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Mixed cation effect in xR_2O–$(40-x)Na_2O$–$50B_2O_3$–$10Bi_2O_3$ (R = Li, K) glasses

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ABSTRACT

Mass density, glass transition temperature and ionic conductivity are measured in xLi_2O–$(40-x)Na_2O$–$50B_2O_3$–$10Bi_2O_3$ and xK_2O–$(40-x)Na_2O$–$50B_2O_3$–$10Bi_2O_3$ glass systems with $0 \le x \le 40$ mol%. The strength of the mixed alkali effect in T_g, dc electrical conductivity and activation energy has been determined in each glass system. The magnitudes of the mixed alkali effect in T_g for the mixed Li/Na glass system are much smaller than those in the mixed K/Na glasses. The impact of mixed alkali effect on dc electrical conductivity in mixed Li/Na glass system is more pronounced than in the K/Na glass system. The results are explained based on dynamic structure model.

1. Introduction

When two types of alkali ions are introduced into a glassy network, a phenomenon known as mixed alkali effect (MAE) is observed. It represents the non-linear variations in many physical properties associated with the alkali ion movement and structural properties, when one type of alkali ion in an alkali glass is gradually replaced by another, while total alkali content in the glass being constant [1,2]. The most evident manifestation of this effect has been observed in DC electrical conductivity as a function of composition where a deep minima is observed in the intermediate mixing ratio of alkali ions [3,4]. Another prominent MAE is observed in the activation energy exhibiting a maximum as the relative composition is changed [5]. Interestingly other "dynamical" properties such as internal friction, viscosity, glass transition, expansion coefficient also exhibit a more or less pronounced deviation. On the other hand, static properties like density appear to be linear [6]. In recent years MAE was found in mixed crystals [7], cation and anion conducting glasses [8,9] and also for glasses containing two glass formers [10]. Recently, Chakradhar et al. [11] and Srinivasa Rao et al. [12,13] studied the EPR and optical absorption spectra of iron and copper doped mixed alkali glasses.

The strength of the MAE depends on many factors [1,6,14–18], e.g., temperature, total alkali content, the size and mass difference of the involved alkali ions, etc. It has also been reported [19–22] that the magnitude of the MAE increases with the difference in size or mass of the involved alkali ions.

Different models for MAE have been proposed in the literature and are compiled in several reviews [1,2,6]. 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. [23] 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. [24,25] 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 the 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 [26] applied the theory of percolative transport to the MAE and predicted a disappearance of mixed alkali effect when temperature is raised. Recently Imre et al. [27] proposed a definition, independent component glass (ICG) and sub-network diffusion concept (SDC) to explain the mixed alkali effect.

The aim of this paper is to study the essence of mixed alkali effect in two mixed alkali glass systems xR_2O–$(40-x)Na_2O$–$50B_2O_3$–$10Bi_2O_3$ with R = Li, K and $0 \le x \le 40$ mol%. The values of x were adjusted so that the compositional parameter defined as $R_{Li} = Li_2O/(Li_2O + Na_2O)$ and $R_K = K_2O/(K_2O + Na_2O)$ takes the values 0, 0.2, 0.4, 0.6, 0.8 and 1.

2. Experimental

2.1. Glass preparation

Two series of glasses having the molar formula xR_2O–$(40-x)Na_2O$–$50B_2O_3$–$10Bi_2O_3$ with R = Li, K and $0 \le x \le 40$ mol%

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Table 1
Density ρ, molar volume V_m, oxygen packing density $\bar{O}$, ionic concentrations N, inter-ionic distance (R) and glass transition temperature for $x$$Li_2O$–$(40-x)$$Na_2O$–$50B_2O_3$–$10Bi_2O_3$ and $y$$K_2O$–$(40-y)$$Na_2O$–$50B_2O_3$–$10Bi_2O_3$ glass systems.

Glass composition	ρ (g/cm^3) (±0.01)	V_m (cm^3/mol) (±0.1)	$\bar{O}$ (g-atm/l)	N_R ($\times10^{21}$/cm^3)		N_T ($\times10^{21}$/cm^3)	R (Å)	T_g (°C) (±0.1)
				Li(K)	Na			
$x=0$	3.62	28.6	76.9	0	16.8	16.8	3.90	441.1
$x=08$	3.34	26.5	82.8	3.6	14.5	18.1	3.80	425.0
$x=016$	4.06	24.0	91.9	8.0	12.1	20.1	3.67	406.9
$x=024$	4.03	23.5	93.7	12.3	18.2	30.5	3.20	403.1
$x=032$	3.76	22.2	99.1	17.4	4.3	21.7	3.58	413.7
$x=040$	3.54	28.9	76.1	16.7	0	16.7	3.91	416.5
$y=00$	3.62	28.2	77.8	0	17.1	17.1	3.88	441.1
$y=08$	3.16	33.2	66.3	2.9	11.6	14.5	4.90	350.0
$y=016$	4.08	26.3	83.5	7.3	10.9	18.2	3.80	334.2
$y=024$	3.76	29.3	75.1	9.9	6.6	16.5	3.92	330.0
$y=032$	3.44	32.7	67.2	11.8	2.9	14.7	4.08	337.6
$y=040$	2.82	40.8	53.8	11.8	0	11.8	4.39	349.2

have been prepared by melt quench technique. The chemical compositions of the studied glass samples are shown in Table 1. Li_2CO_3, Na_2CO_3, K_2CO_3 (all GR grade, Merck), boric acid (GR grade) and Bi_2O_3 (99.8% purity) were mixed together in the required proportion and melted in porcelain crucibles in an electrical furnace maintained at temperature ranging between 1000 and 1150 °C according to the composition. The melt was swirled to ensure homogeneity. The bubble free melt 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 samples were then annealed at 200 °C for about 12 h. The absence of any Bragg peaks in X-ray diffraction pattern confirmed that the glasses are amorphous and homogeneous. The glass composition mentioned is 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.

2.2. Density

Density (ρ) measurements were carried out using Archimedes method with xylene (0.86 g/cm^3) as an immersion liquid at room temperature. Molar volume (V_m), oxygen packing density ($\bar{O}$), alkali ion concentrations (N_R) and inter ionic distance (R) were calculated and are presented in Table 1.

2.3. Glass transition temperature

The thermal behavior of the glass samples was investigated using a differential scanning calorimeter (Du Pont 1090). Glass samples in form of powder weighing about 15 mg were sealed in copper pans and were scanned through their melting temperatures with a heating rate of 10 °C/min. During all runs the sample chamber was purged with dry nitrogen. The transition temperatures of the glass samples are presented in Table 1.

2.4. DC electrical conductivity

Parallel glass discs of thickness around 1.5 mm and diameter 12 mm were polished for DC electrical conductivity measurements. The flat surfaces of the glass samples were painted with silver paste. The current through the sample was measured by using a Keithley 616 digital electrometer. The electrical conductivity was measured as a function of temperature.

3. Results and discussion

3.1. Density and glass transition temperature

The measured densities (ρ) of the lithium sodium borobismuthate and potassium sodium borobismuthate glasses are listed in Table 1. The mass density varies in a non-linear way with the increase in compositional parameter. For glasses containing 40 mol% of alkali content, density follows the order Na > Li > K. The molar volume, oxygen packing density and inter ionic distance for mixed alkali borobismuthate glasses are presented in Table 1.

The glass transition temperature T_g as a function of glass composition is shown in Fig. 1 for both quaternary glass systems. From the above figure it is clear that the glass transition temperature exhibit a negative deviation from linearity. For glasses containing 40 mol% of alkali content, T_g follows the order Na > Li > K. The strength of the mixed alkali effect in T_g can be defined as [28]

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

where ΔT_g and $T_{g,min}$ represent the strength of the mixed alkali effect in T_g and the minimum value, respectively. $T_{g,lin}$ is determined at the composition which corresponds to $T_{g,min}$ and it is obtained by the linear interpolation between the glass transition temperature of the two end members. The magnitudes of the mixed alkali effect in T_g calculated by Eq. (1) for the mixed Li/

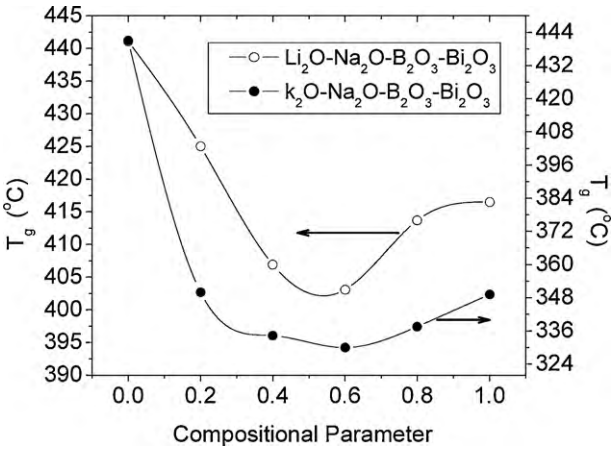

Fig. 1. Compositional dependent glass transition temperature of $x$$Li_2O$–$(40-x)$$Na_2O$–$50B_2O_3$–$10Bi_2O_3$ and $x$$K_2O$–$(40-x)$$Na_2O$–$50B_2O_3$–$10Bi_2O_3$ glasses.