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Enhanced phosphorescence in N contained $Ba_2SiO_4:Eu^{2+}$ for X-ray and cathode ray tubes

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ABSTRACT

A bluish-green color long-lasting phosphorescent phosphor of N contained $Ba_2SiO_4:Eu^{2+}$ for X-ray and cathode ray tubes are prepared with the chemical component formula $Ba_2SiO_4:0.01Eu^{2+} - xSi_3N_4 - 2BaCO_3$ ($x = 0.1$ to 1.0) by the conventional high-temperature solid-state method. The phosphorescence and fluorescence properties as a function of Si_3N_4 content and temperature are investigated. The emission spectra show a single broad band peaking at 505 nm, which are ascribed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Thermoluminescence (TL) glow-curves show that $Ba_2SiO_4:0.01Eu^{2+}$ without N holds a high-temperature peak at 417 K. With increasing the content of Si_3N_4, the phosphorescence grows super-linearly and some new TL peaks appear at low temperatures of about 400, 355, 365, and 335 K. These peaks are ascribed to the formation of new traps related to N substitution for O.

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1. Introduction

Long-lasting phosphorescence (LLP) is a phenomenon that the thermally stimulate recombination of electrons and holes at traps which leave holes or electrons in a long lived excited state at room temperature, is an interesting phenomenon in which the luminescence of LLP material persists after the removal of the excitation source [1,2]. Therefore, LLP phosphors can find application in sign boards, watch dials, etc. where one can see the objects clearly even in the dark [3].

The long-lasting phosphorescence (LLP) phosphors for X-ray and cathode ray tubes (CRT) have their broad application prospect [4,5]. One of the important applications of the phosphors is for displaying radar echoes on the screen due to the long period of electron beam rotation over the screen. At present, the persistent phosphor applied in the radar tube is mainly yellow–green emitting (Zn,Cd)S:Cu,Cl [6]. The persistent phosphor $Zn_2SiO_4:Mn^{2+}$ containing As_2O_3 additive exhibits a green emission at 525 nm, also suitable for radar tubes that operated by random scanning [7]. Some potential LLP phosphors for X-ray or CRT such as the red emitting $Y_2O_2S:Eu^{3+}$ [8] and the green emitting $KY_3F_{10}:Tb^{3+}$ phosphors were also reported [9]. In our previous work, we observed bluish-green LLP in N contained $Ba_2SiO_4:Eu^{2+}$ phosphors for X-ray or CRT excitation [10]. As we known, pure $Ba_2SiO_4:Eu^{2+}$ is a highly efficient bluish-green emitting phosphor for application in phosphor-converted white light-emitting diodes [11,12]. But its thermoluminescence (TL) glow-curve reveals that pure $Ba_2SiO_4:0.01Eu^{2+}$ phosphor holds a strong intrinsic TL peak at 417 K with a weak satellite peaking at 374 K. Due to high-temperature locations of the TL peaks, the filled traps in pure $Ba_2SiO_4:0.01Eu^{2+}$ can hardly be released at room temperature to generate bluish-green LLP. Our previous work demonstrated the preparation of N contained $Ba_2SiO_4:Eu^{2+}$ by the convention high-temperature solid-state reaction method with the nominal composition of either $Ba_2SiO_4:0.01Eu^{2+} - xSi_3N_4$ ($x = 0.03$) or $2BaCO_3 - ySi_3N_4$: $0.01Eu^{2+}$ ($y = 1/4$ to 1). The modified $Ba_2SiO_4:Eu^{2+}$ phosphors appear another new TL peak at low temperature of 355 K, leading to the performance of room temperature bluish-green LLP. The new TL peak is attributed to a new kind of trap related to N substitution for O site [10]. Though the strongest $Ba_2SiO_4:Eu^{2+}$ phase LLP intensity of $2BaCO_3 - ySi_3N_4$: $0.01Eu^{2+}$ ($y = 1.0$) is seven times as strong as that of $Ba_2SiO_4:0.01Eu^{2+} - xSi_3N_4$ ($x = 0.03$), the observed bluish-green LLP still require to be further enhanced.

In this paper, a modified $Ba_2SiO_4:Eu^{2+}$ phosphor is prepared with the nominal composition of $Ba_2SiO_4:0.01Eu^{2+} - xSi_3N_4 - 2BaCO_3$ ($x = 0.1$ to 1.0) by solid-state reaction method. The LLP and TL properties as a function of Si_3N_4 content are investigated. The enhanced bluish-green LLP in $Ba_2SiO_4:Eu^{2+}$ phase is performed.

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2. Experimental

Powder samples were synthesized by using the convention high-temperature solid-state reaction method. A group of modified Ba_2SiO_4:0.01Eu^{2+} (x) samples is prepared with the chemical composition of Ba_2SiO_4:0.01Eu^{2+} – $x$$Si_3N_4$ – 2$BaCO_3$ (x = 0.1, 0.2, 0.3, 0.5, 0.75 and 1.0). The starting materials used in the preparation of these phosphors are $BaCO_3$ (analytical grade), SiO_2 (analytical grade), and Eu_2O_3 (99.99%). The raw materials were taken in an agate mortar in stoichiometric molar ratio and were ground for 1 h, and then the dried powder mixture was loaded into alumina crucibles and was 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 the room temperature, in stoichiometric molar ratio the fired product Ba_2SiO_4:0.01Eu^{2+} was mixed with α-Si_3N_4 (99.9%) and $BaCO_3$, and then the mixtures were ground in ethanol for 1 h and were sintered again at 1300–1500 °C for 4 h in the same reducing gas flow as above. For comparison, the modified Ba_2SiO_4:0.01Eu^{2+} (y = 1.0) samples is also prepared with the chemical composition of 2$BaCO_3$ – Si_3N_4: 0.01Eu^{2+}. $BaCO_3$ 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 powder samples finally were checked using conventional X-ray diffraction (XRD) (Rigaku D/M AX-2500 V) with Cu target (λ = 0.154 nm) radiation at a 0.02° (2θ) scanning step. 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. The photoluminescence excitation (PLE) and emission (PL) spectra were obtained with a Hitachi F-4000 fluorescence spectrophotometer equipped with a monochromator and Xe lamp as the excitation source. LLP emission spectra and the phosphorescence intensity decay curves were measured on the same Hitachi F-4000 fluorescence spectrophotometer with the X-ray operated at 40 kV and 10 mA as an excitation source and the measurements were performed after the samples were irradiated for 5 min. The thermoluminescence (TL) measurements were the same as the LLP measurements and used omega CN76000 thermostat. All measurements except TL spectra were performed at room temperature.

3. Results and discussion

Modified Ba_2SiO_4:0.01Eu^{2+} (x = 0.1 to 1.0) phosphors show a bluish-green light emitting peaking at 505 nm under 400 nm excitation. Fig. 1a and b show the PLE and PL spectra of pure Ba_2SiO_4: 0.01Eu^{2+} and modified Ba_2SiO_4:0.01Eu^{2+} (x = 1.0), respectively. As shown in Fig. 1, the excitation and emission spectra of modified Ba_2SiO_4:0.01Eu^{2+} (x = 1.0) phosphors are in accordance with those of pure Ba_2SiO_4:0.01Eu^{2+}. The PLE spectra are in the region of 220–490 nm, which are attributed to $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} and the emission spectra show a bluish-green emitting peaking at 505 nm, which are ascribed to the $4f^65d^1 \rightarrow 4f^7$ transition of divalent europium [13,14] .

Fig. 2 shows the X-ray diffraction patterns of modified Ba_2SiO_4: 0.01Eu^{2+} (x = 0.1, 0.2, 0.3, 0.5, 0.75, and 1.0) with the standard JCPDS card No. 77-0150 for Ba_2SiO_4. The XRD patterns of samples are collected in the range of $20° \leqslant 2\theta \leqslant 60°$. It is exhibited that XRD patterns of the samples are consistent with the JCPDS card No. 77-0150 for Ba_2SiO_4 orthorhombic phase with the Si_3N_4 content $0.3 \leqslant x \leqslant 1$, indicating that the samples form solid solutions. It is also found that the XRD peaks of $BaCO_3$ (marked with spots in Fig. 2) clearly appear at 23.9° for $x \leqslant 0.2$, implying the occurrence of solubility saturation because of excessive amount of $BaCO_3$. However, when $x > 1/3$, the Si_3N_4 content is superfluous for forming Ba_2SiO_4 phase, but there is no diffraction peaks of Si_3N_4 appearing in the XRD patterns. That may be due to occurrence of reacting of remanent Si_3N_4 with formed CO to produce SiO_2, N_2 and a small quantity of C, and then SiO_2 is reduced to be Si under reductive atmosphere.

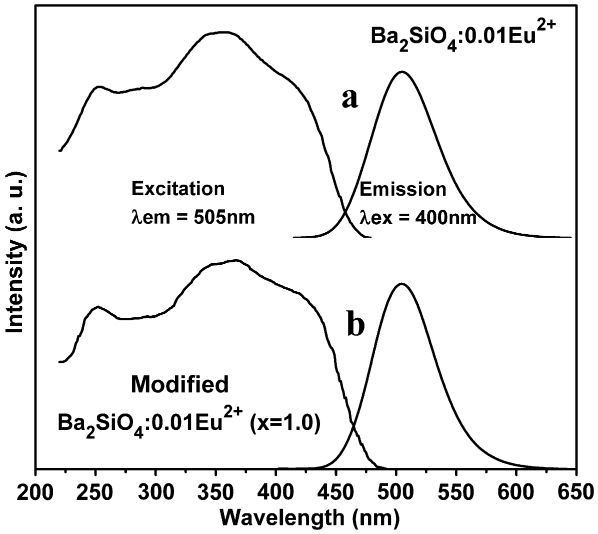

Fig. 1. PLE and PL spectra of pure Ba_2SiO_4:0.01Eu^{2+} (a) and modified Ba_2SiO_4:0.01Eu^{2+} (x = 1.0) (b).

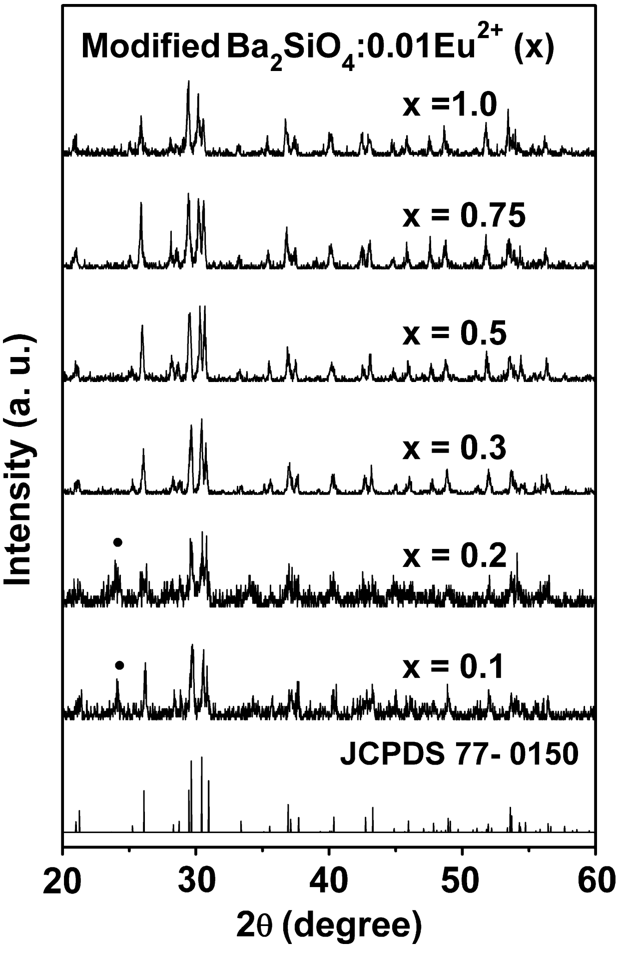

Fig. 2. XRD patterns of modified Ba_2SiO_4:0.01Eu^{2+} (x = 0.1, 0.2, 0.3, 0.5, 0.75 and 1.0) and the JCPDS Card No. 77-0150 (below).

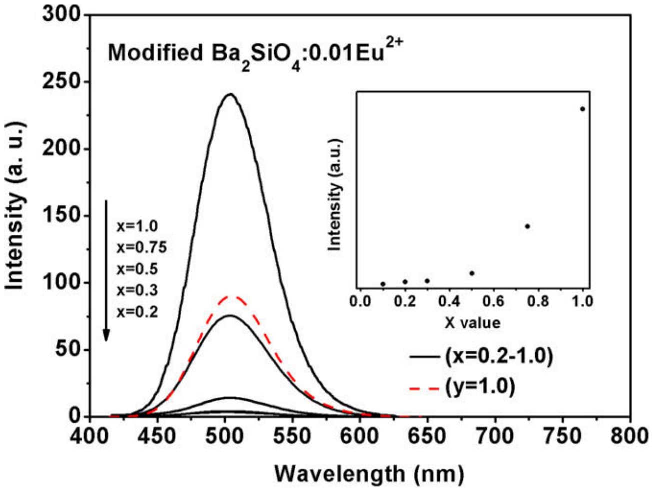

Fig. 3. LLP spectra of modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.2$, 0.3, 0.5, 0.75 and 1.0; $y = 1.0$) and the inset shows the LLP intensity as a function of Si_3N_4 content.

The phosphors with $x \geqslant 0.2$ show an intense bluish-green LLP after irradiated by X-ray or cathode ray excitation source, but no phosphorescence can be detected in the phosphor with $x \leqslant 0.1$. Fig. 3 depicts the LLP spectra of modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.2$ to 1.0, solid; $y = 1.0$, red dashed) detected immediately after the removal of X-ray excitation source. The LLP spectra of phosphors are completely identical with the PL spectrum of pure Ba_2SiO_4:0.01Eu^{2+}, presenting a single broadband peaking at about 505 nm due to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. The phosphorescence intensity of modified Ba_2SiO_4:0.01Eu^{2+} ($x = 1.0$) is about three times as strong as that of modified Ba_2SiO_4:0.01Eu^{2+} ($y = 1.0$). The LLP of modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.2$ to 1.0) are observed to be enhanced continuously with increasing Si_3N_4 content x, as shown in the inset of Fig. 3. It can be seen that the LLP grows super-linearly with increasing x from 0.2 to 1. Fig. 4a shows the decay curves of phosphorescence intensity of modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.75$ and 1.0). After irradiated by X-ray source, the strong bluish-green phosphorescence of samples is observed in the dark by the naked eye. The phosphorescence intensity is 20.8 and 22.8 mcd/m^2, respectively, for $x = 0.75$ and 1.0. The phosphorescence decay time with 50% intensity is 12.7s obtained from the process. The normalized decay curves of modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.75$ and 1.0) are plotted in a double logarithmic coordinate, as shown in Fig. 4b. The decay curves approximatively fit the power law of t^{-n}, with $n \approx 0.69 < 1$. 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_2SiO_4:Eu^{2+} and Ba_3SiO_5:Eu^{2+} [15]. We consider that N can enter into the Ba_2SiO_4:Eu^{2+} lattices to replace O to form a N_O point defect. The defect or their complexes perhaps act as traps for LLP. To know the formation processes of the traps, TL glow-curves of some related phosphors are studied.

Fig. 5 shows the TL glow-curves of pure Ba_2SiO_4:Eu^{2+} and modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.2$ to 1.0; $y = 1.0$). The samples were mounted in the thermostat and heated up with a heating rate about 1.4 K/s in the temperature range of 300–500 K after irradiated by X-ray excitation source. As shown in Fig. 5, the pure Ba_2SiO_4:0.01Eu^{2+} has its intrinsic TL curve that is composed of a dominant peak at 417 K with a shoulder at 374 K. Those peaks should be attributed to the intrinsic defects in the host matrix. Due to high-temperature locations, they can be hardly thermally

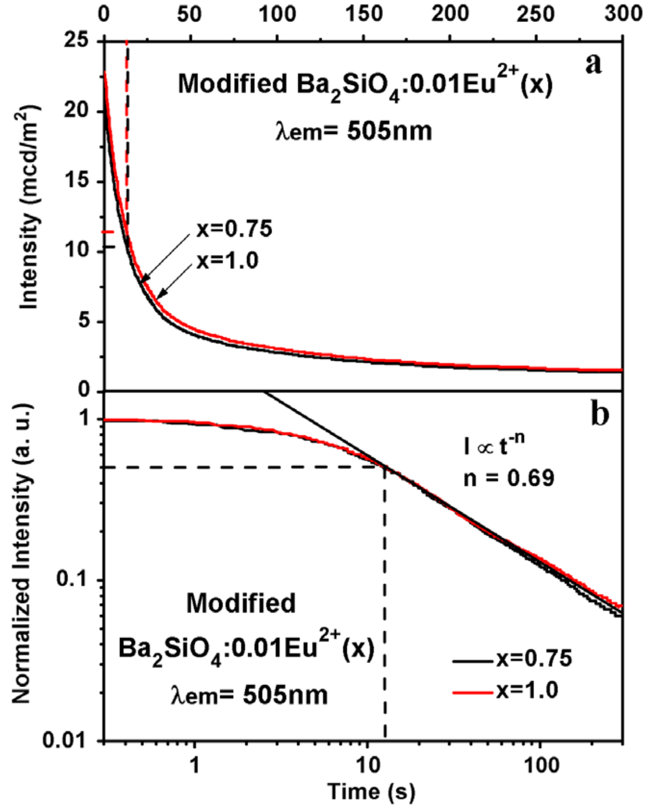

Fig. 4. Decay curves (a) and normalized decay curves (b) of the phosphorescence intensity of modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.75$ and 1.0).

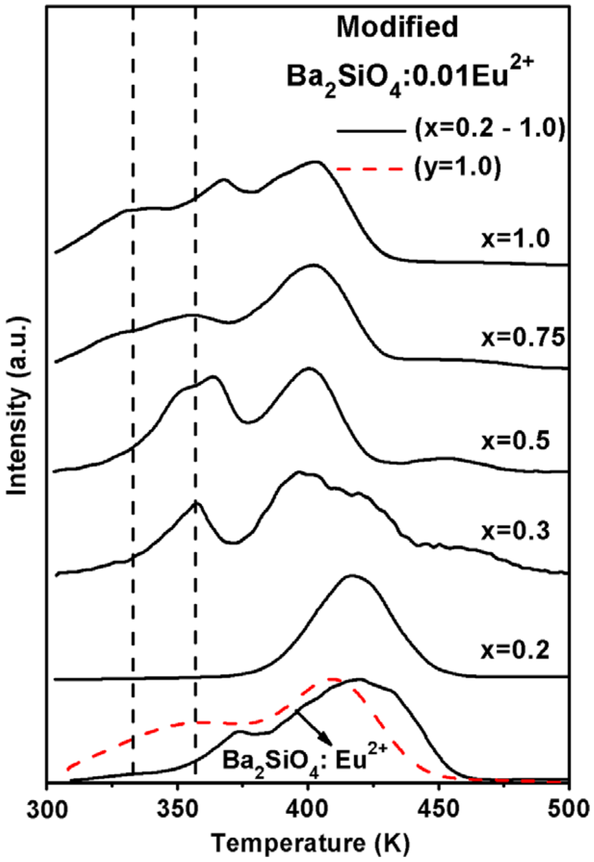

Fig. 5. Thermoluminescence (TL) glow-curves of pure Ba_2SiO_4:0.01Eu^{2+} and modified Ba_2SiO_4:0.01Eu^{2+} ($x = 0.2$, 0.3, 0.5, 0.75 and 1.0; $y = 1.0$).

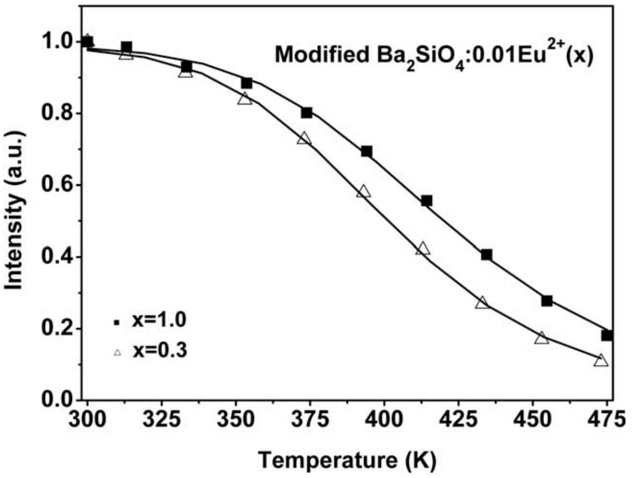

Fig. 6. Temperature dependence of the fluorescence emission intensities of modified $Ba_2SiO_4:0.01Eu^{2+}$ ($x = 0.3$ and 1.0).

released at room temperature to generate LLP. With adding Si_3N_4, the shoulder disappears at $x = 0.2$ and the 417 K peak reduces gradually and finally disappears at $x = 0.5$ in the modified $Ba_2SiO_4:0.01Eu^{2+}$ (x). Instead, some new TL peaks appear successively at about 400, 355, 365, and 335 K, indicating the formation of new traps. It can be seen that these new TL peaks are included in the TL curves (red dashed) of modified $Ba_2SiO_4:0.01Eu^{2+}$ ($y = 1.0$) phosphor. For high content of Si_3N_4 ($x > 0.5$), a peak at low temperature of 335 K appears, leading to the enhancement of room temperature LLP. In the modified $Ba_2SiO_4:0.01Eu^{2+}$ ($x = 0.2$ to 1.0) phosphor, as the mole ratio of $Si_3N_4/BaCO_3$ is less than 1/6, Si_3N_4 may react with $BaCO_3$ completely to form partial Ba_2SiO_4, making N atoms substitute for partial O atoms. When the mole ratio of $Si_3N_4/BaCO_3$ is more than 1/6, Si_3N_4 is excessive for forming Ba_2SiO_4, resulting in more N atoms substitution for O atoms to generate more traps. The increase of the number of traps makes the distance among traps monish. Hence, it is presumed that high Si_3N_4 content promotes two or more traps to form a complex trap, resulting in an exponential growth of LLP with increasing x. In this case, the peak at 335 K appeared for only high Si_3N_4 content is ascribed to the complex traps. Those peaks appeared for low Si_3N_4 content is ascribed to a single trap formed by a N^{3-} substitution for a O^{2-}.

Fig. 6 shows the fluorescence emission intensities of modified $Ba_2SiO_4:0.01Eu^{2+}$ ($x = 0.3$ and 1.0) as a function of temperature under excitation at 400 nm. The fluorescence intensities of phosphors decrease with the temperature increasing from 300 to 473 K. In the sample with $x = 0.3$, the quenching temperature at 50% of initial PL intensity is 401 K and for $x = 1.0$, the quenching temperature is 419 K. This means that the stability of phosphor for $x = 1.0$ is better than that for $x = 0.3$. According to the classical theory of thermal quenching, the temperature-dependent intensity can be described by the expression:

$$I(T) = \frac{I(0)}{1 + R\exp(-\Delta E/k_B T)} \qquad (1)$$

where R is the frequency factor with the unit of radiative rate. ΔE is the activation energy and k_B is the Boltzmann constant [16,17].

Using equation (1), a good fitting result is presented in Fig. 6. The values of ΔE are obtained to be 0.46 eV for $x = 0.3$ and 0.44 eV for $x = 1.0$, respectively.

It is worth noting that the TL property of holding high-temperature traps implies that $Ba_2SiO_4:0.01Eu^{2+}$ and modified $Ba_2SiO_4:0.01Eu^{2+}$ could be materials for X-ray storage. We have observed photo-stimulated bluish-green color luminescence upon 980 nm infrared stimulation in $Ba_2SiO_4:0.01Eu^{2+}$ and modified $Ba_2SiO_4:0.01Eu^{2+}$ phosphor after irradiated by X-ray source.

4. Conclusions

In conclusion, the enhanced bluish-green LLP of N contained $Ba_2\ SiO_4:Eu^{2+}$ is reported in this paper. The modified $Ba_2SiO_4:0.01Eu^{2+}$ phosphors with the chemical compositions of $Ba_2SiO_4:0.01Eu^{2+} - xSi_3N_4 - 2BaCO_3$ ($x = 0.1$ to 1.0) are synthesized by a two-step high-temperature solid-state reaction method under weak reductive atmosphere. The phosphors exhibit a strong bluish-green LLP when are excited under X-ray or CRT. LLP and TL properties of the phosphors after exposure of X-ray have been investigated as a function of Si_3N_4 content. With increasing the content of Si_3N_4, the phosphorescence grows super-linearly and some new TL peaks appear at low temperatures of about 400, 355, 365, and 335 K. These peaks are ascribed to the formation of new traps related to N substitution for O. High Si_3N_4 content may promote two or more traps to form a complex trap to enhance room temperature LLP. Temperature dependence of PL intensity reveals that the thermal stability of phosphors for the relative high Si_3N_4 content is better than that for low Si_3N_4 content.

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