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Dependence of the mixed alkali effect on temperature and total alkali oxide content in $y[xLi_2O \cdot (1-x)Na_2O] \cdot (1-y)B_2O_3$ glasses

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Abstract

The complex conductivity spectra of mixed alkali borate glasses of compositions $y\,[xLi_2O \cdot (1-x)Na_2O] \cdot (1-y)B_2O_3$ (with $x = 0.0$, 0.2, 0.4, 0.6, 0.8, 1.0; $y = 0.1$, 0.2, 0.3) in a frequency range between 10^{-2} Hz and 3 MHz and at temperatures ranging from 298 to 573 K have been studied. For each glass composition the conductivities show a transition from the dc values into a dispersive regime where the conductivity is found to increase continuously with frequency, tending towards a linear frequency dependence at sufficiently low temperatures. Mixed alkali effects (MAEs) in the dc conductivity and activation energy are identified and discussed. It has been *for the first time* found that the strength of the MAE in the logarithm of the dc conductivity *linearly* increases with the total alkali oxide content, y, and the reciprocal temperature, $1/T$.

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Keywords: Mixed alkali effect; Alkali borate glasses; Electrical conductivity spectra

1. Introduction

Physical properties associated with cation movements in ionic conducting materials (including glasses, some crystals and melts), e.g. ionic conductivity, dielectric loss, cation diffusivity and internal friction, show large deviations from additivity when one type of cation is gradually replaced by another, keeping the overall cation content fixed [1–8]. This behavior is known as the mixed cation effect, and it is especially termed as mixed alkali effect (MAE) when only alkali ions are involved. MAEs are also observed in properties associated with structural relaxations, such as glass transition temperature [9–11] and viscosity [1,2].

Although many endeavors have been made to obtain a better understanding on the MAE since the first discovery of the MAE, it is still an outstanding problem in glass science which attracts much attention recently. The strength of the MAE is influenced by many factors, e.g. temperature [12,13], the overall alkali oxide concentration [14–16], the size or mass difference of involved unlike alkali ions [2,17–20]. In order to understand the MAE, many theoretical models have been proposed [1,2], but none of them is able to account for all features of the MAE.

In this paper, the complex electrical conductivity spectra of $y[xLi_2O \cdot (1-x)Na_2O] \cdot (1-y)B_2O_3$ glasses (with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$; $y = 0.1, 0.2, 0.3$) over a wide range in frequency and temperature have been reported. The strong MAEs in the logarithm of the dc conductivity and in the activation energy have been identified in these mixed alkali borate glasses. As pointed out in [21,22], in all studied mixed cation glasses the overall network structure, viz. the number and the distribution of negatively charged boron oxide tetrahedra, remains unaffected by the cation substitution processes. Like the boron oxide groups, the alkali ions are randomly distributed. Therefore, the MAEs are not due to structural peculiarities such as clustering or phase separation.

2. Experimental

Alkali borate glasses of the following compositions $y[xLi_2O \cdot (1-x)Na_2O] \cdot (1-y)B_2O_3$ (with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$; $y = 0.1, 0.2, 0.3$) were prepared from dry mixtures of stoichiometric amounts of reagent grade

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Table 1
Glass transition temperatures, T_g, mass density, ρ, and total cation number density, N_v, of the studied glasses

Sample	y	x	T_g (K)	ρ (g cm^{-3})	N_v (10^{22} cm^{-3})
$0.3\ Na_2O \cdot 0.7\ B_2O_3$	0.3	0.0	755	2.35	1.26
$0.06\ Li_2O \cdot 0.24\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.2	735	2.31	1.28
$0.12\ Li_2O \cdot 0.18\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.4	725	2.29	1.30
$0.18\ Li_2O \cdot 0.12\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.6	733	2.28	1.34
$0.24\ Li_2O \cdot 0.06\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.8	749	2.27	1.38
$0.3\ Li_2O \cdot 0.7\ B_2O_3$	0.3	1.0	782	2.23	1.40
$0.2\ Na_2O \cdot 0.8\ B_2O_3$	0.2	0.0	737	2.18	0.769
$0.04\ Li_2O \cdot 0.16\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.2	723	2.16	0.78
$0.08\ Li_2O \cdot 0.12\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.4	725	2.16	0.793
$0.12\ Li_2O \cdot 0.08\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.6	728	2.15	0.805
$0.16\ Li_2O \cdot 0.04\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.8	735	2.13	0.817
$0.2\ Li_2O \cdot 0.8\ B_2O_3$	0.2	1.0	749	2.11	0.826
$0.1\ Na_2O \cdot 0.9\ B_2O_3$	0.1	0.0	634	2.05	0.358
$0.02\ Li_2O \cdot 0.08\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.2	628	2.03	0.358
$0.04\ Li_2O \cdot 0.06\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.4	628	2.02	0.360
$0.06\ Li_2O \cdot 0.04\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.6	627	2.00	0.359
$0.08\ Li_2O \cdot 0.02\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.8	628	1.99	0.361
$0.1\ Li_2O \cdot 0.9\ B_2O_3$	0.1	1.0	628	1.97	0.361

powder chemicals Li_2CO_3, Na_2CO_3 and B_2O_3 which were heated in a platinum crucible at 1000 °C for about 3 h. The melt was poured into a round stainless steel mould. Then the samples were removed from the mould, immediately annealed at 20 K below their respective glass transition temperatures for 3 h and then cooled to ambient temperature at a rate of 0.5 K min^{-1}.

The glass transition temperatures of the studied glasses were determined by differential thermal analysis (DTA) applying a heating rate of 10 K min^{-1}. The results are shown in Table 1. It is clearly seen that there is a MAE for every glass system, and the MAE in the glass transition temperature becomes less pronounced with decreasing the total alkali content, y. At $y = 0.1$ the MAE in the glass transition temperature has almost vanished.

The glass densities obtained by an Archimedes method via weighing the sample in air and liquid ethylene glycol of high purity are also shown in Table 1.

The number densities of the total alkali ions derived from the mass densities of the studied glasses are also listed in Table 1. In the case of $y = 0.1$ these number densities are constant within 1%. In the other glass systems with $y = 0.2$ and 0.3 the total cation number densities increase continuously if sodium is replaced by lithium. The lithium borate glass with $y = 0.2$ has a cation number density which is 7% higher than that of the binary sodium borate glass. For $y = 0.3$ the corresponding increase is 11%. Therefore, the reported MAE cannot be traced back to these differences in the total cation number density.

Conductivity measurements were carried out using a Novocontrol α-S high-resolution dielectric analyzer covering a frequency range from 10^{-2} Hz to 3 MHz. The conductivities and frequencies attained by the instrument are much lower than those normally accessible in impedance spectroscopy. Cylindrical samples were drilled from the glass plates, and their opposite faces were polished. All samples were of 28 mm diameter and approximately 1 mm thickness. Silver/platinum electrodes were sputtered onto the opposite faces of the glass samples.

3. Results and discussion

Conductivity isotherms of $0.2\ Li_2O \cdot 0.8\ B_2O_3$ and $0.12\ Na_2O \cdot 0.08\ Li_2O \cdot 0.80\ B_2O_3$ glasses in a log–log representation of $\sigma'(\nu)$ versus the experimental frequency ν are presented in Fig. 1. Similar spectra have been obtained for the other studied glasses $y[xLi_2O \cdot (1-x)Na_2O] \cdot (1-y)B_2O_3$ with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ and $y = 0.1, 0.2, 0.3$; some conductivity spectra for glasses with $y = 0.3$ have been published in the previous paper [23].

At sufficiently low frequencies, the conductivity spectra of both the single alkali glass and the mixed alkali glass show a frequency-independent dc conductivity plateau. The temperature dependence of the dc conductivity, σ_{dc}, can be well described by the Arrhenius law, $\sigma_{dc}T = A_{dc} \exp[-E_a/(k_B T)]$, where E_a and A_{dc} represent the activation energy and the temperature-independent pre-exponential factor, respectively. The activation energy and the pre-exponential factor are shown in Table 2. The ac conductivity, $\sigma'(\nu)$, increases monotonically with frequency [24]. The onset frequency ν_o defined as $\sigma'(\nu_o) = 2\sigma_{dc}$ marks the onset of the conductivity dispersion on the frequency scale. In both glasses ν_o shifts to higher frequencies as the temperature is raised. In the dispersive regime, the slope, $d\log(\sigma'(\nu))/d\log(\nu)$, increases continuously. Therefore, the Jonscher power law [25],

$$\sigma'(\nu) \approx \sigma_{dc}(1 + (\nu/\nu_0)^p), \tag{1}$$

which is often used to describe conductivity spectra is only a crude approximation.

With increasing normalized conductivity, $\sigma'(\nu)/\sigma_{dc}$, Eq. (1) becomes more and more inappropriate. In fact,

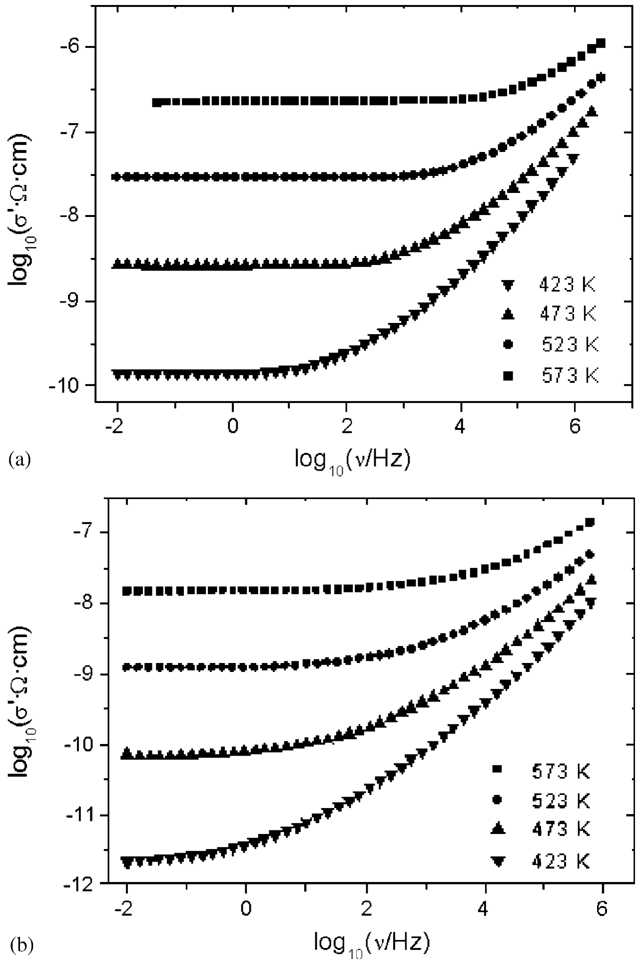

Fig. 1. Experimental conductivity spectra of (a) glassy $0.2Li_2O \cdot 0.8B_2O_3$ and (b) glassy $0.12Na_2O \cdot 0.08Li_2O \cdot 0.8B_2O_3$ at various temperatures.

the apparent exponent varies with the ration $\sigma'(\nu)/\sigma_{dc}$, increasing gradually and tending towards unity for large values of $\sigma'(\nu)/\sigma_{dc}$, while the conductivity becomes decreasingly temperature dependent. As $\sigma'(\nu) \propto \nu$ corresponds to a frequency-independent dielectric loss, this feature has come to be known as nearly constant loss (NCL) behavior [26]. The NCL becomes more pronounced with decreasing temperature and/or increasing frequency.

In spite of these similarities in the spectra of the two different glasses in Fig. 1, careful analysis of the spectral shape shows that there are also significant differences, see the previous paper [14].

Fig. 2 shows that the MAE in the logarithm of the dc conductivity for glassy $0.2[xLi_2O \cdot (1-x)Na_2O] \cdot 0.8B_2O_3$ becomes less pronounced as the temperature is raised. The similar behavior has been found for the other studied glasses $y[xLi_2O \cdot (1-x)Na_2O] \cdot (1-y)B_2O_3$ with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ and $y = 0.1, 0.3$; the result for the mixed alkali glasses with $y = 0.3$ has been published in the previous paper [14].

Fig. 3a shows the composition-dependent dc conductivity of the three glass systems $y[xLi_2O \cdot (1-x)Na_2O] \cdot (1-y) B_2O_3$ (with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$; $y = 0.1$, $0.2, 0.3$) at a constant temperature of 473 K, where the dc conductivities are taken from the low-frequency plateaus of the conductivity isotherms. It can be clearly found that the MAE in the logarithm of the dc conductivity becomes less pronounced as the total alkali oxide concentration decreases, but the effect is still observed even at very low concentration ($y = 0.1$). The similar behavior has been found in mixed alkali germanate glasses [15,16,27]. Fig. 3a shows that for glasses with $y = 0.3$ and 0.2 the minima occur at $x = 0.4$, whereas for glasses with $y = 0.1$ the minimum is found at $x = 0.2$. Fig. 3b shows the

Table 2
The values of the activation energies, E_a, and the pre-exponential factors, A_{dc}, of the dc conductivity of the studied glasses

Sample	y	x	E_a (eV)	$\log_{10}(A_{dc}$ (Ω cm))
$0.3\ Na_2O \cdot 0.7\ B_2O_3$	0.3	0.0	0.791±0.003	4.907±0.036
$0.06\ Li_2O \cdot 0.24\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.2	0.993±0.006	5.569±0.077
$0.12\ Li_2O \cdot 0.18\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.4	1.102±0.005	6.016±0.061
$0.18\ Li_2O \cdot 0.12\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.6	1.088±0.004	6.115±0.052
$0.24\ Li_2O \cdot 0.06\ Na_2O \cdot 0.70\ B_2O_3$	0.3	0.8	0.978±0.002	5.771±0.019
$0.3\ Li_2O \cdot 0.7\ B_2O_3$	0.3	1.0	0.781±0.002	5.279±0.016
$0.2\ Na_2O \cdot 0.8\ B_2O_3$	0.2	0.0	1.029±0.008	4.948±0.089
$0.04\ Li_2O \cdot 0.16\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.2	1.203±0.011	5.683±0.116
$0.08\ Li_2O \cdot 0.12\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.4	1.263±0.014	5.976±0.140
$0.12\ Li_2O \cdot 0.08\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.6	1.251±0.019	5.986±0.192
$0.16\ Li_2O \cdot 0.04\ Na_2O \cdot 0.80\ B_2O_3$	0.2	0.8	1.188±0.014	5.895±0.140
$0.2\ Li_2O \cdot 0.8\ B_2O_3$	0.2	1.0	1.059±0.006	5.383±0.071
$0.1\ Na_2O \cdot 0.9\ B_2O_3$	0.1	0.0	1.455±0.014	5.243±0.137
$0.02\ Li_2O \cdot 0.08\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.2	1.520±0.016	5.600±0.157
$0.04\ Li_2O \cdot 0.06\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.4	1.555±0.028	6.017±0.360
$0.06\ Li_2O \cdot 0.04\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.6	1.498±0.016	5.571±0.151
$0.08\ Li_2O \cdot 0.02\ Na_2O \cdot 0.90\ B_2O_3$	0.1	0.8	1.487±0.022	5.698±0.209
$0.1\ Li_2O \cdot 0.9\ B_2O_3$	0.1	1.0	1.455±0.014	5.793±0.140

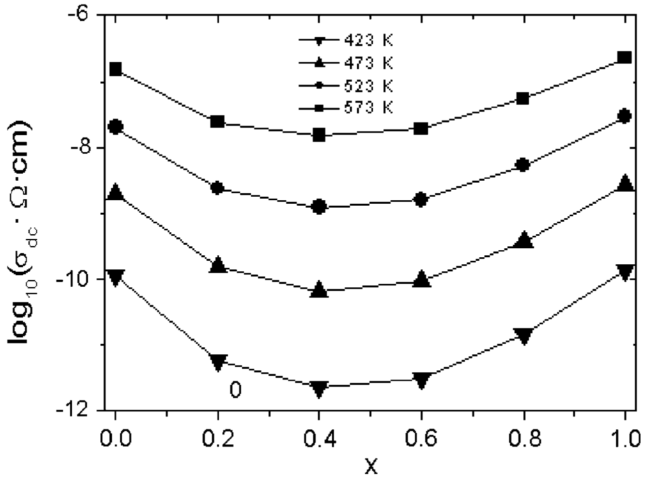

Fig. 2. Composition-dependent dc conductivity of glassy $0.2[x\mathrm{Li_2O}\cdot(1-x)\mathrm{Na_2O}]\cdot 0.8\mathrm{B_2O_3}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) at different temperatures.

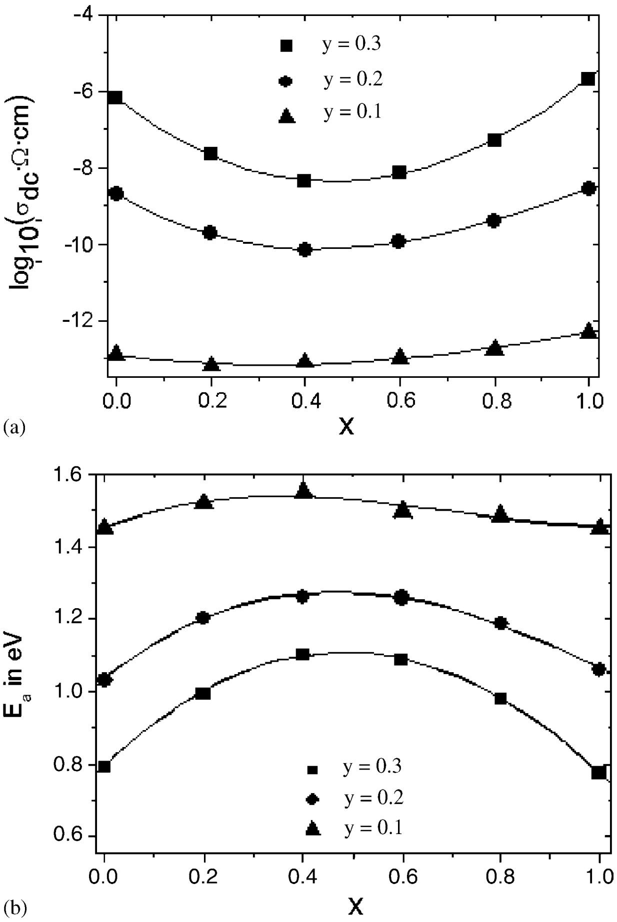

Fig. 3. Composition-dependent (a) dc conductivity at 473 K, (b) activation energy of $\sigma_{dc}T$ of glassy $y[x\mathrm{Li_2O}\cdot(1-x)\mathrm{Na_2O}]\cdot(1-y)\mathrm{B_2O_3}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$, and $y = 0.1, 0.2, 0.3$). Curves are guides to the eyes.

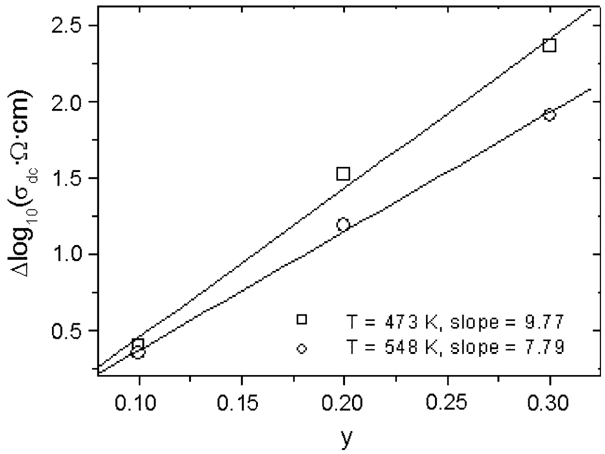

Fig. 4. y-dependent magnitude of the mixed alkali effect in the logarithm of the dc conductivity, $\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$, of glassy $y[x\mathrm{Li_2O}\cdot(1-x)\mathrm{Na_2O}]\cdot(1-y)\mathrm{B_2O_3}$ at 473 and 548 K. The straight lines are obtained by fitting the data using linear regression.

composition-dependent activation energy of the dc conductivity, E_a, where the values of E_a are obtained from conventional Arrhenius plots. It is also clearly found that the MAE in the activation energy becomes less pronounced as the overall alkali oxide concentration is lowered.

Fig. 4 shows y-dependent strength of the MAE in the logarithm of the dc conductivity of $y[x\mathrm{Li_2O}\cdot(1-x)\mathrm{Na_2O}]\cdot(1-y)\mathrm{B_2O_3}$ (with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$; $y = 0.1, 0.2, 0.3$) glasses at 473 and 548 K. Here, the strength of the MAE in the composition-dependent dc conductivity at a given temperature can be defined as

$$\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm}) = \log_{10}(\sigma_{dc,\mathrm{lin}}\,\Omega\,\mathrm{cm}) - \log_{10}(\sigma_{dc,\mathrm{min}}\,\Omega\,\mathrm{cm}), \qquad (2)$$

where $\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$ and $\log_{10}(\sigma_{dc,\mathrm{min}}\,\Omega\,\mathrm{cm})$ represent the magnitude of the MAE in the logarithm of the dc conductivity and the minimum value of $\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$, respectively. The value of $\log_{10}(\sigma_{dc,\mathrm{lin}}\,\Omega\,\mathrm{cm})$ is obtained from a linear interpolation between the experimentally determined logarithmic conductivity values of the two end members (the single alkali borate glasses) at the composition which corresponds to $\log_{10}(\sigma_{dc,\mathrm{min}}\,\Omega\,\mathrm{cm})$. Fig. 4 shows that the magnitude of the MAE, $\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$, *linearly* increases with the total alkali content, y. Furthermore, it is clearly found that the value of $\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$ decreases with increasing temperature at a given value of y, which confirms that the MAE becomes less pronounced with increasing temperature. The two lines in Fig. 4 are obtained by fitting the data points using linear regression, and the value of the slope decreases with increasing temperature.

Fig. 5 shows temperature-dependent magnitude of the MAE in the logarithm of the dc conductivity, $\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$, of the studied mixed alkali glasses. It is found that the strength of the MAE, $\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$, *linearly* increases with the reciprocal temperature, $1/T$. It is also clearly found that the value of $\Delta\log_{10}(\sigma_{dc}\,\Omega\,\mathrm{cm})$ increases with y at a given temperature, which confirms that the MAE becomes more pronounced with y. The lines in Fig. 5 are obtained by fitting the data points using linear

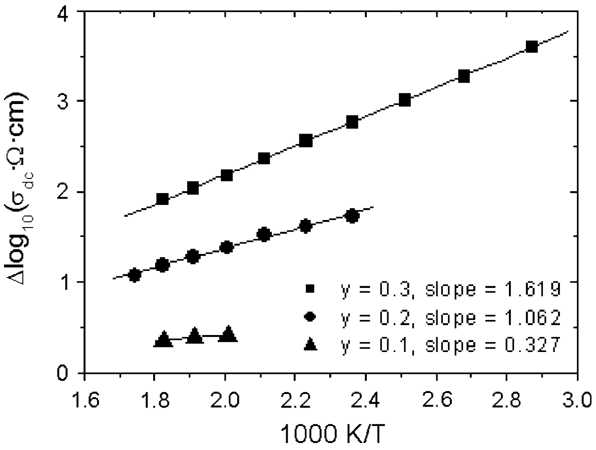

Fig. 5. Temperature-dependent magnitude of the mixed alkali effect in the logarithm of the dc conductivity, $\Delta\log_{10}(\sigma_{dc}\,\Omega\,cm)$, of glassy $y[xLi_2O\cdot(1-x)Na_2O]\cdot(1-y)B_2O_3$. The straight lines are obtained by fitting the data using linear regression.

regression, and the value of the slope decreases as y decreases.

4. Conclusion

The frequency-dependent conductivity spectra of $y[xLi_2O\cdot(1-x)Na_2O]\cdot(1-y)B_2O_3$ glasses show a transition from a dc plateau into a dispersive regime. For the first time the magnitude of the MAE in the logarithm of the dc conductivity is defined. The magnitude of the MAE in the dc conductivity and the activation energy increases with the total alkali content, y. By more careful analysis, it has been for the first time found that the magnitude of the MAE in the logarithm of the dc conductivity *linearly* increases with increasing the total alkali content. Another important finding of this paper is that the strength of the MAE in the logarithm of the dc conductivity *linearly* increases with $1/T$. These new experimental results might provide some help for the understanding of the MAE.

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