures complete collection of the phosphorescence which shows a maximum decay time of about 800 μs. The recorded spectra were averaged over 75 single shot images that were wavelength calibrated using the emission lines of a mercury lamp. Spectra were intensity calibrated using the reference spectrum of a Tungsten lamp. The intensity ratio statistics were computed from the 75 recorded single shot spectra.

Lifetime decay was recorded at room temperature using a photomultiplier tube (PMT) (R955HA, Hamamatsu) attached to a Czerny-Turner monochromator (MonoSpec 18, Jarrell-Ash). The light was collected onto the entrance slit (100 μm) of the spectrometer using a 50 mm Nikon lens. The wavelength

observed at the 100 μm exit slit of the spectrometer could be manually adjusted. The signal from the PMT was digitised by an oscilloscope (PicoScope 3205b) and the data fitted to a single exponential decay using a Levenberg-Marquardt algorithm. At each temperature, 20 measurements composed of 32 single-shot averaged decays were used.

Powder samples were heat treated in an alumina crucible placed inside a temperature controlled chamber furnace and the temperature was monitored using an N-type thermocouple in contact with the powder. Heat treatment temperatures varied from 700 °C to 1200 °C and exposure times from 5 to 120 minutes. When a controlled atmosphere was necessary, the samples were placed inside a quartz tube closed at one side. At the other end a drilled silicon stopper permitted the entrance and exit of the necessary gas flow, which was regulated by mass flow controllers (Fideris), through stainless steel pipes while keeping a closed atmosphere. The quartz tube was slid concentrically within a tube furnace to expose the samples to high temperatures.

3. Results and discussion

3.1. Excitation and emission: definition of a suitable measurand

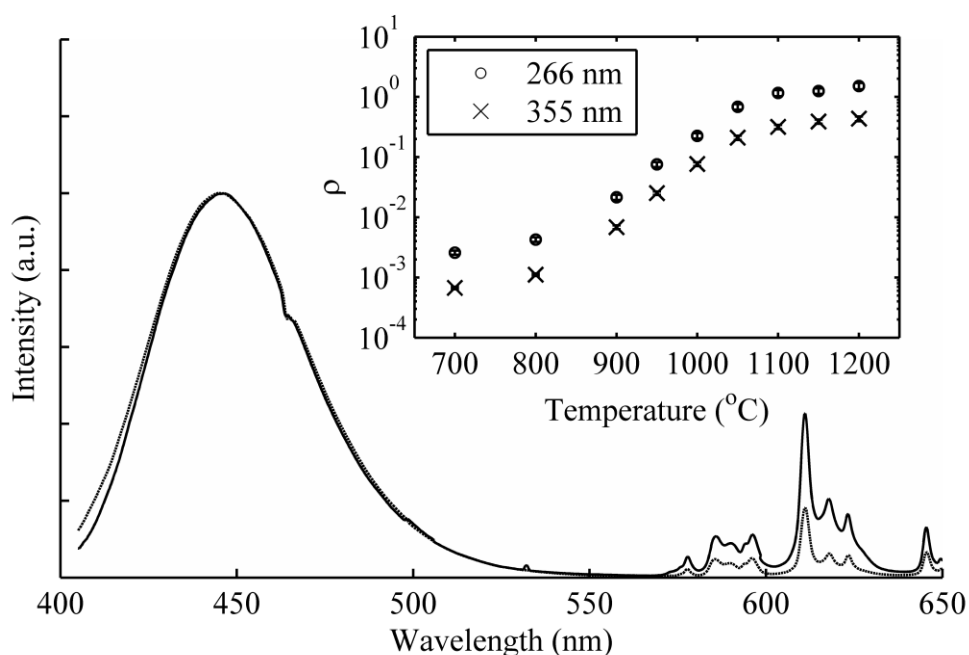The emission spectrum of BAM:Eu after heat treatment in air, as shown in

Figure 2 for a sample heat treated at 1000 °C for 20 minutes, consists of a broad band emission centred at 445 nm (due to $4f^6 5d \rightarrow 4f^7$ transitions of Eu^{2+}) and a series of peaks between 550 nm and 750 nm (due to $^5D_0$ to $^7F_{0,1,2,3,4}$ transitions of Eu^{3+}). The phosphor can be excited using both the third and fourth harmonics of the YAG laser and the shape of the emission spectra obtained for both is the same. Eu^{3+}-based phosphors, such as Y_2O_3:Eu, are normally excited by a Charge Transfer state at short wavelengths (266 nm). In the case of BAM, excitation using 355 nm light is also possible due to an energy transfer mechanism, as shown by the small absorption dip in the Eu^{2+} emission band at about 465 nm (see
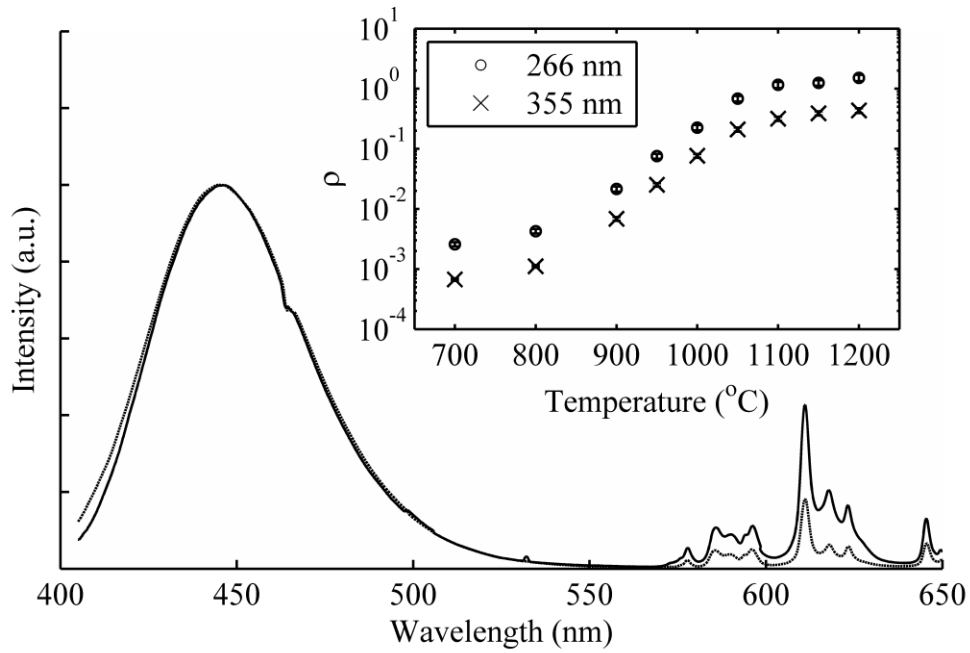
Figure 2). However, the absolute emission intensity obtained using 355 nm excitation is lower (by about 20 % according to the excitation spectra in [23]) and the relative intensity of the peaks due to emission of Eu^{3+} and Eu^{2+} ions is about 50 % lower as shown in the Figure.

The emission spectrum of BAM changes when the phosphor is exposed to high temperatures. The exact nature of the physical/chemical changes that occur as a result of the exposure is not fully understood. The proposed mechanisms were reviewed by the authors [23] and it was concluded that a combination of at least diffusion, oxidation and phase change is likely to occur and that each process will have a rate and activation that are temperature dependent. Sintering is known to occur but at higher temperatures than those employed and thus the microstructure is not affected by this mechanism. Grain growth might also be an issue depending on the synthesis route and initial crystallite size and may be worthy of further investigation. The commercial powder used herein, however, was annealed during manufacture in excess of 1600 °C so that crystallite size was not expected to increase further at the temperatures subsequently studied. The present work provides some additional insights into the nature of those processes but in the context of defining a simple temperature measurand for a thermal history sensor the important consequences are a reduction in intensity in the broad band emission from the Eu^{2+} ions and an increase in output from the narrow emission lines of the Eu^{3+} ions. A suitable temperature measurand can thus be defined as the intensity ratio (ρ) between the integrated intensities of the most intense Eu^{3+} emission peak (611 ± 5 nm) and the Eu^{2+} emission peak (445 ± 5 nm). The ratio increases monotonically with temperature from 700 °C to 1200 °C, as can be seen in the inset of
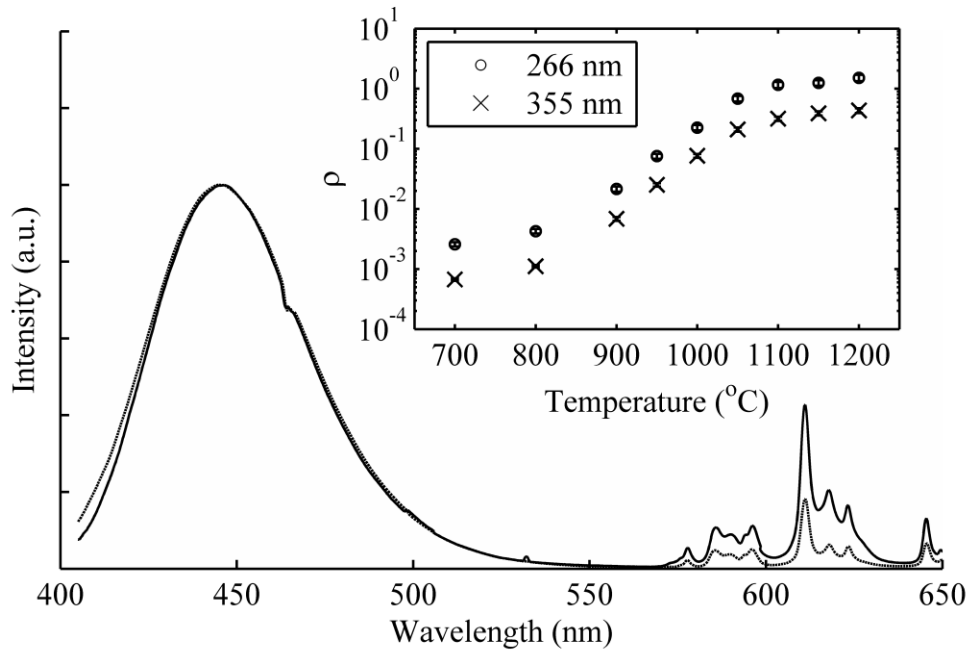
Figure 2, for samples heat treated for 20 minutes. The absolute value of ρ is higher when the phosphor is excited with 266 nm light as a result of the higher relative intensity of the 611 nm peak to the 445 nm band. The sensitivity is however similar for both excitations and they can be equivalently used to perform temperature measurements. The 266 nm excitation is used in this paper because of the higher intensity of the signal.

Alternatively, the lifetime decay method can be used as a measurand of the heat treatment temperature although this has not been previously reported for thermal history sensors using the oxidation mechanism. The lifetime decay was measured for the broadband emission at 445 nm and showed little sensitivity to heat treatment temperature. This lifetime decay was nearly constant with a value of about 1 μs. The lifetime decay was also measured for the Eu³⁺ emission peak centred at 611 nm. This lifetime decay increased monotonically with temperature up to 1100 °C, as shown in
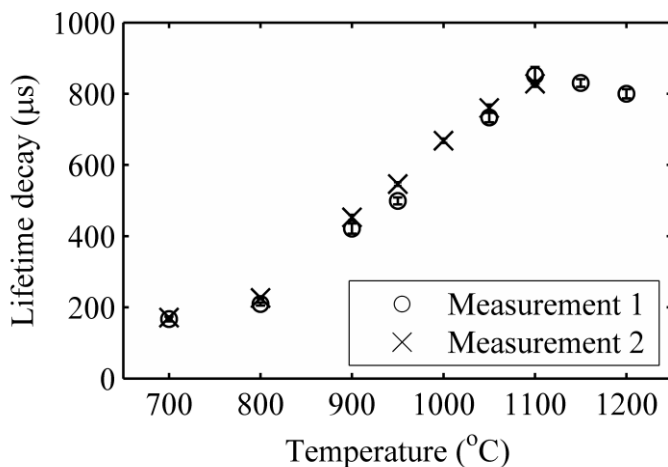

Figure 3 for samples heat-treated for 20 minutes. Above this temperature the lifetime decay decreased again. This effect has been associated, in other materials, with the formation of a second phase, for example in YAG:Eu [26]. In the current work x-ray diffraction (XRD) analysis was performed in order

to identify a second phase but only the BAM phase was observable within the resolution of the equipment.

The intensity ratio, ρ, increases over three orders of magnitude in the studied temperature range while the lifetime decay increases over less than one order of magnitude. Although the lifetime decay method is normally preferred because of its better precision, the precision of the lifetime decay method is in this case is comparable to the ρ based method due to the relatively low signal intensity of the Eu^{3+} emission in BAM. However, both measurands are complementary and could be used simultaneously to improve the accuracy of the method.

3.2. Excitation fluence

The effect of the excitation fluence (energy per unit area) on ρ was studied for samples heat-treated at temperatures of 900 °C, 950 °C, 1000 °C and 1050 °C for 20 minutes and the results are plotted in
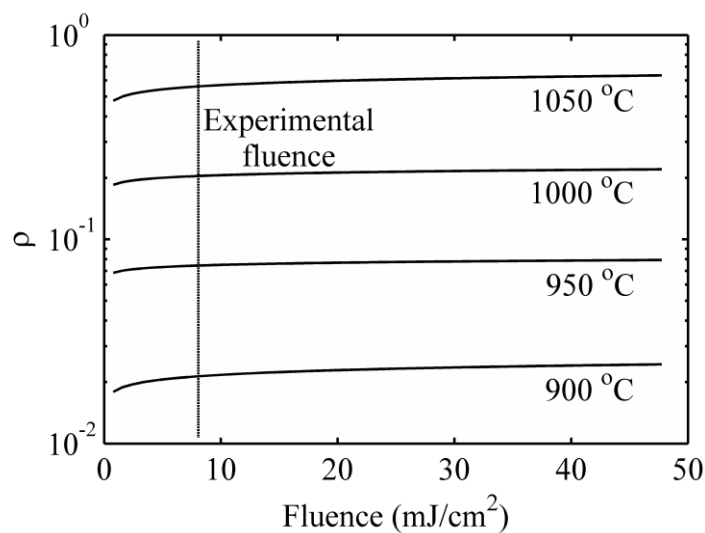

Figure 4. This figure shows ρ against the laser fluence used to excite the samples and the standard fluence condition used throughout experiments is indicated by a vertical dashed line. The intensity ratio increases with fluence, but the maximum increase is small being about the same order of magnitude as the standard deviation of the measurement. This increase was surprising because the two emissions (Eu^{2+} and Eu^{3+}) were expected to behave similarly with fluence and to saturate at the same value, previously reported for the Eu^{2+} emission to occur above 10 mJ/cm^2 [19]. Current experimental measurements are similar to those reported in [19] and extend them by confirming that saturation does not significantly affect the intensity ratio. Indeed, according to the data of
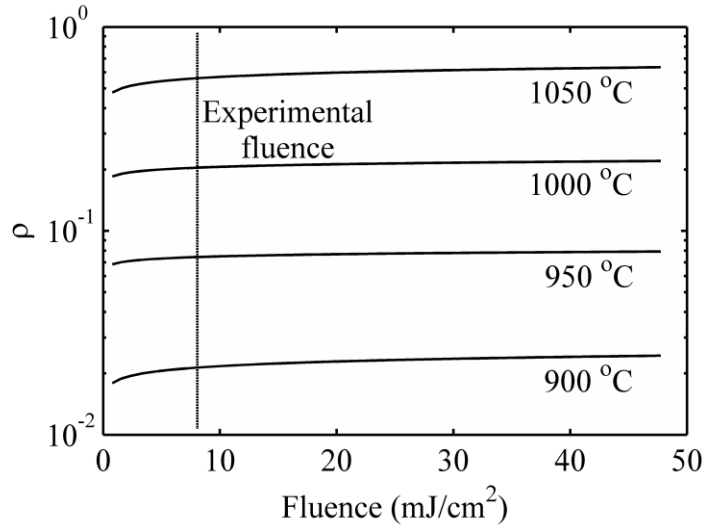
Figure 4 the change is such that the error introduced in a temperature measurement would be less than 0.5 % for a fluence change from 5 mJ/cm^2 to 50 mJ/cm^2. In practical applications the excitation fluence is not expected to vary more than a few percent and therefore this effect can be neglected. Similar conclusions can be obtained for 355 nm excitation although results are omitted for brevity.

3.3.   Exposure time

The response of thermal history sensors depends on their thermal exposure in terms of both temperature and duration. The former is the desired quantity so it would be useful to understand the effect of the exposure time and critical to be able to decouple it from the measurement. The effect of exposure time on ρ was investigated for samples heat-treated at temperatures from 800 °C to 1200 °C for periods from 5 to 120 minutes. The results are shown in
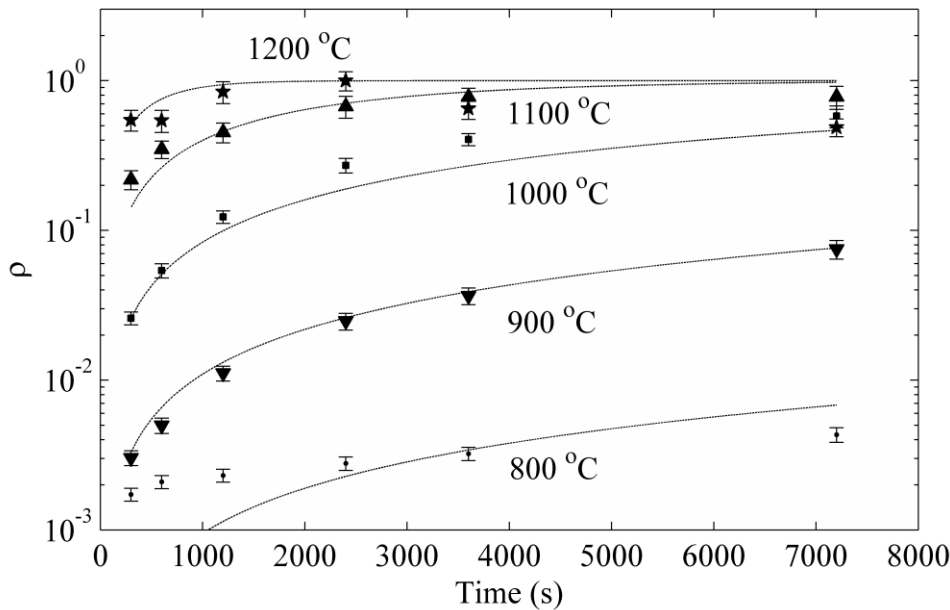

Figure 5. The normalised intensity ratio increases monotonically with time at all temperatures up to 1100 °C. At 1200 °C it decreases slightly for the longer exposure times. At the higher temperatures the normalised intensity ratio tends to 1 as the exposure time is increased indicating saturation whilst for the lowest temperature, 800 °C, this is less obvious or even absent. Saturation might be explained by

the oxidation mechanism proposed by Bizarri and Moine [27], in which oxygen is adsorbed in the BAM lattice and oxidation occurs as a result of Eu^{2+} ions diffusing from the bulk material to the surface [27, 28]. If the amount of oxygen adsorbed is limited so will be the number of Eu^{3+} that can be generated. Equally, the reaction can be slowed if the increasing concentration of Eu^{3+} prevents diffusion of Eu^{2+} to the surface and at this point it would depend on diffusion of the Eu^{3+} ions away from the surface.

An attempt has been made to develop a model of the oxidation process based on the Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory which characterises a process as having initiation, growth and saturation phases. The model is described by Equation (3.1), where k is a temperature dependent growth rate and n is called the Avrami exponent.

$$\rho = 1 - exp(-kt^n) \qquad (3.1)$$

The KJMA process is well known to represent crystallization, phase change and oxidation processes[29].
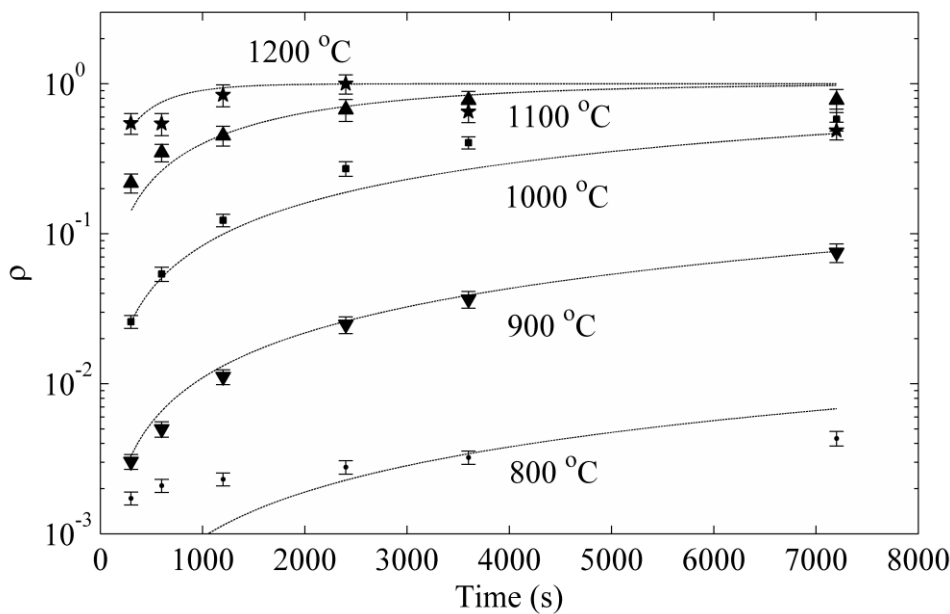

Figure 5 includes curves fitted to the experimental data based on the KJMA equation with the growth term k conforming to an equation of Arrhenius type. At temperatures from 900 °C to 1200 °C there appears to be a good fit with the theory for an exponent of 1. This suggests a process with little or no dependence on the initiation phase as might be the case if it were limited only by the rate of diffusion of Eu^{2+} ions to the surface. Curiously at 800 °C, the data does not conform to the KJMA theory suggesting that at this temperature a different process occurs. Yamada et al.[30] suggested that for temperatures of 900 °C or above a new phase starts to emerge which would explain the change of behaviour.

If a single equation of the KJMA type could be fitted to data covering the entire dynamic range of the phosphor then it would be possible to determine the temperature from the phosphorescent signal and knowledge of the exposure period only and for temperature in the range 900 °C to 1200 °C this appears to be possible. Extending the dynamic range to lower temperatures is still possible but would require more calibration data, perhaps in the form of look-up tables, to be available.
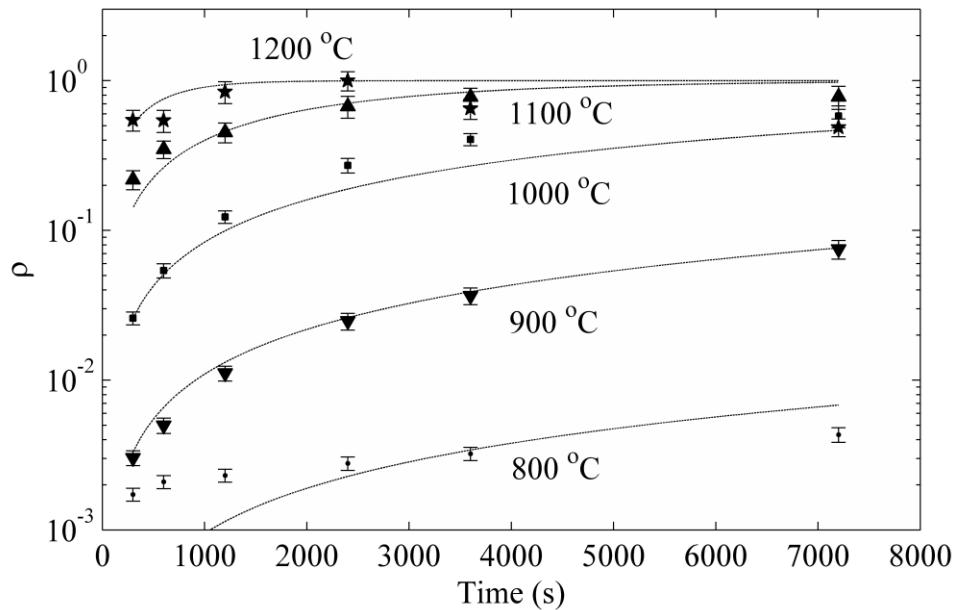
The data presented in

Figure 5 suggest that a-priori knowledge of the likely temperature could be used to improve the precision of the measurements made if it were possible to dictate the exposure period. Of course, the duration of the exposure is normally restricted by other operational requirements so that the precision of the measurement will not normally be open to manipulation in this way. Nevertheless, for temperatures approaching 1200 °C exposure times of less than 20 minutes would provide best precision, while for temperatures in the 700-900 °C range longer exposure times would be preferable. The exposure times discussed for the current sensor compare favourably with those of thermal paints, in that they are longer and permit more cost effective engine tests with other measurement campaigns operating simultaneously. Thermal paints normally offer best results for exposures of only 5 to 10 minutes.

3.4. *Dopant concentration*

The resistance to degradation of BAM:Eu has been previously reported to increase with Eu concentration [31]. Thus, by increasing the dopant concentration the oxidation process should slow making it possible to measure higher temperatures for the same exposure time. This has been investigated in BAM:Eu samples manufactured in-house by the sol-gel method. Three samples were manufactured with dopant concentrations of 5 %, 10 % and 15 % and heat treated in air at different temperatures for 20 minutes. The intensity ratio results are shown in
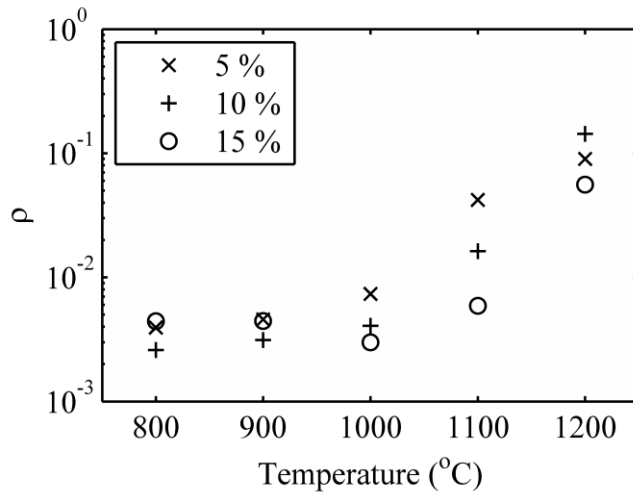
Figure 6. None of the samples respond below 900 °C and ρ remains almost constant. Oxidation becomes apparent above 900 °C for samples with 5 % and 10 % Eu and above 1000 °C for the sample with 15 % Eu. The intensity ratio of the sample with 5 % Eu increases fastest in the 900-1000 °C range which means that this phosphor responds more rapidly at these temperatures. At 1200 °C, the slope of the ρ curve of this sample decreases indicating that the process is slowing. This can be compared to the commercial BAM sample of Figure 1, in which this saturation effect begins at around 1000-1100 °C.

The intensity ratios of the samples with 10 % and 15 % Eu keeps increasing at constant slope up to 1200 °C. The ρ curve of the 15 % sample is effectively shifted to the right compared to the 10% sample which means that this sample only reaches the same level of oxidation at a higher temperature and confirms the hypothesis that dopant concentration can be used to tune the phosphor to measure higher temperatures.

Differences in ρ between sol-gel and commercial BAM samples can be explained considering the different synthesis processes. The different temperatures used for sintering in the solid-state synthesis route of commercial phosphors result in differences in crystallinity and grain size. Crystallinity has been reported as a factor that affects the resistance to thermal degradation of BAM [28] and grain size, which is directly related to surface area, has an influence on the oxygen adsorption process that leads to its thermal degradation.

3.5. Cooling down time

So far powder samples were heat treated in a furnace that was set at the desired temperature and after exposure samples were quenched in air. Typical cooling down times did not exceed 3 minutes. However, in real applications where the component is mounted in an engine, the cooling down time can be significantly longer and this could introduce some measurement error.

To study the effect of cooling down time samples were heat treated at 1000 °C for 20 minutes. These samples were then slowly cooled down inside the furnace. The cooling down rate was controlled by introducing a constant flow of air into the furnace. Temperature of the sample was continuously monitored with the thermocouple and the cooling down time was determined as the time needed to reach 500 °C, a temperature at which the oxidation rate of BAM is considered negligible.

A plot of the intensity ratio of the heat-treated samples versus the cooling down time is shown in
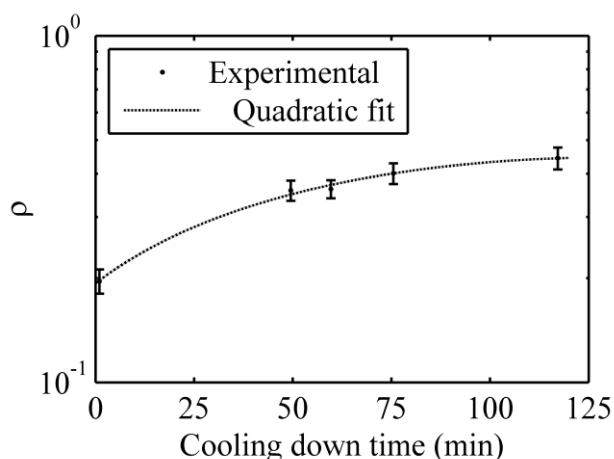
Figure 7. This plot confirms that longer cooling down times result in further degradation of the phosphor, although this degradation is not linear and becomes less significant as cooling down time increases. The difference in the temperature measurement between a sample rapidly quenched and a sample that has cooled down for about 120 minutes is only 4 % and this error could be corrected in real measurements.

Although in this study the cooling down time has been used to analyse the results, the use of a more appropriate variable that simultaneously accounts for the cumulative effects of temperature and time might be advisable, especially if non-uniform cooling down rates are present. This could be achieved by integrating the growth rate (k) over time if the cooling down temperature profile is available. Additionally, the study of the heating up rate is analogous to the cooling down effect and the error can be estimated and corrected in a similar manner.

3.6. Atmosphere

The sensing capabilities of BAM rely on the oxidation of Eu^{2+} ions which is possible in air due to the presence of oxygen. However, the effect that variations in the oxygen partial pressure have in the degradation of BAM has not been previously investigated. This is important since oxygen concentrations in real applications might vary and introduce errors in the measurement.

In this work the effect of oxygen partial pressure was studied for powder samples heat treated at 1000 °C for 20 minutes. The atmospheric composition was adjusted by mixing flows of air, nitrogen and oxygen in the required proportions to obtain oxygen partial pressures that varied from approximately 0.02 bar to 0.31 bar (the normal partial pressure of oxygen in air is about 0.21 bar). The intensity ratio for these samples is plotted against the oxygen partial pressure in
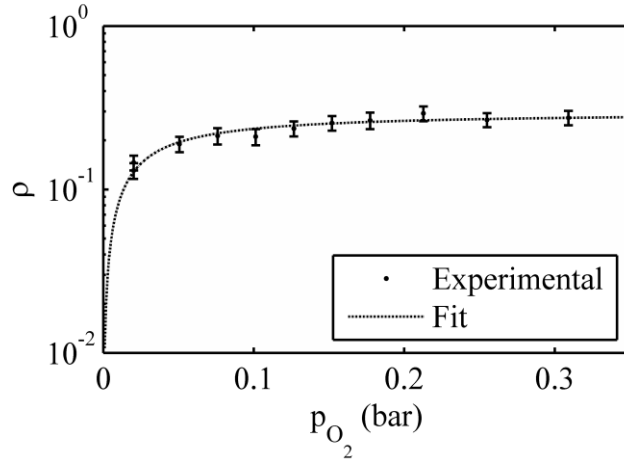
Figure 8. The intensity ratio for these samples is nearly constant for partial pressures of oxygen higher than 0.1 bar and conversion of ρ to temperature gives a temperature difference of less than 2 % in this range. For partial pressures of less than 0.1 bar ρ rapidly decreases and the temperature difference measured at 0.02 bar is of about 4 %.

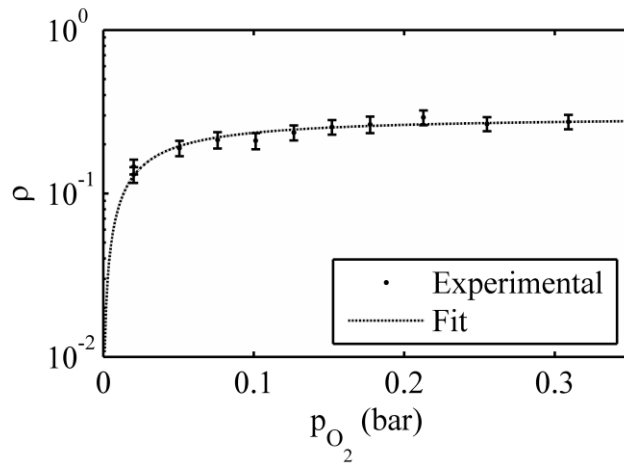The experimental results in

Figure 8 can be explained by the degradation model proposed by Bizarri and Moine [27] in which oxygen adsorption at the BAM surface is the first step. According to this study the adsorption of oxygen can be approximately described by the Langmuir isotherm, which at constant temperature (in this case 1000 °C) can be expressed as:

$$N = \frac{N_0 \alpha p_{O_2}}{1 + \alpha p_{O_2}} \tag{3.2}$$

where N is the number of adsorbed molecules, N_0 is the total number of vacancies that can be filled, α is a constant and p_{O2} is the partial pressure of oxygen. Therefore, if the number of Eu^{2+} atoms oxidised is considered proportional to the number of oxygen ions adsorbed and the intensity of the Eu^{2+} and the Eu^{3+} emissions proportional to the number of each ion present in the material, ρ can be described by an equation which has the same form as the Langmuir isotherm but with different constants. This is confirmed by the fit of the data shown in
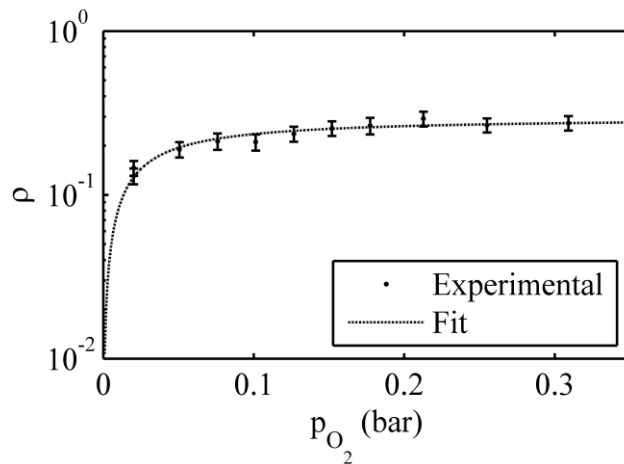
Figure 8. This assumption implies that further increase in the oxygen concentration has no effect in ρ because adsorption has reached saturation.

This is important in the case of gas turbines where compression ratios as high as 45:1 and oxygen consumption in the combustor result in high and variable oxygen partial pressures. According to the data in
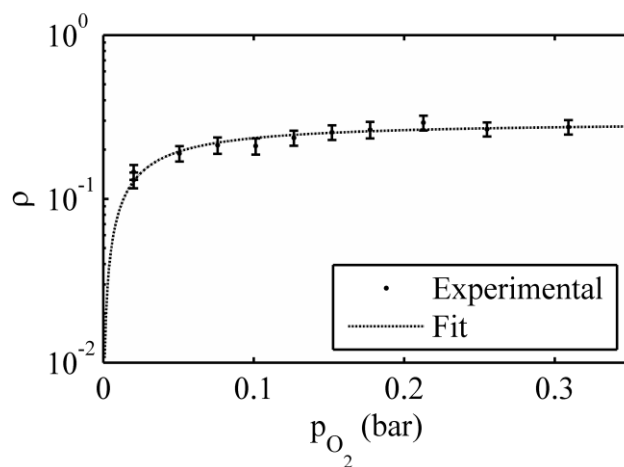

Figure 8, variations in the partial pressure of oxygen in different regions of the gas turbine would not affect the measurement as the partial pressure would in all cases remain much higher than this 0.1 bar threshold.

The results for ρ in a variable oxygen atmosphere, whilst confirming the first step of the three-step mechanism proposed by Bizarri and Moine [27], have implications for the future development of a sensor coating. The density of such a coating, and more importantly the open porosity, would play a major role in the oxidation as the specific surface area determines the amount of oxygen that can be adsorbed. Careful control of the porosity is likely to be crucial to the development of a BAM:Eu coating and is the subject of on-going research by the authors.

4. Conclusions

The performance of the phosphor BAM:Eu as a temperature history sensor has been evaluated in a range of temperatures from 700 °C to 1200 °C. Oxidation of Eu^{2+} to Eu^{3+} generates changes in the optical spectrum and lifetime decay of the phosphor that can both be used to measure the temperature to which the material has been exposed. Measurands composed of the intensity ratio between spectral lines representing the Eu^{2+} and Eu^{3+} ion emissions and the time constant of the lifetime decay of emission from the Eu^{3+} ions can be employed to measure temperatures up to at least 1100 °C.

The effect of the exposure time on the degradation of the phosphor has been investigated in samples heat treated from 800 °C to 1200 °C with exposure times from 5 to 120 minutes. For exposure temperatures in the range 900 °C to 1200 °C the intensity ratio tends to a constant value suggesting saturation and in this temperature regime the results conform to the well-known KJMA process and may be represented by an expression wherein exposure time is the independent variable and temperature the dependent one. At lower temperatures the response does not conform to the KJMA theory although a temperature and exposure time variation in the intensity ratio still occurs. The thermal degradation processes of BAM:Eu are known to be complex with several processes occurring simultaneously, sequentially or in opposition. A change in the mode of behaviour at around 900 °C has been previously reported and the data from the present study support this observation although they do not clearly identify the nature of the change. From the point of view of sensor development, in the range 900 °C to 1200 °C calibration data may be fitted to a KJMA expression but if a wider dynamic range is required raw calibration data, in the form of look-up tables, must be used. The best accuracy at high temperatures would be obtained for exposures of less than 20 minutes, which compares well with current thermal paints.

The response of the phosphor can be adjusted by changing the dopant concentration and thereby it can be tuned to the expected measurement range where a-priori information is available providing greater precision particularly at higher temperatures and longer exposure times.

The effect that excitation energy, cooling down time and atmosphere composition have on the temperature measurement accuracy has been investigated. The error introduced by laser fluence fluctuations can be considered negligible as even unrealistically large changes in fluence from 5 mJ/cm^2 to 50 mJ/cm^2 only affects the temperature reading by 0.5 %. The cooling down time can be regarded as an additional period of exposure and is therefore reflected in a greater degree of reaction and a higher intensity ratio. Differences in response from rapidly quenched samples and samples cooled over a period of 120 minutes were about 4 %. This effect must thus be considered and corrected for in each specific application. Finally, the effect of the bath gas composition has been investigated in samples heat treated in atmospheres with a variable oxygen concentration. It was found that the effect can be considered negligible as long as the partial pressure is higher than a threshold level of about 0.1 bar at 1000 °C.

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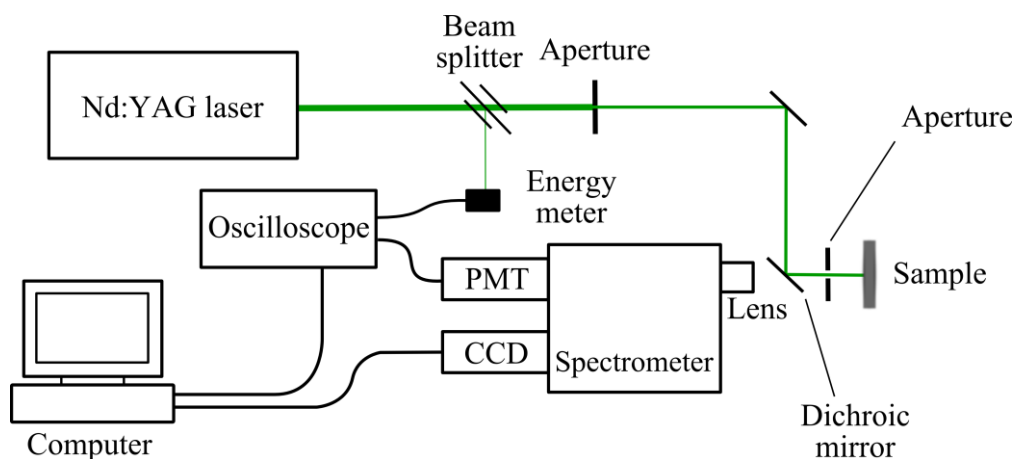
Figures

Figure 1. Experimental set-up for luminescence measurements.
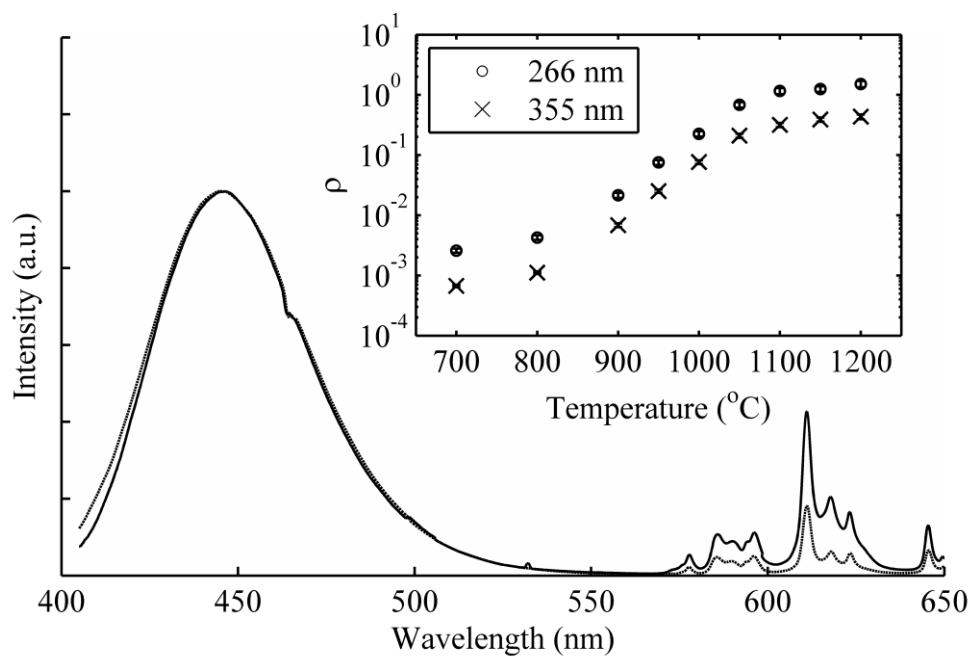

Figure 2. Emission spectra of BAM:Eu excited at 266 nm (continuous line) and 355 nm (dashed line), normalised to the broad band peak. The inset shows the intensity ratio versus heat treatment temperature for samples heat treated for 20 minutes and excited using the two different excitation wavelengths.
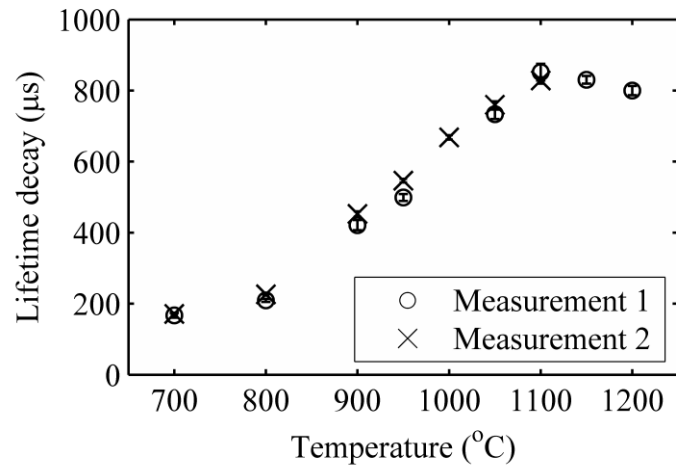
Figure 3. Lifetime decay of the emission at 611 nm versus heat treatment temperature for samples treated for 20 minutes and measured using two different set-ups.
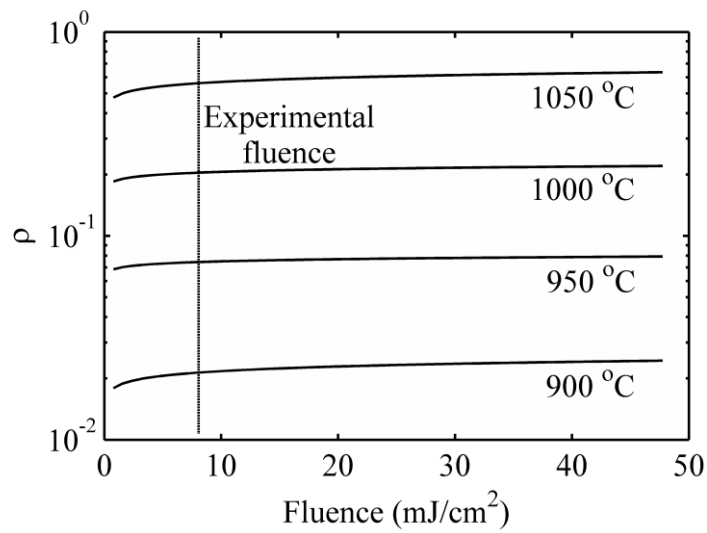
Figure 4. Intensity ratio at different excitation fluences of BAM:Eu samples heat treated at 900 °C, 950 °C, 1000 °C and 1050 °C for 20 minutes. The dashed line indicates the standard fluence condition used throughout experiments.
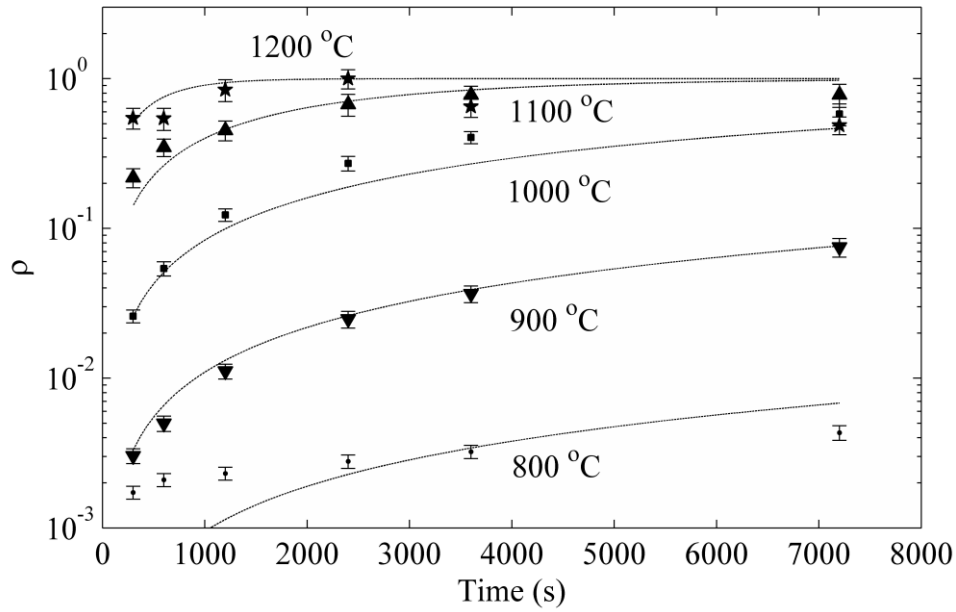
Figure 5. Normalised intensity ratio for samples heat treated at 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C; and exposure times of 5 min, 10 min, 20 min, 40 min, 60 min and 120 min. The data of each time series is fitted according to the KJMA theory.
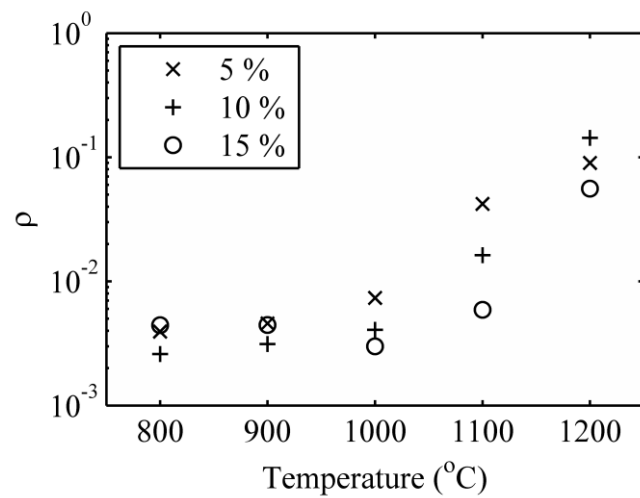

Figure 6. Intensity ratio calibration curve of sol-gel manufactured BAM:Eu with 5 %, 10 % and 15 % Eu content. Samples were heat treated for 20 minutes.
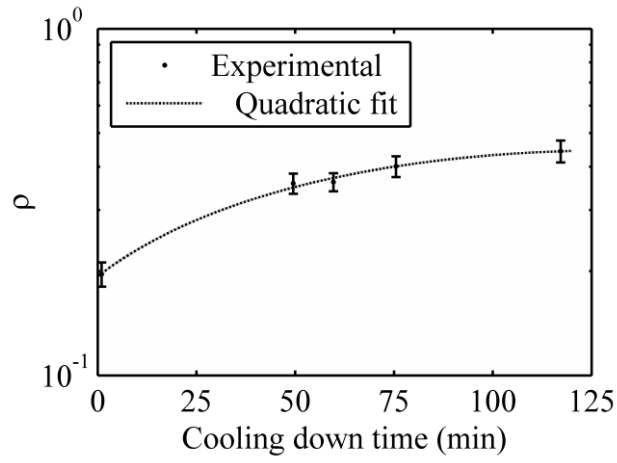
Figure 7. ρ versus cooling down time for the sample heat treated at 1000 °C for 20 minutes.
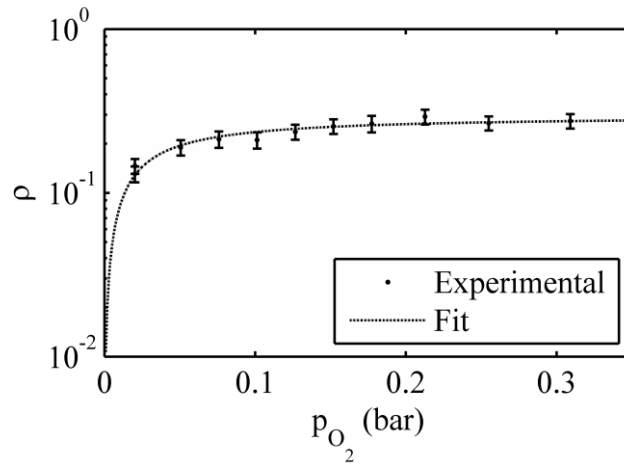

Figure 8. ρ versus oxygen partial pressure for samples heat treated at 1000 °C for 20 minutes in an oxygen controlled atmosphere.