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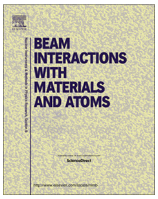

Simulation of alpha decay of actinides in iron phosphate glasses by ion irradiation

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ABSTRACT

A surrogate approach of ion beam irradiation is employed to simulate alpha decay of actinides in iron phosphate nuclear waste glasses. Bismuth and helium ions of different energies have been selected for simulating glass matrix modification owing to radiolysis and ballistic damage due to recoil atoms. Structural modification and change in coordination number of network former were probed by employing Reflectance Fourier-Transform Infrared (FT-IR), and Raman spectroscopies as a consequence of ion irradiation. Depolymerisation is observed in glass sample irradiated at intermediate energy of 2 MeV. Helium blisters of micron size are seen in glass sample irradiated at low helium ion energy of 30 keV.

1. Introduction

The disposal of high-level nuclear wastes (HLW) is global challenge and in most cases these HLW will be immobilised in glass waste forms prior to permanent disposal. World-wide efforts are being made to develop immobilisation matrix with improved radiation resistance. Iron phosphate glasses (IPG) are being considered as candidate material for immobilisation of high level radioactive waste, including minor actinides and plutonium residues [1–5]. Alpha-decay of the incorporated actinides results in the formation of energetic alpha-particles (4.5–5.5 MeV), energetic recoil nuclei (70–100 keV), and some gamma rays. The alpha-particles with energy ranging from 4.5 to 5.5 MeV will predominately deposit its energy by ionization processes and can lead to the permanent displacement of atoms due to the conversion of a localized electronic excitation into atomic motion. Recoil nuclei with an atomic weight of 235–244 and energy 70–100 keV lose most of its energy in ballistic elastic collisions with the nuclei of atoms in the glass. Consequently, interaction of alpha-particles and energetic recoil nuclei will potentially affect the structural integrity of immobilisation matrix [6]. The alpha-decay of actinides lead to (i) radiolysis (due to energetic alpha particles) and (ii) ballistic elastic collisions (due to energetic recoil). Both the processes are responsible for displacement damages inside matrix, and these damages affect the glass durability and its long term performance as an immobilisation matrix [7]. Therefore, it is imperative to explore the effects of radiation damage in glasses. In order to simulate radiation damages in nuclear waste glasses, ion irradiation method can be used. The advantages of this process are the high damage rate and the fact that it does not activate the matrix. Worldwide efforts are being made to simulate radiation damage in glasses by employing ion irradiation method [8,9]. Mendoza et al. have reported depolymerization of the borosilicate network in borosilicate glass specimens irradiated with krypton ions (74 MeV) and xenon ions (92 MeV) [10]. In an another study, structural modification in vitreous SiO_2 by Au ion irradiation is observed and unified thermal spike model consisting of a coherent synergy of the elastic collision spike model with the inelastic thermal spike model is invoked to understand track evolution from the nuclear to the electronic energy regime [11].

2. Experimental details

Iron phosphate glass of composition 60 mol% P_2O_5-40 mol% Fe_2O_3 was synthesised using $NH_4H_2PO_4$ and Fe_2O_3 as starting precursors. The powder in stoichiometric ratio were mixed and melted at 1150 °C for 4 h in recrystallized alumina crucibles in an electric muffle furnace. The molten glass was cast into a steel mold and annealed at 500 °C for 1 h. The glass samples were cut into discs of size 16 mm in diameter and 1.5 mm of thickness, and then optically polished to 1 μm finish using SiC paper and diamond paste before irradiation. Ion irradiation experiments were performed at Ion Beam Centre, University of Surrey. The specimens were

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irradiated with 750 keV and 2 MeV Bi/He ions. To simulate collision cascades induced by heavy recoil atoms during alpha disintegration, Bi ions are chosen as Bi ions have mass closer to recoil atoms. In the case of Bi ions, fluence of $9.2 * 10^{14}$ and $6.2 * 10^{14}$ ions/cm^2 were chosen for 2 MeV and 750 keV Bi ions respectively, to get nearly same damage of 2 dpa at depth of 150 nm inside the glass samples. Except irradiation at 2 MeV with Bi ions, all other samples were irradiated at a fluence of $6.2 * 10^{14}$ ions/cm^2. The ion fluence is measured using four Faraday cups which sit in the periphery of the scan pattern. The electrical charge from the four Faraday cups is integrated in real time. The uniformity of the scan system is at the 1% level for 4″ irradiation areas and the absolute dose control is nearly 5%. The damage profile in IPG obtained from TRIM simulations, for different fluence of bismuth ions having different energy, is shown in Fig. 1 [12].

The damage levels are estimated from TRIM calculations with full cascade option and displacement energy is taken as 50 eV for all atoms in IPG. The electronic and nuclear stopping power of Bi and He ions obtained from SRIM software are given in Table 1. Ion energies for irradiation experiments are chosen in such a fashion that values of electronic and nuclear losses cover three-different loss regimes; (i) mainly nuclear loss for 750 keV Bi ions (ii) nuclear and electronic both for 2 MeV Bi ions (iii) mainly electronic loss regime for 2 MeV He ions. Sample classification and all the irradiation parameters are summarised in Table 2.

The pre-irradiated IPG sample with 2 MeV He ions was later irradiated with 750 keV Bi ions to simulate actual actinide decay in nuclear waste glasses. This sequence of irradiation will allow us to probe concomitant effect of electronic and nuclear losses on structure modification of IPG. The helium concentration in the glass due to alpha decay of actinides will be around 0.1 at.% (neglecting helium diffusion) after around 100,000 years of disposal [13]. Therefore, the sample pre-irradiated with 2 MeV He and 750 keV Bi ions (IPG4), was exposed to low energy (30 keV) He ions at fluence of $2 * 10^{17}$ ions/cm^2 to simulate the helium bubble formation in pre-damaged matrix. All the irradiations were performed at liquid nitrogen temperature to prevent any macroscopic heating of the sample and the local temperature was monitored during the irradiation.

The IPG samples were characterised for their structural and microstructural modifications before and after irradiations. FTIR specular reflectance spectra of pristine and irradiated glass samples were measured in the range 1500–700 cm^{-1} using Perkin Elmer Frontier spectrophotometer. The observed spectra were converted to a normal absorption spectrum using Kramer's–Koenig transformation. Raman spectra in the range of 200–1500 cm^{-1} were taken on inVia Raman microscope using excitation laser light of wavelength 514.5 nm on glass samples before and after irradiation. The obtained IR and Raman spectra were deconvoluted to estimate irradiation induced modifications in the basic unit of IPG samples. The microstructural investigations were performed on Hitachi TM3030 SEM machine.

Table 1
Electronic and nuclear stopping power of Bi and He ions in iron phosphate glass.

Ion type	Energy (keV)	Electronic stopping (Se) (keV/micron)	Nuclear stopping (Sn) (keV/micron)	Sn/Se
Bi	750	1200	3797	3.16
Bi	2000	1899	3146	1.65
He	2000	292	0.276	0.001

Table 2
Details of irradiation parameters: Ion type, energy and fluence.

Sample name	Ion type and energy	Fluence (ions/cm^2)
IPG1	2 MeV Bi ions	$9.2 * 10^{14}$
IPG2	750 keV Bi ions	$6.2 * 10^{14}$
IPG3	2 MeV He ions	$6.2 * 10^{14}$
IPG4	2 MeV He ion irradiation followed by 750 keV Bi ion irradiation	$6.2 * 10^{14}$
IPG5	30 keV He irradiation on pre-damaged IPG sample	$2 * 10^{17}$

3. Results and discussion

IR Spectrum of pristine and irradiated IPG samples were deconvoluted to get quantitative information about the structural modification induced by ion irradiation. Gaussian type function was fitted in spectra for identification of bands and deconvoluted spectrum for pristine IPG sample is shown in Fig. 2.

The deconvolution parameters, band centre and the area of peak, for the pristine and irradiated IPG samples are given in Table 3. The band assignments of IR absorption bands for the pristine and irradiated IPG samples are given in Table 4.

Significant change in stretching vibration of Fe–O–P bonds in Q^1 unit centred around 578–630 cm^{-1} is observed for IPG1 sample.

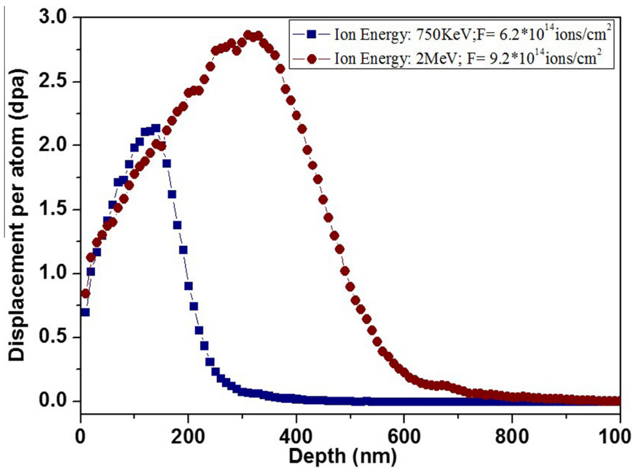

Fig. 1. The damage distribution in iron phosphate glass at 750 keV and 2 MeV Bi ion energy obtained from TRIM simulations.

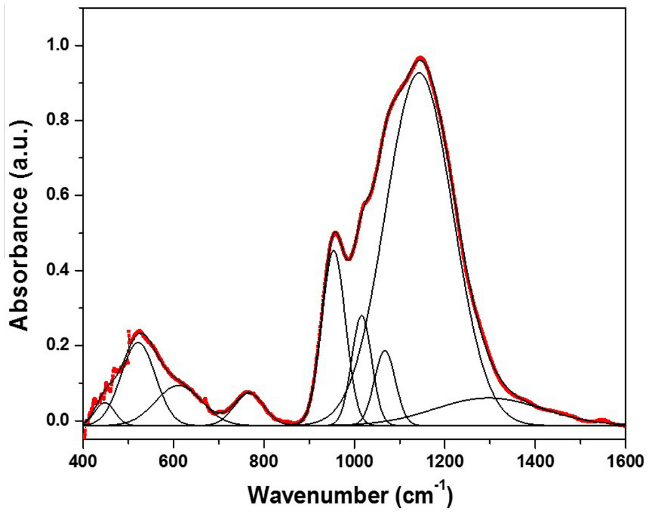

Fig. 2. The deconvoluted infrared spectrum for pristine iron phosphate glass sample.