

By Understanding How Light Emission Depends on Size, Morphology and Phase in Inorganic Phosphor Materials, Can We Deduce Properties to Design Efficient Nanostructures for Tomorrows Industrial Needs

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ABSTRACT

The light emitting properties of a wide variety of Eu^{3+} doped macro and nanostructures that differ in morphology are considered/discussed along with quantum dots (QDs) and quantum rods (QRs). Features that are important in light emission are considered along with their implications for future phosphor design.

1. INTRODUCTION

Over the last fifteen years the needs and applications for new phosphors have undergone dramatic change. In the late 1990's there was a push to develop phosphors for flat screen displays for field emission displays and also for plasma displays. As it became obvious that the former were not going into mass production and the latter would not be on the market for much of the second decade of the twenty first century, the greatest challenge to phosphor researchers/developers became phosphors for lighting applications, principally for use as colour converters for light emitting diodes (LEDs) and laser diodes.

During the course of developing small particles for flat screen displays, we reported studies on a gas method of preparing cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and discussed the morphologies of the resulting particles.¹ We found that for cathodoluminescence (CL), the shape of the particles affected inter-particle conduction. This in turn appeared to affect the light output. Hence the morphology of particles of similar size could have a direct effect on light emission. In more recent times we have studied smaller particles of cubic and monoclinic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and have reported how size may affect phase and in turn light emission properties². In addition we showed how both the particle size and fine control of the concentration of the Eu^{3+} in cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors could be achieved³, how self-assembly could be controlled and how light emission was affected.⁴⁻¹⁴

We have also reported studies on the cathodoluminescence and visualisation of quantum dots (QDs) and quantum rods (QRs).¹⁵⁻¹⁸

More recently, a report on the properties of ultrathin europium oxide nanoplatelets¹⁹ suggested surprising results for the optical properties.

In this work, we report further studies on the Eu^{3+} concentration in cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles; from these results and our earlier work, implications for the design of phosphors for applications in both future displays and lighting applications are derived.

2. EXPERIMENTAL

The cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles were prepared by the urea precipitation method and were characterised by scanning electron microscopy, X-ray powder diffraction, and emission spectroscopy.⁴⁻¹⁴

3. RESULTS AND DISCUSSION

The structures/morphologies of typical nanometer-sized particles of cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ are presented in Figures 1 to 3. In all three images, the particles are very similar in size and shape; this is true of all the $\text{Y}_{1-x}\text{Eu}_x\text{O}_3$ samples studied herein. When fired, the as precipitated amorphous spherical nanoparticles crystallise, and the resultant clusters of nanocrystals (NCs) are around the same size as the precipitated spherical particles.

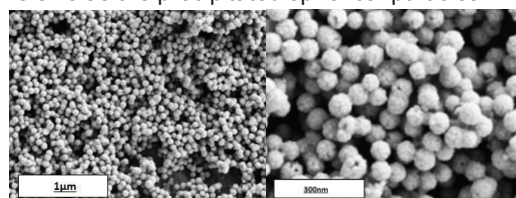


Fig. 1. Scanning electron micrographs of cubic $\text{Y}_{1.99}\text{Eu}_{0.01}\text{O}_3$ NCs (scale bars are 1 μm and 300 nm).

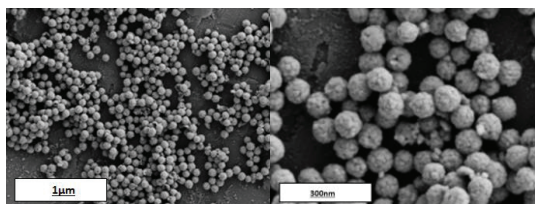


Fig. 2. Scanning electron micrographs of cubic YEuO₃ NCs (scale bars are 1 μm and 300 nm).

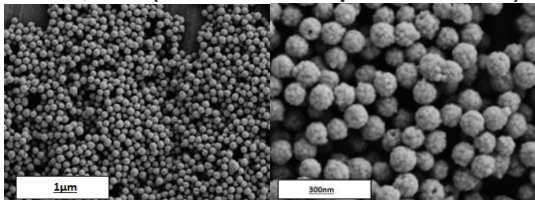


Fig. 3. Scanning electron micrographs of cubic Eu₂O₃ NCs (scale bars are 1 μm and 300 nm).

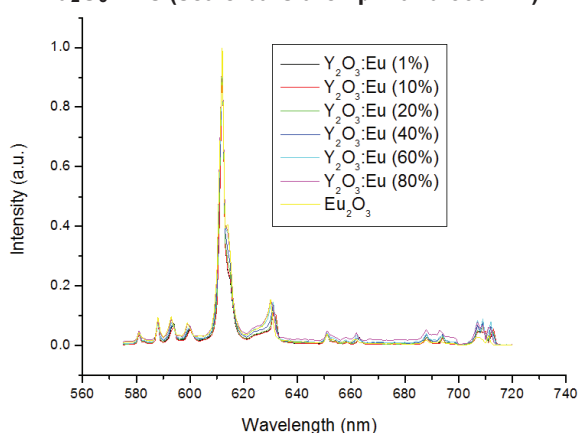


Fig. 4. Normalised (to the 612nm band) emission spectra of the cubic Y_{1-x}Eu_xO₃ NC phosphors (excitation was at 467nm).

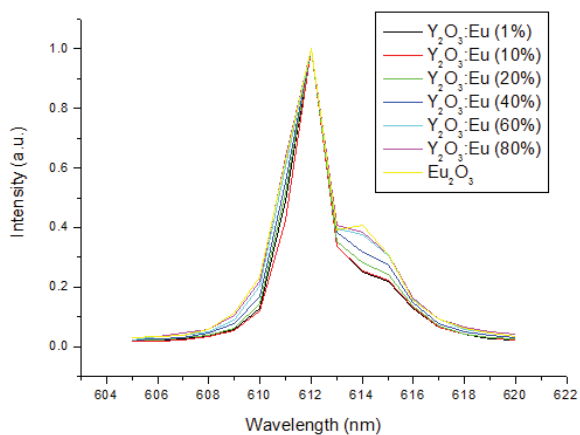


Fig. 5. Emission spectra of the the normalised 612nm band of the cubic Y_{1-x}Eu_xO₃ NC phosphors (excitation was at 467nm).

The emission spectra of some of these Y_{1-x}Eu_xO₃ NC phosphors (excited at 467nm since this is the wavelength widely used in blue emitting LEDs) are shown in Figures 4 to 6. Although the spectra above 5% Eu³⁺ dopant have the same emission bands in the 575nm to 720nm wavelength range, the intensity of the

emission drops as the concentration of the dopant increases due to concentration quenching (as expected). In fact, as we have reported previously, the optimum concentration of the Eu³⁺ dopant is 2% for NCs in this size range. In larger micron-size particles the optimum dopant level rises to between 4 and 8%. The broadening of the 612 nm emission band, seen in Figures 4 and 5, is clear evidence of concentration quenching above 10% Eu³⁺. Thus, even in NCs clusters of roughly spherical phosphors, quenching occurs at doping concentrations greater than 10%.

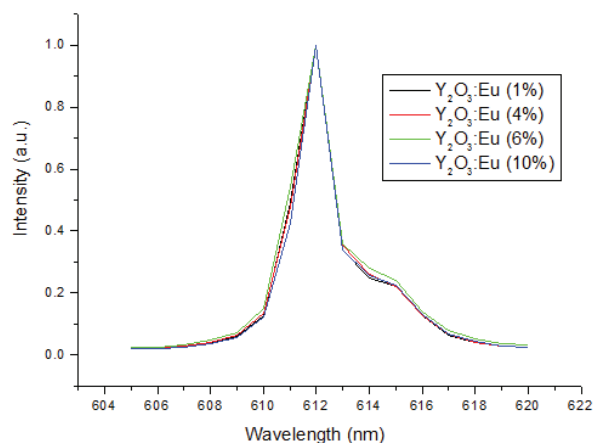


Fig. 6. Emission spectra of the the normalised 612nm band of the cubic Y_{1-x}Eu_xO₃ (where x = 1, 4, 6 and 10%) NC phosphors (excitation was at 467nm).

Figure 6 presents the normalised emission bands of cubic Y_{1-x}Eu_xO₃ (where x = 1, 4, 6 and 10%) NC phosphors; little or no evidence exists of broadening of the 612 nm band and hence no evidence for quenching at the lower Eu³⁺ concentrations.

As we have stated previously, using smaller particles of cubic Y₂O₃:Eu³⁺ is advantageous for some applications since fewer Eu³⁺ cations are needed and, subsequently, the phosphors are cheaper to manufacture^{20, 21}. However, the emission from the 2% doped NCs is only ~70% of the larger micron-sized particles.

All the NC clusters used for the emission spectra shown in Figures 4 to 6 are very similar in size (around 250nm). We have previously shown in CL studies on cubic Y₂O₃:Eu³⁺ that the shape of the particles influences the emission properties. We also showed that the packing of the particles was important to achieve maximum emission. Close-packed, small, spherical particles yielded better results than non-uniformly packed larger particles.

If the exciting energy is applied from behind the phosphor, then for lighting (for example) down converting phosphors that are efficient need to be present in a thick layer to convert the wavelength of the required proportion of incoming light without increasing self-quenching. In the case of efficient phosphors that

have low dopant concentrations, this may mean that thick layers are required, which may affect other optical properties of the system adversely. This, in turn, may be a problem where high intensity lighting is required, and it may well be better to use higher doping ratios (less efficient phosphors) to get around such problems.

The reason that NC phosphors are useful for light emission is that they have higher surface to volume ratios (than larger particles such as micron sized particles) for the light to escape from without being recaptured. Herein, we have shown that at higher dopant levels self-quenching can still be detrimental.

In the case of QDs and QRs, although they have high luminous efficacies, self-absorption between particles is a major problem due to the fact the emission and absorption bands are close together (in wavelength). This has so far limited their use in high intensity lighting. However, they have been successfully used in liquid crystal displays for backlighting as the light intensity needed is much smaller and their colours are very pure. In the case of QDs and QRs, they each emit single photons as each acts as a single emission centre. However, their excitation and emission times are very fast (10^{-7} s), which means that they can emit much faster than Eu^{3+} (10^{-4} s). Although these particles are small and bright, facile manufacturing of multiple, well-packed layers of the particles would be needed to make them cost effective for commercial applications. In addition, QRs tend to manifest their emission as polarized light; this has important implications in their use in backlights for the manufacture of displays. Ideally for next-generation backlighting phosphors, the emission of polarised light would be an objective.

In contrast to QDs, the NCs used in this work were much larger; even the 2%-doped cubic $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ contains more active sites per volume than the QDs, though the latter compete in emission intensity by being much faster emitters. This introduces another consideration in the design of next-generation light emitters: what is needed is an emission centre, such as Eu^{2+} or Ce^{3+} , to offer the emission rate of a QD, the ideal geometry of close-packed spherical nanoparticles. To control of the emission colour from such fast activators, the chemical environments that will facilitate the chosen colour must be carefully selected.

A recent publication on ultrathin europium oxide nanoplatelets containing Eu^{3+} activators¹⁹ comprised a portion of an in-depth study to develop a good understanding of the relationship between the atomic scale structure of ultra-small europium oxide NCs and their photoluminescence properties. Such a study is of major interest in the design and development of innovative Eu^{3+} doped nanophosphors. As a consequence, the preparation of reliable (controlled size and shape distributions) and structurally well-characterized ultrasmall europium oxide NCs was an

essential prerequisite to understand the size effects on their photoluminescence properties¹⁹.

These nanoplatelets can be considered as rafts measuring up to 400 square nanometers in area size but only being around 0.9 nanometers thick. We have recently measured a range of these rafts (nominally based on Eu^{3+} doped yttrium oxide) with different concentrations of Eu^{3+} activators and were surprised to find that the 40% Eu^{3+} concentration was the most efficient. This can be understood when the geometry of the raft is considered. Each raft contains only two or, at most, three layers of cations. Even if 40% of the cations are activators, since the raft is very thin, more directions for the light to escape from each activator cation exist than for light to be absorbed by another activator cation in the material (either within the same layer or in the layer above/below). From this we learn that an ultra-thin layer containing up to 40% of activator cations can be very efficient at emitting light. The rafts are prepared by confining their nucleation and growth with organic ligands. Under such conditions and with such dimensions, these structures are arguably nanoscale macromolecules. Thus, tailoring the chemistry is as important in controlling the shape of the rafts as it is in synthesizing QRs.

As yet, rafts containing Ce^{3+} and Eu^{2+} activators have not been prepared but could well be worth investigating

4. CONCLUSIONS

A number of findings have resulted from this work: 1) the concentration of the activator is important for efficient emission of light from a NC phosphor; 2) the optimum concentration of activator is particle size dependent; 3) the morphology of the particles is important for the emission of light both under CL and photoluminescent conditions.

From the properties of QDs and QRs, the speed of emission from the activation site has been demonstrated to be important for brightness, and the light emitted from QRs may be polarised.

Studies on ultra-thin nanoplatelets have shown that their emission may be higher than expected from a given dopant concentration since light pathways that would lead to concentration quenching are much less likely to occur if the number of M^{3+} cation layers present is very low.

Therefore, to design efficient light emitting structures for tomorrow's marketplace, they must be based on thin layers (like the rafts) that only contain two or three layers of metal cations, allowing the concentration of the activator dopants to be maximised yet keeping concentration quenching to a minimum. The ideal activators are Ce^{3+} or Eu^{2+} as they are very fast emitters (comparable to QDs in speed). To control the emission colour, it will be important to consider the structures of good LED conversion phosphors and how

to facilitate their best properties when they are present only as thin layers.

5. ACKNOWLEDGEMENT

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