Acoustic Attenuation Spectra of Metaphosphate Ion Conductive Glasses

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Abstract. The paper deals with analysing of ultrasonic measurements realised at a constant frequency 13 MHz and the temperature above 300 K – acoustic attenuation of metaphosphate ion conductive glasses. Attenuation measurements have revealed that relaxation peaks from experimental studies of glasses are much broader than those from a Debye process. So, for description of loss peak and distribution of relaxation time, which varies with activation energies were used Double Power Law (DPL) and Gaussian functions. From both of the approaches were estimated the value of activation energies of relaxation processes, which are comparable.

1. Introduction
The properties of amorphous materials are much more complicated from those of crystals and description needs much more effort. In our contribution we are focused on phosphate-based glasses, which are new low-energy alternative to silica-based glass. They bring new benefits in cost and energy saving due to ability to be melted at lower temperatures.

Presently, interest in the dynamics in disordered materials is because of their technological applications, dominate in devices as high-energy, environmentally safe batteries, electronic sensors and high power host materials [1-2]. Also, new application ways are shown for using in vitrification of nuclear waste and biomedical applications [3]. In spite of their advantages, in the manufacturing process is still the lack of industrial application for the phosphate glasses [4] due to their low chemical durability. Many researchers deal with the improvement of their chemical properties with an addition of modifier and better understand their structural properties.

Nowadays, phosphate glasses dominate in application for high power lasers host materials, insulation materials in nuclear fission products with a high level of radiation, optoelectronics devices. Phosphate glasses compared with borosilicate glasses are favourable due to their lower temperature of melting procedure and lower viscosity. Brow in his review points out the needs of spectroscopic studies of the structures of phosphate glasses, which could be benefitting from next structural simulation and molecular dynamics calculations. Mainly information based on molecular-level structures will help improve their chemical properties associated with an addition of modifier and give information about their structural changes [5].

The published investigations have aimed mainly on electric properties, much less measurements are about their mechanical response [6]. Spectroscopic studies with acoustic waves are suitable not only

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for the investigation of materials directly related to musical acoustics [7] but they give deeper insight about structure of materials, moreover, they can be used to study the material properties of magnetic fluids [8] and amorphous glasses [9]. The acoustic attenuation measurements, studied as a function of temperature, of a series of metaphosphate glasses have shown a direct connection between the activation energy of the acoustic relaxation processes and the glass composition and network structure [10]. The investigations of ultrasonic relaxation phenomena have performed in two regions: region at high temperature, where particles that are local mobile by thermally activated movement or region at low temperature where particles are activated by tunnelling. The mostly acoustic relaxation measurements were performed for the region below room temperature. The first published data on phosphate glasses for higher temperature were published by Bridge [11]. In general, loss peak from acoustic measurements occurs at temperature well below the glass transition temperature [12]. In our investigation, we are paying attention to the high temperature region (above 300 K) due to a higher glass transition temperature of alkaline-earth metaphosphate glasses in the range 450-650 K. Ultrasonic measurements, at range MHz frequencies are preferred for attenuation measurements in ionic materials. Metaphosphate glasses have structures that are based on phosphate anion. In the metaphosphate glasses, O/P ratio is equal 3. The average chain-length of an anion in these glasses is infinitive due to the typical metaphosphate stoichiometry. Deeper background about the basic structure of phosphate glasses have been in previous studies [13].

2. Theoretical description
Attenuation measurements have revealed that relaxation peaks from experimental studies are much broader than those from a Debye process. From the shapes of mechanical relaxation peaks, we can acquire the distribution of relaxation times, this distribution can be connected to a distribution of activation energies [12]. For fitting of the attenuation peaks were using two approaches, which are used in literature. Gaussian function:

\[ \alpha = \sum_{n=1}^{\infty} a_n e^{-\left(\frac{E_a - E_{\omega n}}{E_{\text{peak}}}/\tau_0\right)^2} \]  

(1)

where \( \alpha \) is the amplitude, \( E_a \) the activation energy with high estimation is dependent on location, \( E_{\text{peak}} \) is related to the width of the distribution, \( n \) is the number of peaks to fit.

Double power law (DPL) function is given by the equation:

\[ \alpha(\omega, T) \propto \sum_{i=1}^{n} \frac{1}{(\omega \tau)^p + (\omega \tau)^q} \]  

(2)

where \( \omega = 2\pi v \) and \( v \) is frequency of acoustic wave and \( p, q \) are power constants. The quantity \( \tau \) is relaxation time. Then the thermally activated relaxation time has formed:

\[ \tau = \tau_0 \exp\left(\frac{E_a}{k_B T_{\text{peak}}}\right) \]  

(3)

where \( \tau_0 \) is the pre-exponential factor (usually, in the literature is used value: \( \tau_0 \sim 10^{14} \text{ Hz} \), \( E_a \) is the activation energy of the relaxation process, \( T_{\text{peak}} \) is the temperature of peak maxima, \( k_B \) is the Boltzmann constant, in accordance with Arrhenius equation.

From the temperature dependences of acoustic attenuation and positions of the peaks, the activation energy values of dominant processes can be determined by using equation (4):

\[ \nu = \nu_0 \exp\left(-\frac{E_a}{k_B T_{\text{peak}}}\right) \]  

(4)

where \( \nu \) is the characteristic relaxation frequency, \( \nu_0 \) is the pre-exponential factor.

Absorption peaks can be modelled by means of DPL or Gaussian functions and so the activation energy of the different relaxation processes calculated.
3. Experimental description
The investigated sample was prepared within the series of metaphosphate glasses at Department Ceramics and Glass Institute in Madrid, Spain. The metaphosphate glass alkaline earth Ba(PO$_3$)$_2$ with composition 50MO · 50 P$_2$O$_5$ (M = Ba), was prepared using the materials: BaCO$_3$ and (NH$_4$)$_2$HPO$_4$ (Merck, 99%), and the components were mixed to temperature 450 °C in an electric furnace, then melted and mixed in the propane atmosphere for 2 h at the temperature ranging from 900 °C to 1200 °C. The melt was poured onto a brass mould and annealed slightly above its glass transition temperature (T$_g$). The glass transition temperature for Ba(PO$_3$)$_2$ is 490˚C.
The acoustic attenuation measurement was performed at a constant frequency 13 MHz. The experimental equipment consist of modulator and receiver MATEC 7700 (the experiment is provided with longitudinal acoustic waves) and LiNbO$_3$ transducer acoustically coupled directly to the sample. Acoustic measurements were performed at temperatures ranging from 290 K to 650 K at a heating rate of 0.5 K / min. The prepared samples were cylindrical and square in the shape with parameters: thickness h = 2.47 mm and diameter d = 7.1 mm. End of faces was polished to be flat and parallel.

4. Result and discussion
The evaluation of mechanical relaxation process in metaphosphate glasses consists of quantity activation energy, which could be connected to a distribution of relaxation time. Description of their distribution time with accordance Eq. (1) and (2), and sum of a number peaks involved in the relaxation process gives the best fit. Figure 1 and Figure 2 shows the plot of temperature dependence of mechanical attenuation with fits of individual processes.

Figure 1. The fitting data of acoustic attenuation vs. temperature for Ba(PO$_3$)$_2$ sample, where the distribution of relaxation time is calculated by Eq. (1), Gaussian function.

Figure 2) The fitting data of acoustic attenuation vs. temperature for Ba(PO$_3$)$_2$ sample, where the distribution of relaxation time is calculated by Eq. (2), DPL function.

Gaussian peaks are encountered in many areas of science, mainly to describe emission spectra and chemical concentration assays [14]. Theoretical analysis using Gaussian and DPL functions gave the excellent fit of experimental spectra and several different kinds of sites, which are responsible for the ionic hopping motion were discovered. 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 of experimental data and their estimations of activation energies are really close.
5. Conclusion

The sample Ba(PO\textsubscript{3})\textsubscript{2} was examined after thermal excitation in range of temperatures below \( T_g \) and the acoustic attenuation was measured. For characterization distribution of relaxation time, which varies with activation energy, were used DPL and Gaussian functions. From the distribution of relaxation times both of the approaches have estimated the value of activation energies (see Figure 1, 2). The spectroscopic study of the structures of alkaline earth phosphate glasses revealed a quantity of activation energies and could be benefit from next structural simulation and molecular calculation.

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