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Electrical conductivity and glass transition temperature (T_g) measurements on some selected glasses used for nuclear waste immobilization

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ABSTRACT

Borosilicate glass, alumino-borosilicate glass, barium borosilicate glass and lead borosilicate glasses were prepared by melting the glass forming reagents of the respective glass compositions in air ambience. The glasses were characterised by powder X-ray diffractometry. The electrical conductivity of these four glasses was measured by impedance measurements. The conductivities were attributed mainly due to conduction of Na^+ ion in the glass network and were in the range of 9.92×10^{-9}–1.74×10^{-3} Ω^{-1} cm^{-1} at 400–900 K. The activation energies of conduction for these glasses were found to be 0.96 ± 0.01 eV for borosilicate glass, 1.19 ± 0.01 eV for alumino-borosilicate glass, 1.19 ± 0.01 eV for barium borosilicate glass and 1.24 ± 0.01 eV for lead borosilicate glass. Diffusion coefficient of the conducting species (Na^+-ion) was calculated from the conductivity values using Nernst Einstein equation, and the values were in the range of $5.28 \pm 0.03 \times 10^{-13}$–$1.78 \pm 0.01 \times 10^{-8}$ cm^2 s^{-1}. Glass transition temperatures of these glasses were measured by differential scanning calorimetry as well as by dilatometric methods. T_g measured by differential scanning calorimetry were found to be 813 ± 4, 820 ± 4, 785 ± 4 and 749 ± 4 K for borosilicate glass, alumino-borosilicate glass, barium borosilicate glass and lead borosilicate glass respectively, and T_g measured by dilatometric method was 799 ± 5, 818 ± 5, 781 ± 5 and 742 ± 5 K for borosilicate glass, alumina-borosilicate glass, barium borosilicate glass and lead borosilicate glass respectively.

1. Introduction

Borosilicate glass (BSG) is a world wide accepted matrix for the vitrification of radioactive waste for safe storage and disposal [1,2]. Vitrification of waste is carried out by using various melting techniques at and above 1273–1473 K. Joule heated ceramic melting (JHCM) is one of them. Pure borosilicate glass (SiO_2–B_2O_3) exhibits negligibly low conductivity, addition of alkali oxides (Na_2O, Li_2O etc.) as modifiers to the borosilicate glass enhances the electrical conductivity of borosilicate glass [3]. By further increasing the concentration of the modifier oxides, electrical conductivity of the glass increases; conductivity reaches a value of ~3×10^{-3} S/cm by adding 50 mol% of alkali oxides to it [4]. The addition of waste elements (Cs,Sr,Mo,Zr etc.) would influence the structural changes along with the formation of various point defects in the glass matrix. The structural changes will affect the mobility of the cations and anions thereby affecting the electrical conductivity of the glass. A comprehensive understanding on transport properties of the glasses with varying composition and waste loading is essential for the smooth operation of waste vitrification process in the nuclear industry. Various compositions of borosilicate glasses have been explored by researchers by changing the modifier concentrations to see efficacy of the resulting glass in terms of glass formation, durability towards various waste elements, stability at higher temperatures, mobility of ionic species etc. towards nuclear applications. Data on electrical conductivity of the glass compositions at elevated temperatures is essential and is one of the important parameters for the vitrification of the glasses by JHCM process. Electrical conductivity data on some borosilicate glasses containing mainly SiO_2,B_2O_3,Na_2O as the constituents of the glass are available in the literature [5–9]. However, electrical properties of the modified compositions of BSG such as alumino borosilicate glass (AlBSG), barium borosilicate glass (BaBSG) and lead borosilicate glass (PbBSG) are poorly studied at elevated temperatures. Therefore, electrical conductivity measurements on these modified compositions have been carried out at elevated temperatures. These glasses are not only used as waste matrix for nuclear waste vitrification in the glassy state (pure glass phase) but also used as an encapsulating phase to the ceramic waste forms as glass bonded composites. Glass bonded apatites [10,11] and glass bonded sodalites are the examples of such matrices. Alumino borosilicate glass was used for the preparation of glass bonded sodalite [12,13]. Similarly, barium borosilicate glass and lead borosilicate glasses were studied to immobilize sulphate bearing liquid waste and high level radioactive waste containing ^{90}Sr, ^{99}Tc, ^{99}Mo, ^{137}Cs, ^{192}Ir, ^{226}Ra etc. generated from reprocessing of spent nuclear fuel [14,

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15]. Furthermore, in our earlier work [10,11] all these glass compositions were used as the encapsulating phases/bonding material to the Sr-chloroapatite ceramic to form glass bonded composites for the immobilization of pyrochemical chloride waste. Therefore, it is essential to evaluate their thermal and glass transition properties for a better understanding of the system.

Glass transition temperature (T_g) is one of the important properties of the glasses to be evaluated, particularly for nuclear waste immobilization as it determines the process temperature of the waste vitrification process and also the de-vitrifications of the radioactive waste loaded matrices because of the deposition of decay heat released from those long lived fission products into the matrix in due course of time. Some of the T_g values of the glass compositions (especially AlBSG) are not available in the literature. Therefore, attempts were made to prepare BSG, AlBSG, BaBSG & PbBSG and were characterised by various techniques. The electrical conductivities of the glasses were measured by AC-impedance and DC-techniques. The T_g values of these were measured by DSC as well as by dilatometry (thermo mechanical analysis) and compared those with the literature values. The results were discussed on the basis of experimental findings.

2. Experimental

2.1. Preparation of BSG, AlBSG, BaBSG and PbBSG glasses

Borosilicate glass (abbreviated as BSG) was prepared by mixing glass forming reagents (SiO_2: 57 wt%/59.36 mol% + B_2O_3: 25 wt%/22.46 mol% + Na_2O: 18 wt%/18.18 mol%) [16], the mixture was homogenized by grinding in a mortar–pestle for half-an-hour and then calcined at 673 K in an alumina crucible for 1.5 h. The calcined mixture was heated at 1473 K/2 h in the same alumina crucible and quenched to room temperature (298 K). The products were then characterised by powder-XRD to confirm the absence of any crystalline phases present in the final product.

Similarly, aluminoborosilicate glass (AlBSG) [12], barium borosilicate glass (BaBSG) [14,17] and lead borosilicate glass (PbBSG) [15] were also synthesized by mixing their glass forming composition. The details of the glass compositions were given in Table 1. The glass forming agents were mixed well to get a homogeneous mixture in a mortar–pestle for half-an-hour, calcined at 673 K for 1.5 h and then heated to 1473 K/2 h in an alumina crucible and air quenched to get the respective glasses. These products were also characterized by powder-XRD (Siemens D500 X-ray diffractometer employing Cu-K_α radiation) technique.

2.2. Electrical conductivity measurements of the BSG, AlBSG, BaBSG and PbBSG

The electrical conductivity measurements of the prepared glasses (BSG, AlBSG, BaBSG and PbBSG) were carried out by DC and AC impedance techniques at 300–900 K in air. For the electrical conductivity measurements, the cylindrical pellets were prepared by melting the synthesized glasses at 1473 K and then the melt was transferred or poured into a graphite crucible (~ 10 mm dia and 15 mm height) to fabricate pellets of required dimension. The graphite crucible was cut opened to remove the glass pellets. These pellets (~10 mm diameter and 7 mm length) were annealed at 900 K in a platinum crucible for 10 h in air. The pellets were characterised by powder-XRD once again to confirm the absence of any crystalline phases in it and subsequently used for electrical resistivity measurements. The top and bottom flat surfaces of pellets were metalized using Ag-paste. The metalized pellets were put in between the Pt-electrodes as shown in Fig. 1, then loaded into the high temperature conductivity cell and the cell was kept inside the furnace well. The details of the high temperature electrical conductivity cell were reported elsewhere in our earlier studies [18,19,20]. The temperature of the furnace was controlled by a programmable PID temperature controller with ±1 K accuracy. The sample temperature was measured with a K-type (chromel–alumel) thermocouple placed at about 2 mm from the sample in the conductivity measurement cell. Resistances of the sample were measured at each 25 K interval. The impedance (Z) measurements were carried out using an Autolab frequency response analyser (FRA) (Autolab, Eco Chemie BV, Serial no.: AUT83524) in the frequency range of 100 Hz–1 MHz. The impedance/resistance in AC circuit of the samples at various temperatures was determined by fitting the data of $-Z''$ (Ω) versus Z' (Ω) into Nyquist plot using fit and simulates functions available in the Autolab

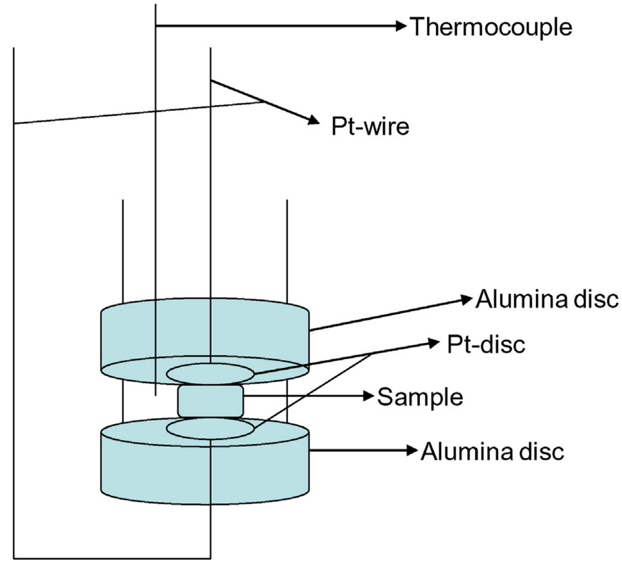

Fig. 1. Schematic of sample pellet and electrode assembly in the high temperature electrical conductivity cell.

Table 1
The nominal compositions of four different glasses.

Nominal composition of glass	Borosilicate glass (BSG) [16] (wt.%/mol%)	Alumino borosilicate glass (AlBSG) [12] (wt.%/mol%)	Barium borosilicate glass (BaBSG) [14,17] (wt.%/mol%)	Lead borosilicate glass (PbBSG) [15] (wt.%/mol%)
SiO2	57/59.36	55/58.08	38.61/47.35	37.5/50.99
B2O3	25/22.47	13.9/12.67	25.32/26.8	25.0/29.34
Na2O	18/18.17	6.5/6.65	12.02/14.29	6.25/8.24
Al2O3	–	9.7/6.04	–	–
PbO	–	–	–	31.25/11.43
BaO	–	–	24.05/11.56	–
CaO	–	13.5/15.28	–	–
K_2O	–	0.8/0.54	–	–
MgO	–	0.4/0.63	–	–
SrO	–	0.1/0.06	–	–
ZrO_2	–	0.1/0.05	–	–
Total	100	100	100	100