THERMO-LUMINESCENCE GLOW CURVE ANALYSIS
AND PHOTOLUMINESCENCE RESPONSE OF $\text{Al}_2\text{O}_3$ IRRADIATED
WITH 100 MeV Ti IONS

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Abstract

Al₂O₃, also known as sapphire, is a very useful material in nuclear environment. The knowledge of its behavior under heavy ion irradiation is thus of primary importance. In this work, thermally stimulated luminescence or thermo-luminescence (TL) glow curves have been recorded at room temperature for single crystal of Al₂O₃ irradiated with 100 MeV Ti ions at fluences in the ranges 1x10¹² to 1x10¹³ ions/cm². The heating rate was kept at 2 K/s. The TL glow curve of the irradiated samples has a simple structure with a prominent peak at ~ 524 K. The intensity of peak increases with the ion fluence. This has been attributed to the creation of new traps on irradiation. Also, a shift of 9 K in the peak position towards the high temperature side has been observed at higher fluence 3x10¹³ ions/cm². The analysis of TL glow curves for irradiated samples has been done by the glow curve deconvolution method to determine trapping parameters. In addition, photoluminescence (PL) spectra of irradiated samples have been recorded at room temperature with 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 has been observed. The intensity of these bands shows an increasing trend up to fluence 1x10¹³ ions/cm² and then a decrease at higher fluence 3x10¹³ ions/cm². The results are interpreted in terms of creation of new defect centers, clustering/aggregation and radiation-induced annihilation of defects.
1. Introduction

Al₂O₃, one of the standard materials for the ceramic science, is considered as radiation resistant material which can be useful under various radiation environments because of its peculiar properties such as high melting point, high thermal conductivities and high electrical resistance [1]. It is a material of technological interest for diverse applications, i.e. as solid state laser, fusion energy devices [2, 3]. The ability of Al₂O₃ for application in optical system of radiation facility strongly depends on the occurrence of radiation induced defects [4].

Furthermore, Al₂O₃ is suggested as an efficient and reproducible thermoluminescence (TL) dosimeter for both ultraviolet and ionizing radiation due to its linear behavior over a wide dose range and easy handling [1]. A number of defects are generated in the growing procedure of sapphire [5] and by ion irradiation [6, 7]. They 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) [6, 7]. There is a consensus that the numerous intrinsic defects present in the crystalline lattice act as trapping centers for charge carriers created by ion irradiation [8]. The presence of impurity ions in the Al₂O₃ matrix induces a big change in the TL characteristic and it has been shown that Al₂O₃ with proper doping (e.g. Fe, Mg, Si, Ti, Cr, Ni etc.) may have optimal high emission linearity over a fairly wide range of radiation dose [8-10]. Al₂O₃ doped with impurity shows the prominent glow peaks of dosimetric importance at temperatures 150 (423 K), 250 (523 K) and 350°C (623 K) [11, 12].

Thermally stimulated luminescence or better known as TL is extensively used as a technique for dosimetry of ionizing radiations [13]. Thermoluminescent materials exhibit differences in their dose response to sparsely ionizing radiation (high energy photons like x-ray and γ-ray) and densely ionizing radiation like swift heavy ions (SHIs). This is due to different spatial dose distributions [14]. The effect of ion beam on the materials depends on the ion energy, fluence and ion species. When energetic ions penetrate through the material they lose their energies through two different modes: (i) nuclear and (ii) electronic stopping. The nuclear stopping is dominant at low energies and the energy lost in this process is called nuclear energy loss. The other mode of energy loss is by exciting or ionizing the atoms by inelastic collisions and the energy spent in this process is called electronic energy loss. Electronic stopping is dominant at high energies, where the displacement of atoms due to elastic collisions is insignificant [15].
Recently, the interest in heavy ion dosimetry is growing because of the increasing human presence in space and the introduction of new facilities for proton and carbon cancer therapy [16, 17]. However, the dosimetry of heavy ions remains one of the most challenging problems in luminescence dosimetry. Hence there is a need to understand their dosimetric properties and the defects caused by such densely ionizing radiation. Thermoluminescent dosimeter phosphors could be employed for this purpose. But, more studies are needed to know their responses and also more knowledge about the defects caused by such densely ionizing radiation like high energy heavy ions. This will also lead to a better understanding of the radiation damage done by heavy ions. Better correlation between thermally or optically stimulated processes and the defects produced by these radiations could be established more realistically for their applications in radiation dosimetry.

In order to use such material in nuclear environment, space and radio-therapeutic applications, it is essential to characterize the radiation damage and/or modification in it by heavy ion irradiation. In the present investigation, the radiation response of Al₂O₃ under 100 MeV Ti ion irradiation has been studied and the subsequent radiation damages, especially defect centers, are being investigated by using TL and photoluminescence (PL) techniques.

2. Experimental procedures

The natural Al₂O₃ 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 100 MeV Ti 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 fluences varying from 1x10¹² to 3x10¹³ 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 TL and PL techniques. TL measurements were made using Harsaw TL analyzer model 3500, connected to a PC to record and process the experimental data. For taking TL the irradiated surface was kept facing towards the detector. 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 discussions

(a) Thermo-luminescence

Fig. 1 shows the recorded TL glow curves of pristine and Al2O3 irradiated with 100 MeV Ti ions at different fluences $1 \times 10^{12}$, $5 \times 10^{12}$, $1 \times 10^{13}$ and $3 \times 10^{13}$ ions/cm² by keeping the heating rate 2 K/s. These spectra have a simple structure with a single prominent peak at ~ 524 K. This is in agreement with the reported value [11, 12]. However, the TL yield and shape of the TL glow curves depend on the amount and nature of the ionizing radiation [14, 18]. The TL glow at ~524 K may be due to the F-type centers. The intensity of prominent TL glow at ~ 524 K is found to increase linearly with the fluence and a supralinear behavior is observed at $1 \times 10^{13}$ 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 Ti ions in Al₂O₃. The primary defect centers generated in Al₂O₃ due to ionizing radiation are F-type centers and their concentrations are found to increase with the ion fluence [6, 7] as a result of dense ionization in it. This linear increase in TL intensity and then supralinear behavior can also be explained by track interaction model (TIM). At low fluence recombination of electron hole pairs occur entirely within the track, and the TL signal is, therefore, simply proportional to the number of ion tracks. At higher fluence, the distance between nearest neighbor tracks decreases and electron escaping the track can reach the neighbouring track resulting in an increased luminescence recombination and an increase in TL efficiency (supralinearity) [19, 20]. The onset of supralinearity occurs at different levels of fluence depending on the type and energy of ions [21].

Also a shift of 9K is observed in the position of TL glow peak (at fluence $3 \times 10^{13}$ ions/cm²) towards the higher temperature side while the shape of spectra remains the same. This may be attributed to the increase in the concentration of defect centers in the lattice that increases the depth of trap. Such shift in the TL glow peaks has been attributed to the disorganization of the
initial energy bands or modification in the trap depth by surrounding defects and impurities forming interacting complexes [22].

The temperature shift has been approximated by A.J.J. Bos [23] by the following equation

\[ T_1 - T_2 = T_1 T_2 \left[ k \frac{(b-1)/E}{\ln f} \right] \]

where \( T_1 \) is the temperature of maximum intensity at a certain fluence and \( T_2 \) the temperature of maximum intensity at an \( f \) times higher fluence. By applying the above approximation we arrive at the value of \( T_1 - T_2 \sim 10K \) for fluence \( 3 \times 10^{13} \) ions/cm\(^2\), which is very close to the value observed experimentally i.e. 9K.

Further, it can be seen from Fig. 1 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, in this way giving rise to a delay in the luminescence emission and spreading out of the emission over a wide temperature range [23]. This is further supported by our observation that a shift in the peak position towards high temperature side and high half width indicates that the TL process is not of first order [24, 25].

The peak shape method and curve fitting have been undertaken to derive the kinetic order (\( b \)), activation energy (\( E \)) and the escape frequency factor (\( s \)) from the measured TL glow curves [25] 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) [13].

The symmetry properties of the TL glow curve can be expressed as a combination of \( T_m, T_1 \) and \( T_2 \), which are the temperature at maximum intensity, the half intensity temperature on the lower temperature side and that on higher side, respectively.

The form factor which is expressed as \( \mu_g = \delta/\omega \), where \( \delta = T_2 - T_m \) and \( \omega = T_2 - T_1 \), can be determined from the shape of the peak [26]. The form factor, which ranges between 0.42 and 0.52, is close to 0.42 for first order kinetics and 0.52 for second order kinetics [27]. The form
factor is found to be independent of the activation energy and strongly dependent on order of kinetics.

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

\[
C_\tau = 1.51 + 3.0(\mu_g - 0.42) \quad b_\tau = 1.58 + 4.2(\mu_g - 0.42)
\]

\[
C_\delta = 0.976 + 7.3(\mu_g - 0.42) \quad b_\delta = 0
\]

\[
C_\omega = 2.52 + 10.2(\mu_g - 0.42) \quad b_\omega = 1
\]

The 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 \((8.6 \times 10^{-5} \text{ eV K}^{-1})\) and \( \beta \) is the heating rate in \( \text{Ks}^{-1} \).

The de-convoluted TL glow curves and experimental one after deconvolution for Al\(_2\)O\(_3\) irradiated with Ti ion at fluence 1x10\(^{13}\) ions/cm\(^2\) are shown in Fig. 3. The kinetic parameters of Al\(_2\)O\(_3\) irradiated at various Ti ion fluence are given in Table 1. One can see from the table 1 that the value of \( \mu_g \) (~0.49 - 0.5) suggests the order of kinetics to be near second order [27]. It appears that a considerable amount of re-trapping has taken place. Also the decrease in activation energy (see Fig. 4) and frequency factor with the fluence suggests that corresponding traps are caused by the complex defects occupying several lattice sites [28] as the TL trapping and recombination mechanism (trapping parameters) are very sensitive to any perturbation in lattice system. 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.
(b) Photoluminescence

The PL spectra for pristine and Al$_2$O$_3$ irradiated with 100 MeV Ti ions at fluences 1x10$^{12}$, 5x10$^{12}$, 1x10$^{13}$ and 3x10$^{13}$ ions/cm$^2$ are depicted in Fig. 5. A broad band, consisting of few bands in it, is observed around 2.3 eV. As the bands observed in the PL spectra are overlapping with each other due to their finite width, curve fitting has been made for all the PL spectra (shown in Fig. 6) 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, 29]. The position of the bands depends on the energy and nature of the bombarding ions [29].

It is seen from the table 2 that pristine contains a reasonable concentration of F$_2$ and F$_2^{2+}$ defect centers. F$_2$ and F$_2^{2+}$ defect centers, also known as F$_2$-type defect centers, are formed by pairing of primary defect centers of similar type when they are sufficiently close [30]. The higher concentration of F$_2$ type defect center in pristine suggests the presence of high concentration of intrinsic defects i.e. 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 and table 2, one can see that the concentration of F$_2$-type defect center increases with Ti ion fluence upto 1x10$^{13}$ ions/cm$^2$. The concentration of F$_2^{2+}$ defect center is more as compared to F$_2$ type. This is due to fact that F centers are converted into F$^+$ centers at sufficient high fluence [31]. 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 [32, 33]. We expect similar behaviour even at higher energy as observed in our earlier work [6]. Therefore, the increase in concentration of F$_2$-type defect center may be due to the increase in concentration of primary centers (F and F$^+$) in the lattice upon 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 [30].

At higher fluence 3x10$^{13}$ ions/cm$^2$, the concentration of defect centers is found to decrease. At sufficiently higher fluence the distances between neighbouring tracks decrease and the tracks begin to merge and overlap. This results into 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, 33, 34]. Or one may say that lattice disorder and associated mechanical stresses are the key parameters affecting the optical emission generated by heavy ion irradiation.

4. Conclusions

The effect of 100 MeV Ti ions on the TL glow curves structure and PL response of Al₂O₃ in the fluence range 1x10¹²- 3x10¹³ ions/cm² have been studied. A linear fluence dependence of the main glow peak at 524 K is observed up to very high level of ion fluence. The shifting of glow peak temperature to higher temperature side and enhancement in TL intensity in irradiated Al₂O₃ may be due to the disorganization of the initial energy levels as a result of dense ionization induced by Ti ions. However, linear response of irradiated material has shown good dosimetric characteristic, such as linear increase of TL intensity as a function of fluence. Therefore, Al₂O₃ can be used for dosimetric applications even at higher fluence value. The increase and decrease in the PL intensity of defect centers (F₂-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. Lattice disorder and associated mechanical stresses, induced by the collective electronic excitations, are the key parameters affecting the optical emission generated by heavy ions.

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References


Table 1

Kinetic parameters of Al₂O₃ irradiated with Ti 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>μ_g</th>
<th>b</th>
<th>Activation energy (eV)</th>
<th>s (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E_r</td>
<td>E_δ</td>
</tr>
<tr>
<td>1x10¹²</td>
<td>524</td>
<td>0.496</td>
<td>2</td>
<td>0.865</td>
<td>0.928</td>
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<tr>
<td>5x10¹²</td>
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<td>0.504</td>
<td>2</td>
<td>0.841</td>
<td>0.901</td>
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<tr>
<td>1x10¹³</td>
<td>533</td>
<td>0.494</td>
<td>2</td>
<td>0.822</td>
<td>0.893</td>
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<tr>
<td>3x10¹³</td>
<td>534.5</td>
<td>0.493</td>
<td>2</td>
<td>0.722</td>
<td>0.804</td>
</tr>
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</table>

Table 2

Gaussian fitted parameters (position, area and FWHM) for F₂ and F₂⁺ defect centers in pristine and irradiated Al₂O₃ samples.

<table>
<thead>
<tr>
<th>Ion fluence (ions/cm²)</th>
<th>Position F₂ (eV)</th>
<th>Area</th>
<th>FWHM</th>
<th>Position F₂⁺ (eV)</th>
<th>Area</th>
<th>FWHM</th>
</tr>
</thead>
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<tr>
<td>Un-irradiated (pristine)</td>
<td>2.50</td>
<td>47</td>
<td>0.22</td>
<td>2.30</td>
<td>37</td>
<td>0.21</td>
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<tr>
<td>1x10¹¹</td>
<td>2.50</td>
<td>53.4</td>
<td>0.21</td>
<td>2.30</td>
<td>82.7</td>
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<tr>
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<td>78.4</td>
<td>0.21</td>
<td>2.31</td>
<td>98.7</td>
<td>0.21</td>
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<tr>
<td>1x10¹³</td>
<td>2.53</td>
<td>112.4</td>
<td>0.20</td>
<td>2.31</td>
<td>315</td>
<td>0.25</td>
</tr>
<tr>
<td>3x10¹³</td>
<td>2.49</td>
<td>75.7</td>
<td>0.20</td>
<td>2.28</td>
<td>257</td>
<td>0.21</td>
</tr>
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Fig. 1. Thermo-luminescence glow curves for pristine and Al₂O₃ irradiated with 100 MeV Ti ions at various fluence. (fluence in ions/cm²).

Fig. 2. Variation of TL glow peak intensity with Ti ion fluence.
Fig. 3. Experimental and fitted glow curve of Al$_2$O$_3$.

Fig. 4. Variation of activation energy with Ti ion fluence.
Fig. 5. Photoluminescence spectra of pristine and Al₂O₃ irradiated with different fluence of Ti ion. (fluence in ions/cm²).

Fig. 6. Gaussian fitted spectra of pristine and irradiated Al₂O₃ at Ti ion fluence 1x10¹², 5x10¹², 1x10¹³ and 3x10¹³ ions/cm².