A novel red emitting phosphor Ca_2SnO_4: Eu^{3+}

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Abstract

A novel red emitting phosphor, Eu^{3+}-doped Ca_2SnO_4, was prepared by the solid-state reaction. X-ray powder diffraction (XRD) analysis confirmed the formation of Ca_2SnO_4: Eu^{3+}. Field-emission scanning electron-microscopy (FE-SEM) observation indicated a narrow size-distribution of about 500 nm for the particles with spherical shape. Photoluminescence measurements indicated that the phosphor exhibits bright red emission at about 615 nm under UV excitation. The excellent luminescence properties make it possible as a good candidate for plasma display panels (PDP) application. Splitting of the $^5D_0-^7F_J$ transitions of Ca_2SnO_4: Eu^{3+} suggests that the Eu^{3+} ions occupied two nonequivalent sites in the crystallite. The luminescence lifetime measurement showed a bi-exponential decay, providing other evidence for the existence of two different environments for Eu^{3+} ions.
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1. Introduction

Plasma display panels (PDPs) are the most promising candidate for large size flat-panel information-display devices. As phosphors play a key role in the performances of the devices, much research has been made in exploring good phosphors for application in PDPs in recent years [1–7]. Alkaline earth stannate is drawing more and more attention for new phosphors. Chau et al. [8] reported Sr_2SnO_4:Eu^{3+} phosphor. Kima and his co-workers [9] reported a new excellent luminescent phosphor, Mg_2SnO_4: Mn^{2+} for application in PDPs. As we all know, the influence of the host lattice, especially the anions, is very important when phosphors are excited by VUV [6]. This opens up the possibility to explore new phosphors for PDPs. Alkaline earth stannate has the advantages of stable crystalline structure and high physical and chemical stability. Since rare-earth (RE) ions have numbers of efficient and narrow emission lines in the visible region, the position

of which is insensitive to their matrices due to the shielding effect of outer $5s$ and $5p$ electrons [10], RE ion doped phosphors are attracting more and more attention in PDPs [11]. As a likely good electron trap, europium is favorable as an activator of phosphors for application in PDPs [1]. So a phosphor, Eu^{3+}-doped Ca_2SnO_4, may provide another choice for these applications. In this article, a novel phosphor, Ca_2SnO_4: Eu^{3+}, was prepared for the first time to our best knowledge by conventional solid-state reaction and the photoluminescence (PL) of the phosphor was investigated.

2. Experimental

2.1. Preparation of $(Ca_{1-x}Eu_x)_2SnO_4$ samples

Materials with general composition of $(Ca_{1-x}Eu_x)_2SnO_4$ ($x = 0.01-0.09$) were synthesized by solid-state reaction. Firstly, a stoichiometric amount of the starting materials, $CaCO_3$ (analytical grade), SnO_2 (analytical grade) and Eu_2O_3 (99.99%) were mixed in an agate mortar using ethanol and then were triturated for a good mixing. The

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mixed power was dried in an oven at 80 °C and heated in a corundum crucible at 1250 °C for 2 h, retriturated and then reheated at 1100 °C for 1 h.

2.2. Apparatuses and measurements

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D/max-IIIA diffractometer, RIGAKU Corporation of Japan. 40 kV and 20 mA, $CuK\alpha = 1.5406$ Å, Rigaku/Dmax-IIIA) for crystal phase identification.

The morphology and size of the calcined particles were observed by field-emission scanning electron-microscopy (FE-SEM, JSM-6330F, JEOL Corporation of Japan). Platinum power was sprayed onto the sample surface before FE-SEM observation.

PL, PL excitation (PLE) spectra and the lifetime of the samples were taken on an FLS920 luminescence spectrometer at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples $(Ca_{0.95}Eu_{0.05})_2SnO_4$ calcined at different temperature. The XRD patterns in Fig. 1 suggests that the sample annealed at 1200 °C for 2 h and reheated at 1100 °C for 1 h has impurity of $CaSnO_3$ and CaO. However, after the sample was annealed at 1250 °C for 2 h and reheated at 1100 °C for 1 h, the peak at $2\theta = 22.539°$ decreased obviously, but the peak at $2\theta = 32.060°$ had not completely disappeared. It showed that there was still
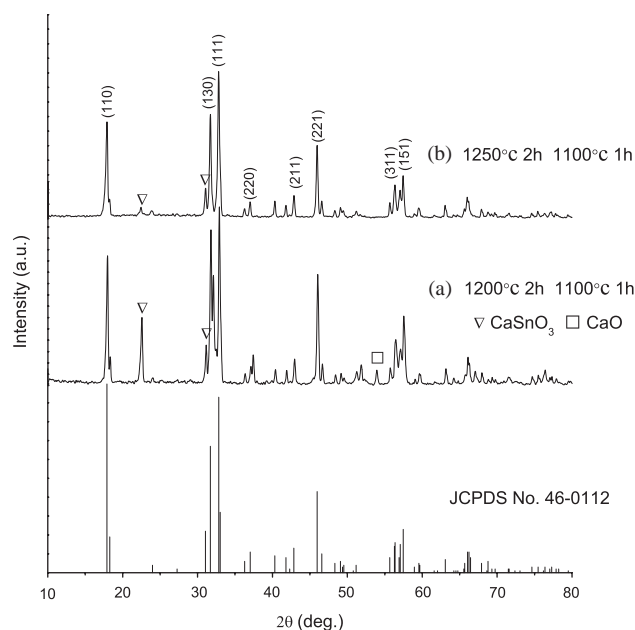
a little $CaSnO_3$ in the samples sintered at 1250 °C. The XRD patterns present the formation of the Ca_2SnO_4 (JCPDS data base No. 46-0112). The diffraction peaks at $d = 4.9407, 2.8751, 2.8168, 2.7251, 2.1064, 1.9722, 1.6302, 1.6133$ correspond to the diffraction face of (110), (220), (130), (111), (211), (221), (311) and (151), respectively. There is an interesting phenomenon that the d value of the sample $(Ca_{0.95}Eu_{0.05})_2SnO_4$ is greater than that of the undoped. Based on the handbook [12], the radius of Ca^{2+} is 99 pm, Eu^{3+} 95 pm (coordination number = 6) and Sn^{4+} 71 pm, and we can conclude that the Eu^{3+} ions substitute for the Ca^{2+} sites, but not the Sn^{4+} sites. The structure of Ca_2SnO_4 consists of SnO_6 octahedra which are linked by edges and the Ca^{2+} which are surrounded by seven oxygen ions in an arrangement of low symmetry [13]. Since the effect of the coordination number on the radius of the ions with unsaturated electron configuration is more than that of the saturated electron configuration ones, the radius of Eu^{3+} ion is larger than that of Ca^{2+}. Thus the substitution of Ca^{2+} ions by Eu^{3+} increases the d parameter.

Fig. 2 shows the FE-SEM image of the $(Ca_{0.95}Eu_{0.05})_2SnO_4$ sample calcined at 1250 °C for 2 h and reheated at 1100 °C for 1 h. The particle exhibits a superfine size of about 500 nm and has a spherical shape, which is favorable to the potential application in PDPs. There was only a little aggregation for the particles because decomposition of $CaCO_3$ and release of a mass of CO_2 gas reduced the aggregation.

Figs. 3 and 4 showed the excitation and emission spectra of the mixed power dried at 80 °C before heating at 1250 °C. Since both $CaCO_3$ and SnO_2 are optical inactivated, and no chemical reaction between the starting materials happened at 80 °C, the sharp lines at 363, 383, and 397 nm in the excitation spectrum
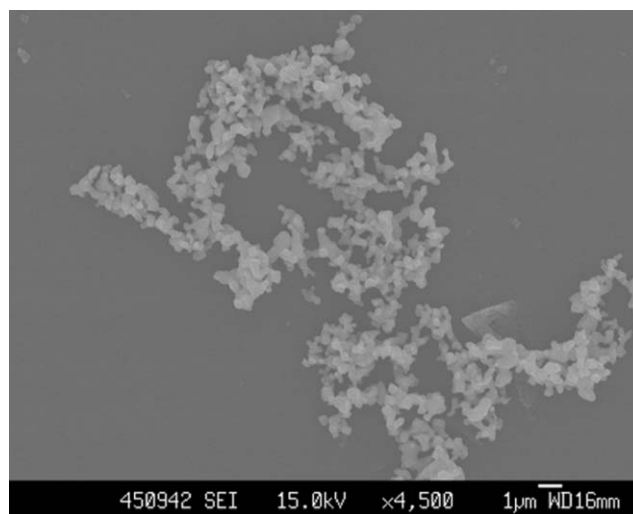

Fig. 1. XRD patterns of the sample $(Ca_{0.95}Eu_{0.05})_2SnO_4$ calcined at different temperatures: (a) at 1200 °C for 2 h and reheated at 1100 °C for 1 h; (b) at 1250 °C for 2 h and reheated at 1100 °C for 1 h.

Fig. 2. FE-SEM image of $(Ca_{0.95}Eu_{0.05})_2SnO_4$ sample calcined at 1250 °C for 2 h and reheated at 1100 °C for 1 h.
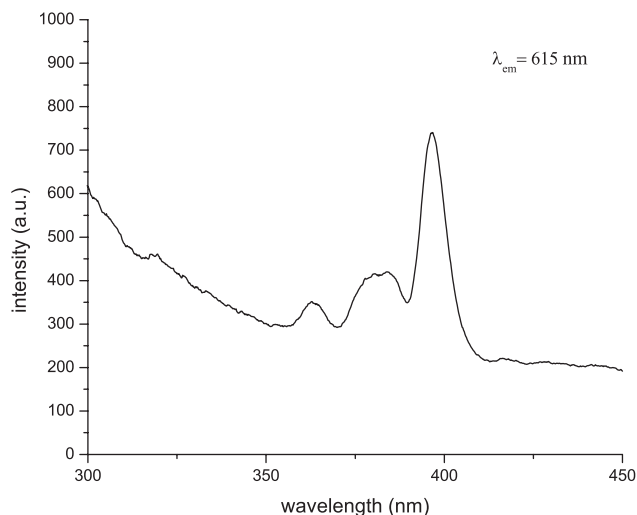
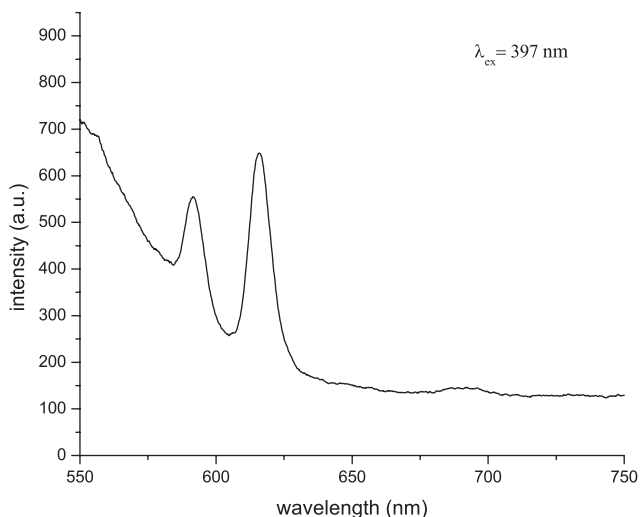Fig. 3. Excitation spectrum of the mixed power dried at 80 °C monitored at 615 nm.

Fig. 4. Emission spectrum of the mixed power dried at 80 °C excited with 397 nm.

Fig. 5. Excitation spectra of $(Ca_{0.95}Eu_{0.05})_2SnO_4$ monitored at different wavelengths.

contribute to the f–f transitions from $^7F_0$ to $^5D_4$, ^5G_J and $^5L_6$ of Eu^{3+} ion itself in Eu_2O_3. Because the f–f transition is forbidden, the emission intensity of the sample is weak, and only two emission peaks at 591 and 615 nm are found. Compared with Eu_2O_3, phosphors, $(Ca_{1-x}Eu_x)_2SnO_4$ exhibit much stronger emissions under UV light excitation. Figs. 5 and 6 showed the excitation and the emission spectra of the $(Ca_{0.95}Eu_{0.05})_2SnO_4$ sample. Phosphors $(Ca_{1-x}Eu_x)_2SnO_4$ with various concentrations of Eu^{3+} were prepared ($x = 0.01-0.09$), the emission of the phosphors enhanced with the increased Eu^{3+} concentration up to $x = 0.05$, then decreased due to the concentration—quenching. As we all know, Eu^{3+} is always used as luminescent probe in the investigation of the crystal structure [14]. Monitored at the $^5D_0$–$^7F_2$ emission bands, the excitation spectrum of
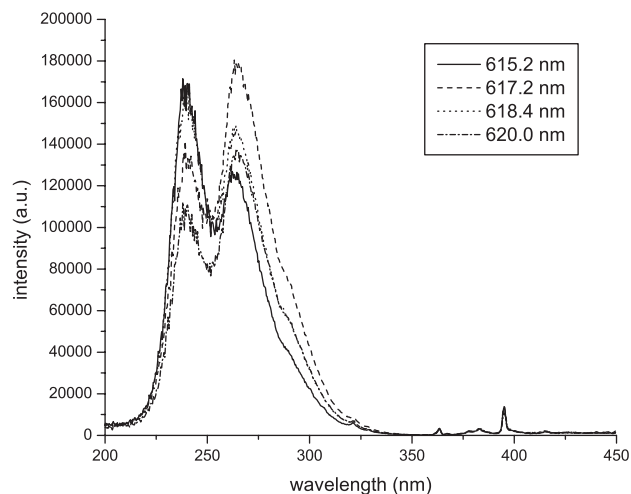
the $(Ca_{0.95}Eu_{0.05})_2SnO_4$ sample consists of two bands at 239 and 263 nm, respectively (Fig. 5). The $^5D_0$–$^7F_2$ transition is the forced electric dipole, which is strongly hypersensitive to the nature of the Eu^{3+} ligand surroundings [15,16]. When the phosphor is excited by 239 nm light, the emission peaks are at 615.2 and 618.4 nm (Fig. 6a) while the emission peaks are located at 617.2 and 620 nm excited by 263 nm (Fig. 6b). Monitored at 615.2 and 618.4 nm, the excitation band at 239 nm is stronger than that at 263 nm, contrary to that situation monitored at 617.2 and 620 nm (Fig. 5). The excitation bands at 239 and 263 nm originate in transitions toward the charge transfer state (CTS) due to europium–oxygen interactions. This result confirms the existence of at least two sites with low symmetry over which the Eu^{3+} dopant is distributed. The $^5D_0$–$^7F_0$ transition may provide further evidence on the eventual existence of more than one site symmetry being occupied by the Eu^{3+} ion [17] since both the excited and ground states are nondegenerated. Splitting of the $^5D_0$–$^7F_0$ transition emission into about 577 and 580 nm suggests that there are two sites occupied by Eu^{3+} ions in the crystalline lattice. Furthermore, appearance of more than $2J+1$ peaks for the $^5D_0$–$^7F_1$ transition confirms that the Eu^{3+} ions occupy two different surroundings (Fig. 6).

The lifetime measurement was taken, and the decay curve of the $(Ca_{0.95}Eu_{0.05})_2SnO_4$ sample exhibits a bi-exponential behavior with $\tau_1 = 0.85$ ms and $\tau_2 = 2.66$ ms, which agrees with two different sites occupied by Eu^{3+} ions.

According to Ref. [12], there is only one site for Ca^{2+} (C_s) in the structure of Ca_2SnO_4, so the substitution of Ca^{2+} by Eu^{3+} will result in only one Eu^{3+} site in the crystal lattice. Where is the other site? The other site may come from the Eu^{3+} substituting for the Ca^{2+} ions sites in the small amount of $CaSnO_3$. In the formation processes of the two sites, when two Eu^{3+} ions

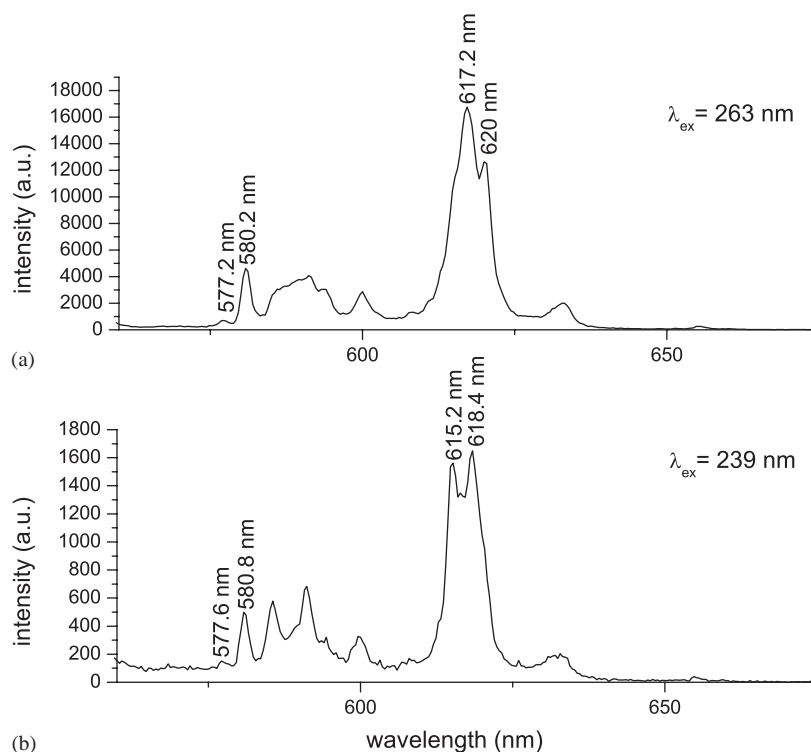Fig. 6. Emission spectra of $(Ca_{0.95}Eu_{0.05})_2SnO_4$ excited with different wavelengths.

substitute for two Ca^{2+} ions, the charge equilibrium is broken. A neighboring Ca^{2+} ion may move to the surface of the material, and leaves a Ca^{2+} vacancy to provide charge compensation. This process may enhance the dissymmetry around Eu^{3+} ions, which is in favor of the red emission of the Eu^{3+} in the phosphor.

4. Conclusions

Eu^{3+}-doped Ca_2SnO_4 was prepared by the solid-state reaction. The particles of the phosphor exhibit a union size-distribution of about 500 nm and an spherical shape. The phosphor is a bright red emitter under UV excitation. Splitting of the $^5D_0$–^7F_J transitions and a biexponential lifetime decay of the Ca_2SnO_4: Eu^{3+} samples suggests that the Eu^{3+} ions occupied two nonequivalents, one is the Ca^{2+} (C_s) in the structure of Ca_2SnO_4 and the other is the Ca^{2+} ions sites in the small amount of $CaSnO_3$.

References

[1] R.P. Rao, D.J. Devine, J. Lumin. 87–89 (2000) 1260–1263.
[2] C. Okazaki, M. Shiiki, T. Suzuki, K. Suzuki, J. Lumin. 87–89 (2000) 1280–1282.
[3] L.H. Tian, B.Y. Yu, C.H. Pyun, H.L. Park, S.I. Mho, Solid State Commun. 129 (2004) 43–46.
[4] E. van der Kolk, P. Dorenbos, C.W.E. van Eijk, H. Bechtel, T. Justel, H. Nikol, C.R. Ronda, U. Wiechert, J. Lumin. 87–89 (2000) 1246–1249.
[5] K.S. Sohn, W. Zeon, H. Chang, S.K. Lee, H.D. Park, Chem. Mater. 14 (2002) 2140–2148.
[6] T. Justel, J.C. Krupa, D.U. Wiechert, J. Lumin. 93 (2001) 179–189.
[7] B. Moine, G. Bizarri, Mater. Sci. Eng. B 105 (2003) 2–7.
[8] P.T.M. Chau, K.H. Ryu, C.H. Yo, J. Mater. Sci. 33 (1998) 1299–1302.
[9] K.N. Kim, H.K. Jung, H.D. Park, D. Kim, J. Lumin. 99 (2002) 169–173.
[10] K. Itoh, N. Kamata, T. Shimazu, C. Satoh, K. Tonooka, K. Yamada, J. Lumin. 87–89 (2000) 676–678.
[11] C.H. Kim, Il-Eok Kwon, C.H. Park, Y.J. Hwang, H.S. bae, B.Y. Yu, C.H. Pyun, G.Y. Hong, J. Alloys Compd. 311 (2000) 33–39.
[12] R.C. Weast, Handbook of the Chemistry and Physics, 69th ed., CRC Press, Boca Raton, FL, 1988–1989, p. F-164.
[13] G. Pfaff, Mater. Sci. Eng. B 33 (1995) 156–161.
[14] M. Gaft, G. Panczer, R. Reisfeld, I. Shinno, B. Champagnon, G. Boulon, J. Lumin. 87–89 (2000) 1032–1035.
[15] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Goncalvese Silva, S. Alves Jr., F.S. Farias Jr., A.V.M. Andrade, J. Lumin. 75 (1997) 255–268.
[16] M. Yin, W. Zhang, L. Lou, S. Xia, J.C. Krupa, Physica B 254 (1998) 141–147.
[17] G.P. Thim, H.F. Brito, S.A. Silva, M.A.S. Oliveira, M.C.F.C. Felintoc, J. Solid State Chem. 171 (2003) 375–381.