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FTIR structural investigation of gamma irradiated $BaO–Na_2O–B_2O_3–SiO_2$ glasses

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ABSTRACT

Fourier transform infrared (FT-IR) spectra of xBaO–15Na$_2$O–(70−x)B$_2$O$_3$–15SiO$_2$ glass system with x=0, 5, 10, 15 and 20 (mol%) has been measured in the spectral range 400–4000 cm^{-1} at room temperature in order to understand the characteristic frequencies of the chemical bonds and bonding mechanisms, which are susceptible to the structural and spectral changes. The effect of gamma irradiation in the dose range 0.1 kGy–60 kGy on the infrared absorption spectra of these glasses is also reported. The change in the glass structure due to the effect of composition is also discussed. It has been observed that irradiation of the glasses with the gamma rays increases the BO$_3$ groups and the non bridging oxygens which make the network loose.

1. Introduction

Irradiation effects on glasses is a growing area of interest nowadays because of the application of glasses in space craft, optical fiber wave guides, image guides for reactor inspection and most importantly for the management and disposal of high level nuclear waste (HLW) [1,2]. Glasses are upcoming and promising materials of excellent radiation resistance and possible alternatives to concrete in the nuclear industry. This is because glasses are transparent to visible light as well as their properties can be largely modified through preparation techniques and by varying the compositional elements in contrast to concrete [3–6]. However, glass and its properties such as physical, electrical, structural and optical are subject to a various changes under the influence of high-energy radiation. Even macroscopic changes like positive or negative volume changes and effect on mechanical properties such as hardness and fracture toughness has been reported by many authors [7,8]. These high-energy radiation effects can lead to the reduction of certain ions to metals to the collapse of the entire glass network. X rays and gamma rays can result in the introduction of defects such as discoloration or fluorescence, rupture of chemical bonds etc. on interaction with the glass [9]. Therefore, the knowledge of the glass structure before and after irradiation leads to better understanding of the glass structure as well as the changes taking place in structure as result of the interaction with radiation [10].

Among various types of glasses, borosilicate glass is considered to be one of the most suitable materials as a matrix for the immobilization of HLW as well as for radiation shielding design [11]. Borosilicate glasses have been studied extensively by various authors [12–14] as they are of technical and scientific interest due to their high density, high resistance to chemicals, low coefficient of thermal expansion and numerous applications in day to day life. An incorporation of heavy metal oxide ions such barium, bismuth and lead is expected to enhance the gamma-ray shielding properties of borosilicate glass due to their higher atomic numbers. Barium is a potential candidate for the development of radiation shielding glass as it strongly absorbs gamma rays, X-rays and is non-toxic as compared to lead [15,16]. Secondly, it prevents the phase separation due to the presence of sulphate in the HLW [17].

The present work has been undertaken with the objectives of studying the use of barium sodium borosilicate glasses as gamma-ray shields and also to explore their structural properties using the FTIR spectroscopy. This work is extended to investigate the effect of varying glass compositions on the infra red spectra. Also, this is in continuation with our previous work where irradiation effects have been investigated on silicate glasses [10,18,19].

2. Experimental

The glasses in the system xBaO–15Na$_2$O–(70−x)B$_2$O$_3$–15SiO$_2$ with x=0, 5, 10, 15 and 20 (mol%) were prepared by conventional

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Table 1
Showing the chemical composition of Ba0, Ba1, Ba2, Ba3 and Ba4 samples in mol%.

Composition	BaO	Na_2O	B_2O_3	SiO_2	$R=Na_2O/B_2O_3$	$K=Na_2O/SiO_2$
Ba0	–	15	70	15	0.21	1
Ba1	5	15	65	15	0.23	1
Ba2	10	15	60	15	0.25	1
Ba3	15	15	55	15	0.27	1
Ba4	20	15	50	15	0.30	1

melt-quenching method using analytic reagents $BaCO_3$ (99.99%), B_2O_3 (99.99%), SiO_2 (99.99%) and Na_2CO_3(99.99%) as raw materials. The composition of glass samples are shown in Table 1. Mixed batches of 30 g were melted in alumina crucibles using an electric furnace in the temperature range 1050–1150 °C for 1 h. The homogenized melts were then poured in disc shaped preheated stainless steel moulds for the required dimensions. The prepared samples were immediately transferred to a muffle furnace regulated at 350 °C and after 1 h, the muffle was switched off to cool at a rate of 25 °C/h to room temperature. The colorless transparent glasses were thus obtained.

All the glass samples were then finely powdered using a clean agate mortar pestle. The powdered glass samples were divided into small portions and packed in polythene sachets. These were then irradiated using a ^{60}Co source of gamma radiation having dose rate of 0.7 kGy/min at room temperature at IUAC, New Delhi. Samples were irradiated for varying radiation doses in the range from 0.1 kGy to 60 kGy. Fourier transform infrared (FT-IR) spectra of all the powdered samples before and after irradiation were recorded at room temperature in the range 4000–400 cm^{-1} using a Thermo Nicolet 380 spectrometer using the conventional KBr pellet technique.

3. Results

Borosilicate glasses have always attracted attention of researchers as there are two glass formers in these type of glasses: silica and boron oxide [20]. While the borate glass structure consists of a random network of BO_3 triangles linked through B–O–B linkages [21], SiO_4 tetrahedra is the main structural unit in silicate glasses [22]. Thus, it is generally expected that borate glasses containing varying amounts of SiO_2 or vice-versa should exhibit composite vibrational modes due to the presence of both silicate and borate units in it. However, the characteristic vibrational frequencies corresponding to either group depend upon the amount of each component added into the glass. Further, the alkali ion (M) which is added into the glass can either attach with silicon as $Si^{-}M^{+}$ resulting in the formation of non-bridging oxygen (NBO) or with boron by forming alkali borate phase. The association of the alkali ion with boron or silicon is governed by the R and K ratios (where $R=[Na_2O]/[B_2O_3]$ and $K=[Na_2O]/[SiO_2]$). The alkali associates with boron till $R<0.5$ and thereafter links itself with silicon. Also it has been observed that in sodium borosilicate glasses if $K>0.5$ and then the alkali (Na_2O) ion links itself only with boron. Thus, it is clear that most of the Na^+ ions in the investigated glasses have associated with trigonal BO_3 where $R<0.5$ and $K>0.5$ (values given in Table 1). This will result in the conversion of BO_3 units to BO_4 units without the creation of any NBO making glass more stable [21,23].

FTIR spectra of the investigated glasses shows prominent absorption bands in the following regions: (i) 400–600 cm^{-1} (ii) 600–800 cm^{-1}(iii) 800–1200 and (iv) 1200–1600 cm^{-1}.

The results are interpreted using the method given by Tarte [24,25] and Condrate [26,27] where the experimental data is compared with the results obtained for the crystalline samples. In the present case, we have compared the results with the absorption bands of vitreous B_2O_3, SiO_2 and crystalline BaO.

To study the presence of these bands and effect of barium oxide, the absorption spectra of each composition before irradiation is discussed below.

3.1. Ba0 glass

3.1.1. Before irradiation

Fig. 1 shows the FTIR spectra of the base ternary $Na_2O–B_2O_3–SiO_2$ glass system. The first absorption region shows small absorption bands at 440 and 530 cm^{-1}.The band at 440 cm^{-1} has been reported to exist in $B_2O_3–SiO_2$, alumino borosilicate glasses and in sodium borosilicate as well [28]. It was assumed that this band is related to Si–O–Si and O–Si–O bending modes of bridging oxygens overlapped with B–O–B bending modes. However this band does not appear in the infrared spectra of vitreous B_2O_3 but has been observed in the spectra of SiO_2 film [29].

Thus two small bands in the region 440–550 cm^{-1} centered at 440 cm^{-1} and 530 cm^{-1} are attributed to the deformation vibration of bonds in Si–O groups containing SiO_4 tetrahedra only [30]. A prominent band observed at about 683 cm^{-1} is due to the bending of Si–O–B linkages in the glass network [31]. The absorption bands in the region extending from 800 cm^{-1} to 1200 cm^{-1} are observed at 954, 1012 and 1054 cm^{-1}.These bands are assigned to the stretching vibrations of the B–O bonds in the structural groups consisting of BO_4 units in di-, tri-, tetra- and penta-borate groups [32,33]. Particularly, the region of 1000–1120 cm^{-1} can arise from overlapping contributions of silicate and borate groups containing BO_3 and BO_4 units [30]. The individual contribution of silicate and borate groups cannot be separated and is assumed to depend on the concentration of each component in the glass system. The bands in the region 1200 and 1500 cm^{-1} are due to the presence of BO_3 structural units in the glass. The component bands in this region appear at 1270 and 1390 cm^{-1} which can be attributed due to stretching vibrations of NBOs of trigonal BO_3 units in metaborate chains and rings, pyro and ortho borate groups [29]. A small absorption edge at around 1625 cm^{-1} is assigned to Si–OH stretching of surface silanol hydrogen bond to molecular water [23]. The presence of water groups is marked by the presence of bands above 2500 cm^{-1}.

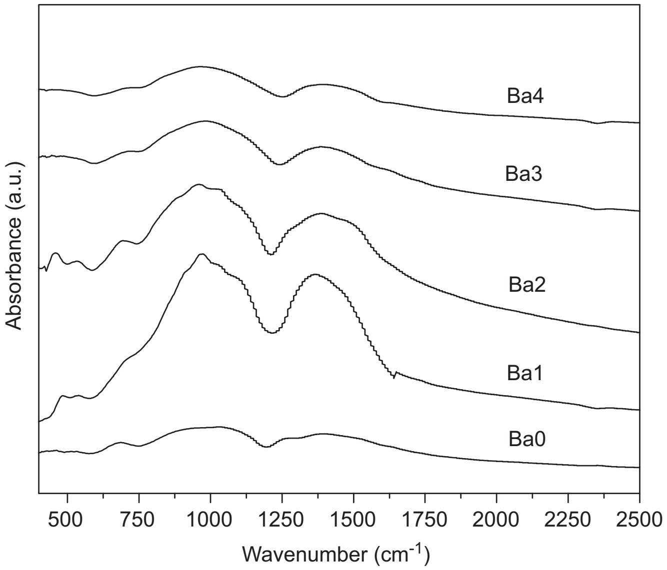

Fig. 1. Shows the IR spectra of the Ba0, Ba1, Ba2, Ba3 and Ba4 glass samples before irradiation.