Available online at www.sciencedirect.com

ScienceDirect

JOURNAL OF RARE EARTHS

JOURNAL OF RARE EARTHS, Vol. 33, No. 5, May 2015, P. 469

www.re-journal.com/en/

Orange-red emitting Eu^{2+}-activated $(Sr_{0.883}Ba_{0.1}Lu_{0.0.17})_3(Si_{0.95}Al_{0.05})O_5$ phosphor: structure, photoluminescence, and application in white LEDs

ZHAO Fengyang (赵凤阳), LÜ Yanpeng (吕雁鹏), ZHOU Guangzhou (周广洲), PIAO Xianqing (朴贤卿)*, SUN Zhuo (孙 卓)

(Engineering Research Center for Nanophotonics & Advanced Instrument, Ministry of Education, Department of Physics, East China Normal University, Shanghai 200062, China)

Received 9 December 2014; revised 2 March 2015

Abstract: Orange-red emitting $(Sr_{0.883-x}Ba_{0.1}Lu_{0.0.17}Eu_x)_3(Si_{0.95}Al_{0.05})O_5$ phosphors were synthesized by conventional solid-state reaction. The effect of NH_4F flux on structural and luminescent properties of phosphors was investigated. Results suggested that the optimal content of NH_4F flux was 3 wt.% and the optimal doping concentration of Eu^{2+} was x=0.023 mol. The phosphors showed intense absorption in near-ultraviolet to blue region and exhibited orange-red emissions. The thermal stability of synthesized $(Sr_{0.86}Ba_{0.1}Lu_{0.017}Eu_{0.023})_3(Si_{0.95}Al_{0.05})O_5$ phosphor were examined and compared with commercial YAG:Ce^{3+} yellow phosphors. Combining an InGaN blue 460 nm chip and a white-emitting $(Sr_{0.86}Ba_{0.1}Lu_{0.017}Eu_{0.023})_3(Si_{0.95}Al_{0.05})O_5$ phosphor produced a white-light LED, demonstrating CIE chromaticity coordinates of (0.314, 0.329) and a color temperature of 5595 K. All results showed that this phosphor is a promising candidate as orange-red emitting phosphor for white light emitting diode (w-LED) application.

Keywords: Eu^{2+}; silicate phosphor; white LED; optical properties; rare earths

Phosphor-converted white LEDs have drawn much attention in recent years for their excellent characteristics, such as low energy consumption, high efficiency, reliability and long lifetime, etc.[1–3]. Up to now, commercial white LEDs are generally realized through combining blue InGaN chip and a yellow-emitting phosphor YAG: Ce^{3+} phosphor. Although the luminescence efficacy and the color rendering index are enough for the use of general illumination, it is not suitable for application in backlight of the liquid crystal display and medical lighting because of the deficiency of red emission[4]. In order to realize the output of warm white lights, one alternative way is near-ultraviolet (n-UV) (350–410 nm) chip combined with RGB (red/green/blue) phosphors. Another way to obtain white light is that a separate red light source can be used to compensate the red deficiency of the output light[5,6].

In the past several years, much attention has been paid to the preparation of tricolor phosphors with luminescent efficiency excited by UV-blue chips. Nowadays, $LiSrPO_4$:Eu^{2+}, $KSrPO_4$:Eu^{2+}, $BaAl_2Si_2O_8$:Eu^{2+},Ce^{3+} were used as blue phosphor for UV-LEDs[7–9]. Some red and orange phosphors such as Y_2O_2S:Eu^{3+} (red), (Ca,Sr)S: Eu^{2+} (red), CaZnOS:Eu^{2+} (red), $CaTiO_3$:Eu^{3+} (red) and SrS:Eu^{2+} (orange) show a much lower efficiency compared with the blue phosphor $BaMgAl_{10}O_7$:Eu^{2+} and green one ZnS:Cu^+/Al^{3+} in the tricolors phosphors under the n-UV irradiation[10–16]. What's more, their stability is not high enough, and their decomposition products are harmful to environment. Therefore, it is urgent to seek for novel and efficient red or orange phosphors for LED application that can be excited in UV-blue light region. A novel orange-yellow phosphor Sr_3SiO_5:Eu^{2+} which emitted efficient light at about 580 nm was firstly reported by Park et al. in 2004, and the Ba^{2+} ions doped in Sr_3SiO_5: Eu^{2+} could shift the yellow emission from about 580 nm to near 600 nm[17,18]. It was a promising candidate for making up those shortcomings of YAG:Ce^{3+} fabricated in warm w-LED. Luo et al. reported that Si^{4+} can be substituted by Al^{3+} to form solid solutions of aluminum oxygen tetrahedrons or silicon oxygen tetrahedrons under some conditions and enhanced photoluminescence of Sr_3SiO_5:Eu^{2+} phosphor[19]. However, the influence of fluxing agents on the luminescence properties of the Ba^{2+}, Lu^{3+} and Al^{3+} co-doped Sr_3SiO_5:Eu^{2+} has not yet been reported to our knowledge.

In the present work, $(Sr_{0.883-x}Ba_{0.1}Lu_{0.0.17}Eu_x)_3(Si_{0.95}Al_{0.05})O_5$ (SBLSAO:$x$$Eu^{2+}$) phosphors which can be efficiently excited by UV-blue light were prepared by a solid state method using NH_4F as a flux. The structural, luminescent, and thermal properties of SBLSAO:Eu^{2+} were studied in detail. The CIE chromaticity coordinates re-

---

Foundation item: Project supported by National Natural Science Foundation of China (51102095) and Research Fund for the Doctoral Program of Higher Education of China (20110076120023)

* **Corresponding author:** PIAO Xianqing (**E-mail:** xqpiao@phy.ecnu.edu.cn; **Tel.:** +86-21-62234321)

DOI: 10.1016/S1002-0721(14)60442-7

sults demonstrated that SBLSAO:xEu^{2+} phosphors might be potential candidates as orange-red emitting phosphors excited by UV-blue light for white LED applications.

1 Experimental

All powder samples were synthesized by high-temperature solid reaction using NH_4F as flux. The raw materials were $SrCO_3$ (A.R. grade), $BaCO_3$ (A.R. grade), Lu_2O_3 (A.R. grade), Al_2O_3 (A.R. grade), SiO_2 (A.R. grade), NH_4F (A.R. grade) and Eu_2O_3 (99.99% purity). Stoichiometric amounts of the reagents were ground and mixed by ball milling for 3 h. And then the mixtures were dried, put into an alumina crucible and subsequently placed in a chamber furnace at 1150 ºC for 2 h to decompose $SrCO_3$ and $BaCO_3$ completely under air condition. The as-obtained precursors were then positioned in a radio frequency (RF) furnace and heated at 1350–1550 ºC for 6 h in a flow of 5% H_2-95% N_2 gas. After firing, these samples were cooled to room temperature with the furnace. Finally, the coarse phosphor samples with orange-red body color were obtained and they were slightly ground with an agate mortar for various measurements. The total reaction involved can be simply expressed as follows:

$$SrCO_3+BaCO_3+Lu_2O_3+Eu_2O_3+Al_2O_3+SiO_2\rightarrow(Sr_{0.883-x}Ba_{0.1}Lu_{0.0.17}Eu_x)(Si_{0.95}Al_{0.05})O_5$$

The crystal phase of the synthesized phosphor was examined using X-ray powder diffraction (XRD) on a Bruker D8 ADVANCE X-ray diffractometer with the Cu Kα radiation at 40 kV and 40 mA (λ=0.15406 nm). The XRD patterns were collected in the 2θ range of 10º–80º. Photoluminescent excitation and emission spectra were measured at room temperature using a fluorescent spectrophotometer (Horiba Jobin Yvon, FluoroMax-4) equipped with a 150 W Xe lamp as an excitation source. To investigate the thermal quenching between 20 and 250 ºC the same spectrometer was equipped with a high-temperature fluorescence controller (Tianjin Orient KOJI Co., Ltd., TAP-02). The sample was kept for 10 min to reach the thermal equilibrium, which would guarantee a uniform temperature both on the surface and in the interior of the sample[20].

2 Results and discussion

2.1 Structure and morphology

Fig. 1 shows the XRD patterns of $(Sr_{0.86}Ba_{0.1}Lu_{0.017}Eu_{0.023})_3(Si_{0.95}Al_{0.05})O_5$ (abbreviated as SBLSAOE23) powders fired at different temperatures ranged from 1350 to 1550 ºC without flux, and fired at 1350 ºC with varying NH_4F flux amounts. (1 wt.%–5 wt.%) and the standard pattern of Sr_3SiO_5 (JCPDS card No. 26-0984).

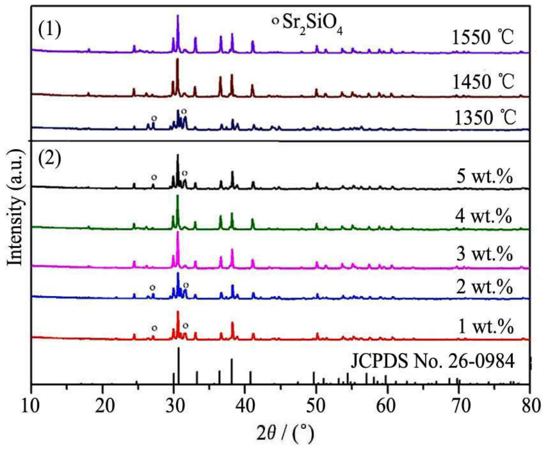

Fig. 1 XRD patterns of SBLSAOE23 powders fired at different temperatures (1350, 1450 and 1550 °C) without flux and fired at 1350 °C with various NH_4F amounts and the standard data of Sr_3SiO_5 (JCPDS card No. 26-0984)

The effect of a flux for the synthesis of phosphors is not only to accelerate uniform distribution of activators in the host materials but also to lower the synthesizing temperature in a solid-state reaction[21]. Without NH_4F flux, a Sr_3SiO_5 phase was dominantly formed at 1350 ºC with a small amount of Sr_2SiO_4 phase observed in the XRD patterns. Pure Sr_3SiO_5 can be obtained with heating temperature above 1450 ºC. But the samples prepared at relatively low temperature 1350 ºC by using NH_4F as flux shows better crystallinity and morphology. The content of Sr_2SiO_4 gradually decreases with increasing the amount of NH_4F flux, and Sr_2SiO_4 phase perfectly disappears with the amount of NH_4F flux increased up to 3 wt.%–4 wt.%. The diffraction patterns of the samples match well with that reported in JCPDS (Joint Committee of Powder Diffraction Standard) card No. 26-0984 for Sr_3SiO_5, indicating that appropriate NH_4F flux successfully reduced the firing temperature. However, the excess flux leads to the formation of an unintended Sr_2SiO_4 impurity when the amount of NH_4F flux is over 5 wt.%.

The Sr_3SiO_5 is a tetragonal crystal structure with a space group of $P4/ncc$ as schemed in Fig. 2. In the Sr_3SiO_5 structure, there are two oxygen sites: O1 and O2. All O2 sites are surrounded by regular octahedra of Sr^{2+} ions (OSr_6) and the O1 ions form the SiO_4 tetrahedron. Unlike the new-emerging nitride or oxynitride hosts, in which the $Si(N,O)_4$ tetrahedrons are connected to form networks or layers, the SiO_4 tetrahedrons in Sr_3SiO_5 structure are completely separated, rather than connected with each other. This to some extent lowered the thermal and chemical stability in the packaging and application process of white LEDs. As the ion radii of Sr^{2+} (11.3 nm), Ba^{2+} (13.5 nm), and Lu^{3+} (8.5 nm) are close, while the radius of Al^{3+} (5.0 nm) is similar to that of Si^{4+} (4.2 nm)[22–24], thus the successful introduction of Ba^{2+} and Lu^{3+} in Sr sites, Al^{3+} in Si^{4+} does not result in a great dis-