Chapter 5

Gamma, UV and ion induced TL properties of CdSiO$_3$:Pr$^{3+}$, Eu$^{3+}$, Ce$^{3+}$ nanophosphors
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Gamma, UV and ion induced TL properties of CdSiO₃:Pr³⁺, Eu³⁺, Ce³⁺ nanophosphors

5.1. Luminescence studies of CdSiO₃:Eu³⁺ (1-5 mol %) nanophosphors prepared by solution combustion method

5.1.1. Introduction

The nanomaterials having significant and unique physical, chemical, electrical, optical and mechanical properties when compared to the bulk materials has fascinated the researchers in the development of organic/inorganic nanomaterials [1]. Therefore, the development of low cost, highly stable, with good yield phosphors is in progress. Now a days, a group of researchers is concentrating on the study of cheaply and abundantly available silicate nano materials in the field the luminescence [2, 3]. A silicate host materials has multi-color phosphorescence, resistance to acid, alkali and oxygen [4]. When silicate doped with active rare earth ions such as Eu, Sm, Dy, Pr, Ce, etc. they become phosphor materials which have potential applications in the field of luminescence, displays, lasers, scintillators, in safety indicators, emergency lighting such as road signs, dosimetric materials, etc [2-4]. Various silicate hosts have been well studied by doping with rare earth and transition metal ions namely CdSiO₃:In³⁺; CdSiO₃:Mn²⁺; CdSiO₃:Sm³⁺; CdSiO₃:Tb³⁺; CaSiO₃:Eu³⁺; Ba₂SiO₄:Eu²⁺; Sr₂SiO₄:Pr³⁺; Mg₂SiO₄:Tb³⁺; Zn₂SiO₄:Mn²⁺; Mg₂SiO₄:Eu³⁺; Mg₂SiO₄:Dy³⁺, Mn; Sr₂SiO₄:Pr³⁺ [4-14] etc.

Among them CdSiO₃ host exhibits a remarkable optical and luminescent properties. It exhibits ionic and covalent nature due to the presence of Cd²⁺ ions and strong interaction between Si-O, present in the SiO₃ group. The crystal structure of CdSiO₃ is having one dimensional chain of edge-sharing SiO₄ tetrahedron as a result transition metal ions can be easily implanted into the host by replacing the Cd site. However for rare earth ions dopant in order to maintain charge neutrality the charge compensation of Cd²⁺ and O²⁻ were considered. These dopants act as an impurity ion which results in the creation of traps at appropriate depths which stores the excitation energy and emit the light in the visible range [15, 16]. However, they show a huge potential practical applications in the field of thermo and photoluminescence.
Thermoluminescence (TL) is a phenomenon of emission of light caused by thermal stimulation of the ionizing radiation induced electrons from the traps of the semiconductors or insulators. TL glow curves gives the information about the defect centers induced due to ionizing radiations in the materials. Hence, TL finds a wide applications in the field of archaeology, radiation dosimetry, defect studies, etc [17, 18]. TL and PL studies mainly depends on particle size, type of dopant, morphology, crystallization, growth mechanism, local symmetry, host matrix, synthesis methods, etc. Therefore, to improve the structural properties of the luminescent materials the exothermic reaction based solution combustion technique [19] which serves as a fast and efficient method is used for the preparation of the CdSiO$_3$:Eu$^{3+}$ nanophosphor materials. In the present chapter synthesis, TL and PL properties of CdSiO$_3$:Eu$^{3+}$ (1-5 mol %) nanophosphor prepared by solution combustion method for the first time and detail results are discussed.

5.1.2. Experimental

5.1.2.1. Preparation

The Eu$^{3+}$ doped CdSiO$_3$ was synthesized by combustion method by using oxalyl dihydrazide (ODH) as a fuel. The preparation of ODH is given elsewhere [20]. Before actual preparation the stiochiometric composition of the redox mixture was calculated by taking the ratio of total oxidizing valencies (O) to the reducing valencies (F) equal to unity i.e., (O/F=1) so that maximum energy is released during combustion. The procedure for the preparation of CdSiO$_3$:Eu$^{3+}$ is shown in flow chart (Fig.5.1.1). The chemicals used for the preparation are of analytical grade and were not purified further. Cadmium nitrate (Cd(NO$_3$)$_2$·6H$_2$O; Sigma Aldrich), silica fumes (SiO$_2$), europium oxide (Eu$_2$O$_3$) and ODH (C$_2$H$_6$N$_4$O$_2$) were used as the starting materials. An appropriate amount of Cd(NO$_3$)$_2$·6H$_2$O, SiO$_2$ and C$_2$H$_6$N$_4$O$_2$ (1:1:1.25 in mole ratio) are well dissolved in a ~300 ml of double distilled water. The homogenized aqueous solution was obtained by magnetic stirring. Then europium oxide was converted into europium nitrate by adding 1:1 HNO$_3$. In the next step, the heterogeneous mixture was rapidly heated in a muffle furnace maintained at 500±10 °C. The reaction takes place within few seconds by heating the redox mixture to incandescence leading to the formation of voluminous foamy white powder. The obtained final product was further calcined at 800 °C for 2 hr for the formation of crystalline nature and used for characterization and luminescent studies. The stiochiometric equation for the formation of Cd$_{1-x}$Eu$_x$SiO$_3$ is given by:
\[(1-x) \text{Cd(NO}_3)_2 + x \text{Eu(NO}_3)_3 + \text{C}_2\text{H}_8\text{N}_2\text{O}_2 + \text{SiO}_2 \rightarrow \text{Cd}_{1-x}\text{Eu}_x\text{SiO}_3(\text{Eu}) + 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g}) + \left(\frac{3-x}{2}\right)\text{N}_2(\text{g}) \]

\[\ldots (5.1.1)\]

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**Fig. 5.1.1. Flow chart for the synthesis of CdSiO\(_3\):Eu\(^{3+}\) (1-5 mol %) nanophosphor by solution combustion technique**

### 5.1.2.2. Measurements

The powder X-ray diffraction (PXRD) patterns were recorded on X’PERT pro Philips analytical diffractometer using CuK\(_\alpha\) radiation (\(\lambda=1.54\) nm). Morphology of the sample was analyzed by using Hitachi Table Top Microscope Model TM3000. TEM and SAED images were measured in TECNAI F-30 TEM at a operating voltage of 200 kV. HRTEM measurements were made using JEOL JEM 2100 HRTEM whose emission gun is operating at voltage of 200 kV. For TL studies samples were exposed to \(\gamma\)-rays (\(^{60}\)Co source) and UV source (254 nm and 15 W) at room temperature. After desired exposure the TL glow curves were recorded using Nucleonix TL reader consisting of a
small metal planchet heated directly using a temperature programmer, photomultiplier, DC amplifier and mV recorder. During TL measurements 5 mg of the samples was taken each time and heated up to 300 °C at a heating rate of 5 °C s⁻¹. PL measurements were carried out using Horiba, USA made model fluoro Log-3, spectrofluorometer.

5.1.3. Results and discussion

5.1.3.1. Structural characterization

Fig.5.1.2. shows the X-ray diffraction pattern of CdSiO₃:Eu³⁺ nanosilicate phosphor. A sharp and intense XRD peaks were observed due to formation of high crystallinity. The obtained peaks are well matched with the standard JCPDS card no.35-0810 [21].

![X-ray diffraction pattern](image)

Fig.5.1.2. X-ray diffraction pattern of 1 mol% Eu³⁺ doped CdSiO₃ nanophosphor

The average crystallite size of the Eu³⁺ doped silicate sample was estimated by using Scherer’s method [22], \( d = \frac{k\lambda}{\beta \cos \theta} \), where \( \lambda \) is the wavelength of X-ray (\( \lambda = 1.54 \) Å), \( \beta \) is full width at half maxima (FWHM) in radians, \( \theta \) is the Bragg’s angle. The average crystallite size was found to be ~25-50 nm. Further, crystallite size was estimated using W-H plots [23] by using \( \beta \cos \theta = \frac{0.9 \lambda}{D} + 4\varepsilon \sin \theta \) where, D is the average particle size, \( \beta \) is the FWHM, ‘\( \theta \)’ is the Bragg ‘s angle, ‘\( \lambda \)’ is the X-ray wavelength, \( \varepsilon \) is the strain. The average crystallite size estimated from Scherer’s method and W-H plots are well matched.
5.1.3.2. Morphology studies

Fig. 5.1.3 (a and b) shows the SEM and TEM images of CdSiO$_3$:Eu$^{3+}$ (1 mol%) nanophosphor. As can be visualized from the Fig. 5.1.3 (a) the product was highly porous, fluffy and agglomerated. The porous and agglomerated morphological behavior was mainly due to the escaping of large amount of gases during combustion synthesis process. The combustion reaction depends on the formation of metal-ligand complex as a result flaming reaction takes place by discharging a large amount of toxic gases. The ligand ODH easily influence the formation of uniform complex structure with Eu$^{3+}$ metal ion than Cd$^{2+}$ metal ion due to its ionic nature and variable coordination. Therefore, the porous nature of the silicate material mainly depends on the type of the metal ion used. The TEM image (Fig. 5.1.3 (b)) shows that the particle size was obtained to be ~20-50 nm. Fig. 5.1.3(c) shows the HRTEM image of the CdSiO$_3$:Eu$^{3+}$ nanophosphor material having clearly defined lattice fringes oriented in different direction. The SAED pattern in Fig. 5.1.3(d) shows the polycrystalline nature of the obtained material.

Fig. 5.1.3. (a) SEM (b) TEM (c) HRTEM and (d) SAED images of CdSiO$_3$:Eu$^{3+}$ (1 mol%) nanophosphor
5.1.4. Thermoluminescence

Fig. 5.1.4 and 5.1.5 shows the effect of different Eu$^{3+}$ concentration (1-5 mol%) in CdSiO$_3$ on TL glow peak intensity was studied by exposing with $\gamma$ (6 kGy) and UV (10 min) respectively at a heating rate of 5 °Cs$^{-1}$. A single well resolved glow peak at 178 °C was recorded for both $\gamma$ and UV exposed samples.

![Graph showing TL glow curves of CdSiO$_3$:Eu$^{3+}$ nanophosphor with varying Eu$^{3+}$ concentrations](image1)

Fig. 5.1.4. TL glow curves of $\gamma$ irradiated (6 kGy) CdSiO$_3$:Eu$^{3+}$ (1-5 mol %) nanophosphor. (Inset: Variation of TL intensity with Eu$^{3+}$ concentration)

![Graph showing TL glow curves of CdSiO$_3$:Eu$^{3+}$ nanophosphor after UV exposure](image2)

Fig. 5.1.5. TL glow curves of 10 min UV exposed CdSiO$_3$:Eu$^{3+}$ (1-5 mol %) nanophosphor. (Inset: variation of TL intensity as a function of Eu$^{3+}$ concentration in UV exposed CdSiO$_3$ nanophosphor).
It is observed that highest TL intensity was registered for 1 mol % Eu$^{3+}$ samples in both γ and UV exposed samples (Inset of Fig.5.1.4 and 5.1.5). Manjunath et al [24] studied the similar behavior when CdSiO$_3$:Ni$^{2+}$ (1-7 mol %) nanocrystalline phosphors was exposed to 20 min UV exposure. They explained the reason for the decrease in TL intensity with increase in Ni$^{2+}$ ions concentration in CdSiO$_3$ host matrix due to lattice perturbation caused by change in trap distribution. On the other hand, the luminescence centers are surrounded by non-luminescent centers so that the released charge carriers cannot combine directly with the luminescent centers therefore energy is transferred non-radiatively. As the activator concentration increases the free charge carrier’s return to the ground state non-radiatively. Hence the decrease of TL intensity with increase of Eu$^{3+}$concentration in CdSiO$_3$ host matrix takes place [25].

Fig.5.1.6 and 5.1.7 shows the effect of different γ (1-6 kGy) and UV (5-25 min) exposures with CdSiO$_3$:Eu$^{3+}$ (1 mol%) phosphor at a heating rate of 5 °C s$^{-1}$ at room temperature. Single well resolved TL glow peak at 178 °C was recorded for the entire range of samples. Further, it is observed that TL glow peak is well resolved in γ irradiated samples. However, in UV exposed samples, TL glow curve is flat for lower UV exposures. Variation of TL glow peak intensity vs γ and UV exposure was studied and shown in insets of Fig.5.1.6 and 5.1.7 respectively.

**Fig.5.1.6. TL glow curves of CdSiO$_3$:Eu$^{3+}$ (1mol %) nanophosphor irradiated with 1-6 kGy γ dose**

(Inset: Variation of TL intensity as a function of γ dose)
Fig. 5.1.7. TL glow curves of Eu$^{3+}$ doped (1 mol%) in CdSiO$_3$ nanophosphor UV exposed for 5-25 min. (Inset: Variation of TL intensity with UV exposure)

It is noticed that the TL intensity was found to be highest in $\gamma$ when compared to UV exposed samples due to the presence of surface defects [26]. In UV exposed phosphors radiations cannot penetrate deep into the lattice and the traps created are surface traps. Further, variation in glow peak position temperature with the $\gamma$ and UV exposures was observed which was due to the disorganization of the initial energy bands created by the ionizing radiations [27]. A wide linear range was observed up to 5 kGy $\gamma$ irradiated samples and after that it becomes sub linear. However, in UV- exposed samples, initially the intensity of the glow curve was quite low but as the exposure time increased the TL intensity also increased up to 10 min and thereafter it decreases. The increase in TL intensity can be explained by Horowitz model (TIM) [28, 29].

According to which the number of traps generated during irradiation depends on the length and cross-section of the tracks in the host matrix. In nanomaterials, the length of the track is nano dimensional therefore for lower exposures the trap centers or luminescent centers (TC/LC) will be less. As we know that the nanomaterials are very tiny and fine particles, therefore some particles may subsist from exposures. However, if we increase the exposure time to the ionizing radiations the particles missed from the radiations will now start generating TCs/LCs resulting in increase in TL intensity.
Further, increase in exposures the overlapping of the tracks takes place due to which the production of TCs/LCs saturates causing saturation or decrease in TL intensity.

Chandrasekhar et al [30] reported the TL studies in γ and UV exposed Dy₂O₃ samples. They observed the similar glow curve structure in both γ and UV exposed samples with varying glow peak temperatures at 376 and 362 °C respectively. For higher γ irradiated samples (5 kGy) an extra glow peaks was observed at 245 and 310 °C respectively. Several authors [31, 32] explained the saturation effect in nanomaterials by using surface to volume ratio. According to which the surface barrier energy created in nanoparticles is more due to high surface to volume ratio. Thus, as the exposure time to the ionizing radiation increases, the energy density crosses the barrier due to which large numbers of defects are produced till the saturation is achieved. In addition, the decrease in TL intensity with further increase in UV exposure is due to radiation damage in the material. The radiation damage is due the competition between radiative and non-radiative centres or trapping centres which occurs during excitation or heating stage.

As well as the effect of different heating rates (β) (5-15 °Cs⁻¹) was studied in 6 kGy γ and 10 min UV exposed CdSiO₃:Eu³⁺ (1 mol %) nanophosphor and shown in Fig.5.1.8 (a) and (b) respectively. It is observed that with increase in heating rate the shift in glow peak temperature towards higher temperature side was observed in γ exposed samples where as in UV exposed samples the shift in glow peak temperature after 8 °Cs⁻¹ of heating rate. The decrease in glow peak area with increase in heating rate is due to thermal quenching [33].

![Fig.5.1.8. Heating rate effect on TL glow curves of (a) 6 kGy γ irradiated and (b) 10 min UV exposed CdSiO₃:Eu³⁺ nanophosphor](image)
The stability of the traps plays an important role in the TL dosimeters because these reflect the storage capacities of the traps. Fading is nothing but the loss of TL glow curve intensity over a span of time [34]. A good TLD material should have low fading characteristics. Fig.5.1.9 and 5.1.10 shows the fading characteristics and fading percentages (Inset of Fig.5.1.9 and 5.1.10) with time (days) in γ and UV exposed CdSiO$_3$:Eu$^{3+}$ (1 mol%) nanophosphor. The fading characteristics were studied over a period of one month after irradiations the samples with 6 kGy γ and 10 min UV exposure.

Fig.5.1.9. Variation of TL intensity with respect to storage time in 6 kGy γ irradiated CdSiO$_3$:Eu$^{3+}$ (1 mol %) nanophosphor. (Inset: Fading percentage vs storage time (days))

Fig.5.1.10. Variation of TL intensity with respect to storage time in 10 min UV exposed CdSiO$_3$:Eu$^{3+}$ (1 mol %) nanophosphor. (Inset: Fading percentage vs storage time (days))
Here, $\gamma$ exposed samples initially showed higher fading and after 15 days the TL intensity was stabilized to $\sim 30\%$ fading due to shallow and deeper traps in $\gamma$ irradiation. However, in case of UV exposed nanophosphors up to 10 days the fading was more ($\sim 35\%$) and stabilized after 20 days. It is observed that the fading is higher in UV exposed samples when compared to $\gamma$ irradiated samples. This was mainly attributed to surface traps. In our previous paper [35], CdSiO$_3$:Pr$^{3+}$ we had done the fading characteristics for 6 kGy $\gamma$ irradiated samples about one month for different intervals of time. Here strong fading was observed up to 15 days and there after the TL intensity of 171 $^{\circ}$C glow peak saturated losing TL intensity around 68%. The TL residual intensity was around 68% of its initial TL intensity. And from literature it is studied that 40% fading of TL intensity is highly sufficient for dosimetric applications.

5.1.4.1. Estimation of kinetic parameters

The TL characteristics of the phosphor material depend on the sensitivity, energy response and kinetic parameters which describes the trapping-emitting centers responsible for TL emission. Therefore, the study of the kinetic parameters such as activation energy/ trap depth, $E$ (metastable state i.e. forbidden band gap between conduction band and valence band) frequency factor, $s$ (attempt to escape an electron frequency) plays an important role in TL dosimetry. Various methods have been used for evaluation of $E$, $b$ and $s$ from experimentally recorded TL glow curves. Among them glow peak shape method follows the simple and easy procedure for the estimation of trapping parameters. Firstly, the glow curves were deconvoluted by using ORIGIN 8.1 (Fig.5.1.11) [24]. Then the glow peak temperature ($T_m$) and the temperatures ($T_1$ and $T_2$) at the lower and higher temperature sides of full width at half maximum of the peak were measured.

The deconvoluted glow peaks were used for the estimation of kinetic parameters by Chen’s set of empirical equation [36]

$$E_c = 2kT_m\left(\frac{1.756T_m}{\omega} - 1\right)$$

...... (5.1.2)

Where, $\tau = T_m - T_1$; $\delta = T_2 - T_m$; $\omega = T_2 - T_1$; $\mu_g = \delta/\omega$

Similarly, the activation energy was also estimated based on the equations given by Luschik and Halperin & Briner equations [37, 38]

$$E_L = 1.706\left(\frac{kT_m^2}{\delta}\right)$$

...... (5.1.3)

$$E_{HB} = \frac{2kT_m^2}{\tau}(1 - 3\Delta_m)$$

...... (5.1.4)
where $\Delta_m = \frac{2kT_m}{E}$.

The frequency factor(s) [39] can be evaluated using the equation

$$s = \frac{\beta E}{kT^2} \exp \left( \frac{E}{kT_m} \right) \left[ 1 + (b - 1)\Delta_m \right]^{-1} \quad \ldots \ldots (5.1.5)$$

Where, $\beta = \frac{dT}{dt}, \Delta = \frac{2kT}{E}$ & $\Delta_m = \frac{2kT_m}{E}$

![Fig.5.1.11. Glow curve deconvolution of γ irradiated Eu$^{3+}$ doped CdSiO$_3$ nanophosphor](image)

The trapping parameters estimated for different $\gamma$ dose and UV exposure are tabulated in Table. 5.1.1 and 5.1.2 respectively. As can be seen from the tables, E, is higher in $\gamma$ irradiated samples when compared to UV exposed samples.

Table 5.1.1. Estimated kinetic parameters of UV exposed CdSiO$_3$:Eu$^{3+}$ nanophosphors by different expressions

<table>
<thead>
<tr>
<th>UV-exposure (min)</th>
<th>Peak</th>
<th>$T_m$ (°C)</th>
<th>$b$ (µg)</th>
<th>Activation energy $E$ (eV)</th>
<th>Frequency factor (s$^{-1}$)</th>
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<td>Lushchik</td>
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Table 5.1.2. Estimated kinetic parameters of γ irradiated CdSiO$_3$:Eu$^{3+}$ nanophosphors by different expressions

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<th>γ-dose (kGy)</th>
<th>Peak</th>
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</table>

5.1.5. Photoluminescence (PL) studies in CdSiO$_3$:Eu$^{3+}$

Fig. 5.1.12 shows the excitation spectra of CdSiO$_3$:Eu$^{3+}$ (4 mol%) nanophosphor which varies from 200-464 nm due to 4f-4f transitions of Eu$^{3+}$ ion. The PL excitation spectra consist of a highly intense broad band at 240 nm and less intense sharp peaks in the range 361-464 nm. The broad band is as a result of O$_{2}^{-}$-Eu$^{3+}$ charge transfer band (CTB), caused due to the electron transfer from 2p orbit of O$_{2}^{-}$ ions to 4f shells of Eu$^{3+}$ ions. Therefore the phosphor materials can be powerfully excited by low pressure mercury lamp. And the small excited peaks at 361, 380, 393 and 464 nm are corresponded to the inter-configurational 4f-4f transitions of Eu$^{3+}$ ions in the host lattices, assigned as $^7$F$_0$$\rightarrow$$^5$D$_4$, $^7$F$_0$$\rightarrow$$^5$G$_2$, $^7$F$_0$$\rightarrow$$^5$L$_6$ and $^7$F$_0$$\rightarrow$$^5$D$_2$ transitions, respectively. It is well known that 4f-4f transition and CTB are two types for excitation of the trivalent lanthanide ions in crystals. The 4f orbital is shielded from the surroundings by the filled 5s$^2$ and 5p$^6$ orbital. Therefore, the influence of the host lattice on the optical transitions within the 4f configuration is small and 4f-4f transitions are sharp lines. While CTB absorption shows a broad band character and is intense than that of 4f-4f transitions [40, 41].
The emission spectra of 1-5 mol% Eu$^{3+}$ doped CdSiO$_3$ nanophosphor measured at 393 nm related to 4f-4f transitions of Eu$^{3+}$ ions are shown in the Fig.5.1.13. The maximum PL intensity is observed in 4 mol% Eu$^{3+}$ doped CdSiO$_3$ nanophosphor (Inset of Fig.5.1.13). The emission bands equivalent to Eu$^{3+}$ are observed at $^5D_0\rightarrow^7F_0$ (577 nm), $^5D_0\rightarrow^7F_1$ (596 nm), $^5D_0\rightarrow^7F_2$ (616 nm), $^5D_0\rightarrow^7F_3$ (659 nm) and $^5D_0\rightarrow^7F_4$ (706 nm) respectively [40-42]. 596 nm emission corresponding to $^5D_0\rightarrow^7F_1$ transmission is mainly due to magnetic dipole transition which is independent of site symmetry where Eu$^{3+}$ is positioned. Whereas, the strongest emission peak at 616 nm corresponding to $^5D_0\rightarrow^7F_2$ is due to hypersensitive forced electric-dipole transition. As we know that Eu$^{3+}$ occupies the centre of symmetry (spherically symmetric site) the $^5D_0\rightarrow^7F_2$ transition intensity is very weak for higher site symmetry as this transition intensity increases the site symmetry decreases [43]. The site symmetry of the nanophosphor also depends on the ratio of electric and magnetic dipole transition ($I_{616}/I_{593}$) as shown in the inset of Fig.5.1.13. The weaker emission peaks at 659 nm and 706 nm are due to the weak interaction between Eu$^{3+}$ and O$^{2-}$ ions present in CdSiO$_3$:Eu$^{3+}$ nanophosphor. The decrease in PL intensity after 4 mol% Eu$^{3+}$ concentration is due to concentration quenching which could be explained by non-radiative transition phenomenon. Non-radiative energy transfer may occur due to radiative reabsorption/ exchange interaction/ multipol-multipole interaction.
Fig. 5.1.3. PL spectra of CdSiO$_3$:Eu$^{3+}$ (1-5 mol %) nanophosphor. (Inset: (a) Variation of PL intensity with Eu$^{3+}$ concentration in CdSiO$_3$nanophosphor (b) Symmetry ratio vs Eu$^{3+}$ concentration)

From inset of Fig. 5.1.3, it is observed that the emission intensity increased with increase in Eu$^{3+}$ concentration up to 4 mol% and there after it decreased with further increase in concentration. Nagabhushana, et al [44], observed the similar behavior in CaSiO$_3$:Eu$^{3+}$nanophosphor prepared by solution combustion technique where the PL intensity was attributed to the ionic radius of Eu$^{3+}$ and Ca$^{2+}$ ions. Which showed that ionic radius and charge state of the impurity ion acts as a major contributors in the emission spectra. Initially, the PL intensity increases with increase in Eu$^{3+}$ concentration because the ionic radius of Eu$^{3+}$ (1.13 Å) was slightly bigger than Cd$^{2+}$ (1.09 Å), therefore a small percentage of impurity ions can only accommodate in the CdSiO$_3$ host matrix. Further, with increase in the Eu$^{3+}$concentration the charge imbalance may occur as a consequence, trapping centres are created. This trapping centres results in cross relaxation due to which concentration quenching takes place.
5.1.6. Conclusion

CdSiO$_3$:Eu$^{3+}$ (1-5 mol%) was prepared by solution combustion technique and was subjected to structural characterization and luminescent studies. PXRD patterns showed that he obtained sample were highly crystalline. The porous and agglomerated structure was seen in CdSiO$_3$:Eu$^{3+}$ (1 mol%) nanophosphor. The porous nature was due to the escaping of gases during synthesis process. TL studies were carried out for both γ and UV exposed samples. A single TL glow peak at ~178 °C was observed. In both the cases 1 mol% Eu$^{3+}$ doped CdSiO$_3$ nanophosphor showed the highest TL intensity. In case of γ irradiated samples the phosphor material showed linearity and good sensitivity where as the in UV exposed samples the TL intensity increased upto 10 min UV exposure and decreased with further increase in exposure time. γ irradiated samples showed lower fading (~30 %) when compared to UV exposed (45 %) samples. Therefore, γ irradiated (1-5 kGy) CdSiO$_3$:Eu$^{3+}$ samples might be useful in TL dosimetry. Deeper traps in γ and surface traps were created in UV exposed samples. The kinetic parameters were calculated by various methods. The PL studies in CdSiO$_3$:Eu$^{3+}$ (1-5 mol%) nanophosphor revealed the Eu$^{3+}$ peaks at 577, 596, 659 and 706 nm excited at 393 nm corresponding to $^5$D$_0$$\rightarrow$$^7$F$_0$, $^5$D$_0$$\rightarrow$$^7$F$_1$, $^5$D$_0$$\rightarrow$$^7$F$_2$, $^5$D$_0$$\rightarrow$$^7$F$_3$ and $^5$D$_0$$\rightarrow$$^7$F$_4$ transitions respectively. The highest PL intensity was observed in 4 mol% Eu$^{3+}$ doped CdSiO$_3$ nanophosphor.
5.1.7. References


5.2. CdSiO$_3$:Pr$^{3+}$ nanophosphor: Synthesis, Characterization and Thermoluminescence studies

5.2.1. Introduction

In recent years, trivalent rare earth (RE) metal ions doped inorganic phosphors have attracted material scientists due to their well-defined transitions within the 4f shell [1, 2]. Among inorganic phosphors, silicate family is an attractive class of materials for a wide range of applications due to their special properties such as acid, chemical resistance, and visible light transparency [3]. In silicate family, the CdSiO$_3$ host material exhibits some interesting applications such as long lasting phosphors, X-ray imaging, displays (plasma display panels, flat panel displays), environmental monitoring, etc., when doped with rare earth ions [4]. The crystal structure of the CdSiO$_3$ is a one dimensional chain of edge-sharing SiO$_4$ tetrahedron. In this kind of low dimensional structure, it is very easy to dope other ions into the host lattice and create traps located at a suitable depth that can store the excitation energy and emit light at room temperature [5, 6].

In general CdSiO$_3$ doped rare-earth ion phosphors were prepared by conventional solid-state, hydrothermal, co-precipitation, sol-gel routes, etc [7-10]. The conventional solid state method for preparing these phosphors requires high calcination temperature (>1200$^o$C), which induces sintering and aggregation of particles. On the other hand, sol-gel method demands complicated precursor and longer duration. Where as hydrothermal method, the final product obtained is very less. Therefore low cost method with high purity, yield end product are required for lamp industry, solution combustion technique is another wet chemical method which offers several advantages such as choice of a wide variety of fuels, homogeneous product in a short time without the use of expensive high temperature furnaces. These synthesis technique make use of the heat energy liberated by the redox exothermic reaction at a relatively low igniting temperature between metal nitrates and fuels [11].

Thermoluminescence (TL) is a powerful technique in identifying the defects and dosimetric properties by using ionizing radiations. Liu et al [12] studied CdSiO$_3$:Dy$^{3+}$ (0.5-10 mol %) white afterglow phosphor prepared by high temperature solid state method and TL measurements were performed by heating the phosphor from room temperature to 637K. The samples were UV exposed at a warming rate of 2 Ks$^{-1}$. Two TL glow peaks at 418 and 358K were recorded.
Manjunath et al. [13] studied CdSiO$_3$:Dy$^{3+}$ (1-9 mol %) nanophosphor synthesized by solution combustion method. TL measurement was carried out by using UV exposure (10-50 min) at a warming rate of 5 °C s$^{-1}$ at room temperature. A well resolved glow peak shape at 170 °C was recorded for all given doses. Further, the glow peak shape was not changed with different Dy$^{3+}$ concentration. However, in different UV exposures, TL glow peak temperature slightly shifted to lower temperature. Further, TL intensity at 170 °C increases with UV exposure up to 20 min and then it decreases. The increase in TL intensity might be due to creation of more number of defect centers/luminescent centers.

Yong et al. [14] have reported the TL properties of pure and In$^{3+}$ doped CdSiO$_3$ nanophosphor prepared by solid state technique fired at 1050 °C. They observed two intrinsic defects associated with TL peaks at 73 and 145 °C appear in the undoped CdSiO$_3$. Whereas, a single cadmium vacancy $V_{\text{cd}}$ was associated with the peak at 75 °C in the CdSiO$_3$:In$^{3+}$ phosphor which is due to the nonequivalent substitution of Cd$^{2+}$ ions by In$^{3+}$ ions. The intensity of a glow peak in a TL glow curve proportional to the amount of radiation dose received by the samples and the glow peak provides information regarding the depth of the charge carriers [15]. Further, addition of suitable rare earth ions will strongly influence the stability and depth of the traps which are needed for radiation dosimetry.

In the present investigation, CdSiO$_3$:Pr$^{3+}$ (1-9 mol %) nanophosphors was prepared by low temperature solution combustion method using oxalyldihydrazide (ODH) as a fuel. The structural, morphological and optical properties were carried out using Powder X-Ray diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and UV-Visible Spectroscopy. Further dosimetric properties were studied by means of Thermoluminescence (TL) technique using gamma irradiation ($^{60}$Co). Trapping parameters are estimated and discussed.

5.2.2. Experimental
5.2.2.1. Preparation of phosphor
The starting chemicals used in the present study were of Analar grade cadmium nitrate (Cd(NO$_3$)$_2$.4H$_2$O), praseodymium nitrate (Pr(NO$_3$)$_3$.4H$_2$O), fumed silica (SiO$_2$, 99.9%, surface area 200 m$^2$/g). The oxalyldihydrazide (ODH: C$_2$H$_6$N$_4$O$_2$) was used as a fuel prepared in our laboratory; the detailed preparation is given in chapter 2. Activator Pr concentrations were varied from 1 to 9 mol%. The stoichiometry of the redox mixture
used for the combustion has been calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for the stiochiometric balance so that the equivalent ratio \( \Phi_e \) is unity and the energy released by the combustion is maximum. According to propellant chemistry [16], the valence of C = +4, H= +1, divalent metal ions = +2, and O = -2. The calculated reducing valence of ODH is +10, the total oxidizing valency of Pr(NO\(_3\))\(_3\) is -15, and that of Cd(NO\(_3\))\(_2\) is -10. The total oxidizing valencies in the mixture of metal salts, mentioned above adds up to -25, whereas the total reducing valence in the ODH, is +10. For the release of maximum energy during the reaction the stiochiometric composition of the redox mixture should be balanced.

The stiochiometric quantities of all the raw materials are taken in a 150 cm\(^3\) cylindrical petri dish containing double distilled water. The aqueous redox mixture is mixed uniformly by stirring for about 5 min on a magnetic stirrer. The uniformly dispersed solution is kept in preheated muffle furnace at 450±10 °C. Initially, solution undergoes dehydration, followed by spontaneous smoldering type combustion with the liberation of large quantity of gases. The process is completed within 5 min. After the completion of the combustion, the product was well grinded using mortar and pestle. Therefore, the grinded powder was fired at 800 °C for 2 hr in boat shaped alumina crucible. The white powder of Pr\(^{3+}\) doped CdSiO\(_3\) was obtained. The typical combustion steps involved for the synthesis of CdSiO\(_3\):Pr\(^{3+}\)nanopowders is given in the Fig.5.2.1. The overall stiochiometric reaction for the formation of Cd\(_{1-x}\) Pr\(_x\)SiO\(_3\) phosphor can be written as:

\[
(1-x)\text{Cd(NO}_3)_2 + x \text{ Pr(NO}_3)_3 + C_2H_2N_2O_4 + \text{SiO}_2 \rightarrow \text{Cd}_x\text{Pr}_{1-x}\text{SiO}_3(s) + 2\text{CO}_2(g) + 3\text{H}_2\text{O}(g) + \left( \frac{3-x}{2} \right) \text{N}_2(g)
\]

**5.2.2. Instruments used**

The phase purity of the nanophosphor is examined by powder X-ray diffractometer (PXRD) (PANalytical X’Pert Pro) using Cu K\(_\alpha\)-radiation with a nickel filter. The surface morphology of the phosphor has been examined using scanning electron microscope (JOEL JSM 840 A) by sputtering technique with gold as covering contrast material. UV-VIS absorption of the samples was recorded on SL 159 ELICO UV - Vis Spectrophotometer. The nanoparticles are uniformly dispersed uniformly in liquid paraffin and recorded in the range 200-800nm. FT-IR studies have been performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. The TL measurements
were measured in a model Nucleonix TLD Reader, Hyderabad with a heating rate of 5 °Cs⁻¹. Before measurement, 100 mg powder samples were exposed to γ - irradiation in the dose range 1-6 kGy.

![Flow chart for the preparation of CdSiO₃:Pr³⁺ nanophosphor by solution combustion technique](image)

**5.2.3. Results and Discussion**

**5.2.3.1 Powder x-ray diffraction (PXRD)**

To check the phase purity of the samples, PXRD measurements were performed for CdSiO₃:Pr³⁺ (1, 5 and 9 mol %) samples. The PXRD patterns calcined at 800 °C for 2 hr are shown in Fig.5.2.2. The diffraction patterns exhibits single phase and is in well agreement with the standard JCPDS card no. 35-0810. The crystal structure of CdSiO₃ is expected to be similar to CaSiO₃ [17], because of very close ionic radii of Ca²⁺ (0.99 Å)
and Cd\(^{2+}\) (0.97 Å) [18]. All the reflection peaks can be perfectly matched with monoclinic crystal system of space group P2\(_1\)/a, no additional peaks can be found in Pr\(^{3+}\) ions doped CdSiO\(_3\).

![Fig.5.2.2 PXRD patterns of CdSiO\(_3\) nanophosphor doped with different concentration of Pr\(^{3+}\) ions](image)

Fig.5.2.2 PXRD patterns of CdSiO\(_3\) nanophosphor doped with different concentration of Pr\(^{3+}\) ions (a) 1 mol% (b) 5 mol% (c) 9 mol%

The average crystallite size (d) of CdSiO\(_3\):Pr\(^{3+}\) doped samples calcined at 800 °C was calculated using Debye- Scherer’s formula [19]

\[
d = \frac{k\lambda}{\beta \cos \theta}
\]

where, ‘\(\beta\)’ is the full width half maximum of the diffraction peak, ‘\(\lambda\)’ is the wavelength of X-ray (1.5418 Å) ‘\(\theta\)’ is the Bragg’s angle, ‘\(k\)’ is the Scherer’s constant varies from (0.88-0.92), therefore the average value of 0.9 is taken for calculation. The crystallite size of the 1, 5 and 9 mol% Pr\(^{3+}\) doped CdSiO\(_3\) samples is found to be 31, 35 and 37 nm respectively.

It is known that the full-width at half-maximum (FWHM) can be expressed as a linear combination of the contribution from the lattice strain and crystalline size [20]. The effects of the strain and crystallite size on the FWHM can be expressed by the following equation

\[
\beta \cos \theta = \frac{0.9 \lambda}{D} + 4 \varepsilon \sin \theta
\]

where ‘\(\beta\)’ is the measured FWHM (in radians), ‘\(\theta\)’ is the Bragg angle of the peak, ‘\(\lambda\)’ is the X-ray diffraction wavelength, \(\varepsilon\) is the strain associated with the nanoparticles.
Equation (5.2.3) represents a straight line between $4 \sin \theta$ (X-axis) and $\beta \cos \theta$ (Y-axis) as shown in Fig.5.2.3. The slope of line gives the strain ($\varepsilon$) and intercept ($0.9/\lambda/D$) of this line on Y-axis gives grain size ($D$). The estimated crystallite size and strain obtained from Scherer and W-H plots are tabulated in Table.5.2.1. It is evident that, the crystallite size obtained from Scherer’s and W-H plots are well matched.

![Williamson-Hall plots of CdSiO$_3$ nanophosphor doped with different concentration of Pr$^{3+}$ ions](image)

Table. 5.2.1. Estimated parameters of CdSiO$_3$:Pr$^{3+}$ nanoparticles using different methods

<table>
<thead>
<tr>
<th>Pr$^{3+}$ (mol %)</th>
<th>Band gap (eV)</th>
<th>Particle size (nm)</th>
<th>Strain ($\times 10^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.15</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>5.20</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>5.36</td>
<td>37</td>
<td>37</td>
</tr>
</tbody>
</table>

5.2.3.2. Scanning electron microscope (SEM)

Fig.5.2.4 (A and B) shows the typical electron micrograph and the corresponding magnified view of the combustion derived CdSiO$_3$:Pr$^{3+}$ (5 mol%) nanophosphor calcined at 800 °C. Agglomerated particles with porous morphology complex structure were observed. Depending upon the type of fuel and metal ions, the nature of combustion differs from flaming (gas phase) to non-flaming (smoldering and heterogeneous) type. Generally, flaming reactions involves liberation of large quantity of gas. Interestingly, it was observed during combustion reaction that the smoldering type of combustion turns to flaming type when the concentration of activator (Pr$^{3+}$) increases from 1-9 mol%. In a
typical combustion reaction, the Pr$^{3+}$ is expected to form a uniform complex with the ODH ligand, more easily than Cd$^{2+}$ because of its variable coordination tendency (coordination number varies from 2 to 7). Therefore, the increase in the porosity of the samples with increase in Pr$^{3+}$ concentration can be assumed due to uniformity in the distribution of ODH which leads to the liberation of large quantity of gas evenly. It is well known that, combustion synthesis reaction is influenced by metal-ligand.

![Image of SEM micrograph](image)

**Fig.5.2.4.** (A) SEM micrograph of CdSiO$_3$:Pr$^{3+}$ (5 mol %) nanophosphor (B) Magnified view

### 5.2.3.3. FT-IR spectral analysis

The FT-IR spectra of CdSiO$_3$:Pr$^{3+}$ (1, 5 and 9 mol %) samples calcined at 800 °C for 2 hr are shown in Fig.5.2.5. The spectra shows the broad band from 840-1240 cm$^{-1}$ is due to asymmetric stretching vibration of Si-O-Si bond and stretching vibrations of terminal Si-O bonds.

![FTIR spectra graph](image)

**Fig.5.2.5.** FTIR spectra of CdSiO$_3$ nanophosphor doped Pr$^{3+}$ (a) 1 mol%, (b) 5 mol% and (c) 9 mol%
The peaks at 458-564, 645 and 680 cm\(^{-1}\) are the characteristic stretching vibrations Si-O-Si bridges. A weak absorption peak at 1655 cm\(^{-1}\) indicates the presence of Cd-O bond in the structure [21]. The sharp peak corresponding to 680 cm\(^{-1}\) can be ascribed to Si-O bond, which exists in the form of SiO\(_5^2^-\).

### 5.2.3.4. UV-Vis absorption and optical band gap energy (\(E_g\))

Fig. 5.2.6(a-c) shows the UV-Vis absorption spectra of Pr\(^{3+}\)doped (1, 5 and 9 mol %) CdSiO\(_3\) phosphor calcined at 800 °C for 2 hr. A strong absorption band in the range 220-260 nm which corresponds to oxygen to silicon (O-Si) ligand-to-metal charge-transfer (LMCT) in the SiO\(_3^2^-\) group was observed. The broad band in the range 350-500 nm are ascribed to the intra configurational 4f - 4f transitions from the ground \(^4\)F\(_0\) level, which corresponds to the excitation spectra. These results are good agreement with those reported in the literature [22]. The direct optical energy band gap (\(E_g\)) of Pr\(^{3+}\)doped (1, 5 and 9 mol %) CdSiO\(_3\) were estimated using Wood and Tauc relation [23]

\[
\alpha(h\nu) \sim (h\nu - E_g)^{1/2}
\]

\[\text{…… (5.2.4)}\]
where ‘\(h\nu\)’ is the photon energy and ‘\(\alpha\)’ is the optical absorption coefficient near the fundamental absorption edge. The absorption coefficients were calculated from these absorption spectra. The values of the optical band gaps of \(\text{Pr}^{3+}\) doped \(\text{CdSiO}_3\) are obtained by plotting \((\alpha E)^k\) versus ‘\(E\)’ in the high-absorption range followed by extrapolating the linear region of the plots to \((\alpha E)^k = 0\). The analysis of the present data showed that the plots give the linear relations, which can for the most part be fitted with the above equation with \(k = 2\) for \(\text{Pr}^{3+}\)-doped samples. This indicates that allowed direct transitions are responsible for the inter band transitions in the doped samples. The optical energy band gap for the \(\text{Pr}^{3+}\) doped (1, 5 and 9 mol\%) phosphors it varies between 5.15-5.36 eV (Inset Fig. 5.2.6(a-c)). These values are well comparable to those reported in the literature [24]. It is noticed that the optical band gap is found to be lower in 1 mol \% \(\text{Pr}^{3+}\) when compared to 9 mol \%.The variation in \(E_g\) values with different mol\% of \(\text{Pr}^{3+}\) in \(\text{CdSiO}_3\) was mainly attributed to structural defects such as vacancies, distortions/ strain in the lattice. 9 mol\% of \(\text{Pr}^{3+}\) doped in \(\text{CdSiO}_3\) host, strain will be more which in turn present more structural defects.

5.2.4. Thermoluminescence (TL)

Fig.5.2.7 shows the TL glow curves of \(\text{CdSiO}_3\): \(\text{Pr}^{3+}\) (1-9 mol \%) \(\gamma\) irradiated for a test dose of 6 kGy.

![Fig.5.2.7.TL glow curves of CdSiO₃ doped with Pr³⁺ (1-9 mol %) nanophosphor irradiated with γ rays of 6 kGy](image-url)
Two glow peaks at 171 and 223 °C were recorded at a heating rate of 5 °Cs⁻¹. It was seen from Fig.5.2.8 that the TL intensity increases with increase of Pr³⁺ ion concentration. This may be due to the increase in number of emitting centers and also due to the increase in the probability of energy transfer from traps to the emitting centers. Fig.5.2.9 shows the TL glow curves of CdSiO₃: Pr³⁺ (9 mol %), irradiated with γ rays in the dose range 1-6 kGy. A well resolved glow peak at 171°C along with the shouldered peak at 223 °C was observed at a heating rate of 5 °Cs⁻¹. From Fig.5.2.10 it is observed that the glow peak intensity increases linearly with increase of γ dose (1-6 kGy).

Fig.5.7.8. Variation of TL intensity as a function of Pr³⁺ concentration in CdSiO₃ nanophosphor

Fig.5.2.9. TL glow curves of Pr³⁺ doped (9 mol %) in CdSiO₃ nanophosphor γ irradiated for 1-6 kGy
The increase in TL intensity at 171 °C suggests that more and more luminescent centers were created with the increase of radiation dose. The linear behavior over a wide range of dose can be explained on the basis of track interaction model (TIM) [25, 26]. Based on this model, the number of traps generated by the high energy (γ rays) radiation in a track depends upon the cross section and the length of the track inside the matrix. In case of nanomaterials the length of the track generated by high energy radiation is of the order of a few tenths of nanometers. At low doses there exist a few trap centers (TC)/luminescent centers (LC). As the dose increases, the TL intensity increases as still some particles exist that would have been missed while targeted by the high energy radiation, owing to the small size of the particles. This gives good linearity over a wide range of dose. On increasing the dose the energy density crosses the threshold value of the surface barrier and thus defects in large numbers are produced in the nanoparticles. The number of defects created in the particles keeps on increasing with dose till saturation is obtained. This explains the linearity in TL response of the nanophosphors over a given dose range [27].

![Graph](image_url)

**Fig. 5.2.10. Variation of TL intensity (Iₘ) and glow peak temperature (Tₘ) as a function of γ dose (1-6 kGy)**

The effect of heating rates between 5-15 °C s⁻¹ on TL response has been investigated in CdSiO₃:Pr³⁺ (1 mol %) sample, γ-irradiated for a test dose of 6 kGy and results are shown in Fig. 5.2.11. It is found that with the increase in heating rates the TL peak intensity and area under the glow peak decreases, however, peak temperature shifts towards higher
temperature side (Fig. 5.2.12). The glow peak ($T_m$) is shifted from 171 to 174 °C with increase of heating rate from 5 - 15 °C s$^{-1}$. The decrease in TL intensity with increase in heating rate is a phenomenon frequently observed in the practice of TL, and has been suggested to thermal quenching [28].

![Graph showing the effect of heating rates on TL glow curve for a sample irradiated for γ radiation.](image)

**Fig. 5.2.11** Effect of heating rates on TL glow curve for a sample irradiated for γ radiation

![Graph showing the variation of TL intensity and glow peak temperature as a function of different heating rates for CdSiO$_3$:Pr$^{3+}$ nanophosphor.](image)

**Fig. 5.2.12**. Variation of TL intensity and glow peak temperature as a function of different heating rates for CdSiO$_3$:Pr$^{3+}$ nanophosphor

The shift of $T_m$ versus heating rate can be empirically explained by the following way. At the low heating rate $\beta_1$, the time spent by the phosphor at a temperature $T_1$, is long enough so that an amount of thermal release of electrons depending on half-life at this
temperature could take place. As heating rate increases to $\beta_2 > \beta_1$ the time spent at same temperature $T_1$ decreases and therefore the thermal release of electrons is also decreased. Then a higher temperature $T_2$ is needed for the same amount of thermal release to take place at $\beta_2$. In this way the whole glow peak is shifted to higher temperatures as heating rate increases in a manner depending on the half-life and time spent at each temperature. Kittis et al [29] have studied the heating rate effects on the TL glow peaks of quartz, TLD-700 and natural CaF$_2$ and reported a similar behavior, but the difference in variation is very small for $T_m$ shifting and it is large in the case of FWHM.

5.2.4.1. Determination of trapping parameters (E & s)

The characteristics of dosimeters used in TL process are related to kinetic parameters and these parameters qualitatively describe the trapping-emitting centers. Detailed studies of the kinetic parameters provide valuable information regarding the TL mechanism responsible for the dosimetric applications. A reliable dosimetric study of a TL material should be based on a good knowledge of the kinetic parameters.

![Glow curve deconvolution of Pr$^{3+}$ doped CdSiO$_3$ exposed to $\gamma$ irradiation at a heating rate of 5 °C s$^{-1}$](image)

For estimation of trapping parameters (s and E), by Luschiks [30] method firstly we did deconvolution of the TL glow peaks using ORIGIN 8.1 software which is shown in the Fig.5.2.13 and the corresponding equations are given by

$$E = \frac{2kT^2}{\delta} \quad \ldots \ldots (5.2.5)$$
\[ s = \left( \frac{\beta}{\delta} \right) \exp \left( \frac{T_m}{\delta} \right) \]  \hspace{1cm} \ldots \hspace{1cm} (5.2.6)

where \( T_1, T_2 \) and \( T_m \) represent the lower, higher and maximum temperatures respectively.

\[ k \] is the Boltzmann constant \( \omega = T_2 - T_1 \), the total half intensity width, \( \delta = T_2 - T_m \), the high temperature half width and \( \tau = T_m - T_1 \), the low temperature half width, \( \mu_g \) is the symmetry factor/Geometric form factor.

Table.5.2.2. Estimated trap parameters of CdSiO\(_3\):Pr\(^{3+}\) (3 mol %) irradiated for different \( \gamma \) dose at a heating rate of 5 °C \text{s}^{-1} by Luschiks method.

<table>
<thead>
<tr>
<th>( \gamma )-dose (kGy)</th>
<th>Peak</th>
<th>( T_m )(°C)</th>
<th>E (eV)</th>
<th>s(Hz)</th>
<th>( n_o )(cm(^{-3}))</th>
<th>( \tau )(ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>167</td>
<td>1.281</td>
<td>2.4 x 10(^{11})</td>
<td>1.1 x 10(^{06})</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>208</td>
<td>0.686</td>
<td>1.9 x 10(^{06})</td>
<td>9.2 x 10(^{06})</td>
<td>161</td>
</tr>
<tr>
<td>2</td>
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<td>6.6 x 10(^{11})</td>
<td>3.1 x 10(^{06})</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>201</td>
<td>0.666</td>
<td>1.6 x 10(^{06})</td>
<td>1.3 x 10(^{06})</td>
<td>167</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>167</td>
<td>1.189</td>
<td>6.7 x 10(^{11})</td>
<td>3.0 x 10(^{06})</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>205</td>
<td>0.727</td>
<td>3.5 x 10(^{06})</td>
<td>73 x 10(^{06})</td>
<td>142</td>
</tr>
<tr>
<td>4</td>
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<td>166</td>
<td>1.274</td>
<td>2.3 x 10(^{11})</td>
<td>3.4 x 10(^{06})</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>202</td>
<td>0.705</td>
<td>2.8 x 10(^{06})</td>
<td>5.3 x 10(^{06})</td>
<td>170</td>
</tr>
<tr>
<td>5</td>
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<td>2.8 x 10(^{07})</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>200</td>
<td>0.699</td>
<td>2.7 x 10(^{06})</td>
<td>1.5 x 10(^{06})</td>
<td>155</td>
</tr>
<tr>
<td>6</td>
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<td>164</td>
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<td>64</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>201</td>
<td>0.690</td>
<td>2.3 x 10(^{06})</td>
<td>8.9 x 10(^{06})</td>
<td>164</td>
</tr>
</tbody>
</table>

Table.5.2.3. Estimated trap parameters of CdSiO\(_3\):Pr\(^{3+}\) (3 mol %) for different heating rate for \( \gamma \) dose by Luschiks method.

<table>
<thead>
<tr>
<th>Heating rate (°Cs(^{-1}))</th>
<th>Peak</th>
<th>( T_m )(°C)</th>
<th>( T_m )(°C)</th>
<th>E (eV)</th>
<th>s(Hz)</th>
<th>( \tau ) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>05</td>
<td>1</td>
<td>165</td>
<td>1.434</td>
<td>2.3 x 10(^{12})</td>
<td>2.8 x 10(^{07})</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>200</td>
<td>0.699</td>
<td>2.7 x 10(^{06})</td>
<td>1.5 x 10(^{06})</td>
<td>155</td>
</tr>
<tr>
<td>07</td>
<td>1</td>
<td>167</td>
<td>1.148</td>
<td>4.1 x 10(^{11})</td>
<td>1.9 x 10(^{06})</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>205</td>
<td>0.727</td>
<td>3.6 x 10(^{06})</td>
<td>7.1 x 10(^{06})</td>
<td>165</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>174</td>
<td>1.108</td>
<td>2.4 x 10(^{11})</td>
<td>4.6 x 10(^{06})</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>201</td>
<td>0.757</td>
<td>6.0 x 10(^{06})</td>
<td>4.7 x 10(^{06})</td>
<td>145</td>
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<tr>
<td>15</td>
<td>1</td>
<td>184</td>
<td>1.330</td>
<td>9.8 x 10(^{10})</td>
<td>5.4 x 10(^{06})</td>
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<tr>
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<td>1.7 x 10(^{06})</td>
<td>6.8 x 10(^{06})</td>
<td>168</td>
</tr>
</tbody>
</table>

The estimated \( E \) and \( s \) values for different \( \gamma \) doses and heating rates are given in Table.5.2.2 & 5.2.3. Variation of \( E \) and \( s \) with different heating rates are shown in Fig.5.2.14 (a & b) respectively. It is observed that (Table.5.2.3) the activation energy corresponding to 171°C peak increase with increase in heating rate. This increase in
activation energy is attributed to temperature lag [31]. However, the activation energy corresponding to 223 °C glow peak decreases with heating rate which is attributed to thermal quenching effect [32].

Fig.5.2.14 (a) Variation of E with β. (b) Variation of s with β in CdSiO₃:Pr³⁺ nanophosphor

Further, the concentration of trapped charges (nₒ) [33] is determined by using equation

\[ nₒ = \frac{\omega I_m}{\beta(2.52 + 10.2(\mu_g - 0.42))} \]  \hspace{1cm} \ldots \ldots \ (5.2.7)

Where \( I_m \) is the glow peak intensity.

The life time of the traps can be estimated using the relation [34]

\[ \tau = s^{-1} \exp\left(\frac{E}{kT}\right) \]  \hspace{1cm} \ldots \ldots \ (5.2.8)

The life time estimated for 171 and 223 °C TL glow peaks are found to be ~ 67 and 158 ms respectively.

Fading is an important characteristic feature of dosimetry, which is the unintentional loss of the TL signal. It leads to an under estimation of the absorbed dose. Fading may be due to several causes. Thermal fading originates from the fact that even at room temperature there is a certain probability of charge carriers escaping from their trapping centers. Fading may also be caused by optical stimulation. In general, high-sensitivity materials should be handled carefully and stored in opaque containers to prevent fading from light exposure. Other types of fading, which are not temperature dependent, are caused by quantum mechanical tunneling of the trapped charge to recombination sites and transitions between localized states, i.e. transitions that do not take place via the delocalized bands [35].
To study the fading effect, the phosphor CdSiO$_3$:Pr$^{3+}$ was given a test dose of 6 kGy from a gamma source ($^{60}$Co), the TL signal was recorded at different intervals of time for nearly 30 days. Fig.5.2.15 shows the plot of TL intensity versus the number of days after gamma irradiation. Strong fading was observed after 15 days with the TL signal losing around 68% of its initial value. Subsequently, the signal decayed slowly and finally stabilized after 20 days.

Pallavi et al. [36] have studied TL properties of β irradiated Sr$_3$Al$_2$O$_6$: Tb$^{3+}$ (1%). The fading effect of the phosphor was measured by giving the sample a test dose of 100 Gy from a Sr-90 beta source. And the TL signal was recorded at different intervals for nearly two months. Strong fading was observed after 10 days of irradiation with the phosphor losing around 59% of the TL signal. After this time, the decay was quite slow and finally stabilized after 30 days. The 41% remnant TL signal is high enough to be considered for dosimetric applications.

![Graph](image_url)

Fig.5.2.15. Effect of fading with number of days in CdSiO$_3$:Pr$^{3+}$ nanophosphor

**5.2.5. Conclusions**

We have demonstrated CdSiO$_3$:Pr$^{3+}$ (1-9 mol %) nanophosphors can be successfully synthesized by a low temperature initiated self-propagation solution combustion method. This method offers wide range of advantages such as high yield (60-70%) purity, simple experimental setup, time and energy saving, when compared to other methods. The PXRD patterns show monoclinic phase. The crystallite size estimated for Scherer’s
method and W-H plots for 1, 5 and 9 mol% Pr$^{3+}$ doped CdSiO$_3$ was found to be 31, 35 and 37 nm respectively. The optical energy band gap is found to be in the range 5.15-5.36 eV. TL studies have been performed for the first time on CdSiO$_3$:Pr$^{3+}$ by irradiating with γ-rays in the range 1-6 kGy. Two TL glow peaks were recorded one at ~171 °C (well resolved) and another one at ~223 °C (shouldered) peak. TL intensity is found to be increase linearly with γ-dose and low fading which are essential properties for radiation dosimetry.
5.2.6. References

5.3. Thermoluminescence properties of swift heavy ions and UV exposed 
CdSiO$_3$:Ce$^{3+}$ nanophosphor synthesized by combustion method

5.3.1. Introduction

Presently there is a huge demand for dosimetry of the heavy ions due to its diagnostic and 
therapeutic purposes [1, 2]. Moreover, the energetic cosmic rays constitute a serious 
dosimetric problem, particularly the high energy particulate radiation, near the low earth 
orbit, where the component used in various subsystems of the space craft get exposed to 
these radiations. Therefore there is a need of measuring doses/fluences of such energetic 
particles with great precision of accuracy, especially, while dealing with human beings. 
Thermoluminescent dosimetry (TLD) phosphors could be employed for this purpose. 
Thermoluminescence (TL) is a well-known technique that is widely used in the dose 
measurement of ionizing radiations namely X-rays, $\gamma$-rays and heavy ion beams.

Thermoluminescent materials exhibit differences in dose response between 
sparingly ionizing radiation (high energy photons like X-ray and $\gamma$ - ray) and densely 
ionizing radiation like heavy charged particles (HCP). This is due to different spatial dose 
distribution [3]. Ion beam effects on the materials mainly depend on the ion energy (GeV, 
MeV and keV), ion fluence, charge state and type ion species. When energetic ion 
penetrates through the material it loses its kinetic energy in two modes, (i) nuclear 
stopping ($S_n$) and (ii) electronic stopping ($S_e$). The nuclear stopping is dominant at low 
energies (keV) and the energy lost in this process is called nuclear energy loss. The other 
mode of energy loss is by exciting or ionizing the atom by inelastic collisions and the 
energy spent in this process is called as electronic energy loss. Electronic stopping is 
dominant at high energies, where the displacement of atoms due to elastic collisions is 
insignificant [4].

An ideal TL dosimetry phosphor is expected to possess certain features such as: a 
relatively simple glow curve having ideally a single peak with its temperature over 
200 °C; same TL response for all energies of ionizing radiation; high sensitivity that 
includes both a high efficiency of light emission and a low threshold dose; low fading; 
good linearity of the TL signal in the specific useful range of radiation dose [5-7]. Till 
date none of the materials have been found to possess all the above characteristic features 
and thus a search in this area is highly needed. Recently, a few reports available suggest 
that nanophosphors are highly suitable compared to their corresponding conventional
micro phosphors for accurately measuring high doses of ionizing electromagnetic as well as particulate radiation [8-10]. Luminescence study of CdSiO$_3$ doped with rare earth/transition metal ion was studied just couple of years ago. In this host matrix, the tetrahedral silicate (SiO$_4^{2-}$) ion provides good mechanical resistance and stability for the phosphor. Therefore, many other silicate-based host lattices have also been used to extract high luminescence yield from rare earth ions.

Thermoluminescence (TL) studies of pure and doped CdSiO$_3$ was investigated with less detail by a very few research groups. Liu et al [11] have prepared pure, rare earth and transition metal ions doped CdSiO$_3$ by solid state method and their attention has been devoted to enhance its luminescence property, e.g., in CdSiO$_3$: Dy$^{3+}$ material the effect of dopant concentration on the TL intensity has been discussed. Lei et al [12] have studied the TL spectra of undoped and Mn$^{2+}$ doped CdSiO$_3$ and reported that the introduction of Mn$^{2+}$ had created different traps. Kuang and Liu [13] have found that the trivalent Pr$^{3+}$ in CdSiO$_3$ host play not only the role of activator, but also as an auxiliary dopant to create traps and they have also studied the effect of co-dopants like trivalent Y, La, Gd, Lu ions in the Mn$^{2+}$ doped CdSiO$_3$ on the enhancement of TL intensity and also the effect of their ionic radii on the formation of traps was discussed. In another study, Kuang et al have observed long-lasting phosphorescence phenomenon by RE$^{3+}$ (RE = Y, Gd, Lu) ions addition in CdSiO$_3$:Mn$^{2+}$ phosphor [14].

As far as preparation of CdSiO$_3$ is concerned, it has been prepared by traditional solid-state method at about 1050 °C for 3h and sol-gel method at 900 °C for 2hr. The powder prepared by solid state method results into large particles, and the method demands repeated grinding followed by firing at very high temperature. However, Qu et al [15] have prepared this material by using sol-gel method. Even this method also not cost effective and eco-friendly, since it demands specific reactant precursors like tetra-orthosilicate (TEOS) as a source of silicate and metal alkoxide and different organic solvents for gel formation and washings. Therefore, in our previous work [16] we have investigated that the solution combustion synthesis could be a best option for the preparation of CdSiO$_3$. Because, it is an effective, low-cost, time saving method and it has been effectively used for the preparation of a variety of industrially important nanomaterials [17]. Today, it has become a very popular approach for preparation of nanomaterials. In this synthesis technique we could able to get nanocrystalline CdSiO$_3$ at very low temperature of 800 °C as compared to others with very less time. Hence in this
work, we report the preparation of Ce$^{3+}$ doped CdSiO$_3$ by combustion technique at a low temperature, its characterization and TL properties by using 100 MeV Si$^{7+}$ swift heavy ions and UV rays for its possible usage in dosimeter applications. To the best of our knowledge, no studies on thermoluminescence luminescence behavior of Ce$^{3+}$ doped CdSiO$_3$ nanophosphor, prepared via combustion method, have ever been discussed.

5.3.2. Starting materials for preparation and characterization

The starting materials used for the preparation of CdSiO$_3$:Ce$^{3+}$ (1-9 mol %) were cadmium nitrate (Cd(NO$_3$)$_2$.4H$_2$O), cerium nitrate (Ce(NO$_3$)$_3$.6H$_2$O), fumed silica (SiO$_2$, 99.9%, surface area 200 m$^2$/g), and diformyl hydrizine (DFH: C$_2$H$_4$N$_2$O$_2$) as a fuel. The dopant concentrations were varied from 1 to 9 mol%. All the starting materials used for the preparation are of analytical grade and not further purified except DFH, which is spectrographically pure. The detailed procedure for the preparation of nanocrystalline CdSiO$_3$ via combustion method has been discussed in detail in our previous report [16, 17].

After desired product was obtained, pellets of approximately 0.5 mm thickness and 6 mm diameter were prepared taking 100 mg of the sample without using any binder and applying tons of pressures each time by a hand pressed hydraulic machine. The pellets were again annealed at ~250 ºC for 1 hr in muffle furnace the deformations, if any, due to applied stress. The samples in the form of pellets were irradiated at room temperature by Si$^{7+}$ swift heavy ion beam at energy of 100 MeV for different ion fluences in the range 3x10$^{11}$ - 3x10$^{13}$ ions cm$^{-2}$, using a 16 MV Tandem Van de-Graff type Electrostatic Pelletron Accelerator at the Inter-University Accelerator Center (IUAC), New Delhi, India. The pelletized samples were mounted on a copper target ladder with a silver paste giving good thermal and electrical conductivity between them. This prevents sample heating during ion irradiation. The ion beam was magnetically scanned on a 10 mm x 10 mm area on samples surfaces for a uniform irradiation and its spot size was ~2 mm$^2$. Two to three pellets were exposed to the same fluence in order to check the receptivity in TL measurements. For taking TL the irradiated surface was kept facing upwards towards the detector (PMT) of the TLD reader every time. TL glow curves were recorded using TLD reader. The heating rate was 5 ºCs$^{-1}$. Three glow curves were recorded for each sample to confirm uniform irradiation. In order to compare the similar dimensioned pellets were taken for UV exposure (254 nm) in the dose range 1-70 min for
TL measurements. The details of instruments used for characterization was given in chapter 2.

5.3.3. Results and Discussion

5.3.3.1. X-ray diffraction

The PXRD patterns of the undoped and Ce$^{3+}$ doped CdSiO$_3$ samples calcined at 800 °C for 2 hr are shown in Fig. 5.3.1.

![Powder XRD patterns](image)

Fig.5.3.1. Powder XRD patterns of solution combustion derived Cd$_{1-x}$Ce$_x$SiO$_3$ (a) un-doped, (b) $x=1$ mol%, (c) $x=3$ mol%, (d) $x=5$ mol%, (e) $x=7$ mol%, and (f) $x=9$ mol%, calcined at 800 °C for 2 hr.

All the diffraction peaks of the CdSiO$_3$:Ce$^{3+}$ (1 to 9 mol%) samples calcined at 800 °C can be assigned exactly to the standard data of CdSiO$_3$ (JCPDS card no. 35-0810). No impurity peaks in the PXRD profile, confirms that the compound is purely monoclinic phase and Ce$^{3+}$ dopant is successfully accommodated in the CdSiO$_3$ host lattice. As Ce$^{3+}$ content increases the crystallinity of the products is found to be increased. Compared to conventional solid-state reactions (1050 °C) and sol-gel method (900 °C), the crystallization temperature can be considerably reduced in the present combustion route. The phase formation temperature is found to be 800 °C, which is one of the appreciable results as for as synthesis part is concerned. The Cd(NO$_3$)$_2$, Ce(NO$_3$)$_3$ and SiO$_2$ are...
homogeneously dispersed at the molecular level during stirring and evenly mixed at some stage during vigorous combustion.

The structure of CdSiO$_3$ is monoclinic with the ‘P21/a’ space group. The ionic radius of Ce$^{3+}$ (1.034 Å) is comparable to that of Cd$^{2+}$ (0.97 Å), but larger than that of Si$^{4+}$ (0.42 Å), [18] so it is assumed that the Ce$^{3+}$ ion replaces Cd$^{2+}$ in CdSiO$_3$. The Ce$^{3+}$ ions upon replacing Cd$^{2+}$ is expected to create some oxygen-related defect centers or Cd$^{2+}$ vacancies for charge compensation. So, it may be assumed that the Ce$^{3+}$ ion will be in a structurally disordered environment and may occupy interstitial positions. However, in our case, the Ce$^{3+}$ doped samples showed similar PXRD patterns (Fig. 5.3.1) without any impurity phase. This clearly suggests the fact that Ce$^{3+}$ ions are certainly occupy Cd$^{2+}$ lattice positions rather than interstitial positions.

The average crystallite size of the samples can be estimated from the Scherer’s equation [19]. The estimated average crystallite size is in the range of 20-60 nm. It is well known that the full-width at half-maximum (FWHM) can be expressed as a linear combination of the contribution from the lattice strain and crystalline size. The effective strain and particle size can be measured by the following equation:

$$\beta \cos \theta / \lambda = 1/\varepsilon + \eta \sin \theta / \lambda$$  …… (5.3.1)

where ‘β’ is the measured FWHM (in radians), ‘θ’ is the Bragg angle of the peak, ‘λ’ is the X-ray diffraction wavelength, ‘ε’ is the effective particle size and ‘η’ is the effective strain. The graph is plotted by taking ($\beta \cos \theta / \lambda$) as y-axis and ($\sin \theta / \lambda$) as x-axis for

![Graph](image_url)
undoped, 1 mol%, 5 mol % and 9 mol% Ce\(^{3+}\) doped CdSiO\(_3\) (Fig.5.3.2). The effective particle size for which the strain has been taken into account can be estimated from the extrapolation of the plot in Fig. 5.3.2 and it is found to be in the range from 20 to 60 nm. The slope of the line indicates the presence of strain in the crystal lattice, which might have an important effect on the optical properties of the samples.

5.3.3.2. Scanning Electron Microscopy (SEM) & Transmission Electron Microscopy (TEM)

Fig. 5.3.3. SEM images of Cd\(_{1-x}\)Ce\(_x\)SiO\(_3\) (A) x= 1mol\%, (B) x=3 mol\%, (C) x=5 mol\%, (D) x=7 mol\% (E) x=9 mol% and (F) TEM of 4 mol % Ce\(^{3+}\) doped CdSiO\(_3\), all are calcined at 800 °C for 2hr
Fig. 5.3.3 (A-D) shows the morphology of Ce\(^{3+}\) doped CdSiO\(_3\) powder, calcined at 800 °C for 2 hr. It can be clearly seen from the low resolution SEM images (Figs. 5.3.3A to 5.3.3D) that this powder shows highly porous in nature with lots of voids and number of pores with uneven shape and size. The darker areas in the micrographs correspond to the pores in the samples. This can be ascribed to the liberation of large quantity of gasses during combustion. This kind of porous network is a typical characteristic of most of combustion derived samples. The formation of pores is due to the escape of gases at very high pressure and unevenness in their distribution is believed to be related to the non-uniform distribution of temperature and mass flow in the combustion flame. It is interesting to note that, there is slightly increase in the porosity, number of voids etc., with increase in concentration of Ce\(^{3+}\) (Fig. 5.3.3C and 5.3.3D). This small variation may be due difference in the concentration of Ce(NO\(_3\))\(_3\) precursor added in the initial stage of the combustion synthesis. The amount of gasses liberated also depends on oxidizing ability of oxidant against the fuel. The cerium nitrate has greater oxidizing tendency as compared to cadmium nitrate, so that the small increase in porosity from 3 to 7 mol % Ce\(^{3+}\) doped CdSiO\(_3\) may be due to increase in the amount of cerium nitrate. The microstructure of the CdSiO\(_3\):Ce\(^{3+}\) observed in the SEM micrographs reflects the inherent property of the self-propagating high temperature solution combustion technique [21]. The TEM image of 7 mol% Ce\(^{3+}\) doped CdSiO\(_3\) calcined at 800 °C is also shown in fig. 5.3.3E and F. The image exhibits a uniform distribution of slightly agglomerated particles of size ranging from 20-60 nm.

5.3.3.3. Fourier transform infrared spectroscopy (FT-IR)

Fig. 5.3.4 displays the FT-IR spectra of un-doped and 5 mol % Ce\(^{3+}\) doped CdSiO\(_3\) samples calcined at 800 °C for 2 hr. The broad band from 840-1170 cm\(^{-1}\) is due to asymmetric stretching vibration of Si-O-Si bond and stretching vibrations of terminal Si-O bonds. The peaks at 448-540 cm\(^{-1}\) and 640 cm\(^{-1}\) are due to symmetric stretching vibrations Si-O-Si bridges [22]. No change in the position of peaks in the spectra of un-doped and 5 mol% Ce\(^{3+}\) doped CdSiO\(_3\) (Fig. 5.3.4) sample confirms that the dopant Ce\(^{3+}\) has occupied the position of Cd\(^{2+}\) ions in crystal.
5.3.3.4. Optical properties

The UV-Vis absorption spectra of Ce\(^{3+}\) doped (1 to 9 mol %) CdSiO\(_3\) phosphor calcined at 800 °C for 2 hr are shown in Fig. 5.3.5. A strong absorption band in the range 220-260 nm was observed, which may be due to ligand-to-metal charge-transfer (LMCT) transition, oxygen to silicon (O-Si) in the SiO\(_3^{2-}\) group. The broad peak from 300-550 nm can be ascribed to the intra configurational 4f - 4f transitions from the ground \(^4F_0\) level, which corresponds to the excitation spectra. The observed results are well matches with that reported in the literature [23,24].

To estimate the direct optical energy band gap (\(E_g\)) of undoped and Ce\(^{3+}\) doped (1 to 9 mol %) CdSiO\(_3\) Tauc relation was used. [25]

\[
a(h\nu) \sim (h\nu - E_g)^{1/k}
\]  \(\ldots \ldots (5.3.2)\)

where ‘\(h\nu\)’ is the photon energy and ‘\(a\)’ is the optical absorption coefficient near the fundamental absorption edge. The values of the optical band gaps of the un-doped and Ce\(^{3+}\) doped CdSiO\(_3\) are obtained by plotting \((ah\nu)^2\) versus ‘\(E=h\nu\)’ in the high-absorption range followed by extrapolating the linear region of the plots to \((ah\nu)^2 = 0\) (Fig.5.3.6).
Fig. 5.3.5. UV-Vis absorption spectra of Cd$_{1-x}$Ce$_x$SiO$_3$ (a) Un-doped, (b) x = 1 mol %, (c) x = 3 mol %, (d) x = 5 mol %, (e) x = 7 mol % and (f) x = 9 mol %

Fig. 5.3.6. The direct optical energy band gap of Cd$_{1-x}$Ce$_x$SiO$_3$ (a) Un-doped, (b) x = 1 mol %, (c) x = 3 mol %, (d) x = 5 mol %, (e) x = 7 mol %, and (f) x = 9 mol %
Further, indirect band gap was estimated using the following relation [26]

$$\alpha \propto \frac{(h\nu + E_p - E_i)^2}{e^{h\nu/kT} - 1} + \frac{(h\nu - E_p - E_i)^2}{e^{h\nu/kT} - 1}$$

…… (5.3.3)

where ‘E_i’ is the band gap energy for indirect transitions, ‘E_p’ the phonon energy, ‘k’ is the Boltzmann constant, ‘h\nu’ is the photon energy, and ‘T’ the absolute temperature. The intersection of the extrapolated linear portion gives the indirect band gap energy (E_i). The plot of (\alpha h\nu)^{1/2} against ‘E= h\nu’ of un-doped and Ce^{3+} doped CdSiO_3 was shown in Fig. 5.3.7. It is noticed that the direct optical band gap is found to be lower in the un-doped samples when compared to the doped samples. The estimated band gap values in indirect method are lower when compared to the direct band gap.

### 5.3.4. Thermoluminescence (TL)

Fig.5.3.8 (a) and (b) shows the TL glow curves of different concentration of Ce^{3+} (1-9 mol %) in CdSiO_3 host irradiated with 100 MeV Si^{7+} ion for a fluence 1x10^{13} ions cm^{-2} and UV exposed for 20 min respectively. Here all the measurements were carried out at RT at a constant heating rate 5 °C s^{-1}. The TL intensity is found to be highest for 5 mol% of Ce^{3+} in ion irradiation and 3 mol% for UV exposure respectively.
(Fig. 5.3.9 (a) and (b)). This may be due to the change in trap distribution due to lattice perturbation caused by the swift heavy ions and UV rays.

![TL glow curves of (a) 100 MeV Si\(^{7+}\) ion irradiated CdSiO\(_3\) doped with Ce\(^{3+}\) (1-9 mol %) nanocrystalline phosphor. (b) UV exposed CdSiO\(_3\) doped with Ce\(^{3+}\) (1-9 mol %) nanocrystalline phosphor](image1)

![Variation of TL intensity as a function of Ce\(^{3+}\) concentration in CdSiO\(_3\) nanocrystalline phosphor (a) for 100 MeV Si\(^{7+}\) ion irradiation (b) for UV exposure](image2)

Fig. 5.3.9 (a) and (b) shows the TL spectra for optimized concentration of Ce\(^{3+}\) ions (5 mol %) in CdSiO\(_3\), irradiated with 100 MeV Si\(^{7+}\) ion for a fluence 3x10\(^{11}\) - 3x10\(^{13}\) ions cm\(^{-2}\) and for 3 mol% is UV exposed for 1-70 min. A shouldered peak 138 °C and a well resolved glow peak at ~ 197 °C was recorded in the entire ion irradiated samples whereas in UV exposed samples, a well resolved glow peak at 159 °C was recorded. It is observed that in UV exposed samples, the glow peak structure is simple and glow peak is shifted towards higher temperature side. The shift of main TL glow peak with increasing dose might be due to the creation of deeper TCs or higher LCs on irradiation. Similar effects have been observed in several other ion beams irradiated materials [27-29]. Further, the observed change in the TL glow peaks position of the
irradiated (ion and UV) materials could be attributed to the incompetence of the initial LCs/TCs, due to use of energetic ions for bombardments.

The variation of TL intensity with 100 MeV Si\(^{7+}\) ion fluence and UV exposure was studied and shown in Fig 3.3.10 (a) and (b) respectively. It is observed that the glow peak intensity increase up to a fluence of \(1 \times 10^{12}\) ions cm\(^{-2}\) then it decreases with further increase of ion fluence. However, in the case of UV exposed samples, the TL intensity increases up to a dose of 20 min, then it decreases with further increase of UV exposure. The TL intensity of glow curves shows non-linear increase in behavior (after \(1 \times 10^{12}\) ions cm\(^{-2}\) and after 15 min for UV exposure (Fig.3.3.10 (a) and (b)).

This suggests that more and more traps responsible for these glow peaks were getting filled with the increase of irradiation dose. These traps release the charge carriers on the thermal stimulation to finally recombine with their counter parts, thus giving rise to different glow peaks [30]. In case of nanoparticles the surface to volume ratio is high which results in a higher surface barrier energy of the nanoparticles [31]. At lower doses
the energy density is not enough to overcome this barrier and create defects or trapping centers in the nanoparticles and therefore a sub-linear response is obtained. On increasing the dose the energy density crosses the threshold value of the surface barrier and thus defects in large numbers are produced in the nanoparticles. The number of defects created in the particles keeps on increasing with dose till saturation is obtained. This explains the linearity in TL response of the nanophosphors over a given dose range [32].

The observed linearity/sub-linearity and saturation of TL signal occurring in this system by ion beam irradiation could be explained by track interaction model (TIM) [33, 34]. Accordingly, at low fluences the recombination of various TCs/LCs (Trap centers/ Luminescent centers) occurs entirely within the tracks. Electrons escaping the tracks are intercepted by the non-radiative competitive centers (CC) in the intermediate region. The TL signal, therefore, is simply proportional to the number of ion beam tracks (the fluence). At higher levels of fluences, the distance between the neighboring tracks decreases and the electrons escaping the track can reach the neighboring track resulting in the increased recombination of the luminescent centers resulting in greater TL intensity. The sub-linearity/ saturation occur due to more overlapping of the tracks at much higher fluences. The overlapping regions do not contribute to additional TL, since they do not result in additional charge carriers due to the full occupancy of the available TCs and/or LCs. This model will be true in the present case too; however, the process becomes little more complicated as the energetic ions also get implanted in the matrix, and might have created new kinds of defects. Therefore, more studies are required to confirm our hypothesis and to identify these defects.

Comparison between the TL glow curve of Si$^{7+}$ ion irradiation and that exposed to UV source (Figs.3.3.9 (a) and (b)) shows that there is a shift in the peak positions. The shift in the TL glow peaks’ positions of UV and ion irradiated phosphors can be attributed to the disorganization of the TCs and LCs, as a result of the use of highly energetic ions for bombardments. Similar effects have been observed in several other ion beams irradiated materials also [35-37].

It is observed that the TL glow temperature and intensity is different in ion and UV exposed samples. In case of UV exposed samples the 159 °C glow peak is more prominent, while in case of Si$^{7+}$ ion irradiated sample the high temperature peak (197 °C) appeared more prominently. This might be due to the change in the population of the
LCs/TCs, as a result of the use of highly energetic ions for bombardment. The rate of energy deposition is high as a result of high degree of ionization takes place and also this may lead to alterations in the traps sites.

The TL glow curves are different in both the irradiated samples (Fig.3.3.9 (a) and (b)). It clearly indicates that, the number of traps responsible for each peak is not in the same proportion in both cases and it might be due to some changes in the recombination center populations due to Si⁷⁺ ions, which have been implanted inside the matrix of CdSiO₃:Ce³⁺ during irradiation. They might also act as a source for new trapping and luminescent centers, which are in turn responsible for these different behaviors.

Effect of fading was studied on CdSiO₃:Ce³⁺ phosphor for a test dose of 30 min UV exposed and TL signal was recorded at different intervals for nearly 30 days. TL intensity as a function of the number of days after exposure is shown in Fig.3.3.11. Initially strong fading was observed (15 days). After 10 days with the phosphor loosing ~40 % of the TL signal. The strong fading is possibly due to the formation of shallow and thermally unstable traps. However, the phosphor irradiated at high doses, deeper traps are formed as a result of which fading will be less. The ~60 % remnant TL signal is high enough to be considered for dosimetric application [38].

![Image](image_url)

**Fig.3.3.11.** TL fading of Ce³⁺ doped CdSiO₃ exposed to 30 min of UV exposed for a period of 30 days

This is due to an increase in the energy barrier in the nanocrystalline phosphor; at lower doses the concentration of defect creation is minimal. The cause of fading at low doses is possibly due to the formation of shallow and thermally unstable traps. However, it is...
further speculated that on irradiating the nanocrystalline phosphor at high doses, deeper traps are formed, as a result of which the fading will be less.

Pallavi et al. [38] have studied the fading effect of Sr$_3$Al$_2$O$_6$: Tb$^{3+}$ (1 mol %) phosphor for nearly two months by irradiating with β-rays for a test dose of 100 Gy. Strong fading was observed after 10 days of β-irradiation with phosphor losing ~59 % of the TL signal. Further, the decay was quite slow and stabilized after 30 days. The 41 % remnant TL signal is enough to be considered for the phosphor in dosimetric application.

TL fading was studied in Y$_3$Al$_5$O$_{12}$ (YAG) irradiating with a 300 Gy β dose [39]. A strong fading was observed in nanocrystalline YAG after 12 hr with the phosphor loosing ~75 % and subsequently, The TL signal stabilized after 48 hr. However, in YAG single crystal strong fading was observed after 56 hr with the phosphor loosing TL signal ~5 % and 35 % remnant considered for dosimetric applications.

The influence of different heating rates between 2.5-7.5 °C s$^{-1}$ on TL response has been studied on CdSiO$_3$: Ce$^{3+}$ (3 mol %) sample, UV exposed for a dose of 20 min and results are shown in Fig. 3.3.12. It is found that with the increase in heating rates the TL peak intensity and area under the glow peak decreases (inset Fig. 3.3.12), however, glow peak temperature shifts towards higher temperature side (Fig. 3.3.12). The glow peak ($T_{\text{m}}$) is shifted from 133 to 175 °C with increase of heating rate from 2.5 to 7.5 °Cs$^{-1}$.

---

Fig.3.3.12. Effect of heating rates on TL glow curve for a sample exposed to UV source for 20 min. (Inset: heating rate vs maximum glow peak temperature)
The decrease in intensity with increase in heating rate is a phenomenon frequently observed in the practice of TL, it has been suggested to thermal quenching [31]. The knowledge of traps with their distribution in the band gap of solids is essential to understand the luminescence process which can be obtained by TL studies. Further, the dosimetric characteristics of TL materials mainly depend on the kinetic parameters such as activation energy, frequency factor and order of kinetics quantitatively describing the trapping emitting centers responsible for the TL emission. The TL glow curves was carried out deconvolution using ORIGIN 8.1 software (Fig.3.3.13 (a) for ion irradiation and (b) for UV irradiation) and then analyzed the individual deconvoluted glow curves using Chen’s peak shape method [40]. The methods for estimation of kinetic parameters and Chens empirical equation are given elsewhere [41].

The evaluated parameters E and b then used as initial parameters in the kinetic equations. These parameters can be modified during the best fit procedure during glow curve deconvolution (GCD) program until the best fit is achieved. Similar studies have been reported by some authors for the calculation of trapping parameters using Chen’s peak shape method applied directly to the peaks which were deconvoluted using origin software without using GCD functions [42].

The trapping parameters (E, b, s) for 100 MeV Si\(^{7+}\) ions and UV exposed CdSiO\(_3\):Ce\(^{3+}\) with various concentrations, different dose and different heating rates are estimated and shown in Table 3.3.1, 3.3.2 and 3.3.3 respectively.
### Table 3.3.1
Estimated kinetic parameters using glow peak shape method in swift heavy ion irradiated (5 mol %) Ce³⁺ doped CdSiO₃

<table>
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<th>Si⁺⁺ ion dose (10¹¹ ions cm⁻²)</th>
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<th>Y</th>
<th>µg</th>
<th>b</th>
<th>E (eV)</th>
<th>E</th>
<th>E</th>
<th>E</th>
<th>s (s⁻¹)</th>
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</thead>
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<td>0.49</td>
</tr>
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<td>1.02</td>
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</tr>
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<td>2.07</td>
<td>2.15</td>
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### Table 3.3.2
Estimated kinetic parameters using glow peak shape method in UV exposed (3 mol %) Ce³⁺ doped CdSiO₃

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<th>UV exposure (min)</th>
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<th>T_m (°C)</th>
<th>Y</th>
<th>µg</th>
<th>b</th>
<th>E (eV)</th>
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<th>E</th>
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<th>s (s⁻¹)</th>
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<td>0.49</td>
<td>2</td>
<td>0.597</td>
<td>0.663</td>
<td>0.632</td>
<td>0.630</td>
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<td>0.614</td>
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<td>0.575</td>
<td>2.4E+07</td>
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Table 3.3.3. Estimated kinetic parameters using glow peak shape method in different heating rates in UV exposure (3 mol %) Ce$^{3+}$ doped CdSiO$_3$

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<th>UV exposure (min)</th>
<th>Peak</th>
<th>$T_m$ ($^\circ$C)</th>
<th>Y</th>
<th>$\mu_g$</th>
<th>b</th>
<th>$E$ (eV)</th>
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The parameter describing the quality of fitting, called Figure of Merit (FOM) was estimated using [43].

$$FOM = \frac{\sum |TL_{\text{Experimental}} - TL_{\text{Fit}}|}{TL_{\text{Fit}}} \quad \ldots \quad (5.3.11)$$

Where $TL_{\text{Experimental}}$ and $TL_{\text{Fit}}$ represent the experimental and TL intensity data values of the fitting function, respectively. The summation extends over all the experimental data points. The resolution of fitting method can be refined by repeating the process of calculating the FOM for different values of $E$ that minimizes the value of FOM. Glow curves with FOM values in excess of 5% are subjected to further investigation to determine the reasons for the poor fit. Hence minimum three peaks are required to get the best fit. These all deconvoluted three peaks show second-order kinetics, i.e. the probability of electron re-trapping during thermoluminescence process was negligible the FOM is found to be $\sim$ 0.037 for theoretical curve fitting which shows that the experimental and theoretical curves are in good agreement and overlap each other well. In the present study we deconvoluted the TL glow curves based on Gaussian functions into
three peaks, which were also confirmed by the thermal cleaning method [44] which is shown in Fig.3.3.14.

![Fig.3.3.14. TL glow curves of Ce$^{3+}$ doped CdSiO$_3$ (a) deconvoluted curve (b-d) thermal cleaning of peaks at different temperatures](image)

It is expected that in high energetic ion beam irradiation (Si$^{7+}$), there will be changes in the TL glow curve structure, since the TL trapping and recombination mechanism are very sensitive to any perturbation. Especially, when atomic displacements are due to non-elastic collisions and ionization due to secondary particles are taking place. Therefore, the observed changes in the trapping parameters (i.e., glow peak temperature, order of kinetics, activation energy and frequency factor) (Table.3.3.1) are perhaps due to the disorganization of the initial energy bands of the silicate host.

5.3.5. Conclusions

In summary, we have successfully synthesized porous CdSiO$_3$:Ce$^{3+}$ (1-9 mol %) nanocrystalline phosphors without any impurity phase using low temperature initiated self propagation solution combustion method. The synthesized phosphor shows monoclinic phase upon calcination at 800 °C for 2 hr. Combined morphology and structural characterizations show that the calcined powder is well crystallized with highly porous morphology. The TEM image clearly demonstrates that the powder is made up of almost spherical shaped nano-particles of size in between 20-50 nm. TL studies have been performed for the first time on CdSiO$_3$:Ce$^{3+}$ by irradiating with 100 MeV, Si$^{7+}$ swift heavy ions and UV rays. Two TL glow peaks were recorded at ~138 °C (shouldered) and 197 °C (well defined) in swift heavy ion irradiation and a single broad well defined TL
peak at 157 °C was recorded in UV exposed samples. The variation in TL glow peak temperatures were observed in swift heavy ions and UV exposed samples. This might be due to the change in population of the luminescent /trapping centers. In swift heavy ion irradiated samples, the TL glow peak intensity increases up to a fluence of $1 \times 10^{12}$ ions cm$^2$ then it decreases with further increase of ion fluence. In the case of UV exposed samples, TL intensity increases up to a dose of 20 min, and then it decreases with further increase of UV exposed. Simple glow peak structure, linear increase in TL intensity and simple trap distribution, less fading indicates that the CdSiO$_3$:Ce$^{3+}$ nanocrystalline phosphor exposed with UV rays can be used in UV dosimeter.
5.3.6. Reference


