

Photoluminescence and Raman studies in swift heavy ion irradiated polycrystalline aluminum oxide

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Abstract. Polycrystalline aluminum oxide is synthesized by combustion technique and XRD studies of the sample revealed the α -phase. The synthesized sample is irradiated with 120 MeV swift Au⁹⁺ ions for the fluence in the range from 1×10^{11} to 1×10^{13} ions cm⁻². A broad photoluminescence (PL) emission with peak at ~447 nm and two sharp emissions with peak at ~679 and ~695 nm are observed in pristine when sample was excited with 326 nm. However, in the irradiated samples the PL intensity at ~447, 679 and 695 nm decreases with increase in ion fluence. The α -Al₂O₃ gives rise to seven Raman modes with Raman intensity with peaks at ~253, 396, 417, 546, 630, 842, 867 cm⁻¹ observed in pristine. The intensity of these modes decreases with increase in ion fluence. However, the Raman modes observed at lower fluences are found to disappear at higher fluence.

Keywords. Al₂O₃; swift heavy ions; Raman spectra; photoluminescence; amorphization.

1. Introduction

Radiation effect in inorganic insulating materials is a subject matter of investigation due to their scientific and technological importance. The major reason of this interest is the need for a better understanding of material performance in radiation environment of nuclear reactors and accelerators. Also, the incorporation of energetic heavy ions as a processing technique improves material properties (Nagabhushana *et al* 2006; Song *et al* 2006). Among the insulators aluminum oxide, also known as alumina, is of high interest due to its superior properties such as very stable structure, good electrical insulation, high strength and chemical inertness etc which provides large potential of applications such as RF windows in fusion reactors, toroidal insulating breaks, diagnostic probes, coatings, abrasives, thermoluminescence dosimeters etc (McKeever *et al* 1999; Mimani 2000; Ryazanov and Kinoshita 2002). Most of the physical properties of aluminum oxide, in particular, its optical and electrical features are dielectric in nature (Kadleikova *et al* 2001). Swift heavy ions (SHI) cause intense electronic excitations along the ion trajectory when they pass through material that may result in defect production or amorphization or phase transformation on nanometer scale (Bolse *et al* 2004; Wang *et al* 2004). Thus, it is interesting to know the effect of strong electronic excitation by high energy

heavy ions in the surface region of materials. With 120 MeV gold ions for aluminum oxide target in the present studies, Se and Sn are calculated using SRIM 2003 program to be 24.83 keV nm⁻¹ and 0.36 keV nm⁻¹, respectively. Here, the Se is higher than the threshold required for the creation of extended defects. Se is dominant up to ~9.1 μ m from the surface (www.srim.org).

Raman and photoluminescence (PL) spectroscopy are known to be nondestructive material characterization techniques. Raman spectroscopy provides unique ways of probing surface and structural properties of ion beam modified materials. The PL spectrum is correlated to the surface amorphization due to SHI irradiation. In the present paper we report the effect of 120 MeV swift Au⁹⁺ ion irradiation on aluminum oxide through glancing angle X-ray diffraction (GAXRD), Raman and PL spectroscopy technique.

2. Experimental

Polycrystalline aluminum oxides were synthesized by combustion technique based on the procedure discussed by Kingsley and Patil (1988). Details of the certificate of guarantee (COG) of chemicals used in synthesis are given elsewhere (Nagabhushana 2008). Where assay 99.95% and other impurities such as chloride (Cl) 0.0005%, sulphate (SO₄) 0.03% and lead 0.005% are present in the ingredient chemicals. However, there are some more impurities which may also be present in the ingredients. However, elemental analysis of the synthesized Al₂O₃ is

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not carried out. Pellets, 6 mm diameter and 1 mm thickness, of Al_2O_3 were prepared using a home-made pelletizer and by applying a pressure of 70 MPa. One of these samples was used as pristine for comparison. The pellets were irradiated with 120 MeV swift Au^{9+} ions for various fluences in the range 1×10^{11} to 1×10^{13} ions cm^{-2} using 15 UD tandem Pelletron accelerator in materials science beam line at the Inter University Accelerator Centre, New Delhi. The structural characterizations of the pristine and SHI irradiated samples are analysed by GAXRD (Bruker X-ray machine, $\text{CuK}\alpha$ rays) technique at a glancing angle of 1° . Raman spectra were recorded using Renishaw, model 1000 Raman spectrometer. A 785 nm laser beam of 0.5 mW from an Ar ion laser is used as excitation source. The micro Raman data was recorded in the range 200–900 cm^{-1} . Luminescence technique is a very sensitive technique to identify trace impurities and point defects, hence PL studies were performed using excitation at 326 nm light from He–Cd laser (KIMMON) and Mechelle900 spectrograph. The PL setup has a cooled CCD array-based detection system. The laser light is made to incident on the sample at 45° and the luminescence light was collected using a collector assembly attached to the spectrograph through optical fibre for detection and analysis.

3. Results and discussion

3.1 Glancing angle X-ray diffraction

The GAXRD patterns of as synthesized unirradiated aluminum oxide are given in figure 1(a). The diffraction peaks at 25.25, 35.16, 37.78, 43.36, 52.58 and 57.52° are due to (012), (104), (110), (113), (024) and (116), respectively. The results compared to those of bulk α -alumina (JCPDS: 82-1468), were found to belong to rhombohedral crystal system with $R\bar{3}c$ space group. Also, the patterns are observed to be in good agreement with polycrystalline Al_2O_3 powders reported by Kingsley and Patil (1988). The GAXRD measurements are carried out on irradiated pellets in order to avoid the effect of pristine part in irradiated part, because X-rays penetrate a few microns in bulk at larger angles. In figure 1, XRD of pristine sample is compared with irradiated one (figure 1b). Careful observation of the XRD of both samples revealed that the intensity of the irradiated sample is lower when compared to that in pristine. The reduction in intensity clearly indicates that the sample starts to amorphize after SHI irradiation at the given fluence. Also, Raman studies clearly indicate the amorphization of the sample. Because, Raman spectroscopy is a very sensitive technique depending on the crystal structure, even a little change in the lattice order leads to change in Raman spectra. Furthermore, alumina being a high radiation resistant material one cannot expect complete amorphization at this fluence.

3.2 Raman studies

Raman spectroscopy provides associated vibrational spectrum of molecular spectra within the irradiated scattering volume. Aluminum oxide has several crystallographic phases. The two important phases are water free Al_2O_3 viz. alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) and gamma alumina ($\gamma\text{-Al}_2\text{O}_3$). Other phases of Al_2O_3 are eta alumina ($\eta\text{-Al}_2\text{O}_3$), theta alumina ($\theta\text{-Al}_2\text{O}_3$) and beta alumina ($\beta\text{-Al}_2\text{O}_3$). Among these $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ does not show any bands in Raman spectrum (Kingsley and Patil 1988). $\alpha\text{-Al}_2\text{O}_3$, also known as corundum, is shown with space group $R\bar{3}c$. The representation of optical modes in $\alpha\text{-Al}_2\text{O}_3$ are given by Krishnan (1947)

$$2A_{1g} + 2A_{1u} + 3A_{2g} + 2A_{2u} + 5E_g + 4E_u. \quad (1)$$

Among these $2A_{1g} + 5E_g$ are Raman active, $2A_{2u} + 4E_u$ are IR active whereas $2A_{1u} + 3A_{2g}$ are neither Raman nor IR active modes. Therefore, $\alpha\text{-Al}_2\text{O}_3$ gives rise to seven Raman active modes. Figure 2 shows the Raman spectra of (a) pristine and SHI irradiated polycrystalline aluminum oxide. Several Raman modes with peaks at ~ 253 , 396, 417, 546, 630, 842, 867 cm^{-1} are observed in pristine. On the basis of Raman polarization study seven Raman active modes have been assigned by Porto and Krishnan (1967). The Raman modes observed in the present studies are assigned and given in table 1. The Raman bands with peaks at 396, 417, 546, 630 and 842, 867 cm^{-1} have been assigned to E_g (external), A_{1g} , E_g (external), A_{1g} , E_g (internal) modes, respectively. The other mode corresponding to E_g (external) at ~ 432 cm^{-1} is not observed in the present studies. However, an extra band with peak at 253 cm^{-1} is observed. This might be due to the fact that, the vibrational spectrum of the crystal is modified even by slight changes in the crystal structure (Kadleikova *et al* 2001). Further, in case of the SHI irradiated samples the intensities of Raman bands decreases

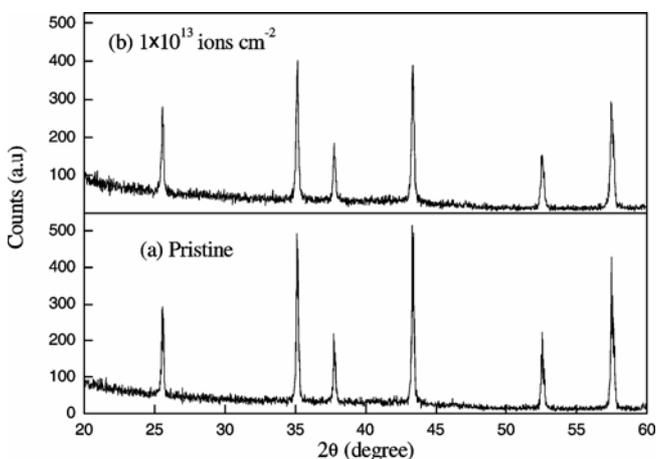


Figure 1. GAXRD patterns of (a) pristine and (b) 120 MeV Au^{9+} ion irradiated polycrystalline aluminum oxide.

with increased ion fluence and at the fluence of 1×10^{13} ions cm^{-2} the samples did not show any Raman bands as can be seen from figure 2(d). This might be due to either change in the crystal phase or surface amorphization. However, XRD studies reveal no phase transformation at the fluence of 1×10^{13} ions cm^{-2} as discussed in §3.1 above. It is well known that Raman spectroscopy is a powerful tool to evaluate the induced amorphization of a crystalline structure. Raman spectra of crystalline with lattice defects and systems having other types of struc-

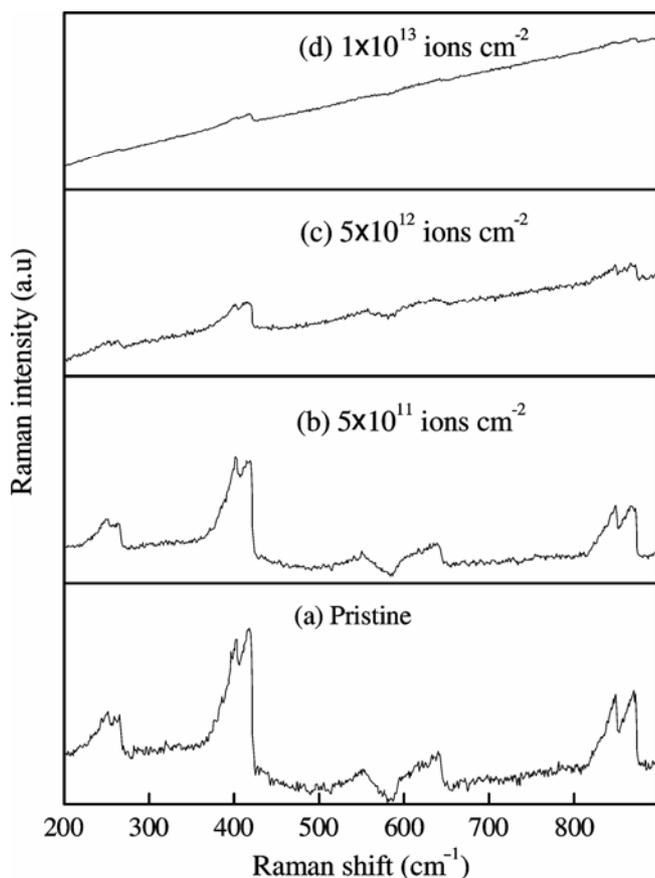


Figure 2. Raman spectra of pristine and SHI irradiated polycrystalline Al_2O_3 .

Table 1. Peak positions of Raman modes of pristine and 120 MeV Au^{9+} ion irradiated combustion synthesized polycrystalline aluminum oxide.

Peak position (cm^{-1})	Pristine	5×10^{11} ions cm^{-2}	1×10^{13} ions cm^{-2}
253	No assignment		–
396	E_g (external)	E_g (external)	–
417	A_{1g}	A_{1g}	A_{1g}
546	E_g (internal)	E_g (internal)	–
630	A_{1g}	A_{1g}	–
842	E_g (internal)	E_g (internal)	–
867	E_g (internal)	E_g (internal)	E_g (internal)

tural disorder usually exhibit a pronounced line broadening in comparison with ordered structures (Brundle *et al* 1992). However, in the present case there is an appreciable line broadening and large decrease in Raman intensity as can be seen from figure 2. This might be attributed to high defect concentrations causing broadened Raman lines. Further, Raman spectra suggest that there is structural damage to Al_2O_3 lattice upon ion irradiation. SRIM results indicate that when the energy of the incident ion is of a few keV then the nuclear energy loss (S_n) is significant as compared to electronic energy loss (S_e) (Ziegler 2004). In the present studies, 120 MeV Au^{9+} ions are used for irradiation and the electronic energy loss is dominant over the nuclear energy loss. The incident ions are expected to break the Al–O bonds in Al_2O_3 . The disordered lattice will contribute to the internal stress and thus the Raman peak intensity decreases. The vibration spectrum of crystal is modified even by slight changes in the crystal structure such as sample of different origin and substitution by different cations and anions and creation of radiation induced defects (Nagabhushana *et al* 2008).

3.3 Photoluminescence

Figure 3 shows PL spectra of pristine and SHI irradiated polycrystalline aluminum oxide. A broad PL emission with peak at 447 nm in the range 400–600 nm and two sharp PL emissions with peak at ~ 679 and 695 nm have been observed in all samples. The two sharp emissions are attributed to well known Cr^{3+} doublet R_1 and R_2 lines. Trace quantities of Cr^{3+} ions are naturally present in ceramic alumina. Cr^{3+} ions are residing in an octahedrally coordinated oxygen environment. The luminescence due to Cr^{3+} ions is used as a probe for the crystalline environment because of its high sensitivity to the variations

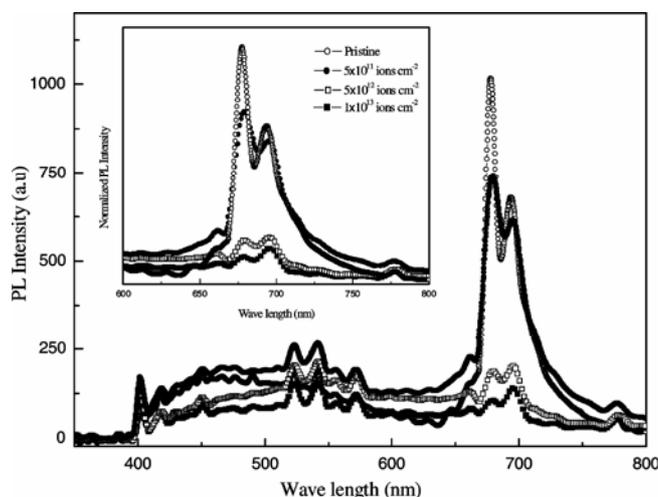


Figure 3. Photoluminescence ($\lambda_{\text{ex}} = 326$ nm) of pristine and SHI irradiated polycrystalline Al_2O_3 .

in crystal field (Jankowiak *et al* 2000). Makhov *et al* (2008) studied the luminescence and radiation effects in electron irradiated Al_2O_3 and $\text{Al}_2\text{O}_3:\text{Cr}$. He observed the emission spectra of both non irradiated and electron irradiated ruby crystals in the red region which show a well known set of narrow emission lines around 700 nm and attributed the emission due to the transitions from the lowest excited 2E state to the ground state 4A_2 of Cr^{3+} . Singh and coworkers (2008) studied the properties of red emitting Cr^{3+} doped barium aluminate phosphor obtained by combustion process. They reported the PL spectrum with a doublet at 701 nm and 705 nm. Such a doublet, an intense R_1 line (705 nm) and partly frozen out R_2 line (701 nm), is the characteristic of Cr^{3+} ions which are caused by the spin forbidden ${}^2E_g \rightarrow {}^4A_{2g}$ transition. Hence in the present investigations the R_1 and R_2 lines are attributed to ${}^2E_g \rightarrow {}^4A_{2g}$ transitions (Nagabhushana 2008).

The PL spectra in the range 600–800 nm due to Cr^{3+} ions in pristine and SHI irradiated one is given as inset in figure 3. It is observed that, the pristine samples show maximum PL intensity due to Cr^{3+} ions whereas it decreases with increase in ion fluence. For the fluence of 1×10^{13} ions cm^{-2} the emission is drastically reduced. The variation of PL intensity of Cr^{3+} doublet R_1 and R_2 lines with ion fluence is given in figure 4. Disorder due to SHI irradiation can be considered responsible for the reduction in PL intensity. As is widely known (Canham 1997), one of the structural changes causing reduction in PL intensity is due to defects acting as nonradiative recombination centres whose concentration certainly increases with increasing ion fluence. Further, Cr^{3+} ions are displaced from octahedrally coordinated oxygen environment due to SHI irradiation which leads to the decrease in volumetric concentration of Cr^{3+} ions. Therefore, the decrease in intensity of PL at 675 nm and

695 nm is attributed to amorphization. Also, the decrease in PL intensity can be attributed to increase in porosity due to SHI irradiation. Further, SHI irradiation creates a latent track in a target material when Se exceeds a threshold value (S_{eth}). Aluminum oxide being a high-band gap insulator, SHI irradiation is expected to create latent tracks in the medium. However, it is reported that the latent tracks were not observed in Al_2O_3 (Skuratov *et al* 2002) using SHI ion beam having Se < 30 keV nm^{-1} . But, discontinuous tracks can be formed when Se exceeds 18 keV nm^{-1} (Ramos *et al* 1998). Therefore, it is believed that, these discontinuous tracks may cause porosity in the sample. At higher fluence the concentration of these discontinuous tracks is higher (Krishna *et al* 2003). Hence, the PL spectrum is correlated to the surface amorphization due to SHI irradiation.

4. Conclusions

Combustion synthesized polycrystalline aluminum oxide shows α -phase. GAXRD studies show decrease in the diffraction peak intensity when irradiated with 120 MeV Au^{9+} ions for a fluence of 1×10^{13} ions cm^{-2} . The Raman bands observed at 396, 417, 546, 630 and 842, 867 cm^{-1} have been assigned to E_g (external), A_{1g} , E_g (external), A_{1g} , E_g (internal) modes, respectively. The intensity of these bands decreases with increase in ion fluence. This may be attributed to surface amorphization. Further, the PL intensity at 679 and 695 nm corresponding to R_1 and R_2 lines of Cr^{3+} decreases with increase in ion fluence. This might be due to surface amorphization by discontinuous tracks created by SHI irradiation. Hence, Raman and PL spectroscopic techniques are applied to understand the surface amorphization in combustion synthesized polycrystalline aluminum oxide.

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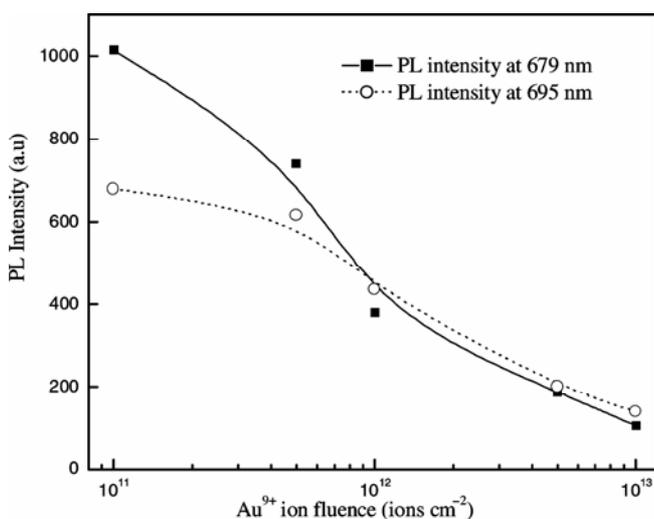


Figure 4. Variation of PL intensity at R_1 and R_2 lines of Cr^{3+} ion emission with irradiation fluence.

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