Chapter 4

Thermoluminescence properties of β-irradiated CaSiO₃ nanophosphor

The work presented in this Chapter is published in:

4.1 Introduction

Following the advent of nanotechnology, there is a considerable amount of research involved in the search for new crystalline phosphor materials with good thermoluminescence (TL) properties. The most widely developed application of such materials is their use in radiation dosimetry [1], which spans the areas of health physics and other biological sciences, radiation protection and personal monitoring [2]. In the recent years, nano crystalline materials are being investigated for luminescence properties as they are known to exhibit enhanced optical, electronic and structural properties. The TL response curves of the nano-materials are linear over a wide range of exposures due to large surface to volume ratio[3]. Nano phosphors are expected to remove the TL saturation effect observed in bulk materials. The linearity of nano phosphors over a wide range of doses is explained on the basis of large surface to volume ratio [3].

CaSiO₃ is a well known ceramic perovskite oxide which has been synthesized and characterized earlier [4]. Based on the results reported by Lars Stixrude et al., the ground state structure of CaSiO₃ perovskite has a distorted phase with symmetry lower than cubic [5]. It appears that the TL properties of CaSiO₃ has not been much exploited. On the other hand, thermo luminescence studies on β-irradiated perovskite fluorides have been reported earlier. The effects of X-ray, β and UV irradiation on TL properties of Tb³⁺ and Eu²⁺ doped KMgF₃ crystals were studied by Kristianpoller et.al.[6]. J. Marcazzo et al. have investigated the luminescent properties of KMgF₃:Sm [7]. The dosimetric properties of a new perovskite LiMgF₃ doped with Ce, Er and
Dy impurities were also reported by Kitis et.al.[8]. In this chapter we report the TL properties of β-irradiated β-CaSiO₃ nanophosphor.

4.2 Experimental

CaSiO₃ polycrystalline powder is synthesized by low temperature solution combustion method as described in Chapter 2. ⁹⁰Sr source is used for irradiation by β-rays. The samples are irradiated four different doses of 30 K Gy, 40 KGy, 50 KGy and 60 KGy. Thermoluminescence measurements are made for the irradiated samples using a TSL analyzer as describes in Chapter 2.

4.3 Results and Discussion

4.3.1 TL studies

TL glow curves of β-irradiated β-CaSiO₃ are shown in Fig 4.1. A well resolved glow peak at 236 °C along with a broad shoulder peak appears at around 172 °C. Further, the TL intensity increases with increasing dose. Also there is no appreciable shift in the glow peak with increase of dose. The appearance of two peaks in the glow curve indicates that there are possibly two kinds of trapping sites generated due to beta irradiation. The shallow trapping center leads to the shoulder peak at lower temperature and the other deeper center gives rise to sharp peak at higher temperature. The intensity of the higher temperature glow peak increases linearly with dose. This might be due of high surface to volume ratio, which results in a higher surface barrier energy for the nanoparticles. On increasing the dose, the energy density crosses the barrier and a large number of defects are produced in the nanophosphor which ultimately keep on increasing with the dose till saturation is reached [9]. For lower dose [30 Gy, shown in the inset of Fig. 4.1] the
traps/defects generated appear to be very less due to surface barrier. Hence the glow curve has minimum intensity and the peak appear at lower temperature of 135 °C. As the temperature increases, the surface barrier energy also increases, and the lower dose (30 Gy) is not sufficient create the defects. Thus we get only a little hump at 224 °C in the glow curve for 30 Gy. As the dose increases, more and more traps or defects are generated at higher temperatures. As a result, glow peak is observed at higher temperature (236 °C) with higher intensity. Figure 4.2 shows the variation of intensity of the glow peaks with β-dose. As is seen, peak intensity increases linearly with dose indicating that the CaSiO₃ nano powder is a good candidate for dosimetry.

![Figure 4.1 Thermoluminescence glow curves for β-irradiated Wollastonite powder for an accumulated doses of (a) 30 Gy (b) 40 Gy (c) 50 Gy and (d) 60 Gy.](image)
The increase in TL intensity with dose can be explained on the basis of track interaction model [10, 11]. According to this model, the number of traps generated by the high energy radiation in a track depends upon the cross section and the length of the track inside the matrix. In the case of nanomaterials, the length of the track generated by high energy radiation is of few tenths of nanometers. At low doses, there exist a few trap centers or luminescent centers are generated owing to the small size of the particles. As the dose increases, the TL intensity increases as the cross section would increase with increase in dose.

TL characteristic of the phosphor requires the knowledge of trapping parameters such as activation energy ($E$) of the traps involved in TL emission and the order of kinetics ($b$) associated with the glow peaks. Here, $E$ is a measure of the energy required to eject an electron from the defect center to the conduction band. The order of kinetics $b$ is a measure
of the probability that a free electron gets retrapped. This retrapping effect increases with
density of empty traps. It is known that, equal concentrations of trapped electrons (n)
and recombination centers (r) lead to give a condition for the first order kinetics.
For second order kinetics, recombination and retrapping probabilities are found to be
equal with the condition \( r < n \) [12]. The trapping parameters were calculated using
Chen’s set of empirical equations [13] for the peak shape method as summarized below.
Figure 4.3 shows the schematic representation of TL glow peak for calculation of trapping
parameters. The activation energy \( E \) and the order of kinetics are estimated using the
following relations (as discussed in Chapter 2)

\[
E_{\alpha} = c_{\alpha} \left( \frac{kT_{m}^{2}}{\alpha} \right) - b_{\alpha} \left( 2kT_{m} \right)
\]  \hspace{1cm} (4.1)

where \( \alpha = \tau, \delta \) and \( \omega \) with \( \tau = T_{m} - T_{1}, \delta = T_{2} - T_{m} \) and \( \omega = T_{2} - T_{1} \)

\[
C_{\tau} = 1.51 + 3.0(\mu_{g} - 0.42), \quad b_{\tau} = 1.58 + 4.2(\mu_{g} - 0.42)
\]
\[
C_{\delta} = 0.976 + 7.3(\mu_{g} - 0.42), \quad b_{\delta} = 0
\]
\[
C_{\omega} = 2.52 + 10.2(\mu_{g} - 0.42), \quad b_{\omega} = 1
\]

The form factor (symmetry factor) is given by

\[
\mu_{g} = \frac{T_{2} - T_{m}}{T_{2} - T_{1}}
\]  \hspace{1cm} (4.2)

The nature of the kinetics can be found by the form factor. Theoretically, the value of
geometrical form factor (\( \mu_{g} \)) is close to 0.42 for first order kinetics and 0.52 for second
order kinetics. In the present study, the value of \( \mu_{g} \) is very close to 0.52 and it falls under
second order kinetics. The trapping parameters of \( \beta \)-CaSiO\(_{3} \) irradiated with 60 Gy \( \beta \)-dose
obtained using peak shape method and deconvolution of the glow curve for the dose
60 Gy shown in figure 4.4 is given in Table 4.1. From the table we see that the activation energy increases with temperature.

Figure 4.3 Schematic representation of TL glow peak for calculation of trapping parameters.

Figure 4.4 Deconvolution of the glow curve for β-dose of 60 Gy
### Table 4.1

<table>
<thead>
<tr>
<th>Glow peak temperature °C</th>
<th>Order of Kinetics (b)</th>
<th>Activation energy (E) (eV)</th>
</tr>
</thead>
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<tr>
<td>145</td>
<td>2</td>
<td>0.0490</td>
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<tr>
<td>174</td>
<td>2</td>
<td>0.1842</td>
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<tr>
<td>208</td>
<td>2</td>
<td>0.1921</td>
</tr>
<tr>
<td>242</td>
<td>2</td>
<td>0.2243</td>
</tr>
</tbody>
</table>

#### 4.4 Summary

TL studies on β-irradiated CaSiO$_3$ exhibit well resolved glow peaks at 236 °C along with shouldered peak at around 172°C. The TL glow curve intensity increases with increasing dose. Deconvolution of the glow curve is employed to estimate the trap parameters. The average activation energy ($E$) of β-CaSiO$_3$ was found to increase as the temperature is increased. The present study demonstrated that the CaSiO$_3$ nano powder can be a good candidate for dosimetry applications.
4.5 References


