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Cathodoluminescent images and spectra of single crystals of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ and $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ nanometer sized phosphor crystals excited in a field emission scanning transmission electron microscope

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Abstract. Cathodoluminescence (CL) spectra have been collected from single nanometer-sized crystals of $\text{Y}_{1.98}\text{Tb}_{0.02}\text{O}_2\text{S}$ and $\text{Gd}_{1.98}\text{Tb}_{0.02}\text{O}_2\text{S}$ using a Gatan Vulcan cathodoluminescence imaging spectrometer. Slight variations observed in the CL spectra taken from the crystals are explained, and discussed in relation to bulk samples.

1. Introduction

$\text{Y}_2\text{O}_2\text{S}$ and $\text{Gd}_2\text{O}_2\text{S}$ crystals are both wide band-gap (4.6 – 4.8 eV) semiconductors that have been considered ideal host matrixes for trivalent rare earth cations [1] where the Ln and the O atoms have C_{3v} site symmetry and the S atoms have D_{3d} symmetry [2,3]. Tb^{3+} activated $\text{Y}_2\text{O}_2\text{S}$ and $\text{Gd}_2\text{O}_2\text{S}$ have been used as bulk phosphor scintillator materials for medical diagnostics because of their inherent properties such as hard radiation stability, high X-ray absorption, high conversion efficiency from X-ray to visible light, short decay times and low afterglow and is used in X-ray intensifying screens [4-8]. In a paper whose subject was “contrasting behaviour of the co-activators in the luminescence spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$, Er^{3+} nanometre sized particles under UV and red light excitation” [9] we reported the properties of nanometre sized particles of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$. Therein we discussed the synthesis and characterisation of the nanometre sized crystals of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$.

A question that phosphor chemists are often asked is “how homogeneous is the phosphor sample?” This question is not easy to answer as PL or CL spectra collected from phosphor samples are the average spectra of the samples making them up. Now that it is possible to collect CL spectra from individual nanometre sized particles the question of homogeneity can begin to be addressed.

The first objective was to compare the spectra of nanometre sized crystals of $\text{Y}_{2-x}\text{Tb}_x\text{O}_2\text{S}$ and $\text{Gd}_{2-x}\text{Tb}_x\text{O}_2\text{S}$ (where x has the value of 0.02) to determine the variability of the emission properties in such crystals made in the same reaction.

2. Experimental

Tb^{3+} activated $\text{Y}_2\text{O}_2\text{S}$ and $\text{Gd}_2\text{O}_2\text{S}$ nanometre sized phosphor particles were synthesized by the two-step method described in our earlier work,[6, 9, 10]. Scanning TEM (STEM) (and CL STEM) was

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carried out at a range of temperatures in a JEOL 2100F analytical TEM operated at 200 kV. STEM was carried out using a JEOL HAADF detector. CL images and the in microscope CL emission spectra were collected using a Gatan Vulcan™ system.

3. Results and Discussion

Figure 1 shows the HAADF STEM images of the nanometre-sized single crystals from which four of the spectra were recorded for the nanometre sized crystals of $Y_{1.98}Tb_{0.02}O_2S$ studied in this work.

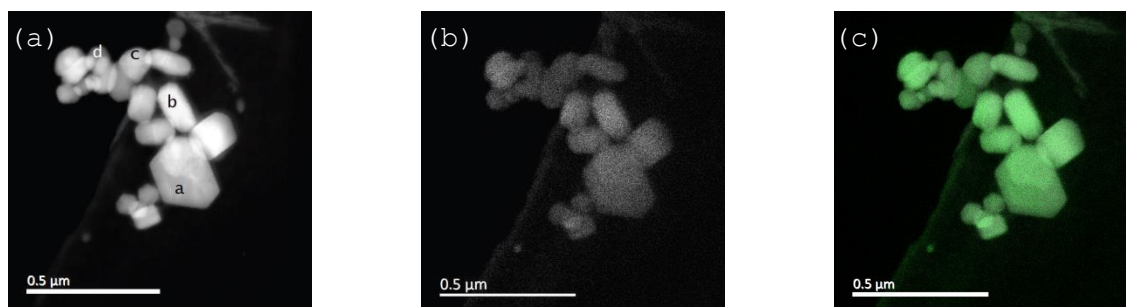


Fig. 1 STEM micrographs of (a) the nanometer sized single crystals of $Y_{1.98}Tb_{0.02}O_2S$; (b) Total visible light (CL) image collected simultaneously with (a) using the VULCAN detector; (c) Overlay of (a) and (b).

In Figure 1a all the crystals can be seen to be discrete with apparently smooth surfaces. In Figure 1b the light distribution image of the cluster is seen, the distribution of the light (generated by CL of the sample) emerging from the crystals is very even. This light originates from the activator sites within the crystals; therefore this possibly indicates an even distribution of the Tb^{3+} cations in the group of crystals. It appears that there is no reason to assume the distribution of the Tb^{3+} cations is not even from this picture. An overlay of Figures 1a and 1b is presented in Figure 1c; additional information is immediately apparent from the overlay which was less obvious on the separate images. For example at the upper left of Figure 1c the small crystal below the larger shows discrete parallel lines. These lines of light may be emitted between lattice stacking planes or fault planes; hence although the crystals appear smooth in Figure 1a the overlay gives more information.

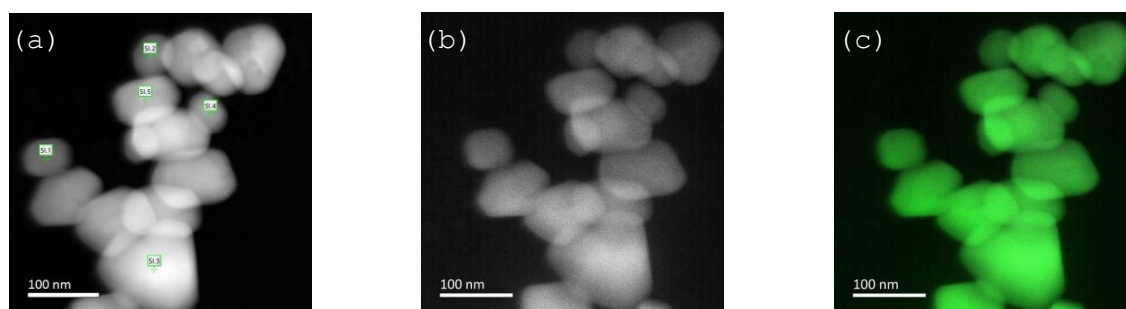


Fig. 2 STEM micrographs of (a) HAADF STEM of single crystals of $Y_{1.98}Tb_{0.02}O_2S$; (b) Total visible light (CL) image collected using the VULCAN detector; (c) overlay of images shown in (a) and (b).

As in Figure 1a all the crystals seen in Figure 2a are discrete with apparently smooth surfaces. In Figure 2b the light distribution image of the cluster is seen, unlike that of Figure 1b although the distribution of the light (generated by CL) emerging from some of the crystals is very even, some areas are brighter. These brighter areas originate from areas of either contact between crystals or from where crystals are overlapping; much less evidence for such effects was seen in Figure 1. From Figure 2b it may be thought that in this cluster there is not such an even distribution of the Tb^{3+} cations in the group of crystals as in Figure 1. To address this point the normalised emission spectra for the crystals shown in Figures 1 and 2 are presented in Figures 3 and 4.

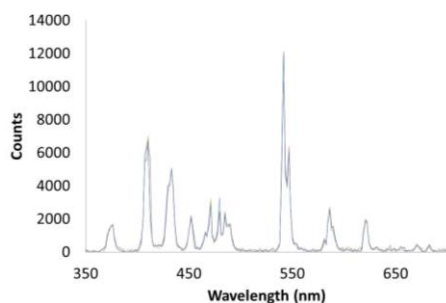


Fig. 3 CL emission spectra of $Y_{1.98}Tb_{0.02}O_2S$ at $20^\circ C$ showing the variation in CL spectra from the 4 separate nanometer sized crystals shown in Figure 1a.

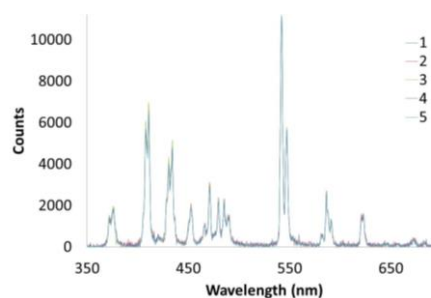


Fig. 4 CL emission spectra of $Y_{1.98}Tb_{0.02}O_2S$ at $20^\circ C$ showing the variation in CL spectra from the 5 positions marked in Figure 2a.

Each CL emission spectrum shown in Figure 3 of $Y_{1.98}Tb_{0.02}O_2S$ was recorded from a different nanometre sized crystal in the group shown in Figure 1a (crystals a-d). Similarly each of the five CL emission spectra presented in Figure 4 were recorded from Figure 2a (marked as crystals 1-5). In both figures 3 and 4 the spectra are all very similar as would be expected with crystals prepared in the same batch. There are no significant differences observed in the spectra in either the $^5D_3 \rightarrow ^7F_J$ or the $^5D_4 \rightarrow ^7F_J$ transitions. [6, 9-11]. These transitions usually lose intensity by a cross relaxation process. In fact for the 1 mol% Tb^{3+} activated Y_2O_3S phosphor the green emission band at 545 nm is the most intense one, the intensity ratio between the $^5D_4 \rightarrow ^7F_J$ and $^5D_3 \rightarrow ^7F_J$ transitions is dependent on the doping concentration of Tb^{3+} cations. Thus the emission colour and intensity of Tb^{3+} emission bands are also strongly affected by the doping concentration [9] and the former can be blue to green. [11] Evidence that the concentration of the Tb^{3+} cations is very similar if not exactly the same in these nanometer sized crystals can be taken from the fact that the spectra all show the same intensity ratio between the $^5D_3 \rightarrow ^7F_J$ transitions and the $^5D_4 \rightarrow ^7F_J$ transitions. So even though there appeared to be some areas of brighter emission in Figure 2b it appears that the activator concentration is the same.

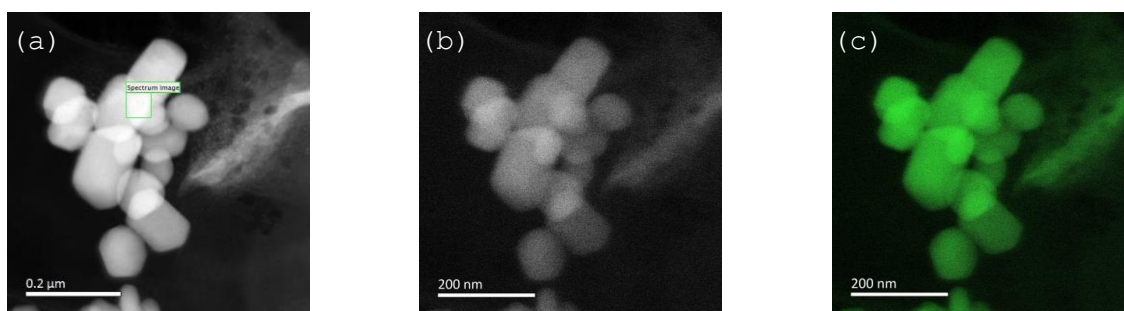


Fig. 5 STEM micrographs of (a) single crystals of $Y_{1.98}Tb_{0.02}O_2S$ used in the CL spectral comparison (spectrum imaging) studies (inset image square shows the area where the 4 different survey positions were taken); (b) Total visible light (CL) image collected using the VULCAN detector; (c) overlay of images shown in (a) and (b).

In Figure 5a all the crystals can be seen to be discrete with smooth surfaces. In Figure 5b the distribution of the light emerging from the crystals is very even with features in common to Figure 2b.

In this case we chose to survey four positions close together across a boundary so we covered different apparent bright areas in close proximity. The four resulting CL emission spectra are presented in Figure 6. These high resolution spectra manifest all the emission bands present in the range 350 nm to 700 nm and the relative intensities of the emission bands in the spectra presented in Figures 3 and 4 are in good agreement with these spectra. The normalised spectra in Figure 6 are all identical which is evidence for an even distribution of the Tb^{3+} activators and shows the even distribution of activator cations. At low Tb^{3+} concentrations the blue emissions from the $^5D_3 \rightarrow ^7F_J$ transitions are predominant in the $Y_{1.98}Tb_{0.02}O_2S$ spectrum while green emissions from $^5D_4 \rightarrow ^7F_J$ transitions are dominant in the equivalent Gd compound's spectrum (Figures 4 and 5). This is due to the positions of the CTSS [11].

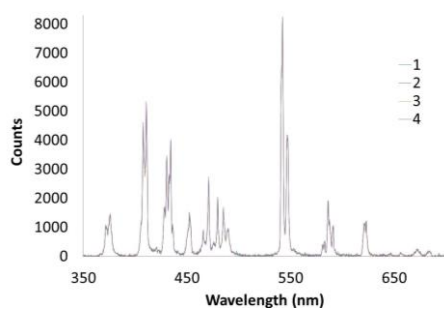


Fig. 6 High resolution CL emission spectra of nanometre-sized single crystals of $Y_{1.98}Tb_{0.02}O_2S$ at $20^\circ C$ showing the variation in CL spectra from the 4 different survey positions in Figure 5a.

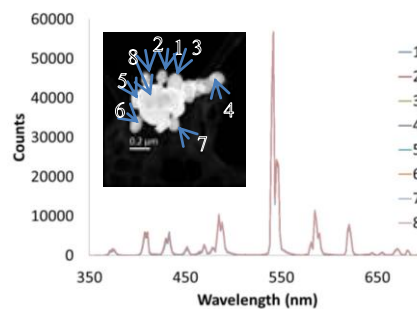


Fig. 7. CL emission spectra of nanometre-sized single crystals $Gd_{1.98}Tb_{0.02}O_2S$ at $-172^\circ C$ showing the variation in CL spectra from 8 separate crystals (Inset image shows the position of the 8 survey positions).

The CL spectra of eight different single nanometre-sized crystals of $Gd_{1.98}Tb_{0.02}O_2S$ are presented in Figure 7. The spectra are all very similar as would be expected with crystals prepared in the same batch. The main differences are observed in the $^5D_3 \rightarrow ^7F_J$ transitions, particularly the $^5D_3 \rightarrow ^7F_5$ and the $^5D_3 \rightarrow ^7F_4$. These transitions usually lose intensity in two ways as discussed above for the 1 mol% Tb^{3+} activated Y_2O_3 phosphor, the first is by the cross relaxation process, but in this case unlike the Y^{3+} compounds the $Gd_{2-x}Tb_xO_2S$ samples are all green as not only does the above relaxation process take place but in addition the second mechanism that loses intensity in the blue bands is more dominant. The CTS in Gd_2O_3 lie closer to the 5D_3 excited state of Tb^{3+} than it does in the Y_2O_3 lattice. Therefore most of the electrons on the 5D_3 excited state of Tb^{3+} in Gd_2O_3 are fed to 5D_4 state at room temperature, yielding a noticeable reduction on the intensities of the $^5D_3 \rightarrow ^7F_J$ transitions [11].

4. Conclusions

The work presented herein has led to a number of important findings:- CL spectra have been easily collected from two clusters of single nanometre-sized crystals (one from four and one from five separate crystals) of $Y_{1.98}Tb_{0.02}O_2S$. In addition CL spectra have been collected from eight single nanometre-sized crystals of $Gd_{1.98}Tb_{0.02}O_2S$; High quality light images demonstrate uniform emission of light from individual phosphor crystals; Evidence the concentration of the Tb^{3+} cations is very similar in these nanometre sized crystals of $Y_{1.98}Tb_{0.02}O_2S$ and $Gd_{1.98}Tb_{0.02}O_2S$ can be taken from the fact that the spectra all show the same intensity ratio between the $^5D_3 \rightarrow ^7F_J$ and $^5D_4 \rightarrow ^7F_J$ transitions.

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