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Preparation and luminescence properties of yellow long-lasting phosphor $Ca_2ZnSi_2O_7:Eu^{2+}$, Dy^{3+}

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ABSTRACT

Long-lasting phosphors $Ca_2ZnSi_2O_7:Eu^{2+}$, Dy^{3+} are prepared by solid-state reaction method assisted with different fluxes. Broadband emission, peaked at 580 nm and originating from 4f to 5d transition of Eu^{2+}, is observed. The emission intensities of the phosphors can be enhanced by 4.84 and 7.73 times with the introduction of H_3BO_3 and CaF_2, respectively. Moreover, their afterglow times are also respectively prolonged to 11 h and 12 h. The yellow afterglow can be excited by both ultraviolet and visible light, thus permitting its application in both room and outdoor environment. In terms of the crystal structure and trap feature of the phosphors added with different fluxes, the mechanism for the improved luminescence and afterglow properties is discussed.

1. Introduction

Long-lasting phosphors, of which the phosphorescence can persist for a long time after removal of excitation source, can be widely applied in emergency lighting, instrumental display, optical memory, imaging storage, decoration, textile printing, and so on [1–5]. Great progress on long-lasting phosphors has been made in the past 100 years, extending the persistence time from minutes to tens of hours [6–9].

Currently the blue ($Sr_2MgSi_2O_7$:Eu, Dy), green ($SrAl_2O_4$:Eu, Dy) and red (Y_2O_2S:Eu, Ti, Mg) long-lasting phosphors are commercially available[10–12]. Besides the three primary color emitting long-lasting phosphors, yellow long-lasting phosphor is also attractive considering its potential application in traffic signs or other warning signs.

$Sr_3SiO_5:Eu^{2+}$, Dy^{3+} [13] is an efficient yellow emitting phosphor. But its afterglow can only be obtained under ultraviolet light (UV) excitation and the afterglow time is very short. Kamioka et al. [14] reported that $Ca_2ZnSi_2O_7:Eu^{2+}$ could emit 600 nm light efficiently under broadband excitation in the region of 250–500 nm. Li et al. further realized the long lasting green-yellow afterglow in Eu^{2+}, Dy^{3+} co-doped $Ca_2ZnSi_2O_7$ [15]. Regretfully, its afterglow lasted for only 1 h.

In order to improve luminescence properties of $Ca_2ZnSi_2O_7:Eu^{2+}$, Dy^{3+} phosphor, the influence of flux H_3BO_3 and CaF_2 on the luminescent intensity and afterglow property have been investigated in this work. The related mechanism is discussed based on excitation and emission spectra, luminescence decay curves and thermally simulated luminescence (TSL) curves.

2. Experimental

$Ca_2ZnSi_2O_7$:1 mol% Eu^{2+}, 2 mol% Dy^{3+} phosphors were prepared by solid-state reaction method. $CaCO_3$ (AR), ZnO (AR), SiO_2 (AR), Eu_2O_3 (4N), Dy_2O_3 (4N), H_3BO_3 (AR), CaF_2 (AR) were used as starting materials. The molar ratio of raw composition were $2CaCO_3$-ZnO-$2SiO_2$-$0.01Eu_2O_3$-$0.02Dy_2O_3$-xH_3BO_3 and $(2-y)CaCO_3$-ZnO-$2SiO_2$-$0.01Eu_2O_3$-$0.02DyO_3$, respectively, in which H_3BO_3 was used as additive flux while CaF_2 was not only used as flux but also composition replacing parts of $CaCO_3$. The H_3BO_3 content (x) varied from 10 mol% to 50 mol% while the CaF_2 content (y) varied from 10 mol% to 100 mol%. Stoichiometrical amounts of starting materials were weighed and mixed homogeneously in an agate mortar, then placed into a corundum crucible and calcined at suitable temperature in the region of 1100–1250 °C for 2 h under weak reductive atmosphere produced by active carbon.

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The structures of the prepared samples were identified by X-ray diffraction (XRD) patterns, which were measured in the 2θ range of 10–80° with a Bruker D8 advance equipment using Cu tube with K_α radiation of 1.5406 Å. A Hitachi F-4500 fluorescence spectrophotometer was used to record excitation and emission spectra. Decay curves of afterglow were measured by combining an R-500 Spectrophotometer with an UT2062CE oscilloscope. TSL glow curves were obtained by an Riso-TL/OSL DA-15 system in the temperature range from 0 to 500 °C at a uniform heating rate of 5 °C/s. Excitation source was Sr-90 β radiation, radiation dose rate was 0.108 Gy/s and irradiation time was 100 s. All the samples were pressed into thin flat disks with the same size (diameter $D = 1$ cm) and smooth surface for luminescence measurement.

3. Results and discussion

XRD patterns of $Ca_2ZnSi_2O_7$:Eu^{2+}, Dy^{3+} added with different contents of H_3BO_3 and CaF2 are shown in Figs. 1 and 2, respectively. In Fig. 1, the major phases of the samples with no flux and with 10 mol% H_3BO_3 are both $Ca_2ZnSi_2O_7$ crystals (JPCDS No. 72-1603). However, low content of $CaSiO_3$ (JPCDS No. 1-720) and SiO_2 (JPCDS No. 86-1563) impurities are also observed. For 30–50 mol% H_3BO_3 added samples, however, no impurity peaks are observed. All diffraction peaks are in good agreement with the standard values of highly crystalline $Ca_2ZnSi_2O_7$. The results indicate that adding 30–50 mol% H_3BO_3 is beneficial for the crystallization of $Ca_2ZnSi_2O_7$. In Fig. 2, there are three impurities phases in 10 mol% CaF_2 doping phosphor, which are $CaSiO_3$, SiO_2 and Zn_2SiO_4. With CaF_2 content increasing from 30 mol% to 70 mol%, these impurities gradually disappear. 50 mol% CaF_2 doped sample presents better crystallization. However, for the sample added with higher content of CaF_2, CaF_2 and Zn_2SiO_4 impurity phases are rapidly present. The results show that proper content of added CaF_2 is also in favor of the formation of $Ca_2ZnSi_2O_7$.

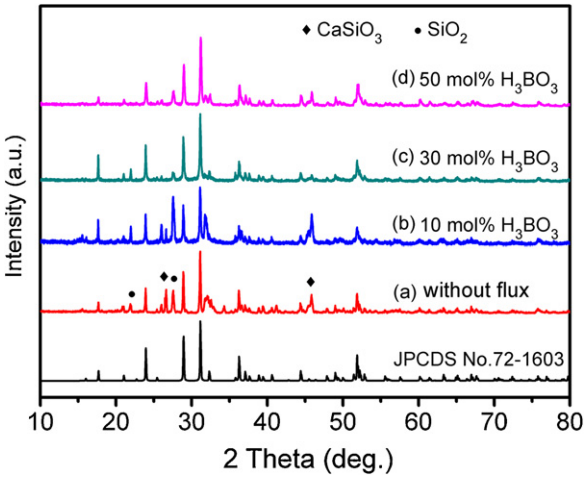

Fig. 1. XRD patterns of $Ca_2ZnSi_2O_7$:Eu^{2+}, Dy^{3+} phosphors added with different contents of H_3BO_3: (a) 0 mol%, (b) 10 mol%, (c) 30 mol%, (d) 50 mol% H_3BO_3.

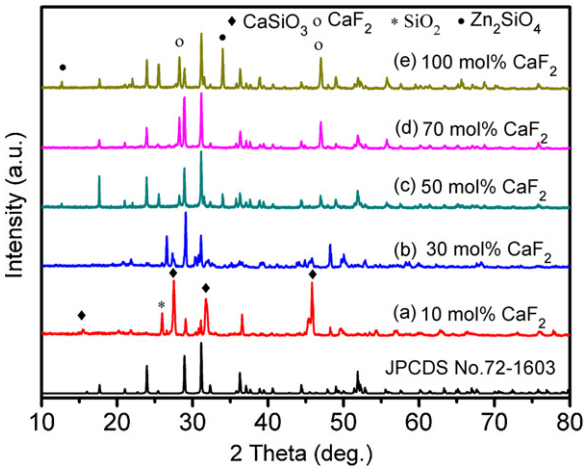

Fig. 2. XRD patterns of $Ca_2ZnSi_2O_7$:Eu^{2+}, Dy^{3+} phosphors added with different contents of CaF_2: (a) 10 mol%, (b) 30 mol%, (c) 50 mol%, (d) 70 mol%, (e) 100 mol%.

Table 1
Lattice parameters of $Ca_2ZnSi_2O_7$ doped with different H_3BO_3 concentrations.

H_3BO_3 concentration	a (Å)	c (Å)
Without flux	7.8308	5.0241
10 mol%	7.8329	5.0209
30 mol%	7.8237	5.0216
50 mol%	7.8292	4.9967

Table 2
Lattice parameters of $Ca_2ZnSi_2O_7$ doped with different CaF_2 concentrations.

CaF_2 concentration	a (Å)	c (Å)
10 mol%	7.9438	4.9004
30 mol%	7.8109	5.0517
50 mol%	7.8255	5.0220
70 mol%	7.8167	5.0188
100 mol%	7.8306	4.9986

The lattice parameters of $Ca_2ZnSi_2O_7$ doped with different concentrations of H_3BO_3 and CaF_2 are carefully calculated, shown in Tables 1 and 2. The $Ca_2ZnSi_2O_7$ phase in all samples has tetragonal structure with space group of P421m (No. 113). However, the lattice constants have slight difference for samples with different contents of H_3BO_3 and CaF_2. Non regularity in the variation of lattice constant is found when the flux content increases, implying that the B^{3+} or F^- ion entered into the lattice sites of $Ca_2ZnSi_2O_7$ is nonlinearly dependent on the flux content.

Fig. 3 shows the excitation and emission spectra of $Ca_2ZnSi_2O_7$:Eu^{2+}, Dy^{3+} synthesized without flux added. The results show that a broad excitation band, with two excitation peaks is centered at 340 and 460 nm. Under 460 nm excitation, these phosphors exhibit yellow light emission peaked at 580 nm, attributed to the broad band 4f–5d transition of Eu^{2+} ions [14].

The effect of different contents of H_3BO_3 or CaF_2 on the luminescence intensity of the phosphors is shown in Fig. 4. With the increase of H_3BO_3 or CaF_2 content, the yellow emission intensity

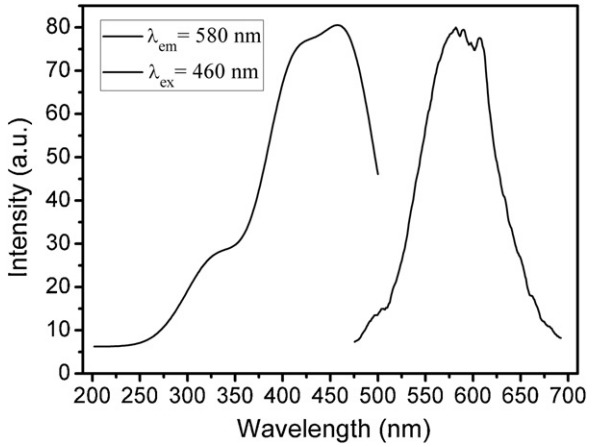

Fig. 3. Excitation and emission spectra for the $Ca_2ZnSi_2O_7$:1 mol% Eu^{2+}, 2 mol% Dy^{3+} sample without flux added.