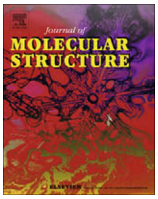
Journal of Molecular Structure 891 (2008) 173–177

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Thermal and electrical properties of mixed alkali in Li_2O–Na_2O–WO_3–P_2O_5 glasses

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ARTICLE INFO

Article history:
Received 27 June 2007
Received in revised form 7 March 2008
Accepted 12 March 2008
Available online 21 March 2008

Keywords:
Ionic conductivity
Glass transition temperature
Phosphate
Tungsten oxide
Glasses
Mixed-alkali effect

ABSTRACT

A series of tungsten-phosphate glasses, $0.5[xNa_2O–(1-x)Li_2O] - 0.5[0.25(WO_3)_2 - 0.75P_2O_5]$ with x varying between 0 and 1, were prepared using the melt quenching technique. They were studied by using powder X-ray diffraction (XRD), differential thermal analysis (DTA) and impedance spectroscopy. The total alkali oxide content is chosen in such a way that the electrical conductivity of the glasses under study is entirely ionic. It was evidenced that the conductivity minimum corresponds to the maximum of the activation energy. The glass transition temperature presents a minimum for the ratio Na/(Na + Li) = 0.5. On the other hand, the density varies linearly versus Na/(Na + Li). The mixed-alkali effect (MAE) is resulting here in a conductivity minimum observed for the composition corresponding to Na/(Na + Li) = 0.5, ($x = 0.5$). It could be attributed to the fact that the two types of alkali ions are randomly mixed and have distinct conduction pathways.

1. Introduction

Mixed-alkali effect (MAE) is a longstanding subject of investigation in oxide glasses. MAE corresponds to a nonlinear evolution of certain properties with the relative cation concentration in oxide glasses including two different alkali cations. Several models for MAE have been proposed in the literature and are compiled in several reviews [1–3]. Recently, Belostotsky [4] has presented a new defect model for the mixed mobile ion effect. The essential physical concept involved is that simultaneous migration of two unlike mobile ions in mixed ionic glass is accompanied by an expansion or contraction of the guest-occupied sites with distortion of the surrounding glass matrix.

Bazan et al. [5] have observed some conductivity anomalies in the system Li_2O–WO_3–P_2O_5. The authors suggested that negatively charged polarons (effectively the d-electron located on a W^{5+} centre) interact with mobile cations (Li^+) to form uncharged diffusing entities minimizing the conductivity. Such reduction of the conductivity is associated with the so-called "ion–polaron effect" (IPE) [5]. In 1978, Kraevskii et al. [6] reported on a similar conductivity anomaly in the Na_2O–WO_3–P_2O_5 glassy system. To the best of our knowledge, there are no reports on properties of glasses in Li_2O–Na_2O–WO_3–P_2O_5 system. However, many works concerning binary and ternary tungsten-phosphate glasses are abundant in the literature [7–13]. A recent investigation of the electrical, glass transition temperature and density properties of homologous glasses in the Li_2O–Na_2O–MoO_3–P_2O_5 system showed the mixed-alkali effect [14]. It was evidenced that the conductivity minimum corresponds to the maximum of the activation energy. The glass transition temperature for the molybdenum phosphate glasses seems to present a minimum for the ratio Na/(Na + Li) = 0.5.

The aim of the present work is to investigate the effect of the substitution of Li_2O by Na_2O on the properties of Li_2O–Na_2O–WO_3–P_2O_5 glasses. In order to avoid potential interferences between MAE and IPE effects, the selected compositions for the present study behave more like ionic rather than electronic or/and mixed ion–polaron conductors. Therefore, our investigations will be focused on the system $0.5[xNa_2O - (1-x)Li_2O] - 0.5[0.25(WO_3)_2 - 0.75P_2O_5]$, with $0 \leqslant x \leqslant 1$.

2. Experimental

The $0.5[xNa_2O - (1-x)Li_2O] - 0.5[0.25(WO_3)_2 - 0.75P_2O_5]$, with $0 \leqslant x \leqslant 1$, compositions were prepared by mixing and finely grinding appropriate amounts of Li_2CO_3 (Merck, 99.5%), Na_2CO_3 (Merck, 99.5%), $NH_4H_2PO_4$ (Merck, 99.5%) and WO_3 (Aldrich, 99.9%). The reactions in a glass melt are known to depend on the size of the melt, the sample geometry, the concentration of the total redox ions, the thermal history and the quenching rate. To keep these parameters constant, all glass samples were prepared under the same conditions as follows: about 10 g of mixture was initially heated at 573 K for about 12 h in order to remove volatile products. Next, the mixture was melted in a platinum crucible in air for 0.5 h at 1100–1200 K depending on the glass composition. The melts were then poured on a stainless steel plate preheated at 450 K, and the vitreous samples obtained were annealed at 650 K to relieve residual internal stress, and slowly cooled at room temperature.

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doi:10.1016/j.molstruc.2008.03.019

The amorphous nature of samples was checked by XRD analysis, using a Seifert XRD 3000 diffractometer. Density measurements were carried out at room temperature, using the Archimede's method with diethyl orthopthalate as the immersion fluid. The relative error in these measurements was about ±0.03 g cm^{-3}. Glass transition temperatures (T_g) were determined by DTA analysis at a heating rate of 10 K min^{-1}, using a Seiko DTA thermal analyzer, these temperatures are reproducible to ±5 K. For measurements of electrical conductivity, silver electrodes were applied onto two opposite sides of the samples. The electrical conductivity was determined from the impedance/admittance spectroscopic method. The spectra were carried out on a Hewlett Packard Model 4284A precision LCR Meter in the frequency range 20–10^6 Hz with temperatures changing from 293 to 533 K. The EPR experiments were made at room temperature on glassy samples using a Brucker EMX spectrometer operating at X-band frequencies (9.5 GHz).

3. Results

The composition dependencies of physical and electrical properties of the glasses have been determined along the series $0.5(x\mathrm{Li_2O} - (1-x)\mathrm{Na_2O}) - 0.5[0.25(\mathrm{WO_3})_2 - 0.75\mathrm{P_2O_5}]$ (x varies from 0 to 1). All the compositions form glasses when cast onto a steel mould; these glasses were subjected to X-ray diffraction studies and no crystalline phases were detected. The density (d) and the molar volume (V) for these glasses are shown in Fig. 1. When Li_2O is replaced by Na_2O, it can be noted that the measured density decreases while the molar volume increases. These variation shapes are similar to those of mixed Li_2O and Na_2O alkalis in the $Li_2O–Na_2O–MoO_3–P_2O_5$ system [14]. The values of the density and the molar volume are consistent with the ionic size, atomic weight of lithium and sodium elements and their amount in these glasses.

Plots of the temperature dependency of the dc electrical conductivity for Li–Na containing tungsten-phosphate glasses are displayed in Fig. 2. Generally, the temperature dependence of electrical conductivity of a vitreous material is due to the thermal activation, i.e., the conductivity increases with temperature according to the Arrhenius law, and/or the structural modification of the glass with temperature [15]. In this study, the conductivity is studied as a function of temperature and found to obey the Arrhenius law: $\sigma T = \sigma_0 \exp(-E_a/kT)$, where σ is the conductivity, σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. This behaviour is close to that observed for molybdenum glasses [14].

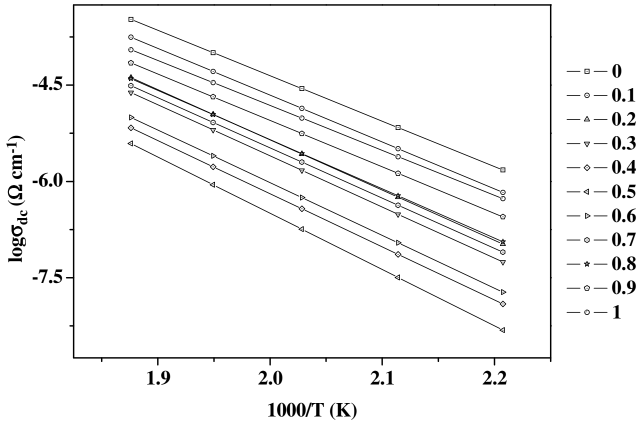

Fig. 2. Thermal variation of the dc conductivity along the system $0.5[x\mathrm{Na_2O} - (1-x)\mathrm{Li_2O}] - 0.5[0.25(\mathrm{WO_3})_2 - 0.75\mathrm{P_2O_5}]$.

Fig. 3 displays the isothermal dc conductivity plots, in a logarithmic scale (at 473 and 453 K). These plots show a minimum centred near $x = 0.5$. It is worth to notice that this minimum is usually observed in mixed-alkali glasses [14,16]. This could be attributed to the maximum of the activation energy (Fig. 3). Such behaviour is compatible with mixed-alkali effect.

Glass transition temperatures T_g were determined by DTA. As can be deduced from Fig. 4, T_g decreases with increasing the ratio Na/(Na + Li) and reaches a minimum for the value Na/(Na + Li) = 0.5. Therefore, a similar trend associated with the conductivity MAE is observed for the glass transition temperature. The conductivity and the glass transition temperature are expected to behave in a similar manner since both properties are associated with the dynamics of the glass system.

The conductivity, as isotherms in a logarithmic scale, was investigated as a function of the frequency for all the compositions; as an example Fig. 5 shows the plot for the composition $x = 0.4$. The dynamic conductivity related to the real part of the complex conductivity showed a typical behaviour [17]: a frequency-independent plateau for low frequency range and a power-law increase at high frequencies. We observed a decrease in the power-law exponent from 0.65 seen in the single-alkali end members to about 0.56 for the mixed-alkali compositions. This decrease cannot be attributed to the average of the power-law exponents found for two single Li- and Na-glasses, since each individually had exponent

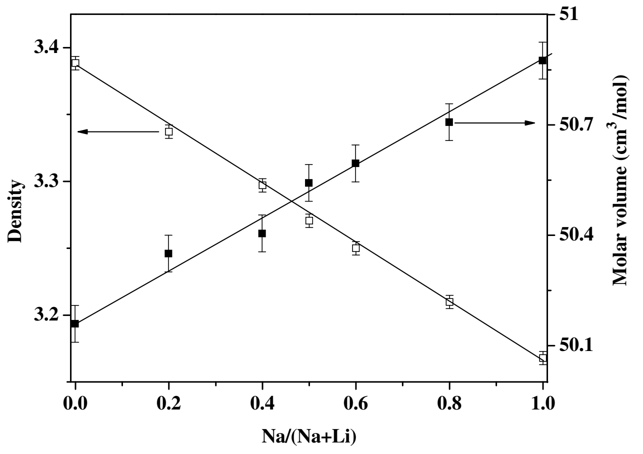

Fig. 1. Plots of density and molar volume versus the molar ratio Na/(Na + Li) along the system $0.5[x\mathrm{Na_2O} - (1-x)\mathrm{Li_2O}] - 0.5[0.25(\mathrm{WO_3})_2 - 0.75\mathrm{P_2O_5}]$.

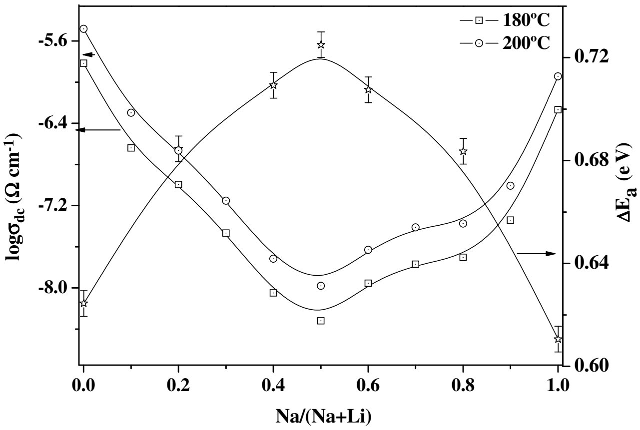

Fig. 3. Plots of conductivity and activation energy versus composition along the glass system $0.5[x\mathrm{Li_2O} - (1-x)\mathrm{Na_2O}]–0.5[0.25(\mathrm{WO_3})_2 - 0.75\mathrm{P_2O_5}]$. Line is drawn as guide to the eye.