Long-Lasting Phosphorescence in BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ and Ba$_2$SiO$_4$:Eu$^{2+}$ Phases for X-Ray and Cathode Ray Tubes

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In this paper, we report the LLP properties of BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ and Ba$_2$SiO$_4$:Eu$^{2+}$ phases for X-ray and cathode ray tubes. LLP is a phenomenon of thermal-stimulated recombination of electrons and holes at traps, which leave holes or electrons in a long-lived excited state at room temperature, in which the luminescence of LLP materials persists after the removal of the excitation source. Since 1996, LLP materials have been greatly reported, but those for X-ray and cathode ray tubes (CRTs) are seldom reported. Now, such LLP phosphors have been greatly reported; more and more attention has been drawn to the exploitation of LLP materials for various displays, signing applications, optical data storage, etc.3-6

Many LLP materials suitable for UV/visible light excitation have been reported, but those for X-ray and cathode ray tubes (CRTs) are seldom reported. Now, such LLP phosphors have been greatly attractive due to their extensive applications.11,12 One of the applications is for displaying radar echoes on the screen due to the long period of electron-beam rotation over the screen;13 the other application is for medical treatment equipments as an X-ray storage material.14-16 The crystal structures, LLP, and thermoluminescence (TL) properties of phosphors are investigated. Due to the similar properties of LLP for X-ray and CRT excitation, X-ray is chosen to be an excitation source in this work.

Experimental

Powder samples can be synthesized by using a high temperature solid-state reaction method. One group of samples, Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (x = 0.03, 0.1, 0.2, 0.3, 0.5, 0.7, and 1.0), is prepared with Ba$_2$SiO$_4$:Eu$^{2+}$ and Si$_3$N$_4$ as precursors, and the synthesized powder mixture was loaded into alumina crucibles and sintered at 1100–1300°C for 4 h in a horizontal tube furnace under weak reducing atmosphere (5% H$_2$ + 95% N$_2$ mixed flowing gas). After slowly cooling to room temperature, in stoichiometric molar ratio, the fired product Ba$_2$SiO$_4$:Eu$^{2+}$ was mixed with α-Si$_3$N$_4$ 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, Ba$_2$CO$_3$:ySi$_3$N$_2$:0.01Eu$^{2+}$ (y = 1/6, 1/4, 1/3, and 1.0) phosphors, was prepared. BaCO$_3$ and α-Si$_3$N$_4$ were ground in ethanol for 1 h in a stoichiometric molar ratio, and then 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° (2θ) 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 CN760000 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 Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$, 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° ≤ 2θ ≤ 60°, as shown in Fig. 1. It exhibits that the XRD patterns of the samples are consistent with JCPDS no. 77-0150 for the Ba$_2$SiO$_4$:Si$_3$N$_4$ orthorhombic phase when the Si$_3$N$_4$ content is equal to or less than 0.1. However, with an increase in the content of Si$_3$N$_4$, the Ba$_2$SiO$_4$:Si$_3$N$_4$ monoclinic phase is gradually formed and finally dominates the crystal phase as x = 1. The powder diffraction patterns of Ba$_2$SiO$_4$:xSi$_3$N$_4$:Eu$^{2+}$ are essentially the same as those reported by Li et al.15 and Bachmann et al.16

At room temperature, no LLP can be detected in Ba$_2$SiO$_4$:Eu$^{2+}$ after removing the X-ray or cathode ray excitation source. However, it is observed that Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ phosphors can generate LLP originating from Eu$^{2+}$ either in the Ba$_2$SiO$_4$ phase or the Ba$_2$Si$_3$N$_2$ phase as x > 0. Figure 2a shows the PL spectra of Ba$_2$SiO$_4$:Eu$^{2+}$ and Ba$_2$Si$_3$N$_2$:Eu$^{2+}$ under excitation at 400 nm. Figure 2b shows the LLP emission spectra of Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (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 Ba$_2$SiO$_4$:Eu$^{2+}$, peaking at around 505 nm. With increasing x from 0.1 to 1, the LLP is enhanced continuously and the emission spectra of LLP are no longer in accordance with the PL spectrum of Ba$_2$SiO$_4$:Eu$^{2+}$ but in accordance with the PL spectrum of Ba$_2$Si$_3$N$_2$:Eu$^{2+}$ 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$^{2+}$–$x$Si$_3$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$_2$SiO$_4$:Eu$^{2+}$,N$^{3-}$, generating traps for room-temperature LLP. For $x \geq 0.1$, Si$_3$N$_4$ reacts with Ba$_2$SiO$_4$:Eu$^{2+}$ to form Ba$_2$Si$_2$O$_2$N$_2$:Eu$^{2+}$ rather than to form Ba$_2$SiO$_4$:Eu$^{2+}$,N$^{3-}$. 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 Ba$_2$Si$_2$O$_2$N$_2$:Eu$^{2+}$ as a sub-phase. This means that LLP prefers to appear in the Ba$_2$Si$_2$O$_2$N$_2$:Eu$^{2+}$ phase.

The decay curves of LLP in Ba$_2$SiO$_4$:0.01Eu$^{2+}$–$x$Si$_3$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 Ba$_2$SiO$_4$:Eu$^{2+}$.

Figure 4 shows the TL glow curves of Ba$_2$SiO$_4$:0.01Eu$^{2+}$–$x$Si$_3$N$_4$ ($x = 0, 0.03, 0.1, 0.2, 0.3, 0.7, and 1.0$) measured above room temper-
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 Ba2SiO4:Eu2+ 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 Ba2SiO4 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 Ba2SiO4:Eu2+ 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 BaSi2O2N2:Eu2+, indicating that it could be the intrinsic TL peak of the BaSi2O2N2:Eu2+ phase. However, the appearance of 320 and 335 K peaks may be originated from the scarcity of N in the incomplete BaSi2O2N2:Eu2+ phase. The TL peak temperature is generally proportional to the trap depth. The depth of the trapping centers can be estimated to be

\[ E = kT_m^2/\beta_T \]

where \( T_m \) is the temperature of the glow peaks, \( \beta_T \) is the high temperature half-width, and \( k \) is Boltzmann's constant. The trap depths of the intrinsic TL peaks of BaSi2O2N2:Eu2+ and BaSi2O2N2:Eu2+ phosphors are calculated by this formula, and the results are 0.493 and 0.484 eV, respectively.

Although the Eu2+ activated LLP of the BaSi2O4 phase is observed in the Ba2SiO4:0.01Eu2+-xSi3N4 phosphors for a low x of 0.03, the LLP is very weak. To obtain a strong LLP in the Ba2SiO4 phase, we synthesized Ba2SiO4:Eu2+,N3− with the starting materials of 2BaCO3–ySi3N4–0.01 Eu2O3 by the solid-state reaction method at a reduction atmosphere. Figure 5 depicts the XRD patterns of 2BaCO3–ySi3N4:0.01Eu2+(y = 1, 1/3, 1/4, and 1.0).

When y is equal to 1, the content of Si3N4 may be too small to form a crystal phase but forms a eutectic mixture. The XRD patterns for x > 1/6 are essentially in accordance with JCPDS card no. 77-0150 for the Ba2SiO4 phase. A strong LLP is observed in the 2BaCO3–ySi3N4:0.01Eu2+ 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 Ba2SiO4:Eu2+ phase because the molar ratio of Ba/Si is 4:1 for y = 1/6, close to that of 3:1 in Ba3SiO6. When y > 1/6, the LLP spectra show a typical emission band at 505 nm of Eu2+ in Ba3SiO6. The phosphorescence intensities increase with the increasing Si3N4 content. Figure 7 shows the TL glow curve of the 2BaCO3–ySi3N4:0.01Eu2+ 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 Ba2SiO4:Eu2+ phase, as shown in Fig. 4. As expected, a new strong TL peak is generated at 355 K. When x is equal to 1/3, the intensity of the 355 K TL peak of 2BaCO3–Si3N4:0.01Eu2+ is much stronger, which results in an increase in LLP at room temperature.

**Conclusions**

The phosphors with compositions of either Ba2SiO4:0.01Eu2+–xSi3N4 (x = 0–1) or 2BaCO3–ySi3N4:0.01Eu2+(y = 1, 1/3, 1/4, and 1.0)
(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. Ba$_2$CO$_3$–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$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (x ∼ 0.03).

3. Pure Ba$_2$Si$_2$O$_5$: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$_2$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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