1. Introduction

Borophosphate glasses may find potential use in different technological applications. They are suitable as host materials in laser applications, solar energy converters or electrode materials in Li secondary batteries [1]. However, the biggest demand of their possible usage is for the development of solid state electrolytes [2, 3]. Next-generation of battery for electronic devices e.g. electrical vehicle, energy storage systems or smart phones, have to possess high energy density, low cost and stable interface between the interphase of the electrodes and electrolyte [4]. Especially for the intercorpotation of Li metal into secondary batteries, it is important to avoid dendrite formation which may lead to safety problems due to possible shortcircuiting [5]. So, the developing of the stable interface is the biggest issue for the solid state electrolyte materials. These glasses have shown to be promising candidates for improved electrolytes of Li-ion batteries due to their physical properties than high ionic conductivity at room temperature (about $10^{-5}$ S/cm), chemical stability and compatibility with the electrode materials [4-6]. The maintainance of stable interface between electrode and electrolyte requires the precise reproduction of components which is based on the good knowledge of physical properties.

From the review of literature we can see several spectroscopy studies such as Raman spectroscopy, X-ray photoelectron spectroscopy or Nuclear Magnetic Resonance which are focused on the relationship between the structural changes and physical properties in alkali borophosphate glasses [6, 8, 9]. The choise of this system is often used for theoretical interest as a model sample for studies of the mixed glass former effect (MGF). The MGF describes the change in ionic conductivity in glasses which can be revealed as decrease or increase in the ionic conductivity with the change of the glass forming oxides while keeping the modifier oxide content constant [2, 3, 8].

As Jonscher has shown in [10] there are wide-reaching similarities between the electrical and mechanical response of system, also shown in [11], although only partially understood. So, this paper represents the first stage of our investigation aiming to compare the electrical and mechanical response of ionic conducting systems Na-B-PO and Li-B-PO. In this paper we present the conductivity and dielectric measurements of glasses of the systems with composition $50R_2O-xB_2O_3-(50-x)P_2O_5$ ($R=Li$ or Na), which are analyzed by several formalisms.

2. Experimental part

The lithium and sodium borophosphate glasses of the systems of composition $50Li_2O-xB_2O_3-(50-x)P_2O_5$ and $50Na_2O-xB_2O_3-(50-x)P_2O_5$ were prepared by the melting and quenching method. Glass batches were obtained through mixing reagent grade raw materials, Li$_2$CO$_3$ and Na$_2$CO$_3$ (Sharlau, ACS), B$_2$O$_3$ (Panreac) and (NH$_4$)$_2$HPO$_4$ (Sharlau, ACS), which were calcined in porcelain crucibles up to 450 °C in an electric furnace and then melted during 2 h at temperatures ranging from 800 °C to 1000 °C depending on their composition. The melts were
which are moving via activated hopping. The rate of hopping is given by the Arrhenius equation:

$$\sigma_{dc} = \sigma_0 \exp \left( - \frac{E_{DC}}{k_B T} \right)$$

(3)

where $\sigma_0$ is the pre-exponential factor, $E_{DC}$ is the activation energy for ionic conduction, $T$ is temperature in Kelvin, and $k_B$ is Boltzmann’s constant. The values of $\sigma_{dc}$ were determined from Equation 2 and used for the evaluation of the activation energy. The calculated values of activation energies for conduction are shown in Table 1.

3. Results and discussion

3.1 Ionic conductivity

Figure 1 shows the results of the ac conductivity measurements provided at the investigated samples which have been studied over wide ranges of frequencies and temperatures for sample 50Li$_2$O-xB$_2$O$_3$-(50-x)P$_2$O$_5$ (x = 5 mol%). Typically, the ionic conduction follows the Jonscher’s power law function:

$$\sigma(\omega) = \sigma_{dc} + A \omega^s$$

(2)

where $A$ is constant related to strength polarizability, $s$ is power law exponent and $\sigma_{dc}$ is dc conductivity and corresponds to the independent frequency part at low frequency. The conductivity dependence exhibits the significant increase according with power law trend in the high frequency region. The motion of charge carried in dc region is related to the long-range diffusion of ions

Figure 2 depicts the real and imaginary parts of complex impedance where characteristic peak of $Z''$ is shifted to higher frequency with the increase of temperature. The graphical inset in the Fig. 2 represents the Nyquist diagram which is plotted as the dependence of real and imaginary part of complex impedance and the intersection of the bulk response semicircle with zero value of $Z''$ at low frequencies give us the value of bulk resistance. For the determination of the dc conductivity the following expression is used: $\sigma_{dc} = \frac{d}{(R \times A)}$, where $d$ is diameter of sample, $A$ is area of electrodes surface and $R$ is bulk resistivity as determined from the intercept with the x-axis in the Nyquist diagram. The calculated values of dc conductivity from Nyquist diagram were in the good agreement with evaluated values from fitted data according Jonscher’s function.

poured onto brass molds and annealed above their corresponding glass transition temperature. The samples were prepared at the Ceramics and Glass Institute of the Spanish Research Council (CSIC) in Madrid, Spain.

The prepared samples were polished to be flat and plane-parallel. The both sides of samples were sputtered with gold electrodes of thickness ~ 1μm.

The dielectric spectroscopy is widely used tool for the investigation of materials [12]. Spectroscopy measurements were done using LCR Meter OT 7600 Plus at frequencies in the range from 10 Hz to 2 MHz (200 measurements for each of the range of temperature in steady state) for increasing temperature in the range below $T_g$- transition point. We performed measurements of chosen temperatures (with time per measurements: 5 min and time per stabilization of measured system: 20 min).

The evaluation of measurements were carried out by different electrical and dielectric quantities $Z'(f), \varepsilon'(f), \sigma'(f)$ and $M'(f)$ which are plotted in the both real and imaginary representation. Also, they are related through their reciprocal representation, then we can write $\sigma'(f) = \varepsilon'(f) + \sigma''(f) = 1/Z'(f)$. $\varepsilon'(f) = \varepsilon''(f) = 1/M'(f)$ and $\sigma''(f)$ is described by the following equation $\sigma''(f) = \omega \varepsilon_0 \varepsilon'(f)$, where $\omega$ is the angular frequency and $\varepsilon_0$ is the permittivity of free space.

According to the symbolic-complex method of circuit analysis we can designate the complex permittivity of the investigated material using the equation:

$$\varepsilon' = \left( \frac{C}{\varepsilon_0 A} \right) \text{ and } \varepsilon'' = \left( \frac{h}{\varepsilon_0 R A} \right)$$

(1)

where $C$ is measured capacitance, $R$ is the value of measured resistance, $A$ denotes the area of the plates and $h$ is thickness of the sample.
3.2 Dielectric behaviour

For the investigation of the dielectric properties, we used two different formalisms, complex permittivity and the reciprocal approach electrical modulus. Figure 3 shows the frequency dependence of complex permittivity in log-log scale for the temperature below $T_g$, for one sample with composition 50Li$_2$O-xB$_2$O$_3$-(50-x)P$_2$O$_5$ (x = 5 mol%). In the plot of frequency dependent $\varepsilon'$, we can observe two characteristic values $\varepsilon_{\infty}'(\omega)$ and $\varepsilon_s'(\omega)$ for a material with ionic conduction. The value $\varepsilon_{\infty}'(\omega)$ is observed in the higher range of frequencies where $\varepsilon'$ reaches a constant value that is the result of a much rapid polarization process in material. The static value $\varepsilon_s'(\omega)$ is observed in the low-frequency plateau before the appearance of electrode polarization. What is more, we can notice that plateau region shifts to higher frequency with the increase of temperature.
The activation energies $E'$, for each glass were determined from the slope of log vs. $1000/T$ using the equation $\tau = \tau_0 \exp(E'/k_BT)$. This Arrhenius type dependence of the relaxation time from which the activation energy was determined is plotted in Fig. 5b. The calculated activation energies are listed in Table 1. The inset in Fig. 4 represents the normalized value of $M_{\text{MAX}}$ and frequency is scaled by $f_{\text{MAX}}$, the collapse of data to a master curve is indicative of a common transport mechanism.

For the investigated systems Na-B-PO and Li-B-PO, dc conductivities (listed in Table 1) increase with the decrease of the alkali cation radius, i.e. conductivity increases from Na to Li containing glasses.

The selected properties of investigated samples 50R_2O-xB_2O_5-(50-x)P_2O_5 (x = 5-25 mol %), R=Li, Na are listed in Table 1. The insets in Figs. 4 and 5 represents the normalized value of $M_{\text{MAX}}$ and frequency is scaled by $f_{\text{MAX}}$, the collapse of data to a master curve is indicative of a common transport mechanism.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E^{oc}$ [±0.01eV]</th>
<th>$\sigma_n$ [S/cm]</th>
<th>$E'$ [±0.01eV]</th>
<th>$\tau^*$ [s]</th>
<th>$s^*$</th>
<th>$\beta^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50Li5B*</td>
<td>0.71</td>
<td>2.99x10^7</td>
<td>0.68</td>
<td>1.28x10^4</td>
<td>0.82</td>
<td>0.51-0.59</td>
</tr>
<tr>
<td>50Li15B*</td>
<td>0.62</td>
<td>2.09x10^4</td>
<td>0.62</td>
<td>2.95x10^4</td>
<td>0.9</td>
<td>0.52-0.6</td>
</tr>
<tr>
<td>50Li25B*</td>
<td>0.61</td>
<td>1.73x10^6</td>
<td>0.61</td>
<td>2.31x10^4</td>
<td>0.91</td>
<td>0.53-0.57</td>
</tr>
<tr>
<td>50Na5B*</td>
<td>0.76</td>
<td>1.63x10^4</td>
<td>0.72</td>
<td>2.96x10^4</td>
<td>0.87</td>
<td>0.58-0.65</td>
</tr>
<tr>
<td>50Na15B*</td>
<td>0.7</td>
<td>8.16x10^6</td>
<td>0.67</td>
<td>5.98x10^4</td>
<td>0.73</td>
<td>0.52-0.59</td>
</tr>
<tr>
<td>50Na25B*</td>
<td>0.67</td>
<td>1.31x10^4</td>
<td>0.64</td>
<td>1.45x10^4</td>
<td>0.5</td>
<td>0.53-0.57</td>
</tr>
</tbody>
</table>

* measured at 348 K; $\Delta$ evaluated for all measured temperatures

The choice of samples 50Li_{2x}O-xB_{2x}O_{5y}(50-x)P_{2x}O_{5y} (x = 5-25 mol %) and 50Na_{2x}O-xB_{2x}O_{5y}(50-x)P_{2x}O_{5y} (x = 5-25 mol %) is due to investigating of the change in ionic conductivity which can be revealed as decrease or increase in the ionic conductivity with

**Fig. 4 Imaginary and real representation of frequency dependent modulus; red lines represent the fitted data with KWW function**

**Fig. 5 Arrhenius dependence of dc conductivity a), and relaxation time for conduction b), depicted for all investigated samples**

### 4. Conclusions

The choice of samples 50Li_{2x}O-xB_{2x}O_{5y}(50-x)P_{2x}O_{5y} (x = 5-25 mol %) and 50Na_{2x}O-xB_{2x}O_{5y}(50-x)P_{2x}O_{5y} (x = 5-25 mol %) is due to investigating of the change in ionic conductivity which can be revealed as decrease or increase in the ionic conductivity with
of composition, which is in accordance with previous structural studies in alkali borophosphate glasses [7]. The activation energies associated to dielectric loss were estimated from the imaginary part of electric modulus, and the both activation energies are supposed to be activated with similar activation energy.

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References