

Comparative Thermoluminescence Study of Rare Earth (Eu^{3+} , Dy^{3+}) and Transition Metal Mn^{2+} with Aluminate Host

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Abstract

The synthesis and characterization of Eu^{3+} Dy^{3+} and Mn^{2+} doped CaYAl_3O_7 phosphor with fixed 1 mol% concentrations are reported herewith to study the kinetic and Thermoluminescence (TL) properties. The TL glow curve exhibit a peak centered around $\sim 350^\circ\text{C}$,for all three dopants. The Mn^{2+} ion is exhibits intensive peak to other dopants. . Determine the activation energy and kinetic parameters of these material using Chen's formula. These results are supported by corresponding X-ray diffraction measurements which exhibit crystalline nature. These comparative analysis suggest the possibility of utilizing this material in futuristic dosimeter application as well as in solid state lighting devices.

Keywords: Thermoluminescence ,Phosphor, Dosimeter

Introduction

Thermoluminescence (TL) technique has wide range of applications such as in radiation dosimeter and also determine the trapping parameter .In the necessity and interest of radiation and personnel dosimeter to develop new phosphor material[1-2].It was shown that the sensitivity of anhydrous magnesium sulphate without dopants is not suitable for use in radiation dosimetry due to its low radiation sensitivity. Rare earth and alkaline earth aluminates have attracted so much attention because they have been widely used as hosts in preparation of dosimeter as well as PDP phosphors [3-5]. In order to develop new phosphor material for radiation dosimeter MgSO_4 with varying concentration of Dy and Mn prepared material . It was found that $\text{MgSO}_4:\text{Dy},\text{Mn}$ has a TL sensitivity compared to com parable to $\text{LiF}:\text{Mg},\text{Ti}$.[6]. Rare earth ions Eu^{3+} doped with LnAlO_3 [7] , YAlO_3 [8] $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ [9] have been reported for optical and thermally stimulated process. Various studies have been performed in order to investigate the possibilities of employing such materials in TLD applications. application of alkaline earth aluminate based phosphors($\text{M}=\text{Ca}, \text{Ba}, \text{Sr}$) $\text{Al}_{10}\text{O}_{17}$ phosphor, when doped with rare earth and transition dopants exhibits high brightness and long life afterglow, which make it useful for plasma devices[10-12]. An important study in this regard was performed by Tanori et. al. who studied $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor in view of its persistent luminescence dosimeter properties. Improvement of luminescence characteristics have been directed toward developing alternative liquid solution techniques including the sol-gel method, combustion technique, spray pyrolysis and micro- wave irradiation, etc. [13]. The combustion technique provides a route to synthesized the improvement of phosphor material as well less preparation time and low cost.

In this paper our aim to develop novel aluminate based phosphor CaYAl_3O_7 . Dy by the low cost combustion method for TLD properties and xed study for the crystal structure and size. These analysis and obtained result applicable for dosimeter and lighting devices.

Experimental Details

The rare earth Eu^{3+} Dy^{3+} and transition metal Mn^{2+} activated CaYAl_3O_7 phosphor was synthesized using combustion process. The $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and were mixed together for 30min. in an agate mortar and then urea added as a fuel. The material was then put into a preheated muffle furnace at 500°C . In 2-3 min. the material turned into a fluffy foam form, which was then processed to produce the desired samples. For the TL measurements sample was gamma irradiated by Co-60 source with 10gy. The temperature range from $50-450^\circ\text{C}$ and heating rate 6.6°C . The thermally stimulated curve was recorded by using TLD 11009 (Nucleonix Sys. Ltd. Hyderabad). XRD pattern was recorded using X-ray diffractometer (Advanced Bruker D8 Diffractometer, $\text{CuK}\alpha$ radiation) to determine the crystalline phase formation.

Results and Discussion

The XRD pattern of aluminate based phosphor is shown in figure 1. The observed peaks CaYAl_3O_7 are in good agreement with those given in JCPDS file number 77-1120, showing hexagonal structure of the host material. No other impurity phase is seen. The x-ray line broadening was used to determine the average crystallite size using the Scherrer formula. The average size of the crystalline particles was found to be $\sim 31.5 \mu\text{m}$.

Figure 2(a-c) shows the TL glow curve of the phosphor plotted as the intensity versus temperature graph for CaYAl_3O_7 with Eu, Dy and Mn doped sample (1mol%). It is clearly seen that there is a single peak in all cases which centered around $\sim 350^\circ\text{C}$ of the fixed dopant 1%(Eu, Dy and Mn). From the all the three TL glow curve of Eu, Dy and Mn the intensities of Eu is very less to compare Dy and Mn. When we compare to Mn doped transition with aluminate host CaYAl_3O_7 is five time intensive to Eu and four time larger to Dy rare earth dopant. Also one shoulder peak of Mn found $\sim 248^\circ\text{C}$ which is applicable for dosimeter purpose.

Using the Chen's peak shape method [14], the kinetic order can be related to the geometrical factor (μ_g) by the relation $\mu = \frac{T_2 - T_m}{T_2 - T_1} = \frac{\delta}{\tau}$, where T_1 , T_m and T_2 represent the temperatures of half intensity at low temperature

side peak temperature and high temperature side of TL peak. And $\delta = T_2 - T_m$, $\tau = T_m - T_1$ and $\omega = T_2 - T_1$. Therefore E_δ , E_τ and E_ω are the corresponding activation energy.

As per the relation the of CaYAl_3O_7 with different dopant phosphor shows the general order of kinetic and the activation energy is given by

$$E = c_\lambda \left(\frac{kT_m^2}{\lambda} \right) - b_\lambda (2kT_m)$$

The frequency factor was calculated by

$$\beta E / kT_m^2 = s[1 + (b-1)2kT_m / E] \exp(-E / kT_m) \dots \dots \dots (2)$$

For general order kinetics, the values of the c_γ and b_γ ($\gamma = \delta, \tau, \omega$) are calculated

$$c_\tau = [1.51 + 3(\mu_g - 0.42)], b_\tau = [1.58 + 4.2((\mu_g - 0.42))]$$

$$c_\delta = [0.976 + 7.3(\mu_g - 0.42)], b_\delta = 0 \text{ and}$$

$$c_\omega = [2.52 + 10.2(\mu_g - 0.42)], b_\omega = 1.0$$

The parameters calculated using these relations are tabulated in table 1.

From the table activation energy between 1.7 to 2.7 eV. However The frequency factor of Mn doped material is higher to Eu and Dy dopant. The results suggested that the maximum TL intensity obtained from CaYAl_3O_7 :Mn dopant with gamma irradiation of 10 Gy. It means that the transfer of charge from deep traps to shallow. The Mn doped phosphor material considerable and provides the prospects for dosimeters purpose and lighting devices.

Conclusion

The CaYAl_3O_7 phosphor material with constant concentrations of rare earth dopant (Eu, Dy and Mn) has been successfully synthesized by combustion method. The intensive and broad TL response exhibited by the sample with 1 mol% of Mn at 349°C with one shoulder $\sim 248^\circ\text{C}$. In the comparison between rare earth (Eu and Dy) and transition metal (Mn) with CaYAl_3O_7 phosphor, the TL glow curve confirms that CaYAl_3O_7 doped with Mn is the best phosphor material within the studied category. This Mn doped phosphor material with comparatively low cost and provides the possibility of its utilization in dosimeters and solid state lighting devices.

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Table 1. Kinetic Parameters for TL glow peak

1mol%	Eu%	Dy%	Mn%
T ₁	313	310	317
T _m	351	350	349
T ₂	323	320	332
μ _g	0.73	0.75	0.70
E _δ	1.9	0.76	1.37
E _τ	0.7	0.65	0.60
E _ω	5.8	5.7	3.1
Avg. Energy(ev)	2.7	2.32	1.7
Fre. Factor	1x10 ⁵	2.5x10 ⁶	4.5x10 ⁷

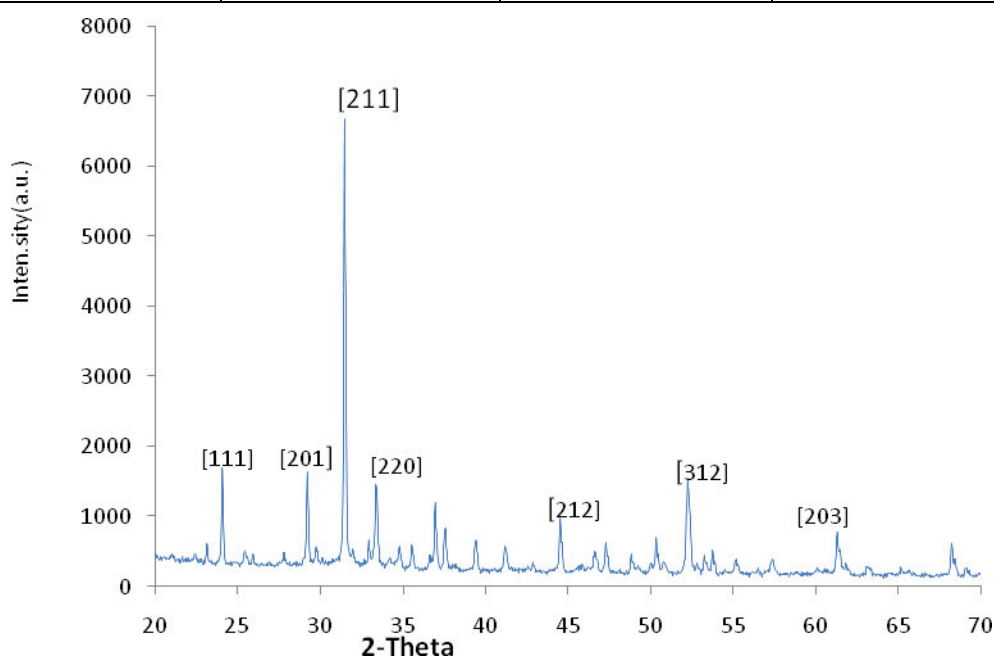


Figure 1. XRD pattern of CaYAl₃O₇

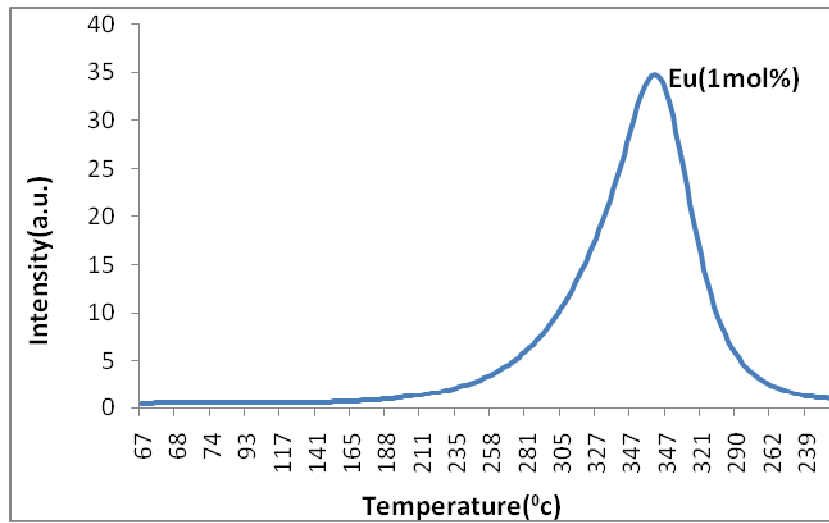


Figure 2(a). TL glow curve of CaYAl₃O₇:Eu³⁺

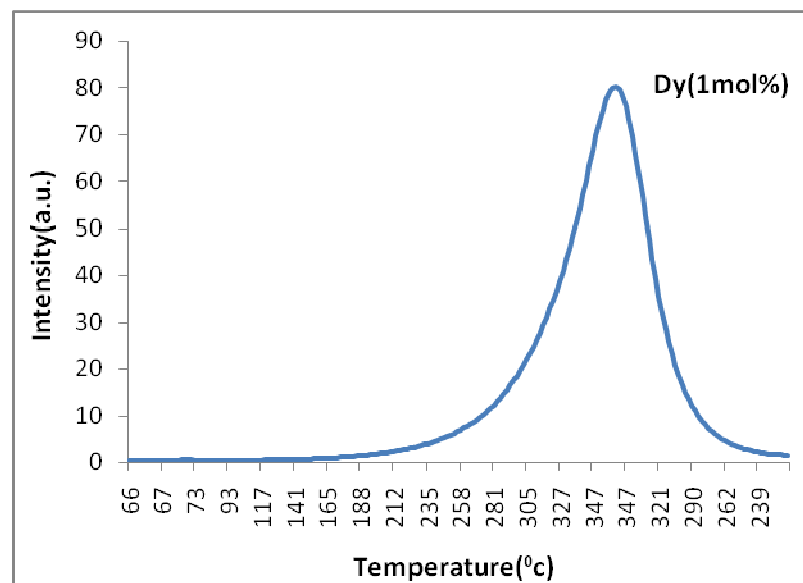


Figure 2(b). TL glow curve of CaYAl₃O₇:Dy³⁺

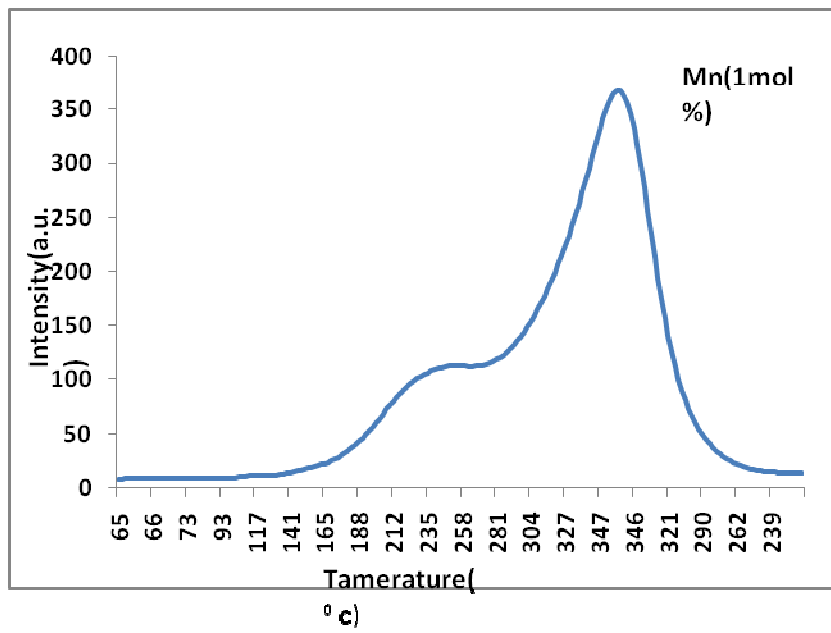


Figure 2(c). TL glow curve of CaYAl₃O₇:Mn²⁺

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