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Long-Lasting Phosphorescence in $BaSi_2O_2N_2$:Eu^{2+} and Ba_2SiO_4:Eu^{2+} 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 Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0–1) or $2BaCO_3$–ySi_3N_4:$0.01Eu^{2+}$ (y = 1/6–1) synthesized by a solid-state reaction. By tuning the Si_3N_4 content, the phosphorescence may originate from Eu^{2+} in $BaSi_2O_2N_2$ (peaking at 490 nm), Ba_2SiO_4 (505 nm), and Ba_3SiO_5 (590 nm) phases. The strong phosphorescence of the Ba_2SiO_4:Eu^{2+} phase in $2BaCO_3$–ySi_3N_4:$0.01Eu^{2+}$ is attributed to N substitution for O to generate a shallow trap. In Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4, however, N prefers reacting with Ba_2SiO_4 to form $BaSi_2O_2N_2$, thereby exhibiting a strong phosphorescence of the $BaSi_2O_2N_2$:Eu^{2+} phase but a weak phosphorescence of the Ba_2SiO_4:Eu^{2+} phase.
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Long-lasting phosphorescence (LLP) is a phenomenon of thermally 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.[1] Since 1996, LLP $SrAl_2O_4$:Eu^{2+},Dy^{3+} with high brightness and long duration was reported;[2] more and more attention has been drawn to the exploitation of LLP materials for various displays, signing applications, luminous ceramics, safety indicators, optical data storage, etc.[3-6]

Many LLP materials suitable for UV/visible light excitation have been reported,[7-10] 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 under IR. Ba_2SiO_4:Eu^{2+} and $BaSi_2O_2N_2$:Eu^{2+} are highly efficient bluish-green emitting phosphors for application in phosphor-converted white light-emitting diodes;[14,15] however, their LLP properties for X-ray or CRT excitation have not been demonstrated.

In this paper, we report the LLP properties of $BaSi_2O_2N_2$:Eu^{2+} and Ba_2SiO_4:Eu^{2+} phases in the materials with the compositions of Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0–1) and $2BaCO_3$–ySi_3N_4:$0.01Eu^{2+}$ (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 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_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0.03, 0.1, 0.2, 0.3, 0.5, 0.7, and 1.0), is prepared with Ba_2SiO_4:Eu^{2+} and Si_3N_4 as precursors, and the synthesized process is described below. The starting materials used were $BaCO_3$ (analytical grade), SiO_2 (analytical grade), and Eu_2O_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 reductive atmosphere (5% H_2 + 95% N_2 mixed flowing gas). After slowly cooling to room temperature, in stoichiometric molar ratio,

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the fired product Ba_2SiO_4:Eu^{2+} was mixed with α-Si_3N_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_3N_4:$0.01Eu^{2+}$ (y = 1/6, 1/4, 1/3, and 1.0) phosphors, was prepared. $BaCO_3$ and α-Si_3N_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° (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 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 Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_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_2SiO_4 orthorhombic phase when the Si_3N_4 content is equal to or less than 0.1. However, with an increase in the content of Si_3N_4, the $BaSi_2O_2N_2$ monoclinic phase is gradually formed and finally dominates the crystal phase as x = 1. The powder diffraction patterns of $BaSi_2O_2N_2$:Eu^{2+} are essentially the same as those reported by Li et al.[16] and Bachmann et. al.[17]

At room temperature, no LLP can be detected in Ba_2SiO_4:Eu^{2+} after removing the X-ray or cathode ray excitation source. However, it is observed that Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 phosphors can generate LLP originating from Eu^{2+} either in the Ba_2SiO_4 phase or the $BaSi_2O_2N_2$ phase as x > 0. Figure 2a shows the PL spectra of Ba_2SiO_4:Eu^{2+} and $BaSi_2O_2N_2$:Eu^{2+} under excitation at 400 nm. Figure 2b shows the LLP emission spectra of Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_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_2SiO_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_2SiO_4:Eu^{2+} but in accordance with the PL spectrum of $BaSi_2O_2N_2$:Eu^{2+} only, peaking at 490 nm. In view of no LLP in pure
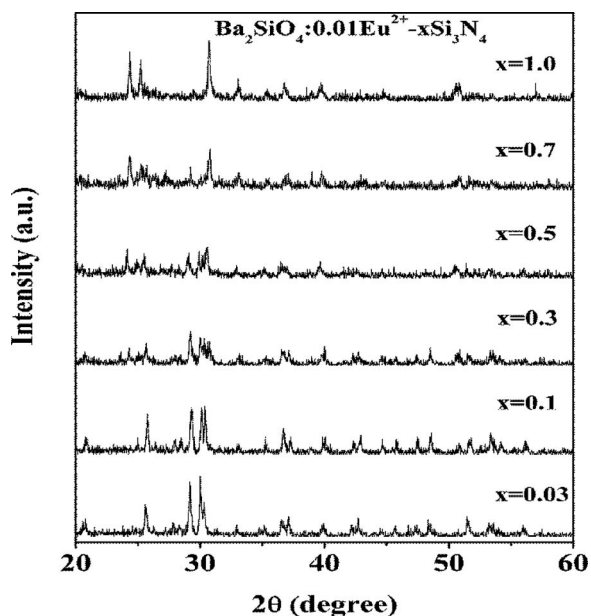
Figure 1. XRD patterns of Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0.03, 0.1, 0.3, 0.5, 0.7, and 1.0).

Figure 3. Decay curves of Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0.1, 0.2, 0.5, 0.7, and 1.0).

Ba_2SiO_4:Eu^{2+} at room temperature, it is speculated for the low Si_3N_4 content (x < 0.1) in Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 that N^{3-} ions may enter into the Ba_2SiO_4:Eu^{2+} lattices to replace O^{2-} ions to form Ba_2SiO_4:Eu^{2+},N^{3-}, generating traps for room-temperature LLP. For $x \geq 0.1$, Si_3N_4 reacts with Ba_2SiO_4:Eu^{2+} to form $BaSi_2O_2N_2$:Eu^{2+} rather than to form Ba_2SiO_4:Eu^{2+},N^{3-}. Although the XRD patterns (see Fig. 1) indicate the Ba_2SiO_4 phase as a main crystal phase for x = 0.1, the LLP exhibits the behavior of $BaSi_2O_2N_2$:Eu^{2+} as a subphase. This means that LLP prefers to appear in the $BaSi_2O_2N_2$:Eu^{2+} phase.

The decay curves of LLP in Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_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 $n \approx 0.75$ < 1. Perhaps this results from the
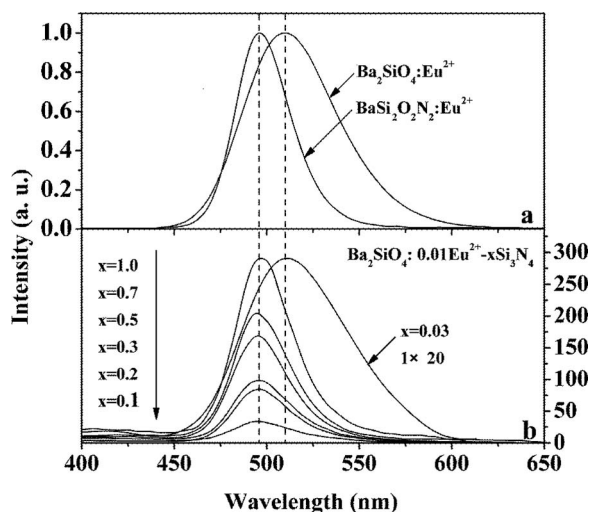
radiative recombination of electrons and holes through tunneling and thermal hopping, as proposed by Yamaga et al.[18] for understanding UV induced phosphorescence in Ba_2SiO_4:Eu^{2+} and Ba_3SiO_5:Eu^{2+}.

Figure 4 shows the TL glow curves of Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0, 0.03, 0.1, 0.2, 0.3, 0.7, and 1.0) measured above room tem-

Figure 2. (a) PL spectra of Ba_2SiO_4:Eu^{2+} and $BaSi_2O_2N_2$:Eu^{2+}, (b) LLP spectra of Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0.03, 0.1, 0.2, 0.3, 0.5, 0.7, and 1.0).
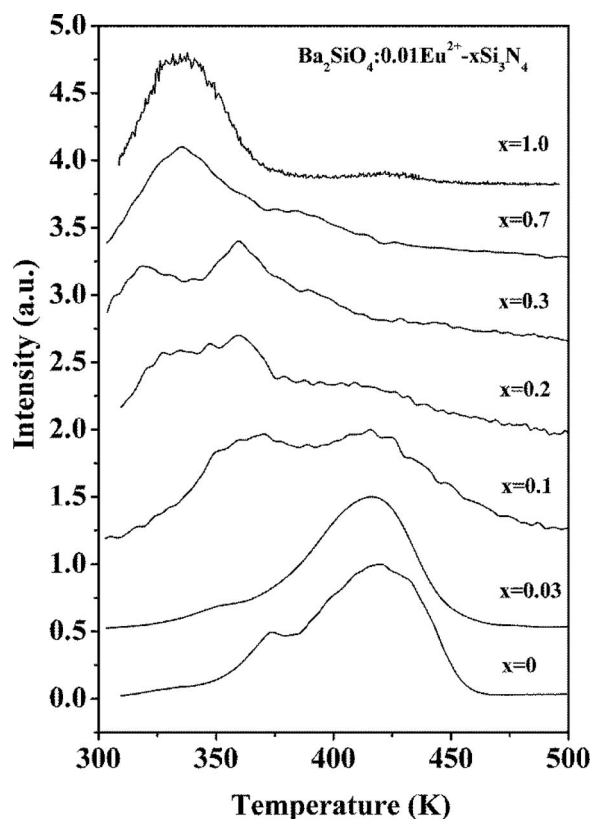
Figure 4. The TL glow curves of Ba_2SiO_4:$0.01Eu^{2+}$–xSi_3N_4 (x = 0, 0.03, 0.1, 0.2, 0.3, 0.7, and 1.0).
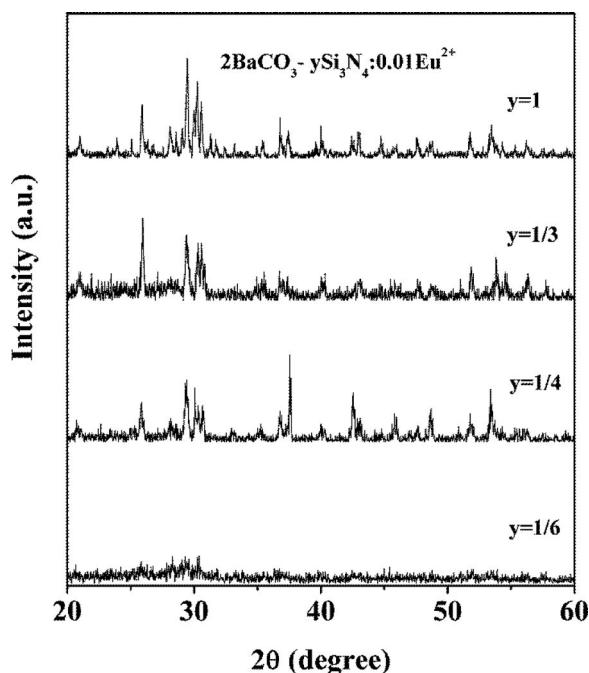
Figure 5. XRD patterns of $2BaCO_3–ySi_3N_4:0.01Eu^{2+}$ ($y = 1/6$, 1/4, 1/3, and 1.0).

Figure 6. LLP spectra of $2BaCO_3–ySi_3N_4:0.01Eu^{2+}$ ($y = 1/6$, 1/4, 1/3, 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 $Ba_2SiO_4:Eu^{2+}$ 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_2SiO_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 $Ba_2SiO_4:Eu^{2+}$ 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 $BaSi_2O_2N_2:Eu^{2+}$, indicating that it could be the intrinsic TL peak of $BaSi_2O_2N_2:Eu^{2+}$. However, the appearance of 320 and 365 K peaks may be originated from the scarcity of N in the incomplete $BaSi_2O_2N_2:Eu^{2+}$ phase. The TL peak temperature is generally proportional to the trap depth. The depth of the trapping centers can be estimated to be

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

where T_m is the temperature of the glow peaks, δ_T is the high temperature half-width, and k is Boltzmann's constant. The trap depths of the intrinsic TL peaks of $Ba_2SiO_4:Eu^{2+}$ and $BaSi_2O_2N_2:Eu^{2+}$ phosphors are calculated by this formula, and the results are 0.493 and 0.484 eV, respectively.

Although the Eu^{2+} activated LLP of the Ba_2SiO_4 phase is observed in the $Ba_2SiO_4:0.01Eu^{2+}–xSi_3N_4$ phosphors for a low x of 0.03, the LLP is very weak. To obtain a strong LLP in the Ba_2SiO_4 phase is our interest. Considering the generation of trap by N substitution for O in the Ba_2SiO_4 phase, we synthesized $Ba_2SiO_4:Eu^{2+},N^{3-}$ with the starting materials of $2BaCO_3–ySi_3N_4–0.01$ Eu_2O_3 by the solid-state reaction method at a reduction atmosphere. Figure 5 depicts the XRD patterns of $2BaCO_3–ySi_3N_4:0.01Eu^{2+}$ ($y = 1/6–1$). When y is equal to 1/6, the content of Si_3N_4 may be too small to form a crystal phase but forms

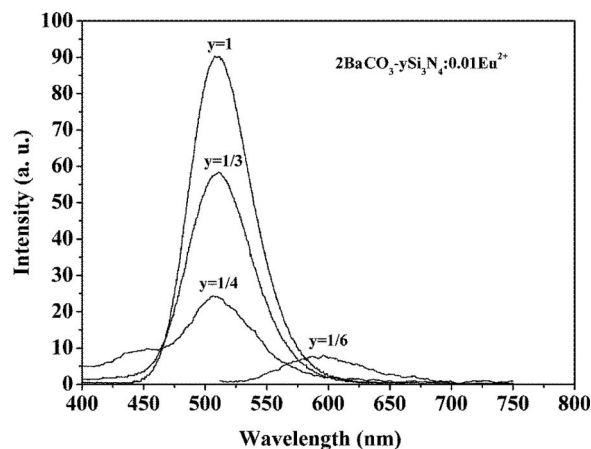a eutectic mixture. The XRD patterns for $x > 1/6$ are essentially in accordance with JCPDS card no. 77-0150 for the Ba_2SiO_4 phase. A strong LLP is observed in the $2BaCO_3–ySi_3N_4:0.01Eu^{2+}$ phosphors after the removal of the X-ray excitation source at room temperature. As shown in Fig. 6, when $y = 1/6$, the LLP spectrum shows a single broad orange-red band with a maximum at 590 nm, which should belong to the $Ba_3SiO_5:Eu^{2+}$ phase[18] because the molar ratio of Ba/Si is 4:1 for $y = 1/6$, close to that of 3:1 in Ba_3SiO_5. When $y > 1/6$, the LLP spectra show a typical emission band at 505 nm of Eu^{2+} in Ba_2SiO_4. The phosphorescence intensities increase with the increasing Si_3N_4 content. Figure 7 shows the TL glow curve of the $2BaCO_3–Si_3N_4:0.01Eu^{2+}$ 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 $Ba_2SiO_4:Eu^{2+}$ 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 $Ba_2SiO_4:Eu^{2+}$ and plays an important role on room-temperature LLP. Compared with the TL glow curve of $Ba_2SiO_4:0.01Eu^{2+}–xSi_3N_4$ for $x = 0.03$, as shown in Fig. 4, the intensity of the 355 K TL peak of $2BaCO_3–Si_3N_4:0.01Eu^{2+}$ is much stronger, which results in an increase in LLP at room temperature.

Conclusions

The phosphors with compositions of either $Ba_2SiO_4:0.01Eu^{2+}–xSi_3N_4$ ($x = 0–1$) or $2BaCO_3–ySi_3N_4:0.01Eu^{2+}$
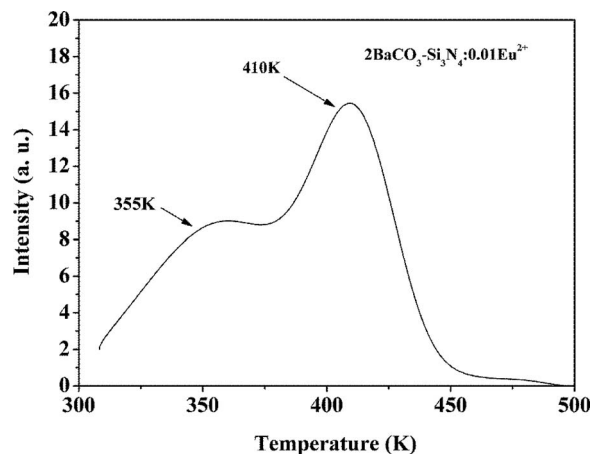
Figure 7. The TL glow curve of $2BaCO_3–Si_3N_4:0.01Eu^{2+}$.

($y = 1/6–1$) 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_2SiO_4:0.01Eu^{2+}–xSi_3N_4 phosphors show a weak LLP peak at 505 nm of the Ba_2SiO_4:Eu^{2+} phase only for a small x ~ 0.03. For $0.1 \leq x \leq 1$, the LLP peak at 490 nm of the $BaSi_2O_2N_2$:Eu^{2+} phase is dominant.

2. $2BaCO_3$–ySi_3N_4:0.01Eu^{2+} phosphors show a weak LLP peak at 590 nm of the Ba_3SiO_5:Eu^{2+} phase only for small y ~ 1/6. For $1/4 \leq y \leq 1$, a strong LLP of the Ba_2SiO_4:Eu^{2+} phase is detected to be enhanced by a factor of 7 in comparison with that of Ba_2SiO_4:0.01Eu^{2+}–xSi_3N_4 (x ~ 0.03).

3. Pure $BaSi_2O_2N_2$: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_2SiO_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_2SiO_4:Eu^{2+} phase in either Ba_2SiO_4:0.01Eu^{2+}–xSi_3N_4 (x ~ 0.03) or $2BaCO_3$–ySi_3N_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_2SiO_4:Eu^{2+} phase. The observed TL peak at 355 K is considered to be the evidence of the new trap.

5. In Ba_2SiO_4:0.01Eu^{2+}–xSi_3N_4, N prefers reacting with Ba_2SiO_4 to form $BaSi_2O_2N_2$ rather than replacing O in the Ba_2SiO_4 phase, therefore exhibiting strong LLP of $BaSi_2O_2N_2$:Eu^{2+} but very weak LLP of Ba_2SiO_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_2SiO_4:Eu^{2+} could also be a material for X-ray storage used in medical application.

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