



THE ROLE OF Dy^{3+} ION IN THE LUMINESCENCE OF $CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$ PHOSPHOR

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ABSTRACT

The phosphors of $CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$ with varying concentrations of Dy^{3+} ion were synthesized by the combustion method. The phase structure of $CaAl_2O_4$ was investigated by X-ray diffraction. The emission spectra of phosphors have a broad band with maximum at 444 nm due to electron transition from the $4f^6 5d^1$ to the $4f^7$ of Eu^{2+} ion; and a small peak of 575 nm due to $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition of Dy^{3+} ions. The excitation spectra and the decay time of phosphors were investigated also. The phosphors of $CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$ have a long persistent luminescence. In these phosphors, Eu^{2+} ions play the role activators. 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+} ions co-doped has a strong influence on the luminescence of phosphor.

Keywords: Alkaline earth, Photoluminescence, Persistence, Phosphorescence, Combustion, Thermoluminescence, Glow-curve.

Contribution/ Originality

This study evaluates the role of Dy^{3+} ion in the luminescence of $CaAl_2O_4: Eu, Nd, Dy$ phosphors by the investigated results. In this material, the Dy^{3+} ions play the role of luminescence centers and hole traps also; this is the new contribution of the paper.

1. INTRODUCTION

In recent years, rare earth doped alkaline earth aluminate phosphors have been extensively studied and widely applied in many fields of technology, such as radiation dosimetry, color display, luminescent porcelain, airport signs, luminous paints on highways and so on [1-3]. 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 $4f^7$ of Eu^{2+} ion [2-5]. The photoluminescence of materials have a strong dependence on crystal field [3-5]. The long-lasting afterglow of these materials have been studied by co-doped the rare earth ions [2-5]. The long persistent phosphors have more important applications with their long afterglow. The phosphors $CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$ have a long afterglow with a single phase monoclinic structure. In these phosphors, Eu^{2+} ions play the role of activators, while Dy^{3+} ions act as hole traps that lead to the long persistent phosphorescence [3]; [5]. In addition, the Dy^{3+} ions also contribute to the photoluminescence of phosphors as the luminescence centres. The concentration of Dy^{3+} ions co-doped has a strong influence on the luminescence of phosphor.

The role of Dy^{3+} ions co-doped in the phosphors of $CaAl_2O_4: Eu^{2+}, Nd^{3+}, Dy^{3+}$ is investigated in this paper. The materials were prepared by the combustion method, which is well known as an important technique for the synthesis of alkaline earth aluminate phosphors with a low initial temperature of combustion and short reaction time [2, 3]; [6].

2. EXPERIMENTAL METHODS

The phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0.5 % mol), Dy^{3+} (z % mol) were synthesized by the combustion method, with $z = 0.5 \div 2.5$. The starting materials to synthesize phosphors CaAl_2O_4 co-doped with rare earth ions were a 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), Nd_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 them 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 as a reducing agent. For the combustion technique, urea is documented as an ideal fuel.

An 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 a microwave is different from a magnetic heating stirrer. The microwave energy mixes and heats the aqueous solution at a molecular level, which leads to uniform diffusing and rapid water evaporation. Next, urea was added and the entire mixture solution was stirred by a magnetic heating stirrer to gel form. Then, the gel was dried at 80°C to dehydrate and combusted at a temperatures of 580°C within 5 minutes. Finally, a white powder product was obtained.

The structure of materials were characterized by a D8-Advance-Bruker X-ray diffract meter, and the photoluminescence spectra was measured by a FL3-22 fluorescence spectrometer. In addition, the glow-curves were analyzed by Harshaw TLD-3500 equipment.

3. RESULTS AND DISCUSSION

The crystalline structures of phosphors $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Dy}^{3+}$ with different concentration of ion Dy^{3+} (z % mol), which were confirmed by X-ray diffraction pattern (XRD). This XRD diagrams is shown in fig. 1.

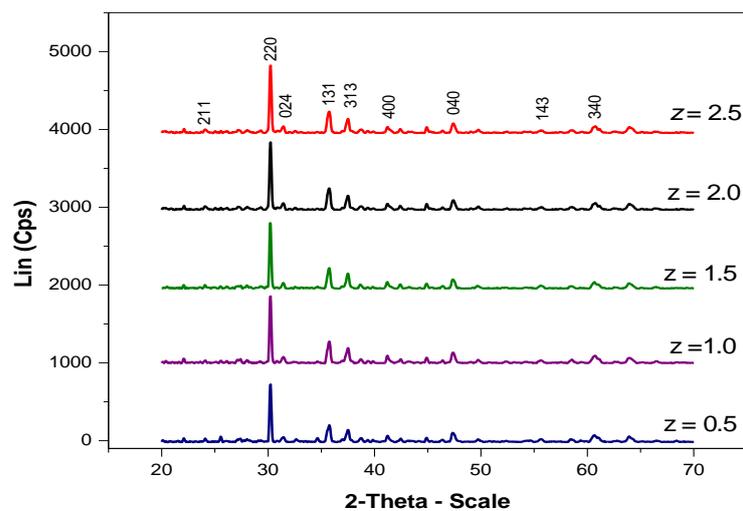


Fig-1. XRD patterns of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0.5 % mol), Dy^{3+} (z % mol)

The phosphors have the monoclinic single phase structure, and the characteristic peaks of CaAl_2O_4 were observed. No other phase was detected and therefore it can be concluded that a small amount of rare earth ions co-doped does not effect the phase composition of the materials.

The photoluminescence characteristics of phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0.5 % mol), Dy^{3+} (z % mol) were investigated and is presented in fig. 2. The samples were excited by the radiation of 365 nm . The results indicated that the emission spectra of the phosphors had the same broad band with a maximum intensity at 442 nm that characterized the transition of electronic configuration from $4f^6 5d^1$ to $4f^7$ of Eu^{2+} ion. In addition, the spectra component also has a small peak at a wavelength of 575 nm due to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} ions [3, 7] (fig. 2). The emission intensity of the Dy^{3+} ion is much lower than that of the Eu^{2+} ion. It indicates that the Dy^{3+} ions act as luminescence centers in the material. However, the density of these centers is much less than those of the Eu^{2+} ions. Thus, the radiation intensity of the Dy^{3+} ion is quite low in comparison with the Eu^{2+} ion radiation in

the luminescence of the material. Besides, the emissions of Eu^{3+} due to the transitions of $f-f$, were not observed in the spectra [8]. This proved that all of the europium ions were completely reduced into Eu^{2+} ions in the combustion process and they play the role activator centers in the lattice. Also, the radiation which characterizes Nd^{3+} ions at a wavelength of 1064 nm is not observed.

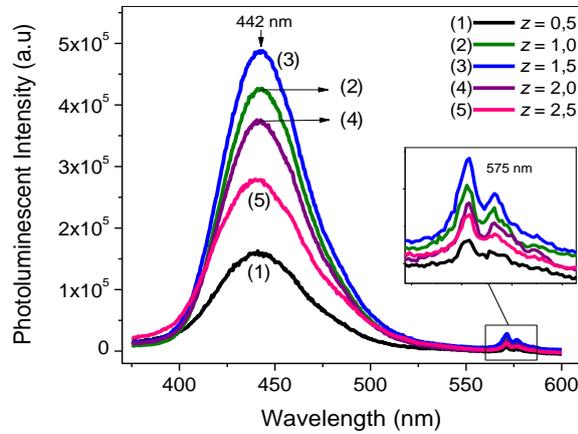


Fig-2. Emission spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0,5 % mol), Dy^{3+} (z % mol); $z = 0,5 \div 2,5$

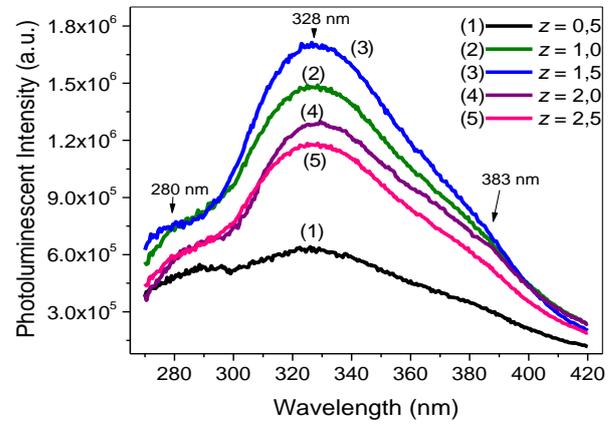


Fig-3. Excitation spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0,5 % mol), Dy^{3+} (z % mol); $z = 0,5 \div 2,5$

The excitation spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$, Nd^{3+} , Dy^{3+} phosphors which were recorded with the emission at 442 nm , are presented in fig. 3. There are two peaks located at 280 nm and 328 nm in the spectra due to transitions from the ground state ($4f^7$) to the excited state ($4f^65d$) of Eu^{2+} ions. Whereas, the sub-peaks appeared within the range of 360 nm to 400 nm , and can be explained as the $4f-4f$ transitions of Dy^{3+} ions. The narrow lines, that characterize the $f-f$ transitions of the valence 3 rare earth ions, do not appear in the spectrum.

In addition, the role of Dy^{3+} ions in the long afterglow of phosphors was also studied. The phosphorescent decay time of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$, Nd^{3+} , Dy^{3+} phosphors with different concentrations of ion Dy^{3+} were investigated, and the results are shown in fig.4. The phosphors were excited by radiation with a wavelength of 365 nm for 2 minutes. It showed that the phosphors of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$, Nd^{3+} , Dy^{3+} have a long afterglow for several minutes after the excitation light is off. In particular, the initial phosphorescent intensity of the sample $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0.5 % mol) outperformed the others which co-doped with Dy^{3+} ion.

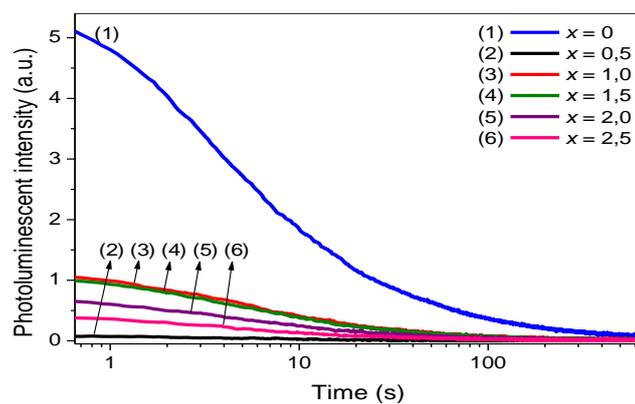


Fig-4. Decay time of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0,5 % mol), Dy^{3+} (x % mol)

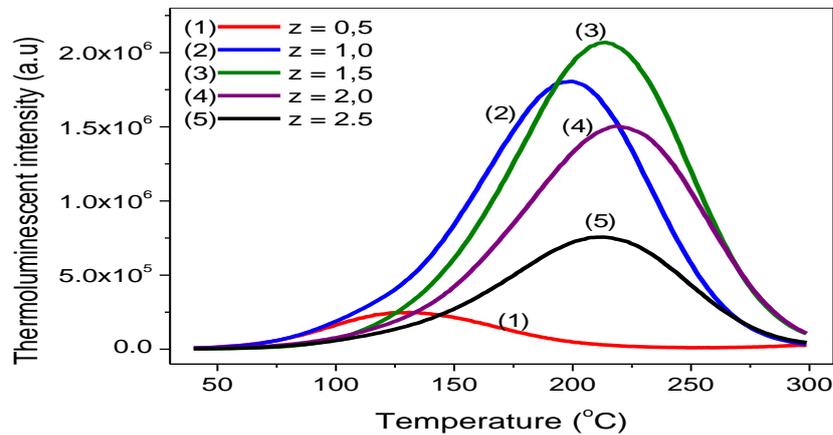
The life-time of phosphors was calculated by fitting the experimental decay time with the combination of three exponential functions. The results are shown in table 1. It indicates that the life-time of phosphors are approximately the same.

Table- 1. The initial photoluminescent intensity and the life-time of CaO: Eu^{2+} (1 % mol), Nd^{3+} (0,5 % mol), Dy^{3+} (x % mol)

Samples	I_{01}	τ_1 (s)	I_{02}	τ_2 (s)	I_{03}	τ_3 (s)
$\text{CaAl}_2\text{O}_4:\text{ENd}0,5\%$	1,95	18,85	7,49	3,37	0,62	127,02
$\text{CaAl}_2\text{O}_4:\text{ENDy}0,5\%$	0,08	7,31	0,05	1,38	0,01	74,33
$\text{CaAl}_2\text{O}_4:\text{ENDy}1,0\%$	0,37	21,62	1,16	4,09	0,11	122,25
$\text{CaAl}_2\text{O}_4:\text{ENDy}1,5\%$	0,38	22,91	1,22	4,29	0,11	131,38
$\text{CaAl}_2\text{O}_4:\text{ENDy}2,0\%$	0,35	16,05	2,23	3,29	0,09	92,91
$\text{CaAl}_2\text{O}_4:\text{ENDy}2,5\%$	0,14	21,65	1,67	3,83	0,04	106,19

The results of research into decay time show that, in these materials, Nd^{3+} and Dy^{3+} ions play the role of hole traps. With co-doping Dy^{3+} ion, the density of generated traps increased significantly, resulting in the probability of carriers captured in the trap are larger than that of those released. Therefore, the initial phosphorescence intensity is relatively low compared to the intensity of CaO: Eu^{2+} (1% mol), Nd^{3+} (0.5% mol). The reason why the phosphorescence is relatively long is due to the carriers being released slowly.

The thermoluminescent properties of the phosphors were also investigated. The results are presented in Fig. 5. The phosphors were irradiated by UV radiation from a D_2 lamp for 20 seconds. The glow-curves were recorded with a heating rate of $5^\circ\text{C}/\text{s}$.

**Figure-5.** Glow-curves of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0,5 % mol) Dy^{3+} (z % mol)

The glow-curves have a single peak with the maximum intensity tending towards the high temperature when the concentration of Dy^{3+} ions increases. The thermoluminescent intensity was at its maximum with the sample of 1.5 % mol Dy^{3+} . Meanwhile, the sample of co-doped Dy^{3+} 0.5% mol had the lowest intensity. This can be explained by the fact that when the Dy^{3+} ions concentration increases, the increased density of traps leads to the probability of more carriers being captured in traps. When heated, the probability of carriers released from the traps also increased, causing a rise in thermoluminescent intensity.

Table-2. The values of the dynamics of CaO: Eu^{2+} (1 % mol), Nd^{3+} (0,5 % mol), Dy^{3+} (z % mol)

Samples	E (eV)	μ_g	s (s^{-1})
$\text{CaAl}_2\text{O}_4:\text{ENDy}0,5\%$	0,54	0,52	$1,03 \times 10^6$
$\text{CaAl}_2\text{O}_4:\text{ENDy}1,0\%$	0,66	0,48	$1,95 \times 10^6$
$\text{CaAl}_2\text{O}_4:\text{ENDy}1,5\%$	0,70	0,50	$3,20 \times 10^6$
$\text{CaAl}_2\text{O}_4:\text{ENDy}2,0\%$	0,69	0,49	$2,11 \times 10^6$
$\text{CaAl}_2\text{O}_4:\text{ENDy}2,5\%$	0,60	0,47	$3,14 \times 10^5$

Besides, the increase in the concentration of Dy³⁺ ions increased the traps depth also, leading to the peak position of the glow-curves that can be driven toward higher temperatures. However, concentration quenching occurs which reduces the thermoluminescent intensity when the Dy³⁺ concentration is greater than 1.5% mol.

Based on the glow-curves, the peak shape method (R. Chen method) [9] was applied to calculate the activation energy of CaAl₂O₄: Eu²⁺ (1 % mol), Nd³⁺ (0,5 % mol), Dy³⁺ (x % mol), and these results, are shown in table 2.

4. CONCLUSION

The phosphors of CaAl₂O₄: Eu²⁺, Nd³⁺, Dy³⁺ were successfully synthesized by the combustion method. The phosphors have a monocline single phase structure of CaAl₂O₄. The emission spectra of CaAl₂O₄: Eu²⁺, Gd³⁺ phosphors have a broad band with a high peak of 444 nm due to electron transition from the 4f⁶5d¹ to the 4f⁷ of ion Eu²⁺, and a lower peak of 575 nm that characterize to the ⁴F_{9/2} → ⁶H_{13/2} transitions of Dy³⁺ ions. The materials of CaAl₂O₄: Eu²⁺ co-doped with Dy³⁺ have a long persistent phosphorescence. In these phosphors, Eu²⁺ ions play the role of activators, and Nd³⁺ ions act as hole traps. In addition, the Dy³⁺ ions play the role of luminescence centers and hole traps also. The concentration of Dy³⁺ ion co-doped has a strong influence on the luminescence of phosphor.

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