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Short communication

Bi^{3+}-doped $Sr_3Al_2O_6$: An unusual color-tunable phosphor for solid state lighting

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Abstract

A $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ phosphor crystallized in space group Pa $\overline{3}$ was prepared by high-temperature solid-state reaction. Two emission bands (λ_{em}=440 nm and 400 nm) and two excitation bands (λ_{ex}=330 nm and 295 nm) were observed, which can be attributed to Bi^{3+} in distinct crystallographic sites. The optimal intensity of 400 nm emission band was observed for the phosphor doped with 1 at% Bi^{3+} (x=0.01), while that of 440 nm emission band was found in the phosphor with 2 at% Bi^{3+} (x=0.02). The emission color varies from the greenish blue to blue and even violet blue as the excitation wavelength increases from 275 to 335 nm. The $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ is a potential blue phosphor for ultraviolet light-emitting diodes.

Keywords: A. Powder: solid state reaction; C. Optical Properties; E. Phosphors

1. Introduction

In recent years, the phosphor has attracted increasing attention because of its applications to solid-state lighting, display devices, detector systems and luminous paint with long persistent phosphorescence. A phosphor is generally composed of a transparent microcrystalline host and a luminescence activator formed by impurity metallic atoms intentionally incorporated. In the case of metallic impurities, a large number of rare-earth ions have been used as the luminescence activators of phosphors, especially trivalent rare-earth ions that generally exhibit stable emission due to the f–f electron transition. Metallic impurities with ns^2 ground state, such as Sn^{2+}, Sb^{3+} and Bi^{3+}, have tunable emission, and are also excellent luminescence activators [1].

The trivalent bismuth ion is considered to be an interesting luminescence activator, which is attributed to the electron transition between the $6s^2$ ground states and the 6s6p excited states [2]. Because the electron transitions from $^1S_0$ to $^3P_0$ and $^3P_2$ are completely spin forbidden, optical absorption is ascribed to the electron transition from $^1S_0$ to $^3P_1$ or $^1P_1$ [3]. The $^3P_1$ excited state has lower energy level and stronger stability than the $^1P_1$ excited state; therefore, the Bi^{3+} emission spectrum at room temperature usually consists of a single broad band due to the $^3P_1$–$^1S_0$ transition [4]. The luminescence of Bi^{3+} can vary from the ultraviolet to blue and even green by choosing appropriate hosts.

Many aluminates with high stability and low thermal quenching have been widely used as host materials for phosphors, such as $Y_3Al_5O_{12}$ and $SrAl_2O_4$ [5,6]. As a commercial product, the yellow $Y_3Al_5O_{12}$:Ce^{3+} phosphor has been widely applied in white light-emitting diodes. With ultraviolet and blue emission, $Y_3Al_5O_{12}$:Bi^{3+} single crystalline films were used as tunable luminescent screens [7]. Among the aluminates, $Sr_3Al_2O_6$ crystallized in space group Pa$\overline{3}$ can form solid solutions with various metal oxides, such as Cr_2O_3 and Eu_2O_3, which results in some modifications in crystal structure, crystal field effect and optical properties [8]. Moreover, there are six distinct

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crystallographic Sr^{2+} sites in $Sr_3Al_2O_6$ lattice, which results in complicated crystal field effects to the activators [9].

According to the above investigation, the analysis of the emission spectrum of Bi^{3+} ions in $Sr_3Al_2O_6$ host crystal is helpful to study the photoluminescence nature of metallic ions with ns^2 ground state. Therefore, we have prepared $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ phosphors by the high-temperature solid-state reaction method, and optimized their luminescence intensity by changing Bi^{3+} concentration. The structure and luminescence properties of $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ phosphors are investigated in detail.

2. Experimental

2.1. Synthesis

Bi^{3+}-doped $Sr_3Al_2O_6$ phosphors were prepared by the conventional solid state reaction method. $SrCO_3$ (A.R.), Bi_2O_3 (A.R.) and Al_2O_3 (99.9%) were used as starting materials, among which bismuth concentration varied from 0.5 to 6 at%. The starting materials were weighed according to the nominal composition of the $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$, and ground in an agate mortar for about 10 min. The homogeneous mixtures were put into alumina crucibles, and heated from room temperature to 1200 °C at the rate of 5 °C/min in a muffle furnace. After calcining at 1200 °C for 5 h in air, the samples were naturally cooled to room temperature.

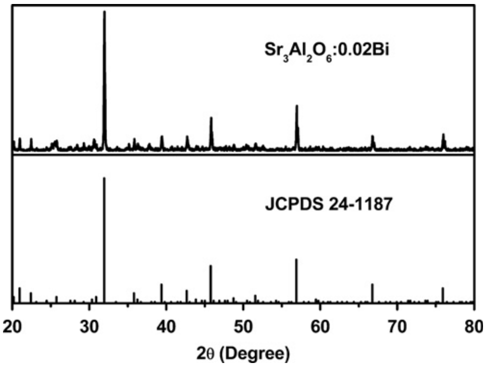

Fig. 1. XRD pattern of $Sr_{2.98}Al_2O_6$:0.02Bi as compared to the standard pattern.

2.2. Characterization

The X-ray powder diffraction (XRD) was performed on a Bruker D8 ADVANCE diffractometer with Cu Kα radiation. Diffraction data were collected by a step scanning with a step size of 0.02° in the 2θ range 10–90°. The excitation and emission spectra were measured by a Fluorolog Fl3-211-P spectrometer with a Xe flash lamp at room temperature.

3. Results and discussion

Fig. 1 shows the XRD pattern of $Sr_{2.98}Al_2O_6$:0.02Bi, whose diffraction peaks match well with the standard card (JCPDS card no. 24-1187). A small amount of doped Bi^{3+} ions has no obvious influence on the structure of the host due to the similar ionic radius of Sr^{2+} (1.12 Å) and Bi^{3+} (1.03 Å). The phosphor is crystallized in space group $Pa\overline{3}$, whose host structure has been reported by Kadyrova and Sirazhiddinov [9]. As shown in Fig. 2, there are 14 independent crystallographic sites, namely, 2 Al^{3+} sites, 6 Sr^{2+} sites and 6 O^{2-} sites. Sr (3), Sr (5) and Sr (6) ions are all in octahedrons with six oxygen ligands, in which average Sr–O distances are 2.416, 2.434 and 2.471 Å, respectively. Sr (3), Sr (5) and Sr (6) ions have similar local environment due to identical coordination number and similar average Sr–O distances. Other Sr^{2+} ions are surrounded by seven, eight or nine oxygen atoms, whose average Sr–O distances are 2.608, 2.712 and 2.783 Å, respectively. Sr (1), Sr (2) and Sr (4) ions are located in large space due to long average Sr–O distances. Six distinct crystallographic sites are available for doped Bi^{3+} ions in the $Sr_3Al_2O_6$, which has a large influence on the luminescence properties of the phosphor.

The $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ phosphor shows two broad absorption bands ($\lambda_{ex}=295$ and 330 nm) and two broad emission bands ($\lambda_{em}=400$ and 440 nm) in Fig. 3. Host

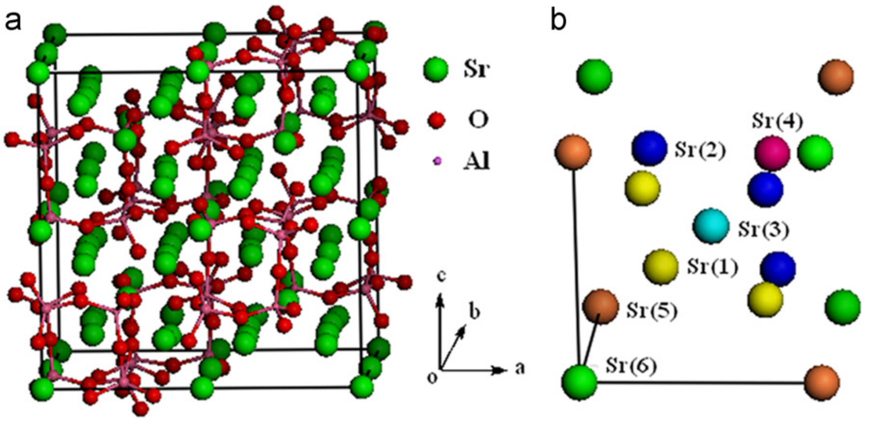

Fig. 2. (a) Unit cell representation of the fully ordered crystal structure of $Sr_3Al_2O_6$ and (b) the six independent crystallographic sites of Sr^{2+} ions.

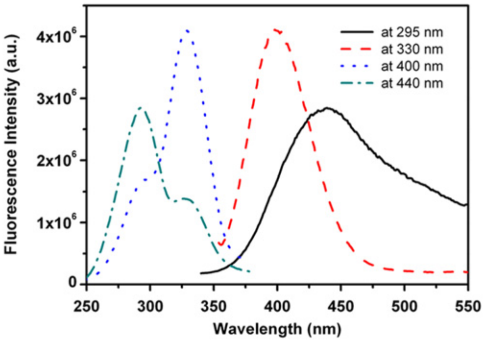

Fig. 3. Excitation and emission spectra of $Sr_{2.99}Al_2O_6$:$0.01Bi^{3+}$ phosphor.

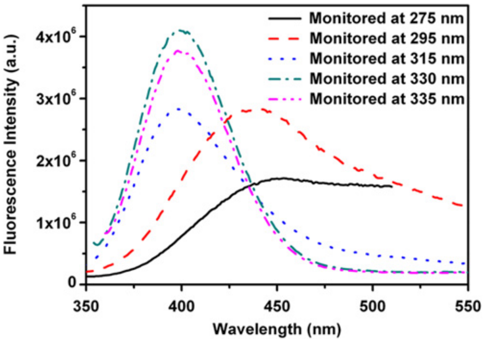

Fig. 4. Emission spectrum of $Sr_{2.99}Al_2O_6$:0.01Bi phosphor excited with different wavelength lights.

lattice absorption is responsible for the high energy excitation band at 295 nm. The low energy absorption band at 330 nm is due to the $^1S_0-^3P_1$ transition, which is allowed due to the mixing of the states in the spin orbit interaction [10]. Although all excitation spectra for the two emission bands exhibit two broad bands, there is a noticeable difference between 295 and 330 nm excitation intensities. As shown in Fig. 3, 400 nm emission is effectively excited by 330 nm; however, the 440 nm emission is excited by 295 nm. The Stokes shifts for the emission at 400 and 440 nm are about 5303 cm^{-1} and 11,171 cm^{-1}, respectively. The 400 and 440 nm emission can be ascribed to the $^3P_1$–$^1S_0$ transition of Bi^{3+} ions in distinct crystallographic sites. The 400 nm emission band is almost symmetrical, which is probably attributed to Bi^{3+} in Sr (3), Sr (5) and Sr (6) sites with similar structure parameters. Because the asymmetrical 440 nm emission band consists of multi-components, we can infer that there is a noticeable difference in the structure parameters of crystallographic Bi^{3+} sites.

The emission spectra under different excitation light are shown in Fig. 4. Excited by ultraviolet light (315–335 nm), the phosphor emits violet blue light centered at 400 nm. However, the phosphor with deep ultraviolet excitation (275–295 nm) emits strong blue light centered at 440 nm. The $Sr_{3-x}Al_2O_6$:xBi^{3+} phosphor shows different optical properties from other phosphors, such as $YNbO_4$:Bi or $SrSb_2O_6$ [11,12]. Long wavelength emission of $YNbO_4$:Bi phosphor is attributed to long wavelength excitation; however, long wavelength emission of $Sr_{3-x}Al_2O_6$:xBi^{3+} phosphor is ascribed to short wavelength excitation. The above optical properties of $Sr_{3-x}Al_2O_6$:xBi^{3+} phosphor are probably ascribed to different luminescence centers that are formed by Bi^{3+} ions in distinct crystallographic sites [13]. The octahedrons with short Sr–O distances offer a very little space for Bi^{3+} ions, which reduces the relaxation effect of Bi^{3+} excitation states and shortens the Stokes shift. Therefore, the 400 nm band with strong emission intensity is most likely attributed to the $^3P_1$–$^1S_0$ transition of Bi^{3+} ions in the octahedrons. Other Sr^{2+} ions have more oxygen ligands and longer average Sr–O distance than Sr (3), Sr (5) and Sr (6) ions, which offers a large space available to Bi^{3+} ions. There is an energy transfer from the host lattice to the excitation state of Bi^{3+} in Sr (1), Sr (2) and Sr (4) sites [14]. However, the excitation states of Bi^{3+} in a large space shift easily to a balanced site due to the pseudo-Jahn–Teller effect, which results in large relaxation effect and long Stokes shift [15].

The intensities of two emission bands are measured separately as a function of Bi^{3+} concentration for the study of the energy transfer mechanism. As shown in Fig. 5, with the increase of Bi^{3+} concentration, the 400 nm emission intensity increases up to 1 at% Bi^{3+}. A further increase in Bi^{3+} concentration results in a decrease of the emission intensity. However, the optimal intensity of 440 nm emission band is observed for material doped with 2 at% Bi^{3+}. Moreover, the emission intensity decreases slowly as the concentration of Bi^{3+} ions is above 2 at%. When Bi^{3+} concentration is in the range 1–2 at%, with the increase of Bi^{3+} concentration, the intensity of 440 nm emission band increases; however, that of 400 nm emission band decreases. There is an energy transfer from Bi^{3+} in Sr (3), Sr (5) and Sr (6) sites to Bi^{3+} in Sr (1), Sr (2) and Sr (4) sites [16]. A rough estimation of the critical distance (R_c) for energy transfer is calculated based on the relation given by Blasse [17]:

$$R_c \approx 2\left[\frac{3V}{4\pi X_c Z}\right]^{1/3} \tag{1}$$

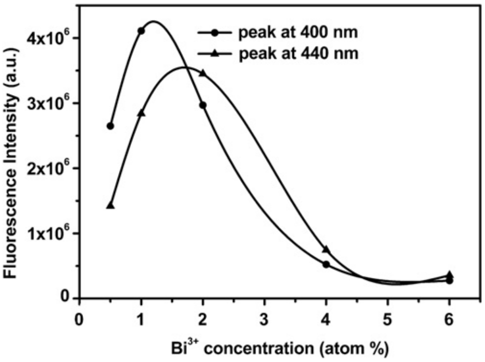

Fig. 5. Emission intensity as a function of Bi^{3+} concentration in $Sr_{3-x}Al_2O_6$:xBi^{3+} phosphors (the 440 nm emission monitored at 295 nm, the 400 nm emission monitored at 330 nm).

where V is the volume of the unit cell, X_c is the critical concentration of Bi^{3+} ions before luminescence quenching, and Z is the number of formula units per unit cell. In the case of $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ phosphor, $V=3921.9$ Å^3, $Z=24$, and $X_c=0.01$ for the 400 nm emission band and $X_c=0.02$ for the 440 nm emission band. Upon inserting the values in Eq. (1), R_c values are determined to be 31.5 Å for the 400 nm emission band and 25.0 Å for the 440 nm emission band. The results indicate that the energy migration of 400 nm emission band is different from that of 440 nm emission band. There is an energy transfer from 400 nm emission to 440 nm emission as Bi^{3+} concentration is in the range 1–2 at%; therefore, the critical concentration of the 440 nm emission band is higher than that of the 400 nm emission band [18]. When Bi^{3+} concentration is above 2 at%, the nonradiative energy transfer predominates.

4. Conclusions

In summary, $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ phosphor was prepared by the conventional solid state reaction method at 1200 °C for 5 h, and its optical properties were investigated. The phosphor had two excitation bands centered at 295 nm and 330 nm. The emission spectrum by 295 nm excitation showed an asymmetrical band at 440 nm, while that by 330 nm excitation exhibited a symmetrical band at 400 nm. The 400 nm emission band can be ascribed to the $^3P_1$–$^1S_0$ transition of the Bi^{3+} ions in crystallographic sites with six oxygen ligands; however, the 440 nm emission band is due to Bi^{3+} ions in other crystallographic sites. With increasing excitation wavelength from 275 to 335 nm, the photoluminescence varies from greenish blue to blue and even violet blue. The variation of Bi^{3+} concentration in the lattice was studied in order to find out the energy transfer mechanism. The energy is transferred from Bi^{3+} in high energy emitting center to Bi^{3+} in low energy emitting center as Bi^{3+} concentration is in the range 1–2 at%. When Bi^{3+} concentration is above 2 at%, the concentration quenching predominates. The $Sr_{3-x}Al_2O_6$:$x$$Bi^{3+}$ phosphor can be used for both white light-emitting diodes pumped by ultraviolet chip and field emission displays.

Acknowledgments

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References

[1] W.M. Yen, S. Shionoya, H. Yamamoto, Phosphor Handbook, second ed., CRC Press, Boca Raton, 2006.

[2] G. Blasse, A.C. Steen, Luminescence characteristics of Bi^{3+}-activated oxides, Solid State Communications 31 (1979) 993–994.

[3] Y. Zorenko, V. Gorbenko, T. Voznyak, V. Jary, M. Nikl, Luminescence spectroscopy of the Bi^{3+} single and dimer centers in $Y_3Al_5O_{12}$:Bi single crystalline films, Journal of Luminescence 130 (2010) 1963–1969.

[4] J. Li, J. Liu, X. Yu, Synthesis and luminescence properties of Bi^{3+}-doped YVO_4 phosphors, Journal of Alloys and Compounds 509 (2011) 9897–9900.

[5] M.S. Lizer, D. Michalik, J. Plewa, T. Juestel, H. Winkler, T. Pawlik, The effect of Al–O substitution for Si–N on the luminescence properties of YAG:Ce phosphor, Journal of European Ceramic Society 32 (2012) 1383–1387.

[6] S.Y. Kaya, E. Karacaoglu, B. Karasu, Effect of Al/Sr ratio on the luminescence properties of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors, Ceramics International 38 (2012) 3701–3706.

[7] Y. Zorenko, V. Gorbenko, T. Voznyak, V. Vistovsky, S. Nedilko, M. Nikl, Luminescence of Bi^{3+} ions in $Y_3Al_5O_{12}$:Bi single crystalline films, Radiation Measurements 42 (2007) 882–886.

[8] A.K. Prodjosantoso, B.J. Kennedy, B.A. Hunter, Phase separation induced by hydration of the mixed Ca/Sr aluminates $Ca_{3-x}Sr_xAl_2O_6$: a crystallographic study, Cement and Concrete Research 32 (2002) 647–655.

[9] Z.R. Kadyrova, N.A. Sirazhiddinov, Preparation and properties of the solid solutions $Sr_3Al_{2(1-x)}Ga_{2x}O_6$, Russian Journal of Inorganic Chemistry 31 (1986) 1114–1115.

[10] W.N. Kim, H.L. Park, G.C. Kim, Lithium solubility limit in $ZnGa_2O_4$:$Bi^{3+}_{0.001}$, Li^+ phosphor, Materials Letters 59 (2005) 2433–2436.

[11] Y. Xia, F. Huang, W. Wang, A. Wang, J. Shi, A reinvestigation of luminescence properties of Bi^{3+}-activated MSb_2O_6 (M=Ca, Sr) phosphors, Journal of Alloys and Compounds 476 (2009) 534–538.

[12] S.H. Shin, D.Y. Jeon, K.S. Suh, Charge-transfer nature in luminescence of $YNbO_4$: Bi blue phosphor, Journal of Applied Physics 90 (2001) 5986–5990.

[13] X. Xu, X. Yu, L. Mao, S. Yang, Z. Peng, Preparation and photoluminescence of Bi^{3+}-doped strontium chloroapatite nanophosphor, Materials Letters 58 (2004) 3665–3668.

[14] C.H. Kim, C.H. Pyun, H. Choi, S.J. Kim, Luminescence of CaS:Bi, Bulletin of the Korean Chemical Society 20 (1999) 337–340.

[15] I. Sioutis, V.L. Stakhursky, G. Tarczay, T.A. Miller, Experimental investigation of the Jahn–Teller effect in the ground and excited electronic states of the tropyl radical. Part II. Vibrational analysis of the $^{2}_{A}E^{\tilde{2}-}_{\tilde{X}}E''_{2}$ electronic transition, Journal of Chemical Physics 128 (2008) 084311.

[16] F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M.H. Whangbo, A. Garcia, T.L. Mercier, Mechanism of phosphorescence appropriate for the long-lasting phosphors Eu^{2+}-doped $SrAl_2O_4$ with codopants Dy^{3+} and B^{3+}, Chemistry of Materials 17 (2005) 3904–3912.

[17] G. Blasse, Energy transfer in oxidic phosphors, Philips Research Report 24 (1969) 131–144.

[18] J.H. Lee, Y.J. Kim, Photoluminescent properties of Sr_2SiO_4:Eu^{2+} phosphors prepared by solid-state reaction method, Materials Science and Engineering B 146 (2008) 99–102.