

Influence of co-doping different rare earth ions on the luminescence of CaAl₂O₄-based phosphors

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Abstract

CaAl₂O₄: Eu, RE³⁺ (RE: Dy, Nd, La) photoluminescent materials with high brightness and long afterglow are prepared by sintering at high temperature and in a reductive atmosphere. The influence of co-doping rare earth ions (Dy, La and Nd) on the luminescence of CaAl₂O₄: Eu was studied. The excitation and emission spectra of these three kinds of phosphors are very similar to that of CaAl₂O₄: Eu phosphor, and all of them have long afterglow phenomenon except for CaAl₂O₄: Eu. Both of initial brightness and persistent afterglow time of CaAl₂O₄: Eu, Nd is better than those of CaAl₂O₄: Eu, Dy, and CaAl₂O₄: Eu, La, which is agreement with the results of thermoluminescence curves. The low temperature photoluminescent spectra indicate that Eu ions occupied only one kind of Ca site in CaAl₂O₄ crystal lattice. © 2002 Published by Elsevier Science Ltd.

Keywords: CaAl₂O₄; Emission spectra; Phosphors; Thermoluminescence

1. Introduction

Calcium aluminates are important cement materials, which have been studied by many researchers.^{1–2} But the use of CaAl₂O₄ as the luminescent host, up to now, is rarely reported. Tanaka et al.³ prepared CaAl₂O₄: Eu phosphors by two-step firing synthesis, and it is expected that CaAl₂O₄: Eu phosphor can be applied to plasma display panels (PDP) due to its excellent resistant to luminance degradation by heating process. Recently, Weiyi Jia et al.⁴ prepared single crystal CaAl₂O₄: Eu, Nd phosphor by the laser-heated pedestal growth method, which shows bright and long persistent purple phosphorescence. Katsumata et al. also grew the single crystal CaAl₂O₄: Eu, Nd by a loading zone technique.⁵ This phosphor shows similar luminescent properties to that of SrAl₂O₄: Eu, Dy phosphor reported previously.^{6,7}

In this paper, four kinds of CaAl₂O₄-based phosphors (CaAl₂O₄: Eu, CaAl₂O₄: Eu, Dy, CaAl₂O₄: Eu, Nd and CaAl₂O₄: Eu, La) were prepared. The luminescent properties of these phosphors were investigated system-

atically, and the mechanism of the long-lasting phosphorescence was also discussed.

2. Experimental procedure

2.1. Phosphors preparation

In this work, CaCO₃, α -Al₂O₃, Eu₂O₃, Dy₂O₃, La₂O₃ and Nd₂O₃ are employed as the raw materials (these materials are all reagent grade). Small quantities of H₃BO₃ (about 5 m/o per of one aluminates) were added as a flux. These powders were weighed as the nominal composition of Ca_{0.955}Al₂O₄: Eu_{0.015}, R_{0.03} (R: Dy, Nd, La). Different CaAl₂O₄-based phosphors were prepared by the traditional ceramic synthesis method at 1380 °C for 3 h in a weak reductive atmosphere of flowing 1.5% H₂–98.5% N₂ gas.

2.2. Phosphors characterization

The prepared phosphor powder was analyzed by X-ray diffraction (XRD) using CuK α radiation at 40 kV and 100 mA to reveal the phase composition. A Hitachi 850 Fluorescence Spectrophotometer was used to detect

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the excitation and emission spectra of products, and emission and excitation spectra were plotted after the correction for the system sensitivity done by conventional methods. The low temperature emission spectrum was measured with H25 spectrophotometer with a He–Cd laser. The decay curves of afterglow were measured by the ST-86LA brightness meter, and the samples were irradiated by the 365 nm light for 5 min. Thermoluminescence glow curves were performed on a brightness meter system equipped with a temperature-controlled stove which is controlled at temperatures between 20 and 300 °C. Measurements were carried out at room temperature, and the relative data were collected on a PC using a program written by ourselves.

3. Results and discussion

Fig. 1 indicates the phase composition of different CaAl_2O_4 -based phosphors co-doped with various rare earth ions. The results proved that all phosphor samples prepared in this work are almost single CaAl_2O_4 phase, and the little amount of co-doped rare earth ions have almost no effect on the CaAl_2O_4 phase composition.

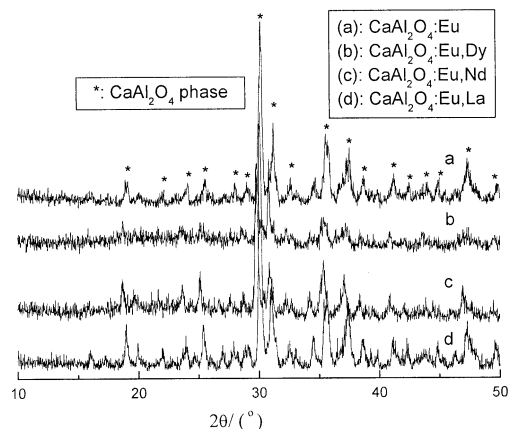


Fig. 1. XRD patterns of different CaAl_2O_4 -based phosphors.

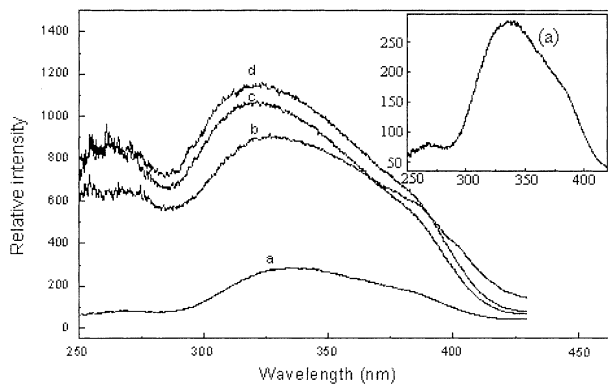


Fig. 2. Excitation spectra of different CaAl_2O_4 -based phosphors. (a) CaAl_2O_4 :Eu; (b) CaAl_2O_4 :Eu, Dy; (c) CaAl_2O_4 :Eu, Nd; (d) CaAl_2O_4 :Eu, La.

The excitation and emission spectra of CaAl_2O_4 :Eu, CaAl_2O_4 :Eu, RE^{3+} (La, Dy, Nd) are shown in Figs. 2 and 3, respectively. Fig. 2 indicates that the excitation spectra of CaAl_2O_4 -based phosphor co-doping various rare earth ions are similar to each other in shape, and contain two main excitation peaks. Fig. 3 illustrates that their emission spectra are all broadband, but the luminescent intensity varies greatly. The results indicate that the luminescent intensity of CaAl_2O_4 :Eu, Nd phosphor is much higher than that of CaAl_2O_4 :Eu phosphor, which may be involved in two sides: Firstly, the co-doped Nd ions can transfer the absorbed energy to the Eu^{2+} emitter efficiently. Secondly, the depth of traps produced by the co-doped Nd ions was more suitable than that of the other two rare earth ions. All of the main emission peaks for these phosphors lie near 440nm, and no other emission peaks can be observed, which indicates that the co-doped Dy, La and Nd elements had little effect on the surroundings of Eu ions in the CaAl_2O_4 host. In addition, the low temperature photoluminescence spectra of CaAl_2O_4 :Eu, Nd phosphor are measured at 5, 50, 150 and 250 K. The results shown in Fig. 4 indicate that CaAl_2O_4 :Eu, Nd phosphor emits only about 440 nm radiation, which can be ascribed to the $4f^7-4f^65d$ transitions of Eu^{2+} ions. These interconfiguration transitions are belong to electric dipole allowed and are about 4–5 orders stronger than

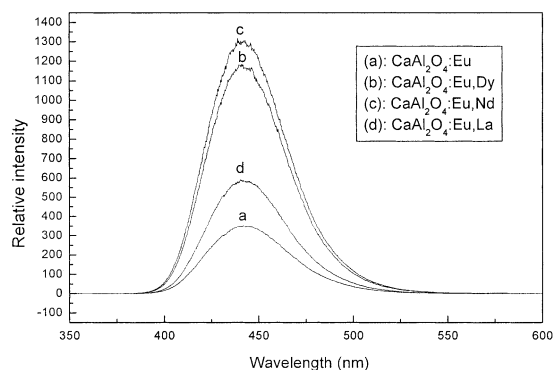


Fig. 3. Emission spectra of different CaAl_2O_4 -based phosphors.

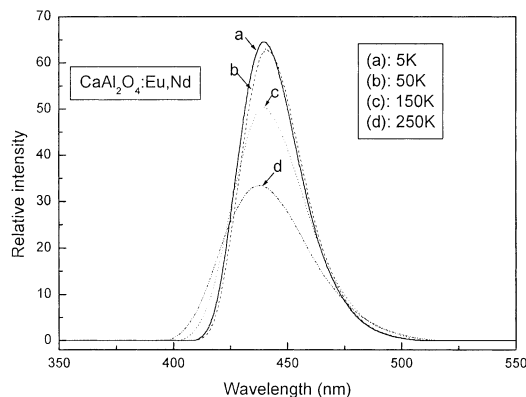


Fig. 4. Emission spectra of CaAl_2O_4 :Eu,Nd at low temperature.

magnetic dipole-allowed transitions. Although the transitions between 4f states of rare earth ions can be partially-allowed electric dipole transition in the distorted lattice environment, its luminescent intensity is still 2–3 orders weaker than the interconfiguration transitions. In addition, Host lattices with Eu^{2+} ions on different crystallographic sites show more than one emission band. The result implies that Eu^{2+} ions occupied only one kind of Ca^{2+} crystal site in CaAl_2O_4 crystal lattice. In fact, as Dougill reports,⁸ CaAl_2O_4 crystal has tridymite structure, which consists of AlO_4 -tetrahedra, and a Eu^{2+} ion substitutes a Ca^{2+} in the CaAl_2O_4 crystal.

The luminescent decay curves of different phosphors at room temperature are showed in Fig. 5. After the removal of the light source, the CaAl_2O_4 : Eu phosphor does not have the property of long afterglow. All of the other phosphors show a rapid decay, and then a long-lasting phosphorescence which can sustain more than 10 h occurred at lower light intensity level. As for the decay curves of the phosphors, we found that the initial luminescence intensity and decay speed of afterglow of phosphors are different from each other. Compared with the CaAl_2O_4 : Eu, Dy and CaAl_2O_4 : Eu, La phosphors, CaAl_2O_4 : Eu, Nd exhibits a relatively higher luminescence intensity and a longer duration than those of the other two phosphors.

As the previous reports,^{9–10} the afterglow time in the aluminates-based phosphor was affected greatly by the depth of trap level formed by the co-doped rare earth ions. The thermoluminescence (TL) glow curves of these CaAl_2O_4 -based phosphors were plotted as shown in Fig. 6. These phosphors samples were irradiated by 365 nm light for 15 min, and the heating rate was controlled at 10 °C/min. The results revealed that their main peaks are located at 336.4, 357.1 and 370.5 K dependent on the co-dopant. The activation energy E_T of a hole from a trap level to the valence band of the host crystal was proportional to kT_m , where T_m is the peak of the TL glow curves.¹¹ And so these values of TL peaks imply that the depth of traps level is $\text{Nd} > \text{Dy} > \text{La}$ in the CaAl_2O_4 -based phosphor, which is agreement with the

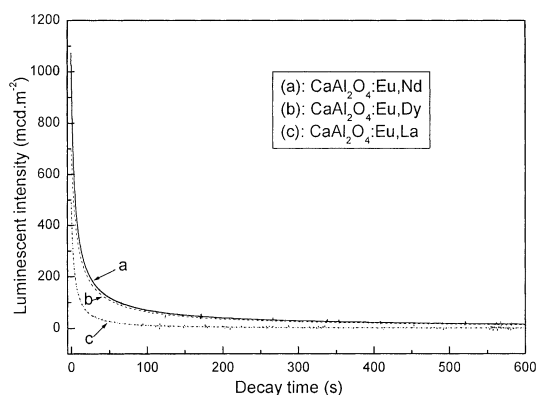
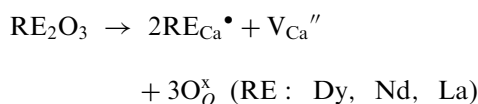


Fig. 5. Decay curves of different CaAl_2O_4 -based phosphors.

afterglow properties given in Fig. 5. And therefore, the luminescent mechanism can be interpreted as shown in Fig. 7. When Eu^{2+} ions are excited by lights, the direct excitation of Eu^{2+} due to $4f \rightarrow 4f5d$ transition occurs, and a great deal of holes are generated. Some free holes are released thermally to the valence band, and some of the released holes are trapped by the co-doped RE^{3+} ions. When the excitation source is removed, the trapped holes are released thermally to the valence band, and the holes migrate and recombine with some of free electrons, which lead to the long afterglow. Additionally, when the rare earth ions (Dy, Nd, La) are co-doped in the CaAl_2O_4 host, the defect chemistry equation can be expressed as following



And therefore, Ca vacancy will be produced for maintaining the charge balance. Probably, the Ca vacancy could have effect on the long afterglow of the

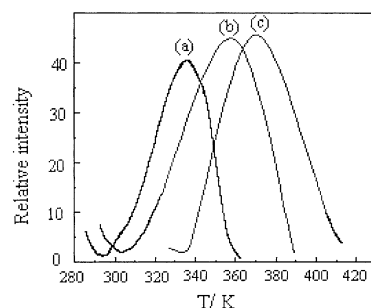


Fig. 6. The thermoluminescence glow curves of different CaAl_2O_4 -based phosphors. (a) CaAl_2O_4 : Eu, La; (b) CaAl_2O_4 : Eu, Dy; (c) CaAl_2O_4 : Eu, Nd.

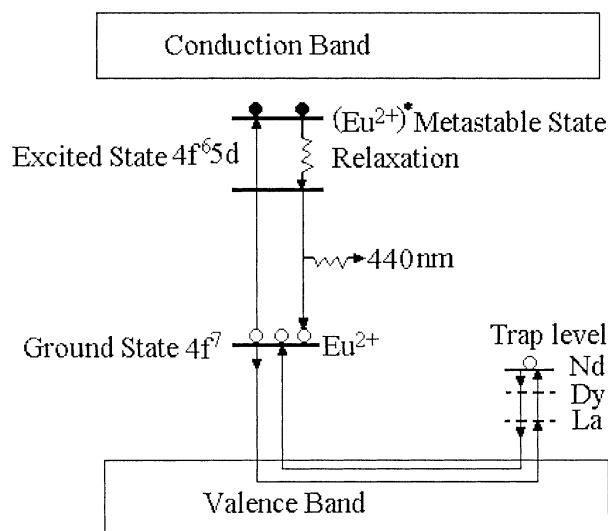


Fig. 7. Schematic graph of mechanism of long afterglow photoluminescence of CaAl_2O_4 -based phosphors.

CaAl₂O₄: Eu, RE phosphors, and the relative work is processing.

4. Conclusions

CaAl₂O₄: Eu, RE (RE: Dy, Nd, La) photoluminescent materials with high brightness and long afterglow are prepared by heating at 1380 °C for 3 h in weak reductive atmosphere of flowing 1.5% H₂–98.5% N₂ gas. The excitation and emission spectra of these four kinds of phosphors are very similar to each other, and ascribe to 4f⁷–4f⁶5d interconfiguration transitions of Eu²⁺ ions. All of them have long afterglow property except for CaAl₂O₄: Eu phosphor. The low temperature photoluminescent spectra of CaAl₂O₄: Eu, Nd phosphor indicate that Eu ions occupied only one kind of crystal site. The initial brightness of CaAl₂O₄: Eu, Nd is brighter and its afterglow time is also longer than those of CaAl₂O₄: Eu, Dy, and CaAl₂O₄: Eu, La, which is agreement with the results of thermoluminescence curves.

Acknowledgements

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