

Mixed mobile ion effect on a.c. conductivity of boroarsenate glasses

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Abstract. In this article we report the study of mixed mobile ion effect (MMIE) in boroarsenate glasses. DSC and a.c. electrical conductivity studies have been carried out for $x\text{MgO}-(25-x)\text{Li}_2\text{O}-50\text{B}_2\text{O}_3-25\text{As}_2\text{O}_3$ glasses. It is observed that strength of MMIE in a.c. conductivity is less pronounced with increase in temperature and frequency. The results were explained on the basis of structural model (SM) proposed by Swenson and his co-workers supporting molecular dynamic results.

Keywords. Glass transition temperature; glasses; a.c. conductivity; mixed mobile ion effect.

1. Introduction

An interesting phenomenon observed in glasses is the so called mixed alkali effect (MAE). Glasses containing two types of alkali ions exhibit highly nonlinear variations of properties when one type of alkali is systematically substituted by the other (Day 1976; Ingram 1987). The most evident manifestation of this effect has been observed in the measured ionic conductivity and diffusion coefficient of glasses (Hunt 1999; Imre *et al* 2002). The same behaviour is often exhibited when alkali ion is substituted by an isovalent non-alkali ion also, and is referred to as mixed mobile ion effect (MMIE). The strength of MAE depends on many factors (Isard 1969; Day 1976; Moynihan 1979; Maass *et al* 1992; Jain and Lu 1996; Cramer and Gao 2005; Gao and Cramer 2005), e.g. temperature, total alkali content, size and mass difference of the involved alkali ions, etc. Several models have been proposed to explain the ‘anomalous’ conductivity behaviour during the mixing of two monovalent cations (Isard 1969; Day 1976; Ingram 1987). These models assume either large structural modification induced by mixing mobile species of different sizes or specific interaction between these dissimilar mobile species. Greaves *et al* (1990) in EXAFS study indicated that the environment of the mobile cations in glasses is well determined by the type of cation that creates the site it occupies. Based on these results, Bunde *et al* (1991, 1994) proposed a new model for ionic migration in glasses, called the dynamic structural model (DSM). The main idea of the DSM model is the existence of mismatches between different types of sites designated by cations in the glass. Ion migration is associated with a “memory effect” of the sites previously occupied, which leads to the creation of ionic pathways. Hunt (1997) applied the theory of percolative transport to the MAE and predicted disappearance of mixed alkali effect when temperature is raised.

Glasses containing As_2O_3 as main glass former has been studied during last two decades (Chowdari and Akhter 1990; Srinivasa Rao and Veeraiah 2001; Ardelean *et al* 2004; Ragavaiah *et al* 2004a,b). To our knowledge all studies are focused on the glass system containing single alkali arsenate glasses (Chowdari and Akhter 1988, 1990) and alkali-free arsenate glasses (Nicula *et al* 1986; Srinivasa Rao and Veeraiah 2002; Ragavaiah *et al* 2004a,b). For the first time the authors reported the optical absorption and ESR studies of copper doped mixed alkali boroarsenate glasses (Srinivasa Rao *et al* 2005) and also the mixed alkali effect in $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{As}_2\text{O}_3$ glasses (Srinivasa Rao *et al* 2007). Recently, Ardelean *et al* (2008, 2010) investigated the arsenate containing glasses by Raman and infrared spectroscopy. However, other than this no mixed alkali effect studies were reported on arsenate glasses.

Many investigations have been reported on MAE in d.c. electrical conductivity of glasses (Ghosh and Ghosh 2002; Mansour 2005; Gao 2006). For the first time Kulkarni *et al* (2000) reported MAE in the a.c. conductivity of glasses. In the present study, we investigate the mixed mobile ion effect in $x\text{MgO}-(25-x)\text{Li}_2\text{O}-50\text{B}_2\text{O}_3-25\text{As}_2\text{O}_3$ glasses by measuring the a.c. conductivity as a function of compositional parameter, R_{Mg} , defined as $R_{\text{Mg}} = \text{MgO mole \%} / (\text{MgO} + \text{Li}_2\text{O}) \text{ mole \%}$, taking the values of 0, 0.2, 0.4, 0.6, 0.8 and 1. The presence of alkali and alkaline earth oxides and their role in conductivity increases the interest in the present study. The authors also report DSC measurements on the present glass system.

2. Experimental

Glass samples of composition, $x\text{MgO}-(25-x)\text{Li}_2\text{O}-50\text{B}_2\text{O}_3-25\text{As}_2\text{O}_3$ (mole %) ($0 \leq x \leq 25$), were prepared using the conventional melt-quench technique. Glasses were prepared by mixing the required proportions of the reagent grade chemicals, Li_2CO_3 , H_3BO_3 , As_2O_3 (May and

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Baker) and MgO (Fluka) in an electrical furnace using silica crucibles. The furnace temperature was varied from 1000–1150 °C depending on the glass composition. The liquids were swirled frequently to ensure homogeneous mixture. In this technique, the clear liquid (free of bubbles) is quickly cast in a stainless steel mould kept at 200 °C and pressed with another steel disc maintained at the same temperature. All the glass samples were annealed at 200 °C for a duration of about 12 h. The glass composition mentioned was the nominal glass composition. The actual composition was calculated from the exact masses of the components in the glass batch, assuming that the glass composition does not change during melting. For samples taken from different regions of the bulk specimen, the absence of any Bragg peaks in the X-ray diffraction pattern confirmed that they were amorphous and homogeneous.

The thermal behaviour of the glass samples was investigated using a differential scanning calorimeter (TA Instruments DSC 2010). Samples in the form of powder weighing about 15 mg were sealed in copper pans and scanned through their melting temperature with a heating rate of 10 °C/min. During all runs the sample chamber was purged with dry nitrogen.

A.C. conductivity measurements were carried out using AUTOLAB (PGSTAT 30) low frequency impedance analyser interfaced to a PC using a frequency response analyser (FRA) software. Parallel glass discs of thickness around 1.5 mm and diameter 12 mm were grounded and polished. The flat surfaces of the samples were painted with silver paste. The samples were scanned in the frequency range 100 Hz–1 MHz and in the temperature range 300–573 K.

3. Results and discussion

Figure 1 shows a typical DSC thermogram of $x\text{MgO}-(25-x)\text{Li}_2\text{O}-50\text{B}_2\text{O}_3-25\text{As}_2\text{O}_3$ glasses at a heating rate of 10 °C/min. Thermodynamical and glass stability

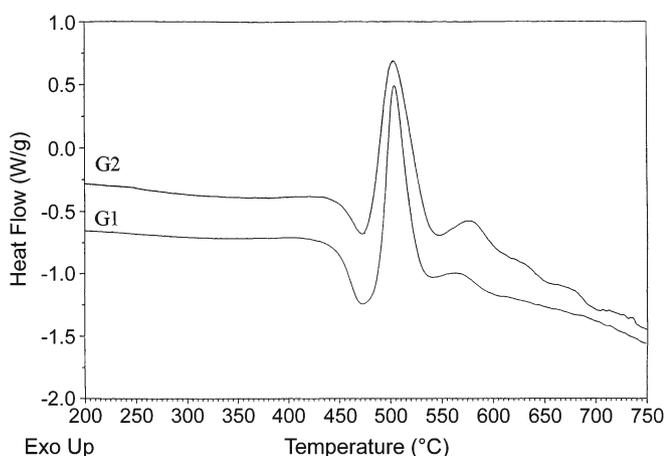


Figure 1. DSC thermograms of G1 and G2 glasses.

parameters such as glass transition temperature, onset of crystallization temperature, peak temperature of crystallization, melting temperature (determined using Kauzmann rule) were evaluated using standard procedures. DSC thermogram shows a single endothermic glass transition peak and a single exothermic crystallization peak. There is an increase of glass transition temperature by about 76 °C as the MgO content is increased.

The empirical parameters used to parametrize stability of the glass are the glass stability, S , defined as the difference between the onset of crystallization temperature and the glass transition temperature and the Hruby parameter defined as

$$K_{gl} = (T_c - T_g) / (T_m - T_c).$$

The Hruby parameter characterizes the tendency of the melts to form glass. The thermodynamical parameters of the present glass system are given in table 1.

The glass transition temperature, T_g , as a function of glass composition is shown in figure 2. From the above figure it is clear that the transition temperature exhibits a negative deviation from linearity, a distinct feature of MMIE. The strength of the mixed mobile ion effect in T_g can be defined as (Gao 2006)

$$\Delta T_g = T_{g,\text{lin}} - T_{g,\text{min}}, \quad (1)$$

where ΔT_g and $T_{g,\text{min}}$ represent strength of the mixed mobile ion effect in T_g and the minimum value, respectively. $T_{g,\text{lin}}$ is determined at the composition which corresponds to $T_{g,\text{min}}$ and it is obtained by the linear interpolation between the glass transition temperature of the two end members. The magnitude of the mixed mobile ion effect in T_g calculated by (1) for the mixed Mg/Li glasses is 20 °C. Similar observations were found in mixed alkali glasses (Gao 2006).

We have analysed the frequency dependence of conductivity for all the glasses as isotherms in the log–log plots. At low temperatures only a.c. conductivity was observed. As the temperature was increased, the dynamic conductivity showed a typical behaviour: a frequency independent plateau and a power law increase at high frequency. Figure 3 shows double logarithmic plots of complex conductivity at 473 K. The plateau of conductivity spread over several decades in the medium frequency range corresponding to d.c. conductivity. All the glasses showed typical power-law behaviour. The variation of a.c. conductivity at 1 kHz, 100 kHz and 1 MHz with the compositional parameter, R_{Mg} , is illustrated in figure 4. It is interesting to note that the a.c. conductivity goes through a minimum at $R_{\text{Mg}} = 0.4$, a distinct feature of mixed mobile ion effect. The strength of the mixed mobile ion effect decreases with increase in frequency. The temperature dependence of a.c. conductivity at 1 kHz is depicted for all mixed mobile ion compositions in figure 5. At higher temperatures, compositions with high conductivity, G1 and G2, show Arrhenius behaviour and at low temperatures, a.c. conductivity shows only a weak temperature dependence. The inset shows the variation of σ_{ac} (1 kHz) with composition at 473 K, 523 K and 573 K. Again the a.c. conductivity shows a minimum with composition confirming the observation in

Table 1. Thermodynamical and glass stability parameters of present glass system.

Glas no.	Glass composition	T_g	T_c	T_p	T_m	S	K_{gl}
G1	25Li ₂ O–50B ₂ O ₃ –25As ₂ O ₃	448	475	505	806	27	0.083
G2	5MgO–20Li ₂ O–50B ₂ O ₃ –25As ₂ O ₃	443	478	504	802	34	0.105
G3	10MgO–15Li ₂ O–50B ₂ O ₃ –25As ₂ O ₃	452	530	550	817	77	0.269
G4	15MgO–10Li ₂ O–50B ₂ O ₃ –25As ₂ O ₃	465	635	676	839	169	0.831
G5	20MgO–5Li ₂ O–50B ₂ O ₃ –25As ₂ O ₃	490	690	–	872	199	1.092
G6	25MgO–50B ₂ O ₃ –25As ₂ O ₃	519	725	–	915	206	1.084

T_g , Glass transition temperature (°C); T_c , crystallization temperature (°C); T_p , peak temperature of crystallization (°C); T_m , melting temperature (°C); $S = (T_c - T_g)$, glass stability (°C); $K_{gl} = (T_c - T_g) / (T_m - T_c)$, Hruby parameter.

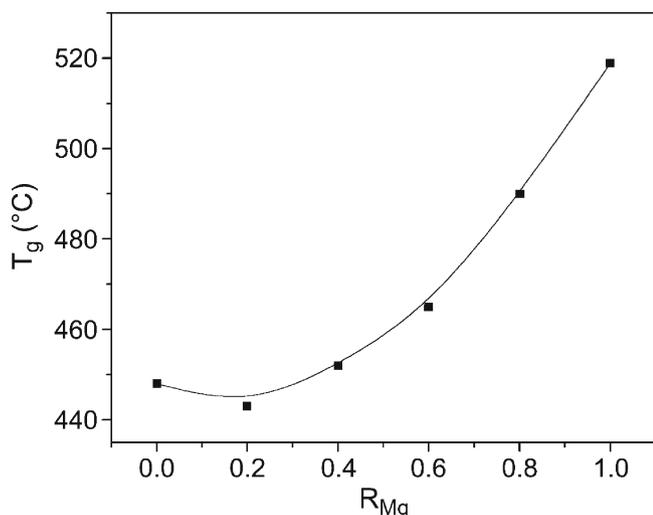
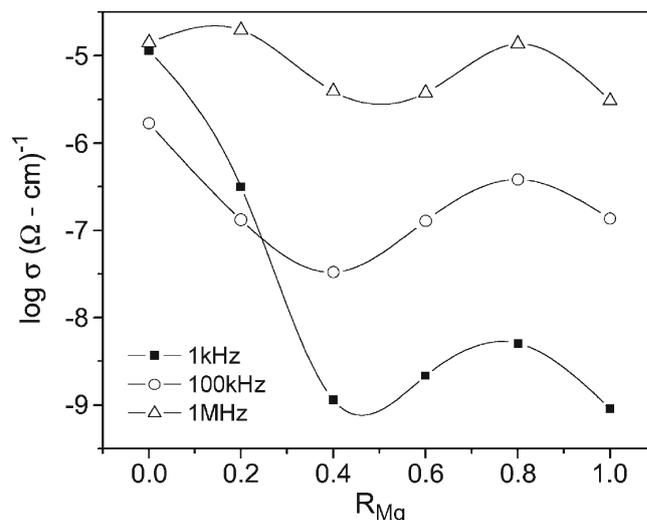
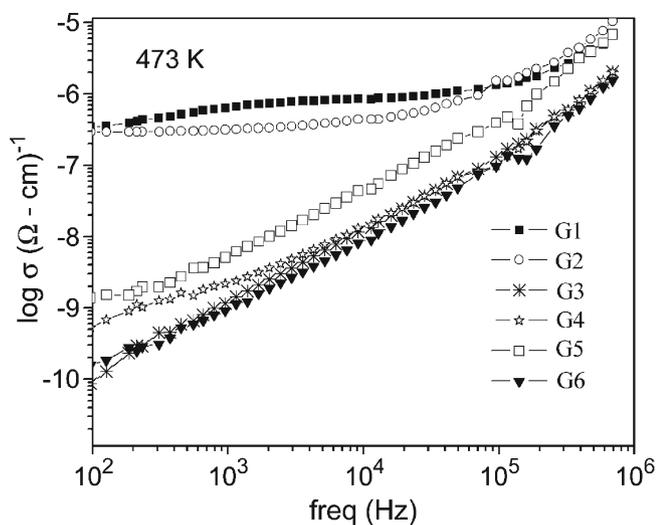
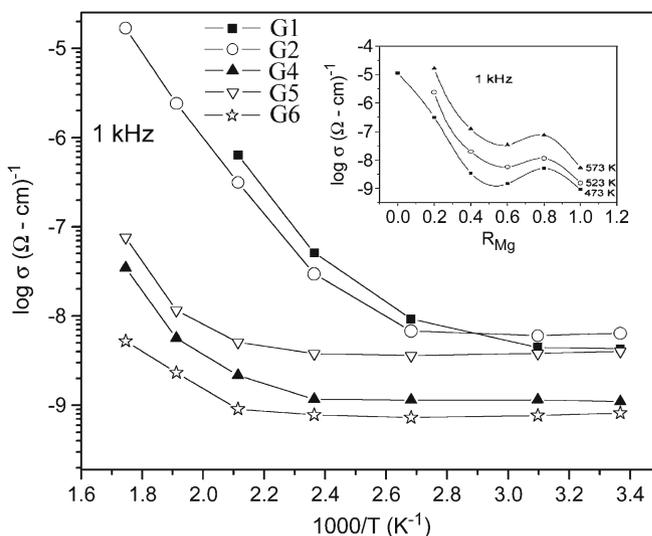
**Figure 2.** Compositional dependent glass transition temperature of $x\text{MgO}-(25-x)\text{Li}_2\text{O}-50\text{B}_2\text{O}_3-25\text{As}_2\text{O}_3$ glasses.**Figure 4.** Variation of a.c. conductivity with compositional parameters at 1 kHz, 100 kHz and 1 MHz.**Figure 3.** Double logarithmic plots of frequency dependent conductivity for $x\text{MgO}-(25-x)\text{Li}_2\text{O}-50\text{B}_2\text{O}_3-25\text{As}_2\text{O}_3$ glasses at 473 K.**Figure 5.** Variation of a.c. electrical conductivity plotted in Arrhenius coordinates for all glasses at 1 kHz. Inset shows isothermal conductivity plots at 473 K, 523 K and 573 K.

figure 4. The strength of MMIE decreases with increase in temperature.

Since mixed alkali behaviour is often referred to as mixed mobile ion effect (MMIE), the results of the present investigation are interpreted on the basis of structural model (SM) proposed by Swenson and his co-workers (Swenson *et al* 2001; Swenson and Adams 2003; Adams and Swenson 2004), of which the essential ideas are shortly summarized in the following. The structure model is constructed directly from experimental data of mixed mobile ion glasses, and by applying the bond-valence method to reverse Monte Carlo simulations. The model suggests that the two types of alkali ions in mixed alkali glasses are randomly mixed and tend to attain the same local structural environment as in the single alkali glasses. The two types of alkali ions have distinctly different low dimensional conduction pathways. This results in a large energy mismatch for ions jumping between dissimilar alkali sites (Uchino *et al* 1992). The mixed alkali effect is mainly due to large mismatch between the local potentials of site *A* and the induced potential of ion *B*, as reflected by a high activation energy for ion jumps to dissimilar sites, viz. *A* ions tend to block the pathways for *B* ions and *vice versa*. Various recent molecular dynamic simulations (Jund *et al* 2001; Habasaki and Hiwatari 2002) have independently confirmed that the large energy mismatch is basically independent of compositions.

When analysed in terms of the structural model, the Li^+ and Mg^{2+} ions in the mixed Li/Mg glasses are taken to be randomly mixed in all the conduction pathways. This random mixing, coupled with the mismatch, results in highly effective blocking of Li pathways by Mg ions, and *vice versa*. This blocking considerably reduces the long range mobility of both Li^+ and Mg^{2+} ions in comparison to the corresponding single component Li and Mg glasses. These effects result in a lower conductivity for mixed Li/Mg glasses relative to their corresponding single component Li and Mg glasses, producing the mixed mobile ion effect shown in figures 4 and 5.

4. Conclusions

The glass transition temperature and a.c. electrical conductivity of $\text{MgO-Li}_2\text{O-B}_2\text{O}_3\text{-As}_2\text{O}_3$ glasses has been investigated. For the first time, mixed mobile ion effect has been detected in the a.c. conductivity of glasses. The strength of the effect decreases with the increase in temperature and also with frequency. MMIE is interpreted on the basis of structural model proposed by Swenson and co-workers.

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