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Atmospheric pressure preparation of red-emitting $CaAlSiN_3:Eu^{2+}$ phosphors with variable fluxes and their photoluminescence properties

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Abstract

A red-emitting Eu^{2+} activated $CaAlSiN_3$ phosphor was successfully prepared via an atmospheric pressure solid-state reaction method with the aid of variable fluxes, namely SrF_2, NH_4F, BaF_2, NaF, AlF_3, CaF_2 and NH_4Cl. The experimental results showed that the addition of SrF_2 flux effectively reduced the formation temperature of $CaAlSiN_3$: Eu^{2+} about 100 °C, improved the morphology of $CaAlSiN_3$: Eu^{2+} and suppressed the appearance of AlN impurity phase, suggesting that SrF_2 flux modifies the formation mechanism of $CaAlSiN_3$: Eu^{2+}. The phosphor of the $CaAlSiN_3:Eu^{2+}$ produced with 4 wt% SrF_2 flux had an enhanced emission intensity, which was a result of the high crystallinity, the absence of AlN secondary phases, and the clean surfaces of the particles in the final product.

Keywords: $CaAlSiN_3:Eu^{2+}$; Fluxes; Atmospheric pressure; Photoluminescence properties

1. Introduction

White light-emitting diodes (LEDs) have drawn much attentions and been widely used in lighting and display fields due to their outstanding merits in high efficiency, low power consumption and long lifetimes [1,2]. The combination of InGaN blue LED chip with YAG: Ce^{3+} yellow phosphor is the dominant mode for the realization of white LED. Nevertheless, these devices are suffering from the disadvantages of higher correlated color temperature (CCT) and lower color rendering index (CRI) because of the deficiency of red light component. Consequentially, red phosphors ranging from sulfides, silicates to nitrides were developed rapidly to compensate red component for fabrication of warm white LED with excellent CRI, especially for those well-known nitrides red phosphors with high luminous efficiency and outstanding thermal stability representative by Eu^{2+} doped (Ca, Sr, Ba)$_2Si_5N_8$ [3,4], (Ca, Sr)$AlSiN_3$ [5,6] and (Ca, Sr)$LiAl_3N_4$ [7,8]. For example, $CaAlSiN_3:Eu^{2+}$ red phosphor shows an high external quantum efficiency up to ~85% at room temperature under the excitation of 460 nm, and has slight decrease up to 160 °C remaining ~87% initial emission intensity at room temperature [5]. With regard to the synthesis of nitrides red phosphors, solid-state reaction was widely used in industry. Although phosphors prepared by SSR method have the better crystallization and luminescence properties [9,10], there are some disadvantages, such as the required high temperature (1600–1800 °C) and pressure (0.5–1.0 MPa) [11,12]. Therefore, facile synthesis route with characters of atmospheric pressure, moderate temperature for nitride phosphors are highly desired. Many laboratory personnel selected variable fluxes to optimize performance of various phosphors. Such as Y.E. et al. synthesized the Ca-doped $BaMgAl_{10}O_{17}$: Eu^{2+},Mn^{2+} blue phosphor using BaF_2 and CaF_2 as co-fluxes

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[13]. In their work, fluxes of BaF_2 and CaF_2 reduced the sintering temperature, improved the size distribution uniformity as well as particle morphology regularity of the phosphors. Simeon et al. synthesized the high performance $CaAlSiN_3:Eu^{2+}$ phosphors with the aid of BaF_2 flux [14], and the addition of BaF_2 flux effectively reduced the temperature of formation of $CaAlSiN_3:Eu^{2+}$ by about 100 K, and suppressed the volatilization of the raw materials. Additionally, Naoto et al. performed the influence of fluxes (Chlorides of NH_4Cl and $SrCl_2$ and fluorides of AlF_3 and SrF_2) in optimizing the optical properties of $Sr_{0.95}Si_2O_2N_2:0.05Eu^{2+}$ green-emitting phosphors [15], and found that that the particle size, particle morphology and photoluminescence intensity of phosphors were largely dominated by the type of flux material and its adding amount. Wako et al. investigated blue-emitting $CaAl_2O_4:Eu^{2+},Nd^{3+}$ phosphor with the addition of H_3BO_3 flux [16], which was found to favor the formation of a monoclinic $CaAl_2O_4$ phase as well as enhancing the luminescence intensity. Khanna et al. used flux (MoO_3) to grow phosphor crystals of Eu^{3+},Dy^{3+} and Tb^{3+} activated calcium sodium molybdenum oxide [17].

Herein, we present the influence of fluxes (NH_4Cl, AlF_3, BaF_2, CaF_2, NH_4F, NaF and SrF_2) in the synthesis process of $Ca_{0.98}AlSiN_3$: $0.02Eu^{2+}$ phosphors on the crystallinity, morphology, and photoluminescence properties as well as the thermal stability.

2. Experimental

Fine powders of CaH_2 (97%, Aladdin), AlN (99%, Ube, Honshu, Japan), Si_3N_4 (α content, 99%, Ube, Honshu, Japan) and EuF_3 (99.99%, Aladdin), and variable fluxes, SrF_2 (99.99%, CP, Aladdin), NH_4F (98%, AR, Aladdin), BaF_2 (AR, Aladdin), NaF (98%, AR, TiandaKewei), AlF_3 (99%, Aladdin), CaF_2 (AR, Aladdin), NH_4Cl (99.8%, GR, Aladdin) were used as raw materials to synthesize $CaAlSiN_3$: Eu^{2+} red phosphors. These starting materials were firstly precisely weighed out according to the $Ca_{1-x}AlSiN_3:xEu^{2+}$ ($x=0.02$, 4 wt% flux) stoichiometry, thoroughly mixed and ground in an agate mortar in indoor environment. And then the powder mixtures were fired in BN crucibles at 1550 °C for 6 h in a horizontal tube furnace under a flowing N_2/H_2 (92/8%) atmosphere. Furthermore, an sintering temperature test from 1300 °C to 1700 °C was demonstrated for the case SrF_2 flux. After firing, the samples were gradually cooled down in the furnace and were ground finely and prepared for measurements.

The crystal structure and the phase purity of sample were measured by X-ray power diffraction (XRD) on a diffractometer (Rigaku D/max-2500/p c, Japan). The photoluminescence (PL) and photoluminescence of excitation (PLE) spectrums of samples were taken out on a fluorescence spectrometer equipped with a Xe flash lamp (Hitachi F-4600, Japan). Temperature dependent emission spectra for the sample were tested by an Exciting spectra and thermal quenching analyser for phosphor (Everfine Co. Ltd, EX-1000, China). The diffuse reflection spectrum (DRS) was recorded by an UV–visible spectrometer (TU-1901, China) with a 60-mm diameter integration sphere. Scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F field emission scanning electron microscope for the particle size and morphology characterization. CIE chromatic coordinates were examined on a PMS-50 Plus UV–vis-Near IR Spectro-photocolorimeter (Everfine Co. Ltd, China) system equipped with phosphor excitation equipment ($\lambda_{ex}=460$ nm).

3. Results and discussion

The crystalline structure of $Ca_{0.98}AlSiN_3$: $0.02Eu^{2+}$ phosphors produced after calcination at 1550 °C for 6 h is shown in the diffractograms in Fig. 1. It is clearly seen that $CaAlSiN_3$ phosphors was predominantly produced under the conditions

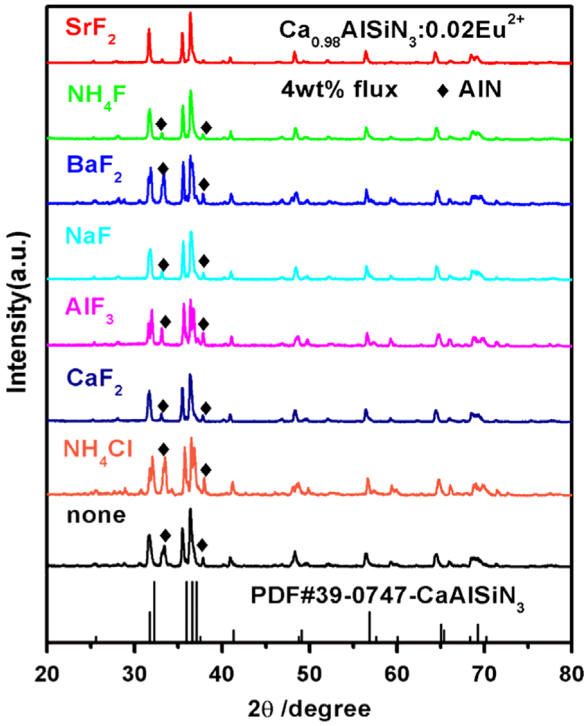

Fig. 1. XRD patterns of $Ca_{0.98}AlSiN_3:0.02Eu^{2+}$ phosphors prepared with variable fluxes (4 wt%).

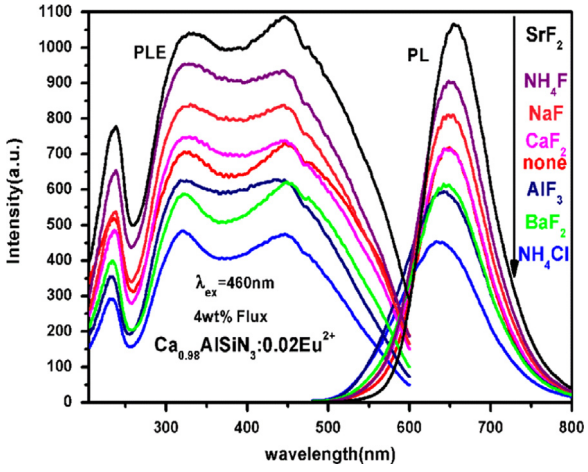

Fig. 2. Fluorescence Spectroscopy of $Ca_{0.98}AlSiN_3:0.02Eu^{2+}$ phosphors prepared with variable fluxes (4 wt%).