

## Hydrothermal synthesis of $\text{Sb}^{3+}$ doped and ( $\text{Sb}^{3+}$ , $\text{Eu}^{3+}$ ) co-doped $\text{YBO}_3$ with nearly white light luminescence

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### Abstract

$\text{Sb}^{3+}$ -doped,  $\text{Eu}^{3+}$ -doped and ( $\text{Sb}^{3+}$ ,  $\text{Eu}^{3+}$ ) co-doped  $\text{YBO}_3$  crystals have been synthesized using  $\text{Y}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SbCl}_3$  and  $\text{Eu}_2\text{O}_3$  as raw materials through a hydrothermal method. Phase-pure  $\text{YBO}_3$  crystal with hexagonal flake shape has been synthesized at 473 K for 3 days. The photoluminescent property of  $\text{YBO}_3$  with different activators were investigated using luminescent spectrometer at room temperature. The color of the ( $\text{Sb}^{3+}$ ,  $\text{Eu}^{3+}$ ) co-doped  $\text{YBO}_3$  crystal could be controlled from blue to red by changing the  $\text{Sb}^{3+}/\text{Eu}^{3+}$  ratio in the initial reactants. The nearly white emission could be obtained through changing the  $\text{Sb}^{3+}/\text{Eu}^{3+}$  ratio in reaction.

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Since lanthanide orthoborates ( $\text{Ln}$ =rare earth and yttrium) is one of the very interesting inorganic materials that show high vacuum ultraviolet (VUV) transparency with exceptional optical damage thresholds, considerable interest has been devoted to the study of these compounds for the past several years [1–3].  $\text{LnBO}_3$  doped with  $\text{Eu}^{3+}$  has been widely used as a luminescent material in plasma display panels (PDP) due to the high quantum efficiency and good color coordinates under 147 nm VUV irradiation [4]. Various synthesis methods have been used to prepare  $\text{LnBO}_3:\text{Eu}^{3+}$  phosphor materials, for example, traditional solid-state reaction [1,5], co-precipitation [6,7], microwave

heating [8], spray pyrolysis [9], sol-gel [6] and hydrothermal [10,11] method. All the above study indicates that  $\text{LnBO}_3$  is a good host material with an excellent luminescent property when it is doped with a suitable activator. For example, it has been well known that  $\text{Eu}^{3+}$ -doped  $\text{YBO}_3$  is a promising orange–red emission luminescent material [2, 10].

Trivalent  $\text{Sb}^{3+}$  ion as a very excellent activator has been widely used in many host materials such as  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$  ( $\text{X}=\text{F}$ ,  $\text{Cl}$ ) [12],  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{X})$ ,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  [13],  $\text{Sr}_3(\text{PO}_4)_2$  [14],  $\text{LnPO}_4$  ( $\text{Ln}=\text{Sc}$ ,  $\text{Lu}$ ,  $\text{Y}$ ) [15] and  $\text{Cs}_2\text{NaMCl}_6$  ( $\text{M}=\text{Sc}$ ,  $\text{Y}$ ,  $\text{La}$ ) [16].  $\text{Sb}^{3+}$  ion is a fine activator for blue light when it is coordinated in a suitable surrounding. The emission peak position of  $\text{Sb}^{3+}$  ion in some of the above mentioned host materials can be changed by controlling the coordinated surrounding in the reaction

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process. It was reported that the emission peak of  $\text{Sb}^{3+}$  in halophosphates can be changed from 467 to 400 nm in our early study [13]. It had been also reported that the emission color can be controlled from blue to yellow through changing the  $\text{Sb}^{3+}/\text{Mn}^{2+}$  ratio in the  $(\text{Sb}^{3+}, \text{Mn}^{2+})$  co-doped  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$  ( $\text{X}=\text{F}, \text{Cl}$ ) commercial phosphor materials due to the blue emission of  $\text{Sb}^{3+}$  ions and the yellow emission of  $\text{Mn}^{2+}$  ions in the compound [12].

Previous reports show that it is possible to produce a new kind of phosphor material when the  $\text{Sb}^{3+}$  ion takes a suitable place in borates by introducing the  $\text{Sb}^{3+}$  ion into borates because of the excellent property of  $\text{Sb}^{3+}$  ion and borates. Therefore, it was tried to synthesize  $\text{YBO}_3$  pure phase and  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped  $\text{YBO}_3$  by hydrothermal method in this study. It was also tried to control the color of the emission light by changing the  $\text{Sb}^{3+}/\text{Eu}^{3+}$  ratios in the  $\text{YBO}_3$  compounds. The nearly white light could be obtained from the  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped  $\text{YBO}_3$ .

In order to synthesize the  $\text{Sb}^{3+}$ -doped,  $\text{Eu}^{3+}$ -doped and  $(\text{Sb}^{3+}, \text{Eu}^{3+})$ -codoped  $\text{YBO}_3$  by hydrothermal method, the  $\text{B}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SbCl}_3$  and  $\text{Eu}_2\text{O}_3$  were used as raw materials. The  $\text{SbCl}_3$  was dissolved in distilled water first and then to which were added the  $\text{B}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  successively under continuous stirring. In a typical synthesis procedure, the molar composition of the initial mixture was 1.4  $\text{B}_2\text{O}_3$ : 1.0  $\text{Y}_2\text{O}_3$ : 0.002  $\text{SbCl}_3$ : 109  $\text{H}_2\text{O}$ . The reactants were stirring for 24 h and then they were sealed in a teflon-lined stainless steel autoclave and heated at 473 K for 3 days under autogenous pressure. The solid product was washed thoroughly with hot distilled water to remove the excess  $\text{H}_3\text{BO}_3$  and dried at room temperature.

For the synthesis of  $\text{Eu}^{3+}$ -doped  $\text{YBO}_3$ , the  $\text{Eu}_2\text{O}_3$  was added into the reaction system instead of the  $\text{SbCl}_3$ , the other procedures are as same as those for the synthesis of  $\text{Sb}^{3+}$ -doped  $\text{YBO}_3$ . For the preparation of  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped  $\text{YBO}_3$ , the synthetic procedures are as same as the above described except that the  $\text{Eu}_2\text{O}_3$  was added in the distilled water after  $\text{SbCl}_3$  added. The amount of  $\text{SbCl}_3$  and  $\text{Eu}_2\text{O}_3$  was changed for varying the ratio of  $\text{Sb}^{3+}/\text{Eu}^{3+}$  to obtain different reaction products that have different color of emission whereas the other reaction conditions were not changed. The ratios of  $\text{Sb}^{3+}/\text{Eu}^{3+}$  in the initial reactants were 0.7 and 1.5, respectively.

The powder X-ray diffraction (XRD) studies were carried out on a Siemens D5005 diffractometer with  $\text{Cu K}\alpha$  ( $\lambda=1.5408 \text{ \AA}$ ) radiation. Photoluminescence property was investigated by a He–Cd laser (excited wavelength is 325 nm, 55 mw) at room temperature. The particle morphology of the crystal was observed by scanning electron microscopy using a Hitachi X-650 scanning electron microscope.

Fig. 1 shows the powder XRD patterns of crystal synthesized from the hydrothermal system at 473 K for 3 days (a) and the simulated XRD of the known structure of  $\text{YBO}_3$  (ICSD code is 84653 [3]) (b). All the peaks in the pattern (a) from synthesized powder are very well consistent

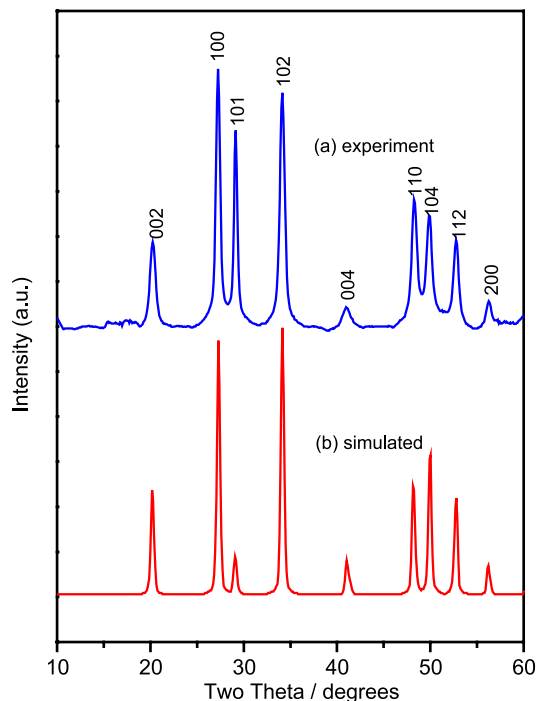


Fig. 1. Powder X-ray diffraction patterns of (a) experimental and (b) simulated of  $\text{YBO}_3$ .

with the peaks from the simulated XRD pattern (b), indicating that the as-synthesized compound is phase-pure  $\text{YBO}_3$  crystal.

Fig. 2 shows the morphology of  $\text{YBO}_3$  particles prepared through the hydrothermal process. The morphology of the particle looks like flowers composed of little hexagonal flakes of which size is about 200 nm.

Fig. 3 shows the photoluminescent spectra of  $\text{Sb}^{3+}$ -doped (a),  $\text{Eu}^{3+}$ -doped (d) and  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped ((b) and (c))  $\text{YBO}_3$  crystals, respectively. The spectrum of  $\text{Sb}^{3+}$ -doped  $\text{YBO}_3$  shows an emission band range from 350 to

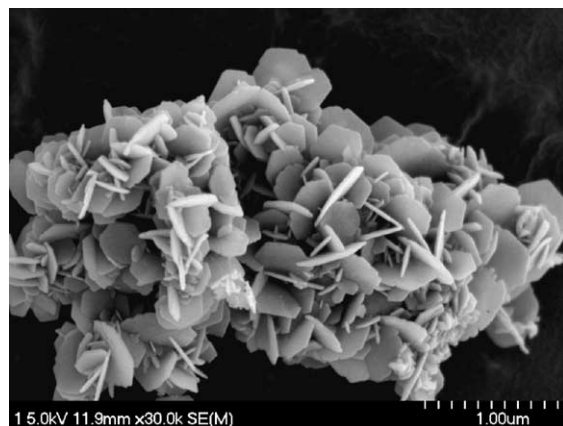


Fig. 2. Scanning electron microscopy (SEM) of the  $\text{YBO}_3$  crystals.

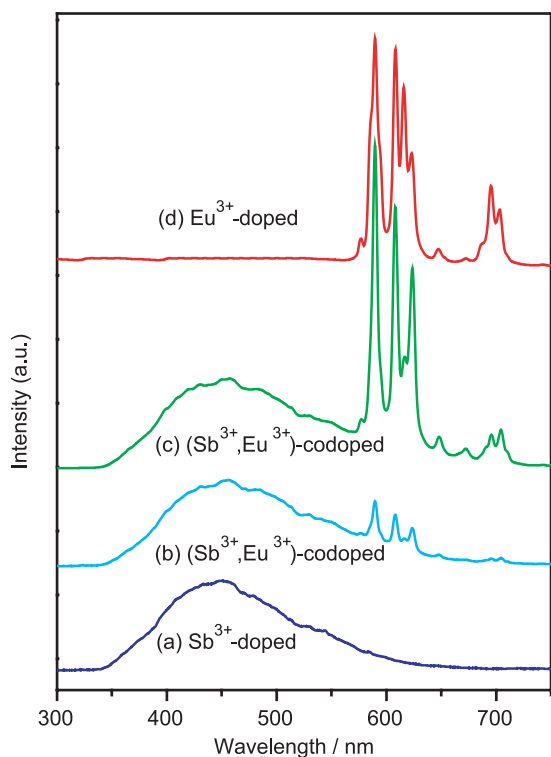


Fig. 3. The photoluminescence spectra of (a)  $\text{Sb}^{3+}$ -doped, (b), (c)  $(\text{Sb}^{3+}, \text{Eu}^{3+})$ -codoped and (d)  $\text{Eu}^{3+}$ -doped  $\text{YBO}_3$  crystals. The variation of ratio of  $\text{Sb}^{3+}/\text{Eu}^{3+}$  in the initial reactants of (b) and (c) is 1.5 and 0.7, respectively.

600 nm with the emission peak at about 450 nm as shown in Fig. 3(a). Full width at half maximum is about 128 nm. This width is broader than that was reported in  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (115 nm) [13], but it is less than that was reported in commercial phosphor calcium halophosphate (140 nm) [12]. According to the reports of Blasse [15, 16], the energy level of ground state of  $\text{Sb}^{3+}$  ( $5s^2$ ) is  $^1\text{S}_0$ , the  $5s5p$  excited state configuration gives rise to the triplet levels  $^3\text{P}_0$ ,  $^3\text{P}_1$ ,  $^3\text{P}_2$  and a singlet level  $^1\text{P}_1$  when the  $\text{Sb}^{3+}$  ions are in the eight-coordination crystallographic position. When the  $\text{Sb}^{3+}$  ion is introduced into the  $\text{YBO}_3$  crystal structure in the hydrothermal process, it takes the  $\text{Y}^{3+}$  ion position coordinated by eight oxygen atoms. In addition, the position of emission peak of  $\text{Sb}^{3+}$  in  $\text{YBO}_3$  (450 nm) is very similar with that in  $\text{Cs}_2\text{NaScCl}_6$  (440 nm) reported by Blasse et al. [16]. Thus, the emission of  $\text{Sb}^{3+}$  should be attributed to the  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition of  $\text{Sb}^{3+}$  ion in  $\text{YBO}_3$  [15,16].

Fig. 3(d) displays the emission spectrum of  $\text{Eu}^{3+}$ -doped  $\text{YBO}_3$  powder. The emission spectrum consists of sharp peaks in the range from 570 to 720 nm, which are corresponding to the transitions from the excited  $^5\text{D}_0$  level to  $^7\text{F}_j$  ( $j=1-4$ ) levels of  $\text{Eu}^{3+}$  ion [17], of which the major

emissions are centered at 589 nm ( $^5\text{D}_0-^7\text{F}_1$ ) and 608, 616 and 622 nm ( $^5\text{D}_0-^7\text{F}_2$ ), which are corresponding to the orange-red and the red color, respectively. The emission peaks at about 650 and 700 nm should be attributed to the transition of  $^5\text{D}_0-^7\text{F}_3$  and  $^5\text{D}_0-^7\text{F}_4$ , respectively, as shown in Fig. 3(d).

The intensity of the transitions between different  $J$  levels of  $\text{Eu}^{3+}$  depends upon the symmetry of the local environment of the activators. The main emission should be come from the electric dipole transition of  $^5\text{D}_0-^7\text{F}_2$  when the  $\text{Eu}^{3+}$  ions occupy the sites without inversion centers such as  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  in which the activators occupy  $\text{C}_2$  sites [12]. When the  $\text{Eu}^{3+}$  site has inversion symmetry, the magnetic dipole transition  $^5\text{D}_0-^7\text{F}_1$  will become stronger. From our results and the reported datum from Yan et al. [10], the emission of  $\text{Eu}^{3+}$  in  $\text{YBO}_3$  is a typical emission of  $\text{Eu}^{3+}$  in a high symmetry crystal field in which the main emission comes from the magnetic dipole transition  $^5\text{D}_0-^7\text{F}_1$  of  $\text{Eu}^{3+}$  ion.

Fig. 3(b) and (c) show the effects of changing the  $\text{Sb}^{3+}/\text{Eu}^{3+}$  ratio on the luminescent property of  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped  $\text{YBO}_3$  powders in which the  $\text{Sb}^{3+}/\text{Eu}^{3+}$  ratios were 1.5 and 0.7 in the initial reactants, respectively. The emission spectra contained the blue light of  $\text{Sb}^{3+}$  ions and the red light of  $\text{Eu}^{3+}$  ions in the  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped  $\text{YBO}_3$  crystal. Fig. 3(b) displays that the emission intensity of  $\text{Sb}^{3+}$  is higher than that of  $\text{Eu}^{3+}$  in  $\text{YBO}_3$ , whereas the emission intensity of  $\text{Eu}^{3+}$  is higher than that of  $\text{Sb}^{3+}$  in  $\text{YBO}_3$  as shown in Fig. 3(c). This result shows that the relative emission intensities from  $\text{Sb}^{3+}$  ions and  $\text{Eu}^{3+}$  ions in  $\text{YBO}_3$  can be controlled by changing the ratio of  $\text{Sb}^{3+}/\text{Eu}^{3+}$  in the initial reactants in the reaction process. Then the nearly white light emission was obtained by the above described method.

In conclusion,  $\text{YBO}_3$  crystal was synthesized through a hydrothermal method at 473 K. In the reaction process,  $\text{Sb}^{3+}$  ions,  $\text{Eu}^{3+}$  ions and  $\text{Sb}^{3+}$  ions together with  $\text{Eu}^{3+}$  ions were introduced into  $\text{YBO}_3$  crystals. And the blue, red and nearly white emission were observed from  $\text{Sb}^{3+}$ -doped,  $\text{Eu}^{3+}$ -doped and  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped  $\text{YBO}_3$  crystals, respectively. The blue and red emission comes from the  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition of  $\text{Sb}^{3+}$  ion and  $^5\text{D}_0-^7\text{F}_1$  and  $^5\text{D}_0-^7\text{F}_2$  of  $\text{Eu}^{3+}$  ion in  $\text{YBO}_3$ . Through controlling the  $\text{Sb}^{3+}/\text{Eu}^{3+}$  ratio in the initial reactants in the hydrothermal system, the nearly white emission was obtained from the  $(\text{Sb}^{3+}, \text{Eu}^{3+})$  co-doped  $\text{YBO}_3$  crystals and the color of the emission can be changed through changing the ratio of  $\text{Sb}^{3+}/\text{Eu}^{3+}$ .

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