

Luminescent Characteristics of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$, Nd^{3+} , Gd^{3+} Phosphors

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Abstract— $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphorescent powder was prepared by the combustion method at 580 °C for 5 minutes. The powder was investigated by X-ray diffractometer, SEM, excitation and emission spectra, decay time and glow curve. The material had monocline single phase structure. The emission spectra were a broad band with peak at 444 nm that due to electron transition from the $4f^65d^1$ to the $4f^7$ configuration of the Eu^{2+} ion. $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphor was a long persistence phosphor with high brightness that was better than $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor. The results have been presented and discussed.

I. INTRODUCTION

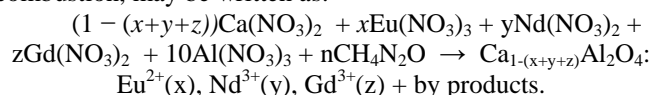
Until recent decade, strontium aluminate phosphors codoped with europium and dysprosium ions have attracted much attention since they show excellent properties [1-3]. Compared with classical sulfide phosphorescent phosphor, aluminates have several valuable properties: high radiation intensity, color purity, longer afterglow, chemical stabilization, safe and no radioactivity, etc. Alkaline earth aluminate doped with rare earth ions (Eu^{2+} , RE^{3+}) have well known as a long afterglow phosphor. In these phosphors, Eu^{2+} ions play role luminescent centers, RE^{3+} ions act as holes that had been discussed by Matsuzawa [1]. The emission color of the phosphor is depended on the alkaline earth ion in the alkaline earth aluminate lattice. The $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ green emitting phosphor is a long persistent phosphorescence with high brightness, the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ blue emitting phosphor is too [4-6]. Therefore, the doping an other trivalent rare earth ion in the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor expect to form a better phosphorescence.

In this paper, the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphors with changed concentration of Gd^{3+} ions were prepared by the combustion process. The results of photoluminescence and thermoluminescence were presented and discussed.

II. EXPERIMENT

Starting materials for the preparation of phosphors CaAl_2O_4 doped with different rare earth ions by urea - nitrate solution combustion synthesis are the mixture of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Eu_2O_3 , Nd_2O_3 , Gd_2O_3 , B_2O_3 , $\text{CO}(\text{NH}_2)_2$. Small quantities of B_2O_3 were used as a flux. Urea was used to supply fuel and reducing agent. Rare earth oxides

have been nitrified by nitric acid. The reaction for the formation of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ assuming complete combustion, may be written as:



With $x = 1$ % mol, $y = 0,5$ % mol, $z = 1$ % mol then $n = 6.69$.

Aqueous solution containing stoichiometric amounts of nitrate metal and urea was mixed by magnetic stirrer and heated at 70 °C for 2 hours to gel. Next, the gel was dried at 80 °C to dehydrate and combusted at temperatures 580 °C within 5 minutes. Urea concentration was 18 times of product mole (theory 6.69). The product was $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ with white powder.

X-ray diffraction, SEM, excitation and emission spectra, decay time and glow curve of the prepared phosphors were measured and discussed.

III. RESULT AND DISCUSSION

The crystalline structure of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphor synthesized by solution combustion was confirmed by X-ray diffraction (XRD), the results showed in figure 1. The phosphor powder has monocline single phase structure. The phase structure of starting materials and other compositions had been observed in the XRD. It showed that a little amount of rare earth ions did not effect on the structure of the lattice.

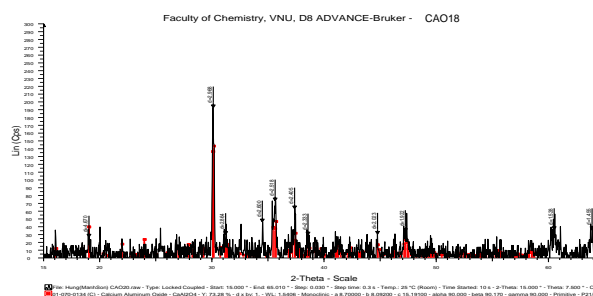


Fig.1: XRD pattern of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$

In order to determine the morphology and particle size of the sample, a scanning electron microscope (SEM) were carried out. Figure 2 displays a typical scanning electron microscope image of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphor. SEM image showed that the sample had loose, foamy, irregular and crowded particles. The surfaces of the particles had many cracked traces and pores that formed by the escaping gases during the combustion reaction. The size particle is about 1-2 μm .



Fig. 2: SEM photograph of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$

Figure 3 shows luminescent spectra of the phosphors $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ and $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ codoped with Nd^{3+} , Nd^{3+} and Gd^{3+} , excited by radiation with wavelength 365 nm. It showed that the emission spectra of the phosphors are a same broad band with maximum intensity at 444 nm that characterize the electronic transition from $4f^65d^1$ to $4f^7$ configuration of Eu^{2+} ion. Emission of Eu^{3+} , Nd^{3+} and Gd^{3+} was not observed in the spectra. It could indicate that europium ions were reduced into Eu^{2+} ions in the combustion reaction and they play role activator centers in the lattice. Whereas, Nd^{3+} and Gd^{3+} ions play role hole trap. A part of Eu^{2+} ions exchanged electric charge in the trap-release process to form the phosphorescence of material. And so, emission intensity of the phosphors $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ codoped with Nd^{3+} , Nd^{3+} and Gd^{3+} were more strong than $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ phosphor.

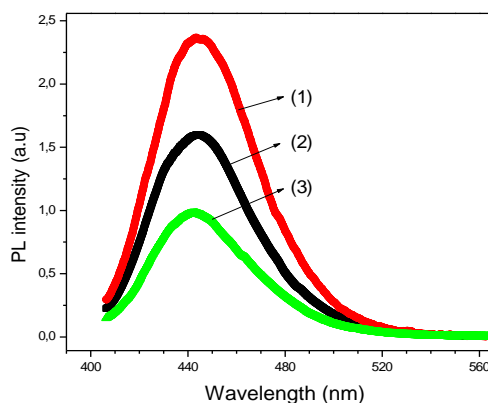


Fig. 3: Emission spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1), $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ (2) and $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ (3)

Emission spectra of phosphors $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ codoped with Gd^{3+} ion have different concentration of Gd^{3+} ion, presented in the figure 4. Maximum luminescent intensity of the spectra change when concentration of Gd^{3+} ion change and optimal emission intensity corresponding with concentration of Gd^{3+} ion 1 % mol. $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0,5 % mol), Gd^{3+} (1 % mol) phosphor not has only high brightness, but also long afterglow is more long than $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0,5 % mol) phosphor.

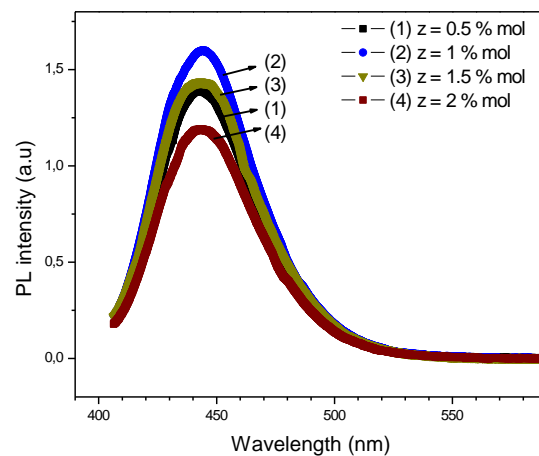


Fig. 4: Emission spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ (z % mol) with $z = 0 \div 2$

Excitation spectra of phosphors CaAl_2O_4 doped and codoped with different rare earth ions at emission wavelength $\lambda_{\text{em}} = 444$ nm show in the figure 5. Excitation spectrum of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ phosphor has two broad band with maximum peak at 270 nm and 325 nm. While Excitation spectra of the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ codoped with Nd^{3+} and $\text{Nd}^{3+}, \text{Gd}^{3+}$ phosphors have only a broad band with maximum at wavelength 325 nm. Disappearance of the peak at 270 nm in these phosphors could due to the peak at 270 nm corresponds with absorption of the $\text{O}^{2-}-\text{RE}^{3+}$ charge transfer band in the oxide host that contains trivalent rare earth ions [7]. Therefore, the absorption of Eu^{2+} ions in this band disappeared in the phosphors codoped with trivalent rare earth ions.

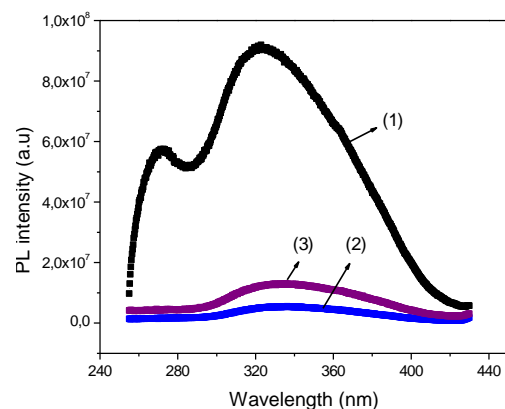


Fig. 5: Excitation spectra of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1), $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ (2) and $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ (3)

Fig. 6 shows the decay times of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphors with different codoped concentration of Gd^{3+} ion after excitation by UV lamp with radiation wavelength 365 nm. The optimal long afterglow is corresponding to the concentration of Gd^{3+} ion 1 %mol. In order to compare the long afterglow of phosphors CaAl_2O_4 doped with different rare earth ions, The decay times of those present in the figure 7. It indicated that $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ phosphors codoped with Nd^{3+} or $\text{Nd}^{3+}, \text{Gd}^{3+}$ ions have more long than persistence the phosphor did not dope, among them $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphor was optimal long persistence. It indicated that all of Nd^{3+} and Gd^{3+} ions formed hole trap in the lattice that trap depth will be determined by thermoluminescent method.

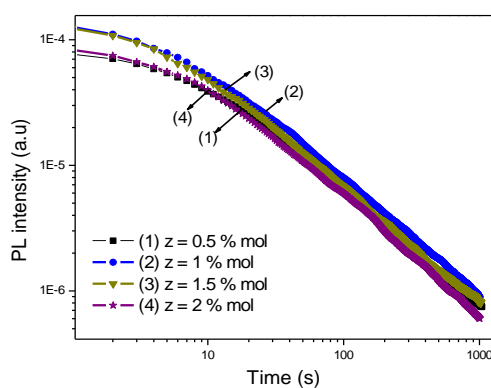


Fig. 6: The decay time of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1 % mol), Nd^{3+} (0.5 % mol), Gd^{3+} (z % mol) with $z = 0 \div 2$

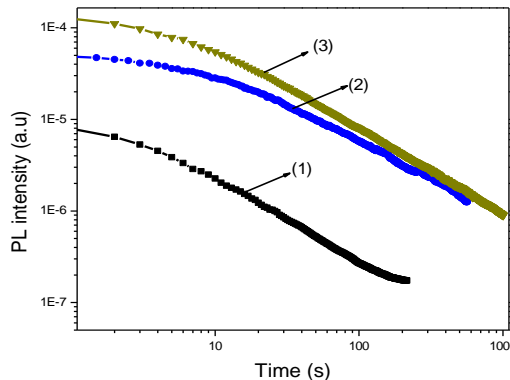


Fig. 7: The decay time of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$ (1), $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ (2) and $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ (3)

The glow-curve of phosphors codoped with rare earth ions have been irradiated by UV radiation of D_2 lamp for 1 minute, showed in Fig. 8. The glow curves of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ and $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphors have a symmetric and single peak with maximum temperature at 129 °C and 118 °C, respectively. Maximum thermoluminescent intensity of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphor is more strong than these of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor. It could indicate that the

Nd^{3+} and Gd^{3+} ions formed hole traps in the lattice. The trap density of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphor is more high than these of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor. Activation energy of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ and $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphors was analyzed by R. Chen method that was 0.68 eV and 0.73 eV, respectively.

The experimental results of the photoluminescence and thermoluminescence showed that the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ phosphor is long persistent phosphorescence with high brightness that is better than $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor.

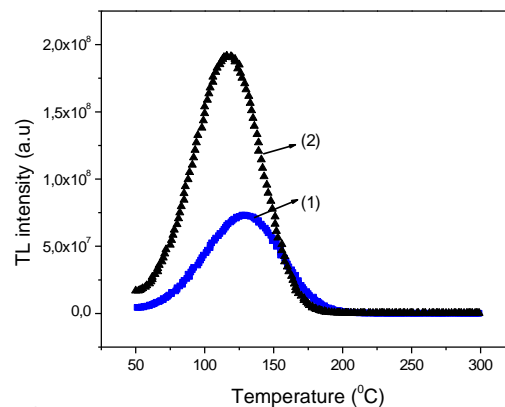


Fig. 8: Glow curve of $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ (1) and $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ (2)

IV. CONCLUSIONS

The phosphors CaAl_2O_4 codoped with different rare earth ions had been successfully synthesized by the urea-nitrate solution combustion method. The materials had monocline single phase structure with average size of particles about 1-2 μm . The $\text{Nd}^{3+}, \text{Gd}^{3+}$ ions formed hole traps with high trap density and suitable trap depth, Eu^{2+} ions was the activator centers in the $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}, \text{Gd}^{3+}$ lattice. This phosphor was a long persistent phosphorescence with high brightness that was better than $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor.

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