Luminescence studies on swift heavy ion irradiated nanocrystalline aluminum oxide

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\textbf{A R T I C L E   I N F O}

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\textbf{A B S T R A C T}

Pellets of nanocrystalline aluminum oxide synthesized by a combustion technique are irradiated with 120 MeV Au\textsuperscript{9+} ions for fluence in the range $5 \times 10^{11} \text{–} 1 \times 10^{13}$ ions cm\textsuperscript{-2}. Two photoluminescence (PL) emissions, a prominent one with peak at $\approx 525$ nm and a shoulder at $\approx 465$ nm are observed in heat treated and Au\textsuperscript{9+} ion irradiated aluminum oxide. The 525 nm emission is attributed to F\textsubscript{2}\textsuperscript{+} -centers. Photoluminescence (PL) and thermoluminescence (TL) in swift heavy ion (SHI) irradiated aluminum oxide gives a strong and broad TL glow with peak at $\approx 610$ K along with a weak shoulder at 500 K. The TL intensity is found to increase with Au\textsuperscript{9+} ion fluence up to $1 \times 10^{13}$ ions cm\textsuperscript{-2} and decreases beyond this fluence.

\section{1. Introduction}

Nanomaterials have attracted many researchers in various fields, including physics, chemistry, material science, biology and genetics [1]. They are considered to be good candidates for optoelectronic applications. There are distinct advantages and issues of using nanoscale phosphors for lighting, displays and related applications. Phosphor nanoparticles and nanostructured films have obvious advantages for greater spatial resolution in high definition displays [2]. Another promising application of nanostructured materials is similar to phosphors in flat panel displays [3]. These flat-panel displays use a cold-cathode ($< 1$ keV) electron emitter tip to excite the phosphor screen. Luminescent nanostructured materials are attractive for FED applications because of their small size that allows complete penetration by the low-voltage electrons for efficient material utilization. The close proximity of the phosphor particles to the emitter tips requires that the phosphor does not outgas or sputter a material that will poison the tips and the high current excitation requires phosphors with low thermal quenching [4]. In addition to lamps and optical displays, a number of phosphor materials is used for long-persistence phosphors, thermometry [5,6] and radiation dosimetry [7]. Thermoluminescence kinetics have been found to be different in nanoparticles [8], and in one report the nanoscale material did not saturate as readily as microcrystals, giving the nanomaterials a larger dynamic range [9]. The interest in nanocrystalline aluminum oxide is due to their potential applications in the fabrication of TLD phosphors and optical devices such as optical amplifiers and display phosphors in opto-electronic devices [10,11]. The luminescence produced in solids due to the impact of high-energy ions was recently the subject matter of investigations [12,13]. 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 the ion path, extremely high energies are deposited in a very small volume of a few hundreds of eV nm$^{-3}$ within an extremely small volume of a few hundreds of eV nm$^{-3}$ within an extremely short time but difficult to reach by any other radiation source. The high electronic excitation density in the core region has strong influence on the defect creation [14]. Good amount of work, though not exhaustive with heavy ion beams on sapphire [15,16] and polycrystalline aluminum oxide [17], has been reported. In this paper, new experimental results are presented on photoluminescence (PL) and thermoluminescence (TL) in swift heavy ion irradiated combustion synthesized nanocrystalline \text{Al}_2\text{O}_3.

\section{2. Experimental}

Nanocrystalline aluminum oxide is synthesized by the combustion technique based on the procedure discussed in detail elsewhere [10]. The stoichiometric amounts of redox mixture (aluminum nitrate, ammonium nitrate and glycine; Merck Chemicals, India) are
dissolved in 100 ml of double-distilled water in a cylindrical Pyrex dish of 300 ml capacity. The dish containing the homogeneous mixture is introduced into a muffle furnace maintained at 400 ± 5 °C. Initially, the solution boils and undergoes dehydration followed by decomposition with evaporation of a large amount of gases, leaving behind a powder. The final product is voluminous and nanocrystalline. To remove the carbon impurities left behind, the sample is annealed at 900 °C in a muffle furnace for 3 h. The pellets of Al2O3 of 6 mm diameter and 1 mm thickness are prepared by applying a pressure of 7 tons per ram of 6 mm diameter, i.e. 70 MPa using a home-made pelletizer. One of these samples is used as pristine for comparison with irradiated ones and the others are irradiated with 120 MeV swift Au9+ ions for various fluences in the range 5 × 1011–2 × 1013 ions cm⁻² using a 15UD tandem Pelletron accelerator in the Materials Science beam line at Inter University Accelerator Center, New Delhi. PL studies performed using a He–Cd laser (KIMMON) and a Michelle 900 spectrophotograph in the range 200–1100 nm. TL measurements are carried out at a heating rate (β) of 5 Ks⁻¹ using PC based TL analyzer (Nucleonix Systems Pvt. Ltd Hyderabad, India).

3. Results and discussion

The structural characteristics of combustion-synthesized nanocrystalline Al2O3 are studied by the XRD technique. Using the Scherer formula, the average grain size of the phosphor is calculated to be ~9 nm. It may be noted that heat treatment of nanomaterials may affect the grain size. However, in the present case, Al2O3 heat-treated at 900 °C does not show much variation in grain size because, nanocrystalline Al2O3 shows gamma phase and it changes to the most stable α-phase only above 1700 °C [18]. Based on SRIM (stopping and range of ions in solids) calculations the electronic energy loss (S_e) and nuclear energy loss (S_n) for 120 MeV gold projectile ions and aluminum oxide target are calculated to be 24.8 and 0.4 keV nm⁻¹, respectively. The range of 120 MeV Au ions in Al2O3 is 9.1 μm, and can be calculated using the SRIM software developed by Ziegler [19]. The software was downloaded from www.srim.org. The luminescence response is extremely sensitive to the nature of defects and their interaction. PL is a well established, nondestructive and widely practiced tool for the identification of defects in opaque materials where optical absorption studies cannot be carried out. Therefore, PL is used as a technique to identify the ion-induced defects. PL emission (λ_ex = 326 nm) spectra of pristine and 120 MeV swift Au9+ ion irradiated nanocrystalline Al2O3 are shown in Fig. 1. A broad and complex PL emission in the range 400–600 nm along with a prominent and well resolved PL emission peak at 770 nm are observed in unirradiated samples. However, when the samples are irradiated with swift Au9+ ions, a prominent PL emission with a peak at ~525 nm along with shoulder at ~465 nm is observed. However, the characteristic 770 nm emission observed in irradiated samples is very weak but well resolved, as can be seen from Fig. 1. A well resolved PL emission with peak at 770 nm observed in unirradiated samples is attributed to Ti3+ impurities [20]. Further, after irradiation, the characteristic 770 nm emission was observed to be very weak, as can be seen from the Fig. 1. As widely known, the structural changes due to SHI irradiation cause reduction in PL intensity due to defects acting as nonradiative recombination centers, whose concentration certainly increases with increasing ion fluence. A weak emission with peak at ~695 nm is observed in all samples and is attributed to C2+ impurities present in the material [21].

Further, oxygen loss may not take place during 120 MeV Au9+ ion irradiation, as Al2O3 is a highly radiation-resistant material. Instead, oxygen is ionized and displaced from its site leading to anion vacancy and subsequently electrons are trapped in it to form color centers (F- and F-aggregate centers).

Al Ghamdi and Townsend [22] have reported two optical absorption bands with peaks at 355 (3.49 eV) and 460 nm (2.70 eV) in He ion irradiated Al2O3 and they are attributed to F2 + and F2 ++ centers, respectively. PL of these centers when excited with 355 and 460 nm gives rise to emission with peaks at 380 and 520 nm, respectively. They observed enhancement in PL intensity with ion fluence. The samples used in the present investigation are opaque in nature and optical absorption studies could not be carried out. However, diffuse reflectance is an excellent sampling tool for powdered materials in the mid-IR and NIR spectral ranges. In the present work, it is observed that PL intensity at 525 nm corresponding to F2 ++-center increases with increase in Au9+ ion fluence and reaches maximum up to about 1 × 1012 ions cm⁻² and then decrease with further increase in ion fluence. Dalmasso et al. [23] reported PL emission at 2.3 eV (540 nm) when polycrystalline Al2O3 was irradiated with 365 and 540 MeV Kr ions followed by excitation at 2.7 eV (460 nm). They attributed the 2.3 eV emission peak to F2 ++-centers (two oxygen vacancies with two electrons). Therefore, it is believed that 525 nm emission observed in the present work might be due to...
$F^2_2^+\text{-centers}$ [17]. Fig. 2 shows the variation in PL intensity at 525 nm with 120 MeV swift $Au^{9+}$ ion fluence in nanocrystalline aluminum oxide. It is observed that, PL intensity increases with increase in ion fluence up to $1 \times 10^{12}$ 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 ($F^2_2^+\text{-centers}$) caused by $Au^{9+}$ ion irradiation. Further, increase in $Au^{9+}$ fluence may annihilate the primary defects and give rise to growth of new defect centers. Hence, decrease in PL intensity in the present work may be attributed to the annihilation of primary defect centers.

Thermoluminescence is a very common and yet simple technique used for estimation of doses of high-energy ionizing radiations absorbed in materials. As-prepared $Al_2O_3$ i.e., pristine samples, did not show any thermoluminescence (TL) response. However, it may be noted that samples irradiated with SHI, UV, X or gamma rays show TL response. Thermoluminescence glow curves of 120 MeV swift $Au^{9+}$ ion irradiated nanocrystalline aluminum oxide annealed at 900°C are shown in Fig. 3. A prominent and well resolved TL glow with peak at 610 K and a shoulder at $\sim$500 K is observed. Fig. 4 shows the variation in TL glow peak intensity and glow peak temperature ($T_{g2}$) with fluence in 120 MeV $Au^{9+}$ ion irradiated nanocrystalline aluminum oxide. It is observed that, the glow peak intensities at $T_{g1}$ and $T_{g2}$ increase with ion fluence up to $1 \times 10^{13}$ ions cm$^{-2}$ and reaches saturation. And the TL intensity is found to decrease with further increase in ion fluence but this decrease is not significant. However, if we irradiate with fluence beyond $2 \times 10^{13}$ ions cm$^{-2}$ the decrease is certainly significant. Further, it may be noted that TL intensity increases rapidly up to $1 \times 10^{13}$ ions cm$^{-2}$. This may be correlated with the observed PL results. The higher temperature glow peak ($T_{g2}$) in the present work is found to be shifted towards lower temperature side with increase in ion fluence.

The evaluation of kinetic parameters such as activation energy ($E$) of the traps involved in TL emission, order of kinetics ($b$) and frequency factor ($s$) associated with the TL glow peaks, is one of the important aspects of studies in condensed matter physics. These parameters are estimated using glow curve shape method based on the modification by Chen et al. [24]. The detailed calculations using a set of equations are discussed elsewhere [25].

Fig. 5 shows deconvoluted glow curve of nanocrystalline aluminum oxide irradiated for the fluence of $1 \times 10^{13}$ ions cm$^{-2}$. The complex glow curve is deconvoluted into two simple curves with peak at 610 K (named as peak B) and 502 K (named as peak A). Following Halperin and Bramer [26], one can define a geometry factor $m_g = \delta / \omega$, where $\delta$ is the high temperature half-width and $\omega$ is the full width at half-maximum (see Fig. 5). This factor would be typically 0.42 for pure first-order glow peak and 0.52 for second order glow peak. The value of $m_g$ for curve A is found to be 0.44, which is closer to 0.42. This implies that curve A (see figure) indicates the first-order kinetics, which obeys Randall–Wilkins first-order expression. $m_g$ for curve B is found to be 0.48, which is closer to 0.52 and it may be inferred that the glow curve B exhibits intermediate kinetics. The trap parameters estimated by glow curve shape method are tabulated in Table 1.

4. Conclusions

Nanocrystalline aluminum oxide irradiated with 120 MeV $Au^{9+}$ ions shows good PL and TL responses. The observed PL emission with peak at 525 nm is ascribed to $F^2_2^+\text{-center}$ emission. A prominent TL glow with peak at 610 K shows intermediate kinetics. The TL glow peak intensity is found to increase with increase in ion fluence up to $1 \times 10^{13}$ ions cm$^{-2}$ and then it saturates. The 610 K glow peak in the present studies finds its importance in dosimetric studies.
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References


Table 1

Kinetic parameters of nanocrystalline aluminum oxide irradiated with swift Au^{+9} ions, obtained using the glow curve shape method (modified by Chen et al. [24]).

<table>
<thead>
<tr>
<th>Ion fluence (ions cm^{-2})</th>
<th>TL glow curve</th>
<th>Tm (K)</th>
<th>kT</th>
<th>b</th>
<th>Activation energy (eV)</th>
<th>s (s^{-1})</th>
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<tr>
<td>A</td>
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<td>0.750</td>
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