

PHOTOLUMINESCENCE CHARACTERISTICS OF THE $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ CO-DOPED WITH ION Dy^{3+} SYNTHESIZED BY COMBUSTION METHOD

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ABSTRACT

The phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ with varying concentrations were synthesized by combustion method. The monoclinic single phase structure of CaAl_2O_4 was investigated by X-ray diffraction. The emission spectra of phosphors had a broad band with maximum at 444 nm due to electron transition from the $4f^6 5d^1$ to the $4f$ of Eu^{2+} ion and a small peak at 575 nm due to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition of Dy^{3+} ions. The excitation spectra and the decay time of phosphors were investigated also. The phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ had long persistence luminescence. In these phosphors, Eu^{2+} ions play the role of activators. Whereas, Dy^{3+} ions generate the hole traps that lead to the long persistent phosphorescence and act as the activators in the phosphors simultaneously. The concentration of Dy^{3+} ion co-doped has strong influence on the luminescence of phosphor.

Keywords: Alkaline earth, Photoluminescence, Persistence, Phosphorescence, Combustion method, Calcium aluminate.

1. INTRODUCTION

The alkaline earth aluminate phosphors doped rare earth ions have been extensively studied and widely applied in the display technology. It was reported that the emission spectra of the phosphors alkaline earth aluminate doped Eu^{2+} ion had a broad band that characterized the transition of electronic configuration from $4f^6 5d^1$ to $4f$ of Eu^{2+} ion [1-3]. The photoluminescence of the materials has strong depend on crystal field [3, 4]. The long-lasting afterglow of these materials has been studied by co-doped the second rare earth ions [1, 2, 4-6]. The trapping mechanism plays an essential role in the persistence of these materials [1, 5, 6]. The long persistence phosphors have more important applications with a long afterglow. The phosphor $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ was a long afterglow phosphor with a single phase monoclinic structure. In these phosphors, Eu^{2+} ions play the role of activators, Dy^{3+} ions act as hole traps that lead to the long persistent phosphorescence [2, 4, 6].

The alkaline earth aluminate materials doped rare earth ions can be synthesized by many methods, such as sol-gel, solid-state reaction, Pechini and combustion [2-5, 7]. In particular, combustion synthesis was well known as an important technique for the synthesis of alkaline

earth aluminate phosphors with low initial temperature of combustion and short reaction time [2, 3, 8]. So, the phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ were prepared by combustion method and the role of Dy^{3+} ion co-doped in the phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ was investigated in this study.

2. EXPERIMENTAL METHODS

The phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Dy^{3+} (x % mol) were synthesized by combustion method, with $x = 0 \div 2.5$. The starting materials were the mixture of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck), Eu_2O_3 (Merck), Dy_2O_3 (Merck), B_2O_3 (AR) and $\text{CO}(\text{NH}_2)_2$ (AR). Rare earth oxides were nitrified by dissolving into HNO_3 . A small quantity of B_2O_3 was added as the flux. Urea ($\text{CO}(\text{NH}_2)_2$) was used to supply fuel and reducing agent. For the combustion technique, urea is documented as an ideal fuel [8].

Aqueous solution containing stoichiometric amounts of nitrate metal and B_2O_3 was mixed and heated by microwave for 10 minutes to evaporate water. The mixing and heating mechanism of microwave is different from magnetic heating stirrer. Accordingly, the microwave energy mixes and heats the aqueous solution on a molecular level, which leads to uniform diffusing and rapid water evaporation.

Next, urea was added, the entire mixture solution was stirred by magnetic heating stirrer to gel form. And then, the gel was dried at 80°C to dehydrate and combusted at 580°C for 5 minutes. Finally, the white powder product was obtained. Urea concentration was 18 times of product mole.

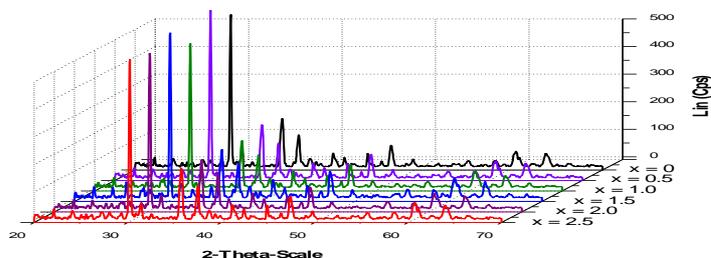
The structure of synthesized products was characterized by D8-Advance-Bruker X-ray diffractometer, and the photoluminescence spectra was measured by FL3-22 fluorescence spectrometer.

3. RESULTS AND DISCUSSION

The phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Dy^{3+} (x % mol) with $x = 0 \div 2.5$ were successfully synthesized by the combustion method. The crystalline structure of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ with different concentration of ion Dy^{3+} were confirmed by X-ray diffraction pattern (XRD) in fig. 1. The characteristic peaks of the CaAl_2O_4 were observed.

The phosphors have the structure of monoclinic single phases. A small amount of doped rare earth ions did not affect on the phase composition of CaAl_2O_4 . Furthermore, there no other phase was detected.

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



The role of Dy^{3+} ion co-doped in the photoluminescence characteristics of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Dy^{3+} (x % mol) phosphors was investigated. The emission spectra of the phosphors was presented in fig. 2. The samples were excited by radiation of 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 $4f^65d^1$ to $4f^7$ of Eu^{2+} ion [1-3]. In addition, the spectra component also had a small peak at wavelength 575 nm due to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} ions [9, 10] (fig. 3). The emission intensity of Dy^{3+} ion is much lower than that of Eu^{2+} ion. The emissions of Eu^{3+} ions were not observed in the spectra. This proved that europium ions were completely reduced into Eu^{2+} ions in the combustion process and they play the role of activator centers in the lattice.

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

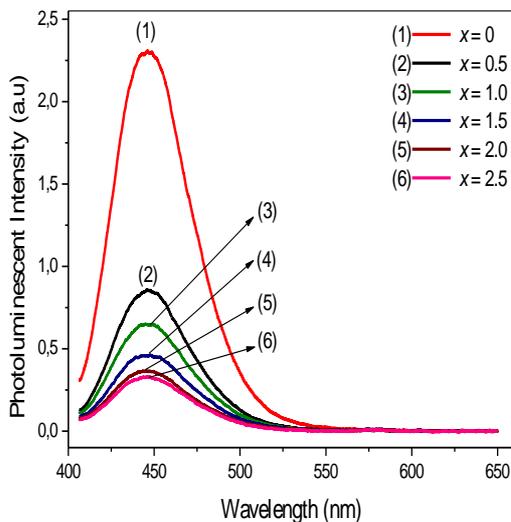


Fig-3. Emission spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Dy^{3+} (z % mol); $z = 0.5 \div 2.5$

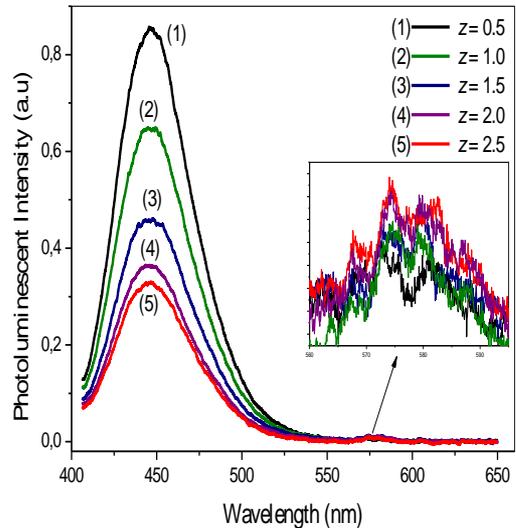


Figure 4 shows the emission spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Dy^{3+} (z % mol) phosphors which were excited by radiation of 450 nm. The emission spectra has two peak groups that located at 485 nm and 575 nm due to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} ions. Accordingly, the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ is known a sensitive transition that is influenced by external environments of Dy^{3+} ion [9, 10]. It is indicated that the Dy^{3+} ions act as luminescent centers for the emission spectra of phosphors.

Fig-4. Emission spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}(1\% \text{ mol}), \text{Dy}^{3+} (\approx \% \text{ mol}); \approx = 0.5 \div 2.5$

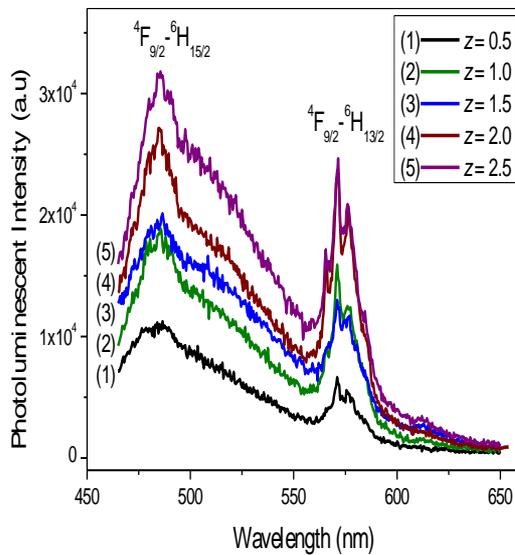
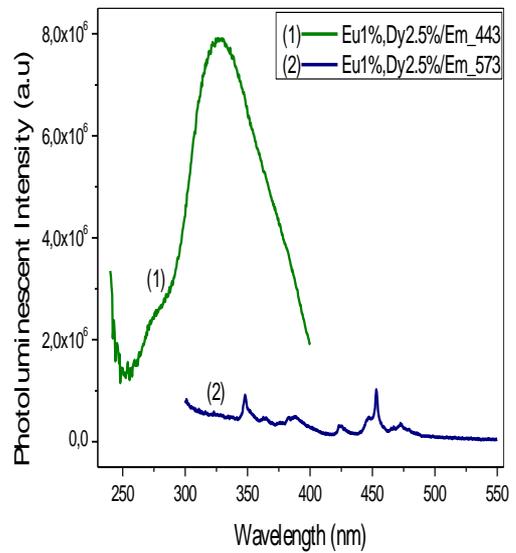


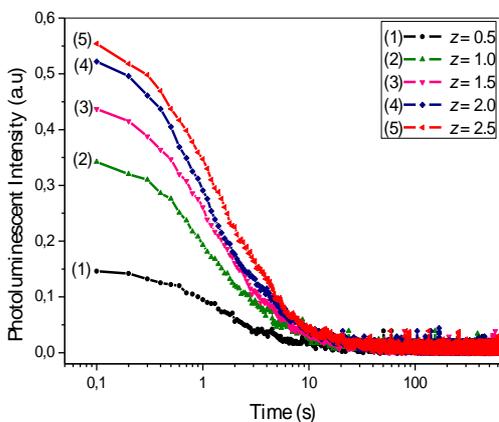
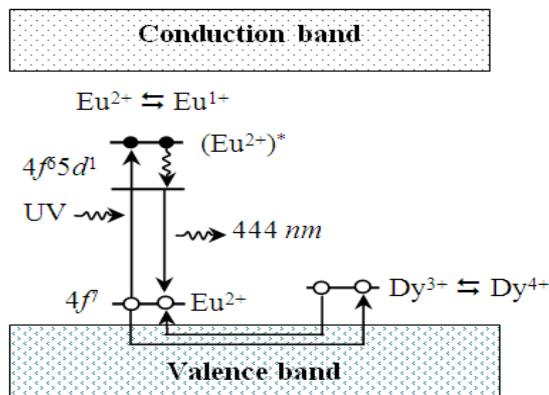
Fig-5. Excitation spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}(1\% \text{ mol}), \text{Dy}^{3+} (2.5\% \text{ mol})$



The excitation spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+} (1\% \text{ mol}), \text{Dy}^{3+} (2.5\% \text{ mol})$ phosphors was shown in fig. 5. When the excitation spectrum was recorded at an emission of 444 nm , there are two peaks located at 275 nm and 330 nm in the spectrum due to transitions from the ground state ($4f^7$) to the excited state ($4f^65d$) of Eu^{2+} ions. Whereas, the peaks appeared from 350 nm to 450 nm , can be explained as the consequence of $4f-4f$ transitions of Dy^{3+} ions when the excitation spectrum was recorded with an emission of 573 nm .

As the results of fig. 3 and 5, for the emission spectra recorded at an excitation wavelength of 365 nm , the phosphors emitted a broad band radiation with maximum intensity at 444 nm that characterized the emission of Eu^{2+} ion. The location of this radiation coincides with the excitation range of Dy^{3+} ion. In this case, it is suggested that the emission of Eu^{2+} ion act as an excitation source of Dy^{3+} ion.

The emission corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of Dy^{3+} ions did not appear because it was overlapped by the emission of Eu^{2+} ion. Besides, the role of Dy^{3+} ions in the long afterglow of the phosphors was studied also. The phosphorescent decay time of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors with different concentrations of ion Dy^{3+} that the results were showed in fig.6. The phosphors were excited by radiation with wavelength of 365 nm for 2 minutes. The results showed that the phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ have long afterglow in several minutes after the excitation light off. The initial phosphorescent intensity of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors increases with increasing concentration of Dy^{3+} ions co-doped.

Fig-6. Decay time of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}(1\% \text{ mol}), \text{Dy}^{3+} (x\% \text{ mol}); x = 0.5 \div 2.5$ **Fig-7.** Phosphorescent mechanism of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ 

The mechanism of the long afterglow is due to the trapped-transported-detrapped process of holes and can be suggested as shown in fig. 7. It is suggested that Dy^{3+} ions generated hole traps near the valence band. These trap levels lie between the excited state and the ground state of Eu^{2+} ion. When the sample was excited by UV radiation, the 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 Eu^{2+} ions. Simultaneously, the Eu^{2+} ions maybe capture electrons to be into Eu^+ : $\text{Eu}^{2+} + e^- \rightarrow \text{Eu}^+$. The Dy^{3+} ions capturing some of free holes from valence band to form the Dy^{4+} cations: $\text{Dy}^{3+} + h^+ \rightarrow \text{Dy}^{4+}$. 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]. It is indicated that the Dy^{3+} ions act as the hole traps in the phosphors.

4. CONCLUSION

The phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ were successfully synthesized by combustion method. The phosphors have monocline single phase structure of CaAl_2O_4 . The materials of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ co-doped with Dy^{3+} have long persistent phosphorescence. In these phosphors, Eu^{2+} ions play the role of activators. The Dy^{3+} ions not only play the role of activator centers but also act as the hole traps in the phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$. The concentration of Dy^{3+} ion co-doped has strong influence on the luminescence of phosphor.

REFERENCES

- [1] Y. Lin, Z. Zhang, Z. Tang, J. Zhang, Z. Zheng, and X. Lu, "The characterization and mechanism of long afterglow in alkline earth aluminates phosphors co-doped by Eu_2O_3 and Dy_2O_3 ," *Materials Chemistry and Physics*, vol. 70, pp. 156-159, 2001.
- [2] N. M. Son, L. T. T. Vien, L. V. K. Bao, and N. N. Trac, "Synthesis of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphorescence nanosized powder by combustion method and its optical properties," *Journal of Physics: Conference Series*, vol. 187, p. 012-017, 2009.

- [3] M. Mothudi, J. R. Ntwaeborwa, Botha, and H. C. Swart, "Photoluminescence and phosphorescence properties of MAl_2O_4 : Eu^{2+} , Dy^{3+} (M: Ca, Ba, Sr) phosphors prepared at an initiating combustion temperature 5000°C ," *Journal of Physica*, vol. 404, pp. 4440-4444, 2009.
- [4] S. H. Choi, N. H. Kim, Y. H. Yun, and S. C. Choi, "Photoluminescence properties of SrAl_2O_4 and CaAl_2O_4 long-phosphorescent phosphors synthesized by an oxalate coprecipitation method," *Journal of Ceramic Processing Research*, vol. 7, pp. 62-65, 2006.
- [5] H. Ryu and K. S. Bartwal, "Photoluminescent spectra of Nd^{3+} codoped CaAl_2O_4 : Eu^{2+} blue phosphor," *Research Letter in Materials Science, Article ID 23643*, vol. 2007, p. 4, 2007.
- [6] T. Matsuzawa, Y. Aoki, N. Takeuchi, and Y. Murayama, "A new long phosphorescent phosphor with high brightness, SrAl_2O_4 : Eu^{2+} , Dy^{3+} ," *J. Electrochem. Soc.*, vol. 143, pp. 2670-2673, 1996.
- [7] N. Avci, K. Korthout, M. A. Newton, P. F. Smet, and D. Poelman, "Valence state of Europium in CaAl_2O_4 : Eu phosphors," *Optical Materials Express*, vol. 2, pp. 321-330, 2012.
- [8] K. C. Patil, M. S. Hegde, T. Rattan, and S. T. Aruna, *Chemistry of nanocrystalline oxide materials – combustion synthesis: Properties and Applications*, World Scientific, 2008.
- [9] H. Choi, C. H. Kim, C. H. Pyun, and S. J. Kim, "Luminescence of (Ca, La)S: Dy," *J. Luminescence*, vol. 82, pp. 25-32, 1999.
- [10] J. Kuang, Y. Liu, and J. Zhang, "White-light-emitting long-lasting phosphorescence in Dy^{3+} -doped SrSiO_3 ," *Journal of Solid State Chemistry*, vol. 179, pp. 266-269, 2006.

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