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Blue and red cathodoluminescent emission of Y_2O_3:Eu phosphor studied as a function of temperature in a transmission electron microscope

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ABSTRACT

Combined EELS, CL and STEM imaging are used to characterize and study Y_2O_3:Eu to confirm the variation in CL properties and photo-luminescent properties observed. The synthetic procedures used have facilitated this material to manifest a strong blue emission at low temperature with the expected red emission dominating at room temperature.

1. INTRODUCTION

We have previously shown how cathodoluminescence can be used inside the transmission electron microscope to study phosphors such as Y_2O_2S:Tb,[1] Gd_2O_2S:Tb[2] and the quantum dots, CdSe/ZnCdS[3] and dot-in-rods CdSe/CdS[4] which have wide ranging applications in scintillation phosphors through to the latest developments in high information content television displays. In order to develop improved synthetic techniques for the fabrication of phosphors it is important to understand the impact of the procedure used and the effect of the materials used to facilitate this. In this work we will show the effect of solvent in synthesizing Y_2O_3:Eu^{3+} and show how this has dramatically influenced the emission properties of the phosphor produced.

In the class of rare earth phosphors europium has a unique position, because it can be divalent or trivalent in a host lattice. Both divalent and trivalent Eu phosphors enjoyed considerable industrial interests: $BaAl_2S_4$:Eu^{2+} as blue phosphor in thin film electroluminescent displays[5] and Y_2O_3:Eu^{3+} as red phosphor in fluorescent lamps and projection cathode ray tubes (CRTs)[6]. The usual way to prepare Eu^{2+} phosphors is by annealing in a reducing atmosphere, while Eu^{3+} phosphors are normally prepared in oxidizing atmospheres, notably air. Besides these normal chemical synthesis methods it has been shown that certain oxygen containing crystals can be doped with Eu^{2+} by annealing in air[7,8]. In many oxygen containing crystals the Eu^{3+} dopant can be reduced to Eu^{2+} by exposure to high energy radiation such as UV[9,10], X-rays[11], β-rays[12], γ-rays[12,13], femtosecond laser pulses[14] and electron beams[15]. A comprehensive theory on the role of the lattice does not exist; however, some properties are supposed to be important. One is the electronegativity difference between oxygen and the cation that is replaced by Eu^{3+}. Another is the crystal structure, i.e. the coordination number of Eu^{3+} in the lattice and finally, the level of the charge transfer (CT) band, although, from the evidence available in the literature it cannot be concluded that a low CT level (as present in Y_2O_3:Eu^{3+}) is enhancing the $Eu^{3+} \rightarrow Eu^{2+}$ reduction in oxygen containing crystals[9,10,12,13].

2. EXPERIMENTAL

Yttrium oxalate and europium oxalate in isopropanol (IPA) were mixed and transferred to a desiccator under vacuum to remove the IPA. The resulting powder with a Eu concentration of 6.37% was oven dried at 100^oC. Portions of the dried powder were fired at 1300^oC for periods of time ranging from 0.5 hours to 3.5 hours.

The samples were characterised using bulk cathodoluminescence (CL) and Photoluminescence (PL) spectroscopy measurements which were carried out using a Bentham Instruments dual excitation and emission monochromator system. CL measurements were made whilst exciting a powder sample mounted onto an SEM stub inside a vacuum chamber with electron beam energies ranging from 1-3 kV impinging on the sample. A Pritchard PR880 photometer was used to measure the luminance.

All electron microscopy measurement were carried out (and CL STEM) at a temperature range of 30^oC to -167^oC) in a JEOL 2100F analytical TEM operated at 200 kV by dispersing the sample onto holey carbon coated copper grids. STEM was carried out using a Gatan HAADF detector. CL images were collected using a Gatan Vulcan™ system. A Gatan Electron Energy Loss Spectrometer was used to map the position of the europium ions.

3. RESULTS AND DISCUSSION

The morphology of the particles produced manifest as large sheets of sintered ~100 nm sized particles as shown in figure 1.

Sample no.	Firing time (hours)	Voltage (volts)			
1	0.5	1000	1500	2500	3000
Cdm^{-2}		3.83	10.00	22.2	29.60
Colour		violet	violet	violet	violet
2	1.0	1000	1500	2500	3000
Cdm^{-2}		5.75	11.8	25.2	31.2
Colour		violet	violet	violet	violet
3	1.5	1000	1500	2500	3000
Cdm^{-2}		6.91	13.50	27.60	34.10
Colour		pink/violet	violet	violet	violet
4	2.0	1000	1500	2500	3000
Cdm^{-2}		5.44	10.40	21.90	27.30
Colour		pink/violet	violet	violet	violet
5	2.5	1000	1500	2500	3000
Cdm^{-2}		7.07	12.50	25.70	31.80
Colour		pink	pink/violet	violet	violet
6	3.0	1000	1500	2500	3000
Cdm^{-2}		6.92	13.20	26.30	30.80
colour		red	pink/violet	violet	violet
7	3.5	1000	1500	2500	3000
Cdm^{-2}		6.92	12.70	24..40	28.00
colour		pink/violet	pink/violet	pink/violet	pink/violet
8	2.0	1000	1500	2500	3000
Cdm^{-2}		8.36	14.90	32.90	36.60
colour		violet	violet	violet	violet
9	3.0	1000	1500	2500	3000
Cdm^{-2}		4.29	8.59	17.20	20.60
colour		violet	violet	blue	blue

Figure 2 1-7 **fired at 1300°C and** 7-8 **fired at 950°C. Luminance and observable colour of samples prepared under various conditions.**
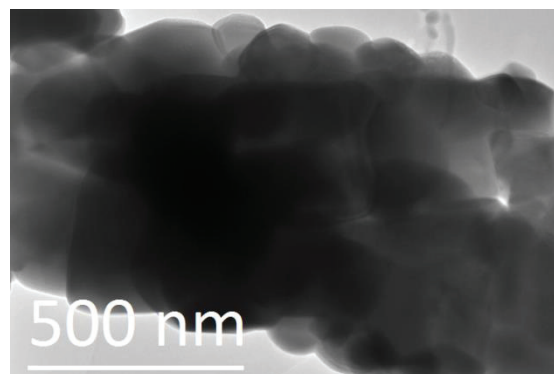

Figure 1 Annular dark field STEM image of Y$_2$O$_3$:Eu phosphor used in this study (Sample 1).

Under electron bombardment from 1kV to 3kV in a vacuum chamber, colours ranging from pink to blue were observed (figure 2). Under ultra violet light (254nm), these phosphors gave a dull red luminescence with a weak blue emission below 400nm (see figure 3).
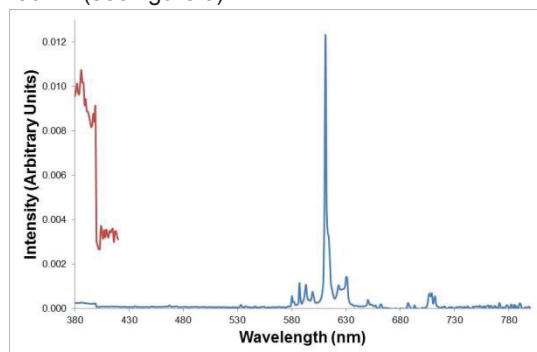

**Figure 3 Photoluminescent spectrum of Sample 1. Red line shows a times 40 expansion from 380-420nm.**
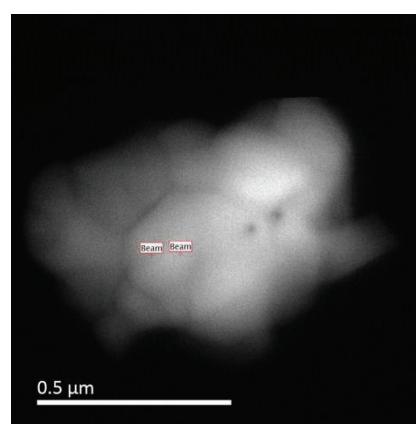
Figure 4 Panchromatic visible light image collected using the Vulcan photomultiplier tube.

In figure 4 the visible light emission from the particles is seen to be uniform across the cluster of particles which is consistent with the expected

uniform emission from this material prepared via a homogeneous precipitation route and indicated by the uniform distribution of Eu ions seen in the EELS map in figure 5.
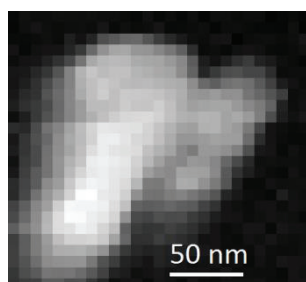
Figure 5 Thickness corrected Eu EELS map of particles showing the homogeneous distribution of Eu ions in Sample 1
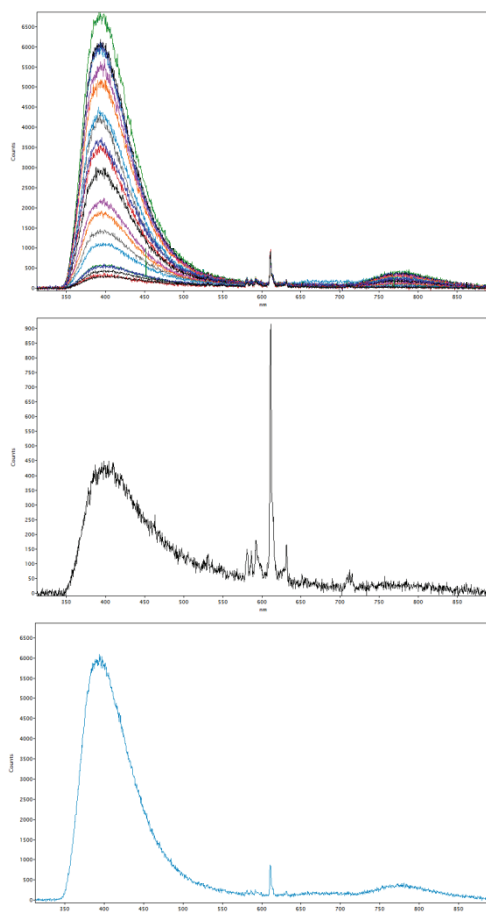

Figure 6 (top) CL spectra as a function of temperature from +30°C to -167°C, (middle) CL spectrum at +20°C, (bottom) CL spectrum at -167°C.

In figure 6 the emission properties of the sample shown in figure 1 are presented. At room temperature the sample manifests the expected Eu^{3+} emission with sharp line at 611 nm but in addition weak blue (394 nm) and deep red (773 nm) emission bands are observed. On reducing the temperature these two bands become dominant whilst the red emission intensity at 611 nm remains unchanged.

These emission bands correspond to those expected for the emission due to $Eu^{2+}(4f^6 5d$ to $4f^7$ transition)[6] the position of which is highly dependent on the host lattice. A plot of the CL emission intensity (Figure 7) over the linear portion gives an activation energy of 1280741 cm^{-1} at 394 nm and 66628 cm-1 at 773 nm. This electron beam reduction has been previously documented in host lattices such as anhydrates, sulfates and fluorites.[15] However we have not seen this behaviour in Y_2O_3:Eu^{3+} under normal synthesis using the urea precipitation method and a firing temperature around 1000°C.
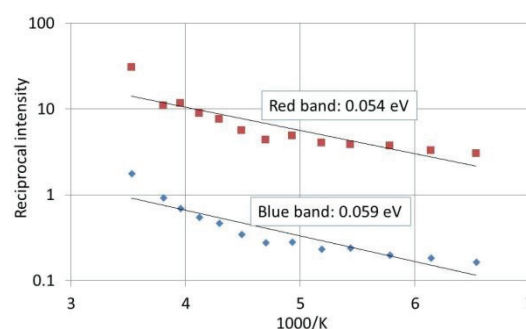
Figure 7 Arrhenius plot of the reciprocal intensity of the bands at 394 nm and 773 nm with trend lines showing the activation energies.

In figure 7 we have plotted the temperature dependence of the CL intensity spectra shown in figure 6. The two activation energies found are very similar which indicates that these two emission bands are related to the Eu^{2+} state. From this we find a small average activation energy of 0.057 eV. It is possible that there are 2 processes describing the temperature dependence, however we do not have enough information to be confident in this conclusion. To our knowledge this is the first time that this reduction of Eu^{3+} has been observed in the yttria lattice.

4. CONCLUSIONS

The reduction of Eu^{3+} to Eu^{2+} in yttria host crystals under electron bombardment has not been observed earlier. At low temperature this reduction is much stronger than at room temperature. Furthermore, it was found that nanosized Y_2O_3:Eu^{3+} made by the urea synthesis or commercial micrometer-sized Y_2O_3:Eu^{3+} could not be reduced under electron bombardment. The usual factory process to produce commercial Y_2O_3:Eu^{3+} is the oxalate precipitation method without an

intermediate step in IPA[6]. This step seems to be essential for the reduction of Eu^{3+}. At this moment we don´t have an explanation for the observed reduction of Eu^{3+} in the Y_2O_3 lattice. CL emission bands at 394 nm and 773 nm are shown to be related and assigned to Eu^{2+} in yttria.

5. AKNOWLEDGEMENTS

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