Photoluminescence and Thermoluminescence Properties of Rare Earth Doped CaAl$_2$Si$_2$O$_8$ phosphors

Geetanjali Tiwari[1], Nameeta Brahme,[2] Ravi Sharma[3], D. P. Bisen[4], Sanjay Kumar Sao[5]

[1][5] *Research Scholar, School of Studies in Physics and Astrophysics, Pt. Ravishankar Shukla*

University Raipur, Chhattisgarh, India

[2][4] *Professor, School of Studies in Physics and Astrophysics, Pt. Ravishankar Shukla*

University Raipur, Chhattisgarh, India

[3] *Department of Physics, Arts and Commerce Girls College, Devendra Nagar,*

Raipur, Chhattisgarh, India

--***---

Abstract - *Tbe doped Calcium alumino silicate (CaAl$_2$Si$_2$O$_8$) phosphor was synthesized by combustion method at initiating temperature of 700^{0}C, using urea as a reducer. XRD, Thermoluminescences, absorption spectra, FTIR and Thermoluminescences spectra were recorded. The X-ray diffraction pattern indicates that the crystal structure of CaAl2Si$_2$O$_8$is mainly triclinic phase. The absorption spectra shows that the absorption edge is at λ = 240nm. The TL intensity was* **recorded for different exposure time of γ** *-irradiation and it was observed that TL intensity is maximum for 1180Gy exposure time. We have calculated the trap depth by initial rise methods. The TL emission spectra has maximum at 540 nm. Mechanism involved in TL is also suggested.*

Key Words: Silicate materials, Combustion Synthesis, Thermoluminescence, Photoluminescence

1. INTRODUCTION

Until 1996, the majority of persistent luminescent applications was based on ZnS doped with copper and cobalt [1, 2]. This material emits a greenish broad-band spectrum centered around 540 nm, which remains visible for several hours after the end of the excitation. However, the afterglow of this material is relatively weak, and it was common to add small amounts of radioactive tritium or promethium in order to sustain the luminescence [3]. In most luminescent materials, the decay of the light emission lasts no longer than a few milliseconds after the end of the excitation. On the contrary, persistent phosphors can continue emitting light for minutes or hours. This phenomenon is used in safety signage, dials and displays and decoration [4], but also in less obvious applications, such as night-vision surveillance [5] or in vivo medical imaging [6]. Since 1996, this ZnS-based

phosphor has been rendered obsolete by Eu^{2+} doped strontium and calcium aluminates exhibiting a much brighter and long-lasting afterglow. The sulfides have the longest recorded history of all persistent luminescent compounds. In fact, the famous Bologna Stone, discovered by Vincenzo Casciarolo in 1997 [7], consisted mainly of copper-doped BaS [8]. Nowadays, the use of ZnS: Cu has much decreased in favor of SrAl2O4:Eu, Dy. The focus has mainly shifted to the oxysulfides, especially Y$_2$O$_2$S:Eu^{3+}, Ti^{4+}, Mg^{2+}, which is currently one of the best red-emitting persistent phosphors. Nevertheless, its afterglow intensity is much weaker than the Eu^{2+}doped aluminates or silicates [9]. The oxides make up the majority of persistent luminescent compounds, but compared to the Eu^{2+}-based materials, many more host compositions (also those in which Eu^{2+} cannot be stabilized) have been explored. Besides the aluminates, also the stannates, titanates and germanates show some interesting properties. The longest afterglow durations have been reached in Ce^{3+}doped CaAl$_4$O$_7$, CaAl$_2$O$_4$, SrAl$_2$O$_4$ and BaAl$_2$O$_4$, all with a blue emission color. The lanthanide ions doped alkaline earth silicates are an important class of phosphorescence materials because of their high quantum efficiency in visible region, long persistence of phosphorescence, good stability, color purity and good chemical, thermal and radiation resistance [10]. The potential benefit of lanthanide ions as activators has now well established in the field of luminescence [11]. Different activators contribute significantly in tailoring the afterglow properties of phosphors from few seconds to many hours [12]. The emission spectra of lanthanide ions almost remain the same in different host, but the luminescent efficiency, chemical stability and durability largely depends on the physical properties of host selected [13]. Ca$_2$Al$_2$SiO$_7$ exhibits a stronger initial intensity and longer duration of afterglow due to the higher liberated probability of the trapped carriers [14]. Kodama has revealed that the Ca$_2$Al$_2$SiO$_7$:Ce^{3+} single crystal has a long

afterglow emission and can be used in tunable solid state laser materials [15]. The present communication deals with synthesis and characterization of silicate based phosphors. Lanthanide ions doped luminescent phosphors namely $CaAl_2Si_2O_8$:Tb^{3+} has been prepared and their Photoluminescence and Thermoluminescence studies are being communicated in this paper. In this work an attempt has been made to prepare the silicate based phosphor activated with rare earth ions. The phosphor of $CaAl_2Si_2O_8$:Tb^{3+} was synthesized by combustion method. To best of our knowledge it is not reported earlier.

2. EXPERIMENTAL PROCEDURES
2.1. SYNTHESIS

Tb^{3+}doped $CaAl_2Si_2O_8$ phosphor were prepared by combustion synthesis. The starting material include $Ca(NO_3)_2.4H_2O$, $Al(NO_3)_3.9H_2O$, SiO_2, $Tb(NO_3)_3.6H_2O$ and NH_2CONH_2 . To prepare $CaAl_2Si_2O_8$:Tb^{3+}phosphor, stoichiometric composition of the metal nitrates (oxidizers) and urea(fuel) were calculated using the total oxidizing and reducing valences of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. The chemical reaction used for the combustion reaction is as follows:

$Ca(NO_3)_2.4H_2O$ + $Al(NO_3)_3.9H_2O$ +SiO_2+ $Tb(NO_3)_3.6H_2O$

+ NH_2CONH_2----------$\rightarrow$ $CaAl_2Si_2O_8$ + N_2 + H_2O + CO_2
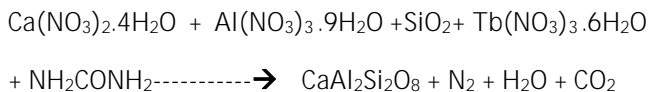
2.2. CHARACTERIZATION

X -ray diffraction of the prepared phosphor was recorded **in a wide range of Bragg angle 2θ using a Bruker D8** advanced X-ray diffraction measuring instrument with Cu **target radiation (λ = 0.154056nm). Absorption spectra** were recorded using Shimadzu UV-1700 UV-Visible spectrophotometer. The stretching mode frequencies data were collected using Perkin Elmer Spectrum 100 FTIR spectrometer and the elemental composition on the surfaces of the phosphor powders were monitored by the PHI 5400 Versaprobe scanning X-ray photoelectron spectrometer. The thermoluminescence (TL) data were collected using a Thermoluminescence Reader (Integral-Pc Based) Nucleonix TL 1009I. Tb^{3+} doped $CaAl_2Si_2O_8$ phosphorwere prepared at temperature of 700ºC. Photoluminescence (PL) data were collected using by RF-5301PC SHIMADZU spectrofluorophotometer (RF-5301PC). Emission and excitation spectra were recorded using a spectral slit width of 1.5nm.

3. RESULTS AND DISCUSSION
3.1 XRD

The XRD patterns of $CaAl_2Si_2O_8$:Tb^{3+} are shown in Fig.1. The diffraction peaks of $CaAl_2Si_2O_8$:Tb^{3+} samples are found

to be in good agreement with corresponding standard data for triclinic phase of $CaAl_2Si_2O_8$ (JCPDS 41–1486; space group: P1 No.2) The diffraction intensity is maximum for **(2 1 1) plane having 2θ = 27⁰.**

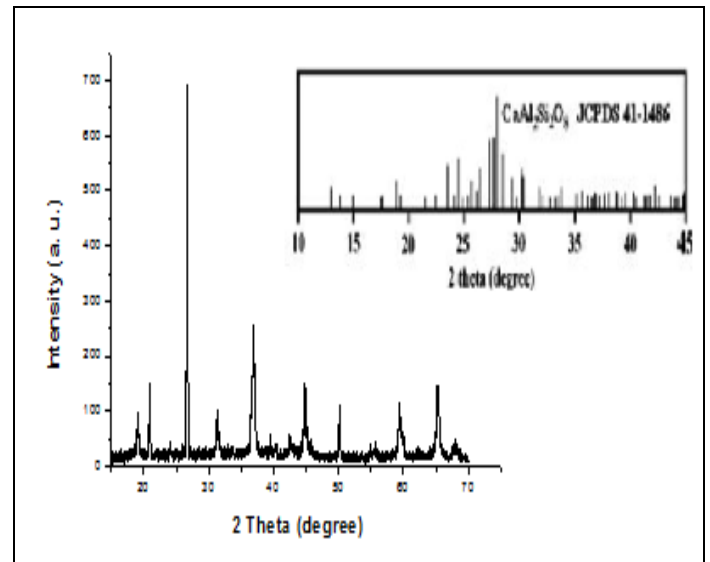Fig.1: X-ray diffraction pattern of $CaAl_2Si_2O_8$: Tb^{3+} Phosphor prepared by 700ºC Matched with JCPDS data file no. 41-1486

3.2 ABSORPTION SPECTRA

An absorption spectrum can be quantitatively related to theamount of material present using the Beer-Lambert law. Determining the absolute concentration of a compound requires knowledge of the compound's absorption coefficient. The absorption coefficient for some compounds is available from reference sources, and it can also be determined by measuring the spectrum of a calibration standard with a known concentration of the target.
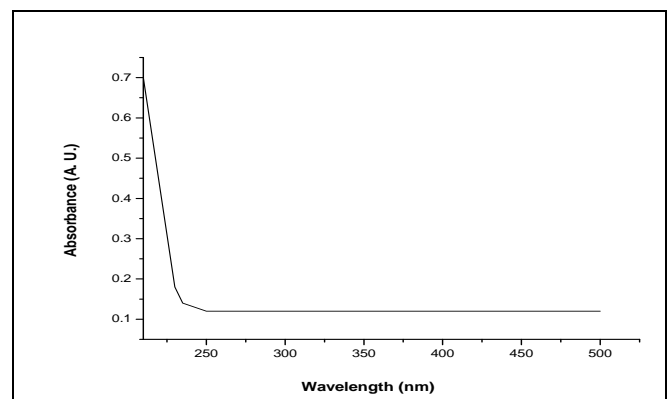

Fig.2: Absorption spectra of $CaAl_2Si_2O_8$:Tb^{3+}

The above Fig.2 shows the optical Absorption spectra of $CaAl_2Si_2O_8:Tb^{3+}$ prepared at initiating temperature 700^0C in range of 230nm-530nm. The absorption edge is found at λ= 245nm and the band gap is calculated by the following relation

$$E_g = hc/ \lambda,$$

$$E_g = 5.06 \text{ eV}$$

From this calculation, it is found that the band gap of the $CaAl_2Si_2O_8:Tb^{3+}$ is 5.06 eV. Since the order of the band gap ~5eV of the material exhibit that is insulator type material, so the $CaAl_2Si_2O_8:Tb^{3+}$ is exactly insulator type material. The estimated absorption edge at λ= 245nm.

3.3 FTIR

Fig. 3 : FT-IR spectra of $CaAl_2Si_2O_8:Tb^{3+}$
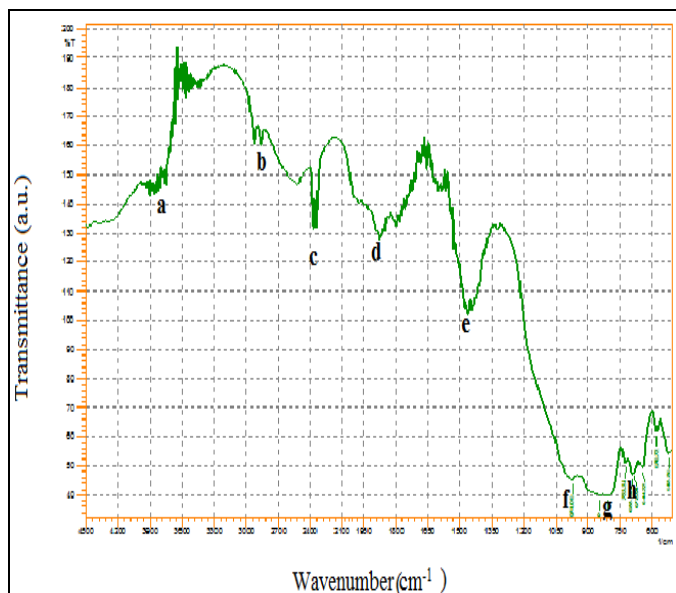
Fig.3 shows the FT-IR spectra of $CaAl_2Si_2O_8:Tb^{3+}$ the first range 3600-3800cm^{-1} (peak a) centered at 36500cm^{-1} is originated from O-H group stretching mode, the most intense transmittance band at around 1350-1500cm^{-1} (peak e) centered at 1400cm^{-1} originate from the absorption of H_2O and NO_3 groups and the peaks in the region 750-1050cm^{-1} (peak g). The band at around 1037cm^{-1} may be attributed to the asymmetric stretching vibration modes of Si-O bond involving bridging oxygen and the peak in the region of 500-750cm^{-1} (peak h) show the stretching and bending modes of AlO_4 and SiO_4 band The IR absorption due to tetrahedral AlO_4 and SiO_4 units can be assigned based on four kinds of modes consisting of symmetric stretching, symmetric bending, anti-symmetric bending and anti-symmetric stretching.

3.4 TL STUDIES WITH Γ IRRADIATION

Thermoluminescence is one of the most useful methods to study the trap level in long lasting phosphors and the measurement of the TL curves could reveal some new facts about the persistent luminescence mechanisms too.
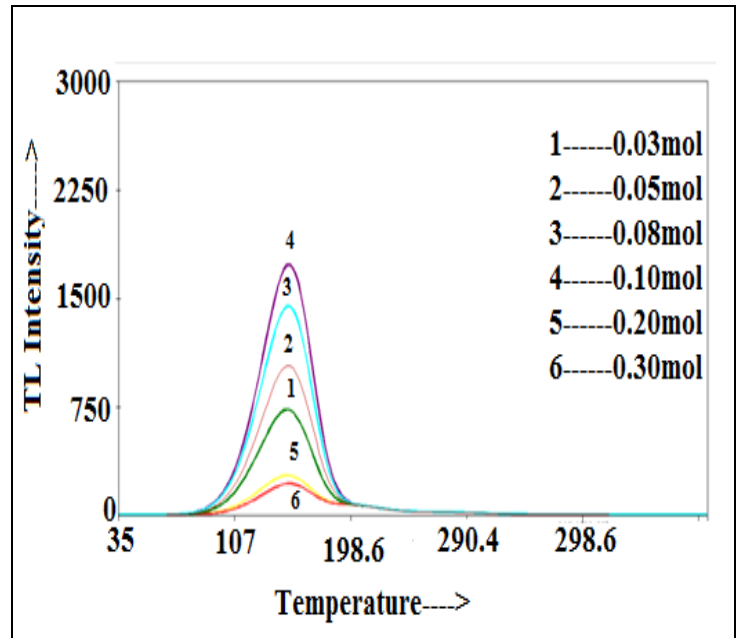

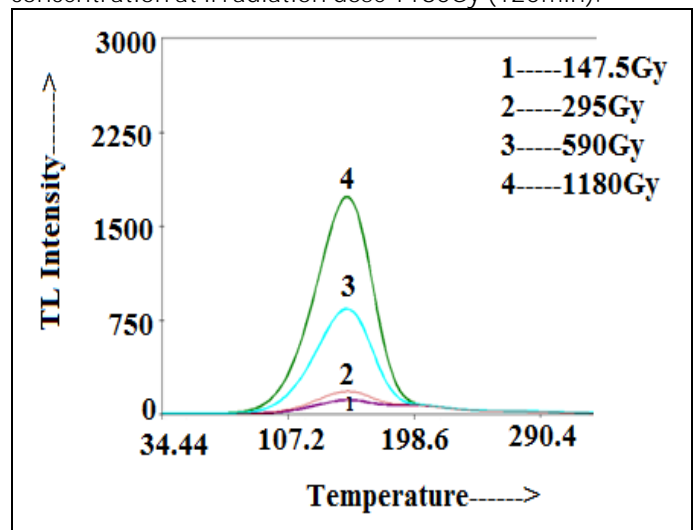Fig. 4(a): TL glow curve of γ- irradiated for different concentration at irradiation dose 1180Gy (120min).

Fig. 4(b): TL glow curve of γ- irradiated for different irradiation time.

Fig.4(a) shows the TL glow curve of γ- irradiated for different concentration at irradiation dose1180Gy (120min.). It is clear that the TL intensity increases with increasing concentration of Tb and attains a maximum value for 10 mole % and it decreases with further increase in concentration of Tb. Because of an increase in the activator concentration, the distance between the

activators gets shorter. The interaction of the ions increases and the energy transfer comes into being. On the other hand, a decrease in the activator concentration decreases the energy stored by the ions. Consequently, there is an optimum in the activator concentration, resulting from the trade-off of the above two factors. As is seen from fig. the favorable concentration of Tb^{3+} in $CaAl_2Si_2O_8$ phosphor is about 10 mole% (relative to Ca^{2+}). Fig.4(b) shows the TL **glow curve of γ**- irradiated at different irradiation time for 10mole% concentration of doping material. The TL intensity of $CaAl_2Si_2O_8:Tb^{3+}$ was **recorded after irradiation with γ light for different interval** of time which has single peak at 151.9^0C suggesting existence for trapping level. Fig. 4(b) shows that the TL intensity increases with increase in **γ exposure time up to 1180Gy.**

INITIAL RISE METHOD

The activation energy of $CaAl_2Si_2O_8:Tb^{3+}$ (10mole %) are calculated by initial rise method. The initial-rise method can be used when the sample has a single glow curve or when there is no overlapping of glow peaks belonging to different trapping states. The method is based on the fact that as the glow curve initially begins to rise, the density of unoccupied recombination centers and the density of trapped electrons remain approximately constant, and hence the TL intensity is strictly proportional to exp(-E/kT).
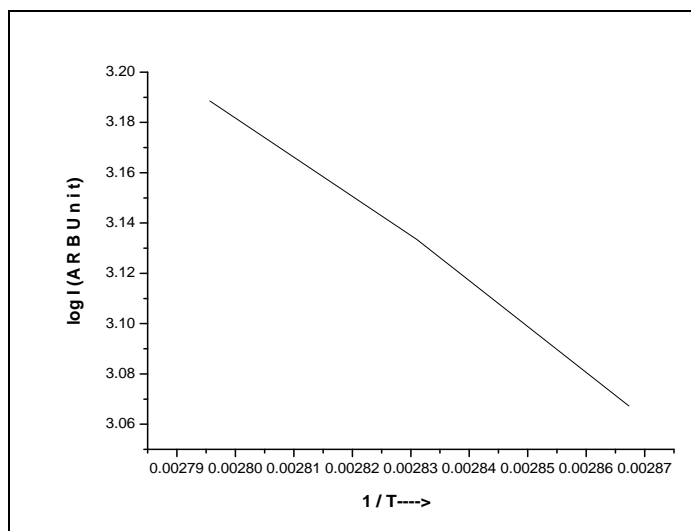

Fig. 4(c): 1/T Vs log (intensity) of $CaAl_2Si_2O_8:Tb^{3+}$ (10 mole%)

Fig.4 (c) shows graph of ln (TL) Vs 1/KT for TL glow peak of fig 4(b). Applying initial rise method, a straight line is obtained. From the slope of line, activation energy E was evaluated. The activation energy was found 0.28eV.

HALF WIDTH METHOD

The shape of the TL glow curve is strongly influenced by the order of the kinetics. In half-width methods, the temperatures T_m ,T_1 and T_2 are respectively, the peak temperature and temperatures on the lower and upper sides corresponding to half the peak intensity shown in fig.3 and dependent on the shape of the glow curve, are utilized to form equations to relate E to all or some of these temperatures. Using only the ascending part of a glow peak, one finds the value of E for the first order kinetics.

$$E = (1.51\ T_m\ T_1)/\ (\ T_m - T_1)$$

Whereas when the descending part of the glow peak is used the value of E is expressed as

$$E = kT_m^2\ /\ (\ T_2 - T_m)$$

The activation energy of $CaAl_2Si_2O_8:Tb^{3+}$ was found to be 0.25eV and frequency factor $S = 0.120*10^{12}$
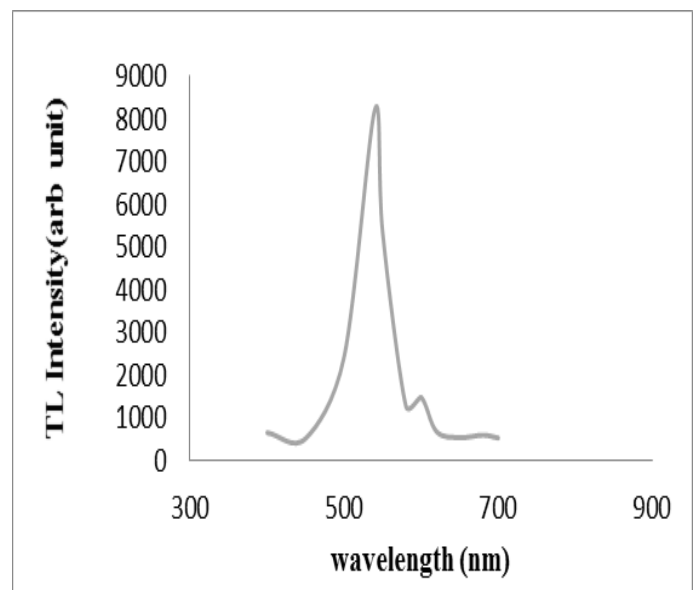
3.4 TL SPECTRA

Fig. 5: TL spectra of $CaAl_2Si_2O_8:Tb^{3+}$ (10 mole %)

Fig. 5 shows that the TL spectra of $CaAl_2Si_2O_8:Tb^{3+}$ exhibits a broad emission band centered around 540nm. These bands result from the $^5D_4 \rightarrow {}^7F_5$ transition configuration of Tb^{3+} ions. It is reported that electron traps in these crystals may be the O^{2-} vacancy and hole traps may be the Al^{3+} vacancies or the bridging oxygen Al – O – Si(Al) [10]. The UV light excites the $^7F_5$ electron of Tb^{3+} to the $^5D_4$ energy levels. The excited electron is expected to be transferred to the nearby O^{2-} vacancy created at the O(2) sites, for example through downward hopping . The electron immediately relaxes to the stable states and is trapped. On

the other hand, the hole produced at Tb^{3+} by the UV excitation moves toward a Si^{4+} vacancy and is self trapped at an Al(2) site, forming Al^{4+} through the electron phonon interaction. Such trapped electron and self – trapped hole are strongly associated with the O^{2-} and Si^{4+} vacancies produced under the crystal growth process. The holes move back to Tb^{3+} in the crystal by thermal excitation and are retrapped at Tb^{3+}. Heating of the phosphor leads to detrapping of the traps and radiative recombination at Tb^{3+} give rise to thermoluminescence. $CaAl_2Si_2O_8:Tb^{3+}$ emits strong green emission.

3.5 PHOTOLUMINESCENCE (PL)

PL characteristics (Fig.6a & Fig.6b) exhibit typical green emission (545nm) when excited by UV- radiation. The appearance of green emission indicates that the activator ion Tb is in trivalent Tb^{3+} state
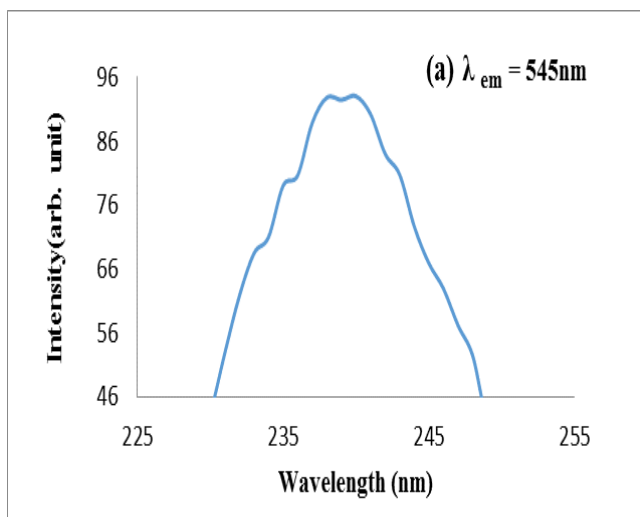

Fig.6(a): Excitation spectra of $CaAl_2Si_2O_8:Tb^{3+}$ (10 mole %) at 240nm
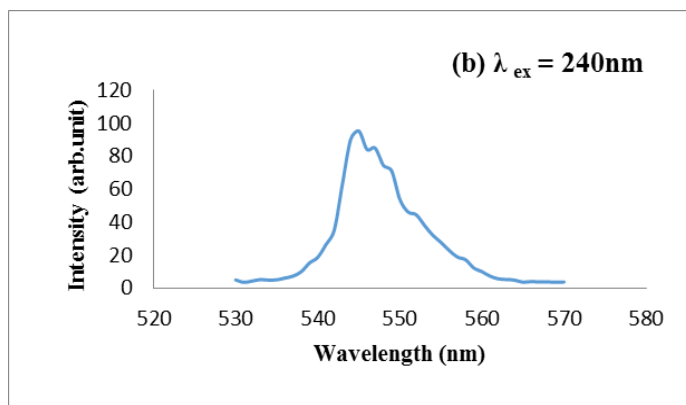

Fig.6 (b): Emission spectra of $CaAl_2Si_2O_8:Tb^{3+}$ (10 mole %) at 545 nm.

The excitation and emission spectra of Tb^{3+} - activated $CaAl_2Si_2O_8$ are given in Fig.6 (a) and Fig.6(b) respectively. The excitation spectra consist of a strong absorption band centered 240nm in the short UV in the range of 200-280nm and f-f absorption lines of Tb^{3+} in the longer wavelength region at the range of 230-250nm (Fig 6a). The former is due to spin-allowed $4f^8$ -$4f^7$ 5d transitions, with their exact position being dependent on the crystal field of the lattice. The emission spectra shows emission at 545 nm which is due to $^5D_4 \rightarrow {}^7F_5$ transition of Tb.

4. CONCLUSIONS

We have investigated the Thermoluminescence and **photoluminescence phenomena in the** γ-irradiated $CaAl_2Si_2O_8:Tb^{3+}$ phosphor (size=50.85nm). From XRD analysis the compound is single phase $CaAl_2Si_2O_8:Tb^{3+}$ with triclinic structure. The phosphor was prepared by combustion method which appears to be a more feasible method for production at initiating temperature 700^oC.The absorption spectra show the absorption edge at $\lambda = 245nm$ **hence the band edge** E_g at 5.06 eV for $CaAl_2Si_2O_8:Tb^{3+}$ phosphor. The TL intensity depends upto **the** γ-dose and it is maximum for 1180 Gy. Further **increasing the** γ-dose the TL intensity decreases. Hence $Ca_2Al_2SiO_7:Tb^{3+}$ phosphor could be used for TL dosimetry upto 1180Gy. Photoluminescence exhibit green emission when excited by UV-light indicating the trivalent state of Tb.

ACKNOWLEDGEMENT

REFERENCES

[1] **Smet, P.F. , Poelman, D., Hehlen, "Introduction: Persistent Phosphors".** Opt. Mater. Express, 2, 452–454, 2012.

[2] **Pan, Z., Lu, Y.Y., Liu, F. "Sunlight**-Activated Long-Persistent Luminescence in the Near-Infrared from Cr^{3+}Doped Zinc Gallogermanates. Nat. Mater. 2012, 11, 58–63.

[3] Le Masne de Chermont, Q.; Chanéac, C.; Seguin, J.; Pellé, F.; Maîtrejean, S.; Jolivet, J.P.; Gourier, D.; Bessodes, M.; Scherman, D. Nanoprobes with Near-Infrared Persistent Luminescence for in vivo Imaging. Proc. Natl. Acad. Sci. USA 2007, 104, 9266–9271.

[4] Matsuzawa, T.; Aoki, Y.; Takeuchi, N.; Murayama, Y. A New Long Phosphorescent Phosphor with High

Brightness, $SrAl_2O_4:Eu^{2+}$, Dy^{3+}. J. Electrochem. Soc. 1996, 143, 2670–2673.

[5] Yen, W.M.; Shionoya, S.; Yamamoto, H. Section 12.3.1, History of Long Persistent Phosphors. In Phosphor Handbook, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2007.

[6] Lastusaari, M.; Laamanen, T.; Malkamäki, M.; Eskola, K.O.; Kotlov, A.; Carlson, S.; Welter, E.; Brito, H.F.; Bettinelli, M.; Jungner, H.; Hölsä, J. The Bologna Stone: History's First Persistent Luminescent Material. Eur. J. Mineral. 2012, 24, 885–890.

[7] Poelman, D.; Avci, N.; Smet, P.F. Measured Luminance and Visual Appearance of Multi-Color Persistent Phosphors. Opt. Express 2009, 17, 358–364.

[8] Liu, F.; Yan, W.; Chuang, Y.J.; Zhen, Z.; Xie, J.; Pan, Z. Photostimulated Near-Infrared Persistent Luminescence as a New Optical Read-Out from Cr3+-Doped LiGa5O8. Sci. Rep. 2013, 3, 1554:1–1554:9.

[9] Bessière, A.; Jacquart, S.; Priolkar, K.; Lecointre, A.; Viana, B.; Gourier, D. ZnGa2O4:Cr3+: A New Red Long-Lasting Phosphor with High Brightness. Opt. Express 2011, 19, 10131–10137.

[10] Haiyan Jiao and Yuhua Wang, "Ca2Al2SiO7: Ce^{3+}, Tb^{3+} A White–Light Phosphor Suitable for White–Light-Emitting Diodes" Journal of the Electrochemical Society, 156 (5) J117-J120 (2009).

[11] CAI Jinjun, PAN Huanhuan and WANG Yi, "Luminescence properties of red-emitting $Ca_2Al_2SiO_7:Eu^{3+}$ nanoparticles pre- pared by sol-gel method" RARE METALS Vol. 30, No. 4, p. 374, 2011.

[12] G.J. Talwar, C.P. Joshi, S.V. Moharil Ã, S.M. Dhopte, "Combustion synthesis of $Sr_3MgSi_2O_8:Eu^{2+}$and $Sr_2MgSi_2O_7:Eu^{2+}$phosphors" Journal of Luminescence 129 1239–1241, (2009).

[13] Haoyi Wu, Yihua Hu, Guifang Ju, Li Chen, Xiaojuan Wang, Zhongfu Yang "Photoluminescence and thermo-luminescence of Ce^{3+} and Eu^{2+} in $Ca_2Al_2SiO_7$ matrix" Journal of Luminescence 131, 2441–2445 (2011).

[14] Le Boulanger P., Doualan J.L., Girard S., Margerie J., Mon corge R, and Viana B. "Excited-state absorption of Er^{3+} in the $Ca_2Al_2SiO_7$ laser crystal" J. Lumin. 86 (1): 15 2011.

[15] Nebiyu Gemechu Debelo, "The role of trap depth and trap centers in thermoluminescence from semiconductor nanostructures" Lat. Am. J. Phys. Educ. Vol. 6, No. 2, June 2012.

BIOGRAPHIES

Geetanjali Tiwari[1]
Ph. D reaserch scholar,
SoS in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur, C.G. 4 years of research experience as a project fellow from CCOST, Raipur, C.G. ,India

Dr. Nameeta Brahme[2] is working as an Prof in SoS in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur, C.G. And she has published many research papers in international and national journals.

Dr. Ravi Sharma[4] is working as an Assistant Prof. in Department of Physics, Govt. Arts and Commerce Girls College, Devendra Nagar, Raipur, C.G. India And he has published many research papers in international and national journals.

Dr. D. P. Bisen[3] is working as an Prof in SoS in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur, C.G.And he has published many research papers in international and national journals.

Sanjay Kumar Sao Ph.D reaserch scholar, SoS in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur, C.G. ,He is GET, NET and SET qualified.