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Investigation of the relationships between acoustic attenuation and ionic conduction of metaphosphate glasses

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ABSTRACT

This paper deals with phosphate-based glasses and summarizes the results obtained from acoustic attenuation and ionic conduction investigations. Several relaxation processes have been found to be connected with different activation energies, for which Double Power Law and Gaussian functions have been used for their modelling. The activation energy of the acoustic relaxations in the metaphosphate glasses increases with the increasing cationic potential of the modifier elements, following a direct relationship between the cationic potential of the modifier in the glasses and their influence on the short and medium range structural arrangements of the PO_4 tetrahedra. On the other hand, the variation of the activation energy for the ionic conduction shows a similar trend than those observed in the acoustic attenuation processes, which indicates that both phenomena are closely influenced by the short and medium range structure of the glasses, particularly through the strength of the modifier-oxygen bonds and the glass network reticulation.

1. Introduction

The study of the fundamental properties and relaxation phenomena of phosphate based glasses has gained very much interest in the recent years due to their special chemical and physical characteristics. Even though they often suffer of a limited chemical resistance because of their high hygroscopicity, phosphate glasses have found application fields where they are more suitable than their silicate counterparts. For instance, they are used in very diverse applications such as biomedicine [1], for the storage of radioactive wastes [2] or for the application as high power lasers host materials [3].

The network of phosphate glasses is known to be built up of PO_4 tetrahedra, which can be represented by the Q^n-type groups, according to the nomenclature of Lippmaa et al. [4], where n is the number of bridging oxygen atoms. Thus, metaphosphate glasses, where the O/P ratio equals 3, have a structure based on chains or rings of Q^2-type species, i.e. having two bridging (BO) and two non-bridging (NBO) oxygens [5]. These chains and rings are connected through non-bridging oxygen atoms to the modifier cations.

Recently, Nuclear Magnetic Resonance (NMR) and Raman spectroscopy were used to get more insights into the relationships between the structure of alkali and alkaline-earth and zinc metaphosphate glasses and their viscosity behaviour [6]. It has been found that there is a close relationship between the strength of the metal-oxygen bonds and the activation energy for the viscous flow. The activation energy seems to be much influenced not only by the bond strength but also through the molar volume of the glasses, suggesting that the medium range order structure of the phosphate network, as represented in the form of chains or rings, does also play a key role in the rheological behaviour within the temperature range studied.

As it has been demonstrated previously, acoustic waves are suitable not only for the investigation of materials directly related to acoustics, but also to study the properties of semiconductor structures [7] and glasses [8–12]. In the particular case of lithium and copper bearing phosphate glasses, the authors showed previously that there seems to be a close correlation between the activation energy for the ionic conduction and the activation energy of the acoustic relaxation process below the glass transition temperature [8,9]. In these glasses, the temperature dependences of acoustic attenuation generally showed one or more peaks which have been attributed to different relaxation mechanisms related to ion hopping processes of mobile cations, the glass network structure and dynamics connected with local distortions and diffusion [13]. As Bridge et al. observed [10], the absorption of the acoustic waves as a function of temperature has been ascribed to the presence of particles or groups of particles moving in double-well potentials.

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The aim of the present work was to investigate the possible relationships existing between both acoustic attenuation and ionic conduction properties and how the short and medium range structure of the previously studied metaphosphate glasses may have an influence on them.

2. Experimental

Alkali, alkaline-earth and zinc metaphosphate glasses were prepared by conventional melt-quenching technique as previously described in [6]. Stoichiometric amounts of reagent grade carbonates and $(NH_4)_2HPO_4$ (Merck, 99%) were weighed and mixed. The batches were calcined in porcelain crucibles, held in an electric furnace up to 450 °C, and then melted in an electric furnace during 2 h at temperatures ranging from 800 °C to 1100 °C depending on the composition. The melts were poured onto brass moulds and annealed slightly above their glass transition temperatures (T_g). The glass transition temperature was determined using the thermal expansion curves of the glasses obtained in air with a *Netzsch Gerätebau* dilatometer, *model 402 PC/1* at a heating rate of 2 $K \cdot min^{-1}$. Prismatic samples around 10 mm in length were used for the measurements.

Longitudinal acoustic waves of 13 MHz frequency generated by the Modulator and receiver MATEC 7700 and $LiNbO_3$ transducer acoustically coupled directly to the sample were used to investigate the glasses. Acoustic measurements were performed at temperatures ranging from 290 K to 650 K at a heating rate of 0.5 $K \cdot min^{-1}$. A computer with system LabVIEW 2010 was employed and the data were processed from digital multimeters. An HP digital multimeter measures the temperature of the sample using a thermocouple type T, and the measured voltage is converted to temperature using Newton interpolation method. A second multimeter measures the output voltage from Box-Car which corresponds to the attenuation of acoustic waves. The prepared samples were either cylindrical or square in shape (thickness h = 2.83 to 3.54 mm and 8.9 to 9.1 mm in diameter for the cylindrical samples and area S = 7.1 × 7.6 mm^2 for square samples). Both faces were cut plane-parallel and polished.

The electrical conductivity of the glasses was calculated through the determination of the bulk resistance by Electrochemical Impedance Spectroscopy in a VMP3 potentiostat from BioLogic, within the frequency range of 10 Hz to 1 MHz. For the measurements, gold electrodes were deposited onto both faces of ca. 1 cm^2 square and 2 to 3 mm thick samples. The resistance of the sample is read in the Nyquist plots of the complex versus real impedance at the intersection point with the horizontal axis and the conductivity is calculated using the equation:

$$\sigma = (1/R)(L/A)(S \cdot cm^{-1}) \quad (1)$$

being L/A the sample geometric factor of the sample, where L is thickness and A is sample area.

3. Results

Fig. 1 shows the measured acoustic spectra of the alkaline-earth and zinc bearing investigated glasses. The relaxation processes characterized by the activation energy E_a for jumps over the barrier between two potential minima as well as the typical relaxation frequency of ion hopping, $v_0 = 1/\tau_0 \approx 10^{13}$–$10^{14}$ s^{-1}, can be described by the Arrhenius relation between peak temperature T_{peak} and applied acoustic frequency v [14,15]. From the temperature dependences of acoustic attenuation and positions of the peaks, the activation energy values of dominant processes can be determined by using Eq. (2):

$$v = v_0 \exp\left(-\frac{E_a}{k_B T_{peak}}\right) \quad (2)$$

where v is the characteristic relaxation frequency, v_0 is the pre-exponential factor, E_a is the activation energy of the relaxation process,

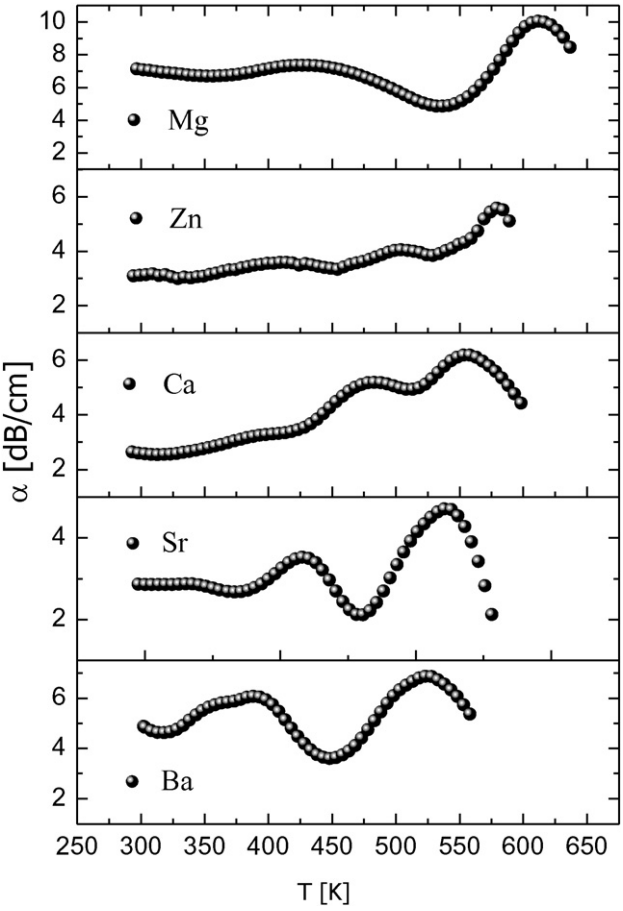

Fig. 1. Acoustic attenuation plots of the alkaline-earth and zinc metaphosphate glasses measured at the frequency of 13 MHz.

k_B is the Boltzmann constant and T_{peak} is the temperature of peak maxima. Theoretical analysis using Double Power Law (DPL) function (Eq. (3)) has given an excellent fit of acoustic attenuation of the different kinds of sites which are responsible for the ionic hopping motion (Fig. 2a), as was pointed in [19].

$$\alpha(\omega, T) \propto \sum_{i=1}^{n} \frac{1}{(\omega\tau)^{-p} + (\omega\tau)^{q}} \quad (3)$$

where n is the number of peaks to fit and p,q are power exponents.

The acoustic attenuation will exhibit a maximum when $\Omega\tau = 1$, where Ω is the angular frequency and τ is relaxation time [19].

Comparatively speaking, the sample $50CaO \cdot 50P_2O_5$ can be fit similarly by four overlapping Gaussian functions (Fig. 2b), as described by Eq. (4),

$$\alpha = \sum_{i=1}^{n} a_i e^{\left[-\left(\frac{x-b_i}{c_i}\right)^2\right]} \quad (4)$$

where a is amplitude, b is centroid (location), c is related to the peak width, n is the number of peaks to fit and x is an independent parameter of temperature dependence of measured acoustic attenuation.

Absorption peaks can be modelled by means of DPL or Gaussian functions and so the activation energy of the different relaxation processes calculated. Fig. 2 (a,b) shows the modelling using DPL and Gauss functions for the glass with composition $Ca(PO_3)_2$. As it can be seen, using different functions, the very close values of activation energies of the same processes were estimated. Both models give a good fit