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Influence of Bi_2O_3 flux in the structural and photoluminescence properties of $SrAl_2O_4:Eu^{2+}$ phosphors

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Abstract

$SrAl_2O_4:Eu^{2+}$ phosphors with various content of Bi_2O_3 flux were synthesized and analyzed. It was observed that the crystallinity and the particle size of the phosphors were increased with the addition of Bi_2O_3 flux. These phenomena are considered to be caused via the melting of the Bi_2O_3 flux particles during the synthesis of the phosphors. The melted Bi_2O_3 flux increased the mobility and homogeneity of solid reactants, thereby enhancing the photoluminescence intensity of the phosphors. $SrAl_2O_4:Eu^{2+}$ phosphors with Bi_2O_3 as the flux exhibited a broad green emission with a peak at 520 nm. The highest photoluminescence emission intensity was observed when 5 mol% Bi_2O_3 flux was added into the phosphors. The emission is due to $4f^65d \rightarrow 4f^7$ ($^8S_{7/2}$) transitions of the Eu^{2+} ions. Moreover, Bi_2O_3 flux extended the application of the ultraviolet excited phosphors toward the blue-light excited phosphors. Nevertheless, the influence of Bi_2O_3 on the afterglow and the emission color of $SrAl_2O_4:Eu^{2+}$ phosphors were not significant. This research indicated that Bi_2O_3 flux is effective flux for synthesizing $SrAl_2O_4:Eu^{2+}$ phosphors.

Keywords: $SrAl_2O_4:Eu^{2+}$ phosphors; Bi_2O_3 flux; Morphology; Photoluminescence

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1. Introduction

Strontium aluminate phosphors recently gathered attention due to the high quantum efficiency, long phosphorescence and considerable thermal and chemical stability [1,2]. Among these strontium aluminate phosphors, diavelent europium (Eu^{2+}) doped $SrAl_2O_4$ are considered as useful bluish-green phosphors in the application of luminous watches and outdoor lighting [3,4]. Compared with classical sulfide phosphorescent phosphors, $SrAl_2O_4:Eu^{2+}$ phosphors have several valuable properties, such as high radiation intensity, color purity, and long afterglow time [5–7].

The solid-state reaction process is used intensively for the synthesis of $SrAl_2O_4:Eu^{2+}$ phosphors. Nevertheless, this process often results in insufficient chemical homogeneity and requires high calcination temperature. In order to overcome the drawbacks of the conventional solid-state reaction process, the flux is introduced into calcination process in this study. It has been reported that the addition of fluxes such as BaF_2, NaF, LiF, and H_3BO_3 optimistically affects the crystallite size distribution and emission intensity [8,9]. Previously, bismuth oxide (Bi_2O_3) has been proved to be a very useful additive for lowering the temperature needed for the reaction to take place during solid-state synthesis [10]. However, there is no detailed study related to the synthesis of $SrAl_2O_4:Eu^{2+}$ phosphors using Bi_2O_3 as flux has been reported in the literatures.

In the present research, $SrAl_2O_4:Eu^{2+}$ phosphors were synthesized via the solid-state reaction process with Bi_2O_3 as the flux. The effects of Bi_2O_3 flux on the crystal structure and particle size of $SrAl_2O_4:Eu^{2+}$ phosphors were investigated intensively. The photoluminescence properties and persistent luminescence of $SrAl_2O_4:Eu^{2+}$ phosphors with various concentration of Bi_2O_3 flux were also discussed.

2. Experimental

A series of $SrAl_2O_4:Eu^{2+}$ phosphors with x mol% Bi_2O_3 flux (x=0, 2.5, 5, and 7.5) were prepared via the solid-state

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reaction process. Mixtures containing analytical grade $SrCO_3$, Al_2O_3 in stoichiometric ratio with 5 mol% Eu_2O_3 and various amounts of Bi_2O_3 were ground into fine powder via using ball milling technique. The mixtures were calcined at 1400 °C for 3 h under reduction atmosphere (5 vol% H_2 and 95 vol% N_2).

The X-ray diffraction (XRD) data for the synthesized polycrystalline phosphors was collected on MAC Science MXP3 Diffractometer with *CuKα* radiation. The morphology of the phosphors was recorded from JSM-6390LV Scanning Electron Microscope (SEM). Emission and excitation spectral properties and persistent luminescence of the phosphors were measured via using a modular fluorescence spectrophotometer (Hitachi F-4500, Tokyo, Japan) with a Xenon lamp as the light source. The Commission International de I'Eclairage chromaticity (CIE) was monitored via an Ocean Optics CIE analyzer attachment (Ocean Optics, Henderson, NV) on the fluorescence spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction and SEM studies

The XRD patterns of the $SrAl_2O_4:Eu^{2+}$ phosphors with x mol% Bi_2O_3 as the flux are depicted in Fig. 1. The sharp and single peaks of all XRD patterns suggest the formation of monophasic $SrAl_2O_4$ compound without the existence of other phase. These results were consistent with the standard ICDD file of $SrAl_2O_4$ (no. 34-0379). The diffraction pattern also reveals that the Bi_2O_3 flux caused no significant changes in the crystal structure. Most importantly, the increment of Bi_2O_3 resulted in the enhanced crystallinity of $SrAl_2O_4$ phase. The samples with 5 mol% Bi_2O_3 flux showed more intense and defined XRD patterns than other three samples. It points out that the optimal dosage of the Bi_2O_3 flux is about 5 mol% for the preparation of single monoclinic phased $SrAl_2O_4:Eu^{2+}$ phosphors. However, the excess flux led to the distortion of crystal structure during the reaction process, and decreased the crystallinity of the sample.

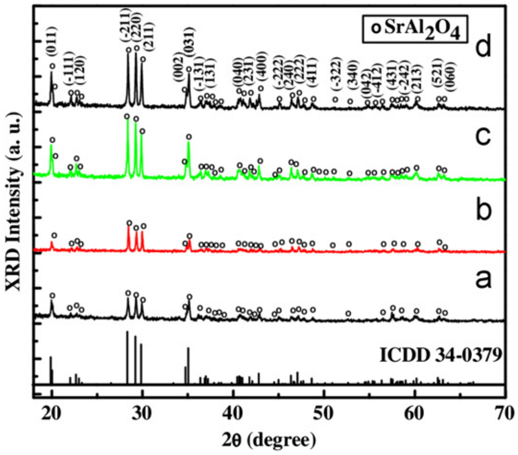

Fig. 1. X-ray diffraction pattern of $SrAl_2O_4:Eu^{2+}$ phosphors with x mol% Bi_2O_3 flux synthesized at 1400 °C for (a) $x=0$, (b) $x=2.5$, (c) $x=5$, and (d) $x=7.5$.

The microscopic images of $SrAl_2O_4:Eu^{2+}$ phosphors with x mol% Bi_2O_3 flux prepared via the solid-state reaction process are shown in Fig. 2. The morphology of the prepared phosphors without Bi_2O_3 flux ($x=0$) displayed micro-granularity with particle sizes in the range of 0.5–4.0 μm sizes (Fig. 2(a)). The particle size increased when the concentration of Bi_2O_3 flux was increased (Fig. 2(b)–(d)). This phenomenon is attributed to the lower melting point of Bi_2O_3 (817 °C) in comparison with the original calcination temperature (1400 °C). The liquid formed via the melted flux increased the surface tension during reaction process, making particles coagulate together. The melt flux also enhanced the slide and rotation of particles. This effect promoted the particle–particle contact and particle growth, and hence increased the particle size [8,11]. The melted flux also increased the mobility and homogeneity of solid reactants significantly during synthesis. These phenomena are considered to be important for eliminating the surface defects of the phosphors and improving the photoluminescence intensity [8,11]. It is concluded that the increase in Bi_2O_3 content directly introduces the enhanced crystallinity and the increment in particle size.

3.2. Photoluminescence studies

The excitation spectra of $SrAl_2O_4:Eu^{2+}$ phosphors with x mol% Bi_2O_3 flux upon emission at 520 nm are depicted in Fig. 3. The excitation spectrum of the sample without Bi_2O_3 flux extended from 200 to 500 nm with most intensive peak at around 360 nm and three shoulders at 270 nm, 325 nm, and 425 nm, respectively. The broadness of the excitation spectrum indicates that the present phosphors can be well excited in the range from 250 to 430 nm. The excitation spectrum ranging from 250 to 450 nm are attributed to the partly allowed $4f^7$ $(^8S_{7/2}) \rightarrow$ $4f^65d$ transitions of the Eu^{2+} ions [12]. In addition, there were no appreciable changes in the positions of intense excitation bands with the addition of Bi_2O_3 flux. However, great enhancement in the emission intensity was observed. The excitation intensity of the phosphors with 5 mol% Bi_2O_3 flux was found to be highest compared with other three samples. The present excitation result suggests that $SrAl_2O_4:Eu^{2+}$ phosphors with Bi_2O_3 flux are suitable for being excited via ultraviolet, near-ultraviolet and blue light as potential green-emitters. It is worth to mention that the blue excitation matches well with GaN-based LED emission, which is essential for improving the efficiency of white LEDs [13].

Fig. 4(a) illustrates the emission spectra of $SrAl_2O_4$: Eu^{2+} phosphors with x mol% Bi_2O_3 flux ($x=0$, 2.5, 5, and 7.5) upon excitation at 425 nm. The emission spectra of present phosphors synthesized with different amount of Bi_2O_3 flux were similar in shape but different in intensity.

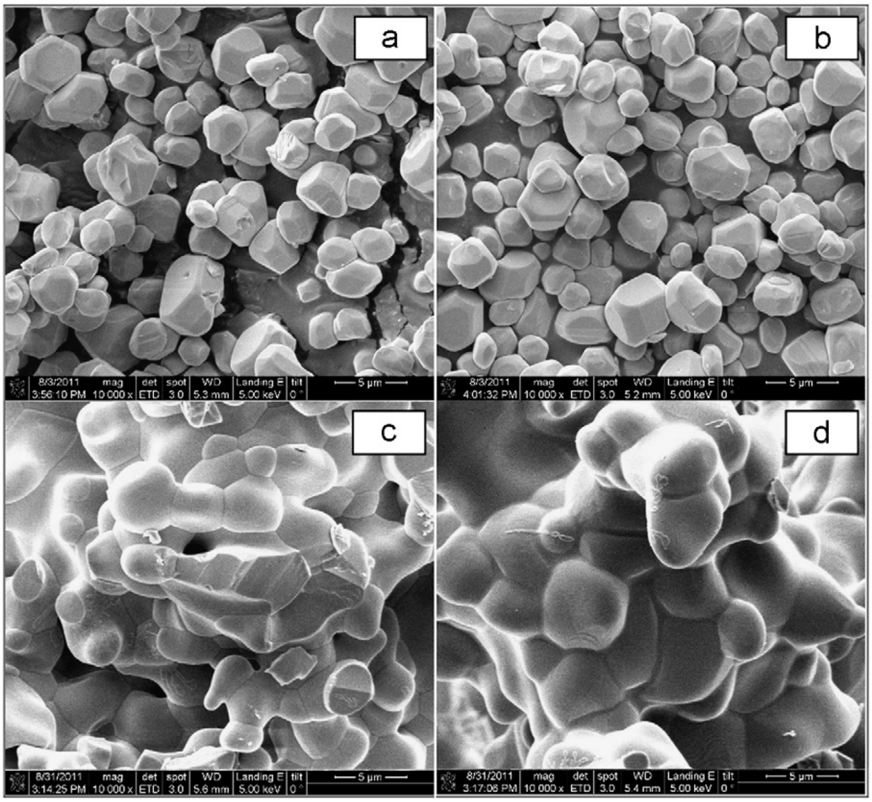

Fig. 2. SEM micrographs of $SrAl_2O_4$:Eu^{2+} phosphors with x mol% Bi_2O_3 synthesized at 1400 °C for (a) $x=0$, (b) $x=2.5$, (c) $x=5$, and (d) $x=7.5$.

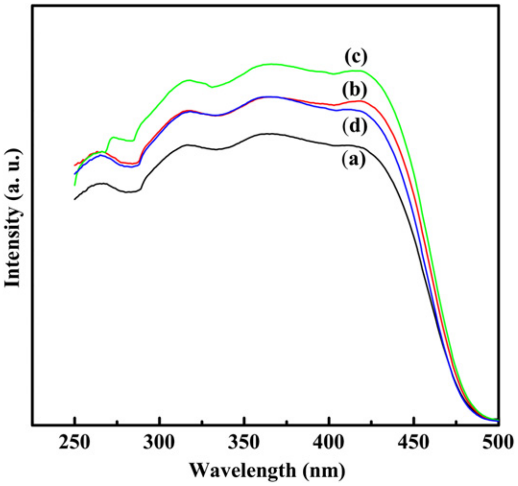

Fig. 3. Excitation spectrum of $SrAl_2O_4$:Eu^{2+} phosphors with x mol% Bi_2O_3 upon emission at 520 nm, where (a) $x=0$, (b) $x=2.5$, (c) $x=5$, and (d) $x=7.5$.

The present samples showed green emission at 520 nm originating from the $4f^65d$ level to $4f^7$ ($^8S_{7/2}$) ground state transition of Eu^{2+} ions. The broad emission band is due to a strong coupling interaction between Eu^{2+} ions and the $SrAl_2O_4$ host matrix [13,14]. The inset of Fig. 4(a) illustrates the emission intensity of the present phosphor as a function of different Bi_2O_3 content under 355 and 425 nm excitations. With increasing the amount of Bi_2O_3, the emission intensity of the present phosphor increased under both near-ultraviolet and blue excitations. The emission intensity of phosphors with 5 mol% Bi_2O_3 flux was the highest compared with other three phosphors. Over this amount of the flux, the emission intensity dropped gradually due to the constituent ion of flux remaining in the host lattice as defects.

The emission spectra of the $SrAl_2O_4$:Eu^{2+} phosphors without and with 5 mol% Bi_2O_3 flux as a function of different excitations are shown in Fig. 4(b). The results showed no spectral shift in emission wavelength under various excitations and gives stable color purity at perfect green-end wavelengths. The fixed emission wavelength suggests that there are only one cation site of Sr^{2+} ions in $SrAl_2O_4$. When Eu^{2+} ions are doped into the $SrAl_2O_4$ host, they are readily substituted for Sr^{2+} sites due to the closeness of ionic radii (Sr^{2+}; 132 pm, Eu^{2+}; 131 pm). As a result, there is only one type of Eu^{2+} emission centers when Eu^{2+} ions are incorporated into Sr^{2+} sites of $SrAl_2O_4$. This effect leads to single and unchanged emission band peaked at 520 nm under various excitations. The addition of Bi_2O_3 flux significantly improved emission intensity. However, the increase in the emission intensity under blue-light excitation was greater than that under ultraviolet and near-ultraviolet excitation (inset of Fig. 4(b)). It is probably because incorporation of Bi_2O_3 flux causes the formation of new defects, facilitating the charge transfer in blue region more than that in ultraviolet and near-ultraviolet region. This indicates that the originally ultraviolet excited phosphors can be extended toward

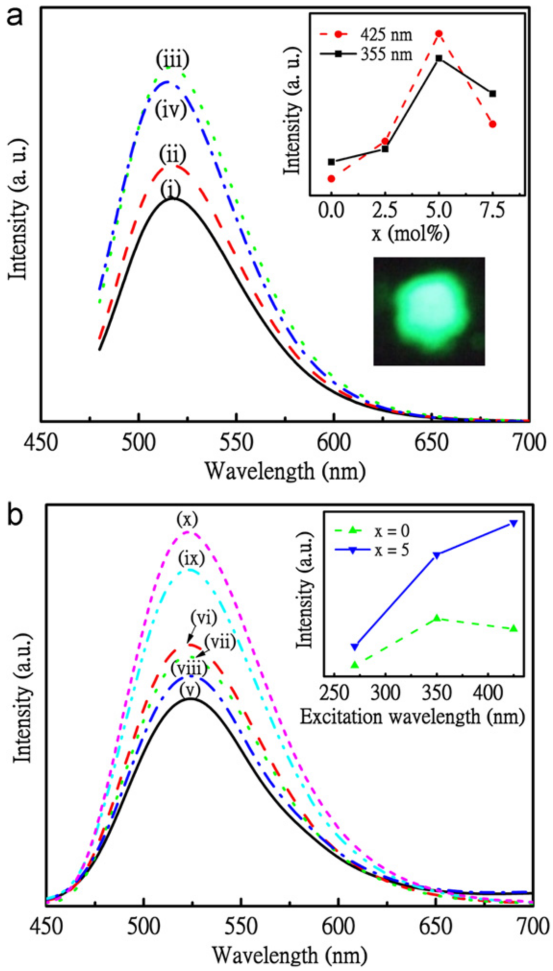

Fig. 4. Emission spectrum of (a) $SrAl_2O_4$:Eu^{2+} phosphors with x mol% Bi_2O_3 upon excitation at 425 nm for (i) x = 0, (ii) x = 2.5, (iii) x = 5, and (iv) x = 7.5 and (b) $SrAl_2O_4$:Eu^{2+} phosphors without Bi_2O_3 upon excitations at (v) 270 nm, (vi) 355 nm, and (vii) 425 nm and with 5 mol% Bi_2O_3 upon excitations at (viii) 270 nm, (ix) 355 nm, and (x) 425 nm. Inset of (a) shows the variation of emission intensity upon excitations at 355 nm and 425 nm as a function of different Bi_2O_3 concentrations. Inset of (b) shows the variation of emission intensity of $SrAl_2O_4$:Eu^{2+} phosphors with x mol% Bi_2O_3 as a function of different excitations for x = 0 and x = 5.

the application as a blue excited green emitter with the addition of Bi_2O_3 flux.

The influence of Bi_2O_3 flux content on the luminescent performance may be attributed to several aspects. The first one is the flux effect of Bi_2O_3, introducing enhanced crystallization and increased grain size and subsequently decreased lattice defects. The oscillating strengths for the optical transitions will be increased enormously due to the improved crystallization and increased grain size. This effect increases the luminescent intensity and also reduces the luminescence quenching due to the surface states [15,16]. On the other hand, the addition of excess Bi_2O_3 may also give rise to the formation of defect centers. Once Bi_2O_3 attains a certain concentration ($x = 7.5$), the defects in the host lattice greatly increase. This phenomenon reduces the crystallinity and increases the inactive center concentration. Hence, it leads to the luminescence quenching [17]. Therefore, the luminescence intensity has great dependence on flux concentration.

The decay properties of 520 nm emissions of $SrAl_2O_4$:Eu^{2+} phosphors with 5 mol% Bi_2O_3 flux are illustrated in Fig. 5(a). The decay curves were fitted via a single-exponential function:

$$I = I_0 \exp(-t/\tau) \tag{1}$$

where I is the intensity of the phosphorescence, τ is the emission life time, t is the measuring time, and I_0 is the initial emission intensity at $t = 0$. The emission life times of present phosphors with x mol% Bi_2O_3 flux are given in Table 1. The reason for $SrAl_2O_4$:Eu^{2+} phosphors with x mol% Bi_2O_3 flux to present mono-exponential nature is due to homogeneous distribution of doping ions inside the host matrix without any cluster formation [18]. The phosphors with Bi_2O_3 flux demonstrated green phosphorescence with afterglow times as long as that of the phosphors without Bi_2O_3 flux. It indicates that the

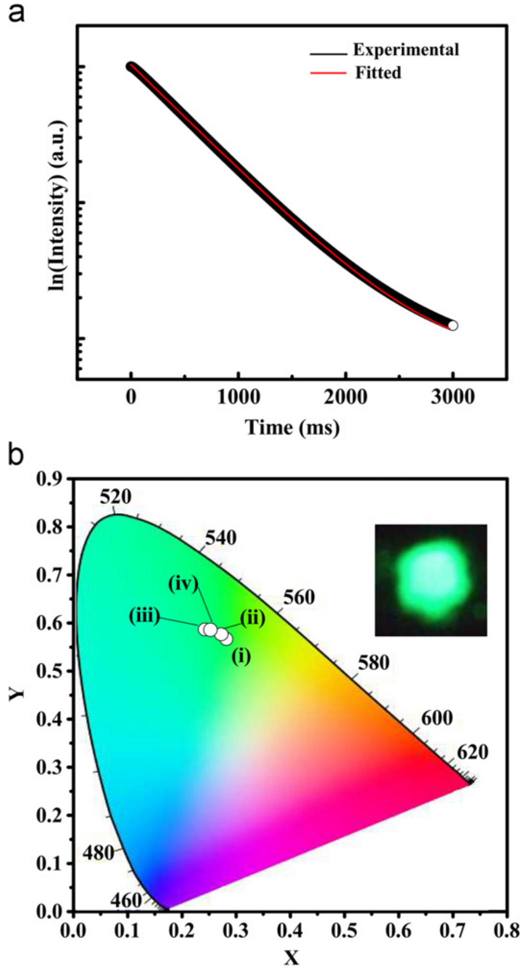

Fig. 5. (a) The decay curves of $SrAl_2O_4$:Eu^{2+} phosphors with 5 mol% Bi_2O_3 (b) chromaticity diagram of $SrAl_2O_4$:Eu^{2+} phosphors with x mol% Bi_2O_3 upon excitation at 425 nm for (i) $x = 0$, (ii) $x = 2.5$, (iii) $x = 5$, and (iv) $x = 7.5$. Inset of (b): The photograph of $SrAl_2O_4$:Eu^{2+} phosphors with 5 mol% Bi_2O_3.

Table 1
The average grain size, photoluminescence life time of 520-nm emission and CIE coordinates of $SrAl_2O_4:Eu^{2+}$ phosphors with x mol% Bi_2O_3 ($x=0$, 2.5, 5, 7.5).

Bi_2O_3 conc. (mole%)	Average grain sizes (μm)	Life time (ms)	CIE co-ordinates	
			X	Y
0	2.5	574.30	0.280	0.570
2.5	2.7	570.01	0.266	0.574
5	3.0	570.96	0.245	0.585
7.5	4.2	576.89	0.253	0.580

incorporation of Bi_2O_3 makes no influence on the type of traps, which are predominantly responsible for the afterglow.

The Commission Internationale de I'Eclairage (CIE) color coordinates of $SrAl_2O_4:Eu^{2+}$ phosphors with x mol% Bi_2O_3 flux excited at 425 nm are shown in Fig. 5(b) and listed in Table 1. For all samples, the CIE color coordinates were in the bright green region. In addition, the strong green emission of the phosphors with 5 mol% Bi_2O_3 flux was even visible to the naked eye (inset in Fig. 5(a)). The color coordinates were almost independent of the Bi_2O_3 concentration, proving the chemical inertness of Bi_2O_3 flux towards the $SrAl_2O_4:Eu^{2+}$ composition.

4. Conclusion

A group of $SrAl_2O_4:Eu^{2+}$ phosphors was synthesized via a conventional solid-state reaction process adding Bi_2O_3 as the flux. The influence of Bi_2O_3 flux on the structural and luminescent properties of $SrAl_2O_4:Eu^{2+}$ phosphors were investigated in detail. The Bi_2O_3 flux promoted the crystallinity and reduced the surface defects of $SrAl_2O_4:Eu^{2+}$ phosphor powders. Under near-ultraviolet and blue excitations, $SrAl_2O_4:Eu^{2+}$ phosphors exhibited a broad green emission at 520 nm. The luminescence intensity of $SrAl_2O_4:Eu^{2+}$ phosphors was enhanced with the addition of Bi_2O_3 flux. The enhancement in the emission intensity under blue-light excitation was greater compared with these under near-ultraviolet and ultraviolet excitation. On the other hand, Bi_2O_3 flux made no significant influence on the persistent luminescence and emission color of $SrAl_2O_4:Eu^{2+}$ phosphors. This study indicates that $SrAl_2O_4:Eu^{2+}$ phosphors with Bi_2O_3 flux are potential light-conversion luminescent materials under both ultraviolet and blue excitations.

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