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Effect of gamma irradiation on the density, glass transition temperature and electrical conductivity of lithium borosilicate glasses with alumina addition

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ABSTRACT

Lithium borosilicate glasses (LBS) with alumina addition have been synthesized. The effect of gamma irradiation on the density, glass transition temperature (Tg) and electrical conductivity of these glasses has been studied. It has been observed that, the density and (Tg) of lithium borosilicate glasses decreases and electrical conductivity increases with addition of alumina. The formation of AlO_4 tetrahedra expands the lattice which explains the decrease in density and Tg. The increase in electrical conductivity has been attributed to the increase in (NBOs). With gamma irradiation the density and Tg increase due to formation BO_4 tetrahedra at the cost of AlO_4 resulting into compact and dense glass network. The electrical conductivity decreases after irradiation due to reduction in the number of NBOs and the formation of more closed network. There is a very good correlation among the density, Tg, FTIR and electrical conductivity for the glasses studied in the present work.

1. Introduction

The electrical conduction in oxide glasses is due to motion of alkali ions present in interstitial position within the glass network. Lithium ion conducting glasses have been widely studied for last four decades due to their potential for application in electrochemical devices [1–5]. Most of the work deals with the compositional dependence of conductivity and other physical properties viz. density, Tg, FTIR. The ionic conductivity in these glasses depends broadly on the concentration of charge carriers and the number of non bridging oxygen (NBOs) which are available vacant sites for lithium ions. The interest in the borate glasses stem from the fast ionic conductivity exhibited by some of them and the attractive possibilities they offer for energy storage applications [6–8]. The lithium borate glasses are hygroscopic in nature and hence their stability is an issue for technical applications. The chemical durability of these glasses can be increased with addition of silica [9]. It has been reported that, the density, Tg and electrical conductivity of the lithium borate glasses are influenced by gamma irradiation [10].Elbatal has studied the effect of gamma irradiation on lithium aluminoborate glasses [10]. However, there are no reports on the effect of gamma irradiation on lithium borosilicate glasses containing alumina. Hence in the present work the study of effect of gamma irradiation on density, Tg and electrical conductivity of lithium borosilicate glasses with alumina addition has been carried out.

2. Experimental

2.1. Preparation of glass sample

The glass series with general formula (30 − x) Li_2O:60B_2O_3:10 SiO_2:xAl_2O_3 (x varying from 0 to 10 at an interval of 2.5 mol%) was prepared by conventional quenching technique. An appropriate amount of Li_2CO_3, B_2O_3, SiO_2 and Al_2O_3 of Merck was taken and mixed thoroughly in acetone. The dried mixture was then put in a platinum crucible and heated to melt in an electric furnace. The melting point of the glasses ranged from 1148 to 1173 K depending on the composition. The melt was then maintained at 40 K above the melting point for 1 h with frequent stirring to ensure homogeneity. The melt was then quenched in an aluminium mould at room temperature to get cylindrical shaped glass samples. The quenched samples were then annealed for 2 h at 573 K.

The glass transition temperature (Tg) was determined with the help of differential thermal analyzer DTG-60 SHIMADZU. Impedance measurements were carried out for all the glass samples as a function of temperature (from 423 K to 573 K) using High Resolution Dielectric Analyzer (Alpha Analyzer) in the frequency range from 100 Hz to 20 MHz with the help of silver electrode. The DC conductivity was determined from impedance plots. The density measurements of these glasses were carried out using Archimedes' principle with toluene as an immersion liquid. The error in this method has been determined based on repetitive measurements. The errors in density were found to be ≤0.3%. The errors in glass transition temperature (Tg) were found to be ≤0.15% and that in electrical conductivity was found to be ≤0.65%.

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The infrared absorption spectra for the glasses were studied at room temperature in the range 4000–500 cm^{-1} by an infrared spectrometer type IR Affinity-1 SHIMADZU by using ATR assembly.

2.2. Irradiation facility

Gamma irradiation was carried out at Bhabha Atomic Research Centre, Mumbai, India. Glass samples were irradiated with gamma rays from a ^{60}Co source for different doses with a dose rate of 12 Gy min^{-1}.

3. Results and discussion

3.1. Density

Fig. 1 shows the variation of density, with alumina addition in lithium borosilicate glasses. Table 1 shows the density of lithium borate glasses of different composition before and after gamma irradiation. The density results of lithium borosilicate glasses of different composition before and after gamma irradiation is listed in Table 1. It is evident from the figure that the density of glass samples decrease with alumina addition. The decrease in density may be attributed to comparatively open network due to formation of AlO_4 tetrahedra created in the glass in place of BO_4 tetrahedra. The metal – oxygen bond distance is larger in AlO_4 than in the BO_4 tetrahedra [11]. The volume of the glass samples thus increases, which results into the decrease in density.

From this figure it can also be seen that, after gamma irradiation, the density of all the glass samples has increased. Shelby has postulated that boron - oxygen bond is affected by the gamma irradiation [12]. In a lithium borosilicate glass system with alumina addition there may be transition of three coordinated boron to four coordinated boron on gamma irradiation. BO_4 forms the compact structure compared to that of BO_3. This also explains the observed increase in density of glasses after gamma irradiation. Another possible reason for the compaction of glasses is the breaking and bonding of bonds of SiO_4 and AlO_4 tetrahedra. The aluminium in these groups may either occupy tetrahedral or octahedral site. It is possible that Al^{3+} ion can give a tetrahedral aluminate site associated with a hole to bond with other atoms like silicon. The bond force constant of the modal Al—O—Si is smaller than the bonding force of the Si—O—Si bond, since the Al—O bond is longer with smaller bonding force than the Si—O bond. The energy of radiation must be of the order of 4–25 eV to break the bonds holding the atom. It has been found that to displace then Si atom bonded to four oxygen atoms requires 26 eV, while to displace of oxygen atom in an SiO_4 tetrahedra network needs 16 eV. In the present study 2 kGy (1 Gy = 6.2 × 10^9 MeV/g) is used to irradiate the glass samples, sufficient to displace Si and O atoms. Such kinds of displacements are responsible to fulfill vacancy and interstices present in the glass network. This consequently results in compaction of glasses [13].

Table 1
Density of glass samples before and after gamma irradiation. Numbers in parentheses gives uncertainty of the density.

Glass sample with mol% Al_2O_3	Density (before irradiation) (g/cm^3)	Density (after irradiation of 1 kGy) (g/cm^3)
0	2.307 (±0.003)	2.327 (±0.007)
2.5	2.290 (±0.004)	2.316 (±0.005)
5	2.282 (±0.006)	2.304 (±0.003)
7.5	2.274 (±0.007)	2.301 (±0.005)
10	2.122 (±0.005)	2.164 (±0.004)

Gamma irradiation causes structural changes, which include displacements, electronic defect and breaking of structural bond. It also causes filling of interstices or combining of defects present in the glass structure. All these parameters are responsible for tightening effect in the glass composition on gamma irradiation [14]. The observed results in the present work are supported by the similar results reported by the Ezz Eldin et al. [15].

Fig. 2 depicts the variation of density as a function of irradiation dose for lithium borosilicate glass with 7.5 mol% Al_2O_3. The density values for glass sample with 7.5 mol% Al_2O_3 with different gamma irradiation dose are compiled in Table 2. It is evident from the figure that the density of the glass increases with the increase of gamma irradiation dose. The increase in density may be due to compaction of glass which increases with higher irradiation dose. The interaction of gamma irradiation cause atomic displacement. The movement of atoms within the glass matrix causes structural changes. The atoms move within the glass matrix till they are absorbed in the defects of glass matrix. This Phenomenon is responsible for the densification of the glass samples, as a function of irradiation dose.

Another reason for significant increase in density of a glass sample as a function dose of gamma irradiation is an indication of a large change in the structure confirmed from the IR spectra. As mentioned before, induced damage by an irradiating species can cause the compaction of B_2O_3 by the breaking of bonds between triagonal elements, allowing the formation of different ring configuration. The average ring size is then decreased leading to the observed increase in density [16].

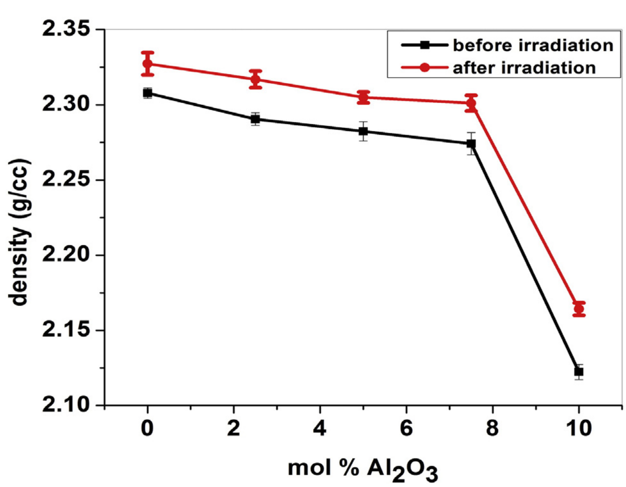

Fig. 1. Variation of density with mol% Al_2O_3 for lithium borosilicate glasses before and after gamma irradiation. Lines in the plot are intended as visual guides.

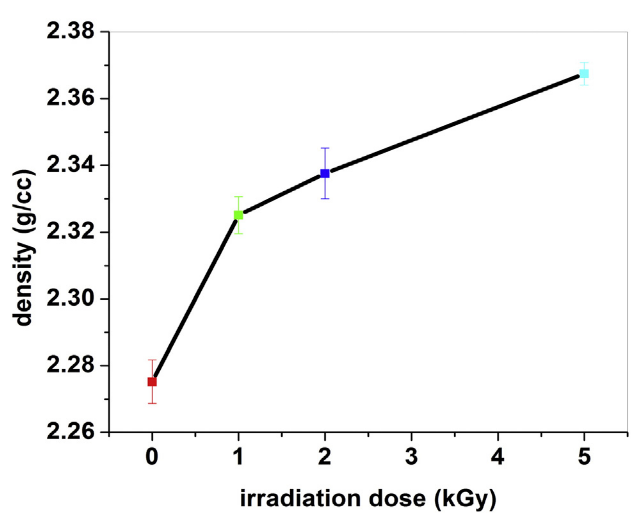

Fig. 2. Variation of density of lithium borosilicate glass with 7.5 mol% Al_2O_3 as a function of irradiation dose. Line in the plot is intended as visual guides.