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Synthesis and Optical Properties of Eu^{2+} and Eu^{3+} Doped SrBP Phosphors Prepared by Using a Co-precipitation Method for White Light-Emitting Devices

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The Eu^{3+} and Eu^{2+}-doped SrBP phosphor powders were synthesized via the co-precipitation method and subsequent reduction of the dopants in N_2/H_2 gas for application in white light-emitting devices (WLED). The as-prepared powders were annealed at a temperature range of 600°C to 1300°C in air ambient to form Eu^{3+}-doped phosphors with an average particle size in the range of 100 nm to 1 μm. The phosphors were then reduced in the forming gas ($90\%N_2$:$10\%H_2$) to achieve Eu^{2+}-doped phosphors. It has been found that typical phases of $Sr_6P_5BO_{20}$, $Sr_2P_2O_7$, and $Sr_3(PO_4)_2$ co-exist in the as-prepared powders. The strong and narrow orange-red emission from 570 nm to 700 nm in the photoluminescence spectra (PL) of the SrBP:Eu^{3+} phosphors are attributed to the $^5D_0 \rightarrow {}^7F_j$ transitions of Eu^{3+} ion (where j gets the value of 1 to 6). In contrast, the broad luminescence band of the SrBP:Eu^{2+} phosphors in the range of 400 nm to 500 nm are attributed to the *5d–4f* transitions of Eu^{2+} ion in the same host crystal. The Eu^{3+}/Eu^{2+}-doped SrBP phosphors are considered to be promising phosphors for WLED. The co-precipitation method is simple and rapid, but allows for the controlling of particle size and composition with ease.

Key words: Eu-doped SrBP phosphor, co-precipitation method, photoluminescence, WLED

INTRODUCTION

The conventional phosphor powder used in fluorescent lamps is known as halophosphate powder ($Ca_5(PO_4)_3(F,Cl)$:Sb^{3+}, Mn^{2+}). This inexpensive fluorescence powder has a broadband of white light emission. However, it has low efficiency and a low color rendering index (~60).[1] During the 1970s, scientists found that a combination of three narrow-band rare earth phosphors can better reproduce the three primary colors of the spectrum. In addition, the use of this tricolorphosphor blend in fluorescent lamps gives a more natural color reproduction to the human eye and a high output of light. Since then, the concept of tricolorphosphor or rare earth-doped phosphor has been widely used in color display devices and in the lighting industry.[2] It is well-known that two out of the three components of the commercial tricolorphosphor are based on Eu-doped phosphors. Eu^{2+} is one of the most important rare earth ions that show typical f–d transitions. The $4f^7 \rightarrow 4f^6 5d^1$ transition of Eu^{2+} is strongly dependent on the host lattice because the outermost 5d shell is involved. The emission bands of Eu^{2+}, therefore, can be varied from ultraviolet (UV) to

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the red region when Eu^{2+} ions are at different lattice sites. The Eu^{2+}-doped phosphors have been reported with excellent luminescence properties, which are promising for applications in light-emitting diodes, tricolor fluorescence lamps, plasma display panels, and wide gamut field emission display.[3–7]

Eu^{2+}-doped $Sr_6B_5PO_{20}$ phosphor has been reported by Murakami et al. as early as 1979, as a phosphor powder emitting in the blue-green region with a color rendering index of up to 99.[8] Its broadband emission with a peak at ~480 nm corresponds to the 5d–4f transition of Eu^{2+} in the crystal lattice. Recently, the $Sr_6B_5PO_{20}$:Eu^{2+} phosphor has attracted a great deal of attention due to its high excitation efficiency in the vacuum UV range, high conversion efficiency into visible light, and high thermal stability.[9,10] This phosphor also has been studied on electron-vibration interaction in the 5d states of Eu^{2+} ions in the $Sr_6B_5PO_{20}$ host matrix.[11] Because of high CRI, the $Sr_6B_5PO_{20}$:Eu phosphor could replace the common tricolorphosphor powders known as Y_2O_3: Eu^{3+} (red), $LaPO_4$: Tb^{3+} (green), and $BaMgAl_{10}O_{17}$:Eu^{2+} (blue) for the production of white fluorescent lamps.[6,7] The $Sr_6B_5PO_{20}$ powder doped with Eu^{2+} ions emitting blue-green light can be combined with another red phosphor such as $(Sr,Ca)_5(PO_4)Cl$: Eu^{2+}, Mn^{2+} (SCAP) to fabricate white light-emitting devices (WLED).[12] However, due to the boundary effect of crystals of different hosts, $Sr_6B_5PO_{20}$ and SCAP in this case may reduce the fluorescence efficiency. To improve the efficiency, it is essential to fabricate a red phosphor with $Sr_6B_5PO_{20}$ as the host material. Because Eu^{3+} ions can emit orange and red light due to $^5D_0 \rightarrow {}^7F_j$ transitions, the $Sr_6B_5PO_{20}$:Eu^{3+} appears to be a potential candidate for white fluorescent powder as well.

In this paper, we synthesized the SrBP:Eu^{3+} and SrBPO:Eu^{2+} phosphors, and investigated their optical properties as well as the possibility of using these phosphors as red and blue-green emitting components in WLED.

EXPERIMENTAL

The Eu-doped SrBPO phosphor powders were synthesized by co-precipitation method using $Sr(NO_3)_2$, $(NH_4)_2HPO_4$, and H_3BO_3 as precursors and Eu_2O_3 as a doping source. The Eu concentration was 2 at.%. Firstly, the precursors $Sr(NO_3)_2$, $(NH_4)_2HPO_4$ and H_3BO_3 and the dopant (Eu_2O_3) were separately dissolved in two different HNO_3 solvents to form two uniform solutions. The solutions were then mixed together by stirring for 1 h to obtain a transparent solution. After that, NH_4OH was gradually dropped into the solution to form a white suspension solution. This solution was stirred again for 2 h so that the chemicals were completely reacted. The precipitates were then filtered and separated from the solvent. At this stage, the powders consist mainly of SrBPO:Eu^{3+}. Subsequently, the Eu^{3+} ions were annealed at several temperatures from 600 to 1300°C in air ambient to form stable phases. Finally, the samples were hydrogen-reduced to Eu^{2+} in the mixture of H_2/N_2 (90%N_2:10%H_2) gas.

The crystal structure of the obtained powders were examined by x-ray diffraction (XRD) using a SIEMEN D5000 system. A field emission scanning electron microscopy (30 kV, JSM-7600F, Jeol) was used to investigate the morphology. The luminescent properties were studied by using an excitation source of a 450 W Xenon lamp of the NanoLog modular spectro-fluorometer (NanoLog, Horiba Jobin–Yvon).

RESULTS AND DISCUSSIONS

First, we analyzed the growth of phosphor particle size by increasing the annealing temperature from 700°C to 1300°C, in air ambient, and for 1 h (see Fig. 1a–f). When the annealing temperature increased from 700°C to 800°C, the products turned into particles with a size ~100 nm (Fig. 1a and b). With the increasing of temperature from 900°C to 1100°C, the particle size was increased further from a few hundred nm to ~1.0 μm (Fig. 1c, d, and e). Thus, the phosphor particles with the size of few micrometers, which are suitable for application in light-emitting devices, were easily obtained via controlling the annealing temperature. With further increases of the anealling temperature to 1300°C (Fig. 1f), the powder turned into bulk due to the aggregation and melt of the powder at high temperature.

Figure 2 presents the XRD pattern of the SrBP:Eu^{3+} (2 at.%) powders annealed at different temperatures. On the basis of the published crystal structures, we can determine that at least three main crystalline phases, namely $Sr_6P_5BO_{20}$, $Sr_2P_2O_7$, and $Sr_3(PO_4)_2$, exist in the sample as indicated by symbols in Fig. 2. It is worth noting that the primary phase $Sr_6P_5BO_{20}$ was thought of as being composed of $Sr_6P_5BO_{20} \equiv Sr_2P_2O_7 + Sr_3(PO_4)_2 + SrBPO_5$, but recently it has been reported as a new phase that is independent of other phases.[13,14]

The XRD pattern also shows that the crystalline phase (or in other words, the composition of the sample) is strongly dependent on the annealing temperature. Content of the $Sr_3(PO_4)_2$ phase increases with an increasing annealing temperature and becomes the major phase in the sample at 1300°C. In contrast, the $Sr_6P_5BO_{20}$ content first increases when the temperature increases from 600°C to 1100°C and then decreases at a higher annealing temperature of 1300°C. In our study, the highest content of the $Sr_6P_5BO_{20}$ phase in the as-prepared samples is ~50 wt.% for the sample annealed at 1100°C.

The optical properties of the Eu-doped SrBP phosphor powders were investigated by photoluminescence (PL) and photoluminescence excitation

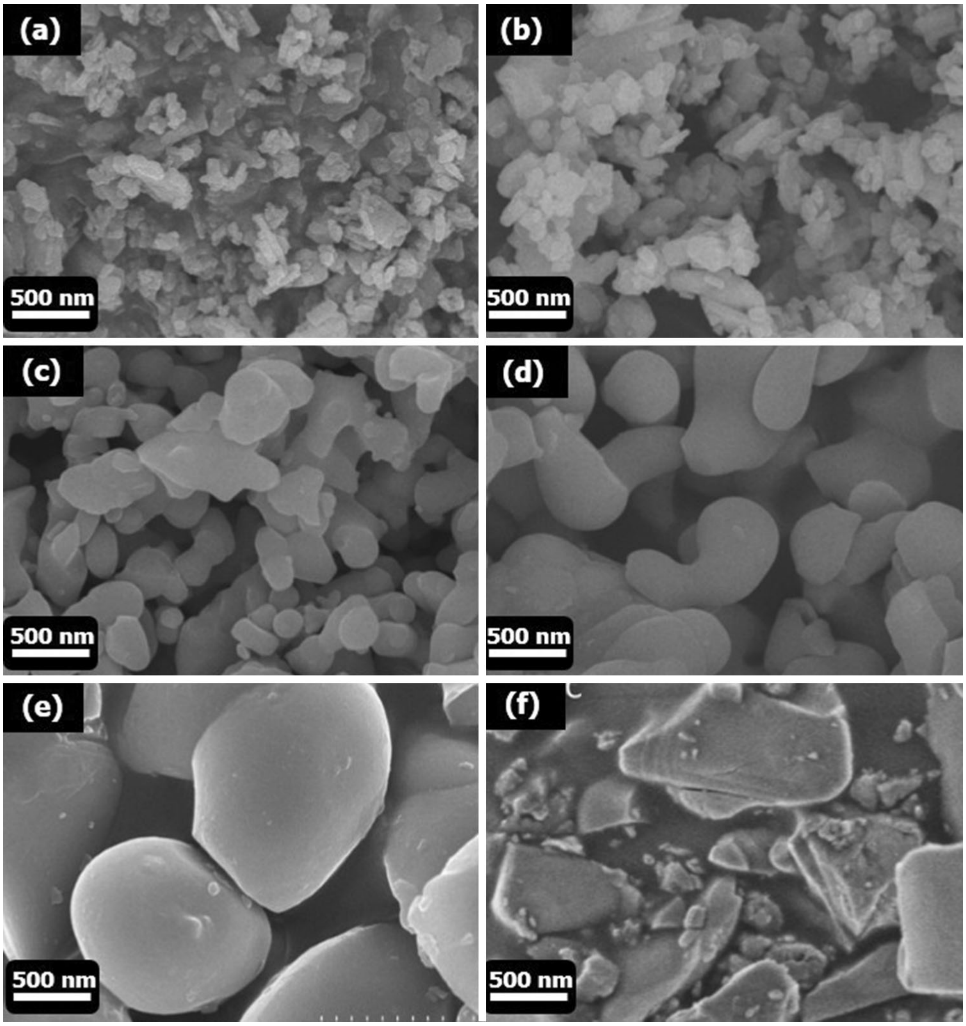

Fig. 1. SEM images of the SrPB phosphors doped 2 at.% Eu, synthesized by co-precipitation method and annealed at various temperatures in air ambient, for 1 h. (a)–(f) the powders annealed at 700°C, 800°C, 900°C, 1000°C, 1100°C, and 1300°C, respectively.

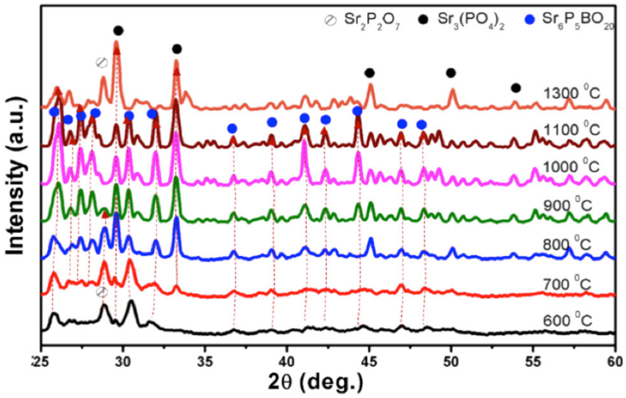

Fig. 2. XRD pattern of SrBPO phosphors doped with 2 at.% Eu as a function of annealing temperature.

(PLE) measurements at room temperature. The emission colors are red and blue-green for the SrBP:Eu^{3+} and SrBP:Eu^{2+} phosphor powders, respectively.

Figure 3a presents the PLE spectrum of the SrBP:Eu^{3+} phosphor doped with 2 at.% Eu, when monitoring the emission wavelength of 605 nm. The PLE spectrum is characterized by several strong and narrow absorption peaks at 361 nm, 393 nm, 415 nm, and 464 nm, corresponding to the transitions of the Eu^{3+} ion from the ground state ($^7F_0$) to $^5D_4$, $^5L_6$, $^5D_3$, and $^5L_2$, respectively. The peak with the greatest intensity corresponds to the $^7F_0 \rightarrow {}^5L_6$ transition. Figure 3b displays the PL spectrum of the SrBP:Eu^{3+} (2 at.%) phosphor annealed at 1100°C under excitation at 254 nm. Seven distinct emission bands are observed with peaks at around 570 nm, 585 nm, 605 nm, 645 nm, 677 nm, 694 nm, and 800 nm, which correspond to typical emissions of Eu^{3+} ion in the host lattice. These emissions are attributed to the $^5D_0 \rightarrow {}^7F_j$ transitions of Eu^{3+} ion (where j gets the values of 0 to 6). In all PL spectra of as-prepared SrBP:Eu^{3+} powders, the emission band peak at 605 nm is always present and of the highest intensity. This emission band corresponds to the $^5D_0 \rightarrow {}^7F_2$ electric-dipole transition.

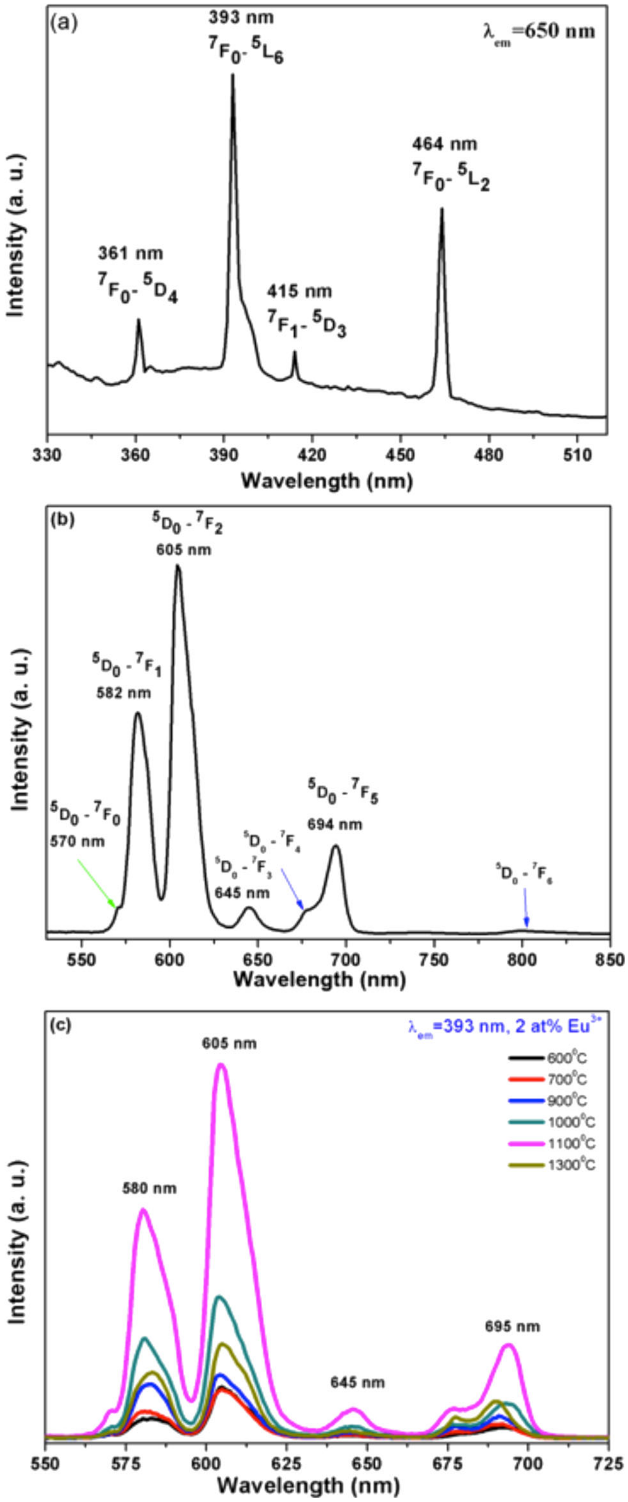

Fig. 3. (a) PLE, and (b) PL spectra of the SrBP phosphor doped with 2 at.% Eu. (c) PL spectra of the phosphor powder as a function of annealing temperature.

In order to examine the optimum annealing temperature for maximum light emission, the PL spectra of the prepared phosphor powders were investigated with different annealing temperatures. Figure 3c presents the PL spectra of the SrBP:Eu^{3+} phosphor powder with the Eu doping concentrations of 2 at.% annealed at various temperatures from 600°C to 1300°C. When the annealing temperature increases from 600°C to 1100°C the PL intensity increases notably. This increasing of the PL intensity can be explained as a result of the development of crystalline phases inside the powder. With increases of the annealing temperature, the structural phase becomes more stable, and the ratio of Eu^{3+} ions replacing Sr molecules increases, making the PL intensity increased. When the annealing temperature rises to 1300°C, the PL intensity decreases because at that temperature, the material tends to melt and aggregate together, causing the PL intensity to be decreased.

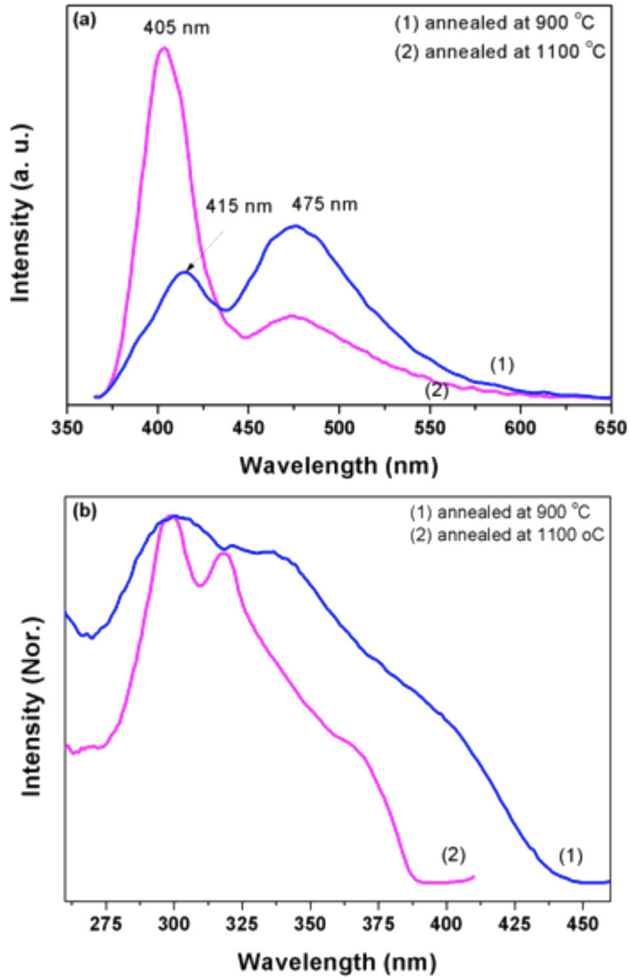

Fig. 4. PL (a) and PLE (b) spectra of the SrBP phosphors doped with 2 at.% Eu^{2+} reduced at 900 (curve 1) and 1100°C (curve 2).

Figure 4a displays the room temperature PL spectra of the SrBP:Eu^{2+} (2 at.%) phosphor annealed at 900°C and 1100°C under excitation with UV light at 300 nm. For the sample annealed at 900°C, two distinct emission bands are observed at around 415 nm and 475 nm. Also, a weaker peak (or a shoulder) in the short wavelength side of the 415 nm band can also be recognized, as indicated by the arrows. At 1100°C, the intensity of this peak increases sharply, and now can be firmly determined at 405 nm. The intensity of the 475 nm band slightly decreases at this temperature. The broad emission band around 475 nm is unambiguously attributed to the 5d-4f transitions of Eu^{2+} ions in the $Sr_2BP_5O_{20}$ lattice.[1,11] In contrast, the two emission bands with peaks around 415 nm and 405 nm, in our opinion, arises from the same transitions of Eu^{2+} but in the $Sr_2P_2O_7$ and $Sr_3(PO_4)_2$ lattices, respectively[15,16] as both of the crystalline phases exist in our sample at this annealing temperature (see XRD data in Fig. 2). The observation of the increases in PL intensity of the 405 nm band with increasing annealing temperature, i.e. increasing the content of the $Sr_3(PO_4)_2$ phase in the sample, is good evidence to support this assignment. Furthermore, no peak related to the presence of Eu^{3+} ions in the red wavelength region is observed. This result indicates that the hydrogen-reduction process had completely reduced Eu^{3+} ions into Eu^{2+} ions. Figure 4b presents the PLE spectra of SrBP:Eu^{2+} phosphor samples that are obtained by reducing the corresponding SrBP:Eu^{3+} powder in forming gas for 2 h and annealed at 900 (curve 1) and 1100°C (curve 2), respectively. The PLE spectra show broad excitation bands from 280–435 nm and 280–385 nm for the sample annealed at 900 and 1100°C, respectively. These broad excitation bands are attributed to the $4f^7 \rightarrow 4f^65d^1$ transitions of Eu^{2+} ion in the crystal field of the SrBP host matrices. From XRD and PL results, the broader excitation band of the sample annealed at 900°C could be explained as due to the contribution of the higher content of the $Sr_6BP_5O_{20}$ in the sample.

CONCLUSION

The SrBP:Eu^{3+} and SrBP:Eu^{2+} phosphor powders have been successfully synthesized using the coprecipitation method combined with subsequent reduction in the forming gas. The XRD patterns showed the existence of three characteristic phases of the powder, namely $Sr_6P_5BO_{20}$, $Sr_2P_2O_7$, and $Sr_3(PO_4)_2$. Depending on the experimental conditions, the SrBP powder with the $Sr_6B_5PO_{20}$ phase as high as 50 wt.% can be obtained. The PL spectra of the SrBP:Eu^{3+} phosphor show strong red emission bands related to the transitions of Eu^{3+} ion in the host SrBP lattice with the maximum peak at 605 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions. The PL spectra of the SrBP:Eu^{2+} phosphor show the broad emission bands peaked at 475, 415, and 405 nm due to the $4f^7 \rightarrow 4f^65d^1$ transitions of Eu^{2+} ion in $Sr_6BP_5O_{20}$, $Sr_2P_2O_7$, and $Sr_3(PO_4)_2$. The red SrBPO:Eu^{3+} phosphor powders can be combined with the blue-green SrBPO:Eu^{2+} phosphor to produce white light for application in WLED, such as fluorescent lamps or light emitting diodes.

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