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Ion conduction in beryllium-alumino-silicate glasses doped with sodium or sodium and lithium ions

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Abstract

Electrical properties of beryllium-alumino-silicate glasses containing sodium ions or sodium and lithium ions were studied with impedance spectroscopy technique over a frequency range from 10 mHz to 1 MHz and at temperature range from 213 to 473 K. The frequency- and temperature-dependent conductivity spectra of individual single alkali glasses were superimposed by means of the Summerfield scaling. Mixed-alkali glasses do not overlap into a single master curve. Glasses doped with sodium ions exhibit significantly higher values of D.C. conductivity and lower activation energy (~0.63 eV) than glasses doped with both sodium and lithium ions (~0.95 eV). The observed mixed-alkali effect can be described by the dynamic structure model (DSM). The conductivity pre-exponential factors and activation energy follow the Meyer-Neldel rule in both glass series. It was observed that the replacement of SiO_2 by BeO in single cation glasses resulted in decrease in activation energy and pre-exponential factor σ_0. In mixed cations glasses similar effect found for D.C. conduction process parameters was assigned to influence of both oxides BeO and Al_2O_3.

1. Introduction

As compared with other alkaline-earth containing glasses very little research has been carried out so far in the glasses doped with the beryllium oxides [1-4] due to the beryllium toxicity, and high melting temperature [5]. However, beryllium oxide-containing ceramics are used for radio equipment, high-performance microwave devices, vacuum tubes, magnetrons and gas lasers, while beryllium metal is used in fusion reactors, nuclear devices, radar systems, and military infrared countermeasure devices [5]. Chemically Be^{2+} is a rather unique cation with the highest field strength charge-to-radius ratio and electronegativity among all alkaline-earth and alkali ions. Be^{2+} is therefore characterized by a small electronic polarizability (α_{Be2+}=0.008), even lower than that characteristic of Si^{4+} (α_{Si4+}=0.033) [6]. Unlike other alkaline earths ions, Be^{2+} is always found to be fourfold coordinated to oxygen in crystalline oxides and to form regular BeO_4 tetrahedra [7].

Wójcik et al. [8] have reported that BeO can play a role of both intermediate glass-forming and glass-modifying oxide in the Na_2O/Li_2O–BeO-Al_2O_3–SiO_2 glasses. The substitution of SiO_2 for BeO up to 5 mol%, leaves the remaining silicate network more polymerized compared to the Be-free glass. The competing glass-modifying role of BeO takes over at increasing BeO contents (10 and 15 mol%) and leads to a progressive destructions of Si-O-Si bridges [8]. An analogous effect on the structure of the alkali silicate network was found for substitution of SiO_2 for $AlO_{3/2}$ [9]. Furthermore, beryllium-alumino-silicate glasses have been reported to have high elastic moduli and strong chemical and thermal shock resistance [10]. However, until now there is a lack of electrical properties data of these glasses.

The electrical conductivity of ion conducting glasses is due to the hopping of monovalent cations under the influence of an external electrical field. The electrical conductivity of Na_2O-SiO_2 glasses increases with an increase in Na_2O content and reaches a value of about 3×10^{-3} Scm^{-1} at 300 °C for a 50 mol% concentration. This increase was assigned to the structure changes caused by an increase of the modifier oxide concentration, which affects the mobility of the monovalent cation [11]. The effect of the glass structure and composition on electrical properties in silicate glasses is still of a great interest [12-17]. Dutta et al. [13] studied the influence of substitution of CaO for Na_2O in silicate glasses and showed that it modifies the glass structure and increases the conductivity not only due to the higher Na^+ ion concentration but also due to an increase of the Na^+ ions mobility. Other studies [14-16] were done with constant level of monovalent cations while modifications were made on the rest of glass composition. For instance electrical conductivity of silicate glasses in which the CaO, MgO or GeO_2 was substituted of SiO_2 was found to decrease due to a reduced number of mobile cations or their mobility [14, 16]. Similar studies were done on the influence of tetravalent cations, Ti, Ge, Zr, Sn and Ce, on the electrical conductivity of soda-lime-silica glasses and the observations were analogous [15]; the differences in electrical conductivity presented by the several glasses were attributed to the effect that the M^{4+} ion has on the mobility of the diffusing Na^+ ion [15]. Kim [17] studied the mixed-alkali effect in A.C. electrical conductivity in Na-K-Si-Al-O melts and reported that the conductivity drop due to mixed-alkali effect increases as the Al_2O_3 content increases. The relationship between the mixed-alkali effect and Al_2O_3 content was explained based on the binding state of AlO_4-R^+ and -O^--R^+ in alkali aluminosilicate melts [17].

To our knowledge, there are so far no reports on electrical properties of alumino-silicate glasses containing beryllium and alkali ions. This study presents the results of the electrical properties of two different glass systems M_2O-BeO-Al_2O_3-SiO_2 where the BeO content is increased on the cost of SiO_2. The first series contains a high content of sodium (35 mol% Na_2O) while a quarter of the sodium ions are substituted by lithium ions in the second series (9 Li_2O–27 Na_2O mol%). Moreover, a thorough study is conducted to investigate the influence of the substitution of SiO_2 for BeO on electrical properties. Furthermore, the single alkali and mixed alkali effect are discussed.

2. Experimental

Two series of silicate glasses containing beryllium were prepared. The first series contains sodium oxide and has a starting composition of $35Na_2O$–xBeO–(65-x)SiO_2 in mol%, where x is 0, 5, 10 and 15. The second one contains sodium and lithium oxides and has starting composition of $9Li_2O$–$27Na_2O$–xBeO–(64-x)SiO_2 in mol%, where x is 0, 5 and 10. Respective amounts of reagents: BeO (99% Alfa Aesar), SiO_2 (99.99% ChemPur GmbH), Na_2CO_3 (99.9+% ChemPur GmbH) and Li_2CO_3 (99.999% ALDRICH) were thoroughly mixed in a mortar. Melting was performed in Al_2O_3 crucibles at 1400-1450 ^oC for 60 min, under air atmosphere. Melts were poured on a cold brass plate and pressed with a steel stamp to obtain flat circular pellets of ~1-2 mm thickness and 10 mm diameter. Afterwards, the samples were annealed in air at a temperature of 400 ^oC for five hours. The cooling rate was 40 °C/h.

The compositions of samples were examined with an inductively coupled plasma optical emission spectrometer (ICP OES) Aviro 200 Perkin Elmer on powdered sample dissolved in HF acid under Ar gas. More detailed descriptions about the measurements of the chemical composition as well as the structure and thermal properties of these glasses can be found in reference [8].

For the electrical measurements, gold electrodes were evaporated at the polished plane parallel surfaces of circular samples, in vacuum. Impedance measurements were carried out in the frequency range from 10 mHz to 1 MHz and the temperature range of 213 K to 473 K, with an AC voltage of 1 V_{rms}, using the Novocontrol Concept 40 broadband dielectric spectrometer Alpha-A equipped with ZG4 dielectric interface. The temperature step was 10 K. Measurements were done during decreasing temperature in nitrogen atmosphere using temperature controlling system Quatro Cryosystem.

3. Results and discussion

Beryllium-silicate glasses containing either sodium or sodium and lithium ions were found to be clear colorless and transparent. Some samples contained small air bubbles inside. Table 1 displays their evaluated chemical compositions. Naming of the samples states the BeO content in mol% (0, 5, 10 or 15) and if they contain only sodium (BN) or sodium and lithium (BNL) ions. It was impossible to obtain a stable circular pellet of sample $9Li_2O–27Na_2O–15BeO–49SiO_2$ due to high internal stresses causing immediate the samples to crack. All glasses dissolved aluminum from the crucible material during melting process, which is included in the analyzed compositions (Tab. 1). It is worth to notice that the basic glasses without beryllium (0BN and 0BNL), contain only trace amount of Al (~0.5 at%), while samples doped with BeO show significantly higher Al-levels. Moreover, xBN glasses exhibit on average significantly less Al than the xBNL series with lithium. The highest dissolution of Al_2O_3 in the melt is found for glasses with the highest Be content [8].

Table 1 Glasses ID and chemical compositions.

Sample ID	Evaluated glass composition (in mol%)	Evaluated glass composition (in at%)
	$35Na_2O–xBeO–(65\text{-}x)SiO_2$	
0BN	$34.1Na_2O–0.8Al_2O_3–65.1SiO_2$	$Na_{22.4}Al_{0.5}Si_{21.1}O_{56}$
5BN	$31.2Na_2O\text{-}5.4BeO–1.2Al_2O_3–62.1SiO_2$	$Na_{20.7}Be_{1.8}Al_{0.8}Si_{20.6}O_{56.2}$
10BN	$31.3Na_2O–10.9BeO–2.1Al_2O_3–55.8SiO_2$	$Na_{21.2}Be_{3.7}Al_{1.4}Si_{18.9}O_{54.8}$
15BN	$30.7Na_2O–15.9BeO–2.6Al_2O_3–50.8SiO_2$	$Na_{21.3}Be_{5.5}Al_{1.8}Si_{17.6}O_{53.9}$
	$9Li_2O–27Na_2O–xBeO–(64\text{-}x)SiO_2$	
0BNL	$10Li_2O–25.5Na_2O–0.6Al_2O_3–63.9SiO_2$	$Li_{6.7}Na_{17}Al_{0.4}Si_{21.3}O_{54.6}$
5BNL	$12.3Li_2O–25.6Na_2O–5.2BeO–4.3Al_2O_3–52.5SiO_2$	$Li_8Na_{16.6}Be_{1.7}Al_{2.8}Si_{17}O_{53.9}$
10BNL	$11.8Li_2O–23.2Na_2O–10.1BeO–9.2Al_2O_3–45.7SiO_2$	$Li_{7.7}Na_{15.1}Be_{3.3}Al_6Si_{14.9}O_{53.1}$

3.1. Conductivity spectra

Figure 1 shows the temperature dependence of the real part of A.C. conductivity (Reσ) at two different frequencies 0.1 Hz (marked by black color) and 1000 Hz (marked by red color) for all glasses. At all temperature and frequency ranges there is no significant difference between conductivity values observed for all glasses of series xBN and the ones of xBNL, respectively. However, glasses doped with lithium ions show conductivity values lower of at least one order of magnitude than glasses containing only sodium ions. The highest difference is visible for low frequency and low temperature regions.

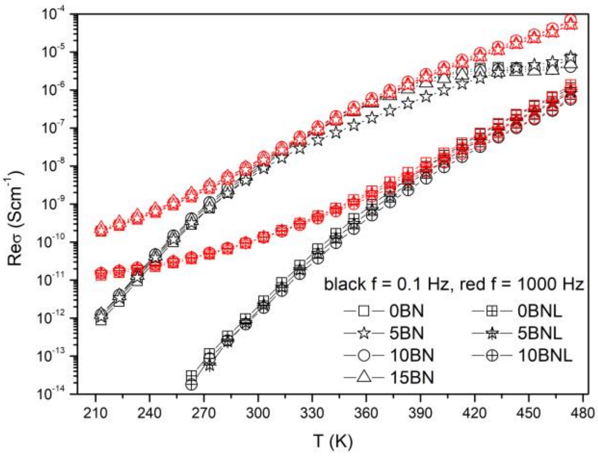
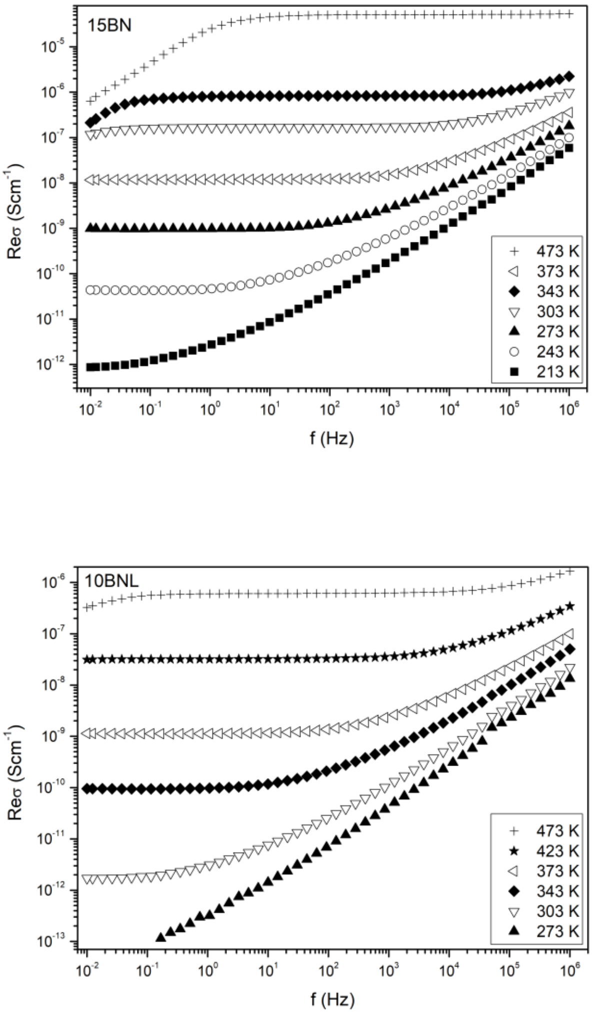


Figure 1 The temperature dependence of the real part of A.C. conductivity at 0.1 Hz (black) and 1000 Hz (red) for all glasses.

Figure 2 presents the frequency dependence of the Reσ at different temperatures for exemplary glasses: 15BN (Fig.2 (a)) and 10BNL (Fig.2 (b)). The other glasses show similar tendencies of their Reσ curves. Their conductivity spectra can be divided into two main parts: the frequency-independent D.C. conductivity (σ_{DC}) and the A.C. conductivity, which increases with frequency. The frequency range of the D.C. plateau increases with the temperature for all studied samples. Additionally, series xBN glasses show also frequency-dependent conductivity part visible at frequencies lower than 1 Hz and temperatures above 343 K, which is correlated with electrode effects. These electrode effects are also found for xBNL glasses but at higher temperatures (above 453 K).

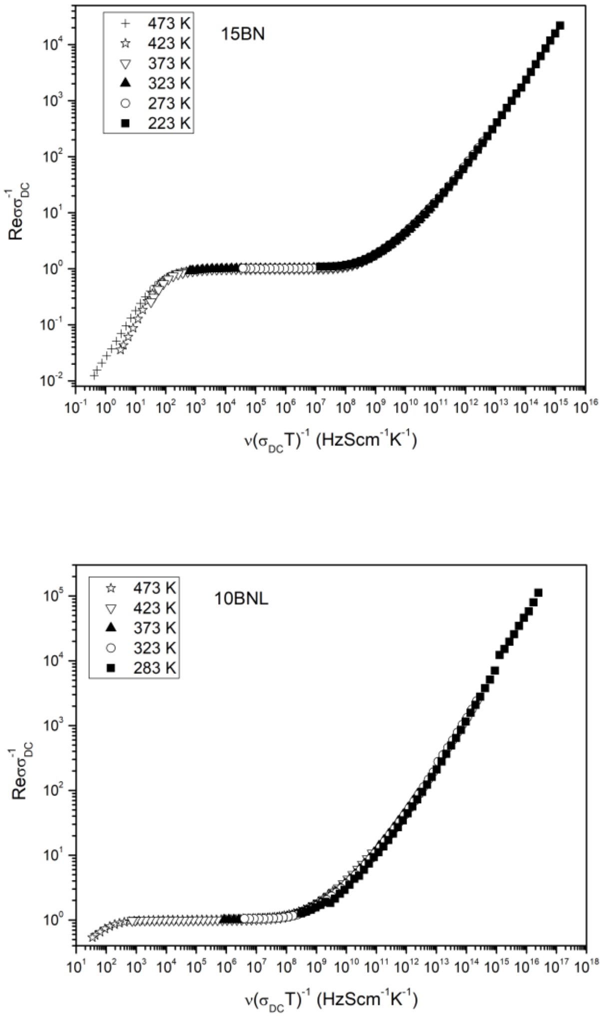


(a)

(b)

Figure 2 The frequency dependence of the real part of A.C. conductivity at different temperatures for glasses: (a) 15BN and (b) 10BNL, respectively.

It is known that in a lot of glasses the A.C. conductivity obeys time-temperature superposition, i.e., the shape of σ´(ω) in log-log plot is temperature independent and it is possible to construct a master curve [12, 18]. Figures 3 (a) and (b) display the master curves of the A.C. conductivity spectra of exemplary glasses: 15BN and 10BNL, respectively. In both cases, the Summerfield scaling has been applied. It can be seen that the slope of d logσ´/ d logν continuously increases with frequency, tending towards 1.0, for both glasses. However, the shape of scaled conductivity spectra is temperature independent only for the single-cation glass 15BN (Fig. 3 (a)), resulting in a single master curve. The same behavior is observed for other xBN glasses. The low frequency part, which does not overlap is due to electrode effects. On the other hand, mixed-alkali glasses xBNL do not overlap into a single master curve (results for 10BNL glass are shown in Fig 3 (b)). The shape of their conductivity spectra is temperature dependent what can be explained by the assumption of differently activated mobility of the two different ionic species. Than an ionic transport is dominated by the more mobile ionic species [19]. Cramer et al. [19] observed similar results for Li-Na-B-O glasses and assumed them that each of the two species contributes separately to the overall conductivity. While the individual spectra of each species follow the time–temperature superposition principle, the shape of the total conductivity spectrum is temperature dependent.



(a)

(b)

Figure 3 Master curves of glasses: (a) 15BN and (b) 10BNL, respectively.

3.2. D.C. conduction process

The σ_{DC} values (obtained from Figs 2) are presented in Fig. 4 for all glasses. They obey the Arrhenius law, over a conductivity range of more than seven magnitudes, which is given by the following relation:

$$\sigma_{DC}T = \sigma_0 \exp(-\frac{E_A}{kT}) \tag{1}$$

The σ_0 is the conductivity pre-exponential factor, E_A denotes the activation energy for the long-range diffusion of mobile ions and k is the Boltzman's constant. The values of σ_0 and E_A derived from fits (Fig. 4 with Eq. 1) and the frequency-independent D.C. conductivity σ_{DC} (estimated at temperatures 293 K and 373 K) are listed in Tab. 2. For all glasses, values of the σ_{DC} have the same order of magnitude at specific temperatures, in series xBN and in series xBNL glasses. The σ_{DC} values obtained for xBN glasses are higher than the ones for glasses doped also with lithium ions, of two or four orders of magnitude, at lower and higher temperatures, respectively. Moreover, the activation energy is lower for glasses containing only sodium ions (~0.63 eV) than the one calculated for xBNL glasses (~0.95 eV). The magnitude of activation energy observed for both series of samples is typical for an ion hopping mechanism. We can therefore conclude that Na^+ ion or both Na^+ and Li^+ ions hopping is the D.C. conduction mechanism in our series xBN and xBNL glasses, respectively.

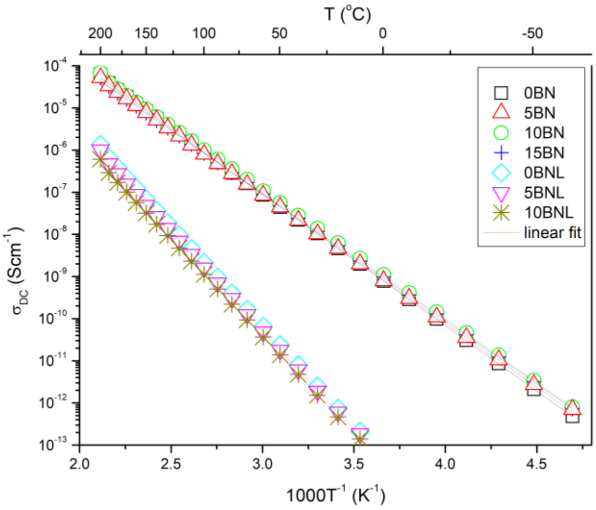


Figure 4 Arrhenius plots of D.C. conductivity for all glasses. Error bars are included in symbol size.

Table 2 D.C. conductivity values at 293 and 373 K, activation energy of D.C. conduction process and σ_0 parameter.

ID	D.C. conductivity			
	σ_{DC} at 293 K (Scm^{-1}) ± 2%	σ_{DC} at 373 K (Scm^{-1}) ± 2%	E_A (σ_{DC}) (eV) ± 2%	σ_0 ($KScm^{-1}$) ± 5%
0BN	$4.64*10^{-9}$	$8.57*10^{-7}$	0.645	$1.75*10^{5}$
5BN	$4.64*10^{-9}$	$7.98*10^{-7}$	0.632	$1.07*10^{5}$
10BN	$6.21*10^{-9}$	$9.98*10^{-7}$	0.629	$1.26*10^{5}$
15BN	$5.34*10^{-9}$	$8.25*10^{-7}$	0.624	$8.77*10^{4}$
0BNL	$7.32*10^{-13}$	$2.14*10^{-9}$	0.974	$1.21*10^{7}$
5BNL	$6.06*10^{-13}$	$1.60*10^{-9}$	0.966	$6.92*10^{6}$
10BNL	$4.65*10^{-13}$	$1.12*10^{-9}$	0.949	$2.84*10^{6}$

The change in values of D.C. conduction parameters observed after quarter of the monovalent cation ions are substituted by different cation ions, observed for the series xBNL glasses, was found before for other mixed-alkali glasses [17, 19, 20]. There is several theories, which try to explain these observations. One of them assumes that the introduction of a second alkali ion into the glass changes the glass structure (a new structural element is formed). The other says that without causing changing in the glass structure, it causes a site exchange between dissimilar alkali ions (defects are formed). These theories consider the pairing of unlike alkali ions about a nonbridging oxygen as essential for the appearance of the mixed-alkali effect [21-24]. However other literature indicate that the non-bridging oxygen content of the glass has no significant role in the mechanism responsible for the mixed alkali effect [25] and the alkali ions are distributed randomly throughout the glass structure rather than combined in alkali-ion pairs [26]. There is also another theory - the dynamic structure model (DSM) described by Bunde et al. [27], which may explain this anomalous behavior. In DSM model, each cation species creates its own chemical environment when glass is formed from a melt. Therefore, a Li^+ site in a glass differs from a Na^+ site. As each cation species prefers to migrate via pathways of sites adjusted to its own requirements, the ionic mobility is drastically reduced if the pathways of the respective species interfere with each other. As a result the effective number of mobile ions is strongly reduced in a mixed-alkali glass as compared to the binary glasses with the same total number of cations, what was observed for Li-Na-B-O glasses by Cramer et al. in [19].

In our previous research about the structure of studied xBN and xBNL glasses [8] we have observed significant changes in the glass structure when comparing glasses containing only Na^+ ions with those containing both Na^+ and Li^+ with a Na:Li ratio of 3:1. Li-containing glasses exhibit higher Q^2 population than the Li-free samples what can be explained by the disproportionation of Q^3 groups into Q^4 and Q^2 units when high field strength cations, such as Li^+, are introduced into the glass. In the presence of both Na^+ and Li^+ ions in 0BNL glass, the higher-field strength cation (here Li^+) forces the low-field strength cation (here Na^+) into energetically less favored sites [28]. However, the content of nonbridging oxygen was found to be similar for both glasses 0BN and 0BNL. Therefore, we think that in the case of our samples the mixed-alkali effect is best explained by the Bunde´s DSM model [19].

The D.C. conductivity of crystalline ionic conductor may be described by the expression obtained from the theory of random walk [29]:

$$\sigma_{DC} = K\omega_p = Ne^2a^2C(1-C)\gamma k^{-1}T^{-1}\omega_p \qquad (2)$$

where e is the electronic charge, a the hopping distance, γ the geometrical factor that may include a correlation factor, ω_p the hopping rate of the ions, N the number of equivalent sites per unit volume, C the fractional occupancy of the mobile ion sites [29]. The hopping rate is thermally activated and is given by:

$$\omega_p = \omega_0 \exp\left(\frac{\Delta S_a}{k}\right)\exp\left(\frac{-E_A}{kT}\right) = \omega_e \exp\left(\frac{-E_A}{kT}\right) \qquad (3)$$

where ΔS_a is the entropy of the hopping process, ω_0 is the vibrational frequency of ions in their lattice sites and ω_p is an effective attempt frequency which includes the entropy term. While compare Eqs (1), (2) and (3) we can obtain the expression for the conductivity pre-exponential factor σ_0:

$$\sigma_0 = Ne^2a^2C(1-C)\gamma k^{-1}\omega_0 \exp\left(\frac{\Delta S_a}{k}\right) = KT\omega_0 \exp\left(\frac{\Delta S_a}{k}\right) \qquad (4)$$

It has been reported that for a wide range of materials the magnitude of the pre-exponential factor σ_0 and the activation energy E_A are related by the Meyer-Neldel rule [30-32]:

$$ln\sigma_0 = \alpha E_A + \beta \qquad (5)$$

where α and β are constants and α is positive. The study of Meyer-Neldel rule helps to rationally understand the activation entropies. It has been shown that in ion conducting glasses [33-35], the entropies and activation energy values for ionic conduction can be expressed as:

$$\Delta S_a = \frac{E_A}{T_d} \tag{6}$$

where T_d is the effective temperature corresponding to an order-disorder transition in mobile ion sub-lattice. From Eqs (4) and (6) we can get:

$$ln\sigma_0 = \frac{E_A}{kT_d} + \ln(KT\omega_0) \tag{7}$$

By combining these equations with the Meyer-Neldel rule (Eq. (5)) we obtain: $\alpha = 1/kT_d$ and $\beta = ln(KT\omega_0)$. The values of $ln\sigma_0$ have been plotted against E_A (Fig. 5) to examine applicability of the Meyer-Neldel rule on the studied materials. The pre-exponential factor increases exponentially with E_A. The linear relationship $ln\sigma_0$ vs E_A indicates that T_d and C are the same for members of a particular family of ionic materials [36]. The slope of the straight lines in the $ln\sigma_0$ vs E_A plots was used to evaluate T_d. The obtained values of T_d were found to be: 373 K and 203 K for xBN and xBNL glasses, respectively.

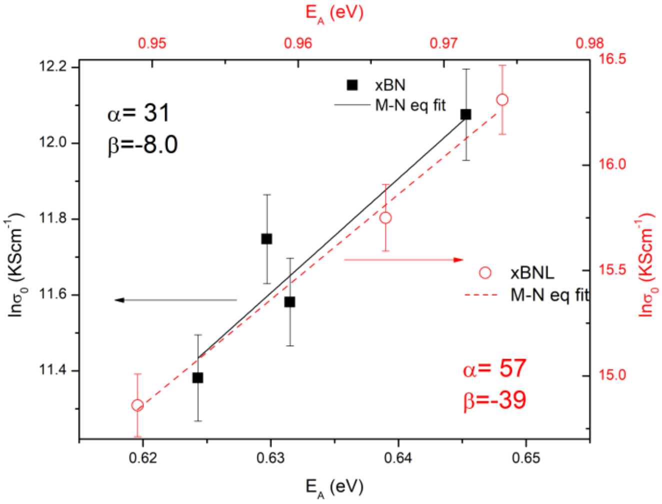


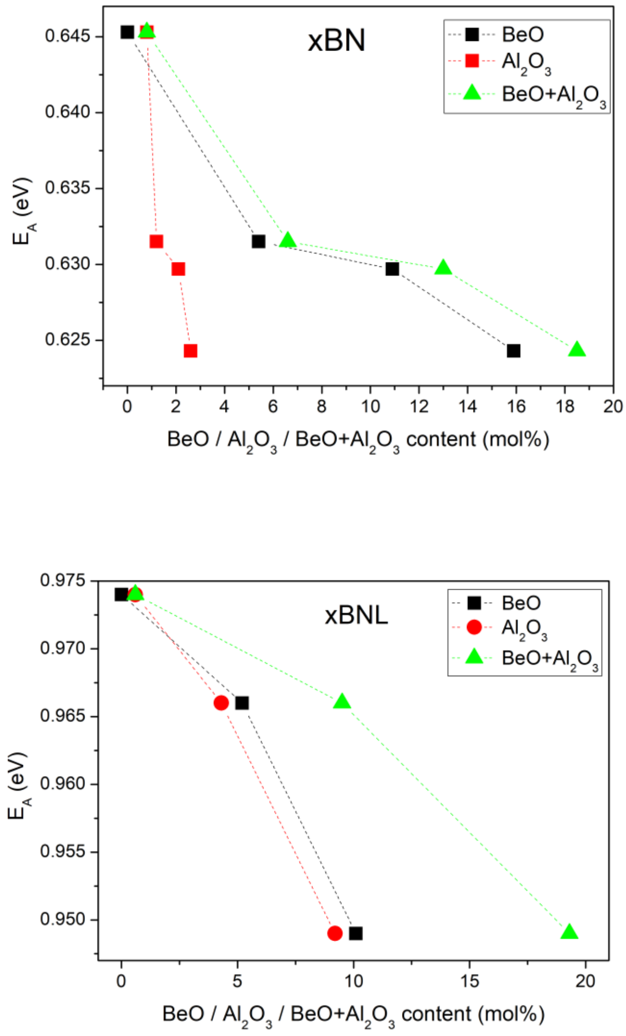
Figure 5 The validity of the Meyer-Neldel rule. The solid line is a fit to Eq.(7).

3.3. Influence of BeO and Al_2O_3 on conductivity

It is known that the magnitude of conductivity depends on concentration of mobile ions *n* and their mobility *μ* ($\sigma_{DC}=n\mu q$) while both of parameters can be influenced by the glass structure as described earlier [14-16]. In our previous paper [8] we have shown that substitution of SiO_2 for BeO in the Na-(Li)-Be-Al-Si-O glass systems resulted in the formation of $[BeO_{4/2}]^{2-}$ tetrahedra which are inserted into the silicate glass network, demonstrating the intermediate glass-forming role of BeO. In that case the BeO requires Na_2O for the formation of the $[BeO_{4/2}]^{2-}$ tetrahedra, leaving the remaining silicate network more polymerized compared to the Be-free base glass. A competing glass-modifying role of BeO takes over at increasing BeO contents (10 and 15 mol%) and leads to the progressive destructions of Si-O-Si bridges. As $[BeO_{4/2}]^{2-}$ tetrahedra are inserted in the silicate network, Si-O-Si bridges are destroyed, and due to the asymmetric nature of the Si-O-Be bridges, IR and Raman spectra show therefore a breakup of the silicate network [8]. An analogous effect on the structure of the alkali silicate network was found for substitution of SiO_2 for $AlO_{3/2}$ [9]. Therefore, we decide to analyze the influence of both oxides BeO and Al_2O_3 on electrical conductivity, especially for the case of series xBNL glasses in which the content of Al_2O_3 and BeO is comparable. Fig. 3 and Tab. 2 displayed the values of σ_{DC}, which were found to be of the same order of magnitude either for all xBN glasses or for xBNL glasses. It is hard to find the regularity in changes between σ_{DC} values observed for xBN glasses and changes in their compositions. However, in series xBNL, the σ_{DC} was found to decrease for glasses in order 0BNL, 5BNL and 10BNL. One of the explanation may be the presence of high level of Al_2O_3 which was found to decrease the conductivity of alkali-silicate glasses [17]. Since BeO has similar influence on silicate glass structure as Al_2O_3, and their contents in xBNL glasses are similar, it is hard to define which if any oxide has dominating influence on values of σ_{DC}.

Figure 6 presents the activation energy as a function of BeO, Al_2O_3 and sum of BeO and Al_2O_3 contents. The activation energy decreases with the increase in BeO, Al_2O_3 and BeO+Al_2O_3 contents for both glass series. In the series xBN glasses the correlation between changes in activation energy with composition is more likely according to change in BeO level. The first decrease observed between glasses 0BN and 5BN

(0.013 eV for doping with 5 mol% of BeO) is higher than observed between glasses 5BN and 15BN (0.008 eV for addition of next 10 mol% of BeO).



(a)

(b)

Figure 6 Activation energy as a function of BeO, Al_2O_3 and Be+Al_2O_3 content for series: (a) xBN and (b) xBNL glasses.

The Anderson and Stuart model describing ion transport in glasses predicts that the total activation energy of D.C. conduction process consists of two terms: the electrostatic binding energy of the original site (E_b) required to remove a cation from a non-bridging oxygen site and the strain energy (E_s) required to dilate the structure as the ion moves from one site to another [37]. The basic idea is that an ion makes a simple jump from one site to another and passes through a "doorway" which opens as it passes through, where cations sites require only the presence of non-bridging oxygens (Eq. 8).

$$E_A = \frac{\beta z z_O e^2}{\gamma(r+r_O)} + 4\pi G r_D (r - r_D)^2 \qquad (8)$$

where z and z_O are the valence of the mobile ion and the fixed counterion in this case alkali and oxygen, respectively; r and r_O are the corresponding Pauling ionic radii for Na^+ or Li^+ and O^{2-}, e is the electronic charge, r_D is the effective radius of the (unopened) doorway, G is the shear modulus, β is a “Madelung” constant, which depends on how far apart the ions are and γ is a covalency parameter, which indicates the degree of charge neutralization between the ion and its immediate neighbors. McElfresh and Howitt [38] have reexamined the E_s term and have suggested a modified form that overcomes certain limitations of the original Anderson and Stuart model. In summary, they [38] include the jumping distance λ as a better parameter:

$$E_A = \frac{\beta z z_0 e^2}{\gamma(r+r_O)} + 4\pi G \lambda (r - r_D)^2 \qquad (9)$$

Based on above model and glass structure studies [8] we can assumed that BeO addition influenced the activation energy as it influenced the glass structure. First, we will discuss series xBN glasses. The comparison of glasses 0BN and 5BN suggests that for glass 5BN, the parameters β and γ increase while λ and r_D decrease due to more polymerized structure of the glass. Moreover, glass 5BN showed also lower value of parameter σ_0 than glass 0BN (Tab. 2). The pre-exponential factor σ_0 (Eq. 4) similarly to E_A, depends on hopping distance, therefore we suppose that it is a hopping/jumping distance which decreases the most due to the 5 mol% substitution of SiO_2 for BeO. Further substitution for next 5 and 10 mol% of BeO (glasses 10BN and 15BN) also influences the E_A and σ_0, however observed changes are significantly smaller than the ones between glasses 0BN and 5BN. It was showed that increasing BeO contents up to 10 and 15 mol% leads to the progressive destructions of Si-O-Si bridges which increasing the depolymerization of the glass structure [8]. The observed structure changes are opposite to the one for the first 5 mol% of BeO substitution. Therefore, the nature of found changes in electrical parameters also should be different. Most probably, in the case of glasses 10BN and 15BN the concentration of not neutralized Na^+ ions is higher and the structure is more open for the ion hopping.

In the case of series xBNL glasses the observed changes in electrical properties cannot be assigned only to substitution of SiO_2 for BeO because of the content of Al_2O_3 is of the same level as BeO. Therefore, the decrease in E_A and σ_0 is an effect of the glass structure changes correlated to the addition of both oxides. Since the contents of both oxides for glasses 5BNL and 10BNL are 9.5 and 19.3 mol%, respectively, than their structure is more depolymerized relative to glass 0BNL. Then in the case of series xBNL glasses, the reason of observed changes in electrical properties is most probably the same as in the case of glasses 10BN and 15BN.

4. Conclusions

The results of the electrical properties of M-Be-Al-Si-O glasses (M = Na and/or Li) showed that the A.C. conductivity obeys time-temperature superposition only for the single-cation glass. The mixed-alkali glasses do not overlap into a single master curve due to differently activated mobility of the two different ionic species. D.C. conductivity was found to be of the same order of magnitude at specific temperatures in both glass series. However, glasses containing only sodium ions exhibit significantly higher values of D.C. conductivity (2 up to 4 orders of magnitude) and lower activation energy (~0.63 eV) than glasses doped with both sodium and lithium ions (~0.95 eV). The observed mixed-alkali effect was assumed to be due to the dynamic structure model (DSM). The linear relationship $ln\sigma_0$ vs E_A was observed and the effective temperature corresponding to an order-disorder transition in mobile ion sub-lattice was evaluated to be: 373 K and 203 K for single alkali and mixed-alkali glasses, respectively. The effect of substitution of SiO_2 for BeO on electrical properties was observed for glasses containing only sodium ions as decrease in the activation energy of D.C. conduction process and conductivity pre-exponential factor σ_0. Addition of low content of BeO (5 mol%) was found to increase the polymerization of glass structure. In the case of glasses doped with a higher level of BeO (10 and 15 mol%), the role of BeO is opposite and caused the increase in depolymerization of the glass structure. The effect of doping with BeO on glasses containing both cations was difficult to deducted due to similar content of Al_2O_3. Therefore, the decrease in E_A and σ_0 was assumed to be an effect of the glass structure changes correlated to the addition of both oxides (BeO and Al_2O_3).

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