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Long-Lasting Phosphorescence in BaSi2O2N2:Eu2+ and Ba2SiO4:Eu2+ Phases for X-Ray and Cathode Ray Tubes

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We report the long-lasting bluish-green phosphorescence for X-ray or cathode ray tubes in the phosphors with compositions of either Ba2SiO4:0.01Eu2+-xSi3N4 (x = 0–1) or 2BaCO3–ySi3N4:0.01Eu2+y (y = 1/6–1) synthesized by a solid-state reaction. By tuning the Si3N4 content, the phosphorescence may originate from Eu2+ in BaSi2O2N2 (peaking at 490 nm), Ba2SiO4 (505 nm), and BaSi2O5 (590 nm) phases. The strong phosphorescence of the Ba2SiO4:Eu2+ phase in 2BaCO3–ySi3N4:0.01Eu2+y is attributed to N substitution for O to generate a shallow trap. In Ba2SiO4:0.01Eu2+-ySi3N4, however, N prefers reacting with Ba2SiO4 to form BaSi4O2N2, thereby exhibiting a strong phosphorescence of the BaSi2O2N2:Eu2+ phase but a weak phosphorescence of the Ba2SiO4:Eu2+ phase.

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In this paper, we report the LLP properties of BaSi2O2N2:Eu2+ and Ba2SiO4:Eu2+ phases in the materials with the compositions of Ba2SiO4:0.01Eu2+-xSi3N4 (x = 0–1) and 2BaCO3–ySi3N4:0.01Eu2+y (y = 1/6–1) for X-ray or CRT excitation. The role of N on the LLP is studied. The LLP phosphors are prepared by a solid-state reaction method under weak reductive atmosphere. The crystal structures, LLP, and thermoluminescence (TL) properties of phosphors are investigated. Due to the similar properties of LLP for X-ray or CRT excitation have not been demonstrated.

Experimental

Powder samples can be synthesized by using a high temperature solid-state reaction method. One group of samples, Ba2SiO4:0.01Eu2+-xSi3N4 (x = 0.03, 0.1, 0.2, 0.3, 0.5, 0.7, and 1.0), is prepared with Ba2SiO4:Eu2+ and Si3N4 as precursors, and the synthesized process is described below. The starting materials used were BaCO3 (analytical grade), SiO2 (analytical grade), and E4H2O (99.99%). These raw materials were taken in an agate mortar in a stoichiometric molar ratio and were ground for 1 h, and then the powder mixture was loaded into alumina crucibles and sintered at 1100–1300°C for 4 h in a horizontal tube furnace under weak reductive atmosphere (5% H2 + 95% N2 mixed flowing gas). After slowly cooling to room temperature, in stoichiometric molar ratio, the fired product Ba2SiO4:Eu2+ was mixed with α-Si3N4 and then the mixtures were ground in ethanol again for 1 h and sintered again at 1300–1500°C for 4 h in the same reducing gas flow as above. The other group of samples, 2BaCO3–ySi3N4:0.01Eu2+y (y = 1/6, 1/4, 1/3, and 1.0) phosphors, was prepared. BaCO3 and α-Si3N4 were ground in ethanol for 1 h in a stoichiometric molar ratio and were sintered at 1300–1500°C for 4 h in the same reducing gas flow as above. The crystal structures of all synthesized samples were finally checked using conventional X-ray diffraction (XRD, Rigaku D/M AX-2500V) with Cu target radiation at a 0.02° (20) scanning step. Photoluminescence, LLP spectra, and the decay curves of LLP were measured at room temperature using a fluorescent spectrophotometer (F-4000, Hitachi Ltd., Japan) equipped with X-ray as an excitation source. TL glow curves were measured using an Omega CN76000 thermostat above room temperature. All measurements except XRD and photoluminescence spectra were performed after irradiated by X-ray excitation source for 5 min.

Results and Discussion

The crystal structures of Ba2SiO4:0.01Eu2+-xSi3N4 with x = 0.03, 0.1, 0.3, 0.5, 0.7, and 1.0, are characterized by XRD. The XRD patterns of the samples are collected in the range of 20° ± 20°, as shown in Fig. 1. It exhibits that the XRD patterns of the samples are consistent with JCPDS no. 77-0150 for the Ba2SiO4 orthorhombic phase when the Si3N4 content is equal to or less than 0.1. However, with an increase in the content of Si3N4, the BaSi2O2N2 monoclinic phase is gradually formed and finally dominates the crystal phase as x = 1. The powder diffraction patterns of Ba2SiO4:0.01Eu2+ are essentially the same as those reported by Li et al.18 and Bachmann et al.17

At room temperature, no LLP can be detected in Ba2SiO4:Eu2+ after removing the X-ray or cathode ray excitation source. However, it is observed that Ba2SiO4:0.01Eu2+-xSi3N4 phosphors can generate LLP originating from Eu2+ either in the Ba2SiO4 phase or the BaSi2O5 phase as x > 0. Figure 2a shows the PL spectra of Ba2SiO4:Eu2+ and Ba2Si2O5:Eu2+ under excitation at 400 nm. Figure 2b shows the LLP emission spectra of Ba2SiO4:0.01Eu2+-xSi3N4 (x = 0.03, 0.1, 0.2, 0.3, 0.5, 0.7, and 1.0) phosphors detected immediately after the removal of X-ray excitation source. When x = 0.03, weak LLP is detected, and phosphorescence emission spectrum is in accordance with the PL spectrum of Ba2SiO4:Eu2+; however, in accordance with the PL spectrum of Ba2Si2O5:Eu2+ only, peaking at 490 nm. In view of no LLP in pure
Ba$_2$SiO$_4$:Eu$^{2+}$ at room temperature, it is speculated for the low Si$_3$N$_4$ content (x < 0.1) in Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ that N$^{3-}$ ions may enter into the Ba$_2$SiO$_4$:Eu$^{2+}$ lattices to replace O$^{2-}$ ions to form Ba$_2$Si$_2$O$_2$N$_2$:Eu$^{2+}$, generating traps for room-temperature LLP. For x = 0.1, Si$_3$N$_4$ reacts with Ba$_2$SiO$_4$:Eu$^{2+}$ to form BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ rather than to form Ba$_2$Si$_2$O$_2$N$_2$:Eu$^{2+}$. Although the XRD patterns (see Fig. 1) indicate the Ba$_2$SiO$_4$ phase as a main crystal phase for x = 0.1, the LLP exhibits the behavior of BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ as a sub-phase. This means that LLP prefers to appear in the BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ phase.

The decay curves of LLP in Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (x = 0.1, 0.2, 0.5, 0.7, and 1.0) are plotted in a double logarithmic coordinate after the X-ray excitation source is switched off at room temperature, as shown in Fig. 3. The decay curves approximatively fit the power law of $t^{-n}$, with $n = 0.75 < 1$. Perhaps this results from the radiative recombination of electrons and holes through tunneling and thermal hopping, as proposed by Yamaga et al. for understanding UV induced phosphorescence in Ba$_2$SiO$_4$:Eu$^{2+}$ and BaSi$_2$O$_2$N$_2$:Eu$^{2+}$.

Figure 4 shows the TL glow curves of Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (x = 0, 0.03, 0.1, 0.2, 0.3, 0.7, and 1.0) measured above room temper-
perature. The samples are mounted in the thermostat and heated up at a heating rate of about 1.4 K/s in the temperature range of 300–500 K. The TL glow curve of Ba$_2$SiO$_4$:Eu$^{2+}$ is composed of a dominant peak at 417 K and a shoulder at 374 K. Those peaks can be attributed to the intrinsic defects in the Ba$_2$SiO$_4$ host matrix. Due to high temperature locations, the two TL peaks therefore can hardly be released at room temperature to generate LLP. When $x = 0.03$, a TL peak at about 355 K appears. Considering the observation of a room-temperature LLP with an emission peak at 505 nm, the new TL peak at 355 K is attributed to the trap generated by N substitution for O in the Ba$_2$SiO$_4$:Eu$^{2+}$ host. With increasing $x$ from 0.1 to 1, the 355 K peak disappears, but three other peaks located at about 365, 320, and 335 K appear. When $x$ is equal to 1, only the 335 K peak is observed in the TL spectrum of BaSi$_2$O$_2$N$_2$:Eu$^{2+}$, indicating that it could be the intrinsic TL peak of the BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ phase, as shown in Fig. 4. As expected, a new strong TL peak is generated at 355 K. This new TL peak is considered to be the N substitution for O in Ba$_2$SiO$_4$:Eu$^{2+}$ and plays an important role on room-temperature LLP. Compared with the TL glow curve of Ba$_2$SiO$_4$:0.01Eu$^{2+}$–$x$Si$_3$N$_4$ for $x = 0.03$, as shown in Fig. 4, the intensity of the 355 K TL peak of 2BaCO$_3$–Si$_3$N$_4$:0.01Eu$^{2+}$ is much stronger, which results in an increase in LLP at room temperature.

Conclusions

The phosphors with compositions of either Ba$_2$SiO$_4$:0.01Eu$^{2+}$–$x$Si$_3$N$_4$ ($x = 0–1$) or 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ form a eutectic mixture. The XRD patterns for $x > 1/6$ are essentially in accordance with JCPDS card no. 77-0150 for the Ba$_2$SiO$_4$ phase. A strong LLP is observed in the 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ phosphors after the removal of the X-ray excitation source at room temperature. As shown in Fig. 6, when $y = 1/6$, the LLP spectrum shows a single broad orange-red band with a maximum at 590 nm, which should belong to the Ba$_2$SiO$_4$:Eu$^{2+}$ phase because the molar ratio of Ba/Si is 4:1 for $y = 1/6$, close to that of 3:1 in Ba$_2$SiO$_4$. When $y > 1/6$, the LLP spectra show a typical emission band at 505 nm of Eu$^{2+}$ in Ba$_2$SiO$_4$. The phosphorescence intensities increase with the increasing Si$_3$N$_4$ content. Figure 7 shows the TL glow curve of the 2BaCO$_3$–Si$_3$N$_4$:0.01Eu$^{2+}$ phosphor, which is composed of two peaks located at 410 and 355 K, respectively. Thereinto, 410 K peak is the intrinsic TL peak of the Ba$_2$SiO$_4$:Eu$^{2+}$ phase, as shown in Fig. 4.

Figures 5 and 6 show the XRD patterns and LLP spectra of 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ ($y = 1/6, 1/4, 1/3, 1/2, 1)$. Figure 7 shows the TL glow curve of the 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ phosphor.
(y = 1/6–1) are synthesized by a high temperature solid-state reaction method. Room-temperature LLP for X-ray or CRT excitation is observed in the phosphors.

1. The Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ phosphors show a weak LLP peak at 505 nm of the Ba$_2$SiO$_4$:Eu$^{2+}$ phase only for a small x ∼ 0.03. For 0.1 ≤ x ≤ 1, the LLP peak at 490 nm of the BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ phase is dominant.

2. 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ phosphors show a weak LLP peak at 590 nm of the Ba$_2$SiO$_4$:Eu$^{2+}$ phase only for small y ∼ 1/6. For 1/4 ≤ y ≤ 1, a strong LLP of the Ba$_2$SiO$_4$:Eu$^{2+}$ phase is detected to be enhanced by a factor of 7 in comparison with that of Ba$_3$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (x ∼ 0.03).

3. Pure Ba$_2$SiO$_4$:Eu$^{2+}$ exhibits a TL peak at 335 K, which is able to contribute to the room-temperature LLP. The TL peak of pure Ba$_2$SiO$_4$:Eu$^{2+}$ is located at a higher temperature of 417 K so that no LLP can be detected at room temperature.

4. The observed room-temperature LLP of the Ba$_3$SiO$_4$:Eu$^{2+}$ phase in either Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (x ∼ 0.03) or 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ (1/4 ≤ y ≤ 1) is attributed to N substitution for O to generate a new trap in the Ba$_2$SiO$_4$:Eu$^{2+}$ phase. The observed TL peak at 355 K is considered to be the evidence of the new trap.

5. In Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$, N prefers reacting with Ba$_2$SiO$_4$ to form BaSi$_2$O$_2$N$_2$ rather than replacing O in the Ba$_2$SiO$_4$ phase, therefore exhibiting strong LLP of BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ but very weak LLP of Ba$_2$SiO$_4$:Eu$^{2+}$.

These results indicate that the blue-green emitting phosphors presented in this paper could be promising LLP phosphors for X-ray or CRT. In view of a strong TL peak located at as high as 417 K, Ba$_2$SiO$_4$:Eu$^{2+}$ could also be a material for X-ray storage used in medical application.

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