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Structural influence of aluminium, gallium and indium metal oxides by means of dielectric and spectroscopic properties of $CaO–Sb_2O_3–B_2O_3$ glass system

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Abstract

Dielectric constant (ε'), loss ($\tan\delta$), ac conductivity (σ) of $CaO–Sb_2O_3–B_2O_3:M_2O_3$ (Al_2O_3, Ga_2O_3 and In_2O_3) glasses with varying concentrations of M_2O_3 (0–5 mol%), were measured as a function of frequency and temperature over moderately wide ranges. The analysis of results of these studies along with IR, Raman and optical absorption spectra and also DTA studies indicated that in the concentration ranges, $0 \leq Al_2O_3 \leq 4$, $0 \leq Ga_2O_3 \leq 2$ and $1 \leq In_2O_3 \leq 5$, Al^{3+}, Ga^{3+} ions occupy tetrahedral positions whereas In^{3+} ions take up octahedral substitutional positions, cross-link with the other structural units in the glass network and increase the rigidity of the glass network.

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1. Introduction

The study of dielectric properties, such as constant, loss and ac conductivity over a wide range of frequency and temperature will not only help in assessing the insulating character of the glasses but also being used as a powerful tool in understanding the structural aspects of the glasses. Work along these lines was carried out in recent years on a variety of inorganic glasses by a number of researchers [1–4].

Sb_2O_3 based borate glasses are well known due to their potential applications in non-linear optical devices due to the fact that these glasses possess large non-linear optical susceptibility coefficient χ^3 [5]. Quite recently we have reported the influence of some transition metal ions like, Cu, Ni, Cr, Fe, etc., on various physical properties of some antimony glass systems [6–9]. These studies have yielded valuable information regarding the structural role of the dopant ions in these glasses. Addition of the oxides of IIIA group elements like Al_2O_3, Ga_2O_3 and In_2O_3 is predicted to improve the physical properties of these glasses, to a substantial extent and is further, expected to increase the range of practical utility of these glasses.

The introduction of Al_2O_3 in to antimony glass network is anticipated to enhance the chemical durability of these glasses while simultaneously increasing the glass transition temperature and reducing the thermal expansion coefficient. The presence of aluminium oxide in the glass network makes the glasses to be more resistant to attack by alkali metal ions like Li^+, Na^+, etc. This is obviously because of entering of Al_2O_3 in to the glass network with AlO_4 structural units that cross-link the neighbouring borate chains. In the IR spectra, the bands due to ν_3 vibrations of SbO_3 structural units and also B–O–B stretching vibrations of borate groups lie around 700 cm^{-1}; incidentally, the vibrational frequency of Al–O stretching in AlO_4 structural units is found to exhibit band in the same region [10]. Hence, it is quite likely that tetrahedral Al ion to cross-link with the neighbouring SbO_3 structural units also. In view of this we may expect $CaO–Sb_2O_3–B_2O_3$ glass network mixed with Al_2O_3 to be consisting of Sb–O–Al and B–O–Al linkages. The occurrence of such linkages may increase the rigidity of the glass network and improve insulating strength of the glasses. The Al_2O_3 mixed glasses are widely being used in precession mirror-blanks for space, microwave cavities, etc. [11]. A considerable number of

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recent investigations on some Al_2O_3 based glasses are available [12–15].

Ga_2O_3 is a heavy metal oxide and when it is introduced in the glass matrix, is expected to alter the physical properties like refractive index, thermal expansion coefficient, chemical resistance and glass transition temperature, infrared transmittance and the insulating strength of the glasses spectacularly and further makes the glasses suitable for the applications in infrared windows, ultra fast optical switches, optical isolators and other photonic devices for communication and advanced computer applications. Many recent devoted studies on the role of Ga_2O_3 in various glass matrices are available in literature [16–21]. In_2O_3 is yet another interesting oxide that participates in the glass network as network modifier and also as network former. The presence of In_2O_3 bring interesting changes in the properties of the glasses, for example, enhance the region of transparency [22–25].

The desired properties of CaO–Sb_2O_3–B_2O_3 glasses can be achieved by tailoring the concentration of these additive metal oxides (Al_2O_3, Ga_2O_3 and In_2O_3), to provide necessary structural units in the glass network. For example, earlier it was shown that the chemical durability of borosilicate glasses can be improved by minimizing the concentration of BO_3 structural units and maximizing BO_4 structural units.

The objective of the present study is, to explore the structural influence of Al_2O_3, Ga_2O_3 and In_2O_3 on CaO–Sb_2O_3–B_2O_3 glass system through a detailed investigation on dielectric properties over a range of frequency and temperature with the aid of data on spectroscopic (optical absorption, Raman, IR) studies.

2. Experimental

The following five particular compositions of the CaO–Sb_2O_3–B_2O_3:M_2O_3 glass system with different concentration of M_2O_3 (Al_2O_3, Ga_2O_3 and In_2O_3) are chosen for the present study: the details of the composition are

- Series A: 20CaO–$(40 - x)$ Sb_2O_3–40B_2O_3:$x$$Al_2O_3$
- Series G: 20CaO–$(40 - x)$ Sb_2O_3–40B_2O_3:$x$$Ga_2O_3$
- Series I: 20CaO–$(40 - x)$ Sb_2O_3–40B_2O_3:$x$$In_2O_3$,

all in mol%, with five values of x values ranging from 0 to 5. The samples are labeled as M_1 (x = 1 mol%), M_2 (x = 2 mol%), M_3 (x = 3 mol%), M_4 (x = 4 mol%), M_5 (x = 5 mol%), where M stands for A, G and I.

Appropriate amounts of Analar grade reagents of $CaCO_3$, H_3BO_3, Sb_2O_3, Al_2O_3, Ga_2O_3 and In_2O_3 were thoroughly mixed in an agate mortar and melted in a thick walled platinum crucible between 1050 and 1100 °C for about 1 h until a bubble free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 350 °C. X-ray diffraction and scanning electron microscopy studies were used to confirm that the samples prepared were vitreous and free of crystallinity.

The glasses were then ground and optically polished. The final dimensions of the glasses used for electrical and optical absorption measurements were about 1 cm × 1 cm × 0.2 cm. The details of methods adopted for recording DTA, IR, Raman optical absorption and dielectric measurements were similar to those reported in our earlier papers [26,27].

3. Results

The samples prepared were free from visible inhomogeneities, such as inclusions, cracks or bubbles. Based upon the visual examination, the absence of peaks in the X-ray diffraction pattern, the existence of glass transition temperature (T_g) and crystallization temperature (T_c) in the differential thermal analysis traces of the glasses, we could come to the

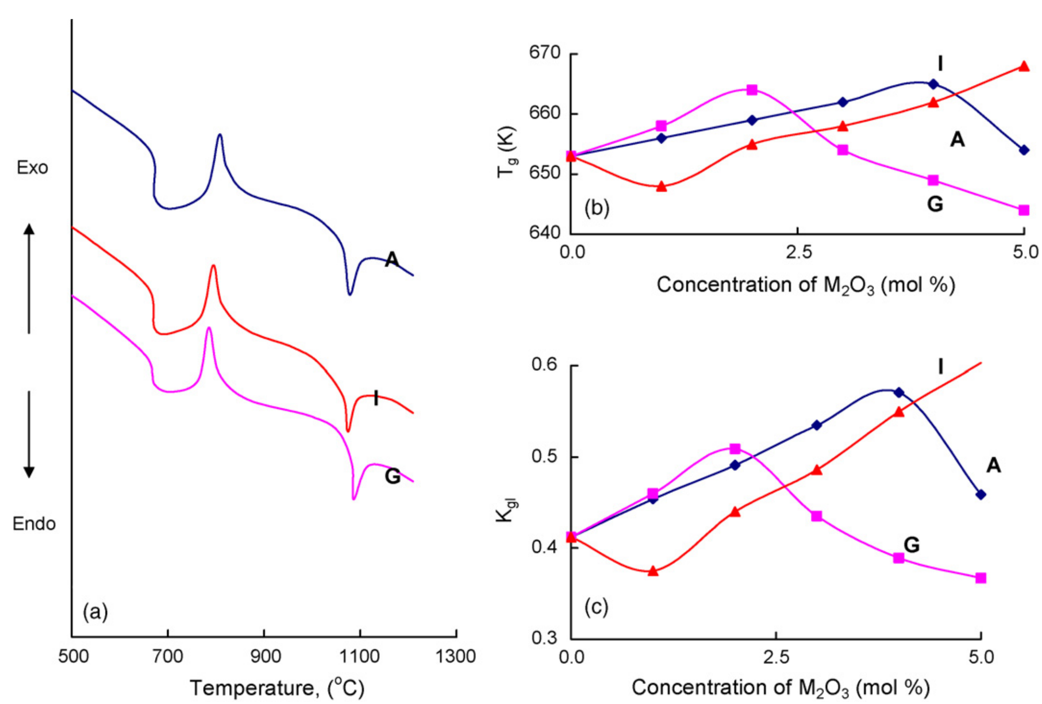

Fig. 1. (a) DTA traces of CaO–Sb_2O_3–B_2O_3 glasses containing 3 mol% of M_2O_3 (b) and (c) represent the variation of T_g and K_{gl} of the three series of the glasses with the concentration of M_2O_3 (M = Al, Ga, In) respectively.

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