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Investigation of the conductivity of the lithium borosilicate glass system

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Abstract

The lithium borosilicate system $(Li_2O)_{0.4}(B_2O)_{(0.6x)}(Si_2O_4)_{0.6(1-x)}$ with $x = 0$, 0.2, 0.3, 0.4, 0.6, and 0.8 was investigated using impedance spectroscopy. Impedance spectra were taken in the frequency range from 50 Hz to 1 MHz and in the temperature range from 100 to 280 °C. The ac- and dc-conductivity, relaxation frequency and activation energy of the dc-conductivity were extracted from the impedance spectra. The dc-conductivity of the investigated glass samples increases almost linearly from silica rich ($x = 0$) to the boron rich ($x = 0.8$) samples. Activation energy (E_a) was found to be 0.65 eV for high conducting sample and 0.8 eV for low conducting sample, respectively. The mixed glass-former effect was not observed on the samples studied. The effect of temperature scaling of ac-conductivity was observed, which indicates, that ionic conductivity relaxation mechanism is temperature independent for samples with $x = 0$, 0.2, 0.3. However, some deviations from scaling were found for the samples with higher x ($x = 0.4$, 0.6, 0.8).

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1. Introduction

In recent years the ionic conductivity of glasses has been investigated, both theoretically and experimentally, due to their potential applications as materials in the solid state ionic devices. Among those glass systems, special attention has been devoted to lithium ionic conducting glasses, e.g. Li-borosilicates (LBS), as candidates for solid electrolytes in lithium cells [1,2]. Full understanding of all conduction and relaxation processes in Li^+ conducting glasses is however still a challenging problem. For example, the effect of phase separation on electrical conductivity of the LBS glasses has not been reported yet.

Impedance spectroscopy (IS) is a powerful method for characterization of many electrical properties of materials and their interfaces [3]. It may be used to investigate any kind of solid or liquid material [1–5].

In the present study we report the electrical properties of glasses from the lithium borosilicate system $(Li_2O)_{0.4}(B_2O)_{(0.6x)}(Si_2O_4)_{0.6(1-x)}$ with different composition parameter $x = 0$, 0.2, 0.3, 0.4, 0.6, 0.8. A boron former is substituted by two atoms of the silicon former in this system, thus keeping constant the lithium concentration and the number of former atoms in the ternary system Li_2O–B_2O_3–SiO_2. IS was employed to measure ac- and dc-conductivity and impedance of studied glass samples. The activation energy of dc-conductivity was also extracted from experimental data.

2. Theory

In IS an electrical impedance Z (both real and imaginary parts) over a wide frequency range f is measured and resulting curve, Z vs. f, provides valuable information about the electrical properties of investigated system. Experimental data are commonly visualized through Nyquist diagrams [3]: Im(Z) vs. Re(Z). Nyquist diagrams are usually semicircles (RC semicircles) or semicircle arcs. Important param-

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eters of the sample, such as dc-resistance R_0, relaxation time constant τ_R and depression angle Θ, which characterizes non-Debye relaxation behavior, can be easily obtained from analysis of these diagrams [3].

Experimental impedance data $Z(f)$ may well be approximated by the impedance of an equivalent circuit made of ideal resistors, capacitors, perhaps inductances, and possibly various distributed circuit elements. Equivalent circuit can be physically interpreted, which leads to insight into the processes in the sample. In such a circuit the resistances represent the bulk conductivity of the material. Capacitances are generally associated with space charge polarization regions and with specific processes on an electrode. The physical interpretation of the distributed elements is somewhat more elusive. Non-local processes, such as diffusion, can be represented by Warburg impedance. Constant-phase element (CPE)

$$Z_{\mathrm{CPE}} = \frac{1}{(i\omega C)^n}, \tag{1}$$

where C and n are constants ($0 < n < 1$), accounts for distribution of microscopic properties. For example, when a given time constant is thermally activated with a distribution of activation energies one passes from simple RC circuit to a parallel CPE/resistance circuit.

For ionic glasses the real part of ac-conductivity σ as a function of frequency f is well approximated by equation [4,7,8]

$$\sigma(f) = \sigma_{\mathrm{dc}}[1 + (f/f_0)^s] + Af. \tag{2}$$

The first term (Jonscher term) in Eq. (2) results from the relaxation of dissociated ions in the glass matrix. Diffusion of these ions results in the frequency independent dc-conductivity σ_{dc} at low frequencies. With increasing frequency, the conductivity increases as a power law with exponent s close to 2/3. The last term ('near constant loss' – NCL term) in Eq. (2) represents additional contribution from processes, which are not yet completely understood [7,8]. In regimes where the NCL term can be neglected, the ac-conductivity follows a scaling law given by equation

$$\frac{\sigma}{\sigma_{\mathrm{dc}}} = F\left(\frac{f}{\sigma_{\mathrm{dc}}T}\right). \tag{3}$$

All different curves, representing the dependence of the ac-conductivity on frequency at different temperatures T, collapse into one common 'supercurve' after scaling them using of Eq. (3).

3. Experimental

The glasses $(Li_2O)_{0.4}(B_2O)_{(0.6x)}(Si_2O_4)_{0.6(1-x)}$ for $x = 0$, 0.2, 0.3, 0.4, 0.6, and 0.8 were melted in a platinum crucible. Melting temperature varies from 800 to 1300 °C, depending on glass composition. The molten glasses were poured into a metal mould and the glass blocks were then annealed at temperatures around 400 °C for 1 h.

Morphology of the samples was examined using scanning electron microscopy (SEM) Tesla BS 300 with digital unit Tescan. SEM images of the surface of samples studied were taken at accelerating voltage 15 kV and magnifications 50–20 000×. Before the SEM microscopy the surface of the samples was etched in 3 M HCl (aq.) at room temperature for 168 h. After drying, the sample surface was sputtered with Au in vacuum.

IS measurements were taken on approx. 2 mm thick samples coated on both surfaces with graphite paste. Measurements were performed using programmable automatic RCL meter FLUKE PM6306 in the frequency range from 50 Hz to 1 MHz and in the temperature range from 100 to 280 °C.

4. Results and discussion

From morphology point of view, the samples with $x = 0$, 0.2, and 0.3 were homogeneous and optically transparent, whereas the phase separation was observed for the samples with $x = 0.4$, 0.6, and 0.8, as documented by SEM microscopy (Fig. 1). Rapid crystallization has occurred in the sample with $x = 1$ (lithium–borate glass).

The Nyquist diagrams of experimental IS data of the samples show a single semicircle followed by a straight line at higher temperatures (Fig. 2). The centre of each semicircle is found to be depressed bellow the real axis. This suggests that associated relaxation of ions is non-Debye in nature. Depression angle Θ decreases from 22–19° to 13–11° as temperature increases from 100 to 280 °C and the values are almost independent on the glass composition.

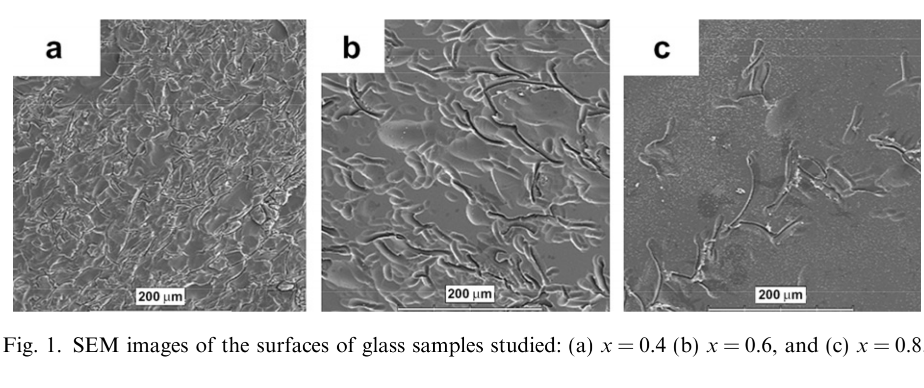

Fig. 1. SEM images of the surfaces of glass samples studied: (a) $x = 0.4$ (b) $x = 0.6$, and (c) $x = 0.8$.