The Effect of the Flux B_2O_3 and the Role of Ion RE^{3+} in $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$ Phosphor (RE: Dy, Gd, Tb)

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Abstract: The long afterglow phosphors $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$ (RE: Dy, Gd, Tb) were prepared by the combustion method at 580 °C for 5 min. In this method, the B_2O_3 oxide was used as flux. The influences of the flux B_2O_3 quantity and the role of ion RE^{3+} (RE: Dy, Gd, Tb) in the phosphor $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ were studied systemically. The X-ray diffraction pattern, scanning electron microscopy graphic, the photoluminescence spectra and decay time were presented. The emission spectra of phosphors had a broad band with maximum at 444 nm due to electron transition from the $4f^65d^1$ to the $4f^7$ of ion Eu^{2+} . It is showed that Nd^{3+} and RE^{3+} ions generated traps that resulted in the long persistent phosphorescence. Simultaneously, when the concentration of RE^{3+} ion was high, they generated also emission centers in the phosphor.

Key words: Long afterglow, phosphorescence, aluminate, combustion method.

1. Introduction

In recent years, rare earth doped alkaline earth aluminate phosphors have been extensively studied and used in many of applications, such as radiation dosimetry, color display, luminescent porcelain, airport, luminous paints in highway and so on [1-3]. This material has strong photoluminescence at the blue region with maximum at 444 nm. Calcium aluminate codoped with rare earth ions ($Eu^{2+}, Nd^{3+}, RE^{3+}$) has well known as a long afterglow phosphor. The long afterglow and luminescent intensity can be enhanced by codoped with the third rare earth ion. In these phosphors, Eu^{2+} ions play a role luminescent centers and RE^{3+} ions act as holes [4-6]. The mechanism of persistent phosphorescence in these aluminate is considered to include the photoionization of the Eu^{2+} ion and a subsequent transfer of the electrons to traps formed by the lattice defects as oxide

ion vacancies and possibly also the auxiliary RE^{3+} ion codopants [7, 8]. It is showed that Nd^{3+} and RE^{3+} ions generated the hole traps that resulted in the long persistent phosphorescence.

In this paper, the influence of the flux B_2O_3 concentration on the crystalline structure and luminescent properties of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ phosphor were investigated. The role of RE^{3+} in $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$ (RE: Dy, Gd, Tb) phosphors were also studied systemically. The materials were prepared by urea-nitrate solution combustion method.

2. Experiments

The powder samples with the general formula $CaAl_2O_4: Eu^{2+}$ (1% mol), Nd^{3+} (0.5% mol) and $CaAl_2O_4: Eu^{2+}$ (1% mol), Nd^{3+} (0.5% mol), RE^{3+} (1% mol) (RE: Dy, Gd, Tb) were prepared by urea-nitrate solution combustion method. Starting materials for synthesized phosphors $CaAl_2O_4$ codoped with rare earth ions were the mixture of $Ca(NO_3)_2 \cdot 4H_2O$,

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$Al(NO_3)_3 \cdot 9H_2O$, Eu_2O_3 , Nd_2O_3 , Dy_2O_3 , Gd_2O_3 , Tb_2O_3 , B_2O_3 and $CO(NH_2)_2$. Rare earth oxides were nitrified by dissolving into HNO_3 . A small quantity of B_2O_3 was added as the flux. Urea was used to supply fuel and reducing agent.

Aqueous solution containing stoichiometric amounts of nitrate metal and urea was mixed by magnetic stirrer and heated at 70 °C for 40 min to gel. Next, the gel was dried at 80 °C to dehydrate and combusted at temperatures 580 °C within 5 min. Urea concentration was 18 times of product mole (theory 6.69). The white powder product was obtained.

The prepared products were characterized by D8-Advance-Bruker X-ray diffractometer. The scanning electron microscope (SEM) graphs were taken by FE-SEM Hitachi S4800. The photoluminescence spectra were measured by FL3-22 fluorescence spectrometer. The glow curves were analyzed by Harshaw TLD-3500 equipment. The samples were irradiated by β -ray with dose 1.5 Gy, preheated at 50 °C for 200 s, heating rate 5 °C/s.

3. Experimental Results

3.1 The Effect of the Flux B_2O_3 Concentration on the $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ Phosphor

The crystalline structure of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ with different concentration that were confirmed by X-ray diffraction pattern (XRD), the XRD diagrams were showed in Fig. 1.

The phosphor had monocline single phase $CaAl_2O_4$ structure. The XRD diagrams also indicated that no impurity phase was detected in the lattice. When the concentration of the flux B_2O_3 was small, the XRD diagram exist a small quantity of $CaAl_4O_7$ phase.

SEM was carried out to investigate the surface morphology and crystalline sizes of the synthesized phosphor powder.

The SEM graphs taken for $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ with different B_2O_3 concentrations (2%, 3%, 4% and 5% wt.) were showed in Figs. 2a-2d, respectively. It showed that the powder had the irregular, foamy and

agglomerate particles. The foamy structure of the materials reflects the inherent nature of the combustion reaction. The surface of powder (Figs. 2a, 2b and 2d) shows a lot of voids and pores which may be formed by the evolved gases during combustion reaction. However, the crystal has sharp surface morphology like single crystalline bars (Fig. 2c). It is clearly seen from these micrographs that the crystalline sizes are about several hundreds of nanomet.

The photoluminescent spectra of the phosphors $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ with B_2O_3 x% wt. (x = 2, 3, 4, 5) were investigated and presented in Fig. 3. The phosphors were excited by radiation with wavelength 365 nm. The results showed that the emission spectra of the phosphors had a same broad band with maximum intensity at 444 nm that characterized the transition of electronic configuration from $4f^6 5d^1$ to $4f^7$ of Eu^{2+} ion. The photoluminescent intensity of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ phosphors depend on the concentration of B_2O_3 and the luminescent intensity is optimal with B_2O_3 4% wt. Simultaneously, Eu^{2+} ions play a role emission centers and Nd^{3+} ions act as hole traps that trap and release charges to form the phosphorescence of materials.

Fig. 4 shows the phosphorescent decay time of the $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ phosphors with different B_2O_3 concentrations. The phosphors were excited by radiation with wavelength 365 nm for 1 min. The results indicated that the phosphor of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ with B_2O_3 4%wt. has long afterglow and high

Fig. 1 XRD of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ with different concentration of B_2O_3 .

Fig. 2 SEM graphs of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ with different B_2O_3 (x% wt.) concentrations: (a) $x = 0.2$, (b) $x = 0.3$, (c) $x = 0.4$ and (d) $x = 0.5$.

Fig. 3 Photoluminescence spectra of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ phosphors with B_2O_3 (x% wt.) $x = 2, 3, 4, 5$.

brightness. And so, their thermoluminescent properties were studied. The glow curves of the phosphors were recorded in the Fig. 5. The thermoluminescent intensity of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ the phosphor with B_2O_3 4% wt. is the strongest. It is indicated that the activator centers and the density of

Fig. 4 Decay time of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ phosphors with different B_2O_3 concentrations.

traps produced were more suitable than that of the other concentrations of B_2O_3 .

3.2 The Effect of RE^{3+} Ions in $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$

Fig. 6 shows the photoluminescent spectra of the phosphors $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$. The radiation

Fig. 5 Glow curve of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ phosphors with different B_2O_3 concentrations.

Fig. 6 Photoluminescence spectra of $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$ (RE: Dy, Gd, Tb).

with wavelength 365 nm was used to excited the phosphors. The results showed that the emission spectra of the phosphors had a same broad band with maximum intensity at 444 nm that characterized the electronic transition of Eu^{2+} ion. The emissions of Eu^{3+} , Nd^{3+} , Dy^{3+} , Gd^{3+} and Tb^{3+} ions were not observed in the spectra. In the $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ codoped with RE^{3+} phosphors, the photoluminescent intensity of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ codoped with Gd^{3+} or Tb^{3+} are stronger than the uncoded phosphor. Whereas, the photoluminescent intensity of the phosphor $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ codoped with Dy^{3+} is lower. These results related to their phosphorescent characteristic.

The decay time of $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$

phosphors were presented in Fig. 7. It is showed that the brightness of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ codoped with Gd^{3+} or Tb^{3+} are higher than the uncoded phosphor. Otherwise, brightness of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ codoped with Dy^{3+} is lower.

The lifetime of phosphors were calculated from fitting experimental decay time with the combination of three exponential functions. The results showed in Table 1. It is indicated that the lifetime of phosphors are approximate to each other.

The thermoluminescent properties of the phosphors were also investigated. The results were showed in Fig. 8. The peak of glow curves were around from 50 °C to 270 °C. By preheated at 50 °C within 200 s, the glow curves had symmetric single peaks. Beside, the thermoluminescent of $CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$ was quite low and consisted of two peaks that located at 148 °C and 201 °C. That is the reason of quite low phosphorescent property. The peak shape method (R. Chen method) [9] was applied to calculate the activation energy that the results showed in Table 2.

Fig. 7 Decay time of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ and RE^{3+} (RE: Dy, Gd, Tb).

Table 1 The values of the lifetime of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ and RE^{3+} phosphors.

Sample	τ_1 (s)	τ_2 (s)	τ_3 (s)
$CaAl_2O_4: Eu^{2+}, Nd^{3+}$	17.3	2.4	114
$CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$	18.3	3.5	112
$CaAl_2O_4: Eu^{2+}, Nd^{3+}, Gd^{3+}$	14.3	2.6	106
$CaAl_2O_4: Eu^{2+}, Nd^{3+}, Tb^{3+}$	15.7	2.9	107

Fig. 8 Glow curve of $CaAl_2O_4: Eu^{2+}, Nd^{3+}, RE^{3+}$ (RE: Dy, Gd, Tb).

Table 2 The values of the activation energy of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ and RE^{3+} phosphors.

Sample	E (eV)
$CaAl_2O_4: Eu^{2+}, Nd^{3+}$	0.79
$CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$	0.85
$CaAl_2O_4: Eu^{2+}, Nd^{3+}, Gd^{3+}$	0.84
$CaAl_2O_4: Eu^{2+}, Nd^{3+}, Tb^{3+}$	0.74

4. Conclusions

The B_2O_3 is not only a flux but also changes emission intensity of $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ phosphor. The optimum concentration of the flux B_2O_3 was found to be 4% wt. for maximum luminescent intensity. The phosphors of $CaAl_2O_4: Eu^{2+}$ codoped with RE^{3+} have long persistent phosphorescence. Inside, $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ codoped with Gd^{3+} or Tb^{3+} had long afterglow with high brightness and their photoluminescent intensity are better than $CaAl_2O_4: Eu^{2+}, Nd^{3+}$. In these phosphors, Eu^{2+} ions play a role of activators and RE^{3+} ions act as hole traps.

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