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Mixed alkali effect in quaternary K_2O–Li_2O–BaO–B_2O_3 glasses containing V_2O_5

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Abstract

DC conductivity and density measurements have been carried out for xK$_2$O–(25 − x)Li$_2$O–10BaO–20V$_2$O$_5$–45B$_2$O$_3$ glasses and compared with K_2O–Li_2O–Fe_2O_3–B_2O_3 and K_2O–Na_2O–Fe_2O_3–P_2O_5 glasses. The results showed a pronounced mixed alkali effect (MAE) although polaronic conduction was observed in these glasses. There is a deviation from linearity in $\ln\sigma - 1/T$ plots at a certain temperature (T_d) at which the transition from polaronic to ionic conduction occurs. The derivative $\partial T_d/\partial X(X = K_2O/(K_2O + Li_2O))$ shows a dramatic change at nearly equal concentrations of alkali oxides and can be taken as a characteristic feature of MAE in these glasses. The type and concentration of both the transition metal and alkali ions as well as the host glass matrix govern how the relative mobilities of alkali ions and polarons suppress one another. Both density and molar volume change linearly with composition in opposite directions.

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Keywords: Mixed alkali effect; Polaronic conduction; Transition metal ions

1. Introduction

Interesting physical effects have been observed in studying the behavior of glassy ionic conductors. The understanding of the microscopic mechanism for ion conduction in glass is a long-standing problem in glass science. Many glasses exhibit a roughly linear behavior with changing chemical composition. Glasses containing two different alkali oxides are a major exception to this trend. For these glasses, the deviation from linearity in property trends may be so great that maxima or minima occurs. The mixed alkali effect (MAE) was observed as a dramatic non-linear

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variation in isotherms of several dynamic properties of ions when a fraction of one type of the mobile ions is substituted by another type, keeping the total alkali content constant [1–3]. Those properties are based on the diffusivities of the alkali species, e.g. ionic diffusion, electrical conductivity, dielectric loss and internal friction.

Maxima for activation energy and minima in electrical conductivity isotherms are commonly found in mixed alkali (MA) oxide glasses [2]. Moynihan [4] suggested that the essence of the MAE on conductivity is not necessarily that σ versus composition isotherm exhibits a minimum, but more generally that the conductivities of MA glasses exhibit negative departures from additivity on a linear σ vs. composition plot. In general, the physical properties of MA glasses, such as density, microhardness and thermal expansion, only show slight deviations from linearity [3].

MAE in borate glasses free from transition metal ions (TMIs) has been extensively studied [5–10]. MAE in borate glasses doped with minor quantities of TMIs (0.25 mol% CuO [11], 0.5 mol% CuO [12], and 1 mol% MnO [13]) has been studied by EPR [12,13] and optical absorption [11–13].

Little effort has been made to study MAE in oxide glasses containing higher contents of TMIs [14,15]. Electrical conductivity in $(20-x)K_2O$–xNa_2O–$20Fe_2O_3$–$60P_2O_5$ glasses was dominated by electron hopping between Fe^{2+} and Fe^{3+} sites and the mobilities of the sodium and potassium ions were so low that they make no detectable contribution to the overall electrical conductivity [14]. Recently, the DC electrical conductivity of $(25-x)Li_2O$–xK_2O–$10Fe_2O_3$–$65B_2O_3$ and $(25-x)Li_2O$–xK_2O–$15Fe_2O_3$–$60B_2O_3$ [15] has been measured and investigated. The results show a pronounced MAE although polaronic conduction was observed in these glasses. This result is dissimilar to that for Na_2O–K_2O–Fe_2O_3–P_2O_5 glasses [14].

The aim of this paper is to study the essence of MAE in glasses containing TMIs by measuring the DC electrical conductivity of xK_2O–$(25-x)Li_2O$–$10BaO$–$20V_2O_5$–$45B_2O_3$ glass system and comparing the results with the available data for K_2O–Li_2O–Fe_2O_3–B_2O_3 and K_2O–Na_2O–Fe_2O_3–P_2O_5 glasses.

2. Experimental

One series of glass having the molar formula xK_2O–$(25-x)Li_2O$–$10BaO$–$20V_2O_5$–$45B_2O_3$, with $0 \leqslant x \leqslant 25$ mol% has been prepared by the quenching technique. The chemical compositions of the studied samples are shown in Table 1. Reagent grades H_3BO_3, $BaCO_3$, V_2O_5, Li_2CO_3 and K_2CO_3 were mixed together and melted in porcelain crucibles in an electric furnace at temperature ranging between 1050 and 1100 °C according to the composition. To assure homogeneity the melt was swirled from time to time. The homogenized melt was quenched by pouring it onto a steel plate and quickly pressed by another one to obtain disks having a thickness of 1–2 mm. The obtained samples are of glassy appearance and free from air bubbles. However, a trial was performed to prepare glasses with the same chemical components without adding BaO. But the prepared samples were found to be hygroscopic. The 10 mol% BaO was added to the compositions to make the glasses less hygroscopic in ordinary atmosphere.

Plates of about 1–2 mm thickness were used to measure the DC conductivity. A silver paste coating was applied to the flat surfaces to serve as electrodes. The radius of the coated area is 5 mm. The resistance was measured using an insulation tester-type TM14 (Levell Electronics Ltd.) with 10^3–$10^{13}\,\Omega$ range. As a rule, three samples of each glass were used to measure the resistance as described in detail elsewhere [15,16]. The experimental error in determining the high temperature activation energy for conduction is estimated to be less than 0.02 eV, whereas the

Table 1
Chemical compositions of the studied glasses in mol%

Glass no.	K_2O	Li_2O	BaO	V_2O_5	B_2O_3
1	0	25	10	20	45
2	5	20	10	20	45
3	10	15	10	20	45
4	12.5	12.5	10	20	45
5	15	10	10	20	45
6	20	5	10	20	45
7	25	0	10	20	45