2010

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

Meiyuan Wang  
*Chinese Academy of Sciences*

Xia Zhang  
*Chinese Academy of Sciences*

Zhendong Hao  
*Chinese Academy of Sciences*

Xinguang Ren  
*Chinese Academy of Sciences*

Yongshi Luo  
*Chinese Academy of Sciences*

See next page for additional authors

Follow this and additional works at: [https://digitalcommons.georgiasouthern.edu/physics-facpubs](https://digitalcommons.georgiasouthern.edu/physics-facpubs)

Part of the Physics Commons

Recommended Citation


[https://digitalcommons.georgiasouthern.edu/physics-facpubs/71](https://digitalcommons.georgiasouthern.edu/physics-facpubs/71)

This article is brought to you for free and open access by the Department of Physics at Digital Commons@Georgia Southern. It has been accepted for inclusion in Physics Faculty Publications by an authorized administrator of Digital Commons@Georgia Southern. For more information, please contact digitalcommons@georgiasouthern.edu.
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

Meiyuan Wang, Xia Zhang, Zhendong Hao, Xinguang Ren, Yongshi Luo, Haifeng Zhao, Xiaojun Wang, and Jiahua Zhang

Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China
Graduate School of Chinese Academy of Sciences, Beijing 100029, China
Department of Physics, Georgia Southern University, Statesboro, Georgia 30460, USA

We report the long-lasting bluish-green phosphorescence for X-ray or cathode ray tubes in the phosphors with compositions of either Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ (x = 0–1) or 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ (y = 1/6–1) synthesized by a solid-state reaction. By tuning the Si$_3$N$_4$ content, the phosphorescence may originate from Eu$^{2+}$ in Ba$_2$SiO$_4$:N$_2$ (peaking at 490 nm), Ba$_2$SiO$_4$ (505 nm), and Ba$_3$SiO$_5$ (590 nm) phases. The strong phosphorescence of the Ba$_2$SiO$_4$:Eu$^{2+}$ phase in 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ is attributed to N substitution for O to generate a shallow trap. In Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$, however, N prefers reacting with Ba$_2$SiO$_4$ to form Ba$_3$SiO$_4$:N$_2$, thereby exhibiting a strong phosphorescence of the BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ phase but a weak phosphorescence of the Ba$_2$SiO$_4$:Eu$^{2+}$ phase.

© 2009 The Electrochemical Society. [DOI: 10.1149/1.3267513] All rights reserved.

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 process is described below. The starting materials used were BaCO$_3$ (analytical grade), SiO$_2$ (analytical grade), and E$_2$O$_3$ (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 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, 2BaCO$_3$–ySi$_3$N$_4$: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 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 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 ICPDF no. 77-0150 for the Ba$_2$SiO$_4$:Eu$^{2+}$ 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$_4$:N$_2$ monoclinic phase is gradually formed and finally dominates the crystal phase as x = 1. The powder diffraction patterns of Ba$_2$SiO$_4$:N$_2$:Eu$^{2+}$ are essentially the same as those reported by Li et al. and Bachmann et al.

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$_3$SiO$_4$:N$_2$ phase as x > 0. Figure 2a shows the PL spectra of Ba$_2$SiO$_4$:Eu$^{2+}$ and Ba$_3$SiO$_4$: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 about 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$_2$SiO$_4$: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$^{2+}$–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$_2$SiO$_4$:Eu$^{2+}$,N$^{3-}$, 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$_2$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 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 tem-

---

**Figure 1.** XRD patterns of Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ ($x = 0.03$, 0.1, 0.3, 0.5, 0.7, and 1.0).

**Figure 2.** (a) PL spectra of Ba$_2$SiO$_4$:Eu$^{2+}$ and BaSi$_2$O$_2$N$_2$:Eu$^{2+}$. (b) LLP 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).

**Figure 3.** Decay curves of Ba$_2$SiO$_4$:0.01Eu$^{2+}$–xSi$_3$N$_4$ ($x = 0.1$, 0.2, 0.5, 0.7, and 1.0).

**Figure 4.** 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).
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 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. The TL peak temperature is generally proportional to the trap depth. The depth of trapping centers can be estimated to be

$$E = kT_m^2/\delta_T$$

where $T_m$ is the temperature of the glow peaks, $\delta_T$ 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 Ba2SiO4 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 is our interest. Considering the generation of trap by N substitution for O in the Ba2SiO4 phase, we synthesized Ba2Si2O4:Eu2+,N3− with the starting materials of 2BaCO3–ySi3N4–0.01Eu2O3 by the solid-state reaction method at a reduction atmosphere. Figure 5 depicts the XRD patterns of 2BaCO3–ySi3N4:0.01Eu2+ (y = 1/6, 1/4, 1/3, and 1.0). When y is equal to 1/6, 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+ phase18 because the molar ratio of Ba/Si is 4:1 for y = 1/6, close to that of 3:1 in Ba2SiO4. When y > 1/6, the LLP spectra show a typical emission band at 505 nm of Eu2+ in Ba2SiO4. The phosphorescence intensities increase with the increasing Si3N4 content. Figure 7 shows the TL glow curve of the 2BaCO3–xSi3N4:0.01Eu2+ 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. This new TL peak is considered to be the N substitution for O in Ba2SiO4:Eu2+ and plays an important role on room-temperature LLP. Compared with the TL glow curve of Ba2SiO4:0.01Eu2+-xSi3N4 for $x = 0.03$, as shown in Fig. 4, 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+ are of interest. The phosphors show strong LLP at room temperature with emission maxima at 505 nm for x = 0–1, and at 590 nm for y = 1/6. The trap depth is estimated to be 0.493 eV for Ba2SiO4:0.01Eu2+ and 0.484 eV for Ba2Si2O2N2:Eu2+. The phosphor with composition 2BaCO3–ySi3N4:0.01Eu2+ (y = 1/6) shows a strong LLP at room temperature with an emission maximum at 590 nm, which is attributed to the intrinsic defects in the Ba2SiO4 host matrix.
(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$^{2+}$–$x$Si$_3$N$_4$ phosphors show a weak LLP peak at 505 nm of the Ba$_2$SiO$_4$:Eu$^{2+}$ phase only for a small $x \sim 0.03$. For 0.1 $\leq x \leq 1$, 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 $\leq y \leq 1$, 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$^{2+}$–$x$Si$_3$N$_4$ ($x \sim 0.03$).

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$_2$SiO$_4$:Eu$^{2+}$ phase in either Ba$_2$SiO$_4$:0.01Eu$^{2+}$–$x$Si$_3$N$_4$ ($x \sim 0.03$) or 2BaCO$_3$–ySi$_3$N$_4$:0.01Eu$^{2+}$ (1/4 $\leq y \leq 1$) 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$^{2+}$–$x$Si$_3$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.

Acknowledgment
This work was financially supported by the National Natural Science Foundation of China (10834006 and 10774141) and the MOST of China (2006CB601104 and 2006AA03A138).

Chinese Academy of Sciences assisted in meeting the publication costs of this article.

References