The acoustic attenuation spectra which reflect the basic features of the relaxation and transport processes of the mobile ions of investigated phosphate and oxynitride phosphate glasses are analyzed. Suitable theoretical models and mathematical fit of acoustic spectra are used for characterization of the ionic hopping motion, relaxation processes and transport mechanisms connected with the mobility of conductive ions. Results from acoustic measurements are compared with results obtained from electrical conductivity measurements.

2. Experiment

2.1. Characterisation of the glasses

Lithium phosphate glasses with composition $x\text{Li}_2\text{O}(1-x)\text{P}_2\text{O}_5$ ($x = 55, 57.5 \text{ mol}\%$), were obtained by conventional melt-quenching technique. Stoichiometric amounts of reagent grade raw materials Li$_2$CO$_3$ (Aldrich, 99 %) and (NH$_4$)$_2$HPO$_4$ (Merck, 99 %) were weighed and mixed. The batches were calcined in porcelain crucibles in an electric furnace up to 450 °C, and then melted in a gas furnace (propane/air) during 1 h at temperatures ranging from 800 °C to 1000 °C depending on composition. The compositions of the glasses are given by their molecular formula as Li$_{1.22}$PO$_{3.11}$ and Li$_{1.35}$PO$_{3.18}$ for Li$_2$O contents of 55 and 57.5 mol%, respectively [2].

Oxynitride lithium phosphate glasses were obtained through ammonolysis of the base glasses in an Al$_2$O$_3$ gas-tight tube furnace.
at temperatures from 600 °C to 750 °C and treatment times of 3 h. Base glasses were placed in graphite moulds acting as individual “crucibles” of 2 cm in diameter and 5 mm deep. The furnace was heated up to the treatment temperature at a constant heating rate of 10 K min⁻¹ under N₂ flow. In the present work only two glass compositions of prepared set of samples [2] are studied by acoustic spectroscopy: Li₁₁.₃₅PO₃.₁₈ (C) and Li₁₁.₂₂PO₂.₈₀N₀.₂₁ (BN).

Electrical conductivity measurements were performed by Electrochemical Impedance Spectroscopy (EIS) in a Solartron SI1260 impedance analyzer, in the frequency range from 10 Hz to 10 MHz at temperatures between 40 and 200 °C [2]. The samples were cut into discs of 1–2 mm in thickness and 10 mm in diameter and gold electrodes were sputtered on both faces as contacts for electrical measurements.

2.2. Acoustic measurements

The longitudinal acoustic waves of frequency 13, 17 and 29 MHz were generated by Pulse Modulator and Receiver – MATEC 7700 and LiNbO₃ transducer acoustically bonded to the quartz rod buffer. Acoustic measurements were realized at the temperature range of 290 – 530 K at a heating rate of 0.5 K/min on the same samples that were used previously for electrical measurements. The quartz buffer was used to separate the acoustic signal from thin sample (Fig. 1). The samples for acoustical attenuation measurements were cylindrical in shape (thickness ≈ 1.8 mm and 8.7 mm in diameter) and end faces were polished to be flat and parallel.

3. Theoretical principles

In a dilute system containing a low concentration of mobile ions the acoustic attenuation spectrum may be described as a Debye-like, single relaxation time process in which the individual ion hops occur independently of each other. In such cases, the attenuation α for a wave of angular frequency ω takes the form

\[ \alpha = \Delta \left( \frac{\omega \tau}{1 + \omega^2 \tau^2} \right), \]

where the parameter \( \Delta \) is the relaxation strength and it determines the magnitude of the attenuation peak [8].

The term in the equation (1) in the round brackets describes a Debye peak. The acoustic attenuation will exhibit a maximum when the condition \( \omega \tau \) is equal to 1 and

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

is the most probable relaxation time, \( T \) thermodynamic temperature and \( k_B \) the Boltzmann constant [9]. The relaxation processes, described by the Arrhenius equation (2), are characterized by the activation energy \( E_a \) for jumps over the barrier between two potential minima and typical relaxation frequency of ion hopping \( 1/\tau_0 \approx 10^{13} - 10^{14} \text{ s}^{-1} \).

All the glasses we studied using acoustic spectroscopy exhibit the Arrhenius - type relaxation between the temperature of the peak maximum \( T_{peak} \) and the applied frequency \( f \) of acoustic waves

\[ f = f_0 \exp \left( \frac{E_a}{k_B T_{peak}} \right), \]

where \( f_0 \) is the preexponential factor.

In fact all the investigated relaxation peaks are much broader than Debye peak. It can be interpreted as arising from the existence of a distribution of relaxation times due to random deviations in the local arrangement of the system.

In solid electrolytes the mobile ion concentrations are large and conduction mechanisms are thought to be cooperative. The relaxation phenomena observed in a wide variety of materials exhibit then a power-law type of frequency dependence. The relationship corresponding to the Debye behaviour is expressed in the form [8]

\[ \alpha \approx \frac{1}{T} \left( \frac{\omega \tau}{1 + (\omega \tau)^m} \right)^n. \]

where \( m \) and \( n \) are power-law exponents, which take values between 0 and 1. When \( m = 1 \) and \( n = 0 \), equation (4) reduces to the equation for a single Debye-like process. One of the functions which were mainly used to fit mechanical loss data is the double power law (DPL) [10]

\[ \alpha(\omega, T) \propto \frac{1}{(\omega \tau)^m + (\omega \tau)^n}. \]
Using this function, we can fit also the acoustic attenuation spectrum of the lithium phosphate glasses. Applying the method of genetic algorithm [11] with binary representation of the theoretical attenuation DPL function of variables in connection with the visual construction of the acoustic attenuation model we analyzed then the acoustic spectra obtained on copper phosphate glasses.

4. Experimental results and discussion

The acoustic spectra are illustrated for investigated sample BN and measured at various frequencies in Fig. 2. All acoustic measurements indicate one broad attenuation peak at higher temperature, however, for some dependences we can distinguish two separated peaks.

Applying DPL function (5) we simulated acoustic attenuation spectra at constant frequency as a superposition of individual peaks (Figs. 3–5) and determined the values of activation energies (Tab. 1) of the individual relaxation processes connected with ion hopping.

Using the theoretical double power law (DPL) model we tried to fit the whole acoustic attenuation spectra of investigated samples measured at various frequencies as a superposition of two relaxation processes, respectively. The whole temperature dependence of acoustic attenuation cannot be fitted applying only one DPL function in any case. The whole temperature dependence of acoustic attenuation was analyzed then assuming the existence of at least two thermally activated relaxation processes of Li$^{+}$/H$_{11001}$ ions in connection with different kinds of sites.
There are several categories of relaxation processes connected with temperature peaks of individual processes. Comparing the activation energies obtained from acoustic and electrical measurements (Tab. 1), it seems that essentially the same microscopic processes can be responsible for the electrical and one of the acoustic relaxation processes (the same or very close values of \( E_{a1} \) and \( E_{a2} \)). However, the acoustic spectra are able to detect also other processes compared with electrical spectroscopy.

From acoustic measurements we found lower activation energies for the sample BN in comparison with the sample C. It was found that nitrogen affected the electrical conductivity according to the structural modifications of the glass network induced by nitrogen [2]. Some authors [14] supposed that the decrease in the electrostatic energy when P-O bonds are replaced by more covalent P-N bonds may cause the decrease in the electrostatic activation energy and increase in ionic conductivity. The effect of nitrogen on conductivity can be explained by higher cross-linking density introduced by nitrogen atoms, which should facilitate the lithium transfer between phosphate units. The higher amount of non-bridging oxygen atoms created by nitridation could increase the number of hopping positions for Li\(^{+}\) ions creating conduction paths with lower activation energy and the rising of the electrical conductivity as a consequence of this [2].

### 5. Conclusion

The experimental investigation of the lithium phosphate and oxynitride phosphate glasses proved that acoustical spectroscopy can be a very useful technique for the study of relaxation and transport mechanisms in ion conductive glasses. Using the theoretical model of Double Power Law function for the simulation of acoustic spectra we can better determine and describe the relaxation processes and transport mechanism of mobile ions. Several different kinds of sites responsible for ionic hopping motion were discovered and described. The comparison of activation energies obtained from acoustic and electrical measurements showed that the same microscopic processes can be responsible for the acoustic and electrical relaxation processes, however the acoustic spectroscopy can detect also some minor processes. It was found that the activation energy connected with main attenuation peak decreases with increasing content of nitrogen. Nitridation increases the amount of non-bridging oxygen atoms and cross-linking density which increases the electrical conductivity of the oxynitride phosphate glasses connected with decrease of the activation energy.

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