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

Anupam Selot (Corresponding author)
Dept. of Physics, Sadhu Vaswani College, Bhopal , 462030 India
e-mail address:selotanupam14@rediffmail.com
Mahendra Aynyas
Dept. of Physics .C.S.A. Govt P. G. College Sehore , 466001,India
e-mail address: aynyas@rediff.com
Pushpraj Pathak
Dept of Medical Physics, Jawaharlal Nehru Cancer and Research Hospital Bhopal, 462001, India
e-mail address: prpathak14@gmail.com

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 ~350°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 aluminatess 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 MgSO4with varying concentration of Dy and Mn prepared material . It was found that MgSO4:Dy,Mn has a TL sensitivity compared to com parable to LiF:Mg,Ti.[6]. Rare earth ions Eu^{3+}doped with $LnAlO_3$[7] ,$YAlO_3$ [`8] BaMgAl10O17: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(M= Ca, Ba, Sr)$Al_{10}O_{17}$ 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 $SrAl_2O_4$: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 $Ca(NO_3).6H_2O$, $Y(NO_3)$, Al $(NO_3)_3$. $9H_2O$ 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° 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 Brucker D8 Diffractometer, CuKα 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 ~31.5 µm.

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~ 350^0c 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 CaYAl3O7 is five time intensive to Eu and four time larger to Dy rare earth dopant. Also one shoulder peak of Mn found ~248^oc which is applicable for dosimeter purpose.

Using the Chen's peak shape method [14], the kinetic order can be related to the geometrical factor ($\mu_{g)}$ 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 $\delta = T_2\text{-}T_m$, $\tau = T_m\text{-}T_1$ and $\omega = T_2\text{-}T_1$ 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

$$\beta E / kT_m^2 = s[1+(b-1)2kT_m / E]\exp(-E / kT_m) \text{-----------} \quad (2)$$

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

c_τ= [1.51+3(μ_g - .42), b_τ= [1.58+4.2((μ_g -0 .42)]

c_δ = [0.976+7.3(μ_g -0 .42), b_δ= 0 and

c_ω = [2.52+10.2(μ_g - 0.42), b_ω= 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 t he 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 ~248^0c.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.

Acknowledgement

The authors would like to thank Dr. M. Gupta (XRD), UGC-DAE CSR, Indore (M.P.) and Dr. Jagjeet Kaur, VYVT P.G. College, Durg (TL) for the respective measurements.

References

[1] Mckeever S.W.S., *Thermoluminescence of Solids*, Cambridge University Press, 1985.

[2] Arellano- Tanori O.A. , Mel'endrez R, Pedroza-Montero M,. Castaneda B, Chernov V, Yen W. M. & Barboza-Flores M (2008) Persistence luminescence dosimetric properties of UV irradiated $SrAl_2O_4$:Eu^{3+} ,Dy^{3+} phosphor, *J. Lumin.* 128, 173-184.

[3] Salah N., (2011) Nanocrystalline materials for the dosimetry of heavy charged particles: A review Radiation Physics and Chemistry, 80, 1–10.

[4] Singh V., Gundu Rao, T.K.(2008), Studies of defects in combustion synthesized europium –doped LiAl5O8 red phosphor, J. Solid State Chemistry,181,1387-1392.

[5] Suryamurthy N., Panigrahi B.S, Natarajan A , (2005),Luminescence study of iron dopedlithium aluminate phosphor, Material Science and Engineering ,A 403,182-185.

[6] Daling L., Chunxiang Z, Zouping D, Guozhen L ,"(1999), Thermoluminescence characteristics of

MgSO4:Dy,Mn phosphor, Radiation Measurements, 30, 59-63.
[7] Han S. D., S.P. Khatkar S.P. Taxak , V.B., Kumar D, Park J.Y.,(2006),combustion Synthesis and luminescent properties of Eu3+ LnAlO3 (Ln= Y and Gd) phosphors, Materials Science and Engineering B, 127, 272–275.
[8] Zhydachevskii . Ya., Suchocki A., Berkowski M., Bilski P., Warchol S. (2010), CharacterizationofYAlO3:Mn2þ thermo luminescent detectors Radiation Measurements 45, 516–518.
[9] Zhou J. ,Wangn Y., Liu B., Liu (2001), Photoluminescen properties of BaMgAl10O17:Eu3+ phosphor prepared by the flux method, J. of Physics and Chemistry of Solids, 72 ,995–1001.
[10] Dongdong Jia et al., (2007), Trapping processes of 5d electrons in Ce3+ doped SrAl2O4 J. Luminescence ., 122- 123, 311-314.
[11] Singh V. et. al., (2006) Gundu Rao, T.K., Zhu J.J., , Preparation, luminescence and defect studies of Eu2+-activated strontium hexa-aluminate phosphor prepared via combustion method, J. of Solid State Chemistry. 179 ,2589-2594.
[12] Wanjun T., Donghua C., Ming W.,(2009) , Luminescence studies on SrMgAl10O17:Eu, Dy phosphor crystals, Optics & Laser Technology, 41 ,81– 84.
[13] Ekambaram, S., Patil K.(1997),Synthesis and properties of Eu3+ activated blue phosphor, J. Alloys Compd. ,248, 7-12
[14] Chen, R., 1969. Glow curves with general order kinetics. *J. Electrochem. Sco: Solid Atite Sci*. ,16, 1254-1257.

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	$1x10^5$	$2.5x10^6$	$4.5x10^7$

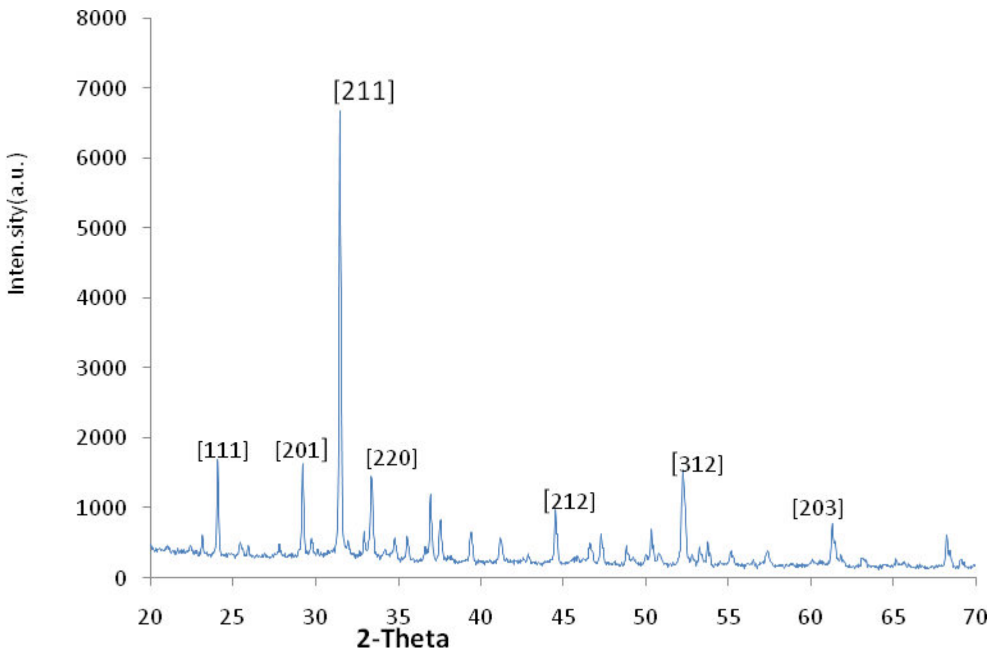

Figure 1. XRD pattern of $CaYAl_3O_7$

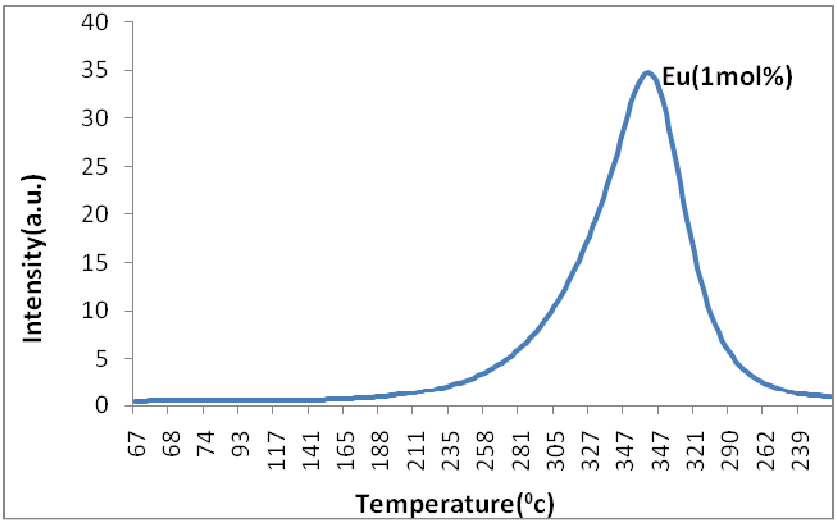

Figure 2(a). TL glow curve of $CaYAl_3O_7$:Eu3+

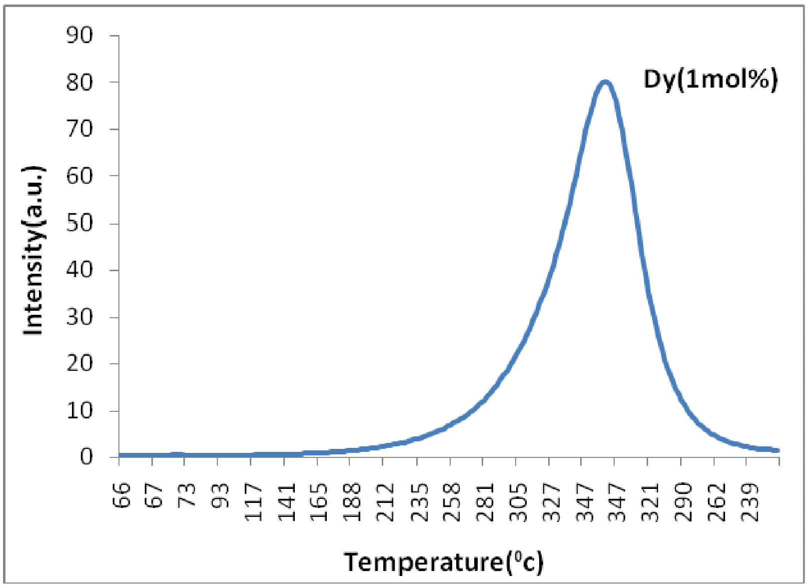

Figure 2(b). Tl glow curve of $CaYAl_3O_7:Dy^{3+}$

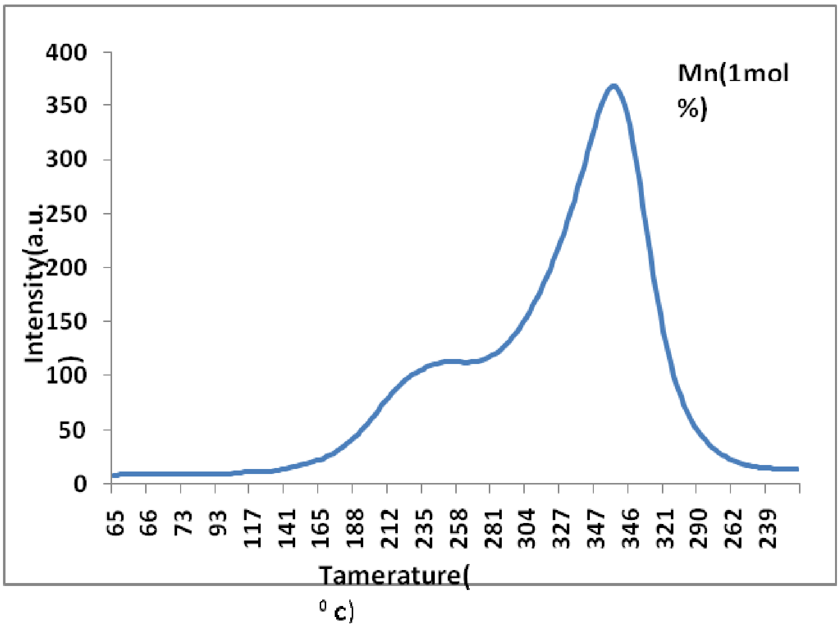

Figure 2(c). TL glow curve of $CaYAl_3O_7{:}Mn^{2+}$