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Effects of fluxes on the synthesis of $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ green phosphors for white light-emitting diodes

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ABSTRACT

Different fluxes were added in preparation of $Ca_3Sc_2Si_3O_{12}:0.01Ce^{3+}$ phosphors with a solid-state method and the different influences of the fluxes on phase formation, morphology, and photoluminescence properties of the phosphors were studied. The results show that CaF_2 flux is the best flux as it can decrease single phase-forming temperature, improve morphology and enhance photoluminescence of the $Ca_3Sc_2Si_3O_{12}:0.01Ce^{3+}$ phosphors remarkably. White light-emitting diode was fabricated with the $Ca_3Sc_2Si_3O_{12}:0.01Ce^{3+}$ phosphor prepared with CaF_2 flux, and good performances of this WLED confirm that CaF_2 is a good flux for preparing $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$, and the phosphor is an efficient green component for fabrication of white LEDs.

1. Introduction

Recently semiconductor white light-emitting diodes (LEDs) have emerged as the fourth generation of illumination technology [1–4]. It is an obvious tendency for white LEDs to occupy the lighting domain and replace the conventional lamps sooner or later. Most currently commercially available white LEDs are obtained mainly by combining a 460 nm blue-emitting GaN chip with a yellow emitting yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped Ce^{3+} phosphor [5]. However, such white LEDs still encounter the following problems: low color-rendering index, low color reproducibility, and high color temperature [6,7]. To resolve these problems, use of green and red phosphors instead of a yellow phosphor has been proposed [8,9]. As the first example of a silicate garnet host crystal in which Ce^{3+} shows efficient luminescence at room temperature, Ce^{3+} activated $Ca_3Sc_2Si_3O_{12}$ host system represents a huge potential for developing new efficient phosphors suitable for this purpose. In 2007 and 2008, $Ca_3Sc_2Si_3O_{12}$ (CSSO):Ce^{3+} phosphors were prepared by Shimomura et al. [10] and Suzuki et al. [11] with solid-state method or hydrothermal silicon alkoxide gelation method, respectively. Mikami et al. [12] used a charge compensation method to improve the efficiency of CSSO:Ce^{3+} to a great extend.

In the most popular solid-state (SS) preparation method of phosphors, using a flux may improve the morphology and enhance the photoluminescence of the products. Lin [13] and Chen [14] reported the effects of fluxes on YAG:Ce^{3+} and $Tb_3Al_5O_{12}:Ce^{3+}$ (TAG:Ce^{3+}) phosphors. However, to our best knowledge, there is, as yet, no report on using fluxes in preparation of CSSO:Ce^{3+} phosphor so far. In this paper, different fluxes were added when synthesizing CSSO:Ce^{3+} phosphors by SS method and the effects of these fluxes on the phase formation, morphology and photoluminescence of CSSO:Ce^{3+} phosphors were investigated. Several bright green LEDs and highly efficient, high color-rendering index, low color temperature white LED were fabricated.

2. Experimental

Sc_2O_3 (99.99%), CeO_2 (99.99%), $CaCO_3$ (A. R.) and SiO_2 (A. R.) were used as starting materials and LiF (A. R.), H_3BO_3 (A. R.), CaF_2 (A. R.) and NH_4Cl (A. R.) were used as fluxes, respectively. Stoichiometric amounts of starting materials were mixed in an agate mortar in a molar ratio of 2.97:2:3:0.03 (Ca:Sc:Si:Ce), and then different fluxes – H_3BO_3 (H), LiF (L), H_3BO_3 and LiF with 1:1 weight ratio (HL), CaF_2 (C), NH_4Cl (N) – were added in different contents. After repeated grinding, each mixture was transferred to a corundum crucible and fired at 1100–1450 °C for 4 h in an electric furnace under a reducing atmosphere created by burning an excess of activated carbon. For the purpose of comparison, a CSSO:Ce^{3+} sample without using flux was also prepared by the same process. The synthesis conditions of different samples were shown in Table 1. After the reaction ended, H_3BO_3 (H), LiF (L) and NH_4Cl (N) fluxes can be removed by sublimation, melt and boiling or decomposition with loss of the halogen or maybe even the halide. The reason for removal of CaF_2 may be

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Table 1
The synthesis conditions of different samples.

Sample no.	Flux composition	Flux content/wt.%	Temperature/°C	Time of synthesis/h
01	No flux	0	1250	4
02	H (H_3BO_3)	1	1250	4
03	L (LiF)	1	1250	4
04	HL (H_3BO_3 + LiF)	1	1250	4
05	C (CaF_2)	1	1250	4
06	N (NH_4Cl)	1	1250	4
07–11	C (CaF_2)	1, 3, 5, 7, 9	1150	4
12–16	C (CaF_2)	1, 3, 5, 7, 9	1250	4
17–21	C (CaF_2)	1, 3, 5, 7, 9	1350	4
22–26	C (CaF_2)	1, 3, 5, 7, 9	1450	4
27	No flux	0	1450	4

due to the formation of some intermediate-phase in the reaction process.

X-ray powder diffraction (XRD) patterns of the products were recorded on a Rigaku D/max-IIIA diffractometer with Cu Kα radiation (λ = 0.15403 nm). The morphology of each sample was inspected using a JEOL JSM-6330F field emission scanning electron microscope (FESEM), and the samples were gold-coated before the inspection. The photoluminescence signals of the samples were detected by an FLS920 Combined Fluorescence Lifetime and Steady State Spectrometer from EDINBURGH Inc. with a Xe900 lamp as the light source.

Several LEDs were fabricated by combining the synthesized CSSO:Ce^{3+} phosphors with ~460 nm-emitting InGaN chips. The emission spectra of the LEDs under 20 mA forward bias were recorded on a PMS-80 LED spectrophotocolorimeter (EVERFINE, China).

3. Results and discussion

3.1. The phase formation and luminescence properties of $Ca_3Sc_2Si_3O_{12}$:Ce^{3+} phosphors prepared with different fluxes at 1250 °C

Fig. 1 shows the X-ray diffraction patterns of the CSSO:0.01Ce^{3+} sample nos. 01–06. Firing without flux at 1250 °C (sample no. 01) produced a material that shows no diffraction peaks relatable to the $Ca_3Sc_2Si_3O_{12}$ phase. In contrast, sample nos. 02–05 presented diffraction peaks which are nearly consistent with the presence of crystalline $Ca_3Sc_2Si_3O_{12}$. All of the peaks are in agreement with PDF card 72-1969 (calcium scandium silicate, cubic, $I_{a-3d(230)}$) except some minor Sc_2O_3 peaks. The square symbols denote the minor peaks derived from the starting material Sc_2O_3. According to these patterns, the CSSO crystallized in the presence of H, HL, L, C flux but not without flux. There are no diffraction peaks from the flux phases.

All products obtained show similar profiles in the excitation and the emission spectra, and the excitation and emission spectra of CSSO:0.01Ce^{3+} sample no. 03 are shown in Fig. 2(a) and (b) as a representative. The excitation spectrum, monitored at 505 nm, exhibits a broad and intense excitation band at 400–500 nm, with a maximum near 450 nm that originates from the *f–d* electron transition of Ce^{3+}. Excited with 450 nm-light, the samples show intense green emission in a broad range of 500–700 nm centering near 505 nm which belongs to the characteristic $5d(^2D)$–$4f(^2F_{5/2}, ^2F_{7/2})$ transitions of Ce^{3+} ions. All the photoluminescence characteristics indicate that the prepared CSSO:0.01Ce^{3+} is a good candidate for fabrication of InGaN-based LEDs. The effects of different fluxes on emission intensities of CSSO:0.01Ce^{3+} phosphors were also investigated. The emission spectra of CSSO:0.01Ce^{3+} sample nos. 02–06 and no. 27 are shown in Fig. 2(c)–(h) for a comparison. The sample no. 05 shows the highest improvement compared with the sample without flux. The emission levels in the other phosphors are in the following order 1%HL > 1%H > 1%L ≈ no flux > 1%N.

3.2. The phase formation, morphology and luminescence properties of $Ca_3Sc_2Si_3O_{12}$:Ce^{3+} phosphors prepared with CaF_2

Because of the best effect on the photoluminescence of the phosphor, further investigation concentrated on CaF_2 flux. Different phosphors were prepared from the starting materials listed above with different amounts of CaF_2 flux and with firing at differ-

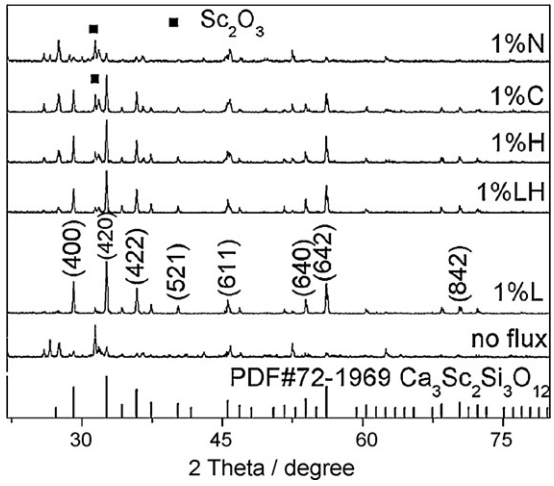

Fig. 1. The XRD patterns of CSSO:0.01Ce^{3+} phosphors prepared at 1250 °C with of without fluxes at the wt.% of 1%.

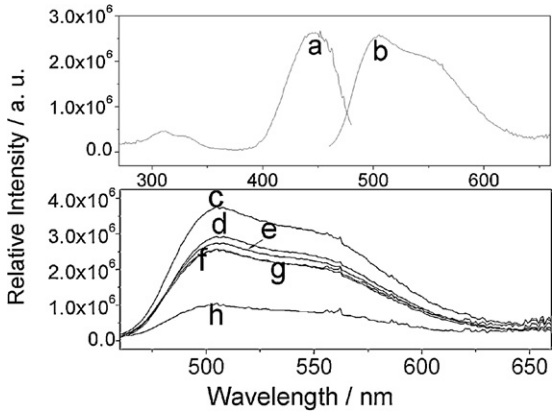

Fig. 2. The excited (a, λ_{em} = 505 nm) and emission (b, λ_{ex} = 450 nm) spectra of CSSO:0.01Ce^{3+} phosphor prepared at 1250 °C with 1% L and emission spectra of the CSSO:0.01Ce^{3+} phosphor prepared with or without fluxes at 1250 °C (c, 1%C; d, 1% HL; e, 1% H; f, 1% L; g, no flux; h, 1% N, λ_{ex} = 450 nm).