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Electron beam irradiation effects in Trombay nuclear waste glass

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ABSTRACT

Spectroscopic investigations were carried out on electron beam irradiated sodium barium borosilicate glasses, which is the base glass for immobilization of nuclear high level radioactive waste, generated from the research reactors at Bhabha Atomic Research Centre, Trombay. This was done in order to access the defects generated in it under long term irradiation. Electron paramagnetic resonance was used to identify the defect centers generated in the borosilicate glass after irradiation. In addition, positron annihilation spectroscopy and infrared investigations were done on the samples to evaluate the radiation induced changes in the glass. It was found that, boron–oxygen and silicon based hole centers along with E' centers are getting formed in the glass after irradiation due to the breaking of the Si—O bonds at regular tetrahedron sites of Si—O—Si. The positron annihilation spectroscopy data gave an idea regarding the free volume size and fraction of the glasses before and after irradiation. It was seen that, after irradiation the free volume size in the glass increased with creation of additional sites. Microwave power variation and temperature variation studies suggested the formation of at least five different radicals in the irradiated glasses. The spin Hamiltonian parameter of all the radical species were determined by computer simulation. An electron paramagnetic resonance spin counting technique was employed to evaluate the defect concentration in the glasses after irradiation.

1. Introduction

Most of the radioactivity present in the entire nuclear fuel cycle is associated with the high level radioactive liquid waste (HLW), generated during reprocessing of spent nuclear fuel, whose composition largely depends on off reactor cooling of the fuel, its type, burn up and chemistry of reprocessing flow sheets [1]. Development of matrices for fixing the HLW to ensure complete isolation of radionuclides from human environment for extended period of time is a scientific and technological challenge. Borosilicate based glass formulations are being adopted worldwide for vitrification of the HLW [2]. An aluminum based borosilicate glass formulation has been developed in the United States during the 90s at Aiken, SC (the Defense Waste Processing Facility, DWPF) and in West Valley, NY (the West Valley Demonstration Project, WVDP) [3–5]. Similarly a French nuclear waste glass has been developed where along with oxides of boron and silicon, oxides of calcium, sodium and aluminum were also added to form the glass [6,7]. In BARC (Bhabha Atomic Research Centre), Trombay, the HLW generated from the research reactor nuclear waste, is characterized by the presence of high sulfate ion content. This poses a serious problem during glass vitrification as sulfate forms a separate phase owing to its low solubility in the borosilicate glass. To countercheck this higher sulfate content, a barium based alkali borosilicate glass composition has been developed which takes care of the problem of phase separation of sulfate [8]. Because of the decay of the radioactive components such as fission/activation products and minor actinides present in the waste, the glass experiences radiation damage. These damages can significantly alter the glass structure which may influence their long term leaching behavior. A comprehensive review has been given in this aspect by Weber et al. in their classical paper [9]. Several other reports are also available where glasses irradiated by high-energy electron beams and gamma rays have undergone changes in their structure, caused mostly by ionization and ballistic interaction of high-energy radiation with solid constituents of the glass matrix, that introduce disorders in the original structure causing formation of defect centers accompanied with volume changes, phase separation or gas accumulation in the irradiated glasses [10–12]. It is pivotal to study these changes so as to predict the long term leaching behavior of the vitrified waste product. Moreover, it is well known that the optimal engineering performance of a glass is dominated by its structure. So, the knowledge of the glass structure before and after

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irradiation is a prerequisite for understanding the structural evolution of glasses under long term irradiation [13]. In addition, these studies on the borosilicate glasses will lead to an understanding of the nature of the damage which can further lead to fabrication of materials in which the deleterious effects of radiation can be minimized or favorable effects can be maximized. Moreover, careful study of radiation induced defects can help to elucidate certain structural aspects of the glassy state which cannot be readily accessible by other means.

Electron beam irradiations can simulate the effects of beta irradiation in HLW glasses to a great extent if not in totality. Several effects such as the rates of alkali ion exchange in radiation fields do show a non-Arrhenius behavior depending on both the irradiation dose and dose rate as suggested by Ojovan and Lee [14]. Nevertheless, many literature reports are available where nuclear waste glasses of varying compositions were irradiated by high energy electron beams to simulate the beta irradiation effects [15–18]. In the present work, alkali barium borosilicate glasses, having similar composition to the Trombay waste base glass were irradiated with high energy electron beam and the changes were studied by electron paramagnetic resonance (EPR) spectroscopy. In addition, positron annihilation spectroscopic technique (PAS) was utilized to study the changes in the free volume size and free volume fraction of the glass. IR technique was used to monitor the changes in the overall glass structure. EPR spin counting technique was used to quantify defect centers formed in the glasses on irradiation.

2. Experimental

2.1. Sample preparation

All the chemicals used for the preparation of glass samples were of AR grade. At first, required amounts of glass network formers namely SiO_2 and H_3BO_3 and network modifiers, e.g. $Ba(NO_3)_2$ and $NaNO_3$, were taken and mixed thoroughly in an agate mortar so as to get a base glass with the composition (in wt.%) $(SiO_2)_{0.39}(B_2O_3)_{0.25}(Na_2O)_{0.12}(BaO)_{0.24}$. The powder mixtures were well ground and then transferred into a platinum crucible and heated at 700 °C for 2 h for the completion of calcination and then melted at 1000 °C. The melt was maintained at 1000 °C for 4 h to ensure homogenization. The free flowing melt was quenched between two stainless steel plates. Details regarding the development of the glass matrix and finer details of sample preparation are mentioned elsewhere [8].

2.2. Irradiation facility

The electron beam irradiations were done at room temperature in an industrial 2 MeV and 20 kW electron beam accelerator facility, ILU 6 (Budker Institute of Nuclear Physics, Russia) at Vashi, Navi Mumbai, India. The irradiations were done in a stationary mode under 1.8 MeV of energy and 400 mA of current. For the present investigations, glass discs of 10 mm diameter were prepared and irradiated at the electron beam facility. The samples were irradiated for varying time periods so as to get three different doses viz 10^5, 10^6 and 10^8 Gy (J/kg).

2.3. Instrumentation

EPR experiments were performed on a Bruker ESP 300 spectrometer operated at X-band frequency (9.60 GHz) equipped with 100 kHz field modulation. The '*g*' values were calibrated relative to a 2,2 diphenyl-1 picryl hydrazil (DPPH) standard having $g = 2.0036$. The EPR parameters for different free radicals have been precisely determined from the calculated spectra, which were obtained with Bruker SIMFONIA computer program based on perturbation theory. The theoretical EPR signals were calculated using the spin Hamiltonian parameter (H) as per the following equation.

$$H = \beta H_j S_j g_j \quad (1)$$

here j is the component along one of the axis x, y and z; H is the applied field, S is the total spin of the electron, g is the g factor (spectroscopic factor) and β is Bohr magneton. In the glass samples, EPR signals were simulated by generating 9000 random orientations of the magnetic field and by summing the corresponding 9000 absorption signals. The final signal was obtained by performing a convolution (Gaussian or Lorentzian line shape) of each transition line adding all contributions and calculating the first derivative of the signal. The line width of each component was optimized in order to obtain a best fit between the simulated and the experimental data. Temperature variation studies of the EPR spectra were conducted using a B-VT 2000 Eurotherm temperature controller unit attached to the spectrometer.

For PAS measurements, ^{22}Na positron source in the form of NaCl folded in kapton foil was sandwiched between the two identical pieces of borosilicate glass samples. Positron annihilation lifetime measurements were carried out using plastic scintillation detectors coupled to fast–fast coincidence system with a time resolution of 235 ps as measured with ^{60}Co source in ^{22}Na energy window setting. Data analysis was carried out using PATFIT program [19].

IR absorption spectra of the glass samples before and after irradiation were recorded at room temperature in the 400–4000 cm^{-1} range using a Bruker Vertex 80 V Fourier transform infrared (FTIR) spectrometer by the KBr pellet technique (2% sample in KBr powder). The spectra were obtained at a resolution of 4 cm^{-1} using a globar source, KBr beam splitter and DTGS detector. The spectrum of each sample was normalized with the spectrum of the blank KBr pellet.

3. Results

3.1. EPR results

Fig. 1a shows the room temperature X-band EPR spectra of the sodium barium borosilicate glasses irradiated with electron beam at varying doses. The spectrum is characterized by two sets of signals one at g ca 2 and the other at g ca 4.3. In the unirradiated glass sample except the sharp and intense signal at g ca 4.3, no other signal was observed. Thus the line at g ca 2 was only attributed to the various paramagnetic centers generated due to electron beam irradiation whose intensity increased with increase in the radiation dose as depicted in the figure. It was seen that the nature of the paramagnetic defects formed on irradiation remained almost same on irradiation with higher doses, however, the intensity of EPR signal almost increased twice on increasing the dose from 10^5 to 10^8 Gy suggesting that the paramagnetic defect concentration strongly increases as a function of irradiation dose. Fig. 1b shows the EPR signal generated due to defect centers in the borosilicate glasses in a smaller scale. This '$g \sim 2$' signal was very complex in nature and consisted of superposition of several contributions from different paramagnetic centers induced by external irradiation. The free radicals formed during the radiolysis were identified on the basis of their g factors and hyperfine coupling constants (A). The deconvoluted spectra were used for obtaining the spin Hamiltonian parameters of the paramagnetic defects. On the other hand, the resonance at g ca 4.3 was attributed to tetrahedrally coordinated Fe^{3+} ions in the glass [20]. The iron impurity might be coming from the stainless steel plates used for the quenching of the glass samples during preparation.