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# Fluorescence intensity and color purity improvement in nanosized $\text{YBO}_3:\text{Eu}$

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In order to improve the color purity of  $\text{YBO}_3:\text{Eu}$ , which is practically used as a plasma phosphor, the lowering of the structural symmetry is proposed and subsequently realized in nanosized  $\text{YBO}_3:\text{Eu}$  so as to increase the contribution of  ${}^5D_0-{}^7F_2$  transition of the luminescent centers,  $\text{Eu}^{3+}$  ions. Spherical  $\text{YBO}_3:\text{Eu}$  nanocrystals were fabricated *via* thermal decomposition of complex precursors and could be crystallized at lower temperature than required by the bulks. The particle size could be controlled by adjusting the annealing temperature and time. Unlike the bulk  $\text{YBO}_3:\text{Eu}$  synthesized by solid-state reaction, the quenching concentration increased with the decrease of the particle size. Furthermore, the fluorescence intensity and color purity were significantly improved in nanocrystals. Possible mechanisms responsible for these improvements were proposed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1452787]

Recently, much attention has been paid to phosphors for vacuum ultraviolet (VUV) ( $\lambda < 200$  nm) excitation due to the demands of plasma display panels and a possible new generation of Hg-free fluorescent lamps.<sup>1,2</sup> Higher efficiency and stronger VUV absorption are two important aspects of an ideal VUV phosphors. It has been discovered that  $\text{Gd}^{3+}$  can be used as an efficient quantum cutter to realize two visible red photon emission of  $\text{Eu}^{3+}$  in a series of fluorides.<sup>3-5</sup> However, the efficiency and the VUV absorption of these materials are still not high enough. Recent studies indicate that the overall quantum efficiency of  $\text{LiGdF}_4:\text{Eu}$  is only 32%.<sup>6</sup>

Rare earth orthoborates,  $\text{REBO}_3$  (RE=lanthanide and yttrium), represent an interesting class of materials due to their high VUV transparency and exceptional optical damage threshold.<sup>7</sup> Among them,  $\text{YBO}_3$ , which possesses the hexagonal vaterite-type structure and shows a good VUV absorption, has been a promising candidate of desired host materials for VUV phosphors. Studies show that the VUV absorption of rare earth borate depends strongly on the structure of the borate ions.<sup>8</sup> Compared with  $\text{REBO}_3$ , the VUV absorption of the other rare earth borates, such as  $\text{Y}_3\text{BO}_6:\text{Eu}$ ,  $\text{YCaB}_9\text{O}_6:\text{Eu}$ , etc., is quite weak. However, in practical applications, although  $\text{YBO}_3:\text{Eu}$  presents strong absorption and high efficiency under VUV excitation, the characteristic emission of  $\text{YBO}_3:\text{Eu}$  is composed of almost equal contributions of  ${}^5D_0-{}^7F_1$  and  ${}^5D_0-{}^7F_2$  transitions, which gives rise to an orange-red emission instead of red and thus hampers its application. In this letter, we intend to improve the color purity of  $\text{Eu}^{3+}$  doped luminescent materials by lowering the structural symmetry so as to increase the contribution of  ${}^5D_0-{}^7F_2$  transition and therefore improve the color purity. The earlier attempt is successfully realized in nanosized  $\text{YBO}_3:\text{Eu}$  materials. Our research reveals that

nanosized  $\text{YBO}_3:\text{Eu}$ , which maintains the hexagonal vaterite-type structure and possesses lower symmetry simultaneously, should have higher fluorescence intensity and better color purity.

The nanosized  $\text{YBO}_3:\text{Eu}$  was obtained by thermal decomposition of complex precursors. The advantage of this method is that pure phased  $\text{YBO}_3:\text{Eu}$  can be obtained at a relatively lower annealing temperature than by any other methods.<sup>9,10</sup> Appropriate amount of  $\text{Y}(\text{NO}_3)_3$ ,  $\text{Eu}(\text{NO}_3)_3$ ,  $\text{H}_3\text{BO}_3$ , and  $(\text{NH}_4)_2\text{-EDTA}$  (ethylenediaminetetraacetic) aqueous solutions were mixed together, and kept stirring for hours to prepare the precursor complexes. Aliquots of these precursors were calcined at 700 °C for 2.5 and 5 h, 900 °C for 5 h in air to obtain nanosized  $\text{YBO}_3:\text{Eu}$ , and at 1100 °C for 5 h in air to obtain submicron-sized sample. These samples are denoted as a, b, c, and d, respectively, in the following descriptions. For comparison, the bulk  $\text{YBO}_3:\text{Eu}$  was obtained by direct solid-state reaction from the mixture of  $\text{Y}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$  at 1100 °C for 5 h in air.

X-ray diffraction (XRD) studies were carried out on a Rigaku D/max-2000 x-ray powder diffractometer using  $\text{Cu } K_\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation. Transmission electronic microscopy (TEM) images were taken on a Hitachi H-8000 NAR transmission electron microscope under a working voltage of 300 kV. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer at room temperature.

Figure 1 shows the XRD patterns of the  $\text{YBO}_3:\text{Eu}$  samples, in which all of the peaks could be indexed to the hexagonal phased  $\text{YBO}_3$  with vaterite-type structure, and no excessive traces of rare earth oxide were observed. By applying the Scherrer formula to the full width at half maximum of the diffraction peaks, the mean particle size could be calculated as 22.6, 40.8, and 88.6 nm for samples a, b, and c, respectively. Obviously, the size of  $\text{YBO}_3:\text{Eu}$  samples increases with annealing temperature and time. The TEM image of sample b is shown in Fig. 2. It reveals that the

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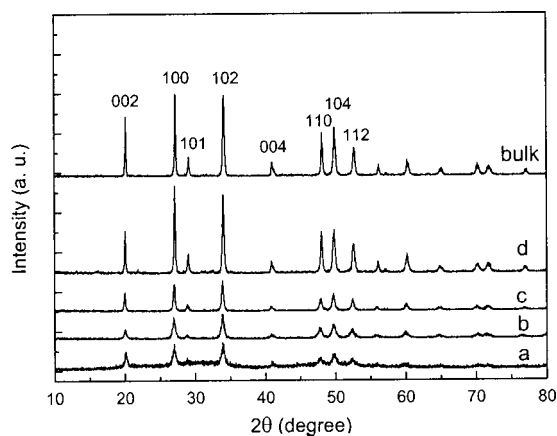


FIG. 1. XRD patterns for  $\text{YBO}_3:\text{Eu}$  samples. Complex precursors are decomposed at 700 °C for 2.5 h (a), 700 °C for 5 h (b), 900 °C for 5 h (c), and 1100 °C for 5 h (d), respectively. Bulk sample is obtained by direct solid-state reaction at 1100 °C for 5 h.

$\text{YBO}_3:\text{Eu}$  nanocrystals are spherical-like in configuration and there is almost no amorphous constituents. The grain size is distributed in the range of 30–50 nm, which is consistent with the mean particle size obtained from XRD. The electron diffraction pattern shown in the inset of Fig. 2 also indicates a hexagonal structure.

Figure 3 displays the emission spectra of  $\text{YBO}_3:\text{Eu}$  under 240 nm UV irradiation. The spectra consists of sharp lines ranging from 580 to 720 nm, which are associated with the transitions from the excited  ${}^5D_0$  level to  ${}^7F_J$  ( $J = 1, 2, 3, 4$ ) levels of  $\text{Eu}^{3+}$  activators.<sup>3,6</sup> The major emissions of  $\text{YBO}_3:\text{Eu}$  are at 591 nm ( ${}^5D_0-{}^7F_1$ ) and 610, 625 nm ( ${}^5D_0-{}^7F_2$ ), which correspond to orange-red and red color, respectively. The luminescent intensity of  $\text{YBO}_3:\text{Eu}$  increases with increasing the decomposition temperature, and the highest intensity is obtained for sample d, which is about twice as high as that of the bulk  $\text{YBO}_3:\text{Eu}$ . Although the major peak positions in the emission spectra are identical to each other, the intensity patterns are quite different. For the bulk and submicron-sized samples, the  ${}^5D_0-{}^7F_1$  transition is by far the most intense.<sup>9</sup> But the relative intensity of  ${}^5D_0-{}^7F_2$  increases with decreasing particle size. It is obvious that with the particle size decreasing, the red emission come from  ${}^5D_0-{}^7F_2$  increases, and as a result, a better color

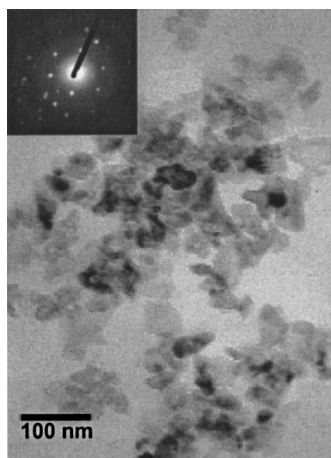


FIG. 2. TEM image and electron diffraction of  $\text{YBO}_3:\text{Eu}$  nanocrystals prepared at 700 °C for 5 h.

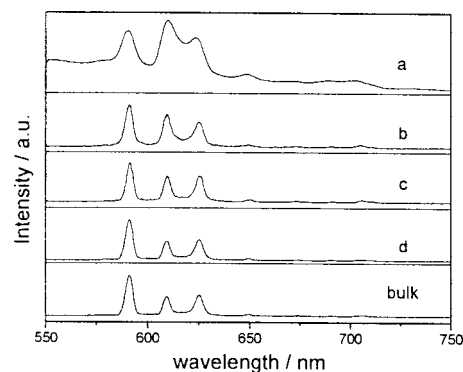


FIG. 3. Emission spectra of  $\text{YBO}_3:\text{Eu}$  samples. Samples a–d and bulk are denoted in Fig. 1.

purity, i.e., a redder fluorescence, in chromatic sense, can be obtained from the small particle sized  $\text{YBO}_3:\text{Eu}$ .

The intensity of transitions between different  $J$  levels depends on the symmetry of the local environment of the  $\text{Eu}^{3+}$  activators and can be described in terms of the Judd–Ofelt theory.<sup>11</sup> Magnetic dipole transition is permitted and electric dipole transition is forbidden, but for the most cases, the local symmetry of the  $\text{Eu}^{3+}$  activators do not have an inversion center and the parity forbidden is partially permitted, such as  $\text{Eu}^{3+}$  ions occupying  $C_2$  sites in  $\text{Y}_2\text{O}_3:\text{Eu}$ .<sup>12</sup> It is well known that the relative intensity of  ${}^5D_0-{}^7F_1$  transition (a typical magnetic dipole transition) or  ${}^5D_0-{}^7F_2$  transition (a typical electric dipole transition) depends strongly on the local symmetry of  $\text{Eu}^{3+}$  ions. Subsequently, when  $\text{Eu}^{3+}$  ions occupy the inversion center sites, the  ${}^5D_0-{}^7F_1$  transition should be relatively strong, while the  ${}^5D_0-{}^7F_2$  transition is parity forbidden and should be very weak. The abnormal luminescent behavior of the nanosized  $\text{YBO}_3:\text{Eu}$  must be correlated to the microstructure of the nanoparticles. More atoms are located at the particle surface as the particle size is reduced. In addition to the limited coherence length of the nanoparticles, numerous surface defects exist as a consequence of the low temperature synthesis. These defects may increase the degree of disorder and lower the local symmetry of  $\text{Eu}^{3+}$  ions located at the surface of the particles. This will increase the transition probability of  ${}^5D_0-{}^7F_2$  and enhance the red emission in visual although the luminescent spectra are still the mixture of orange-red and red emission bands in the nanosized  $\text{YBO}_3:\text{Eu}$ .

The relationship between luminescence intensity and dopant content is shown in Fig. 4. The dependence of  ${}^5D_0-{}^7F_2$  and  ${}^5D_0-{}^7F_1$  transitions on the activator concentration is identical for different sized  $\text{YBO}_3:\text{Eu}$  samples, but the quenching concentration varies with the particle size. It is about 8% for the bulk  $\text{YBO}_3:\text{Eu}$  and increases to 15% and 20% for 88.6 and 40.8 nm  $\text{YBO}_3:\text{Eu}$  nanoparticles, respectively. It is worth noting that quenching concentration increases with decreasing the particle size, as have been observed in other nanosystems.<sup>13</sup> It is understandable that the concentration quenching effect is due to the possible nonradiative transfer between neighboring  $\text{Eu}^{3+}$  ions, which increases the mobility of the excited state within the host matrix and therefore increases the probability of nonradiative de-excitation via quenching centers (traps).<sup>14</sup> In nanosized materials, the deficiency of the traps due to the limited primi-

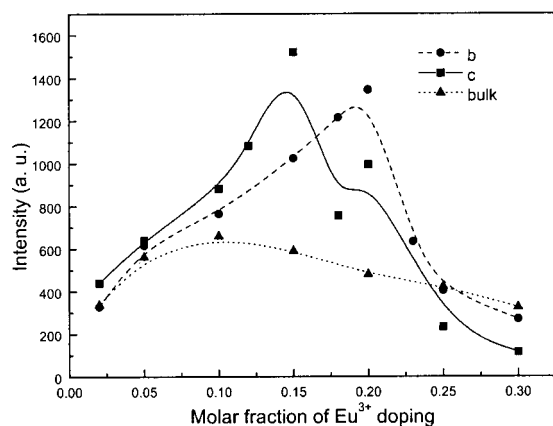


FIG. 4. Quenching concentration of  $\text{YBO}_3:\text{Eu}$  for samples b, c, and bulk obtained by monitoring the emissions of  ${}^5D_0-{}^7F_2$ .

tive cells per particle results in the fact that the traps distribute randomly with a considerably large fluctuation between particles: there must be many traps in some of the particles while fewer traps in others.<sup>15,16</sup> Resonance energy transfer only occurs within one particle due to the hindrance by the particle boundary. Therefore, with increasing the concentration of luminescent centers, quenching occurs first in particles containing many traps, while those particles containing few or no traps quench only at high concentration or do not quench at all. Therefore, quenching occurs at higher Eu concentration in smaller particles. In other words, higher quenching concentration does not lead to stronger luminescence, just as what was observed in smaller particles. The quantum efficiency is another important factor to be studied and the detailed investigation is under way.

In conclusion, pure hexagonal phased  $\text{YBO}_3:\text{Eu}$  nanocrystals with vaterite-type structure are fabricated by thermal decomposition of complex precursors. The emission spectra of nanosized  $\text{YBO}_3:\text{Eu}$  are distinct from that of the bulk in

the intensity patterns. Detailed analysis tentatively explained the relatively high contribution of  ${}^5D_0-{}^7F_2$  transition resulted from decreasing the particle size, which is of great benefit to the color purity. Compared with the bulk  $\text{YBO}_3:\text{Eu}$ , the quenching concentration, fluorescence intensity and color purity were significantly improved in nanocrystals, which can be very beneficial for applications.

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