J Electroceram (2011) 26:112–115
DOI 10.1007/s10832-011-9637-8

Luminescent properties of $Sr_2ZnSi_2O_7$: Eu^{2+} phosphors prepared by combustion-assisted synthesis method

Shan-shan Yao · Li-hong Xue · You-wei Yan

Received: 26 November 2009 / Accepted: 22 March 2011 / Published online: 19 April 2011

Abstract A blue-emitting phosphor $Sr_2ZnSi_2O_7$: Eu^{2+} was prepared by combustion-assisted synthesis method and an efficient blue emission under from ultraviolet to visible light was observed. The emission spectrum shows a single intensive band centered at 475 nm, which corresponds to the $4f^65d^1 \rightarrow 4f^7$ transitions of Eu^{2+}. The excitation spectrum is a broad band extending from 250 to 450 nm, which matches the emission of ultraviolet light-emitting diodes (UV-LEDs). The effect of doped Eu^{2+} concentration on the emission intensity of $Sr_2ZnSi_2O_7$: Eu^{2+} was also investigated and the corresponding concentration quenching mechanism is verified to be an electric multipole-multipole interaction.

Keywords Silicates · Optical materials · Phosphors · Luminescence

1 Introduction

In recent years, alkaline earth silicates $A_2BSi_2O_7$ (A = Ca, Sr, Ba, B = Mg, Zn) codoped with rare earth ions have attracted research interests in the field of photoluminescence since they are suitable hosts with excellent thermal and chemical stability [1–5]. Eu^{2+}, Dy^{3+} co-doped $Sr_2MSi_2O_7$ (M = Mg, Zn) phosphor was found to emit blue light upon ultraviolet (UV) illumination and show long afterglow [6, 7]. Toda et al. prepared $Sr_2MgSi_2O_7$: Eu^{2+}, Dy^{3+} and Ca_2Mg-Si_2O_7: Eu^{2+}, Dy^{3+} phosphors, and they showed bright and long-lasting phosphorescence [8]. In the light-emitting diodes (LED) phosphors, the long persistent property is not necessary [9, 10]. Zhang et al. reported the luminescence properties of $M_2MgSi_2O_7$: Eu^{2+} (M = Ca, Sr) phosphors and found their effects on yellow and blue LEDs for solid-state lighting [11]. Hayato et al. prepared the $Ca_2ZnSi_2O_7$: Eu^{2+} phosphors for white light generation by blue ray excitation [12]. So we considered the $Sr_2ZnSi_2O_7$: Eu^{2+} phosphor without the Dy coactivator as a potential blue phosphor for UV-LED.

The optical properties of luminescent materials are frequently affected by the preparation method [13, 14]. The conventional solid-state reaction for preparing phosphors requires a high calcining temperature, which induces sintering and aggregation of particles. Furthermore, the milling process to reduce to the particle size leads to decreasing of luminescence properties. It has been observed that the preparation of the powders by sol-gel procedures leads to significant reinforcement of the photoluminescence intensity [15]. For sol-gel techniques, processing routines to prepare the phosphors are complicated and the duration is long. The combustion method to synthesize the phosphors, however, can produce a homogenous product in a short time without the use of expensive high-temperature furnaces [16, 17]. In the present work, we synthesized the $Sr_{2-x}ZnSi_2O_7$: Eu_x^{2+} blue-emitting phosphor by combustion-assisted synthesis method and investigated its luminescent properties.

S.-s. Yao · L.-h. Xue (✉) · Y.-w. Yan
State Key Laboratory of Materials Processing and Die & Mould Technology,
College of Materials Science and Engineering,
Huazhong University of Science & Technology,
Wuhan 430074 Hubei, People's Republic of China
e-mail: xuelh@mail.hust.edu.cn

2 Experimental

2.1 Sample synthesis

$Sr(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $Si(OC_2H_5)_4$, Eu_2O_3, H_3BO_3, and NH_2CONH_2, all in analytical grade, were used as the starting materials in the experiment. Small quantities of H_3BO_3 were used as a flux and amounts of urea were added as a fuel. Powders were weighted according to the stochiometry. $Sr(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, H_3BO_3 and NH_2CONH_2 were dissolved into enough deionized water to obtain transparent solution, the Eu_2O_3 was dissolved into concentrated nitric acid, then mixed the two solutions. $Si(OC_2H_5)_4$ and appropriate amount of ethanol was added slowly into the above solution under vigorous stirring. The mixture solution was allowed to react at 80°C for 2 h to obtain a homogenous solution. And then the solution was introduced into a muffle furnace preheated at 600°C. Within a few minutes, the solution boiled and was ignited to produce a self-propagating flame. The product obtained was post-annealed in a reducing atmosphere at 1000°C for 3 h.

2.2 Characterization

The synthesized phosphors were ground to powder and passed through a 200 mesh sieve prior to the characterization. The crystal phase of the synthesized powders prepared in the process was characterized by X-ray powder diffraction using an X′ Pert PRO X-ray diffractometer having a Cu Kα radiation (λ=1.5406Å) at 40 kV tube voltage and 40 mA tube current. The XRD patterns collected in the range of 10°≤2θ≤90°. The emission spectrum was performed on a RF-5301 fluorescence spectrophotometer equipped with a xenon discharge lamp as an excitation source. The excitation and emission slits were set to 3.0 nm. All the luminescent properties of the phosphors were studied at room temperature.

3 Results and discussion

3.1 Phase composition of the obtained phosphor

The XRD patterns of the phosphors $Sr_{2-x}ZnSi_2O_7$: Eu_x^{2+} samples post-annealed 1000°C for 3 h are shown in Fig. 1. There are no observable differences between the two diffraction patterns, indicating that the small amount of doped rare-earth ions has almost no effect on the $Sr_2ZnSi_2O_7$ crystalline structure. Its diffraction peak is consistent with the standard JCPDS card of tetragonal $Sr_2ZnSi_2O_7$ phase (JCPDS, 39–0235) and also with that reported in the literature (space group $P\bar{4}21_m$, a=8.007Å, c=5.168Å) [19]. In this work, the structure of $Sr_2ZnSi_2O_7$ with space group $P\bar{4}21_m$ was taken as the starting model for the synthesized phosphors.

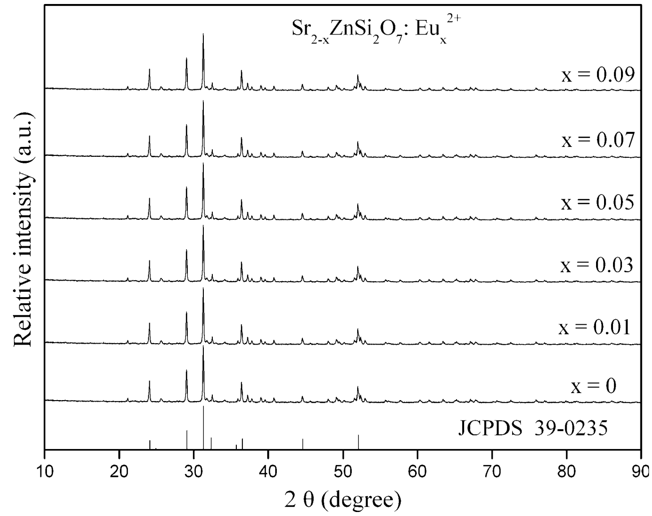

Fig. 1 Powder X-ray diffraction patterns of $Sr_{2-x}ZnSi_2O_7$: Eu_x^{2+} (x=0, 0.01, 0.03, 0.05, 0.07, 0.09)

In the $Sr_2ZnSi_2O_7$ crystal structure, the zinc atoms are in tetrahedral of oxygen, all four of which are shared by adjacent $[SiO_4]$ tetrahedral, which themselves are linked in pairs to form $[Si_2O_7]$ groups [20, 21]. The calculations of the radius percentage difference (Dr) between the doped ions (Eu^{2+}) and possible substituted ions (Sr^{2+}, Zn^{2+}) in $Sr_2ZnSi_2O_7$ are summarized in Table 1. The values are based on the following formula:

$$Dr = [Rm(CN) - Rd(CN)]/Rm(CN)$$

where CN is the coordination number, $Rm(CN)$ is the radius of the host cation, and $Rd(CN)$ is the radius of the doped ion. We take the date of Eu^{2+} with CN=6 as a responsible approximation [22]. The value of Dr between Eu^{2+} and Sr^{2+} is 0.8%. While that between Eu^{2+} and Zn^{2+} is −95.00%.

Table 1 Ionic radii difference percentage (Dr) between matrix cations and doped ions

Doped ions	Rd(CN) (Å)	Dr = [Rm(CN) − Rd(CN)]/Rm(CN)(%)	
		$R_{Sr}^{2+}(8) = 1.26$(Å)	$R_{Zn}^{2+}(4) = 0.60$(Å)
Eu^{2+}	1.170 (6)		−95.00
	1.250 (8)	0.8	

CN stands for coordination number, Rm(CN) and Rd(CN) for the radii of matrix and doped cations, respectively, and the data of the effective ionic radii are from Ref. [23]

Thus, doping ions of Eu^{2+} will preferentially substitute the strontium sites.

3.2 Luminescent properties

A series of $Sr_{2-x}ZnSi_2O_7$: Eu_x phosphors with various Eu^{2+} concentrations (x=0.01–0.09) were prepared and the effect of doped Eu^{2+} concentration on the excitation and emission intensity was investigated. The excitation and emission intensities of $Sr_{2-x}ZnSi_2O_7$: Eu_x with different Eu^{2+} concentrations are shown in Fig. 2. The positions of excitation and emission bands have no obvious changes for all the samples. With increasing Eu^{2+} concentration, the emission intensity increase and the maximum is at x= 0.05 mol. Concentration quenching occurs, when the Eu^{2+} concentration is more than 0.05 mol.

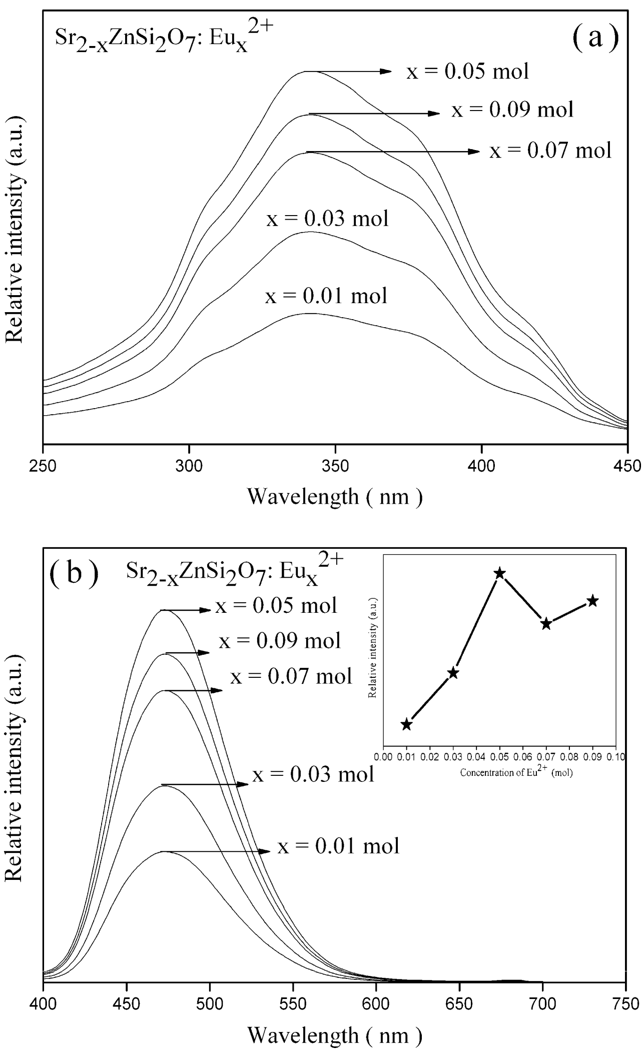

Fig. 2 (**a**) Excitation (λ_{em}=475 nm) and (**b**) emission (λ_{ex}=342 nm) intensity of $Sr_{2-x}ZnSi_2O_7$: Eu_x^{2+} with different Eu^{2+} concentrations

With respect to the mechanism of energy transfer in phosphors, Blasse has pointed out the critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume [24]:

$$Rc \approx 2\left(\frac{3V}{4\pi\chi_c N}\right)^{\frac{1}{3}}$$

where χ_c is the critical concentration, N the number of cations in the unit cell and V is the volume of the unit cell. By taking the experimental and analytic values of V, N and χ_c (331.10Å^3, 4, 0.05 mol, respectively), the critical transfer distance of Eu^{2+} in $Sr_2ZnSi_2O_7$ phosphor is calculated to be about 15Å. Qiu et al. showed that the probability of energy transfer among Eu^{2+} ions increases when the Eu^{2+} concentration increases [25]. A non-radiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion occurs as a result of an exchange interaction, radiation reabsorption, or a multiple-multiple interaction. The exchange interaction is generally responsible for the energy transfer to forbidden transitions and the typical critical distance is about 5Å [26]. The mechanism of radiation reabsorption comes into effect only when there is a broad overlap of the photoluminescence spectra of the sensitizer and activator. In the present case, Eu^{2+} ion shows the allowed 4*f*-5*d* transition and there is little overlap between excitation and emission spectra. Therefore the exchange and reabsorption interaction can not account for the energy transfer of Eu^{2+} in $Sr_2ZnSi_2O_7$. The process of energy transfer between Eu^{2+} ions in phosphor should be controlled by the electric multipole-multipole interaction according to Dexter's theory [26].

The photoluminescence spectra of $Sr_{1.95}ZnSi_2O_7$: $Eu_{0.05}^{2+}$ is shown in Fig. 3. It can be observed that a broad

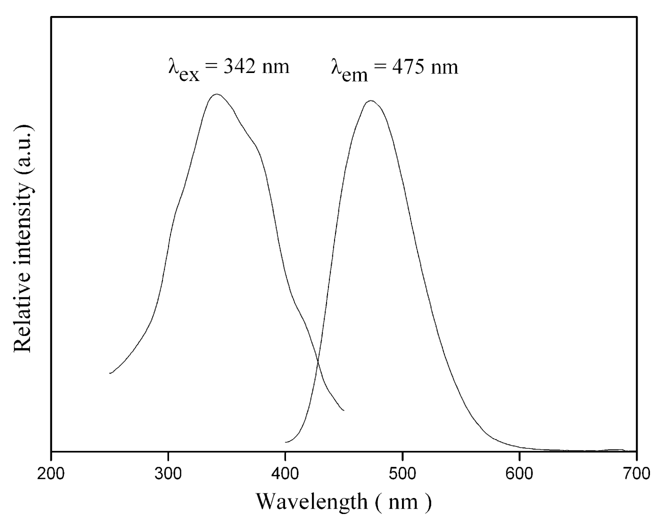

Fig. 3 Photoluminescence spectra of $Sr_{1.95}ZnSi_2O_7$: $Eu_{0.05}^{2+}$

absorption band extends from 250 to 450 nm. The results show a broad excitation band, centered at 342 nm. The excitation band is due to $4f^7$ ground state to the $4f^6 5d^1$ excited state transition of Eu^{2+} ions. The 5d energy level of Eu^{2+} and the lower level of 4f state overlap, so the electron of 4f state can be excited to 5d state. The broad luminescence of Eu^{2+} is due to $4f^6 5d^1 \rightarrow 4f^7$ transitions, which is an allowed electrostatic dipole transition. However, the 5d state is easily affected by the crystal field, that is to say, different crystal fields can split the 5d state in different ways. This makes Eu^{2+} emit different wavelengths light in different crystal fields and the emission spectrum can vary from the ultraviolet to the red region [27]. Since the codopant Eu^{2+} ions are substituted for the Sr^{2+} sites and are exposed to a strong crystal field, the excitation band of Eu^{2+} can extend into the visible region. With the excitation wavelengths of 242 nm, the emission spectra is located at 475 nm, consistent with the fact that there is only one kind of Sr site in the host material $Sr_2ZnSi_2O_7$. Owing to its excellence in excitation spectrum profile, it is believed that $Sr_{1.95}ZnSi_2O_7$: $Eu_{0.05}{}^{2+}$ phosphors would have applications in the UV-LEDs.

4 Conclusions

$Sr_2ZnSi_2O_7$:Eu^{2+} phosphor powders have been synthesized by the combustion-assisted synthesis method. With an increase in the Eu^{2+} concentration, quenching of the excitation energy occurs. The critical quenching concentration of Eu^{2+} in $Sr_2ZnSi_2O_7$: Eu^{2+} phosphor is determined as 0.05 mol. The critical transfer distance is calculated as 15 Å. The photoluminescence spectrum of $Sr_{1.95}ZnSi_2O_7$:$Eu_{0.05}{}^{2+}$ contains board excitation bands extending from 250 to 450 nm, resulting from the strong crystal field imposed on the Eu sites. Under ultraviolet and visible excitation, $Sr_{1.95}ZnSi_2O_7$:$Eu_{0.05}{}^{2+}$ shows a blue emission band centered at 475 nm. According to its excellence in excitation spectrum profile, we have demonstrated that the optimized phosphors $Sr_{1.95}ZnSi_2O_7$:$Eu_{0.05}{}^{2+}$ is a potentially useful blue phosphor for UV-LEDs.

Acknowledgement The financial support from the Natural Science Foundation of China under grant No. 50574042 for this work is greatly appreciated, the Natural Science Foundation of Hubei Province of China (No.2008CB252), and by the Scientific Research Foundation for the Returned Overseas Chinese Scholar, Sate Education Ministry.

References

1. Z.Y. Zhang, Y.H. Wang, J. Electrochem. Soc. **154**, J62 (2007)
2. T. Aitasalo, D. Hreniak, J. Hölsä, T. Laamanen, M. Lastusaari, J. Niittykoski, F. Pellé, W. Strek, J. Lumin. **122/123**, 110 (2007)
3. S.S. Yao, Y.Y. Li, L.H. Xue, Y. You, Y.W. Yan, Cent. Eur. J. Phys. **7**, 800 (2009)
4. L. Jiang, C.K. Chang, D.L. Mao, C.L. Feng, Mat. Sci. Eng. B. **103**, 271 (2005)
5. S.S. Yao, Y.Y. Li, L.H. Xue, Y. You, Y.W. Yan, Appl. Phys B **96**, 32 (2009)
6. Y. Lin, Z. Tang, Z. Zhang, X. Wang, J. Zhang, J. Mater. Sci. Lett. **20**, 1505 (2001)
7. L. Jiang, C.K. Chang, D.L. Mao, B. Zhang, Mater. Lett. **58**, 1825 (2005)
8. K. Toda, Y. Imanari, T. Nonogawa, J. Miyoshi, K. Uematsu, M. Sato, J. Ceram. Soc. Jpn. **110**, 283 (2002)
9. H.A. Höppe, Angew. Chem. Int. Ed. **48**, 3572 (2009)
10. K.Y. Jung, H.W. Lee, H.K. Jung, Chem. Mater. **18**, 2249 (2005)
11. M. Zhang, J. Wang, W.J. Ding, Q.H. Zhang, Q. Su, Opt. Mater. **30**, 571 (2007)
12. K. Hayato, Y. Takashi, H. Masahiro, K. Toshio, H. Hideo, J. Lumin. **122/123**, 339–2007 (2007)
13. T.H. Gho, H.J. Chang, J. Ceram. Int. **29**, 611 (2003)
14. C.H. Lu, W.T. Hsu, C.H. Huang, S.V. Godbole, B.M. Cheng, Mater. Chem. Phys. **90**, 62 (2005)
15. P.T. Diallo, K. Jeanlouis, P. Boutinaud, R. Mahiou, J.C. Cousseins, J. Alloys Compd **323/324**, 218–2001 (2001)
16. S.S. Yao, Y.Y. Li, D.H. Chen, W.J. Tang, Y.H. Peng, Cent. Eur. J. Phys. **7**, 96 (2009)
17. S.S. Yao, D.H. Chen, Cent. Eur. J. Phys. **5**, 558 (2007)
18. Y. Hao, Y.H. Wang, Mater. Res. Bull. **42**, 2219 (2007)
19. L. Jiang, C.K. Chang, D.L. Mao, C.L. Feng, Opt. Mater. **27**, 51 (2004)
20. G. Bergerhoff, M. Berndt, K. Brandenburg, J. Res. Natl. Inst. Stand. Technol. **101**, 221 (1996)
21. K. Brandenburg, M. Berndt, J. Appl. Cryst. **32**, 1028 (1999)
22. R.D. Shannon, Acta Crystrallogr. A. **32**, 751 (1976)
23. F. Liebau, *Structural chemistry of silicates, structure, bonding and classification* (Springer, Berlin, 1985)
24. G. Blasse, J. Solid St. Chem. **62**, 207 (1986)
25. J. Qiu, K. Miura, N. Sugimoto, K. Hirao, J. Non-Cryst. Solids **213/214**, 266 (1997)
26. D.L. Dexter, J. Chem. Phsys. **21**, 836 (1953)
27. R.J. Xie, N. Hirosaki, Sci. Technol. Adv. Mater. **8**, 588 (2007)