Measuring the optical thermometry properties of La_2O_2S:Eu phosphor material

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Abstract. This paper is focused on the investigation and measurement of optical thermometry properties of Lanthanum Oxysulphide doped with Europium (La_2O_2S:Eu) by utilising the Photoluminescence (PL) technique. After a literature study it was concluded that the optical thermometry properties of phosphor materials can be measured by several techniques. The technique used in this paper is the fluorescence intensity ratio technique. This technique consists of obtaining the fluorescence spectra of a phosphor material and monitoring the intensity ratio between two thermally coupled levels as a function of temperature. The PL system in the Physics department at the University of the Free State was modified to measure the fluorescence spectra of a phosphor material at temperatures range from room temperature to 700 K. The modified PL system was used for the measurements of the optical thermometry properties of La_2O_2S:Eu for this paper.

1. Introduction

It is generally known that the energy to light conversion efficiency of some inorganic phosphor materials is temperature dependent and therefore gives these phosphor materials their temperature sensing characteristics. Phosphor materials that exhibit this characteristic are also known as thermographic phosphors. [1] A generic phosphor thermometry system consists of an excitation source that is used to excite the phosphor material that is bonded to the surface of interest. [2] The emission of the phosphor material is then analysed and compared to pre-calibrated data to determine the temperature of the surface in question.

The system design in terms of the excitation source, phosphor material and detector will depend on the application in interest. The excitation source can vary between a flash lamp, Light Emitting Diode and a laser that can also be a continuous or a pulsed source depending on the technique that is used as will be explained in the theory section. [2] There are a large number of phosphor materials that have different responses in comparison to temperature range and sensitivity that can be matched to a variety of applications. A Photo Multiplier Tube (PMT) or a Charge Couple Device (CCD) can be used for detection of the emitted light from the phosphor material. [2]

Thermographic phosphors that are used in the thermometric technique are adaptable to the needs of a wide variety of situations. It provides a *non-contact* optical alternative for measuring temperature in contrast to other conventional techniques and can therefore also be employed in systems where other thermographic techniques are not suitable. [1]

2. Theory
There are several ways the temperature dependence of phosphor materials is manifested. The properties measured to characterise the temperature dependence of the phosphor materials are the intensity, rise and decay lifetime and the line shift and width of selected spectral features. [1] A summary of each of these techniques is given below.

2.1 Fluorescence Intensity and Fluorescence Intensity Ratio technique
When a light source excites a phosphor material, electrons are transferred to higher energy states which also return back to their ground states. This is known as electron transitions. Usually equilibrium between excitation and de-excitation is reached which results in a steady emission intensity that is emitted by the phosphor material. If the temperature increases a decrease in emission intensity is observed. This is due to an increase in the probability of non-radiative processes with an increase in temperature. Thus by calibrating the fluorescence intensity response as a function of temperature, temperature measurements can be made of the emission intensity. [2]

The fluorescence intensity based approach generally requires the simplest instrumentation and is therefore relatively cheap to implement. However difficulty arises with the maintaining of intensity calibration since the intensity of emission is also a function of other variables. These variables include non-homogenous illumination, light source instabilities, distance and angle of detector. [2] Thus a better approach that eliminates most of these variables is the Fluorescence Intensity Ratio (FIR) technique.

The FIR technique uses the ratio of two or more fluorescence emission lines at different wavelengths of a phosphor material to determine the temperature response. Phosphor materials that are good thermographic phosphors exhibit multiple emission response where some emission lines being less or more sensitive to change in temperature which makes the use of the FIR technique possible. [2-4]

2.2 Fluorescence Lifetime technique
When a phosphor is excited by a pulsed source, the resulting fluorescence can be observed as the fluorescence intensity rises and decays exponentially. The lifetime of the fluorescence is a function of temperature and is therefore a useful method of thermometry. The fluorescence lifetime approach does not suffer the same disadvantages as the intensity based approach because rise and decay rates can be measured in terms of time and therefore offers less uncertainty since this quantity can generally be determined with greater accuracy than optical intensities. However to measure the fluorescence intensity rise and decay one must use a fast analog-to-digital converter which could be costly. [1]

2.3 Fluorescence Line Shift and Line Width technique
Each emission line of a phosphor is characterised by a wavelength for which the intensity is a maximum. Line shifts may occur with a change in temperature. Each emission line also has a finite width, which is often designated as the full width half maximum which also changes with a change in temperature. Line shift and line width changes as a function of temperature are usually small and therefore not often used in fluorescence thermometry as compared to the intensity and lifetime techniques. [1]

In this study only the fluorescence intensity and FIR technique was used to characterise the temperature response of Lanthanum Oxysulphide doped with Europium (La_2O_2S:Eu). [5]

3. Experimental
Commercially available La_2O_2S doped with Eu, from Phosphor Technology, was selected for this study since it was reported in a previous study to shown a decrease in emission intensity for the temperature range 292 K to 333 K. [2] An X-ray diffraction (XRD) pattern of the La_2O_2S:Eu was measured with the D8 Advance Bruker XRD apparatus. The emission spectra containing the different emission peaks were monitored for the La_2O_2S:Eu from 200 nm to 580 nm by using a Cary Eclipse fluorescence spectrophotometer (Varian).

The Photoluminescence (PL) system in the Physics department at the University of the Free State is capable of measuring fluorescence spectra of a phosphor material at room temperature and thus it was necessary to modify the system for this study. Figure 1 shows a basic layout of the modified PL system. At the top left corner is the (a) Helium-Cadmium (Kimmon IK Series, model KR1801C) laser. The laser beam was filtered with a (b) band-pass filter (Newport 10LF10-325) to pass only a 325 nm laser beam that was used as the excitation source. The laser beam was directed (c) onto the La_2O_2S:Eu phosphor material (Phosphor Technology SKL63/F-R1) and the emitted light of the phosphor was directed towards (d) a fibre optic cable that was connected to (e) a spectroscope (Ocean Optics, Model USB2000+). The spectroscope uses a diffraction grating to divide the emitted light into its different wavelength components and a (f) CCD to generate an electrical signal from the light spectrum and the spectrum is then displayed and stored on (g) a computer.

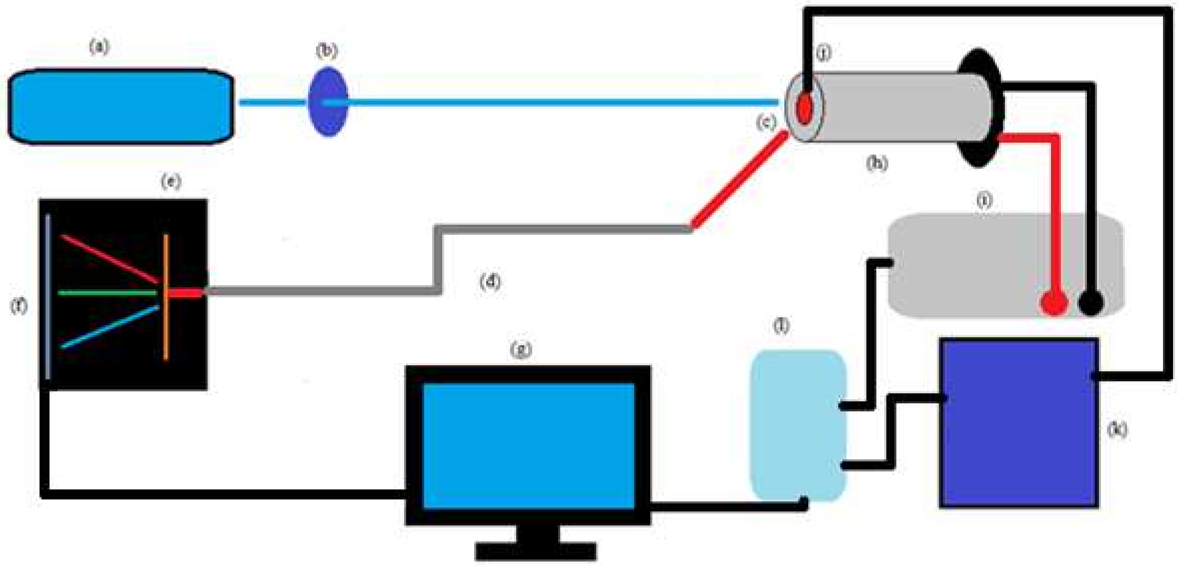

Figure 1. Experimental setup for analysing temperature dependent fluorescence intensity, (a) Helium-Cadmium laser, (b) filter, (c) La_2O_2S:Eu phosphor material, (d) fibre optic cable, (e) diffraction grating, (f) CCD, (g) computer, (h) heating element, (i) power supply, (j) thermocouple, (k) temperature display unit and (l) digital-to-analog and analog-to-digital converter.

The La_2O_2S:Eu phosphor material's temperature was changed by placing it in (h) a custom build heater and the temperature was controlled by a software program developed by the author. The temperature control software controlled (i) the power supply (Manson Switching Mode Power Supply, 1-30 VDC, 15 A, model HCS-3302) for (h) the heater. The temperature of the phosphor material was measured by a thermocouple (K-type) that was connected to (k) a unit that displayed the temperature as can be seen in figure 1. Both the temperature display unit and power supply was connected to (l) a digital-to-analog and analog-to-digital converter (uDAQ Lite Micro DAQ Data Acquisition, Serial D1000014395) that was also connected to a computer. The temperature control program uses a proportional-integral-derivative (PID) controller to control the temperature of the phosphor material.

The setup was used to excite the La_2O_2S:Eu phosphor material at a wavelength of 325 nm and to record the emission spectra at temperatures ranging from 300 K to 500 K in 10 K steps.

4. Results and Discussion

The XRD pattern of the La_2O_2S:Eu is shown in figure 2. As it can be seen in figure 2 there is a good correlation between the measured pattern and the known data for La_2O_2S (PDF-Number 27-0263). Therefore the La_2O_2S:Eu phosphor material can be recognised as well-crystallised particles in the hexagonal phase with cell parameters of a=4.051 Å and c=6.944 Å. The peak that is marked with a dash appears if it may be from Lanthanum Oxide (La_2O_3) (PDF-Number 05-0602) impurity.

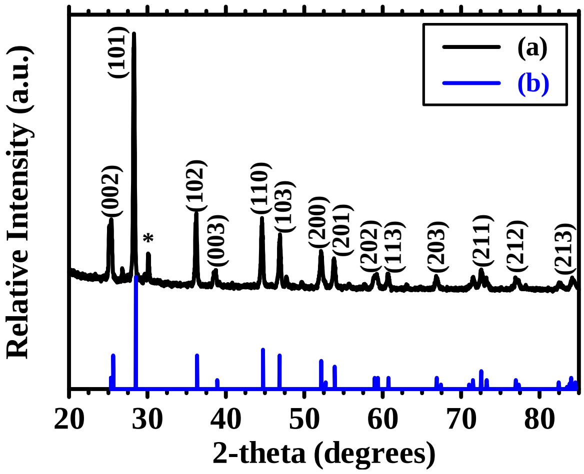

Figure 2. (a) Measured XRD pattern for the La_2O_2S:Eu phosphor material and (b) the standard data of the XRD pattern for the La_2O_2S:Eu phosphor material with peak indexing.

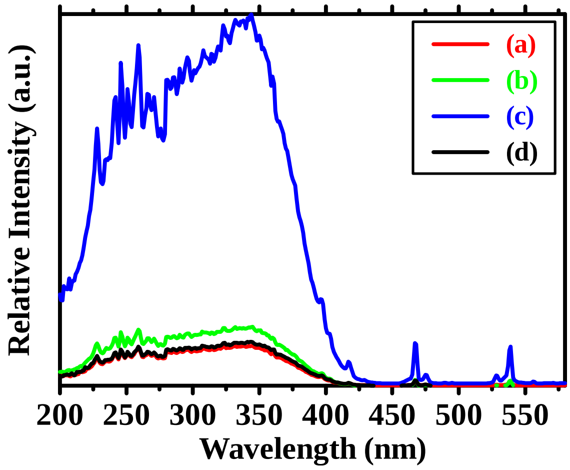

Figure 3. Excitation spectra of the (a) 594 nm, (b) 616 nm, (c) 624 nm and (d) 704 nm emission lines of La_2O_2S:Eu.

The excitation spectra (figure 3) of the 594 nm, 616 nm, 624 nm and 704 nm emission peaks were monitored for the La_2O_2S:Eu from 200 nm to 580 nm. It can be seen in figure 3 that the 325 nm He-Cd laser wavelength used in the PL system falls in the correct range for efficient excitation of the current phosphor.

The emission spectra of the La_2O_2S:Eu phosphor material was measured by the PL system at different temperatures as explained in the experimental section. Figure 4 shows the emission spectra for 5 different temperatures and it can be seen that the intensities of the emission lines decreased as the temperature increased. The integrated intensities were calculated for the six main peaks (that are numbered in figure 4) and plotted as a function of temperature in figure 5.

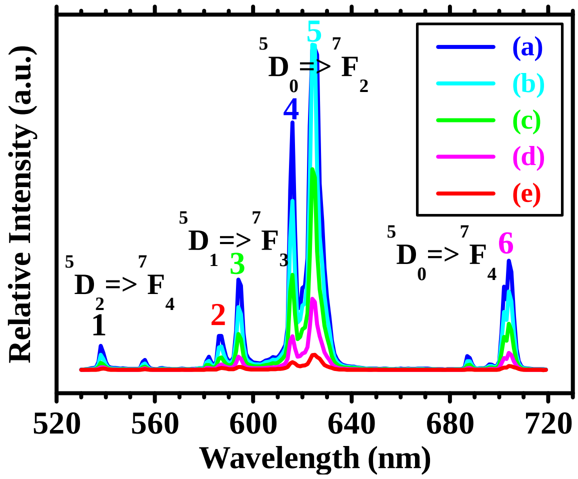

Figure 4. Emission spectra of La_2O_2S:Eu at 325 nm wavelength excitation at (a) 300 K, (b) 350 K, (c) 400 K, (d) 450 K and (e) 500 K with peak indexing corresponding to transitions of the Eu^{3+} ions. [6]

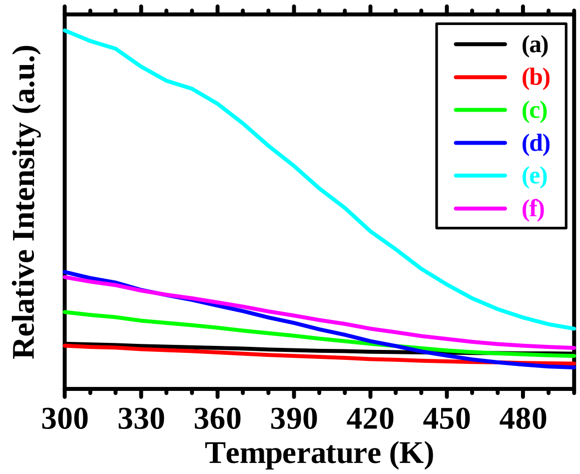

Figure 5. Emission intensity as a function of temperature for the (a) Peak 1 (535 nm - 544 nm), (b) Peak 2 (585 nm - 591 nm), (c) Peak 3 (591 nm - 599 nm), (d) Peak 4 (614 nm - 618 nm), (e) Peak 5 (618 nm – 630 nm) and (f) Peak 6 (699 nm – 709 nm) as numbered in figure 4.

To employ the FIR technique the intensity ratio of the different peaks were taken. The intensity ratio between some of the peaks as a function of temperature can be seen in figure 6. Figure 7 shows the Arrhenius plot for the same data as in Figure 6.

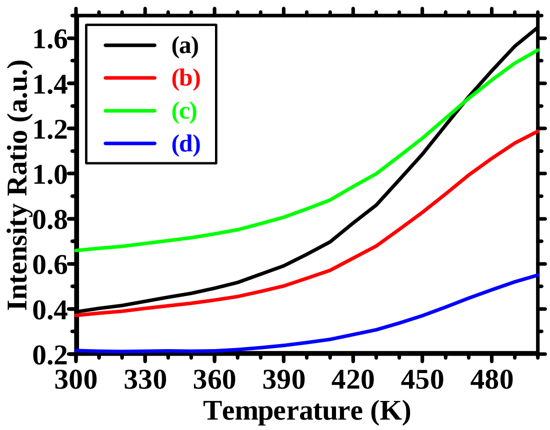

Figure 6: Intensity ratios between (a) Peak 1 / Peak 4, (b) Peak 2 / Peak 4, (c) Peak 3 / Peak 4 and (d) Peak 3 / Peak 5 as a function of temperature.

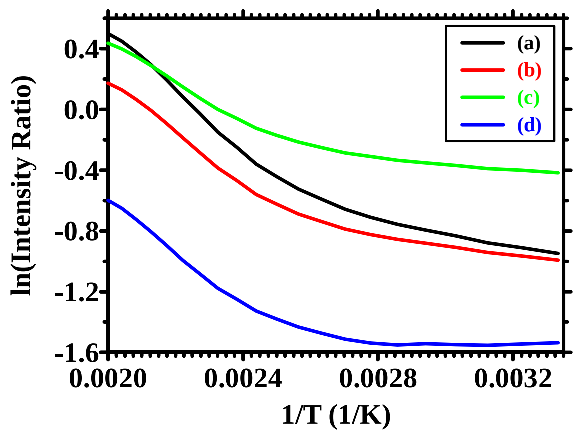

Figure 7: Arrhenius plot for intensity ratios between (a) Peak 1 / Peak 4, (b) Peak 2 / Peak 4, (c) Peak 3 / Peak 4 and (d) Peak 3 / Peak 5.

It can be seen in figure 6 that the ratios between different peaks intensities vary sufficiently that La_2O_2S:Eu could be used as a temperature sensor in the 300 K to 500 K temperature range. Thus by using the FIR technique the effect of the environmental variables could be eliminated and allow La_2O_2S:Eu to be used as a temperature sensor.

5. Conclusion

In this paper the measurement of optical thermometry properties of La_2O_2S:Eu by utilising the PL technique was successfully demonstrated. The fluorescence intensity technique where the fluorescence spectra of a phosphor material is obtained and monitored as a function of temperature was used to achieve this and by using the FIR it was shown that La_2O_2S:Eu could be used as a temperature sensor in the 300 K to 500 K temperature range. The PL system in the Physics department at the University of the Free State was also enhanced to allow the investigation of thermographic phosphors by using the fluorescence intensity technique. However the spectroscope must be replaced with a device that is capable of measuring higher resolution emission spectra to allow higher quality data.

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