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Effects of $SrCl_2$ as a flux on the structural and luminescent properties of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors for AC-LEDs

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ABSTRACT

$SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors were prepared by a high temperature solid state reaction method. $SrCl_2$ with various amounts was used as a flux to improve the optical properties of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors. The crystal structure, particles size, optical properties and decay curve of the products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectra, respectively. It is revealed that the addition of $SrCl_2$ flux can alter the morphology and then improve the photoluminescence of the phosphors. Compared to the commercial phosphors obtained by 0.6% H_3BO_3, maximum improvement of 13.56% is achieved in the integrated emission intensity of the phosphors when the amount of $SrCl_2$ is 9%. Meantime, the average lifetime of this phosphor can be shorten from 845.86 ms to 428.83 ms. It can be indicated that the phosphor prepared with 9% $SrCl_2$ is more suitable for applications in AC-LEDs with a time gap of 5–20 ms. The results are also confirmed by the fabricating and characterizing LEDs with $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors. These findings show that $SrCl_2$ is an excellent flux for the synthesis of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors.

1. Introduction

The emergence of alternate current light emitting diodes (AC-LEDs) is a major breakthrough in the field of semiconductor lighting, owing to its small drive current, low cost, high efficiency and long lifetime [1–3]. However, AC-LEDs cannot emit immediately until the voltage across circuit is higher than their turn-on voltage [2–5]. The flickering effects of AC-LEDs with a time gap of 5–20 ms are caused by AC cycles [3–5]. Therefore, people's eyes will be tired and damaged if they work for a long time under this environment. Very recently, long afterglow phosphors have been studied to resolve this problem [4,5]. The long afterglow materials can store the energy of light, and then they will emit slowly for a certain time [6]. It seems more promising to eliminate the periodic scintillation phenomena of AC-LEDs by compensating the dark duration with the persistent luminescence of phosphors.

$SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor is considered to be a very important long persistence material due to its high brightness, long afterglow, good heat and radiation resistance, high stable physical and chemical properties, which can be widely used for direction indicators, signs and other public facilities [7–12]. Among the preparation method of phosphors, high temperature solid-state reaction method is the most popular and easiest way to achieve industrialization, owing to its simple process, low cost and good performance. Commercial $SrAl_2O_4:Eu^{2+}$, $Dy3^{+}$ powders are usually prepared by a solid-state reaction method around 1200–1500 °C, and H_3BO_3 is mostly used as the flux [10,13]. But the serious agglomeration would be discovered by using H_3BO_3 flux. The phosphors must be grinded, which can cause the destruction of the crystalline structure and greatly reduce the luminous efficiency [4]. Several researches reported that a certain amount of flux, such as BaF_2 and LiF, can decrease the reaction temperature, improve the morphology and enhance the optical properties of phosphors [14–16]. However, there are few reports on using $SrCl_2$ fluxes in preparation of phosphors so far.

This paper aims to use $SrCl_2$ as fluxes to improve the performance of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors. For this purpose, $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors were prepared by the high temperature solid state method with $SrCl_2$ flux. The influence of the weight ratio of $SrCl_2$ on the morphology, optical properties and decay of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors were investigated in details. The electroluminescent properties of LEDs with $SrAl_2O_4$: Eu^{2+},

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Dy^{3+} phosphors were also studied. It is revealed that $SrCl_2$ is an excellent candidate for flux to improve the optical performance of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphor.

2. Experimental sections

2.1. Synthesis

$SrAl_2O_4$:Eu^{2+}, Dy^{3+} samples with different weight ratio of $SrCl_2$ as fluxes (3%, 6%, 9%, 12%, 15%) were prepared by the high temperature solid-state method. Stoichiometric amount of $SrCO_3$ (99.99%), Al_2O_3 (99.99%), $SrCl_2{\cdot}6H_2O$ (99%), Eu_2O_3 (99.99%), Dy_2O_3 (99.99%), H_3BO_3 (99%) were used as the starting materials and mixed in an agate mortar. After a good mixing, the mixtures were calcined at 800 °C for 2 h in an air atmosphere. After regrinding, they were sintered at 1400 °C for 4 h under a reducing atmosphere created by burning activated carbon. As for the commercially available long lasting green phosphor, $SrAl_2O_4$:Eu^{2+}, Dy^{3+} was popularly synthesized by using 0.6% H_3BO_3 flux [4,8,10]. For comparison, $SrAl_2O_4$:Eu^{2+}, Dy^{3+} without flux and 0.6% H_3BO_3 were prepared with the same process.

2.2. Characterization

The phase purity of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} samples were collected by X-ray powder diffraction (XRD) using a Diffractometer (X′ Pert PRO, Panalytical) with Cu K_α radiation at 40 kV and 30 mA. The XRD patterns were collected in the range of 10°–80°. The photoluminescence (PL) spectra and decay curves were obtained using a spectrofluorometer (F-4600, Hitachi) equipped with a 150-W Xe lamp. The morphology and size of particles were examined using a Scanning Electron Microscope (NoVaTM Nano SEM 430).

The phosphors were precoated on near-UV chips with 365 and 395 nm emission peaks, respectively. The emission spectra and the Commission Internationale de l'Eclairage (CIE) color coordinates of all LEDs were measured using the LED spectrophotocolorimeter (PMS 50, Evergreen Photo-E-Info Co. Ltd.) with an integrating sphere of 50 cm diameter. The forward-bias current is 20 mA. All measurements were conducted at room temperature.

3. Results and discussion

3.1. Phase identification

Fig. 1 depicts XRD patterns of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} with different weight ratio of $SrCl_2$ (denoted as sample a–f, respectively) and 0.6% H_3BO_3 (denoted as sample g). The XRD patterns were compared with the JCPDS standard cards of the possible phase, which have been marked with different symbols. The diffraction peaks of all samples can be indexed, and the dominant phase is monoclinic $SrAl_2O_4$ (JCPDS card No.74-0794). There are no obvious peaks of the used fluxes. However, minor content of the raw material Al_2O_3 (◇) and $Sr_4Al_{14}O_{25}$ (○) is clearly observed in Fig. 1a for the sample prepared without flux.

Fig. 1b–f shows the XRD patterns of the powders synthesized in the addition of $SrCl_2$ with various concentrations. When the weight ratio of $SrCl_2$ flux increases, Al_2O_3 phase disappear initially and the impurity of $Sr_4Al_{14}O_{25}$ phase can be seen from sample b–c, respectively. By further increasing concentration of $SrCl_2$ flux (sample d–f), the impurity of $Sr_4Al_{14}O_{25}$ phase disappear gradually, but Al_2O_3 phase emerges again. From the diffraction integrated intensity, it also can be concluded that all of fluxes except 15% $SrCl_2$ are beneficial to the formation of $SrAl_2O_4$ phase. And the diffraction integrated intensity of phosphor with 9% $SrCl_2$ can reach the maximum, indicating it is helpful for the crystallinity enhancement

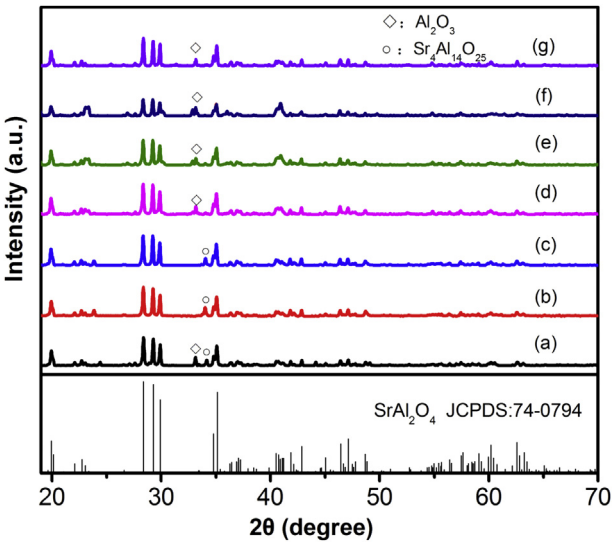

Fig. 1. (a) The XRD patterns of $SrAl_2O_4$:0.05Eu^{2+}, 0.05Dy^{3+} phosphors (a) without $SrCl_2$, (b) 3% $SrCl_2$, (c)6% $SrCl_2$, (d) 9% $SrCl_2$, (e)12% $SrCl_2$, (f) 15% $SrCl_2$, (g) 0.6% H_3BO_3.

of the phosphors. In addition, the impurity of Al_2O_3 phase can also be seen from the sample by adding 0.6% H_3BO_3 flux. Al_2O_3 have probably not been completely reacted, and the impurity of $Sr_4Al_{14}O_{25}$ phase may originate from the complex reaction. The by-products are greatly influenced by the flux.

3.2. SEM images and particles size distribution

Fig. 2a–d illustrates the SEM images and particles size distribution histograms of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors with different fluxes. The phosphors without $SrCl_2$, 9% $SrCl_2$, 15% $SrCl_2$ and 0.6% H_3BO_3 were chosen as representatives. The average size of phosphors was estimated by approximately measuring 230 particles in each phosphor. Size was dependent on the diagonal length of particles. All of the phosphors prepared with $SrCl_2$ fluxes exhibit regular spherical morphologies of microcrystalline structure, but platelike for that of H_3BO_3. It can be seen that the addition of fluxes can increase the particle size, especially for the phosphors prepared with 0.6% H_3BO_3. The added flux melt and increase the surface energy during the reaction process, which is expected to slow down the particles growth rate, so the morphology of the particles and the crystallinity can be improved [15]. However, the phosphors synthesized by adding H_3BO_3 as flux are agglomerate and the distribution of granularity is broad, which is harmful to the LEDs fabrication. No obvious agglomeration can be found among the samples prepared with $SrCl_2$ fluxes, the particles increase gradually, which present more regular morphology and narrower distribution than that of sample without flux. And phosphor prepared with 9% $SrCl_2$ exhibits the best uniformity among all of these four products.

To further evaluate the particle size distribution of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors as mentioned above, the standard deviation (SD) and standard error (SE) were calculated. The measurement details have been described in our previous work [17]. Calculated values of the SD, SE and SE% for four phosphors are listed in Table 1. For phosphors prepared with H_3BO_3, the value of SD, SE and SE% was 5.27 μm, 0.35 μm and 3.95%, respectively. The average size and the value of SD, SE increases when $SrCl_2$ concentration increases. But there is an obvious tendency that the value of SE% of the phosphors with fluxes is smaller than that of the sample without flux. And the minimum value of SE% was 2.70%, obtained from the sample synthesized with 9% $SrCl_2$ flux. It confirms that this sample have good