Chapter 4

Luminescence properties of CaSiO$_3$:Eu$^{3+}$, Dy$^{3+}$ nanophosphors induced by Si$^{7+}$ ions
Chapter 4

Luminescence properties of CaSiO₃: Eu³⁺, Dy³⁺ nanophosphors induced by Si⁷⁺ ions

4.1. Thermo, Iono and photoluminescence properties of 100 MeV Si⁷⁺ ions bombarded CaSiO₃:Eu³⁺ nanophosphor

4.1.1. Introduction
The successful applications of inorganic luminescent materials such as CaSiO₃, CdSiO₃, Zn₂SiO₄, etc in display, energy, environmental and biological studies [1-3] have inspired great research interest in their nanoscale counterparts. It is expected that the nanosized luminescent materials can improve not only the luminescence quantum yield but also the resolution of display. Among these luminescent materials, rare-earth ion doped phosphors have been widely studied for their superior luminescence properties [4-6]. In the case of rare-earth ion doped phosphors, the electronic wave functions of rare-earths 4f-4f transitions are strongly localized, and they are not affected by quantum confinement effect. Reducing the size to a few nanometers, rare-earth doped phosphors may exhibit electron–photon interaction related spectral behavior as has been observed in rare-earth oxides. Specifically, the luminescence spectra related to 4f-5d transitions which involve broad spectral line width as occurred for low valence rare-earth ions are crystal field related and can be tuned by the size and the crystal structure [7].

In recent years, the irradiation of nanomaterials with swift heavy ions (MeV range) has become one of the most important methods for surface modification. In MeV irradiation, electronic energy loss in the materials can be varied from tens of eV/A⁺ up to a very high energy value keV/A⁺ by choosing appropriate ions and energy. This provides a remarkable flexibility and adequate opportunities to manipulate the properties of materials to acquire desired structural, optical, electrical and luminescent properties. Further, Ion beam techniques such as proton induced X-ray emission (PIXE), Rutherford back scattering (RBS), iono beam induced luminescence (IBIL), are very powerful tool due to their high flexibility and the possibility to control exactly technological important parameters like energy, fluence, beam size, charge state, type of ion, etc [8]. However, extension of the energy to the MeV range, many interesting features are expected such as radiation damage, radiation induced phase transition, generation of deep levels and their relation to the implant distribution in crystalline solid. An understanding of associated
physics processes involved in MeV irradiation is still a matter of great concern in nanocrystalline materials. Moreover, swift heavy ions also produce various types of defects in the materials for modifying the structural, electrical, optical and mechanical properties of the materials [9].

In this chapter we report the swift heavy ion bombarded thermo, iono and photoluminescence properties of 100 MeV Si$^{7+}$ ions on nanocrystalline CaSiO$_3$:Eu$^{3+}$ phosphor. The silicate phosphors have been paid considerable attention because of their multi-color phosphorescence and resistance to acid, alkali and oxygen [10] and have been widely used in lighting and display for luminescent applications [11]. In this host matrix, the tetrahedral silicate (SiO$_4$)$^{2-}$ ion provides good mechanical resistance and stability for the phosphor. Moreover, silicate-based host lattices have also been proposed for the efficient luminescence yield from rare earth ions.

4.1.2. Experimental
The nanocrystalline CaSiO$_3$:Eu$^{3+}$ (1-5 mol %) phosphors were synthesized by a low temperature solution combustion method which was given in our earlier paper [12]. 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 2.5 tons of pressures per ram on each time by a hand pressed hydraulic machine. The pellets were again annealed at ~250 °C for 1 hr in muffle furnace the deformations, if any, due to applied stress. The pellets were irradiated at room temperature by Si$^{7+}$ swift heavy ion beam at energy of 100 MeV for different ion fluences using a 16 MV Tandem Van de Graff type Electrostatic Pelletron Accelerator at the Inter-University Accelerator Center (IUAC), New Delhi, India [13]. The detail description of the instruments used for ion irradiation and IL, PL and TL instruments used for luminescent measurements are given in chapter 2.

4.1.3. Results and Discussion
4.1.3.1. Thermoluminescence (TL)
Fig.4.1.1. shows the TL glow curves of 100 MeV swift Si$^{7+}$ ion irradiated CaSiO$_3$:Eu$^{3+}$ in the fluence range 1x10$^{11}$-1x10$^{13}$ ions cm$^{-2}$. A single well resolved glow peak at ~304 °C is recorded at a heating rate (β) of 5 °Cs$^{-1}$. The variation in TL glow peak intensity with Si$^{7+}$ ion irradiated CaSiO$_3$:Eu$^{3+}$ is shown in Fig.4.1.2. It is observed that the glow peak intensity increase sub linearly with ion fluence up to 1x10$^{12}$ ions cm$^{-2}$ and thereafter it reaches saturation. The sub-linear region is attributed to large surface to volume ratio in CaSiO$_3$:Eu$^{3+}$ nanophosphor which results in a higher surface energy barrier.
Fig. 4.1.1. TL glow curves of CaSiO$_3$:Eu$^{3+}$ (5mol %) in 100 MeV Si$^{7+}$ ion irradiation for a fluence range $1 \times 10^{11}$-$1 \times 10^{13}$ ions cm$^{-2}$.

Fig. 4.1.2. Variation of TL intensity and Glow peak temperature of CaSiO$_3$:Eu$^{3+}$ phosphor with 100 MeV Si$^{7+}$ ions in the fluence range $1 \times 10^{11}$-$1 \times 10^{13}$ ion cm$^{-2}$.

At lower ion fluences the energy density is not enough to overcome this energy barrier and create luminescent / trapping centers as a result of sub-linear response. A similar sub-linear TL response was observed in proton and gamma irradiated K$_2$Ca$_2$(SO$_4$)$_3$: Eu$^{3+}$ [14]. Further, at high ion fluences, saturation of defects produced due to very high local dose around the ion path [15]. It is evident from the Fig.4.1.2 the glow peak temperature shifts...
towards the lower temperature side with increase of ion fluence. This might be attributed to the increase in concentration of trapped electrons ($n_o$) in CaSiO$_3$:Eu$^{3+}$ lattice. Further, shift in TL glow peak positions might be attributed to disorganization of the trapping and luminescence centers [14].

The linear/sublinear/supralinear/saturation of TL intensity by swift heavy ion irradiation was observed by many authors and can also be explained on the basis of track interaction model (TIM) [16, 17]. Accordingly, at lower ion fluences, the recombination of various trapping or luminescence centers in the intermediate region. The TL intensity therefore, is simply proportional to the number of ion beam track. At higher ion fluences, the distance between the neighbouring tracks decreases and the electrons escaping the track can reach the neighboring track results in the increased recombination of the luminescent centers resulting in TL intensity. The sublinear /saturation occurs due to more overlapping of the tracks at 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 luminescent centers. However, the process becomes more complicated as the energetic ions get imported in the matrix and might have created new and complicated defects. Therefore, more studies are required to confirm our hypothesis and identify these defects.

The evolution of kinetic parameters ($E$, $b$, $s$) associated with the TL glow peak is one of the important parameter. Any complete description of TL characteristics of the material requires the knowledge of these parameters. TL glow curve analysis leads to the estimation of localized trap depth. The analysis further leads to the estimation of the frequency factor ($s$), which gives information about the electrons that are released from the trap due to thermal energy, that is released electrons may get retrapped at the trapping centre, which is known as second order kinetics ($b=2$). On the other hand the thermally released electrons may reach the conduction band without getting retrapped and it is known as first order kinetics ($b=1$). Further, it has been observed that the glow curves are more symmetric in nature on a wide temperature range. This is one of the characteristic features of a second order kinetics and it is due to the fact that in second order kinetics, significant concentration of released electrons are retrapped before they recombine with hole centre’s. This might be the reason for the delay in the luminescence emission and hence spreading out the emission over a wide temperature range [18].
To obtain the parameters (E, b and s) the glow curves are deconvoluted using commercially available ORIGIN 8.1 software (Fig.4.1.3) then analyzed the individual deconvoluted glow curves using Chen’s peak shape method [19] by the following equations.

\[ E_a = C_a \left( \frac{K m^2}{\alpha} \right) - b_a (2K m) \]  

\[ \text{Where } \alpha = \tau, \delta, \omega \]

\[ \delta = T_2 - T_m \quad \omega = T_2 - T_1 \quad \tau = T_m - T_1 \quad \mu g = \frac{\delta}{\omega} \]  

\[ C_\tau = 1.51 + 3.0(\mu_g - 0.42) \quad C_\delta = 0.976 + 7.3(\mu_g - 0.42) \]  

\[ C_\omega = 2.52 + 10.2(\mu_g - 0.42) \]  

\[ b_\tau = 1.58 + 4.2(\mu_g - 0.42) \quad b_\omega = 0 \quad b_\delta = 1 \]  

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 8.1 software without using GCD functions [20].

Fig.4.1.3. Deconvoluted TL graph for a fluence of 30x10^{11} ions cm^{-2}
The isolated peaks were analyzed by Chen’s peak shape method to evaluate the peak parameters using above equations. The calculated parameters were then used as initial parameters for the GCD basic function suggested by Kittis et al [21] for the second order kinetics glow peaks given by

\[
I(t) = 4I_m \exp\left(\frac{E}{kT} T - T_m \right) \times \left[\frac{T_m^2}{T^2} (1 - \Delta) \exp\left(\frac{E}{kT} \frac{T - T_m}{T_m}\right) + 1 + \Delta \right]^2 \quad (4.1.6)
\]

Here \(I_m\) is the main peak intensity, \(E\) is the activation energy (eV), \(k \) is the Boltzmann constant. Once the activation energy \((E)\) and order of kinetics \((b)\) were determined, the frequency factor \((s)\) was calculated from the equation:

\[
\frac{BE}{kT_m^2} = s \exp\left(\frac{E}{kT_m^2}\right) \left[1 + (b - 1)\Delta_m \right] \quad \text{…….. (4.1.7)}
\]

Where \(\Delta = \frac{2kT}{E}\); \(\Delta_m = \frac{2kT_m}{E}\) and \(\beta\) is the linear heating rate and \(k\) is Boltzmann constant \((8.6 \times 10^{-5} \text{ eV K}^{-1})\). The trapping parameters \((E, b, s)\) of CaSiO\(_3\):Eu\(^{3+}\) for 100 MeV Si\(^{7+}\) ions irradiated with different ion fluences are shown in Table.4.1.1.

From the table, it is obvious that a considerable amount of retrapping takes place in all second order peaks. It is believed that there are some deep and shallow traps, for this reason there could be retrapping of the electrons at deep traps going to upper shallow traps by stimulation due to thermal energy. The competition among them might have resulted in different frequency factors. The traps could be either electron traps or hole traps or of both kinds.

<table>
<thead>
<tr>
<th>Si(^{7+}) Ion fluence (x10(^{12})ions cm(^{-2}))</th>
<th>Peak</th>
<th>(T_m) (°C)</th>
<th>(b) (μg)</th>
<th>(E) (eV)</th>
<th>(s) (s(^{-1}))</th>
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<td></td>
<td></td>
<td></td>
<td>(E_\tau)</td>
<td>(E_\delta)</td>
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<tr>
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<td>2</td>
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<td>2(0.51)</td>
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<td>1.297</td>
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<tr>
<td></td>
<td>3</td>
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<td>0.658</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>338</td>
<td>2(0.48)</td>
<td>1.657</td>
<td>1.498</td>
</tr>
<tr>
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<td>0.818</td>
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<tr>
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<td>269</td>
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<td>336</td>
<td>2(0.51)</td>
<td>1.224</td>
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### Table 4.1.3.1: Ionoluminescence (IL) Parameters

<table>
<thead>
<tr>
<th>Si(^{7+}) Ion fluence (x10(^{12}) ions cm(^{-2}))</th>
<th>Peak</th>
<th>T(_m)(°C)</th>
<th>b ((\mu_g))</th>
<th>E (eV)</th>
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<td></td>
<td></td>
<td>(E_t)</td>
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<td>233</td>
<td>2(0.50)</td>
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<tr>
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<td>2</td>
<td>267</td>
<td>2(0.50)</td>
<td>1.687</td>
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<tr>
<td></td>
<td>3</td>
<td>299</td>
<td>2(0.48)</td>
<td>1.731</td>
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<tr>
<td></td>
<td>4</td>
<td>333</td>
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</tr>
<tr>
<td>30</td>
<td>1</td>
<td>230</td>
<td>2(0.48)</td>
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</tr>
<tr>
<td></td>
<td>2</td>
<td>273</td>
<td>2(0.49)</td>
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</tr>
<tr>
<td></td>
<td>3</td>
<td>303</td>
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</tr>
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<tr>
<td></td>
<td>4</td>
<td>341</td>
<td>2(0.51)</td>
<td>1.612</td>
</tr>
</tbody>
</table>

#### 4.1.3.2. Ionoluminescence (IL)

When an ion beam with energy of a few MeV/u bombarded on a crystalline materials, visible light is often observed. This light induced by the energetic ions is termed as ionoluminescence. IL can mainly be used for materials modification, creation of intrinsic defects and structural defects, identification of emitting impurities, differentiation of synthetic and natural materials, crystalline and vitreous material, identification of polymorphs etc [22]. The main difference between IL and other luminescence techniques is that it uses more energy (MeV range) for excitation of the sample, so it is possible to reach higher electronic levels [23]. IL is especially sensitive towards the presence of cation elements such as transition metal ions and rare earths.

Fig. 4.1.4 shows the optimized IL spectra for various concentrations of Eu\(^{3+}\) in CaSiO\(_3\) nanophosphor bombarded with 100 MeV Si\(^{7+}\) ions for fluence of 5.2 x10\(^{12}\) ions cm\(^{-2}\). The maximum IL yield was observed in 5 mol% Eu\(^{3+}\) doped CaSiO\(_3\) nanocrystalline phosphor. Fig.4.1.5 shows the IL spectra of nanocrystalline CaSiO\(_3\):Eu\(^{3+}\) (5 mol %) acquired during 100 MeV Si\(^{7+}\) ion irradiation in the fluence range 1.30 x10\(^{12}\) - 5.2 x10\(^{12}\) ions cm\(^{-2}\) at room temperature. The spectra consist of bands at 581, 593, 614, 654 and 724 nm which can be assigned to \(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_J\) (J=0, 1, 2, 3 and 4) transitions of Eu\(^{3+}\) ions namely the \(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_0\) (581 nm), \(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_1\) (593 nm), \(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_2\) (614 nm), \(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_3\) (654 nm) and \(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_4\) (724 nm) respectively [24-26].
Fig. 4.1.4. Variation IL intensity of CaSiO$_3$: Eu$^{3+}$ phosphor as a function of Eu$^{3+}$ content for 100 MeV Si$^{7+}$ ions bombarded with a fluence of $5.2 \times 10^{12}$ ions cm$^{-2}$.

The variation of IL yield in different emissions peaks (581-724 nm) with different Si$^{7+}$ ion fluence was studied and shown in Fig. 4.1.6. It is observed that IL yield increases up to fluence $5.20 \times 10^{12}$ ions cm$^{-2}$, then it decreases with further increase of fluence. The increase in IL yield is due to an increasing number of intrinsic defects produced by the Si$^{7+}$ ion irradiation. Further, at higher fluences, the saturation of defect centers is reached.
the sample becomes defect-rich, which influences the radiative transitions. Due to the high defect concentration, the radiative transition rate decreases, resulting in the reduction of IL intensity from the sample.

![Graph](image)

**Fig. 4.1.6. Variation of IL intensity with 100 MeV Si\(^{7+}\) ions for the fluence range 4.16 \times 10^{12}-6.77 \times 10^{12} \text{ ions cm}^{-2}**

The decrease in IL intensity with increase of ion fluence might also be due to lattice disorder produced by dense electronic excitations under swift heavy ion (SHI) irradiation [27]. This might due to amorphization of the material and it may be explained on the basis of thermal spike model (TSM). When the heavy ion strikes the lattice of the material, most of its energy is employed for the creation of an excited electron cloud. The excited material then stabilizes by emitting energy in different forms. There are two important mechanisms suggested. (i) Non-radiative emission of phonons from the lattice. This process would increase the temperature in the crystal if the irradiation is continuous i.e., increase in ion fluence and would lead to amorphization of the crystalline (ii) Alternatively the radiative emission by an impurity atoms located in the matrix of the crystal takes place from their excited levels to the ground level.

This emission is very sensitive towards the valence state, ion species and distance from the emitting atom to the element to which it is coordinated. The light emission generated in this way fades with the ion fluence and an increment in temperature is observed. A proton beam colliding in a crystalline material (lattice + impurities) generates some electron cloud that appears localized in the lattice. Certain different relaxing mechanisms are available for the material to return to its ground state, namely non-
radiative and radiative emissions coming either from the lattice or from the impurities. These mechanisms are dependent on irradiation time. The final effect is that of the heating of the lattice that thermally quenches all the forms of emission [28].

Lakshminarasappa et al [29] studied IL of combustion synthesized nanocrystalline Mg$_2$SiO$_4$:Dy$^{3+}$ bombarded with 100 MeV Si$^{8+}$ ions with fluences in the range (1.124-22.480) $\times$ 10$^{12}$ ions cm$^{-2}$. The decrease in IL intensity with Si$^{8+}$ ion fluence was observed. The decrease in IL intensity with increase of ion fluence was attributed to amorphization of the material and same may be explained on the basis of TSM. In the present studies amorphization was not achieved for the studied fluences. IL yield depend on type of ion species, luminescence activators/quenchers, current beam used, etc [30].

Calvo del Castillo et al [31] studied IL of trivalent rare-earth-doped strontium barium niobate single crystals have been induced with a 3 MeV proton beam for a variety of beam current intensities (45, 40 and 20 nA). The emission at 350–570 nm was not observed in 20 nA of beam intensity. However, same spectral features observed for 40 and 45 nA beam intensities with trivalent rare-earth features, increases with the current intensity. Further, beam current as a function of emitted intensity was observed to be linear with different slope. This different behavior is probably associated with the different nature of the emitting centres that contribute to the whole IL spectrum that can involve slightly different excitation steps.

Demarche et al [32] studied IL measurements on fused silica samples containing Si-nc using an 18 keV proton beam with excitation fluence of 1.2 $-10^{15}$ H$^+$cm$^{-2}$. The IL spectra of pure SiO$_2$ reference sample and SiO$_2$ samples with Si-nc grown under N$_2$ and Ar atmosphere was studied. Two emission peaks was observed around 485 and 650 nm, as well as a significant reduction of the IL response in the Ar-annealed samples than N$_2$ annealed samples. The reduction in IL signal under Ar may come from several effects, as a less efficient trapping mechanism of the carriers generated by ionization, a stronger non-radiative recombination rate, and/or the presence of a lower density of residual defects within this sample [33].

In recent studies, [13] of IL of iron-rich kyanite mineral during 100 MeV Si$^{8+}$ ion irradiation in the fluence range 1.87-7.50 $\times$10$^{11}$ ions cm$^{-2}$, sharp IL peaks at 689 and 706 nm were recorded. These sharp peaks were attributed to luminescence centers activated by Fe$^{2+}$ and Fe$^{3+}$ ions. The IL intensity at these peaks increases with increase of
Si$^{8+}$ ion fluence. The increase of IL intensity might be due to O–Si–H and –OH type bonds covering the surface of the sample and providing a protective and passivating effect; as a result the number of non-radiative recombination centers can be reduced. More recently, the Nagabhushana et al [34] also studied IL of two natural Kyanite (Al$_2$SiO$_3$) minerals collected from different regions of India by bombarding 120 MeV Au$^{9+}$ ions in the fluence range 1.50-10.5x10$^{11}$ ions cm$^{-2}$. Identical emission peaks were observed in both the samples at ~ 416, 463, 530-540 nm along with other emission peaks at ~ 689, 706 (sharp) and 770 nm (broad). The sharp emission peaks at 689 nm correspond to R lines of Cr$^{3+}$ impurities and are related to transition of $^2E_g \rightarrow ^4A_{2g}$. The sharp and broad emission peaks in the range 706-770 nm are attributed to Fe$^{3+}$ impurities and are related to the transition of $^4T_{1g} \rightarrow ^6A_{1g}$. The peak in the range 530-540 nm is attributed to Mn$^{2+}$ impurities and is related to transition of $^4T_1 \rightarrow ^6A_1$. IL peak intensity decreases with the Au$^{9+}$ ion fluence which might be due to the thermal quenching/amorphization, caused by the ion beam irradiation. Therefore, IL is very sensitive and informative for impurity characterization and differentiation of the origin of minerals.

4.1.3.3. Photoluminescence (PL)

Fig. 4.1.7. shows the PL response in different Eu$^{3+}$ concentrations in CaSiO$_3$ nanophosphor bombarded with 100 MeV Si$^{7+}$ ions for a fluence of 1x10$^{13}$ ions cm$^{-2}$.

Fig. 4.1.7. PL spectra of different molar concentrations of Eu$^{3+}$ ions doped CaSiO$_3$ irradiated with 100 MeV Si$^{7+}$ ions for a fluence of 1x10$^{13}$ ions cm$^{-2}$ (a) 1 mol % (b) 2 mol % (c) 3 mol % (d) 4 mol % (e) 5 mol % (Inset: PL spectrum of un-doped CaSiO$_3$ nanophosphor)
The maximum PL response was observed in 5 mol % Eu$^{3+}$ ions (Fig. 4.1.8). PL spectra of nanocrystalline pelletized CaSiO$_3$: Eu$^{3+}$ phosphor (5 mol %), irradiated with 100 MeV Si$^{7+}$ ions at different fluences in the range 1x10$^{11}$ - 1x10$^{13}$ ions cm$^{-2}$, upon 326 nm laser beam excitation and the results are presented in Fig. 4.1.9. The spectra consist of bands at 581, 593, 614, 654 and 724 nm which can be assigned to $^5$D$_0 \rightarrow ^7$F$_J$ (J = 0, 1, 2, 3 and 4) transitions of Eu$^{3+}$ ions namely the $^5$D$_0 \rightarrow ^7$F$_0$ (581 nm), $^5$D$_0 \rightarrow ^7$F$_1$ (593 nm), $^5$D$_0 \rightarrow ^7$F$_2$ (614 nm), $^5$D$_0 \rightarrow ^7$F$_3$ (654 nm) and $^5$D$_0 \rightarrow ^7$F$_4$ (724 nm) [24-26] respectively.

Fig. 4.1.8. Variation of Eu$^{3+}$ ion concentration as a function of PL intensity in 100 MeV Si$^{7+}$ ions irradiation for a fluence of 1x10$^{13}$ ion cm$^{-2}$

Fig. 4.1.9. PL spectra of CaSiO$_3$: Eu$^{3+}$ (5 mol %) irradiated with 100 MeV Si$^{7+}$ ions for fluence in the range 1x10$^{11}$-1x10$^{13}$ ions cm$^{-2}$
The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is allowed as magnetic dipole transition. This is the only transition when Eu$^{3+}$ is situated at a site coinciding with a centre of symmetry. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is allowed as forced electric dipole transition and is induced when Eu$^{3+}$ is situated at a site which lacks the inversion symmetry. This transition is much stronger than that of the transition to $^7\text{F}_1$ state. The PL spectrum of pure CaSiO$_3$ was also studied for same excitation wavelength. A broad emission peak at 447 nm along with weak emission peaks at 574 and 578 nm was observed. The variation of PL intensity as a function of Si$^{7+}$ ion fluence was studied and shown Fig. 4.1.1.0. It is observed that, the PL emission peaks intensity (581, 593, 614, 654 and 724 nm) increases with ion fluence. The increase in PL intensity is due to increase in defect concentration caused by Si$^{7+}$ ion irradiation [35].

Nagabhushana et al [36] studied the PL studies on swift heavy ion irradiated nanocrystalline aluminum oxide irradiated with 120 MeV Au$^{9+}$ ions for fluence in the range 5x10$^{11}$-1x10$^{13}$ ionscm$^{-2}$. PL intensity increases with increase in ion fluence up to 1x10$^{12}$ ions cm$^{-2}$ and thereafter it decreases with further increase in ion fluence. The increase in PL intensity might be due to increase in defect concentration caused by Au$^{9+}$ ion irradiation. Further, the decrease in PL peak intensity with increase of ion fluence which is due to defects acting as non-radiative recombination centers, whose concentration certainly increases with increasing ion fluence. Chowdhury et al [37] have studied the 160 MeV Ni$^{12+}$ ion irradiation on PbS quantum dots between fluences
$10^{12}$-$10^{13}$ ions cm$^{-2}$. The PL intensity is significantly increased in irradiated sample which is due to increase in defect concentration after ion irradiation. Further, no shift in peak positions has been observed with increase in particle size upon ion irradiation. The increase in luminescence intensity may be due to the combined effect of surface state emission as well as emission from the large defects generated during SHI irradiation. Therefore, in the present study, the increase in PL intensity is due to increase in defect concentration caused by Si$^{7+}$ ion irradiation.

4.1.4. Conclusions

Thermo, iono and photoluminescence properties of nanocrystalline CaSiO$_3$:Eu$^{3+}$ (1-5 mol %) bombarded with 100 MeV Si$^{7+}$ ions have been studied for first time. A well resolved TL glow peak at $\sim$ 304 °C was recorded in all the ion bombarded samples at a warming rate of 5 °C s$^{-1}$. The TL intensity is found to increase sub linearly with shifting of glow peak towards lower temperature with ion fluence. The characteristic emission peaks $^5$D$_0 \rightarrow ^7$F$_j$ ($j = 0, 1, 2, 3, 4$) of Eu$^{3+}$ ions was recorded in both PL ($1\times10^{11}$ - $1\times10^{13}$ ions cm$^{-2}$) and IL ($4.16 \times 10^{12}$ - $6.77\times10^{12}$ ions cm$^{-2}$) spectra. PL emission peaks intensity increases with Si$^{7+}$ ion fluence, whereas in IL the peaks intensity increases up to fluence $5.20 \times 10^{12}$ ions cm$^{-2}$, then it decreases with further increase of ion fluence. IL is a very sensitive method, for characterization of nanocrystalline materials using heavy ion beams. IL and PL spectroscopy together with TL have been shown to be very promising characterization/defect probes in material science studies. Further experiments are in progress for obtaining a better understanding of these aspects in detail.
4.1.5. References


4.2. Swift heavy ion induced structural, ionic and photoluminescence properties of \(\beta\)-CaSiO\(_3\):Dy\(^{3+}\) nanophosphor

4.2.1. Introduction

Rare earth ions activated phosphors have attracted much attention of scientists due to their unique electronic, optical and chemical properties resulted from the 4f shell of the ion; and the progress in the development of the phosphors is directly related to the understanding of the physical processes of energy absorption and relaxation [1–3]. Therefore, the f–f transitions of the trivalent lanthanide ions in crystalline hosts is receiving more attention as optical materials emitting in the visible and near-IR regions [4, 5]. Among rare earth ions, Dy\(^{3+}\) is one of the most investigated ions, and has been studied extensively because it provides two typical emission bands in blue (480 nm) and yellow (570 nm) regions, which are necessary for full color displays [6–8]. In addition, the emission probability of electric dipole transition is greatly affected by the crystal field and radial integral of 4f and 5d electrons. Thus it is interesting to study the luminescence properties of Dy\(^{3+}\) in different host lattices.

Due to its excellent chemical and thermal stability, long persistence time, better formability, multicolor phosphorescence, easy preparation, resistance for alkali and oxygen, silicates are considered to be one of the best host materials for luminescence centers [9, 10]. When doped with rare-earth ions or transition metal ions, silicate becomes phosphor material, which produces intense luminescence in the blue, green and red emission peak [11, 12]. The luminescence produced in this type of phosphor by swift heavy ions (SHI) is the subject of recent investigations. When SHI pass through a solid target, a large amount of energy is deposited due to inelastic collision with target electrons, which in turn induce new damage process. In particular close to ion path, extremely high energies are deposited in a small volume of a few hundreds of eV nm\(^{-3}\) within an extremely short time but difficult to reach by any other radiation source [13].

Ionoluminescence (IL) is non-thermal light emission induced by bombardment with accelerated particle beams. The main advantage of this method is that no sampling is required and an object of any size can be easily analyzed by placing it in front of the ion beam. During ion beam implantation there is associated luminescence from insulators which contains information on the crystallinity of the host lattice, the structural perfection of the surface region, impurity content, intrinsic defects, local symmetry studies and variations in phase, lattice stability. Hence, ion beam luminescence can provide both an
immediate diagnostic probe of the changes which occur during implantation and an independent means of analyzing defects in the near surface region. The technique is similar to Cathodoluminescence (CL) but it has several advantages that it probes a greater depth of material with a more controllable rate of energy deposition in the layer [14-16]. Photoluminescence (PL) technique is a versatile tool to understand the defect production mechanism. This is very sensitive compared to optical absorption for the lower concentration of defects. Further, from PL studies one can identify the defects whose optical absorption bands overlap [17].

Extensive literature survey has been made and to the best of our knowledge no reports are available on SHI irradiated CaSiO$_3$:Dy$^{3+}$ and the mechanism responsible for light emission due to ion irradiation. Calcium silicate (CaSiO$_3$) also called wollastonite has mainly two phases one is the low temperature (β-phase) and the other is the high temperature phase pseudo wollastonite (α-phase). It is used in high temperature applications, to its high surface area, low thermal expansion, good chemical stability and excellent insulation properties even at elevated temperature. In the present paper an attempt has been made to study the effect of SHI irradiation in β-CaSiO$_3$:Dy$^{3+}$ nanophosphor on its structural, ionic and photoluminescence properties.

### 4.2.2. Experimental

Nanocrystalline β-CaSiO$_3$:Dy$^{3+}$ phosphor was prepared by low temperature solution combustion method and described elsewhere [18]. Pellets of approximately 0.5 mm thickness and 6 mm diameter were prepared taking 680 mg of the sample without using any binder and applying 50 Kg cm$^{-2}$ of pressures on each time by a hand pressed hydraulic machine. The pellets were again annealed at ~250 °C for 1 hr in muffle furnace in order to remove the deformations, if any, due to applied pressure. The pellets were irradiated at room temperature by Si$^{7+}$ swift heavy ion beam at energy of 100 MeV for different ion fluences using 16 MV Tandem Van de-Graff type Electrostatic Pelletron Accelerator at the Inter-University Accelerator Center (IUAC), New Delhi, India [19]. The pellet samples were mounted on a copper target ladder with a silver paste giving good thermal and electrical conductivity between them. The XRD measurements are carried out using powder X-ray diffractometer (PANalytical X’Pert Pro) using Cu K$_α$ (1.541Å) radiation with a nickel filter. For on-line ionoluminescence (IL) and photoluminescence (PL) measurements, a point beam was used with a beam current of 3 PnA in the fluence range (7.81-15.62) x $10^{12}$ ions cm$^{-2}$. The detailed IL and PL setup
used in the present studies was described in chapter 2. The FTIR measurements were recorded using Perkin Elmer Spectrometer (Spectrum 1000). For all measurements, one pellet was un-irradiated and it is used as the pristine sample.

4.2.3. Results and discussion

Fig.4.2.1 shows the XRD patterns of pristine and 100 MeV Si⁷⁺ ion irradiated (7.8 x 10¹² -15.62 x 10¹² ions cm⁻²) CaSiO₃:Dy³⁺ nanophosphor. The XRD patterns of pristine CaSiO₃:Dy³⁺ has an intense peak at 2θ = 31°; (320) and it is the prominent peak for monoclinic β-CaSiO₃:Dy³⁺ Along with the intense peak other peaks at (400), (002) (202), (521), (204) are also observed. The observed XRD patterns are in well agreement with the standard JCPDS card No. 43-1460. Further, it is observed that in XRD patterns of the irradiated sample the intensity of the prominent is decreasing on irradiation at the fluence of 7.81x 10¹² ions cm⁻² and finally vanish completely at the fluence of 15.62 x 10¹² ions cm⁻². The full width at half maxima (FWHM) of the prominent peak at (320) is found to increase significantly with increasing Si⁷⁺ ion irradiation (inset of Fig.4.2.1). The broadening is due to the stress induced agglomeration due to swift heavy ion irradiation.

Further, the intensity variation of XRD pattern in pristine and ion irradiated samples (Fig.4.2.1) can be attributed to the creation of defects such as ion tracks [20]. The ion tracks were created from the ion induced melt due to the mechanical stress arising from the thermal expansion [21]. The observed decrease in peak intensity (320) indicates the stress induced point/cluster defects are produced during irradiation. The similar type of observation was reported for sapphire at 190 MeV of Ag ions irradiation in the fluence range 10¹¹-10¹³ ions cm⁻² [22].

Fig. 4.2.2 shows the optimized ionoluminescence spectra for various concentrations of Dy³⁺ in CaSiO₃ nanophosphor bombarded with 100 MeV Si⁷⁺ ions for fluence of 7.81x10¹² ions cm⁻². The maximum IL yield was observed in 3 mol% Dy³⁺ doped β-CaSiO₃ nanocrystalline phosphor. Fig. 4.2.3 and 4.2.4 shows the IL and PL spectra of nanocrystalline β-CaSiO₃:Dy³⁺ (3 mol %) acquired during 100 MeV Si⁷⁺ ion irradiation in the fluence range (7.81 -15.62) x10¹² ions cm⁻² at room temperature respectively.
Fig. 4.2.1 (A) XRD pattern of β-CaSiO$_3$:Dy$^{3+}$ (a) pristine (b) 7.81 x 10$^{12}$ ions cm$^{-2}$ (c) 15.62 x 10$^{12}$ ions cm$^{-2}$. (B) Broadening of (320) peak

Fig. 4.2.2. Variation of IL intensity as a function of different Dy$^{3+}$ concentrations in β-CaSiO$_3$ bombarded with 100 MeV Si$^{7+}$ ions for a fluence of 7.81 x 10$^{12}$ ions cm$^{-2}$
Fig. 4.2.3. IL spectra of $\beta$-CaSiO$_3$:Dy$^{3+}$ bombarded with 100 MeV Si$^{7+}$ ions in the fluence range (7.81-15.62) x 10$^{12}$ ions cm$^{-2}$

The IL spectra consisting of three main groups of lines in the blue region (481 nm) and yellow region (574 nm) and red region (664 nm) along with weak lines observed at 754 nm. These blue, yellow and red emissions are assigned to the electronic transitions $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$ and $^4F_{9/2} \rightarrow ^6H_{11/2}$ respectively.

Fig. 4.2.4. PL spectra of $\beta$-CaSiO$_3$:Dy$^{3+}$ bombarded with 100 MeV Si$^{7+}$ ions in the fluence range (7.81-15.62) x 10$^{12}$ ions cm$^{-2}$ (Inset: PL spectrum of pure $\beta$-CaSiO$_3$:Dy$^{3+}$ nanophosphor)
Similar emission peaks were observed in PL studies bombarded with same ion fluences. The blue (\(\text{^4F}_{9/2} \rightarrow \text{^6H}_{15/2}\)) emission corresponds to the magnetic dipole transition and the yellow (\(\text{^4F}_{9/2} \rightarrow \text{^6H}_{13/2}\)) emission belongs to the hypersensitive (forced electric dipole) transition with the selection rule \(\Delta J = 2\) [23-25]. The assignment of emission spectra is based on earlier results of Carnall et al [26]. The crystal field splitting components of \(\text{Dy}^{3+}\) can be observed and are well correlated with the Kramer’s doublets \((2J+1)/2\), where \(J\) is the angular momentum of the electrons. It indicates that \(\text{Dy}^{3+}\) ions are well substituted in to calcium sites, because the ionic radius of the \(\text{Dy}^{3+}\) (0.103 nm) is smaller than \(\text{Ca}^{3+}\) (0.106 nm). In this \(\text{CaSiO}_3:\text{Dy}^{3+}\) nanophosphors, the intensity of the yellow (574 nm) emission is greater than that of the blue (481 nm) emission, and this can be explained according to the following reason: It is well known that the hypersensitive (forced electric dipole) transition is strongly influenced by the outside surrounding environment and the magnetic dipole transition is insensitive to the crystal field strength around the \(\text{Dy}^{3+}\) ions. When \(\text{Dy}^{3+}\) is located at a low symmetry local site (without inversion symmetry), the yellow emission is often dominant in the emission spectrum and when \(\text{Dy}^{3+}\) is at a high symmetry local site (with inversion symmetry center), and the blue emission is stronger than the yellow emission and is dominant in the emission spectrum.

The variation of IL and PL intensity as a function of different ion fluences was studied and shown in Fig.4.2.5 and 4.2.6 respectively. At the beginning of the ion irradiation the IL intensity increases rapidly, stabilizes and then decreases and thereafter remains constant for higher fluences.

![Fig.4.2.5. Variation of IL intensity with Si\(^{7+}\) ion fluence in \(\beta\)-CaSiO\(_3\):Dy\(^{3+}\) nanophosphors](image-url)
Fig. 4.2.6. Variation of PL intensity with Si\textsuperscript{7+} ion fluence in $\beta$-CaSiO\textsubscript{3}:Dy\textsuperscript{3+} nanophosphor

The rapid increase in IL intensity is caused due to the increasing number of intrinsic defects produced by ion irradiation and the decrease in IL intensity with Si\textsuperscript{7+} ion fluence might be due to the disorder produced by dense electronic excitation under swift heavy ion (SHI) irradiation [27]. It is noticed that PL intensity in un-doped CaSiO\textsubscript{3} is three times higher, when compared to Dy\textsuperscript{3+} doped samples.

Another important result to be mentioned here is that the IL spectra disappear with the irradiation time. This fact must be due to IL thermal quenching as a result of an increase in the sample temperature caused by the ion-beam irradiation. The results reported here can be explained in the frame of thermal spike model to describe the crystal damage and amorphization due to swift ion-beam irradiation [28]. Within this model, in the first step of ion excitation, an excited electron cloud is formed followed by electron thermalization. Then the excited energy can be (a) directly transferred to the crystal lattice (phonons) and/or (b) delivered to populate excited states of excitons and dopant ions. These localized excited states can relax by radiative recombination (light production) and/or by non-radiative recombination (phonons) results in the production of light and phonons.

The decrease in IL and PL emission intensity was further confirmed by means of FTIR spectroscopy. An FTIR spectroscopy provides the information with regard to bending, bonding and stretching of molecules in the given sample. Fig.4.2.7 shows the FT-IR spectra of pristine and 100 MeV Si\textsuperscript{7+} ion irradiated $\beta$-CaSiO\textsubscript{3}: Dy\textsuperscript{3+} for a fluence of...
The peaks observed are fundamental IR active modes consistent with previously reported literature [29]. The data obtained for pristine and ion irradiated $\beta$-CaSiO$_3$:Dy$^{3+}$ are summarized in Table 4.2.1.

![Fourier transform infrared spectra of (a) pristine and irradiated pellets of $\beta$-CaSiO$_3$:Dy$^{3+}$](image)

**Fig. 4.2.7.** Fourier transform infrared spectra of (a) pristine and irradiated pellets of $\beta$-CaSiO$_3$:Dy$^{3+}$ (b) $7.81 \times 10^{12}$ ions cm$^{-2}$ (c) $11.71 \times 10^{12}$ ions cm$^{-2}$ (d) $13.67 \times 10^{12}$ ions cm$^{-2}$ and (e) $15.62 \times 10^{12}$ ions cm$^{-2}$

**Table 4.2.1.** Assignment of the band positions of the infrared spectra of pristine and 100 MeV Si$^{7+}$ ion irradiated $\beta$-CaSiO$_3$:Dy$^{3+}$

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Absorption modes (cm$^{-1}$)</th>
<th>Pristine</th>
<th>Ion-irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>415-600</td>
<td>Si-O</td>
<td>Si-O</td>
</tr>
<tr>
<td>2</td>
<td>463-1030</td>
<td>Si-O-Si</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>750-1170</td>
<td>O-Si-O</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1462-1700</td>
<td>Ca-O</td>
<td>Ca-O</td>
</tr>
<tr>
<td>5</td>
<td>3445</td>
<td>-OH stretching</td>
<td>-OH stretching</td>
</tr>
</tbody>
</table>

It is observed that with increase in the Si$^{7+}$ ion fluence, the intensity of the peaks (560, 648, 741, 1020 cm$^{-1}$) decreases, the decrease in peak intensity which is due to the breaking of $\beta$-CaSiO$_3$:Dy$^{3+}$ molecules. The area under the IR active peaks was studied.
with ion fluence. It is observed that 560, 648, 741, 1020 cm\(^{-1}\) decreases with the ion fluence (Fig.4.2.8. (a)) and it is observed that the decrease in rate is different for the different peaks. It means that different modes have different sensitivities to ion irradiation. It is noticed that there are no new peaks in the ion irradiated $\beta$-CaSiO\(_3\): Dy\(^{3+}\) spectra. The lack of new peaks and the peak shifts give strong evidence that no substantial amount of intermediate fragmentation occurs. In ion irradiated samples, the IR modes at 1020 cm\(^{-1}\) (Si-O-Si) and 560 cm\(^{-1}\) (O-Si-O) completely destructed (Table.4.2.1) at higher fluences and the destruction of these modes with irradiation may further enhance the amorphous in nature of the sample. The variation of FWHM of different modes as a function of Si\(^{7+}\) ion fluence in $\beta$-CaSiO\(_3\):Dy\(^{3+}\) nanophosphor is shown in Fig.4.2.8.(b).

From Transport of ions in mater (TRIM) calculations, when the energy of the incident ions is of few keV then nuclear energy loss ($S_n$) are significant as compared to electronic energy loss ($S_e$). In present studies, we have used 100 MeV energy for irradiation and the electronic excitation effect is more dominant over the nuclear energy transfer interactions in the near surface region. The irradiation effect may lead to the restructuring of the surface chemical species because of the energy deposited through electronic energy loss during the process of heavy ion irradiation and formation of ion induced defects leading to non radiative recombination centers [30]. These two processes are simultaneous.
consequences of irradiation and they compete with each other. Enhancement / degradation of IL and PL intensity in the present studies might be due to the balance between these two effects [31]. It is observed from the FTIR spectra there is no change in peak position of OH bond and this stretch bond remains stable with heavy ion irradiation (Fig.4.2.7). These results confirm that SHI irradiation leads to only surface amorphization instead bulk amorphization of the crystalline sample.

4.2.4. Conclusions

Ion implantation is an efficient means of exciting luminescence in $\beta$-CaSiO$_3$:Dy$^{3+}$. The reduction in IL and PL emission intensity with increase of Si$^{7+}$ ion fluence might be attributed to degradation of Si-O-Si and O-Si-O bonds present on the surface of the sample as well as due to lattice disorder produced by dense electronic excitation under SHI irradiation. Being a very sensitive probe for structural imperfections, the spectral structure and emission intensities of ion beam induced luminescence in nano materials are strongly affected by accumulated radiation damage. The characteristic IL and PL emission peaks at 488, 580 and 670 nm are attributed to transition of $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$ and $^4F_{9/2} \rightarrow ^6H_{11/2}$ Dy$^{3+}$ ions. Luminescence techniques especially IL has several advantages such as study of amorphization, mechanism of defect formation, material modification, phase transformation etc.
4.2.5. References


