

## Studies of UV stimulated luminescence from phosphors of commercial importance

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### Introduction

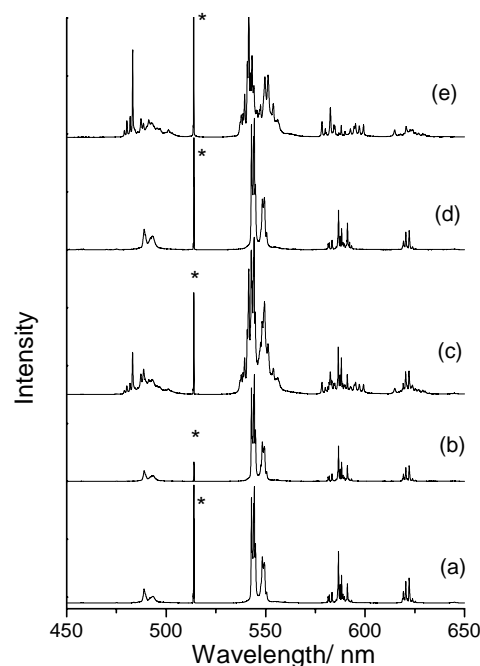
Field emission displays (FEDs) are flat panel displays that offer many of the advantages of CRT TV such as wide viewing angle, low power consumption and good colour gamut. However, in order for the FED TV to make significant advances, two technological challenges have to be met<sup>1)</sup>. First, the electron emitters need to be improved so that they have long lifetime and provide high current density when manufactured by a reproducible, cost effective process. Second, new low voltage cathodoluminescent phosphors need to be developed that are robust enough to withstand the relatively high current densities that are employed in FEDs. In an ongoing program of work we are currently investigating the synthesis and characterisation of new phosphors for FED applications. In addition to the above characteristics, the phosphors are required to have small particle sizes both for high definition of the image on the FED screen and for making up ink formulations that can be used for printing the phosphor on to the anode. Here we report the UV stimulated photoluminescence of red and green emitting low voltage cathodoluminescent phosphors,  $Y_2O_2S:Eu$  and  $Y_2O_2S:Tb$  respectively, which we have recently synthesized in small particle sizes. These photoluminescence spectra provide a convenient quality control for the synthetic methodology which is being developed.

### Experimental

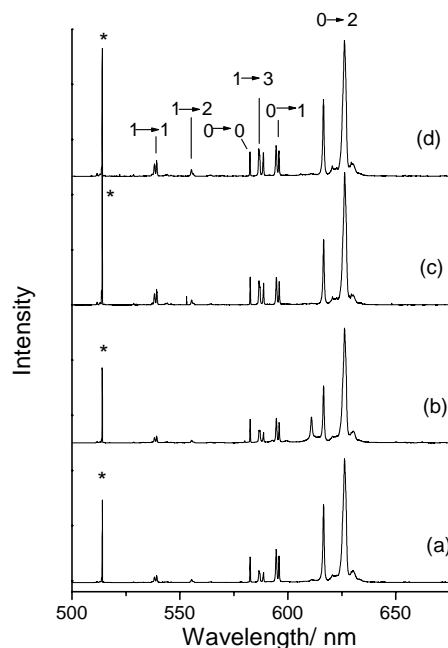
The urea homogeneous precipitation method was used to prepare spherical  $Y_2O_3:REE$  hydroxy-carbonate sub-micrometre phosphor precursor powders. Stock solutions of yttrium nitrate and REE nitrate were prepared from the respective oxides and nitric acid. Following the addition of urea the mixture was heated to boiling and this was maintained for two hours after precipitation had begun. The precipitated rare earth hydroxy carbonate was filtered, washed with distilled water and air dried. The rare earth hydroxy carbonate was then mixed with 3/2 mole equivalents of sodium carbonate and 2 mole equivalents of sulfur. A mixture of yttrium oxide, 1.5 mole equivalents of sodium carbonate and 2 mole equivalents of sulfur was ground together and added loose powder to the crucible in order to exclude as much air as possible. The crucible was covered and fired in a muffle furnace at a temperature of 900°C for 1 hour. After firing and cooling, the loose mixture at the top of the crucible was discarded and the tightly packed mixture was boiled with distilled water to remove flux and other impurities. The  $Y_2O_2S:REE$  samples were then fired in a tube furnace either in air in the temperature range of 900-1100°C or under an argon atmosphere at a temperature of 1100°C.

$Y_2O_3:Tb$  phosphor was prepared by firing the Tb doped yttrium hydroxy carbonate precursor at 980°C for 6 hrs to convert it to the oxide.

The resultant phosphors were excited with 257 nm laser light provided by an intracavity frequency-doubled argon ion laser (Coherent Ltd.) which is a loan pool laser (CWL3) from the Central Laser Facility. Emission spectra were collected with a Spex 1877 Triplemate Raman spectrometer equipped with a Peltier-cooled open electrode CCD detector (Wright instruments).



**Figure 1.** Photoluminescence spectra of  $Y_2O_2S:Tb$  under 257 nm excitation after firing for 1 hour at (a) 900°C in air, (b) 1000°C in air, (c) 1100°C in air, and (d) 1100°C under an argon atmosphere. The spectrum shown in (e) has been obtained from  $Y_2O_3:Tb$  under 257 nm excitation.

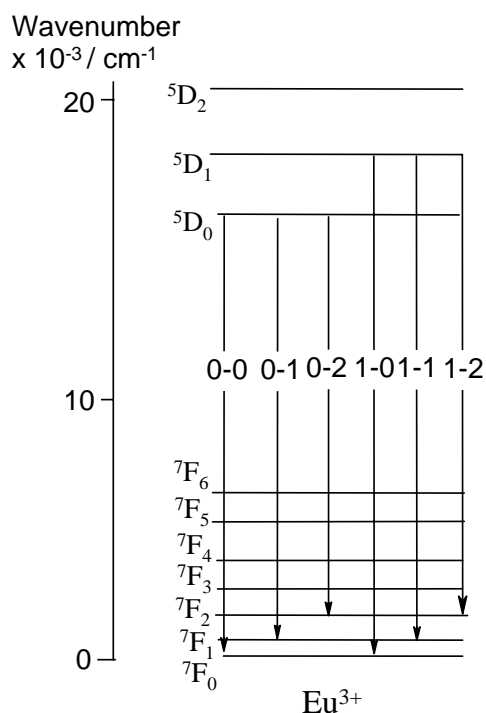


**Figure 2.** Photoluminescence spectra under 257 nm excitation of (a)  $Y_2O_2S:Eu$  (8 mol%) fired in air at 900°C, (b)  $Y_2O_2S:Eu$  (8 mol%) fired in air at 1000°C, (c)  $Y_2O_2S:Eu$  (4 mol%) fired in air at 900°C, and (d) a commercial sample of  $Y_2O_2S:Eu$ .

## Results and Discussion

Photoluminescence spectra of samples of  $Y_2O_2S:Tb$  have been obtained under 257 nm excitation (see Figure 1). Firing the phosphor samples in air at 900 and 1000°C for 1 hour gave similar photoluminescence spectra (see Figures 1a and 1b), but a different spectrum was obtained after firing in air at 1100°C for 1 hour (see Figure 1c). This spectrum was similar to that obtained from a sample of  $Y_2O_3:Tb$  (see Figure 1e). Clearly the yttrium oxysulfide lattice decomposes to yttria when fired at 1100°C in air. However, this decomposition does not occur if the yttrium oxysulfide is fired at 1100°C for 1 hour under an argon atmosphere, as is made evident by the photoluminescence spectrum (see Figure 1d) which is similar to those of Figures 1a and 1b. These spectra together with XRDs of the samples indicate that single phase terbium doped yttrium oxysulfide phosphor can be prepared by the novel two stage process described above. Pure phase yttrium oxysulfide can be obtained at the relatively low firing temperature of 900°C and when fired in an argon atmosphere at a higher temperature of 1100°C, in order to give improved cathodoluminescent brightness, the purity of the original phase is not affected.

Photoluminescence spectra of samples of  $Y_2O_2S:Eu$  have been obtained under 257 nm excitation (see Figure 2). The line at 514 nm, denoted by an asterisk in Figures 1 and 2 is due to the 257 nm laser line in second order. The spectra of  $Y_2O_2S:Eu$  (8 mol%) fired in air at 900 and 1000°C are shown in Figures 2a and 2b, respectively. An extra emission feature occurs in Figure 2b at 611 nm which is due to  $Y_2O_3:Eu$ <sup>2,3</sup>, suggesting that some partial oxidation occurs transforming the oxysulfide to the oxide. The emission lines observed in the spectra of Figure 2 have been assigned to the various  $^5D_J \rightarrow ^7F_J$  electronic transitions of the  $Eu^{3+}$  cation and these transitions are shown in the energy level diagram of Figure 3. As can be seen from the spectra of Figure 2, the emissions from  $^5D_1$  are quenched when the  $Eu^{3+}$  concentration is increased. This is manifested by a decrease in intensity of the 1-1, 1-2 and 1-3 emission lines relative to those of the 0-0, 0-1 and 0-2 lines on going from  $Y_2O_2S:Eu$  (4 mol%) (see Figure 2c) to  $Y_2O_2S:Eu$  (8 mol%) (see Figures 2a and 2b).



**Figure 3.** Energy level diagram for the low-lying levels of  $Eu^{3+}$ .

The emissions are quenched at higher  $Eu^{3+}$  concentrations due to a cross-relaxation process, ( $^5D_J \rightarrow ^5D_0$ )  $\rightarrow$  ( $^7F_0 \rightarrow ^7F_J$ ), between  $Eu^{3+}$  cations<sup>4</sup>. The commercial sample of  $Y_2O_2S:Eu$  gave a spectrum (see Figure 2d) that was similar to that of Figure 2c, suggesting that the  $Eu^{3+}$  concentration was approximately 4 mol%.

## Conclusions

UV stimulated photoluminescence spectra have been shown to be useful for monitoring the purity of the oxysulfide lattices of the commercially important  $Y_2O_2S:Tb$  and  $Y_2O_2S:Eu$  phosphors that have been prepared using different firing regimes.

The photoluminescence spectra obtained from  $Y_2O_2S:Eu$  phosphors show increasing quenching of emissions from the  $^5D_1$  level relative to those from the  $^5D_0$  level with increasing  $Eu^{3+}$  activator concentration. This emission quenching is due to a cross-relaxation process, ( $^5D_J \rightarrow ^5D_0$ )  $\rightarrow$  ( $^7F_0 \rightarrow ^7F_J$ ), between  $Eu^{3+}$  cations and it can be used to estimate the activator concentration from the UV stimulated photoluminescence spectrum.

## Acknowledgements

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## References

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