The internal friction of lithium and sodium borophosphate glasses

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ARTICLE INFO	ABSTRACT
	Alkali borophosphate glasses have recently gained strong interest, not only for their fundamental importance due to the mixed glass former effect but also because of their potential applicability as solid state electrolytes in energy harvesting devices. In the present work, internal friction measurements of lithium and sodium borophosphate glasses have been performed in order to look for further insights on the relationships between the ionic conduction mechanism and the structure of the glasses that has been previously determined. Absorption of acoustic waves shows two marked internal friction peaks with activation energy in the range of the activation energy for the ionic conduction of the glasses between 0.5 and 0.7 eV. Furthermore, the substitution of phosphorus by boron network former results in the decrease of the activation energy associated to both processes in parallel to the E_a of the ionic conduction of alkali cations; and the relationship between the areas of both peaks suggests a change of the distribution of alkali ions between positions energetically different in agreement with the structural changes of the glass network.

1. Introduction

The internal friction of glasses has not traditionally been one of the mostly studied or easily accessible techniques to the glass research community. However, it can provide valuable results that, in conjunction with measurements of diffusion coefficients or impedance spectroscopy analysis of the conducting species, may allow one to distinguish and quantify between the different structural motifs of the glass networks. Basically, the internal friction measures the relaxations occurring around atomic positions after they are submitted to a stress. Thus, the classical peaks associated to atomic relaxations are due to the motion of cationic species, the interactions between different cations, including protons, and those from non-bridging oxygen atoms as well as the viscoelastic character of the network [1]. As it was studied in binary alkali silicate glasses, McVay and Day [2] showed that the internal friction curves of Na_2O-Rb_2O-SiO_2 glasses presented two peaks: a first below 0 °C and attributed to the alkali ions and a second near 200 °C corresponding to the non-bridging oxygen atoms. In these mixed alkali glasses, they also observed the appearance of a third peak that was attributed to the mixed alkali effect when the two alkalis are present in the composition and as it was proved by means of diffusion coefficient measurements of the two alkalis. Other authors have instead studied the effect of dissolved water on the internal friction results, and demonstrated that the two usually observed peaks are affected by the amount of remaining water [3]. As the phosphate-based glasses are highly

sensitive to hydration and may dissolve relatively large amounts of water, the authors proved that the presence of proton affects simultaneously both internal friction peaks reported in literature.

In alkali borate glasses, however, the first peak can be found at higher temperatures, above room temperature, and the agreement of the activation energies with those for the ionic conduction reveals that the relaxation mechanisms are the same as in silicate glasses [1]. In any case, the relaxations attributed to the more mobile species are seen at lower temperatures and present smaller activation energy, while those coming from structural units or cationic pairs have greater activation energy and appear at higher temperatures.

We have recently studied the acoustic attenuation and electrical properties of metaphosphate glasses [4] as well as of lithium oxynitride phosphate glasses, where part of the oxygen atoms is substituted by nitrogen atoms after a remelting reaction under flowing ammonia [5]. In all previous cases the attenuation spectra were simulated using the Double Power Law (DPL) function or Gaussian functions [4] and we obtained generally two peaks between room temperature and the glass transition temperature of the glasses, being attributed to relaxations of the modifier cations and with activation energies similar to those for the ionic conduction from impedance measurements. The analysis of the spectra turned out more complicated as the number of chemical environments or structural motifs of the network was increased. Furthermore, the sometimes observed overlapping of neighbouring peaks or very low energy relaxations of others makes the spectra to show a

clear different number of peaks between compositions.

Lithium borophosphate glasses have notably been studied recently due to their interesting improved properties as a consequence of the mixed glass former effect (MGFE), through which the electrical conductivity, for instance, increases upon substitution of phosphorus by boron for constant Li_2O containing glasses [6]. This has originated numerous studies concerning their usefulness as solid state electrolytes for lithium secondary batteries in either bulk or thin-film forms [7]. Meanwhile the absolute values of conductivity at room temperature are not as high as other solid electrolytes under use, these glasses are thought as potential candidates for a range of electrochemical devices that may profit of the advantages of glasses, such as chemical variability and homogeneity with absence of grain boundaries and simple preparation. Similarly, sodium borophosphate glasses do also present an increase of their conductivity in parallel with a decrease of the conduction activation energy as shown by Mizerakova et al. [8], and these could also find application in sodium ion batteries.

The MGFE phenomenon describes the nonlinear changes observed in glass properties, i.e. ionic conductivity or viscosity, upon the change in the fraction of two different glass former oxides while keeping the concentration of modifier oxide constant [6, 9]. When B_2O_3 substitutes for P_2O_5, the boron atoms may be either four or three fold-coordinated in the form of $[BO_3]$ or $[BO_4]$ groups, respectively. The influence of the MGFE on the electrical conductivity of lithium borophophate glasses has been explained as a consequence of the formation of four-fold coordinated borate groups to which modifier cations, being either lithium or sodium, may be associated under a smaller electrostatic attraction [6], and has also been manifested in the behaviour of the viscosity and kinetic fragility [9]. Thus, the overall bonding of alkalis to non-bridging oxygens results smaller and gives rise to a net increase of the mobility of the alkali ions. The aim of the present work was to investigate the influence of the mixed glass former effect onto the internal friction of alkali borophosphate glasses with compositions $50R_2O$-xB_2O_3-$(50$-$x)$ P_2O_5 (R = Li or Na) by means of its relationships with the atomic structure of these glasses and their known properties such as electrical conductivity and viscosity.

2. Experimental

The lithium and sodium borophosphate glasses of the systems of composition $50Li_2O$-xB_2O_3-$(50$-$x)P_2O_5$ (x = 5,10,15,20,25,50) and $50Na_2O$-xB_2O_3-$(50$-$x)P_2O_5$ (x = 5,10,15) were prepared by the melting and quenching method. Glass batches for 100 g were obtained through mixing reagent grade raw materials, Li_2CO_3 and Na_2CO_3 (Sharlau, ACS), B_2O_3 (Panreac) and $(NH_4)_2HPO_4$ (Sharlau, ACS), being firstly calcined in porcelain crucibles up to 450 °C, then melted during 2 h at temperatures ranging from 800 °C to 1000 °C depending on their composition. The melts were poured onto brass moulds and annealed above their corresponding glass transition temperature. Chemical analysis through X-ray Fluorescence spectroscopy did not show variation of the nominal molar oxide contents, neither contamination from the ceramic crucibles.

After annealing, glass specimens were obtained through cutting and polishing as plane-paralell plates of ca. 1 cm^2 and sputtered with gold layers of 1 μm thickness.

The conventional pulse-echo experimental equipment for measurement of acoustic attenuation and velocity was implemented in the investigation. Longitudinal acoustic waves with frequency 13 MHz were produced by a HF pulse generator Matec 7700. The sample was acoustically coupled to a piezoelectric transducer $LiNBO_3$, which possesses the properties such large piezoelectric coefficient and very low acoustic losses.

The multiple reflections were observed, and generated signal was amplified and displayed on the oscilloscope. The velocity was measured from the transit time between the reflected pulses and their corresponding distance in the investigated samples. The attenuation was

obtained from the amplitude of selected echoes received by attenuation recorder [10]. The consequential errors were minimized according McSkimin method [11].

The measured acoustic attenuation is dependent on temperature. The heating rate was 0.1 $K \cdot min^{-1}$ and the raising temperature was monitoring by digital multimeter using a thermocouple (type T). Acoustic measurements were performed at temperatures below T_g of the investigated glasses, in the range from 290 K to 550 K.

Tan δ is called as internal friction or mechanical attenuation (electrical analogue), it represents the absorption of vibrational energy in a substance and is related to the vibrational (acoustic) spectrum [1].

$$\tan \delta = Q^{-1} = \Delta \frac{\omega \tau}{1 + \omega^2 \tau^2} \tag{1}$$

where ω is angular frequency and τ is relaxation time, the centred position of peak is given by expression $\omega \tau = 1$. Internal friction analysis gives us the useful information about the structural relaxation of glass below T_g. Internal friction is defined with following equation:

$$\phi = \alpha \lambda / \pi \tag{2}$$

where α is the amplitude absorption coefficient per unit distance and $\lambda = v/f$.

3. Results

The acoustic absorption of longitudinal waves with frequency of 13 MHz is represented in terms of the internal friction and depicted in Fig. 1 as a function of temperature for the investigated group of lithium borophosphate glasses. Broad peaks with characteristic temperatures of the maximum of absorption were observed. As it can be seen, the temperature of peak maxima (both at low and high temperatures) for lithium borophosphate system decreases for B_2O_3 contents up to 20 mol %, then increases between 25 and 50 mol% B_2O_3 contents.

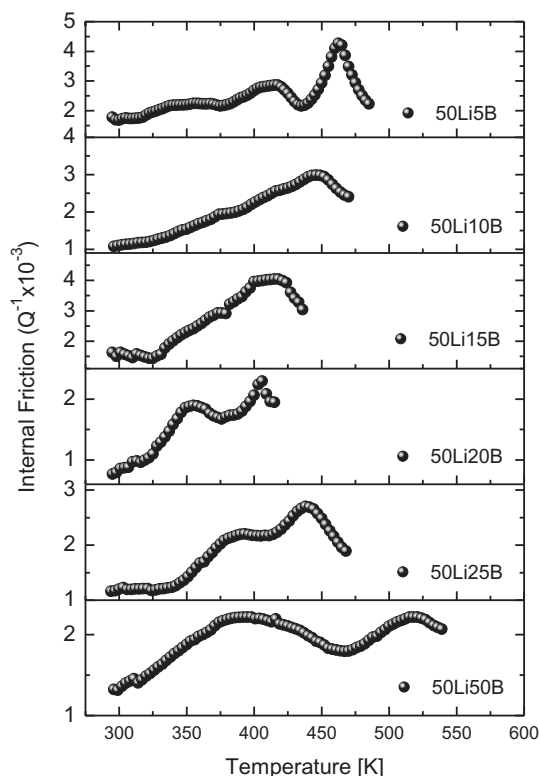Fig. 2 shows the temperature dependence of the internal friction for

Fig. 1. Temperature dependence of internal friction for the investigated samples of the lithium borophosphate glasses measured at the frequency of 13 MHz.