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Luminescent properties of Na-codoped Lu_2SiO_5:Ce phosphor

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ABSTRACT

Lu_2SiO_5:Ce_x,Na_y ($x = 0.002–0.016$ and $y = 0.01–0.08$) phosphor was prepared by sol–gel method. The effect of Na^+ ions on the crystallization behavior and luminescence properties of LSO:Ce phosphor was investigated by X-ray diffraction (XRD) and spectral measurement. The results indicated that the crystallization temperature of LSO was reduced from 1200 °C to 1000 °C by Na^+ doping. The luminescence intensity of LSO:Ce phosphor under UV and X-ray excitation was much improved by Na-doping and the dopant concentration of the sample with maxima luminescent intensity was at $x = 0.006$ and $y = 0.02$. And the relationship between Na-doing concentration and the luminescent properties is discussed.

1. Introduction

The cerium doped lutetium oxyorthosilicate (LSO:Ce) is a well-known scintillator that is widely used for gamma-ray detection in positron emission tomography (PET) as well as in other applications[1–5]. The host of LSO has a monoclinic structure. In this lattice, the Lu atoms occupy two equally populated, crystallographically independent sites, which have oxygen coordination numbers of 6 and 7.When doped with cerium, the Ce is assumed to substitute for the two different Lu sites, designated Ce1 and Ce2 [6]. The scintillator light is due to the parity-allowed electric dipole 5d → 4f transition of the Ce^{3+} ion, which is strongly affected by the crystal field [4].

In recent years, considerable work has been done by a number of researchers on the use of codoping to improve the scintillation properties or growth of various inorganic scintillators [7–12]. LSO:Ce has been doped with Ca^{2+} or Mg^{2+} by Zavartsev et al., who reported some improvement in light yield, relative to LSO:Ce with no codoping [10–12]. Li^+ or Na^+ also frequently plays an important role in the influence of the luminescent efficiency for some luminescent materials [7–9]. More recently, we found that the luminescence intensity of LSO:Ce had been remarkably enhanced by doping Li^+ ions [13]. So far, however, there are few reports on the effect of Na^+ on the scintillation properties of LSO:Ce.

In present work, LSO:Ce,Na phosphor was prepared by Pechini sol–gel technique. The impact of Na^+ codoping on scintillation properties was discussed.

2. Experimental

Stoichiometric amount of Lu $(NO_3)_3 \cdot 6H_2O$ (99.99%, A.R.) and Ce $(NO_3)_3 \cdot 6H_2O$ (A.R.) were dissolved in a water–ethanol (v/v = 1:4) solution with vigorously stirring. Certain amount of Si $(OC_2H_5)_4$ (A.R.) was added in. The molar composition was Lu^{3+}:Si^{4+}:Ce^{3+} = 2:1:x ($x = 0.002–0.016$). The solution was set aside for 24 h at room temperature to form a sol. After drying, the gel was put into alumina crucible, and the gels in reducing atmosphere were covered with graphite and alumina lids. Then the gel was heated up to 1200 °C for 6 h. Finally, phosphor was cooled to room temperature and then was re-milled using an agate mortar. The Na-codoped samples were prepared by similar process. The source of Na^+ was from $NaNO_3$ (A.R.), and the molar composition was described as Lu^{3+}:Na^+ = 2:y ($y = 0.01–0.08$). In addition, the value of x and y is calculated according to the molar mass of Lu^{3+}.

The crystal structure of LSO:Ce_x,Na_y phosphor was examined by a Rigaku D/max-2550 X-ray powder diffractometer with Cu Kα radiation ($\lambda = 0.15405$ nm) operated at 40 kV and 100 mA. The morphology was measured by a Philips XL-30 scanning electronic microscopy (SEM). The photoluminescence spectra were recorded with a PerkinElmer LS-55 luminescence spectrometer. The X-ray excited luminescence spectra were measured by X-ray Excited Spectrometer, Fluor Main, where an F-30 X-ray tube (W anticathode target) was used as the X-ray source, and operated under 50 kV and 2 mA. Luminescence spectra were recorded with 44 W plate grating mnochromator and Hamamatsu R928-28 photomultiplier with the data acquired by a computer. In spectra measurements mentioned above, the samples were placed on a fixed sample stage. These measurements were carried out at room temperature. The thermoluminescence glow curve was recorded up to a temperature of 600 K with a heating rate of 2 K s^{-1} on FJ427A1 produced by Beijing Nuclear Instrument Factory.

3. Results and discussion

The XRD patterns of the LSO:Ce samples were shown in Fig. 1. As illustrated in Fig. 1(a), the LSO:Ce samples sintered at 1100 °C and 1200 °C. When sintered under 1100 °C, the cubic Lu_2O_3 phase could be obtained (PDF43-1021). And the LSO phase appeared when they were sintered at 1200 °C (PDF41-0239). It is indicated that the Pechini sol–gel chemistry is suitable to prepare LSO material. For

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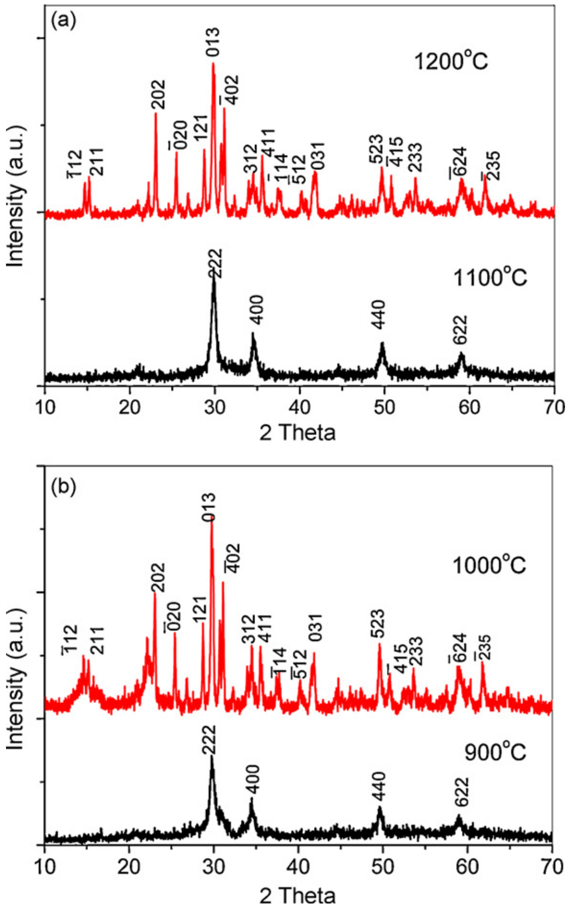

Fig. 1. XRD patterns of phosphors (a) LSO:$Ce_{0.006}$ sintered at different temperatures and (b) LSO:$Ce_{0.006}$,$Na_{0.02}$ sintered at different temperatures.

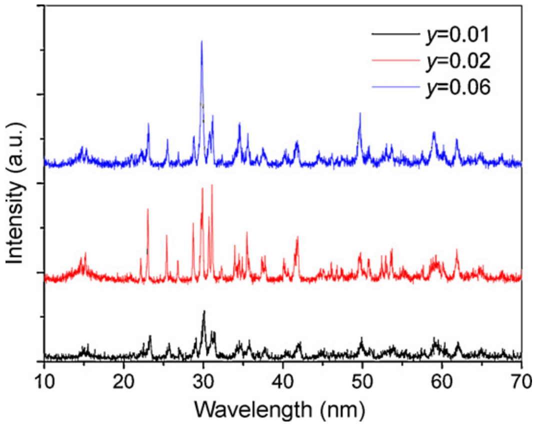

Fig. 2. XRD patterns of LSO:$Ce_{0.006}$,Na_y with different Na-doping concentrations.

the preparation of LSO:Ce,Na_y powders, the samples were sintered at 900 °C and 1000 °C. Under the condition of sintering at 900 °C, LSO:$Ce_{0.006}$,$Na_{0.02}$ shows the cubic Lu_2O_3 phase, and the LSO phase appeared at temperature of 1000 °C, see in Fig. 1(b). Pure LSO phase achieved by Na^+ codoping at 1000 °C illustrates that it is favorable for reducing the crystallization temperature of LSO. This is favorable from an economical point of view.

In order to analyze the effect of Na-doping concentration on crystallization of LSO:Ce phosphor, XRD patterns of LSO:$Ce_{0.006}$,Na_y samples sintered at 1000 °C are given in Fig. 2. It can be seen that the relative intensity of diffraction peak was improved due to the Na^+ doping. And the crystallization is much improved at $y = 0.02$. The codoping of Na^+ to LSO:Ce shows a shift to lower 2θ, implying that bigger Na^+ ions substituted the smaller Lu ion [14]. Reduced crystallization temperature and better crystallization can be regarded as the result of flux effect of Na^+ ions [15].

Fig. 3 illustrates the SEM images obtained from LSO:$Ce_{0.006}$,Na_y phosphors ($y = 0.00$, 0.01,0.02 and 0.06). In comparison with Fig. 3(a), whose grains agglomerated apparently, the grains in Fig. 3(b)–(d) gradually get larger and more fine-shaped particles

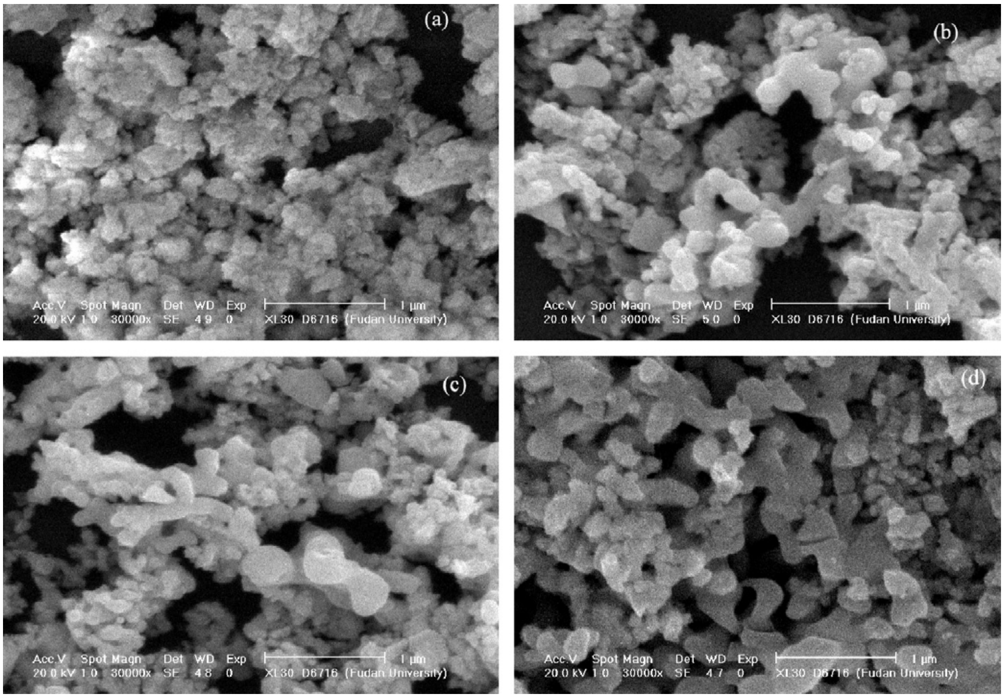

Fig. 3. SEM images of LSO:$Ce_{0.006}$,Na_y phosphors (a) $y = 0.00$, (b) $y = 0.01$, (c) $y = 0.02$, (d) $y = 0.06$.

appear which is consistent with Fig. 2 and is also regarded as the flux effect of Na^+ dopant.

It is established that the Ce^{3+} luminescence in the LSO host exhibits excitation and emission spectra of two distinct types under UV-excitation, with contributions from two luminescent centers Ce1 and Ce2 [4]. In order to measure the spectra of the samples, the LSO:Ce and LSO:Ce,Na_y powders were shaped into pellets ($\phi = 8$ mm, $h = 2$ mm) under the pressure of 2 MPa at room temperature.

The photoluminescence spectra of LSO:Ce phosphor are shown in Fig. 4(a). The excitation spectra of Ce^{3+} emission consists of three sub-bands of 5d states peaking at 264 nm, 296 nm and 358 nm. These bands are related to the transitions from the 4f ground state to the lowest 5d sublevel of the Ce^{3+} ion, subjected to the crystal filed splitting of the host. Moreover, the peaks at 264 nm and 296 nm are related to Ce1 and the peak at 358 nm is associated with both Ce1 and Ce2 [5].

As shown in Fig. 4(a), the emission band of Ce^{3+} can be decomposed into three components by using Gaussian fittings [16]. Two bands peaking at 392 nm and 420 nm originate from Ce1 center and one band peaking at 452 nm is from Ce2 center. The double structure for Ce1 is due to the electronic transition from the lowest 5d energy level to two 4f ground levels from the spin–orbit interaction. The double structure for Ce2 is mostly washed out at room temperature because of the thermal broadening effect [16,17]. All the spectra were normalized to their peak intensities and were shown in Fig. 4(b). The emission spectra all possessed very similar shapes. Based on assume that the integral of the emission spectra is directly proportional to the luminous intensity [6]. The relationship between the luminescence intensity and the Ce^{3+} doping concentration is obtained, as shown in inset Fig. 4(b), the optimal concentration of Ce^{3+} is about $x = 0.006$. The excitation and emission spectra of LSO:$Ce_{0.006}$,Na_y ($y = 0$, 0.02) phosphors are shown in Fig. 5(a). It is found that the luminescence intensity for Na-doped LSO:$Ce_{0.006}$ phosphor is much improved. The relationship between the luminescence intensity and the Na-doping concentration is given in Fig. 5(b). With the increase of Na^+ content, the total intensity increases and then decreases, and the climax appears at $y = 0.02$, where the emission intensity is a factor of 2.8 larger than that of the Na^+-undoped sample. On the basis of the results of XRD, the enhanced luminescence can be attributed to the improvement of crystallization of LSO:Ce phosphor due to the flux effect, which induces in higher oscillation strengths for the optical transitions [18] and brings on the enhancement of the luminescence intensity.

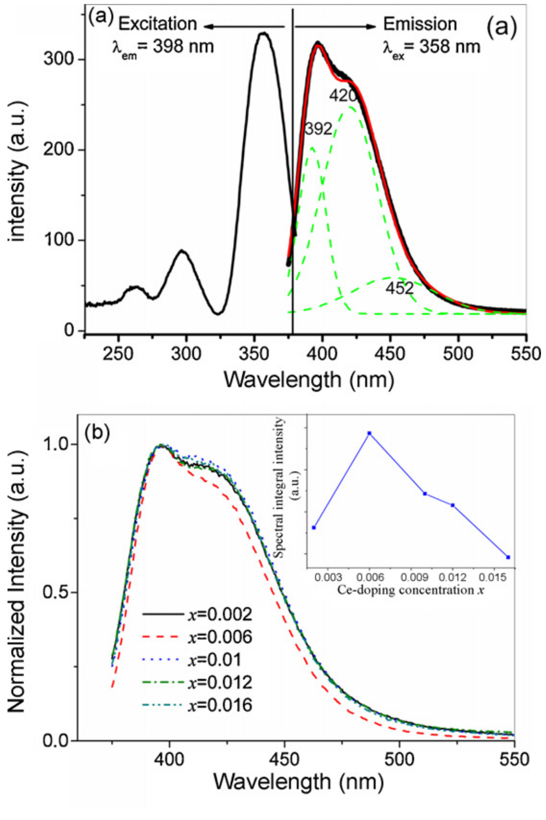

Fig. 4. (a) Typical excitation and emission spectra of LSO:$Ce_{0.006}$ phosphors and (b) the normalized emission spectra. Each spectrum is normalized to its peak intensity. The inset shows the dependence of spectral integral intensity on the Ce^{3+} content x.

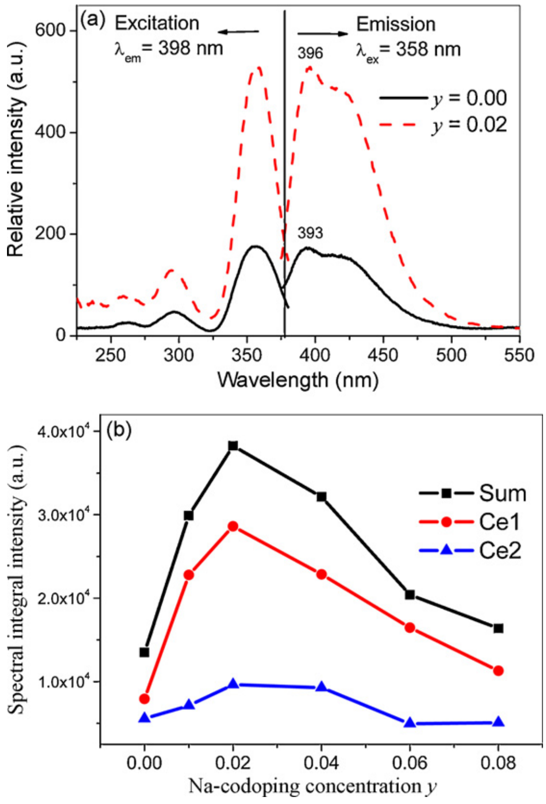

Fig. 5. (a) Typical excitation and emission spectra of LSO:$Ce_{0.006}$, Na_y phosphor, and (b) the relationship of Na^+-codoping content y and the emission of two sites (Ce1, Ce2 and sum of Ce1 and Ce2).

Compared to Na-uncodoped sample, a slightly red shift of Ce^{3+} emission band is observed in Na-doped LSO:$Ce_{0.006}$ phosphors, as shown in Fig. 5(a). The emission of Ce^{3+} is sensitive to the crystal field of the host lattice. It has been reported that the substitution of larger ions for smaller ions shifts the band of Ce^{3+} emission toward to red, while substitution of smaller ions shift the band toward to blue [19]. Although the particular sites occupied by Na^+ ions in LSO lattice are not clear, the probable sites might be substitution for Lu^{3+} sites because the effective radius of Na^+ ion (0.97 Å) is just slightly larger than that of Lu^{3+} ion (0.85 Å). This means that the incorporation of Na^+ into LSO:Ce lattice would induce in an alteration of the crystal field surrounding the Ce^{3+} ions, leading to a red shift for Ce^{3+} emission band, and even affecting the luminescence properties of LSO:Ce phosphors. The red shift was also observed in YAG:Ce,La(Gd) when smaller ion Y^{3+} was substituted by La^{3+} or Gd^{3+} [20].

To judge the relative trends between intensities of Ce1 and Ce2 centers and their dependence on the Na codoping, the Gaussian decomposition of the spectra was used. The emission bands of Ce^{3+} in LSO:$Ce_{0.006}$,Na_y ($0 \le y \le 0.08$) can be divided into three com-

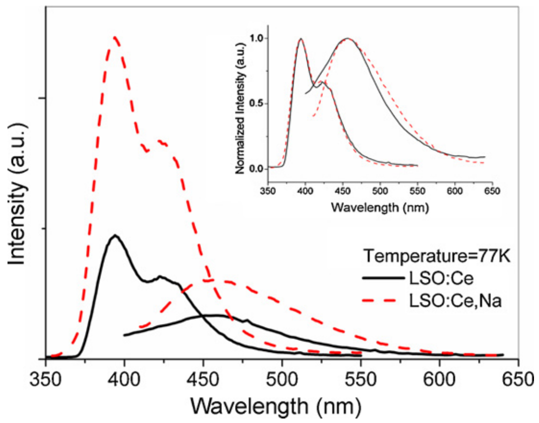

Fig. 6. The UV-excited Ce1 (excited at 296 nm) and Ce2 (excited at 376 nm) emission spectrum at 77K. The inset shows the normalize emission spectra. Each spectrum is normalized to its peak intensity.

ponents by using Gaussian fittings at room temperature, peaking at 392 nm, 420 nm and 452 nm, which two of them (392 nm and 420 nm) originated from Ce1 and one (452 nm) is from Ce2 [16]. Based on assume that the integral of the emission spectra is directly proportional to the luminous intensity [6], the relationship of the luminous intensity of two sites (Ce1 and Ce2) and the Na-doping concentration was given in Fig. 5(b). It can be seen that the increasing magnitude of emission intensity for Ce1 site is much larger than that for Ce2 site, and the relative ration of Ce1/Ce2 presents increasing trend. In order to investigate the influence of Na^+ doping on the population of two sites, the spectra of Ce1 and Ce2 at low temperature (77 K) were measured on an Edinburgh FLS920 as seen Fig. 6.

Fig. 6 displays two emission spectra excited at 296 nm (Ce1) and 376 nm (Ce2). The spectra of Ce1 have two emission peaks at 393 nm and 423 nm, showing the characteristic transition of the Ce^{3+} ion from the 5d levels to the two 4f ground states. The spectrum of Ce2 has an emission peak at 455 nm, for which the Ce^{3+} doublet structure cannot be seen. The spectra were shown inset in Fig. 6 normalized to their peak intensities and the emission spectra all possessed very similar shapes; the only difference between them is the relative height of the lower energy peak of Ce2 spectra. And the results are in accordance with the published data [6]. Based on assume that the integral of the emission intensity from a given type of Ce center is directly proportional to the concentration of that type of Ce center [6], the integral of the emission intensity and the relative ratio of Ce1/Ce2 were calculated. The population of two sites increased by Na^+ doping and the population of Ce1 increased faster than that of Ce2, which also could be speculated from the spectrum in Fig. 6. This means that more Ce^{3+} might enters into Lu1 sites by Na^+ doping, which also can enhance the luminescence intensity. This will be very useful to reach the requirement of practical application [21].

In order to further understand the influence of Na^+-doping on the luminescence properties of two sites, it is necessary to analyze the decay time of the two sites (Ce1 and Ce2) separately, for Ce2 and Ce1 sites have individual decay times, and they would be affected by the luminescent intensity [4,16]. The light emission decay curve of LSO:$Ce_{0.006}$,Na_y ($y \leq 0.02$) phosphors for two sites were measured with the time correlated single photon counting technology on a Edinburgh FL920 spectrofluorimeter and all of decay curves could be fitted by using single exponential function as $y = A\exp(-t/\tau)$, where τ is the decay time. The scanning excitation and emission wavelengths for Ce1 center were fixed at 296 nm and 392 nm, and they were fixed at 376 nm and 480 nm for Ce2, which are the most effective excitation and emission wavelengths for the two sites [4].

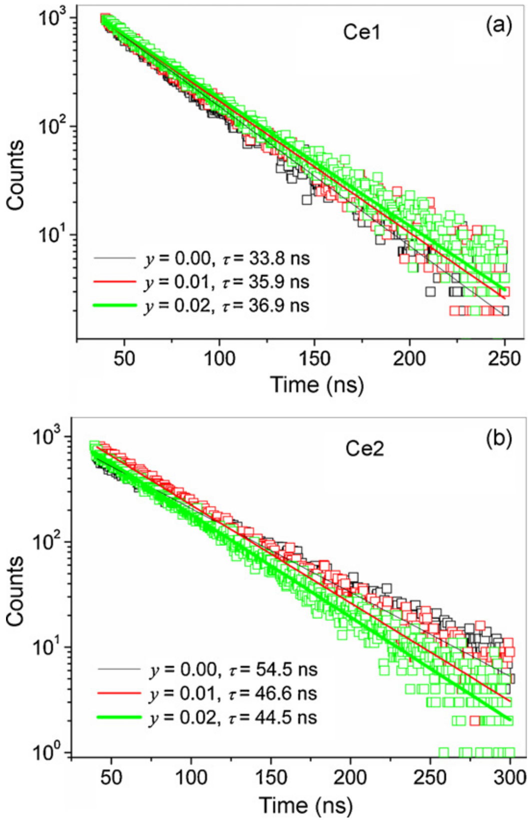

Fig. 7. Decay curves of LSO:$Ce_{0.006}$,Na_y ($y \leq 0.02$) phosphors for Ce1and Ce2.

As shown in Fig. 7, with the increase of Na^+ content, the decay time of Ce1 emission increases from 33.8 ns to 36.9 ns, whereas that of Ce2 emission decreases from 54.5 ns to 44.5 ns. The decreasing rate of the decay time for Ce2 site is larger than the increasing rate for Ce1 site, which corresponds to the tendency of the emission intensities of Ce1 and Ce2 sites. This can be attributed to the different speed of luminescence enhancement and population of two sites.

The emission spectra of LSO:$Ce_{0.006}$,Na_y under X-ray excitation are shown in Fig. 8. The luminescence intensities of LSO:$Ce_{0.006}$,$Na_{0.02}$ phosphors are also greatly enhanced by Na^+ codopant and the intensity is increased by a factor of 3.3 in comparison with that of undoped sample. And the spectra were normalized to their peak intensities and they all possessed very similar shapes.

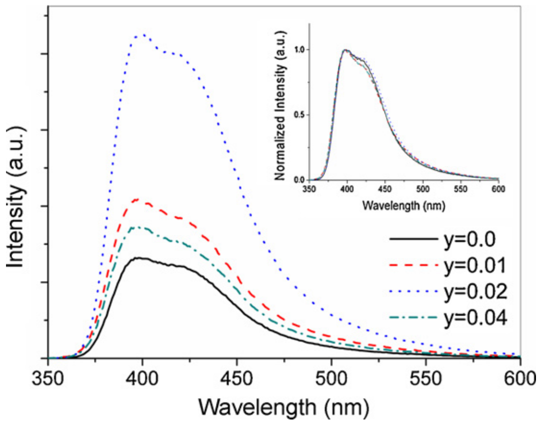

Fig. 8. Emission spectra of LSO:$Ce_{0.06}$,Na_y phosphors under X-ray excitation. The inset shows the normalize spectra and each spectrum is normalize to its peak intensity.

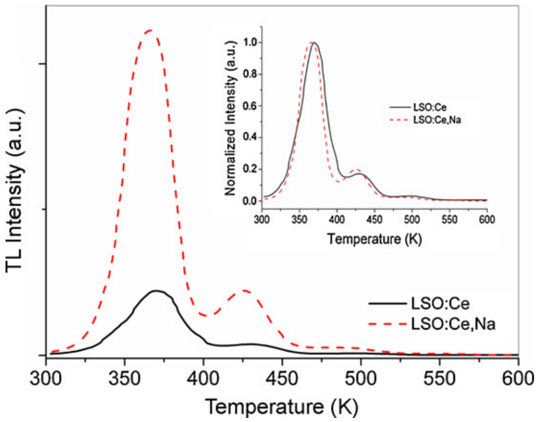

Fig. 9. The thermoluminescence glow curves of LSO:$Ce_{0.006}$,Na_y ($y = 0.00$ and 0.02).

The Na-codoped LSO:Ce phosphor with highly enhanced luminescence is promising in practical applications.

It is known that the valence and the radius of Na^+ are different from that of Lu^{3+} and the Na^+ doping may introduce defects. Moreover, oxygen vacancies are likely to be introduced in sample preparation. The samples were exposed to X-rays (80 kV, 6 mA) for 20 s at room temperature in air and the curves were recorded at a heating rate of 2 K s^{-1}, and the thermoluminescence (TL) glow curves of LSO:$Ce_{0.006}$,Na_y ($y = 0.00$ and 0.02) were given in Fig. 9. As shown in Fig. 9, the TL glow curve of LSO:Ce exhibited three peaks with maxima near 370 K, 430 K and 500 K. And the results are in consistent with the published data [22]. In comparison with undoped sample, there is a little shift in the curves of Na-doped sample, which exhibited three peaks near 365 K, 425 K and 485 K. But the two curves are strikingly similar. As proposed by Dorenbos [23], the first peak near 375 K is responsible for the afterglow, which has some relationship with oxygen vacancies [10,11]. It is possible that Na^+ compensates for oxygen vacancies that would otherwise diminish light output by trapping electrons in competition with Ce [11]. And this may also have some influence on the emission of the relative populations of the two Ce sites [11], which cannot be ruled out but requires further investigation.

4. Conclusions

Lu_2SiO_5:Ce_x, Na_y phosphor was successfully prepared by Pechini sol–gel technique. The XRD patterns show that codoping LSO:Ce phosphor with Na^+ can reduce the crystallization temperature of LSO phosphor and favorable for crystallize. With respect to the luminescence enhancement by Na-doping, it is possible that Na^+ compensates for oxygen vacancies or the flux effect of Na^+. However, it is not obvious that why Na^+ could affect the relative populations of the two Ce sites, which also can influence the luminous intensity. To fully explain our results, Na^+ would need to perform both of the above functions and some unknown traps introduced by Na-doping, which needs further investigation.

Acknowledgments

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References

[1] C.L. Melcher, J.S. Schweitzer, IEEE. Trans. Nucl. Sci. 39 (1992) 502–505.
[2] C.L. Melcher, Nucl. Instrum. Methods Phys. Res. A 537 (2005) 6–14.
[3] W.W. Moses, Nucl. Instrum. Methods Phys. Res. A 487 (2002) 123–128.
[4] H. Suzuki, T.A. Tombrello, C.L. Melcher, J.S. Schweitzer, IEEE Trans. Nucl. Sci. 40 (1993) 380–383.
[5] D.W. Cooke, B.L. Bennett, K.J. McClellan, Phys. Rev. B 61 (2000) 11973–11978.
[6] J.D. Naud, T.A. Tombrello, C.L. Melcher, J.S. Schweitzer, IEEE Trans. Nucl. Sci. 43 (1996) 1324–1328.
[7] O.A. Lopez, J. McKittrick, L.E. Shea, J. Lumin. 71 (1997) 1–11.
[8] X.L. Liu, K. Han, M. Gu, L.H. Xiao, C. Ni, S.M. Huang, B. Liu, Solid State Commun. 142 (2007) 680–684.
[9] Shinya Oikawa, Chiharu Hidaka, Takeo Takizawa, J. Phys. Chem. Solids 69 (2008) 400–403.
[10] Y.D. Zavartsev, S.A. Koutovoi, A.I. Zagumennyi, J. Cryst. Growth 275 (2005) e2167–e2171.
[11] M.A. Spurrier, P. Szupryczynski, K. Yang, A.A. Carey, C.L. Melcher, IEEE Trans. Nucl. Sci. 55 (2008) 1178–1182.
[12] M.A. Spurrier, P. Szupryczynski, H. Rothfuss, K. Yang, A.A. Carey, C.L. Melcher, J. Cryst. Growth 310 (2008) 2110–2114.
[13] Lingchun Jia, Mu Gu, Xiaolin Liu, Shiming Huang, Bo Liu, Chen Ni, IEEE Trans. Nucl. Sci. 57 (3) (2010) 1–4.
[14] R.D. Shannon, Acta Cryst. A-32 (1976) 751–767.
[15] Yinzhen Wang, Qinyu He, Benli Chu, J. Alloys Compd. 479 (1–2) (2009) 704–707.
[16] Bo Liu, Chaoshu Shi, Min Yin, et al., J. Lumin. 117 (2006) 129–134.
[17] Eric Bescher, S.R. Robson, J.D. Mackenzie, B. Patt, J. Iwanczyk, E.J. Hoffman, J. Sol–Gel Sci. Technol. 19 (2000) 325–328.
[18] K.C. Misbra, J.K. Berkowitz, K.H. Johnson, P.C. Schmidt, Phys. Rev. B 45 (1992) 10902–10906.
[19] W. Holloway, M. Kestigan, J. Opt. Soc. Am. 59 (1969) 60–63.
[20] M. kottaisamy, P. Thiyagarajan, J. Mishra, M.S. Ramachandra, Mater. Res. Bull. 43 (2008) 1657–1663.
[21] A. Saoudi, C. Pepin, D. Houde, R. Lecomte, IEEE Trans. Nucl. Sci. 46 (6) (1999) 1925–1928.
[22] D.W. Cooke, R.E. Muenchausen, B.L. Bennett, K.J. McClellan, J. Appl. Phys. 86 (1999) 5308–5310.
[23] P. Dorenbos, C.W.E. van Eijk, A.J.J. Bos, C.L. Melcher, J. Lumin. 60–61 (1994) 979–982.