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Effect of fluxes on synthesis and luminescence properties of $BaSi_2O_2N_2:Eu^{2+}$ oxynitride phosphors☆

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ABSTRACT

Eu^{2+} activated $BaSi_2O_2N_2$ oxynitride bluish-green phosphor was synthesized adopting conventional high-temperature solid-state reaction method, in which BaF_2, Na_2CO_3 and NH_4Cl were used as the fluxes. The phase formation, size distribution and microscopic morphology were characterized to investigate the influence of adding fluxes on photoluminescence properties. The results indicate that with the addition of BaF_2 flux, the particle morphology becomes regular and size distribution narrows and the phase purity of $BaSi_2O_2N_2:Eu^{2+}$ phosphor can be improved effectively. The photoluminescence intensity of $BaSi_2O_2N_2:Eu^{2+}$ phosphor with BaF_2 as flux gets enhanced obviously, which is much higher than that of Na_2CO_3, NH_4Cl and without flux. The optimum content of BaF_2 flux is 4 wt%, and the maximum photoluminescence intensity of the $BaSi_2O_2N_2:Eu^{2+}$ phosphor prepared with BaF_2 flux rises to 141%, meanwhile, the phosphors with BaF_2 flux exhibits low thermal quenching. The results indicate that the $BaSi_2O_2N_2:Eu^{2+}$ is sort of promising bluish-green phosphor for application in full-spectra LED.

1. Introduction

White light emitting diodes (W-LEDs) have attracted significant attention over the past decades due to their considerable impact on issues such as energy consumption, environment and even the health of individuals.[1,2] Therefore, W-LEDs are promising to replace conventional light sources such as incandescent and fluorescent lamps in the near future.[3] Typically, the common approach to making phosphors-converted W-LEDs is combining blue LED chips and yellow-emitting phosphors, $Y_3Al_5O_{12}:Ce^{3+}$ (YAG). In white LEDs, the phosphor is one of key parts and determines the color rendering index value and correlated color temperature.[4] Whereas YAG is not that ideal because of weak luminescence in the red spectral region, resulting in poor color rendition.[5,6] Therefore, a wide variety of nitride or oxynitride phosphors have been developed recently in W-LEDs applications,[7–12] such as Ca-α-SiAlON:Ce^{3+},[7] Ca-α-SiAlON:Eu^{2+},[8] β-SiAlON:Eu^{2+},[9] $M_2Si_5N_8:Eu^{2+}$ (M = Ca, Sr, Ba),[10] and $CaAlSiN_3:Eu^{2+}$,[11] $SrSiN_2:Eu^{2+}$.[12] Thus, these rare-earth doped nitride phosphors are popularly used as efficient conversion phosphors for W-LEDs owing to strong absorption from ultraviolet (UV) to blue region, high quantum efficiency, as well as excellent thermal quenching characteristics compared to oxide phosphors.

Because of the simple operation, lower cost and much less environmental wastes, the conventional high temperature solid-state reaction method is the most desirable synthetic process for industrial production of the phosphor. However, the phenomenon of cluster of the phosphor particles prepared by high temperature solid phase method is serious, which will seriously affect the luminous efficiency and morphology of the phosphor. Therefore, for the phosphor synthesized by high-temperature solid-phase method, it is necessary to add appropriate amount of flux to improve the phosphor particle morphology and further enhance its luminous intensity.[13–16] However, the mechanism of the influence of different fluxes on $BaSi_2O_2N_2:Eu^{2+}$ phosphor has not been reported so far.

Therefore, the $BaSi_2O_2N_2:Eu^{2+}$ bluish-green phosphor was synthesized by solid-state reaction at high temperature. The effects of different fluxes on the purity, luminescence intensity and particle morphology of the phosphor were studied. In present work,

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different fluxes (BaF_2, Na_2CO_3, and NH_4Cl) were added when synthesizing $BaSi_2O_2N_2:Eu^{2+}$ phosphors by solid-state reaction method and the effects of these fluxes on the phase formation, morphology, particle size, and PL intensity of the $BaSi_2O_2N_2:Eu^{2+}$ phosphors were investigated. We concentrated on finding the appropriate flux material which can improve the optical performance of $BaSi_2O_2N_2:Eu^{2+}$ blue-green phosphors. Finally, the thermal quenching of the $BaSi_2O_2N_2:Eu^{2+}$ phosphor with the appropriate flux was also measured.

2. Experimental

2.1. Preparation

A series of $BaSi_2O_2N_2:0.05Eu^{2+}$ samples added with fluxes of 0.5 wt%–5 wt% of BaF_2, Na_2CO_3, and NH_4Cl were synthesized by solid state reaction method. Stoichiometric mixtures of Eu_2O_3 (Sinopharm Chemical Reagent Co., Ltd, 99.99%), α-Si_3N_4 (UBE, SN-E10), $BaCO_3$ (Aladdin, AR), SiO_2 (Aladdin, 99.99%), BaF_2 (Sinopharm Chemical Reagent Co., Ltd, AR), Na_2CO_3 (Sinopharm Chemical Reagent Co., Ltd, 99.99%), and NH_4Cl (Sinopharm Chemical Reagent Co., Ltd, AR) were weighted out according to the stoichiometric ratio. The mixed powder was ground evenly in an agate mortar, and then homogeneous mixtures were put in an alumina crucible and continually fired at 1350 °C in a reducing atmosphere (CO) for 4 h.

2.2. Characterization

The crystalline phase of the samples was analyzed by an X-ray powder diffraction (XRD, Advance D8, Bruker, Karlsruhe, German) using the Cu Kα, $\lambda = 0.15418$ nm, operating at 40 kV and 40 mA in the 2θ range of 10°–70° with a step size of 0.02° and 0.2 s per step. PL spectra were measured at room temperature using a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Tokyo, Japan) with a 150 W Xe lamp as an excitation source at room temperature. The morphology of the samples was observed by a scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). The particle size was analyzed on a particle size analyzer (S3500-special, Microtrac, USA). The QE of phosphors was determined on a quantum yield measurement system (QE-2100, Hamamatsu Photonics K. K., Japan) under the excitation of 450 nm and a white plate $BaSO_4$ was used as a reference material. The thermal quenching of the prepared phosphor was measured using a QE-2100 (QE-2100, Hamamatsu Photonics K. K., Japan) and the reflection spectrum of $BaSO_4$ white standard was used for calibration. The thermal quenching measurements were conducted under the excitation of 450 nm from 50 to 200 °C at an interval of 25 °C with holding time of 10 min at each temperature.

3. Results and discussion

3.1. Effect of fluxes on the luminescence properties and phase formation of $BaSi_2O_2N_2:Eu^{2+}$

The emission intensity of the $BaSi_2O_2N_2:Eu^{2+}$ phosphors with 1 wt% adding amount of different fluxes (BaF_2, Na_2CO_3, and NH_4Cl) firing at various temperatures are presented in Fig. 1. In all cases, the emission intensities of all the samples increase firstly, and then fall down after the emission intensity reaches a maximum value. For the phosphors with no flux, BaF_2, Na_2CO_3 and NH_4Cl fluxes, the optimal sintering temperatures seemed to be 1400, 1400, 1400 and 1450 °C, respectively. At the optimal sintering temperatures, it was likely to obtain the highest crystallinity. It indicated that the photoluminescence intensity of the phosphor was deeply affected by the crystallinity.

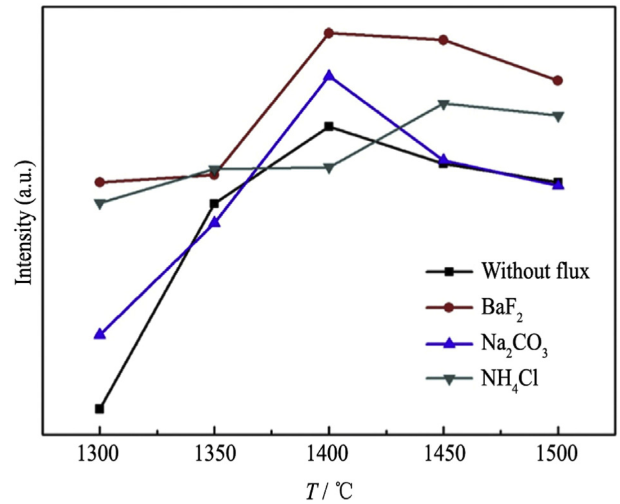

Fig. 1. Photoluminescence intensity of the $BaSi_2O_2N_2:Eu^{2+}$ phosphor sintered without flux and with 1 wt% flux as a function of the calcination temperature ($\lambda_{ex} = 450$ nm).

The XRD patterns of $Ba_{0.95}Si_2O_2N_2:0.05Eu^{2+}$ synthesized without flux and with BaF_2, Na_2CO_3, NH_4Cl at the optimum temperature are shown in Fig. 2. The reference XRD pattern of $BaSi_2O_2N_2$ was calculated by the crystallographic conversion program Powder Cell using the crystallographic data reported by Kechele et al.[17] The XRD analysis shows that the $BaSi_2O_2N_2:Eu^{2+}$

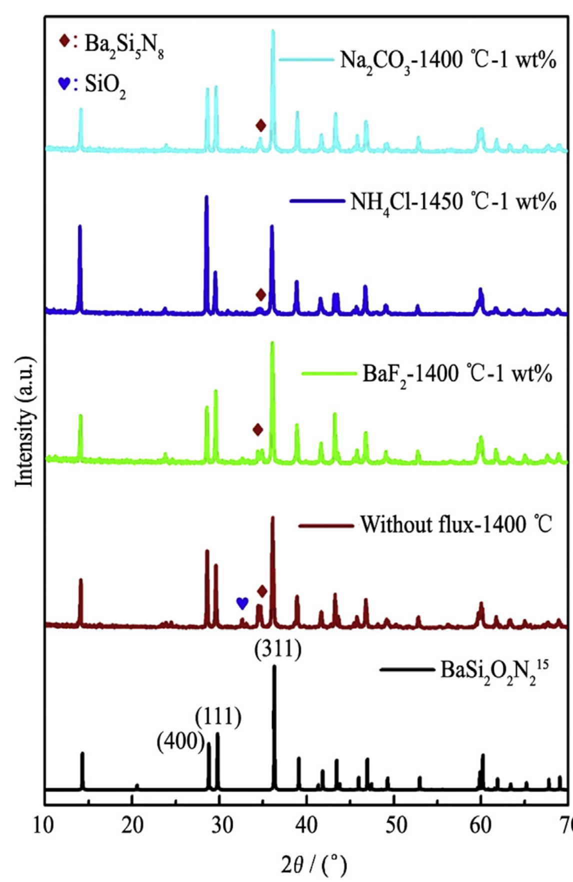

Fig. 2. XRD patterns of the $BaSi_2O_2N_2:Eu^{2+}$ phosphor sintered at various temperatures without flux and with 1 wt% flux.