Preparation of $(Sr_{0.5}Ba_{0.5})Si_2N_2O_2:Eu^{2+}$ Phosphor and Its Luminescence Properties

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Eu^{2+} ion-doped oxynitride phosphor, $(Sr_{0.5}Ba_{0.5})Si_2O_2N_2:Eu^{2+}$, was prepared by solid-state reaction using metal alloy as precursor. Owing to the relatively high activity of the metal alloy precursor compared with the inert Si_3N_4, a single phase of solid solution phosphor $(Sr_{0.5}Ba_{0.5})Si_2O_2N_2:Eu^{2+}$ was easily obtained at 1400 °C under atmospheric pressure. It showed a broad excitation band originating from the $4f^7 \rightarrow 4f^6 5d$ transition of Eu^{2+} ion, extending to 520 nm, and centering at 460 nm and a strong emission band peaking at 565 nm. The high emission and small thermal quenching allow this material to be used for phosphor-converted white LEDs.

Recently, the development of InGaN-based white-light-emitting diodes (LEDs) with huge industrial applications due to their many advantages over conventional incandescent and fluorescent lamps has increased the demand for phosphors with better stabilities, longer lifetime, and higher efficiency.[1–4] Of all the phosphors developed for LED applications, Eu^{2+}-activated $MSi_2O_2N_2$ phosphors with yellow, green to yellow, and blue-green emission for M = Ca, Sr, and Ba, respectively, have been proven to be a new series of excellent phosphors for LEDs because of their advantages of better flexibility, composition-tunability, high thermal stability, and high luminescence intensity.[4–8] They have strong absorption in the UV–visible spectral region and exhibit a broad emission band located at the green to yellow region.[4,5,8] The unusual optical properties of $MSi_2O_2N_2:Eu^{2+}$ phosphors meet the requirements of LEDs, making them good candidates for materials to be used for phosphor-converted white LEDs.

Compared with other reported nitrides and oxynitrides, $MSi_2O_2N_2:Eu^{2+}$ (M = Ca, Sr, and Ba) phosphors can be prepared at a comparatively low firing temperature, as reported by Li et al.[4] However, except for $BaSi_2O_2N_2:Eu^{2+}$, it turns out that by starting with MCO_3, SiO_2, Eu_2O_3, and α-Si_3N_4 following the reported preparation method, it is difficult to obtain a single phase of $MSi_2O_2N_2:Eu^{2+}$ (M = Ca, Sr, and Ba) having X-ray diffraction (XRD) peak intensities that match the reported XRD patterns.[4–7] This difficulty was ascribed to the low chemical reactivity of Si_3N_4, which decomposes at about 1900 °C.[3,5]

In the present work, we prepared the solid solution phosphor $(Sr_{0.5}Ba_{0.5})Si_2O_2N_2:Eu^{2+}$ using a novel metal alloy precursor. Owing to the relatively high activity of the metal alloy precursor compared with the inert Si_3N_4, a single phase of solid solution phosphor $(Sr_{0.5}Ba_{0.5})Si_2O_2N_2:Eu^{2+}$ was easily obtained. The photoluminescence properties and thermal quenching behavior of the obtained phosphor were investigated as an efficient phosphor for white LED application.

The alloy precursors of $Sr_{1-x}Ba_{1-x}Eu_{2x}Si_2$ were prepared by repeated arc melting of strontium (Nilaco, 99.9%), barium (Nilaco, 99.9%), silicon (Wako, 99.999%), and europium

(Wako, 99.99%) metal shot to form homogeneous alloy ingots under an Ar-gas atmosphere. An excessive amount of Sr metal (5 mol %) is better for obtaining high-quality alloy due to the sublimation of Sr metal at high temperature during arc melting. In this work, the Eu doped concentration was set to 5 atom % with respect to the metal ions. The ground alloy powders were subsequently homogeneously wet-mixed with stoichiometric SiO_2, and then the mixture was dried in a glove box filled with purified Ar. Finally, the fine powder mixtures were transferred to a BN crucible and loaded into a radio frequency (RF) furnace (ZrB_2 heater). The heating chamber was pumped down to high-vacuum, back filled with high purity N_2 (6 N), and heated under continuous N_2 flow with a rate of 40 mL min^{-1}. The temperature was increased up to 800–850 °C for 2 h, and then the product was calcined at 1400 °C for 5 h for further nitridation. After firing, the samples were cooled to room temperature in the furnace and were ground again with an agate mortar.

The structure was identified by X-ray powder diffractometry (XRD, RINT2200, Rigaku) with Cu Kα irradiation. The room-temperature photoluminescence spectra of the phosphor were measured by a fluorescence spectrometer (Model F-4500, Hitachi). Variable temperature emission spectra were recorded with a USB2000 (Ocean Optics) spectrometer and a homemade thermocontroller combined with a vacuum chamber.

In this work, alloy powders were used as precursor for the preparation of solid solution phosphor $(Sr_{0.5}Ba_{0.5})Si_2O_2N_2:5\%Eu^{2+}$. Figure 1 shows the XRD patterns of the alloy precursor and the final product. The alloy precursor is single phase and the XRD peaks match well with the JCPDS Card No. 74-0119 (strontium silicon, SrSi, orthorhombic). Owing to the solid solution effect of SrSi (74-0119) and BaSi (65-1369, barium silicon, orthorhombic), which have the same crystal structure, obvious broadening of the Bragg peaks can be observed. After further nitridation, the final product crystallized in a single phase. As shown in Figure 1, all the diffraction peaks are consistent with previous reports.[4,5] The introduction of Eu^{2+}
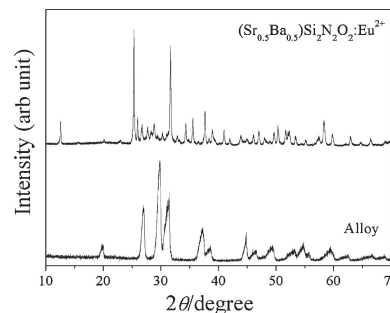
Figure 1. XRD patterns of the alloy precursor and the $(Sr_{0.5}Ba_{0.5})Si_2N_2O_2:5\%Eu^{2+}$ phosphor.
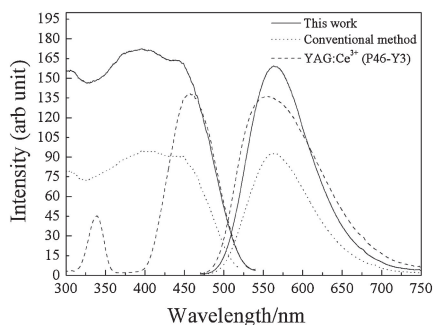
Figure 2. Comparison of the luminescence spectra ($\lambda_{ex} = 460$ nm, $\lambda_{em} = 565$ nm) of $(Sr_{0.5}Ba_{0.5})Si_2N_2O_2$:5%$Eu^{2+}$ prepared by different methods and YAG:Ce^{3+} (P46-Y3) phosphor (dashed line, $\lambda_{ex} = 460$ nm, $\lambda_{em} = 555$ nm).

Figure 3. Temperature dependences of the emission intensity of $(Sr_{0.5}Ba_{0.5})Si_2N_2O_2$:5%$Eu^{2+}$ and YAG:Ce^{3+} (P46-Y3) phosphor.

is found without disturbing the crystal lattice due to the good solution of Eu^{2+} in the $(Sr_{0.5}Ba_{0.5})EuSi_2O_2N_2$.[6]

Figure 2 gives the excitation and emission spectra of the $(Sr_{0.5}Ba_{0.5})Si_2O_2N_2$:5%$Eu^{2+}$. It is clear that the emission spectrum exhibits an intense broad band ranging from 470 to 750 nm centering at 565 nm, which is attributed to the transition from the lowest component of the 5d excited states to the ground state ($^8S_{7/2}$) of Eu^{2+} ion.[4–6] At the same excitation of 460 nm, the integrated PL emission area of present sample is about 94.3 and 172% of those of the YAG:Ce^{3+} (P46-Y3) standard phosphor and the $(Sr_{0.5}Ba_{0.5})Si_2N_2O_2$:5%$Eu^{2+}$ sample prepared by conventional method, respectively. The PL spectra of these two materials are also given for comparison in Figure 2. The higher PL emission intensity is related to its good crystallinity and purity because the oxygen-rich impurity phases, which generally formed in those samples prepared from conventional solid-state reaction and greatly suppress the emission intensity, are absent. Monitored at 565 nm, an intense broad excitation band extending to 520 nm was observed in the excitation spectrum. The excitation and emission spectra suggest that the $(Sr_{0.5}Ba_{0.5})$-$Si_2O_2N_2$:Eu^{2+} solid solution is an efficient phosphor with broad absorption bands, matching well with the widely used near-UV LED chips (ca. 400 nm) and blue LED chip (ca. 460 nm), which provides the basis for developing this kind of phosphor for LED conversion applications. Upon irradiation at different wavelengths within the excitation spectrum, the emission spectra exhibit similar emission of Eu^{2+} in peak shape and position, indicating the occurrence of energy transfer between the matrix and the Eu^{2+} activators.[2]

In the white LED application, the thermal stability of phosphor is a crucial factor to keep the stability of the chromaticity and brightness of white LEDs device, of which the joint-temperature is generally around 150 °C.[9] Due to the electron–phonon interaction between both the ground state and excited states of the luminescence center at high temperature, the emission intensity decreases with increasing temperature. The dependence of photoluminescence intensity on temperature is shown in Figure 3. The temperature-dependent emission intensity of YAG:Ce^{3+} (P46-Y3) phosphor is also given as comparison. When the temperature was increased from room temperature to 200 °C, the emission peak at 565 nm shifted to high energy by about 3 nm, and the intensity decreased slowly. When the samples is heated up to 150 °C, the emission intensity of
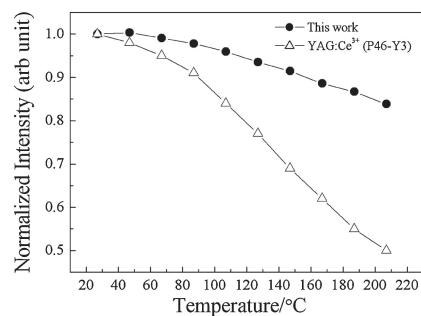
$(Sr_{0.5}Ba_{0.5})Si_2O_2N_2$:5%$Eu^{2+}$ remains at about 90% of that measured at room temperature, while at about 68% for the YAG:Ce^{3+} (P46-Y3) phosphor. Such a preferred small temperature quenching effect indicates weaker electron–phonon interaction in this solid solution phosphor, which is supported by the rigid lattice with a more extended network of SiN_3O tetrahedra.[10]

In conclusion, efficient solid solution phosphor $(Sr_{0.5}Ba_{0.5})$-$Si_2O_2N_2$:Eu^{2+} is successfully prepared by solid-state reaction using metal alloy as precursor instead of the inert Si_3N_4 raw material. As expected, well-crystallized single-phase product was obtained. The product can be efficiently excited by 460 nm blue light of InGaN LED chips and gives an intense emission band centering at 565 nm. The integrated emission area is about 94.3% compared with that of YAG:Ce^{3+} (P46-Y3) under the same 460 nm excitation. As an oxynitride phosphor, the obtained product exhibits a small temperature quenching effect. The emission intensity remains its 90% of original at 150 °C, which is better than that of YAG:Ce^{3+} (68% at 150 °C).

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