Thermo-luminescence (TL) spectra of single crystals of Al₂O₃ (sapphire) irradiated with 200 MeV swift Ag ions at different fluence in the range 1×10¹¹ to 1×10¹³ ions/cm² has been recorded at room temperature by keeping the warming rate 2K/min. The TL glow curve of the irradiated samples has a simple structure with a prominent peak at ~ 500 K with one small peak at 650 K. The intensity of main peak increases with the ion fluence. This has been attributed to the creation of new traps on irradiation. Also, a shift of 8 K in the peak position towards low temperature side has been observed at higher fluence 1×10¹³ ions/cm². In addition, photoluminescence (PL) spectra of irradiated samples have been recorded at room temperature upon 2.8 eV excitation. A broad band consisting of mainly two emission bands, respectively at 2.5 and 2.3 eV corresponding to F₂ and F₂⁺ defect centers is observed. The intensity of these bands shows an increasing trend up to fluence 5×10¹² ions/cm² and then decreases at higher fluence 1×10¹³ ions/cm². The results are interpreted in terms of creation of newly defect centers, clustering/aggregation and radiation-induced annihilation of defects.
1. Introduction

Al₂O₃ is a well known insulator material of great interest in electrical and optical technology [1]. Also, Al₂O₃ doped with impurity is a useful tunable solid state laser material in the near infrared region [2]. The electric trap structure of the material is a basic quantity of importance, because this material is used as substrate in the fabrication of silicon on sapphire microelectronic devices [3]. The high dielectric strength of sapphire causes it to be used as an insulator and its high melting point and low atomic number make it a good candidate for the first wall of proposed fusion reactor [4]. More relevant for our purposes, Al₂O₃ is suggested as efficient and reproducible thermo-luminescence (TL) dosimeter for both ultraviolet and ionizing radiation [1]. A number of defects are generated in the growing procedure of sapphire [5] and by ion irradiation [6, 7]. These are mainly F centers (oxygen vacancy with two electrons), F⁺ center (oxygen vacancy with one electron), F₂ center (two oxygen vacancies with four electrons), F₂⁺ center (two oxygen vacancies with three electrons) and F₂²⁺ centers (two oxygen vacancies with two electrons) centers [6, 7]. These defect centers affect the electrical and optical properties of the crystal [8, 9]. In addition, when a solid sample is irradiated by some kind of radiation, defect traps can be filled by charge carriers. Then, if the sample is heated at a constant heating rate, the trapped carriers are thermally released giving rise to thermo-luminescence [10, 11].

It has been shown that the vacancy centers (F-type) play an important role in the TL glow curves of Al₂O₃ [1, 12]. A large number of TL peaks have been detected in the different types of Al₂O₃ indicating that different traps and recombination centers are possible in the Al₂O₃ host, but it is interesting to note that most of the peaks appear in the temperature range between -60 to 0°C and 100 to 250°C. Although other peaks are also observed at other temperatures, usually they are very small [1]. It has been found that the presence of impurity ions in the Al₂O₃ matrix induces a big change in the characteristic of the TL glow curve and in some cases very high intensity peaks are observed [13].

When heavy charged particles penetrate into the matter, they interact with the atoms of the medium losing their energy by ionization and excitation and nuclear collision. Point defects, defect clusters and/or ion track can be created in the irradiated material along the range of ion and the defect structures depend on the energy loss value and ion fluence [14].

The purpose of this paper is to characterize the radiation damage produced by heavy ions in sapphire. Therefore, we have undertaken the irradiation of sapphire by Ag ions of 200 MeV at various fluence and subsequent changes are evaluated by using TL and PL techniques as these are very sensitive techniques for the estimation of the concentration of defect centers in solids.

2. Experimental procedures

The natural sapphire of South Africa origin of sizes 5x5x1 mm³ are taken for this study. These were cleaned using ethanol in an ultrasonic vibrator before irradiation. These samples consist of 1500 wt. ppm of Fe, 750 wt. ppm of Ti and Cr in traces. The plane (0001) of sapphire, being parallel to foil surface, were irradiated with 200 MeV Ag ion beam at room temperature under high vacuum (6x10⁻⁶ torr) using the 15 UD pelletron tandem accelerator at Inter-University Accelerator Centre (IUAC), New
Delhi, India. The ion beam was magnetically scanned on an area of 10x10 mm² for uniform irradiation. The samples were mounted on a copper target ladder with silver paste giving good thermal conductivity between them in order to prevent the melting of samples. The ion flux was 10⁹ ions / (cm²s). Samples were irradiated at fluence varying from 1x10¹¹ to 1x10¹³ ions/cm². The ion beam fluence was measured by integrating the ion charge on the sample. Two un-irradiated samples were kept as pristine samples. The pristine and irradiated samples were characterized with thermo-luminescence and photoluminescence techniques. TL measurements were made using Harsaw TL analyzer model 3500, connected to a PC to record and process the experimental data. The TL signal was integrated from room temperature to 673 K at a heating rate of 2 Ks⁻¹. The kinetic parameters were obtained using only glow peak shape method (modified by Chen) i.e. deconvolution of glow curves is done first using origin 6.0 software. Then, the kinetic parameters are calculated using the equations as suggested by Chen.

PL measurements were carried out for two samples of same fluence and average value of the intensity is plotted. PL measurements were carried out using Mechelle-900 spectrograph, using 442 nm (2.8 eV) He-Cd laser excitation at IUAC, New Delhi, India.

3. Results and discussion

(a) Thermo-luminescence study

Fig. 1 shows the TL glow curves of pristine and sapphires irradiated with Ag ions at fluences 1x10¹¹, 5x10¹¹, 1x10¹², 5x10¹² and 1x10¹³ ions/cm². Two well resolved glow peaks are observed at ~ 500 K and ~650 K with a heating rate of 2 Ks⁻¹. The TL glow curve of the irradiated samples has a simple structure with a prominent peak at ~ 500 K with one small peak at 650 K. These values are very close to the earlier reported values [11, 14, 15]. The TL glow at ~500 K may be due to the F-type centers. The intensity of prominent TL glow at ~ 500 K is found to increase with the fluence till 1x10¹³ ions/cm² (see Fig. 2). This is probably due to the creation of new defect centers/ traps as a result of high density ionization induced by Ag ions in sapphire. The primary defect centers generated in sapphire due to ionizing radiation are F-type centers and their concentrations are found to increase with the ion fluence [6, 7, 16] as a result of dense ionization /displacement process in the sapphire. Hence, the enhancement in the TL glow intensity is expected. Further, it has been observed that the TL glow curves are very symmetric over a wide temperature range. This feature shows the characteristic of second order glow. In a second order reaction, concentration of released electrons are getting re-trapped before they recombine with the hole centers. This might be the probable reasons of spreading out of the emission over a wide range because of delay in luminescence [17].

Also, a shift of 8 K in the position of prominent TL glow at ~ 500 K towards low temperature side has been observed at higher fluence 1x10¹³ ions/cm² as can be seen from Fig. 3 and table 1. This may be attributed to the increase in the concentration of defect centers/or trapped electrons in the lattice [17]. The observation of a shift over a fluence range coupled with the symmetric shape of the peak has lead some of the authors to conclude that the kinetics of TL production are non-first order [18, 19]. It
has been observed by Bos and Diehfof [20] that the maximum temperature shifts to lower energy side as the number of trapped electrons at time T=0 increases.

The kinetic parameters such as activation energy (E), order of kinetics (b) and frequency factor (s) are also evaluated by deconvoluting the curves using origin 6.0 programme and are given in table 1, as these parameters are indeed very important for the complete description of any TL characteristic of material. Here, the activation energy is the energy required to eject an electron from the defect center to the conduction band and S is the rate at which the electron are ejected. The probability that a free electron is getting re-trapped is governed by the order of kinetic (b). The re-trapping increases with the density of empty traps. The trap parameters of deconvoluted curves are obtained by using the glow curve shape method (modified by Chen) [10].

The order of kinetics (b) is calculated by using

\[
\mu_g = \frac{T_2 - T_m}{T_2 - T_1}
\]

where \(T_1\) and \(T_2\) are the temperature corresponding to the half of the maximum intensities on either side of the glow peak maximum \(T_m\).

The activation energy (E) can be calculated by the following sets of equations, which are independent of the order of kinetics;

\[
E_\alpha = c_\alpha \left[ \frac{kT_m^2}{\alpha} \right] - b_\alpha \left( 2kT_m \right)
\]

where \(\alpha = \tau, \delta, \omega\) with \(\tau = T_m - T_1\), \(\delta = T_2 - T_m\), \(\omega = T_2 - T_1\)

\[
\begin{align*}
C_\tau &= 1.51 + 3.0(\mu_g - 0.42) \\
C_\delta &= 0.976 + 7.3(\mu_g - 0.42) \\
C_\omega &= 2.52 + 10.2(\mu_g - 0.42)
\end{align*}
\]

\[
\begin{align*}
b_\tau &= 1.58 + 4.2(\mu_g - 0.42) \\
b_\delta &= 0 \\
b_\omega &= 1
\end{align*}
\]

The frequency factor (s) is obtained from the relation

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

where \(\Delta_m = \frac{2kT_m}{E}\), \(b\) is the order of kinetics, \(k\) is the Boltzmann constant (8.6 x 10^{-5} eV K^{-1}) and \(\beta\) is the heating rate in Ks^{-1}.

From table 1, one can see that the value of \(\mu_g\) (~0.5) suggests the order of kinetics to be of second order [21]. It appears that a considerable amount of re-trapping is taking place. Also the
activation energy and frequency factor increase with the fluence and exhibit maximum at $1 \times 10^{12}$ ions/cm$^2$ suggesting that corresponding traps are caused by the complex defects occupying several lattice sites [22]. This is in accordance with our results shown in the PL study. It is believed that there are some deep and shallow traps as induced by ion irradiation. Further decrease in the parameters at higher fluence (beyond $1 \times 10^{12}$ ions/cm$^2$) may be due to the stress and strain induced in the lattice as a result of dense ionization at sufficient high fluence (or overlapping of the ion tracks) that reduces the TL efficiency.

**b) Photoluminescence study**

Photoluminescence spectra for pristine and sapphires irradiated with 200 MeV Ag ions at fluence $1 \times 10^{11}$, $5 \times 10^{11}$, $1 \times 10^{12}$, $5 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$ are depicted in Fig. 4. Curve fitting has been made for all the PL spectra (shown in Fig. 5) as bands observed in the PL spectra are overlapping with each other and the resultant parameters such as position, area and FWHM corresponding to each band are presented in table 2. Mainly four bands $2.11$, $2.30$, $2.50$ and $2.64$ eV can be seen in the spectra. The bands at $2.50$ and $2.30$ eV can be assigned to $F_2$ (oxygen vacancy with four electron) and $F_2^{2+}$ defect centers (oxygen vacancy with two electron), respectively as they are in agreement with the earlier reported values at $2.46$ and $2.27$ eV [6, 7, 23]. The position of the bands depends on the energy and nature of the bombarding ions [23].

It is seen from table 2 that pristine contains a reasonable concentration of defect centers $F_2$ and $F_2^{2+}$. $F_2$ and $F_2^{2+}$, also known as $F_2$-type defect centers, are formed by pairing of primary defect centers of similar type when they are sufficiently close [24]. The higher concentration of $F_2$ type defect center in pristine suggests the presence of high concentration of $F$-type centers in the un-irradiated sample i.e. pristine.

The area under the curve is a proper measure of concentration of defects. From Fig. 5, one can see that the concentration of $F_2$-type defect center increases on increasing the Ag ion fluence upto $5 \times 10^{12}$ ions/cm$^2$. This increase in concentration of $F_2$-type centers may be associated with the increase in radiation damage that creates new defect centers in the lattice. Such behavior has been reported in sapphire irradiated with energetic H, He, Ar and Kr ions at keV energies [16, 25]. We expect similar behaviour even at higher energy as observed in our earlier work [6]. Therefore, this increase in concentration of $F_2$-type defect center may be associated with the increase in number of primary centers ($F$ and $F^+$) in the lattice on ion irradiation. Under high radiation environment, probability of aggregation of $F$-type defect centers becomes high due to lowering of vacancy activation energy and as a result, concentration of $F_2$-type centers is expected to increase [24].

The low concentration of $F_2$-type center at higher fluence may be associated with the clustering of $F$-type and $F_2$-type defects leading to formation of void and/or diffusion of defect centers into un-irradiated part of the material. The formation of voids and diffusion of defect centers at higher fluence probably occurs due to disorder in crystal structure or stress produced along the ion track [6, 25, 26].
A band at 2.11 eV, not reported earlier, appears at longer wavelength region in all the PL spectra. The behavior of this band on irradiation is quite similar to that of both the defect centers discussed earlier but the concentration is quite less. The positions of higher order oxygen vacancies occur at longer wavelength side [27]. Absorption band corresponding to higher order vacancy center is reported at 2.17 eV (572 nm) in MgO crystal [28]. From these observations, it may be associated to a higher order oxygen vacancy center.

4. Conclusions
Single crystals of Al$_2$O$_3$ were irradiated with the 200 MeV Ag ions to various fluence and radiation induced defect centers were investigated by thermo-luminescence and photoluminescence techniques. It is found that the TL glow intensity increases with increase of Ag ion fluence. This is associated with the creation of new traps by Ag ions. The main peak shows a second order kinetics. Also, a shift of 8K is observed in the position of main peak towards lower temperature region on increasing ion fluence. This may be due to the increase in the concentration of defect centers/or trapped electrons in the lattice. The increase and decrease in the PL intensity of defect centers (F$_2$-type) are associated with the creation of defect centers and their annihilation by forming a large defect complexes or diffusion of the same in the un-irradiated part of the crystal.

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References
Table 1: Kinetic parameters of sapphires irradiated with Ag ions, obtained by using the glow curve shape method (modified by Chen).

<table>
<thead>
<tr>
<th>Ion fluence (ions/cm²)</th>
<th>T_m (K)</th>
<th>μg</th>
<th>b</th>
<th>Activation energy (eV)</th>
<th>s (s⁻¹)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E₁</td>
<td>E₂</td>
</tr>
<tr>
<td>1x10¹¹</td>
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<td>0.489</td>
<td>2</td>
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<td>5x10¹¹</td>
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<td>0.7762</td>
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<td>2</td>
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<td>0.749</td>
</tr>
</tbody>
</table>

Table 2: Gaussian fitted parameters (position, area and FWHM) for F₂ and F₂²⁺ defect centers in pristine and irradiated sapphire samples.

<table>
<thead>
<tr>
<th>Ion fluence (ions/cm²)</th>
<th>F₂</th>
<th>F₂²⁺</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Position (eV)</td>
<td>Area</td>
</tr>
<tr>
<td>Un-irradiated (pristine)</td>
<td>2.50</td>
<td>54</td>
</tr>
<tr>
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</tr>
<tr>
<td>1x10¹³</td>
<td>2.50</td>
<td>75.7</td>
</tr>
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</table>
Fig. 1. Thermo-luminescence glow curves for pristine and sapphires irradiated with 200 MeV Ag ions at various fluence (fluence in ions/cm$^2$).

Fig. 2. Variation of TL glow peak intensity with ion fluence.
Fig. 3. Variation of TL glow peak temperature with ion fluence.

Fig. 4. Photoluminescence spectra of pristine and sapphires irradiated with different fluence of Ag ion. (fluence in ions/cm²).
Fig. 5. Gaussian fitted spectra of pristine and irradiated sapphires at Ag ion fluence $1 \times 10^{11}$, $5 \times 10^{11}$, $1 \times 10^{12}$, $5 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$. 