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Ionic conductivity in borate glasses with three types of mixed alkali cations

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ABSTRACT

We have investigated the temperature- and frequency-dependent ionic conductivity in $(Li_{0.67-x}Na_{0.33}Rb_x)_2B_4O_7$ (LNRBO) glasses with $x=0$, 0.07, 0.2, 0.33, 0.47, and 0.6. The mixed alkali effect of the ternary mixed alkali system LNRBO is compared with that of the binary mixed alkali systems $(Li_{1-x}Na_x)_2B_4O_7$ (LNBO), $(Li_{1-x}Rb_x)_2B_4O_7$ (LRBO) and the single alkali glass $Rb_2B_4O_7$ (RBO). From the results of the dc conductivity and dc activation energy, we observe that the LNRBO system exhibits the combined characteristic of binary mixed alkali systems LNBO and LRBO. It is found that the power-law exponent n for binary alkali glass is the same as that for ternary alkali glass but it is lower than that for single alkali glass. This indicates that the dimensionality of conducting pathway in the mixed alkali glasses of LNBO, LRBO and LNRBO is lower than that in the single alkali RBO. We discuss the concentration dependence of the dc conductivity and dc activation energy in the framework of the bond valence technique to reverse Monte Carlo produced structural model [Phys. Rev. Lett. 90, 155507 (2003)].

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1. Introduction

The high ionic conductivity in glasses plays a major role for potential applications as solid electrolytes in electrochemical devices such as batteries, memory devices, chemical sensors, and smart window [1].

It has attracted much attention how the transport dynamics is working for mixed cations because the study of the mixed alkali effect (MAE) related to the ionic transport is important for the purposes of applications and understanding the diffusion mechanism of alkali ions. The MAE causes the pronounced changes in properties resulting from the addition of extra alkalis to a single alkali glass [2–10].

The understanding of mechanisms of ionic migration through solids is of fundamental importance in many branches of materials science. However, despite a comprehensive experimental and theoretical effort, the conduction mechanism in glass system is still not fully understood [11]. A major barrier is partly due to the paucity of knowledge of the microscopic structure, especially of the distribution and local environment of the mobile cations, which contain information about the most likely migration pathways. For the ionic conducting glass in theory, it is important to understand the nature of the Coulomb repulsion in the complex structured medium and the hopping mechanism for the interstitial or vacant sites through the network structure.

In experiment, therefore, the measurement of archetypal combinations in the alkali material is needed for better understanding of the ionic transport dynamics in the mixed alkali glass system. Previous conductivity MAE studies based on phosphate and borate network formers have been reported for the glasses with two and three types of alkali ions systems in the temperature range 240–523 K [4,5,12,13]. The strength of MAE is strongly dependent on the annealing temperature and alkali element. The effect becomes stronger with decreasing temperature and increasing the mismatch of the element size [10].

In this paper, we present the experimental results of the composition dependence of the conductivity properties of $(Li_{0.67-x}Na_{0.33}Rb_x)_2B_4O_7$ (LNRBO), $(Li_{1-x}Na_x)_2B_4O_7$ (LNBO), $(Li_{1-x}Rb_x)_2B_4O_7$ (LRBO) and discuss the effects of mixed cation in glasses by comparing the dc and ac conductivities of three types of cations (ternary mixed alkali glasses) with two types of cations (binary mixed alkali glasses), thus extending the study in the previous report [14,15]. We will also discuss the concentration dependence of the activation energy of the dc conductivity in the framework of reverse-Monte-Carlo (RMC) produced structural models in combination with the bond valence technique [16].

2. Experimental

Samples were prepared by mixing stoichiometric amounts of $Li_2B_4O_7$, $Na_2B_4O_7$, Rb_2CO_3, and B_2O_3. The powders were mixed well for an hour. The powder sample was melted in a Pt crucible in an electric furnace for 15 min at 1273 K. The melt was quenched onto copper plate.

Binary mixed alkali borate glasses of $(Li_{1-x}Na_x)_2B_4O_7$, $(Li_{1-x}Rb_x)_2B_4O_7$ (LRBO) with $x=0$–1.0 and ternary mixed alkali glass systems $(Li_{0.67-x}Na_{0.33}Rb_x)_2B_4O_7$ with $x=0$–0.6 were prepared by a melt-quenching method. The obtained samples were transparent with 1 mm thickness.

The glasses were identified by X-ray diffraction (Rigaku, Japan) measurements. The frequency-dependent conductivity spectra at

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various temperatures were determined by using an impedance/gain-phase analyzer (Hewlett-Packard LF4194A, U.S.A).

Gold electrodes with radius 1.5 mm were deposited on both of the surfaces of the polished samples by vacuum evaporation, and gold leads were attached to them with silver paste. The frequency range was from 100 Hz to 15 MHz, with a heating rate of 2 K/min.

3. Results and discussion

Within the framework of the conductivity representation, the bulk frequency-dependent conductivity $\sigma(\nu)$ from the movement of dissociated cations in the glass matrix is described by

$$\sigma(\nu) = \sigma_{dc}[1 + (\nu/\nu_h)^n], \quad (1)$$

where σ_{dc} is the dc conductivity from the power-law fit, ν_h is the hopping frequency of the charge carriers, and n is a frequency exponent parameter in the range $0 \le n \le 1$ characterizing the deviation from Debye behavior and measurement of the inter-ionic coupling strength [17–20].

Frequency spectra of the real conductivity $\sigma(\nu)$ for typical compositions of the glass systems $(Li_{0.5}Na_{0.5})_2B_4O_7$, $(Li_{0.5}Rb_{0.5})_2B_4O_7$, and $(Li_{0.33}Na_{0.33}\ Rb_{0.33})_2B_4O_7$ are shown in Fig. 1 at a given temperature 613 K. The solid lines are obtained from fits of the Jonscher's power law of ac conductivity in glass with Eq. (1).

At low frequency, the conductivity of Li–Na–B–O glass is almost frequency independent, approaching the dc conductivity, whilst the conductivity of Li–Na–Rb–B–O and Li–Rb–B–O systems show dispersion at this frequency range. At high frequency, the conductivity has dispersion, and onset of the dispersion shifts to higher frequencies in the order of LNBO, LNRBO, and LRBO.

In Fig. 2, we present the composition dependence of dc conductivity σ_{dc} for the glass systems LNBO, LRBO, and LNRBO at three different temperatures. The Jonscher's power law in Eq. (1) is mainly adopted to obtain the dc conductivity, which is sensitive to MAE. We also used the complex impedance Cole–Cole plot to calculate the dc conductivity, and the result was the same as the one from the Jonscher's power law. A typical MAE can be seen with the exhibition of a negative deviation.

The drop in conductivity for LRBO is 4 order of magnitude, whilst the one for LNBO is 2.5 order of magnitude with $x = 0.5$ compared with the corresponding single alkali glass LBO. The drop in conductivity for an intermediate composition tends to increase with increasing the mismatch of the element size between the two types of alkali ions. For example, the atomic radii of Li, Na and Rb are 1.52 Å, 1.86 Å and 2.48 Å, respectively. The average bond distances of Li–O, Na–O and Rb–O are

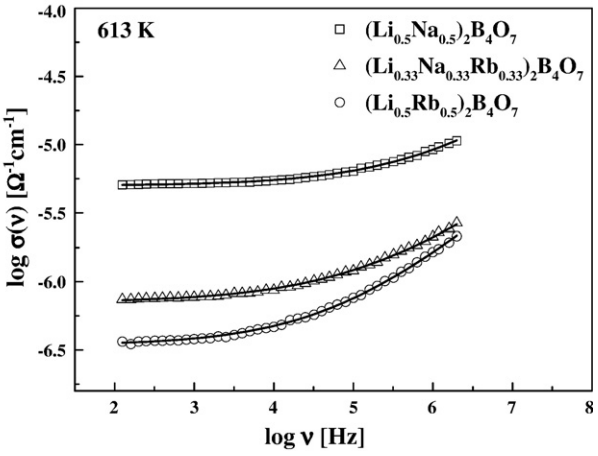

Fig. 1. Frequency spectra of the real conductivity for $(Li_{0.5}Na_{0.5})_2B_4O_7$, $(Li_{0.5}Rb_{0.5})_2B_4O_7$, and $(Li_{0.33}Na_{0.33}\ Rb_{0.33})_2B_4O_7$ at temperature 613 K. Points are the data, and the lines are fits using the Jonscher's power law.

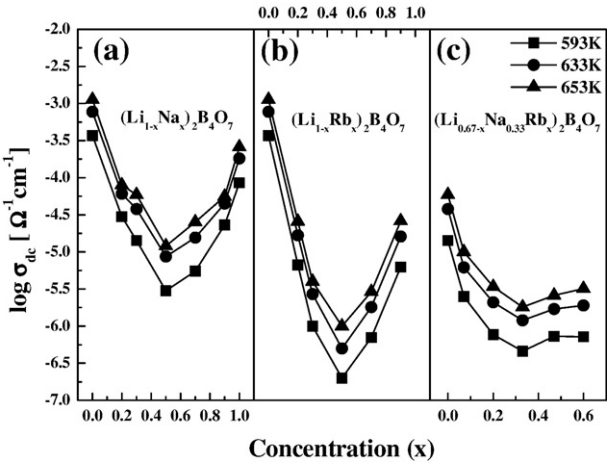

Fig. 2. Comparison of dc conductivity of glassy $(Li_{1-x}Na_x)_2B_4O_7$ (LNBO) with that of $(Li_{1-x}Rb_x)_2B_4O_7$ (LRBO) and $(Li_{0.67-x}Na_{0.33}\ Rb_x)_2B_4O_7$ (LNRBO) glass systems at various temperatures. Points are obtained from the power law, and the lines are guides to the eyes.

2.05 Å, 2.50 Å and 2.90 Å, respectively, as obtained from reverse Monte Carlo (RMC) simulation for phosphate glass [3]. Correspondingly, the order of the mismatch between Li–O and Rb–O is approximately 1 Å. The asymmetry of the dc conductivity curves as function of concentration of compositions is large for heavy element of Rb alkali ion.

It is reported that MAE is more pronounced in glass with the ternary alkali borate glasses of type xLi_2O–$(0.2-x)Na_2O$–0.1 K_2O–$0.7B_2O_3$ ($x = 0$, 0.04, 0.08, 0.10, 0.12, 0.16 and 0.20) than that in glass with two types of cations (Li–Na, Li–K, and Na–K glass series) [5,21]. However, the glass system LNRBO, which has the large relative mismatch of the element size, does show the combined characteristics of binary mixed alkali systems LNBO and LRBO, as shown in Fig. 2. The asymmetric dc conductivity of mixed alkali glasses may be due to the mass effect in partial, as it is expressed in the bond-valence RMC method in glass system [22]. It is also worth emphasizing that the small amount change of Rb with $x = 0.07$ in LNRBO in Fig. 2(C) makes significant difference in the dc conductivity.

We illustrate some typical values for the samples of single alkali glass, binary, and ternary mixed alkali glasses in Table 1. The hopping rates are obtained from the conductivity spectrum in Eq. (1) by the substitution $\sigma(\nu_h) = 2\sigma_{dc}$, and the other parameter n by a linear least-square fitting procedure.

As shown in Table 1, the hopping rate decreases as the following order of samples, $Rb_2B_4O_7$, $(Li_{0.5}Na_{0.5})_2B_4O_7$, $(Li_{0.33}Na_{0.33}\ Rb_{0.33})_2B_4O_7$, and $(Li_{0.5}Rb_{0.5})_2B_4O_7$. We note here that the hopping rates are related to the ac conductivity in the systems. In reality, conduction takes place on some complex subset of the fat percolation cluster that is termed the diffusion cluster [11]. Recently, Swenson and Adams show that the ions move through the conduction pathways of fractal-structured geometry by applying the bond valance technique to reverse Monte Carlo (RMC) produced structural models for a system of mixed alkali phosphate glasses [16]. They show that the two types of alkali ions are randomly mixed and have distinctly different conduction pathways of low dimensionality. They have shown that A ions tend to block the pathways

Table 1
Typical values of dc conductivity, σ_{dc}, the hopping frequency of the charge carriers, ν_h and a frequency exponent parameter, n, in selected glasses at 613 K.

Samples	σ_{dc} (Ω^{-1} cm^{-1})	ν_h (MHz)	n
$Rb_2B_4O_7$	1.3×10^{-6}	2.20	0.72 ± 0.02
$(Li_{0.5}Na_{0.5})_2\ B_4O_7$	5.2×10^{-6}	1.46	0.45 ± 0.02
$(Li_{0.5}Rb_{0.5})_2\ B_4O_7$	3.6×10^{-7}	3.55×10^{-2}	0.45 ± 0.02
$(Li_{0.33}Na_{0.33}Rb_{0.33})_2\ B_4O_7$	7.5×10^{-7}	1.87×10^{-1}	0.45 ± 0.02

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