

# The Role Of Co-Doping Rare Earth Ion $Gd^{3+}$ In The Photoluminescence Characteristics Of $CaAl_2O_4: Eu^{2+}, Gd^{3+}$ Phosphors

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**Abstract--**  $CaAl_2O_4: Eu^{2+}$  (1 % mol),  $Gd^{3+}$  (x % mol) phosphors, with  $x = 0 \div 2.5$ , were prepared by solution combustion method. The structure and luminescent properties were investigated by X-ray diffraction pattern, emission spectra, decay time and glow-curve. The materials had monocline single phase structure. 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  $Eu^{2+}$  ion.  $CaAl_2O_4: Eu^{2+}, Gd^{3+}$  was a long persistence phosphor with high brightness. In these phosphors,  $Eu^{2+}$  ions play the role activators. Whereas,  $Gd^{3+}$  ions generate the hole traps that resulted the long persistent phosphorescence and also act as a sensitizer in the phosphor. The concentration of  $Gd^{3+}$  ion co-doped has strong influence on the luminescence of phosphor.

## I. INTRODUCTION

The alkaline earth aluminate phosphors doped with  $Eu^{2+}$  ions have strong photoluminescence at the visible region. The emission spectra of the phosphors had a broad band that characterized the transition of electronic configuration from  $4f^65d^1$  to  $4f^7$  of  $Eu^{2+}$  ion. The photoluminescence of material have strong depend on crystal field [1-3]. In recent years, the influence of  $Eu^{2+}$  on the photoluminescent characteristics of  $MA_2O_4: Eu^{2+}$  materials have been extensively studied (M: Sr, Ca, Ba, Mg). Besides, the effect of trivalent rare earth ions codoping on the phosphorescence of alkaline earth aluminate materials were investigated also [4-6]. The persistent lifetime and luminescence intensity of phosphor can be enhanced by co-doping with the second rare earth ions. The trapping mechanism plays an essential role in the persistence of these materials [5-7]. The phosphorescence phosphors have important applications with a long afterglow. The  $CaAl_2O_4: Eu^{2+}, Gd^{3+}$  phosphor is one kind of the long afterglow phosphors. In these phosphors,  $Eu^{2+}$  ions play the role activators. Whereas,  $Gd^{3+}$  ions generated hole traps that resulted the long persistent phosphorescence and also act as a sensitizer in the phosphor [4-5]. The concentration of  $Gd^{3+}$  ion co-doped has strong influence on the luminescence of phosphor.

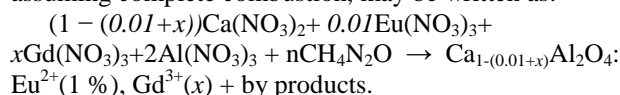
In this paper, the influence of  $Gd^{3+}$  ion co-doped with different concentration on luminescent properties of  $CaAl_2O_4: Eu^{2+}, Gd^{3+}$  phosphor was investigated. The materials were prepared by combustion method. Combustion synthesis has emerged as an important technique for the synthesis and processing of advanced materials that was characterized by

high-temperature, fast heating rates and short reaction times [8].

## II. EXPERIMENTS

The powder samples with the general formula  $CaAl_2O_4: Eu^{2+}$  (1 % mol),  $Gd^{3+}$  (x % mol) 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  $Ca(NO_3)_2 \cdot 4H_2O$  (Merck),  $Al(NO_3)_3 \cdot 9H_2O$  (Merck),  $Eu_2O_3$  (Merck),  $Gd_2O_3$  (Merck),  $B_2O_3$  (AR) and  $CO(NH_2)_2$  (AR). Rare earth oxides were nitrified by dissolving into  $HNO_3$ . A small quantity of  $B_2O_3$  was added as the flux. Urea ( $CO(NH_2)_2$ ) was used to supply fuel and reducing agent. For the combustion synthesis, urea is documented as an ideal fuel [8].

The reaction for the formation of  $CaAl_2O_4: Eu^{2+}, Gd^{3+}$  assuming complete combustion, may be written as:



With  $n = 6.69$ .

Aqueous solution containing stoichiometric amounts of nitrate metal, urea and  $B_2O_3$  was mixed and heated by microwave for 10 minutes to gel form. The mixing and heating mechanism of microwave is different from magnetic heating stirrer. The microwave energy mixes and heats the aqueous solution on a molecular level, which leads to uniform diffusing and rapid water evaporation. Next, the gel was dried at  $80^\circ C$  to dehydrate and combusted at temperatures  $580^\circ C$  within 5 minutes. Finally, the white powder product was obtained. Urea concentration was 18 times of product mole (The concentration was calculated by theory: 6.69 times).

The structure prepared products were characterized by D8-Advance-Bruker X-ray diffractometer. The photoluminescence spectra were measured by FL3-22 fluorescence spectrometer. The glow curves were analyzed by Harshaw TLD-3500 equipment.

## III. RESULTS AND DISCUSSION

The phosphors of  $CaAl_2O_4: Eu^{2+}$  (1 % mol),  $Gd^{3+}$  (x % mol) with  $x = 0 \div 2.5$  were successfully prepared by the combustion method. The crystalline structure of  $CaAl_2O_4: Eu^{2+}, Gd^{3+}$  with different concentration of ion  $Gd^{3+}$  were

confirmed by X-ray diffraction pattern (XRD), the XRD diagrams were showed in Fig. 1. The phosphor had monocline single phase  $\text{CaAl}_2\text{O}_4$  structure. There no other phase was observed. The XRD diagrams also indicated that a little amount of rare earth ions did not effect on the structure of the lattice.

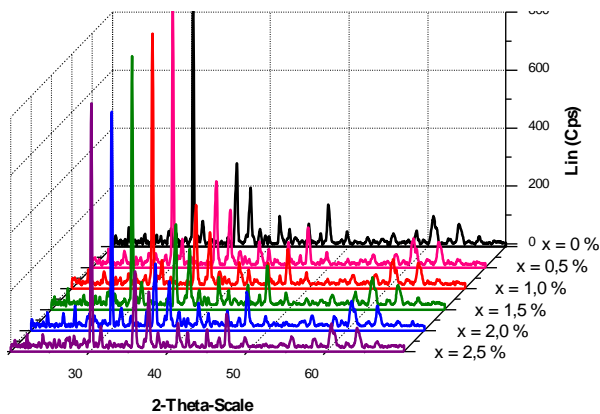


Fig. 1. XRD of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  (1 % mol),  $\text{Gd}^{3+}$  (x % mol)

The role of  $\text{Gd}^{3+}$  ion co-doping in the photoluminescence characteristics of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  (1 % mol),  $\text{Gd}^{3+}$  (x % mol) phosphors was investigated. The emission spectra of the phosphors were and presented in Fig. 2. The samples were excited by radiation with wavelength 285 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  $4f^65d^1$  to  $4f^7$  of  $\text{Eu}^{2+}$  ion. The emissions of  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  ions were not observed in the spectra, europium ions were reduced into  $\text{Eu}^{2+}$  ions in the combustion process and they play the role activator centers in the lattice. The emission spectra of ion  $\text{Gd}^{3+}$  has a sharp peak at 320 nm when the sample was excited by a radiation with wavelength 285 nm [9]. The both maximum of excitation spectra and emission spectra of ion  $\text{Gd}^{3+}$  were covered by excitation spectra of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$ . On the other hand, when the sample was excited by radiation with wavelength 285 nm, its emission spectra has a broad band with a peak at 444 nm that characterized for emission of  $\text{Eu}^{2+}$  ion (fig. 3).

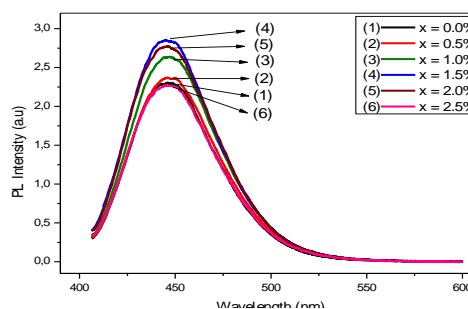


Fig. 2. Emission spectra of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  (1 % mol),  $\text{Gd}^{3+}$  (x % mol); x = 0 ÷ 2.5

The emission intensity of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$  phosphors increases with increasing concentration of  $\text{Gd}^{3+}$  ions co-doped, and the luminescence intensity is optimal with 1.5 % mol  $\text{Gd}^{3+}$ . This suggests that the energy transfer from  $\text{Gd}^{3+}$  to  $\text{Eu}^{2+}$  ions occurs and  $\text{Gd}^{3+}$  ions act as sensitizers. When the concentration of  $\text{Gd}^{3+}$  ions increases over 1.5 % mol, the luminescence intensity of phosphor decreases due to the concentration quenching occur.

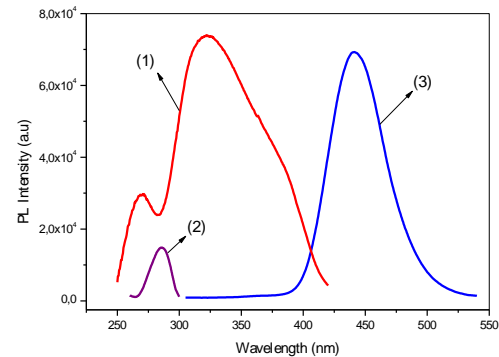


Fig. 3. Excitation and emission spectra of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  (1 % mol),  $\text{Gd}^{3+}$  (1.5 % mol)  
(1) : Excitation spectra of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$   
(2) : Excitation spectra of  $\text{Gd}^{3+}$  was recorded corresponding to maximum emission at wavelength 320 nm.  
(3) : Emission spectra of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$  when it was excited by radiation with wavelength 285 nm

Fig. 4 shows the phosphorescent decay time of the  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$  phosphors with different concentrations of ion  $\text{Gd}^{3+}$ . The phosphors were excited by radiation with wavelength 365 nm for 2 minutes. The results showed that the phosphor of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$  have more long afterglow and high brightness. Whereas, the initial photoluminescence intensity and the lifetime of the phosphor  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  is quite low.

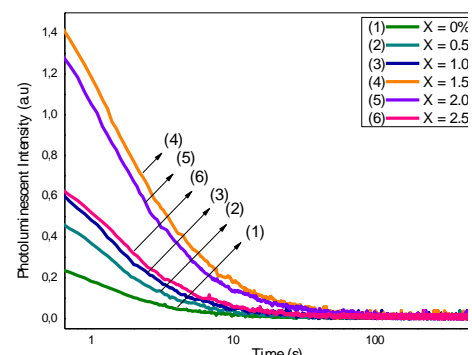


Fig. 4. Decay time of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  (1 % mol),  $\text{Gd}^{3+}$  (x % mol)

The phosphorescent mechanism of material can be suggested as shown in fig. 5. It is indicated that  $\text{Gd}^{3+}$  ions generated hole traps near the valence band that resulted the long persistent phosphorescence. These trap levels lie in between the excited state and the ground state of  $\text{Eu}^{2+}$  ion. When the sample was excited by UV radiation, the  $\text{Eu}^{2+}$  ions are excited from the ground state ( $4f^7$ ) to the excited state

( $4f^65d^1$ ):  $\text{Eu}^{2+} + h\nu \rightarrow \text{Eu}^{2+*}$  and thereby leaving a hole in the valence band, the electron – hole pairs are produced in  $\text{Eu}^{2+}$  ions. Simultaneously, the  $\text{Eu}^{2+}$  ions maybe capture electrons to be reduced to  $\text{Eu}^+$ :  $\text{Eu}^{2+} + e^- \rightarrow \text{Eu}^+$ . The  $\text{Gd}^{3+}$  ions capture some of free holes from valence band to form the  $\text{Gd}^{4+}$  cations:  $\text{Gd}^{3+} + h^+ \rightarrow \text{Gd}^{4+}$ . When the excitation was cut off, these captured holes are released slowly at room temperature and recombine with some free electrons, which lead to the persistent afterglow [5-6], [10].

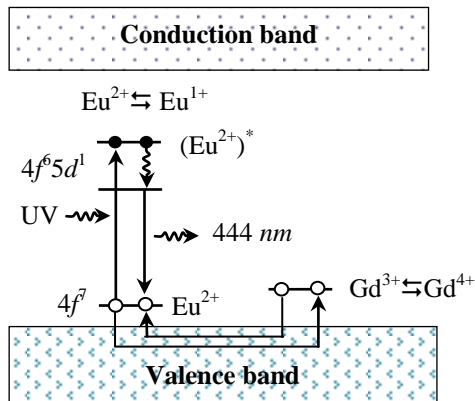


Fig. 5. Phosphorescent mechanism of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Gd}^{3+}$

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.

$$I = I_0 + I_{01}e^{-t/\tau_1} + I_{02}e^{-t/\tau_2} + I_{03}e^{-t/\tau_3}$$

TABLE I. THE VALUES OF LIFETIME OF  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Gd}^{3+}$  PHOSPHORS

Sample	$\tau_1$ (s)	$\tau_2$ (s)	$\tau_3$ (s)
CAO: Eu1%, Gd0.5%	6.56	1.27	42.93
CAO: Eu1%, Gd1.0%	6.79	1.38	32.55
CAO: Eu1%, Gd1.5%	8.44	1.59	48.73
CAO: Eu1%, Gd2.0%	7.06	1.54	41.78
CAO: Eu1%, Gd2.5%	6.77	1.34	44.69

And so, their thermoluminescent properties were studied. The glow curves of the phosphors were showed in the fig. 6.

The phosphors were irradiated by UV radiation of D<sub>2</sub> lamp for 20second. The results were recorded with heating rates 2°C/s. The glow curves of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Gd}^{3+}$  phosphors have a single peak with maximum intensity at around 104°C.

The thermoluminescence intensity of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Gd}^{3+}$  phosphor with 1.5 % mol is the strongest. It is indicated that the activator centers and the density of traps produced were more suitable than that of the other concentrations  $\text{Gd}^{3+}$  ion. The activation energy was calculated by the Reuven Chen method [11] and the results showed in table 2.

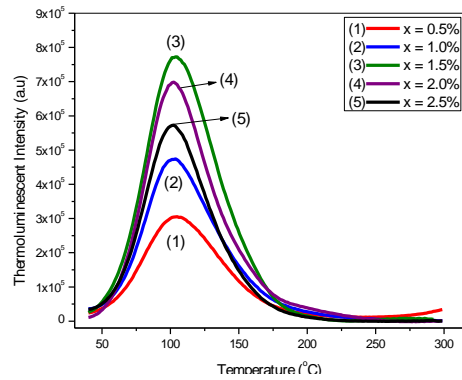


Fig. 6. Glow curves of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  (1 % mol),  $\text{Gd}^{3+}$  (x % mol)

TABLE II. THE VALUES OF THE ACTIVATION ENERGY OF  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Gd}^{3+}$  PHOSPHORS

Sample	E (eV)
CAO: Eu1%, Gd0.5%	0.63
CAO: Eu1%, Gd1.0%	0.64
CAO: Eu1%, Gd1.5%	0.66
CAO: Eu1%, Gd2.0%	0.65
CAO: Eu1%, Gd2.5%	0.64

#### IV. CONCLUSION

The phosphors of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Gd}^{3+}$  were successfully synthesized by combustion method. 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  $\text{Eu}^{2+}$ . The materials of  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  co-doped with  $\text{Gd}^{3+}$  had long persistent phosphorescence. Inside,  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  codoped with  $\text{Gd}^{3+}$  had long afterglow with high brightness and their photoluminescent intensity are better than  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ . In these phosphors,  $\text{Eu}^{2+}$  ions play the role activators and  $\text{Gd}^{3+}$  ions act as hole traps and sensitizers also.

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