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Letter

Photoluminescence properties of YBO_3:Eu^{3+} phosphors prepared via the solvothermal synthesis under supercritical conditions

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ABSTRACT

The preparation process and photoluminescence properties of YBO_3:Eu^{3+} powders synthesized via a solvothermal process using isopropanol as a solvent are reported in this study. Raising solvothermal temperatures resulted in a significant increase in crystallinity of YBO_3 phase. Single-phased YBO_3:Eu^{3+} phosphor powders were obtained under a supercritical condition. The morphology of the prepared powders varied from a flower-like to a spherical shape with raising the solvothermal temperatures. The photoluminescent intensity of the obtained phosphors increased with a rise in solvothermal temperatures due to enhanced crystallinity and purity of YBO_3 phase. The supercritical condition has been demonstrated to facilitate the formation of spherical YBO_3:Eu^{3+} phosphors with high emission intensity.

1. Introduction

Orthoborate phosphors are widely used in various optical devices such as field emission displays (FED), plasma display panels (PDPs) and a new generation of Hg-free fluorescent lamps. Among the orthoborate phosphors, YBO_3-based phosphors demonstrate strong absorption in vacuum ultraviolet (VUV) range and high emission intensity upon VUV excitation [1,2]. YBO_3:Eu^{3+} phosphors are regarded as one of the potential red phosphors to be utilized in PDPs [3]. YBO_3:Eu^{3+} phosphors have been synthesized via various routes, such as the co-precipitation [4], spray pyrolysis [5] and hydrothermal methods [6]. It is known that the photoluminescent properties of the phosphors are significantly influenced by the particle size and morphology [7]. Spherical phosphors have high packing density, good slurry property and low scattering of light. These advantages indicate that spherical phosphors are considered to be advantageous in improving the luminescent intensity [8,9]. However, employing conventional processes barely yields spherical rare-earth orthoborate phosphors [10,11]. Therefore, it is crucial to develop a new route for synthesizing YBO_3:Eu^{3+} phosphors with a spherical shape in order to meet the demands of optical devices.

A solvothermal process, which has the advantages of short reaction time and low reaction temperatures, has been employed to synthesize phosphors recently [8]. In addition, supercritical fluids (SCFs) have been reported to facilitate the formation of inorganic particles with controlled particle size and shape [12,13]. Under supercritical conditions, the low viscosities of SCFs and high diffusivities of solutes in SCFs enhance the mass transfer of the ions in SCFs [14]. It is considered that SCFs can produce inorganic particles with high phase purity, high crystallinity and homogeneous composition [15]. In this study, SCFs were incorporated into the solvothermal process to prepare YBO_3:Eu^{3+} phosphors. The effects of various preparation conditions on the luminescent characteristics and microstructures of the prepared samples were investigated in detail.

2. Experimental

Europium-ion doped yttrium borate (YBO_3:Eu^{3+}) phosphors were prepared via the solvothermal route. The synthesis procedures of the solvothermal process are summarized in the flowchart as illustrated in Fig. 1. Y_2O_3 and Eu_2O_3 were dissolved in dilute nitric acid. The doping amount of Eu^{3+} ions was fixed at 5 mol% with respect to Y^{3+} ions. The solution was mixed with an appropriate amount of urea. Urea was employed to control the pH values and acted as the precipitant. The molar ratio of metal ions (Y^{3+} and Eu^{3+}) to urea was maintained at 1:20. Excess urea was used to assure complete precipitation of metal ions (Y^{3+} and Eu^{3+}). The precipitates were obtained after heating the solution at 90 °C for 12 h, followed by washing with deionized water and drying in a vacuum oven at 70 °C.

Excess H_3BO_3 was dissolved in isopropanol solution, and the above prepared precipitates were added into this solution. The molar ratio of H_3BO_3 to metal ions (Y^{3+} and Eu^{3+}) was set at 2:1. CH_3COONH_4 was added to adjust the pH values of the solution to reach 8. After stirring for 2 h, the solution was transferred into a stainless autoclave with a Teflon lining. The autoclave was heated at temperatures ranging from 200 to 240 °C for 6 h. The critical temperature of isopropanol is about 235 °C. Hence, the SCFs were achieved by heating the autoclave to 240 °C. The obtained powders were washed and dried, followed by heating at 1100 °C in air for 2 h. For comparison, YBO_3:Eu^{3+} with the same composition was also synthesized via the conventional hydrothermal method at 240 °C for 6 h and the derived powders were calcined at 1100 °C for 2 h.

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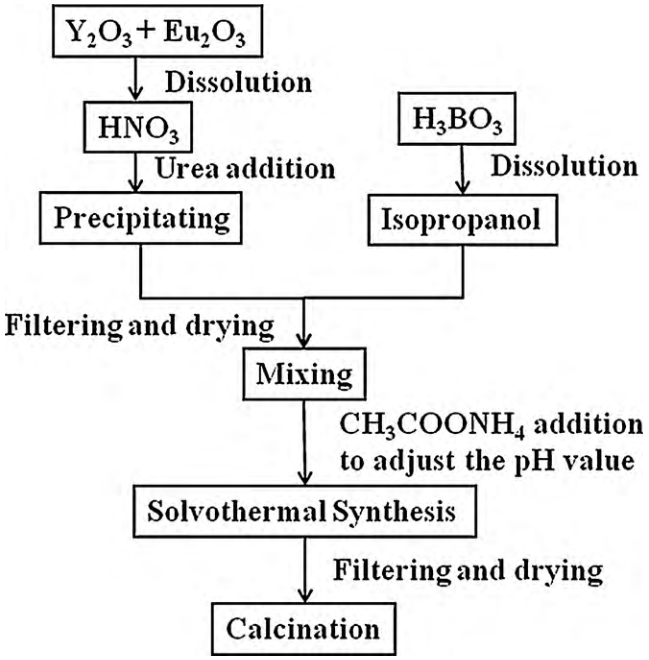

Fig. 1. Synthesis flowchart of YBO_3:Eu^{3+} phosphors prepared via the solvothermal method at 200–240 °C for 6 h with the calcination at 1100 °C for 2 h.

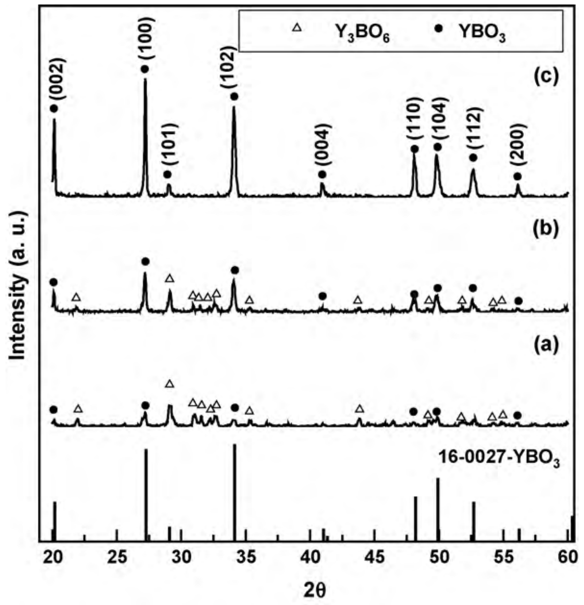

Fig. 2. X-ray diffraction patterns of YBO_3:Eu^{3+} phosphors prepared via the solvothermal method at (a) 200 °C, (b) 220 °C and (c) 240 °C for 6 h and calcined at 1100 °C for 2 h.

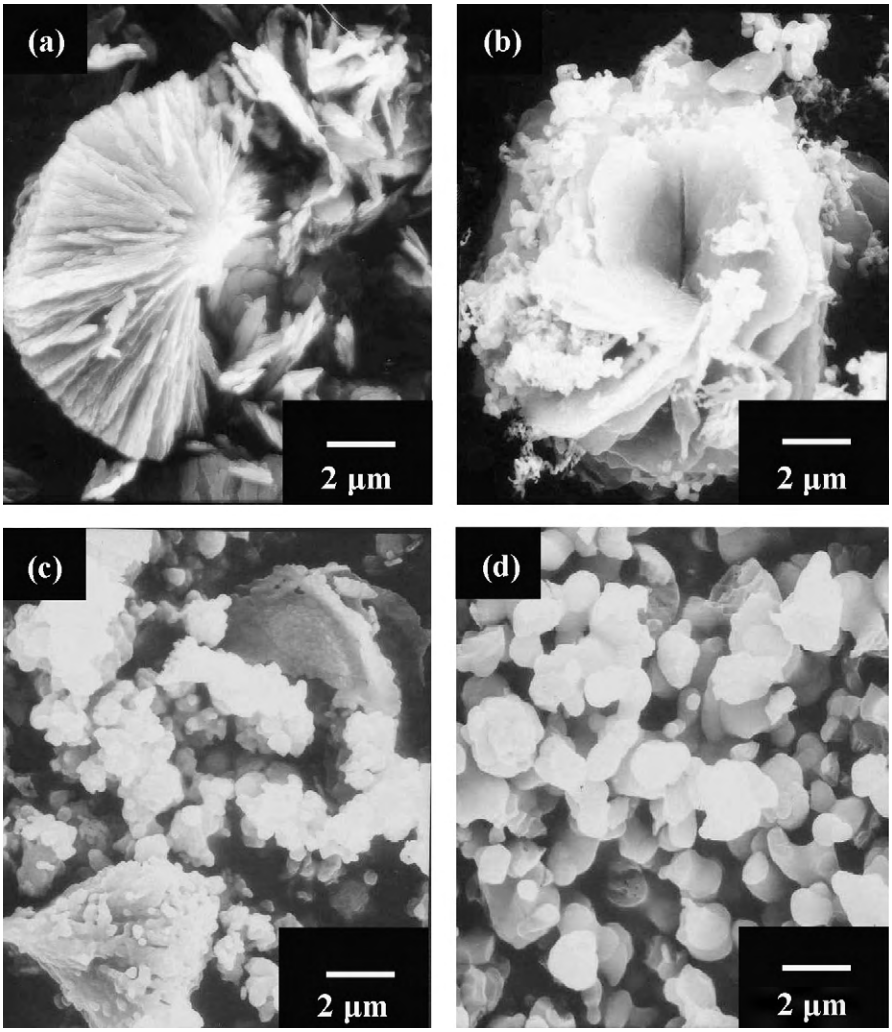

Fig. 3. Microstructures of YBO_3:Eu^{3+} phosphors prepared via the (a) hydrothermal method at 240 °C for 6 h and solvothermal method at (b) 200 °C, (c) 220 °C, (d) 240 °C for 6 h with the calcination at 1100 °C for 2 h.

The formed phases of the synthesized powders were identified using an X-ray diffractometer (XRD, Philips X'Pert/MPD). The morphology and particle size of the obtained powders were examined using a scanning electron microscope (SEM, Hitachi S-800). The photoluminescence spectra of the phosphors were measured via a fluorescence spectrophotometer (Hitachi, F-4500) that used a 150 W xenon lamp as the excitation light source.

3. Results and discussion

Fig. 2 illustrates the XRD patterns of the solvothermal-derived samples calcined at 1100 °C. When the solvothermal temperature was 200 °C, YBO_3 was found to coexist with the impurity phase—Y_3BO_6 (Fig. 2(a)). As the solvothermal temperature was raised to 220 °C, the amount of YBO_3 phase increased along with a decrease in the amount of Y_3BO_6 phase (Fig. 2(b)). When the solvothermal temperature reached to the supercritical level (240 °C), single-phased YBO_3:Eu^{3+} was successfully obtained after calcination at 1100 °C (Fig. 2(c)), and the recorded diffraction pattern was well consistent with the data reported for YBO_3 in the ICDD file No. 16-0027. It is considered that the low solubility of metal ions and the high reaction rate under the supercritical condition lead to rapid nucleation in the reaction [16]. Furthermore, the rapid nucleation occurred in supercritical fluids, promoting the formation of YBO_3 phase.

The microstructures of YBO_3:Eu^{3+} particles prepared via the conventional hydrothermal method at 240 °C for 6 h with the calcination at 1100 °C for 2 h are shown in Fig. 3(a). This sample exhibited a flake-like shape with a size of 4–5 μm. When the solvothermal temperature was kept at 200 °C, the morphology of the obtained powders changed drastically to be flower-like (Fig. 3(b)). As the temperature was raised to 220 °C, the amount of flower-like particles decreased along with the appearance of some spherical particles as shown in Fig. 3(c). Further raising the temperature to the supercritical level (240 °C) resulted in complete transformation into spherical particles with a size of 1–2 μm (Fig. 3(d)). The sizes of the powders obtained after solvothermal processes without calcination were about 0.3–0.5 μm. In addition, the solvothermally treated powders with and without calcination exhibited almost the same morphology. Therefore, the morphology of YBO_3 phosphors was not affected by the calcination process. On the other hand, it was found that the formed morphology and particles sizes of prepared YBO_3:Eu^{3+} via the conventional hydrothermal process and those via the supercritical condition were clearly different. These results indicate that both the size and shape of the obtained particles can be controlled by adjusting the solvothermal temperatures.

Fig. 4 depicts the excitation spectra of the solvothermal-derived YBO_3:Eu^{3+} phosphors calcined at 1100 °C. The excitation spectra were recorded at an emission wavelength of 592 nm. It was found that all the excitation spectra exhibited a broad band in the range of 220–280 nm with a maximum at 240 nm. This broad band is attributed to the $O^{2-} \rightarrow Eu^{3+}$ charge transfer transition, and several weak excitation peaks ranging from 350 to 450 nm are assigned to the ^7F–^5H inner-shell transitions of Eu^{3+} ions [17]. When the solvothermal temperature was below 240 °C, a weak shoulder at 272 nm was observed. On the basis of the XRD patterns of the samples prepared at 200 and 220 °C, this shoulder may be attributed to the excitation band of the impurity Y_3BO_6:Eu^{3+}. With elevating the solvothermal temperatures, the excitation intensity at 240 nm of the YBO_3:Eu^{3+} samples was found to increase in conjunction with a decrease in the intensity of 272 nm peak owing to increased amount of YBO_3 phase formed.

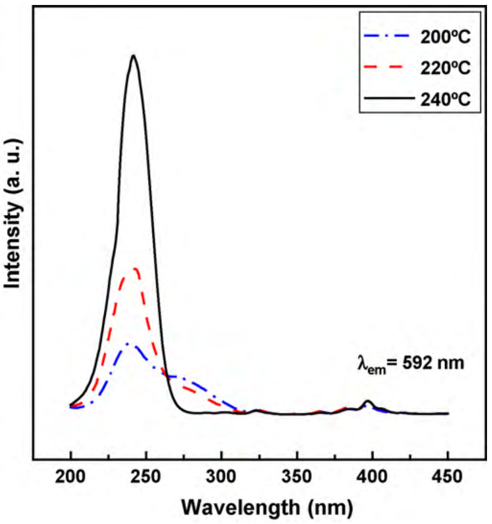

Fig. 4. Excitation spectra of YBO_3:Eu^{3+} phosphors prepared via the solvothermal method at various temperatures for 6 h and calcined at 1100 °C for 2 h.

The emission spectra of the samples for 240 nm excitation are shown in Fig. 5. In the emission spectra of YBO_3:Eu^{3+}, sharp lines ranging from 580 to 720 nm were found. These lines are associated with the transitions from the excited $^5D_0$ level to ^7F_J (J = 1–3) levels of Eu^{3+} [6]. The orange emission peak centered at 592 nm is due to the $^5D_0 \rightarrow {}^7F_1$ magnetic-dipole transition, while the red emission at 611 nm, which is originated from $^5D_0 \rightarrow {}^7F_2$ transition, is assigned to the forced electric-dipole transition [18]. It was found that the orange emission intensity at 592 nm of YBO_3:Eu^{3+} phosphors synthesized under the supercritical condition was much higher than that of the samples with the coexistence of the impurity phase-Y_3BO_6. The emission intensity ratio of $^5D_0 \rightarrow {}^7F_1$ to $^5D_0 \rightarrow {}^7F_2$ transition (I_{611}/I_{592}) can be used to evaluate the site symmetry of Eu^{3+} ions [19]. The ratios calculated for the samples are given in the inset of Fig. 5. The decrease in the I_{611}/I_{592} ratio was observed with increasing the solvothermal temperatures. It is suggested that the anionic environment around Eu^{3+} ions in the host of YBO_3 is more symmetrical than that in the samples with the coexistence of Y_3BO_6 phase. When the synthesis temperatures are low,

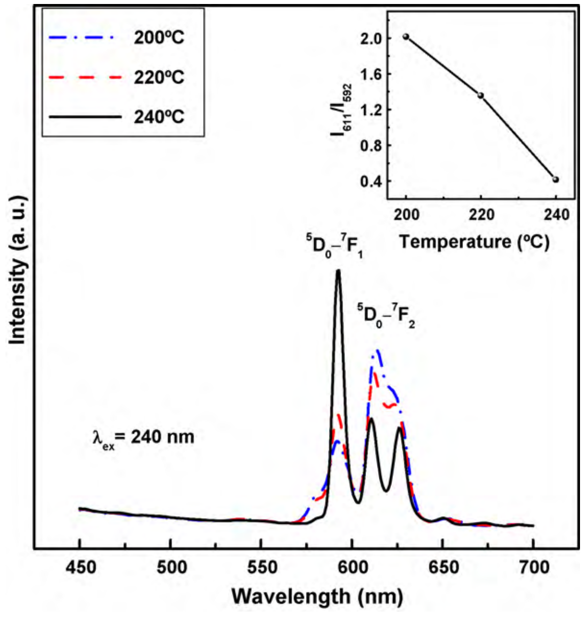

Fig. 5. Emission spectra of YBO_3:Eu^{3+} phosphors prepared via the solvothermal method at various temperatures for 6 h and calcined at 1100 °C for 2 h. Inset shows the dependence of the emission intensity ratio of peaks at 611–592 nm (I_{611}/I_{592}) on solvothermal temperatures.

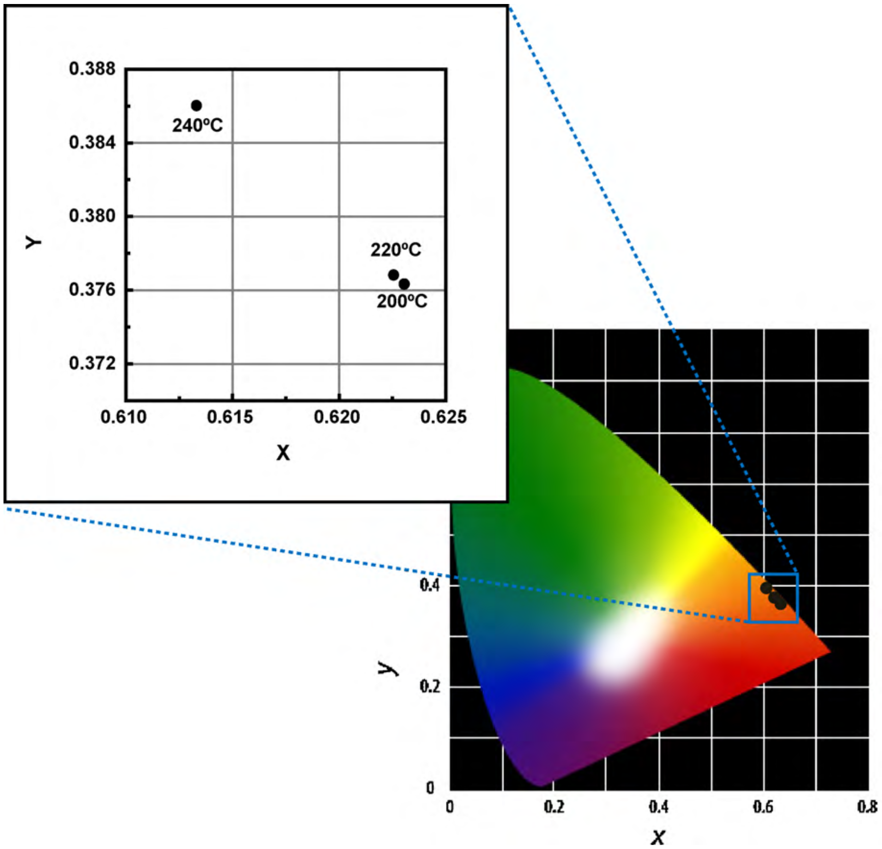

Fig. 6. CIE chromaticity diagram of $YBO_3:Eu^{3+}$ phosphors prepared via the solvothermal method at various temperatures for 6 h and calcined at 1100 °C for 2 h.

the peaks at the red region could be partially overlapped because of the location of Eu^{3+} at low symmetric sites in Y_3BO_6. On the other hand, as the synthesis temperatures are high enough, single-phased $YBO_3:Eu^{3+}$ forms. In the single-phased compound, the peaks at the red region spectra would clearly split because Eu^{3+} ions locate at high symmetric sites in YBO_3. The above result indicates that raising the solvothermal temperatures lead to enhanced crystallinity of YBO_3 and thereby an increase in the emission intensity at 592 nm of the obtained samples. The fluorescence decay time of the $^5D_0 \rightarrow {}^7F_2$ transition for 240 nm excitation was measured at room temperature. It is found that the fluorescence decayed nearly exponentially. The decay time of single-phased $YBO_3:Eu^{3+}$ phosphors prepared under the supercritical condition was 2.08 ms. It was shorter than that of $YBO_3:Eu^{3+}$ phosphors obtained via the solid-state method in the literature. It is indicated that the decay time for Eu^{3+} ions decreases with decreasing the size of particles [20].

The Commission International de I'Eclairage (CIE) chromaticity coordinates of the prepared samples upon excitation at 240 nm are illustrated in Fig. 6. The CIE chromaticity coordinates of the samples prepared via the solvothermal route at 200, 220 and 240 °C were at (0.623, 0.376), (0.622, 0.376) and (0.613, 0.386), respectively. With raising the solvothermal temperatures, the emitting color shifted from red to reddish orange. This observation was consistent with our earlier findings that the orange emission intensity at 592 nm increased as the solvothermal temperature was elevated. This study has proven that the luminescent intensity of color-tunable $YBO_3:Eu^{3+}$ phosphors can be increased by controlling the solvothermal temperatures.

4. Conclusions

$YBO_3:Eu^{3+}$ phosphors were successfully prepared via the solvothermal route under the supercritical condition. With a rise in the solvothermal temperatures, the amount of YBO_3 phase increased with the decrease in the amount of Y_3BO_6 phase. When the solvothermal temperature was elevated from sub-supercritical to supercritical level, the morphology of the obtained YBO_3 powders transformed from flower-like to spherical. Increasing the solvothermal temperatures resulted in enhanced emission luminescence intensity and a symmetrical anionic environment for Eu^{3+} ions. In comparison with the similar commercial red $Y_2O_3:Eu^{3+}$ phosphors (P22), $YBO_3:Eu^{3+}$ phosphors obtained under the supercritical condition had more uniform morphology and a smaller size (1–2 μm). The decay time of $YBO_3:Eu^{3+}$ phosphors synthesized under the supercritical condition was 2.08 ms. The crystallinity and photoluminescent properties of $YBO_3:Eu^{3+}$ phosphors were significantly improved when the samples were synthesized under the supercritical condition.

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