Photoluminescence (PL) and Thermoluminescence (TL) studies of γ-irradiated CaAl₂O₄: Eu²⁺ phosphor synthesized by combustion technique

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Abstract - *Rear earth Eu²⁺ activated alkaline earth aluminate CaAl₂O₄: Eu²⁺ phosphor synthesized by combustion technique using urea as a reducer at temperature of 600°C. Photoluminescence (PL) and Thermoluminescence (TL) properties of γ-irradiated Eu doped calcium aluminate have been studied. In photoluminescence (PL) spectrum a broad peak of Eu²⁺ ion was observed in blue region at 441 nm, under350 nm excitation due to transition from the 4f⁶5d¹ to the 4f⁷ configuration of the Eu²⁺ ion. Optimum intensity of photoluminescence (PL) is found for 0.05 mol% concentration of Eu²⁺. Thermoluminescence (TL) studies have been done for different concentrations of Eu. It was found that initially the peak TL intensity increases with increasing concentration of Eu in CaAl₂O₄ host and attains maximum value for 0.05 mol% concentration and decreases with further increase in the doping concentration due to concentration quenching.*

Key Words: *Thermoluminescence (TL), Photoluminescence (PL), Solution-Combustion, Rear Earth, CaAl₂O₄: Eu²⁺.*

1. INTRODUCTION

Alkaline earth aluminates MAl_2O_4 doped with Eu^{2+} activator ion possess safer, chemically stable and intense photoluminescence (PL) in visible region [1,2], compared to the conventional sulfide-based phosphors. These properties makes them use in many applications, such luminous paints in highway, airport, buildings and ceramics products, in textiles, dial plate of glow watch, warning signs and the escape routes [3]. Rare earth and non-rare earth inorganic phosphors are widely used in a variety of applications, such as lamp industry, radiation dosimetry, X-ray imaging and color display [4].Various aluminates are used as host for doping rare earth ions in luminescent applications.

$CaAl_2O_4$ is a member of the large family of stuffed tridymite tetrahedral framework structure, where there are three Ca^{2+} sites. One Ca^{2+} site is coordinated with nine oxygen atoms [5]. Recently many studies on phosphors with calcium aluminate as a host based on their persistent luminescence and photoconductivity spectrum have been reported [6]. Many phosphors such as $CaAl_2O_4:Eu^{2+}$, Dy^{3+} [7] and $CaAl_2O_4:Ce^{3+}$ [8] were developed for their photoluminescence and high chemical stability.

Thermoluminescence is the emission of light from an insulator or semiconductor when they are thermally stimulated following the previous absorption of energy from radiation [9]. It is very important and convenient method of investigating the nature of traps and trapping level in crystals [10].

The synthesis of oxide phosphors has been achieved by a variety of routes: Solid-state reaction [11], sol-gel technique [12], micro-wave heating technique [13], hydroxide precipitation [14], an electric arc method [15] and combustion synthesis [16-18]. Combustion process is very simple, safe, energy saving and takes only a few minutes. The method makes use of the heat energy liberated by the redox exothermic reaction at a relative low igniting temperature between metal nitrates and urea as fuel. It was found that the $CaAl_2O_4:Eu^{2+}$ prepared at initiating temperature 600°C exists as a single phase monoclinic structure [19].

Thermo luminescent materials are used as passive dosimeters in a wide range of radiological applications. Alkaline earth aluminate ceramics are important host materials that have been prepared and studied by several researchers for luminescence applications. Several reports dealing with the luminescence studies of $SrAl_2O_4$, $BaAl_2O_4$ and $MgAl_2O_4$ are available in the literature [13-14]. However, there are very few researchers reported $CaAl_2O_4$ as a TL material. In the present work, we report the Thermoluminescence properties of gamma irradiated ($CaAl_2O_4$: Eu^{2+}) phosphor to find out its suitability in dosimetry applications.

In this paper, a facile combustion process was chosen to prepare Eu^{2+} doped $CaAl_2O_4$ phosphor. Thermoluminescence (TL) and Photoluminescence (PL) properties of γ-irradiated Eu^{2+} doped $CaAl_2O_4$ phosphors have been investigated.

2. EXPERIMENTAL

The flow chart for a quick material screening and material elaboration shown in figure 1.Analytical grade calcium nitrate $Ca(NO_3)_2$, aluminum nitrate $Al(NO_3)_3.9H_2O$, Europium oxide Eu_2O_3 and urea $CO(NH_2)_2$ were used as the staring materials. The starting materials were weighted according to the stoichiometry. First of all Eu_2O_3 was converted into $Eu(NO_3)_3$ by mixing Eu_2O_3 into 2 ml of dil. HNO_3. Then weighed quantities of each nitrate and urea were mixed together and crushed into mortar for 1 hour to form a thick paste. The resulting paste was transferred to crucible and introduced into a vertical cylindrical muffle furnace maintained at 600ºC initiating temperature. Initially the mixture boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases (oxides of carbon, nitrogen and ammonia). The process being highly exothermic continues and the spontaneous ignition occurs. The solution underwent smoldering combustion with enormous swelling, producing white foamy and voluminous ash. The foamy product can easily be milled to obtain the precursor powder.

The crystalline structure of the synthesized samples was investigated by X-ray diffraction analysis (XRD model D2 PHASER, Bruker AXS) using Cu/Kα radiation (λ = 1.54060Å). Data have been collected by step scanning 2θ from 10° to 80° and 9.6 s swept time at each step at room temperature. In order to study the surface morphology of phosphor scanning electron micrograph (SEM) was taken

on a JOEL-JSM-6390A analytical scanning electron microscopy. PL was recorded using fluorescence spectrophotometer (Shimadzu RF-5301 XPC). For thermoluminescence measurement, samples were irradiated with γ-rays using a ^{60}Co source having an exposure rate of 0.59×10^3 Gy/hr. A routine TL setup (Nucleonix TL 1009I) was used for recording TL glow. Absorption spectrum was recorded using Shimadzu UV-1700 UV- visible spectrophotometer. For the measurement of TL spectra of sample interference filters of different wavelength were used.
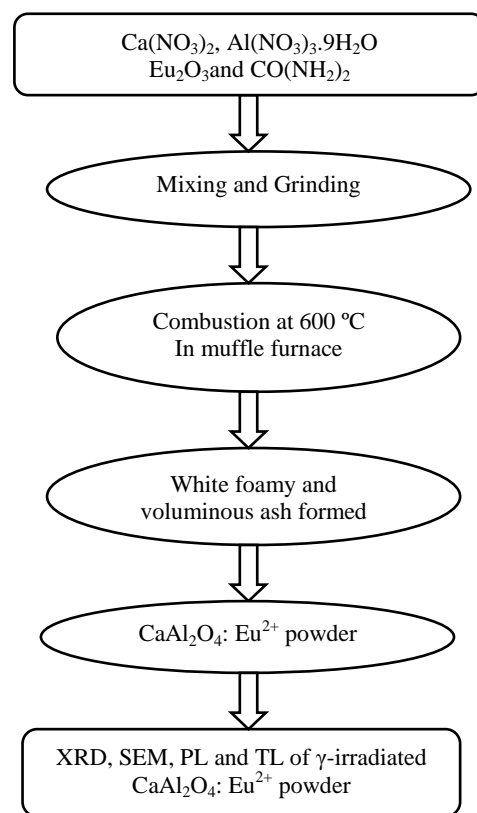
Fig. 1: Flowchart for the preparation and characterization of $CaAl_2O_4$: Eu^{2+} phosphor

3 RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

The XRD pattern of the prepared $CaAl_2O_4$:Eu^{2+} synthesized by combustion process at initiating temperature of 600ºC is shown in fig. 2. All the diffraction peaks in figure 2 are in good agreement to the pure monoclinic phase structure of $CaAl_2O_4$. Calculated lattice parameters are: a = 8.700, b =

8.0920, c = 15.19100 and β = 90.170. The XRD pattern matched well with that reported for $CaAl_2O_4$ (JCPDS File No. 00-70-0134). Furthermore, a small amount of doped rare earth ions has almost no effect on $CaAl_2O_4$ phase composition.

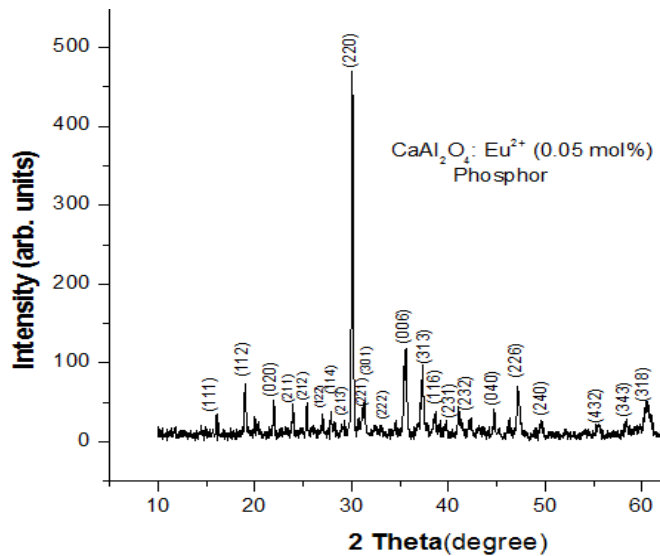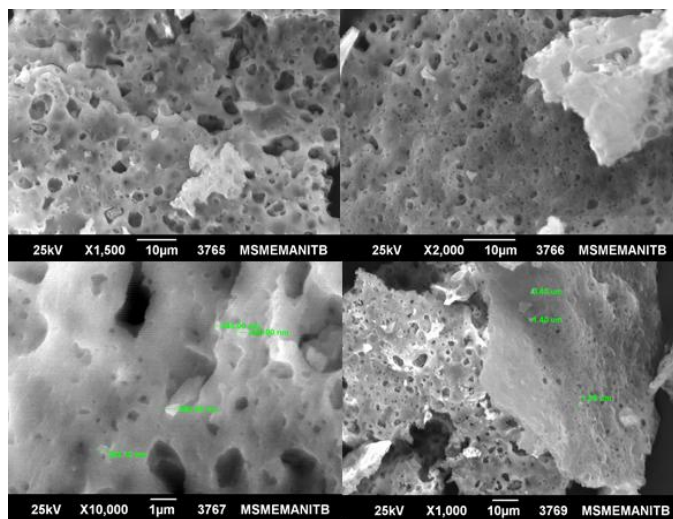**Fig. 2:** X-ray diffraction (XRD) pattern of $CaAl_2O_4$:Eu^{2+} (0.05 mol %) phosphor.

Fig. 3: SEM photograph of $CaAl_2O_4$: Eu^{2+} (0.05 mol %) phosphor.

3.2   Morphology Analysis

Figure (3) shows the SEM micrograph of the sample reflects the foamy and agglomerate particle nature of the powder. The foamy structure of monoclinic $CaAl_2O_4$: Eu^{2+} reflects the inherent nature of the reaction. Urea enhances

combustion and this process results in crystal facets growing in different directions. The surface of the powder shows lots of voids and pores, which may be formed by the evolved gases during combustion. The non-uniform and irregular shapes of the particle can be attributed to the non-uniform distribution of temperature and mass flow in the combustion flame.

3.3   Photoluminescence (PL) spectra

Figure 4(a) shows the excitation spectra of $CaAl_2O_4$: Eu^{2+} phosphor. In excitation spectra a broad peak centered at 353 nm is observed. The Photoluminescence emission spectra of synthesized phosphors with different doping concentration are shown in figure 4(b). The PL emission spectra of phosphors were recorded at the excitation wavelength λ_{ex} = 350 nm. Generally the access concentration of activators (rare earth elements) quenches the Photoluminescence, so it is necessary to experimentally find the critical concentration of Eu^{2+} to optimize the luminescence efficiency of $CaAl_2O_4$: Eu^{2+} under UV excitation. The emission spectra of $CaAl_2O_4$: Eu^{2+} phosphor show one strong peak at 441 nm under 350 nm excitation. A broad peak of Eu^{2+} ion was observed in the ultra violet region and attributed to 4f → 5d electronic transition. The observed emission peak at 441 nm is due to the transition of Eu^{2+} from excited state of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ of $4f^7$configuration. The optimized PL intensity is found for 0.05mol % concentration of Eu in $CaAl_2O_4$ host. For higher doping concentration PL intensity decreases due to concentration quenching.

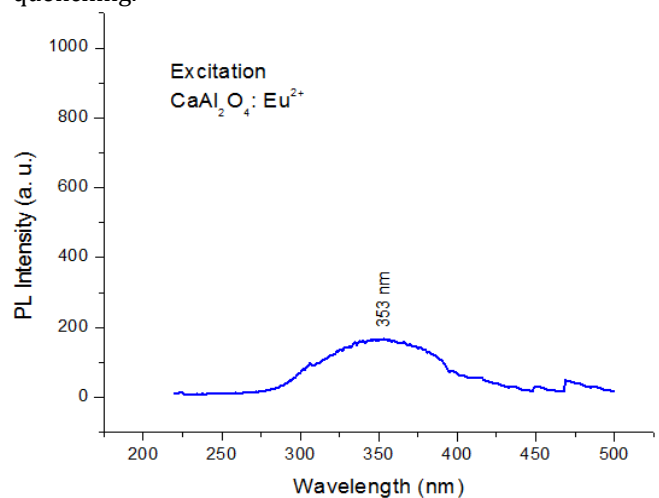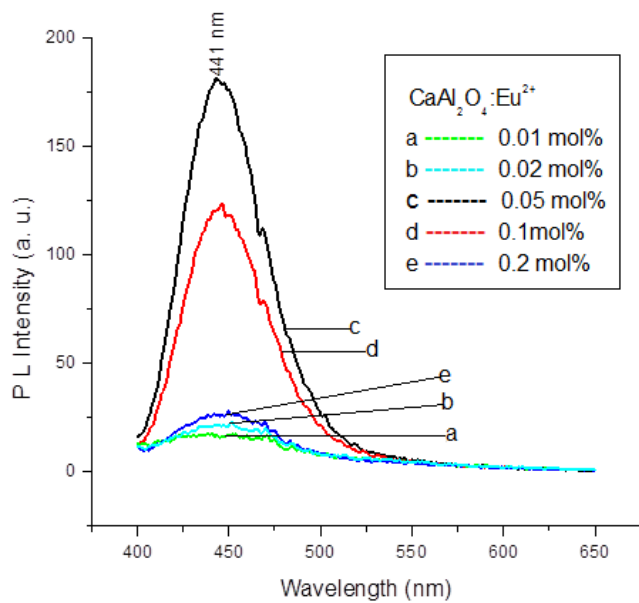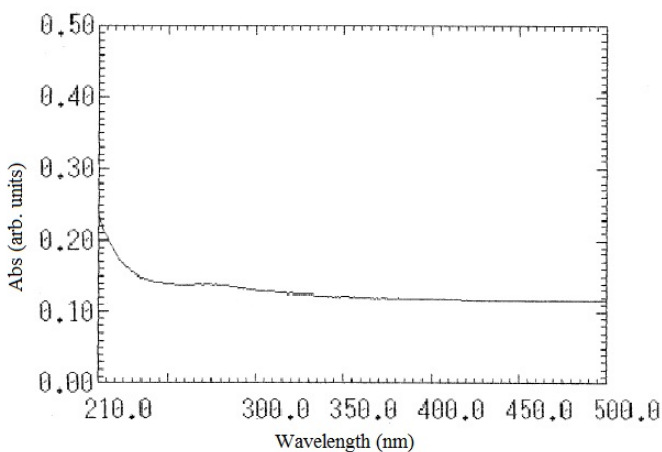**Fig. 4(a):** Excitation spectra of $CaAl_2O_4$:Eu^{2+} phosphor with 446 nm excitation

Fig. 4(b): Emission spectra of $CaAl_2O_4:Eu^{2+}$ phosphor for different doping

**Fig 5.** Absorption spectra of $CaAl_2O_4$: Eu^{2+} having absorption edge at 230 nm

3.4 Optical absorption spectra

The study of optical absorption is important to understand the behavior of crystal. A fundamental property is the band gap, the energy separation between the filled valence band and the empty conduction band. Optical excitation of electron across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge. Figure (5) shows the optical absorption spectra of $CaAl_2O_4$: Eu in the range of 210 nm-500 nm. It can be seen that the spectra is featureless and no absorption occur for wavelength $\lambda > 390$ nm (visible). The optical absorption edge was found at $\lambda = 230$ nm. The

band gap was calculated corresponding to absorption edge (230 nm). The band gap E_g was found to be 5.40 eV.

3.5 Thermoluminescence studies

Figure 6 shows comparative study of the TL glow curve of Eu^{2+} (0.05mol %) doped $CaAl_2O_4$ phosphor for different γ-dose. It is seen that the TL intensity increases with γ-dose and attains maximum for 590 Gy. Further increasing γ-dose intensity decreases. The pattern of the TL glow peaks appear in all glow curves with hardly any changes in peak temperature. The peak temperature is found around 394°C.
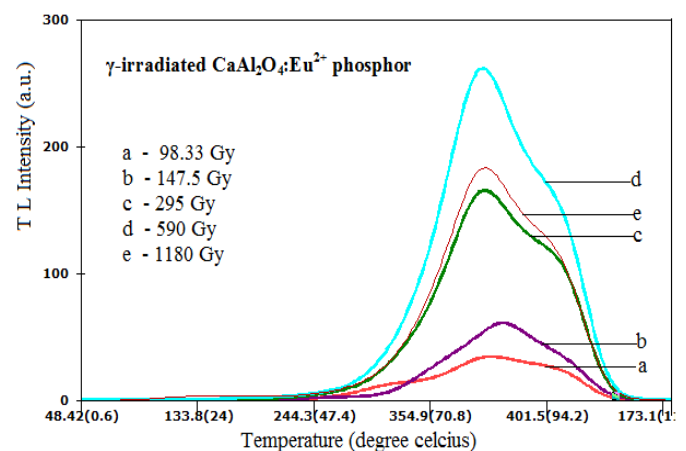
Fig. 6: The comparative studies of TL glow curve of $CaAl_2O_4:Eu^{2+}$ (0.05 mol %) phosphor for different γ- dose.
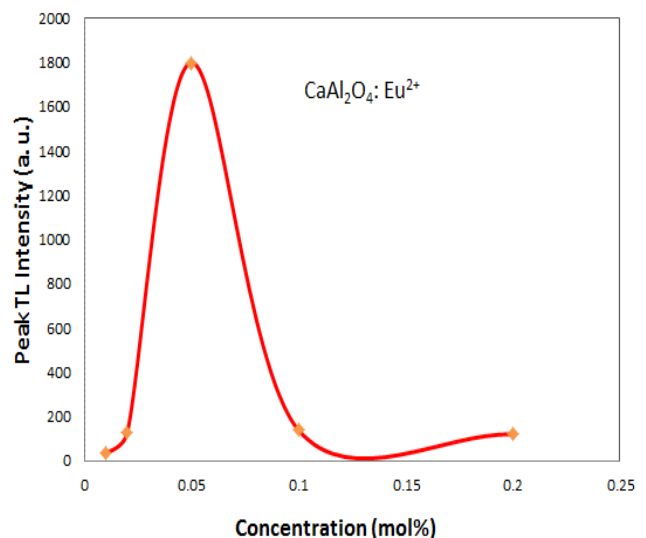
Fig.7: Concentration Vs Peak TL Intensity curve of $CaAl_2O_4:Eu^{2+}$ phosphor for 1770 Gy   gamma dose

All solids contain imperfections in the form of impurities and intrinsic defects. Upon excitation of suitable radiation these imperfections capture electrons/holes whose radiative recombination can be studied by the technique of Thermoluminescence (TL). Each TL peak is associated with certain trapping levels whose intrinsic parameters may be retrieved by analyzing the TL data. Figure 7 shows the variation in peak TL intensity as a function of Eu concentration in $CaAl_2O_4$ host lattice. It is seen that Peak TL intensity increases with increasing the concentration of activator (Eu) and attains a maximum value for 0.05 mol% concentration of Eu and decreases for higher concentrations of Eu. The drop in Peak TL intensity for higher doping concentration of Eu can be explained by the fact that the trapping probability is reduced if the density of the activator ion is increased due to the statistical reduced spatial distance between the activator ions and the excitons formed after band absorption.

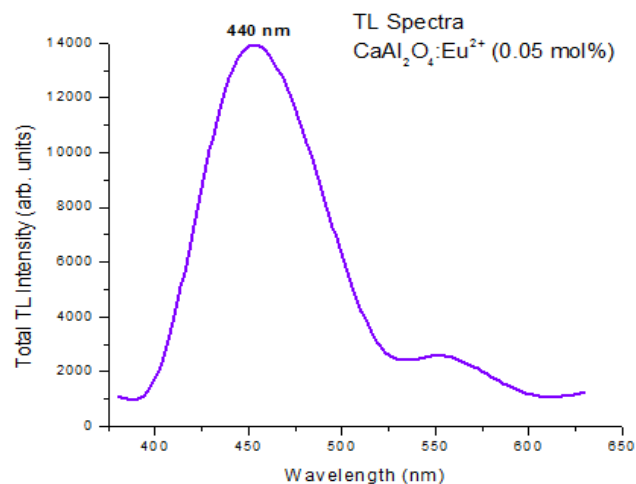### 3.5.1 Thermoluminescence emission spectra

Fig. 8: TL Spectra of $CaAl_2O_4:Eu^{2+}$ (0.05 mol %) phosphor

Fig. 8 shows the TL emission spectra of $CaAl_2O_4:Eu^{2+}$ phosphor. TL emission spectra show a broad peak around

440 nm corresponds to blue region. In crystals of $CaAl_2O_4:Eu^{2+}$, the Ca^{2+} ion is the only metal that could be replaced by Eu^{2+} , because there is such great difference between the radii of Al^{3+} and Eu^{2+} that the replacement of Al^{3+} by Eu^{2+} is impossible. To maintain the electrical neutrality of the compounds, two Eu^{2+} ions would be substituted for three Ca^{2+} ions. So the Ca^{2+} vacancies are created in the combustion process [22]. Furthermore the oxygen vacancies are also present. All these vacancies present make up trap levels. In $CaAl_2O_4$, the most probable centers which can be observed are the V centers (a hole trapped at a cation vacancy) and F centers (an electron trapped at an anion vacancy).When the sample is irradiated with gamma radiation most of the excitation energy associated with the excited carriers (electrons or holes) will be transferred via the host directly to the luminescence centers of Eu^{2+} followed by characteristic emission of Eu^{2+} immediately. However part of the excitation energy will be stored when electrons and holes are trapped in the trap levels. When the sample is heated, the thermal energy excites the filled traps to release carriers and transferred via the host to the Eu^{2+} followed by the recombination of electrons and holes in the luminescence centers (L) and give rise to luminescence. In the practical system the electron traps and the hole traps may not be both equally important in terms of their contribution to the light emission [23].

3.5.2 Calculation of TL parameters using Chen empirical method

For the calculation of various TL parameters such as activation energy, frequency factor etc. we have chosen the TL glow curve of CaAl2O4:Eu^{2+} (0.05 mol %) phosphor for 590 Gy gamma dose. The calculated values of different TL parameters are given in table 1. From Chen empirical method activation energy E was found 1.31 eV. The value of shape factor μ is found to be 0.11 which indicate that the TL glow curve represents first order kinetics.

Table 1: TL parameters

T_1 (k)	T_2 (k)	T_m (k)	$\tau = T_m-T_1$ (k)	$\delta= T_2-T_m$ (k)	$\omega= T_2-T_1$ (k)	Shape Factor $\mu= \delta/\omega$	Activation Energy (eV)	Frequency factor S (s⁻¹)
623.13	66.95	664.05	40.92	4.6	45.9	0.11	1.31	4.3×10^9

4. CONCLUSIONS

The $CaAl_2O_4:Eu^{2+}$ phosphors were successfully synthesized by combustion method and thermoluminescence (TL) and photoluminescence (PL) of $CaAl_2O_4:Eu^{2+}$ were studied. The XRD pattern of synthesized $CaAl_2O_4:Eu^{2+}$ phosphor matched well with standard data. The observed emission peak at 441 nm is due to the transition of Eu^{2+} from excited state of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ of $4f^7$ configuration. PL intensity is optimum for 0.05 mol% concentration of Eu. A TL spectrum was observed around 440 nm. TL intensity is optimum for 0.05 mol% concentration of Eu. The TL response found nearly linear with gamma dose up to 1475 Gy. Above this particular gamma dose linearity destroys. So, it is suggested that $CaAl_2O_4:Eu^{2+}$ (0.05 mol %) phosphor can be used in TL dosimetry for gamma radiation up to 1475 Gy.

XRD pattern of $CaAl_2O_4$: Eu phosphor prepared by combustion synthesis matched well with standard data. In the PL spectrum of $CaAl_2O_4$:Eu phosphor emission at 441 nm is due to the transition of Eu^{2+} from excited state of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ of $4f^7$ configuration. In the TL glow curve a distinct peak is observed around 394 ^0C which is optimum for 590 Gy.

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