The research of lithium conducting glasses has recently seen an increase due to their potential application mainly as solid-state amorphous electrolytes in secondary batteries and the advantages they may offer [1]. In a secondary lithium ion battery, Li metal can be used as the anode material allowing higher energy and power densities than when graphitized anodes are used as anode materials, and one of the most important requirements of the electrolyte material in such a system is to have a high ionic conductivity and being compatible with the electrode materials. The use of solid electrolytes in rechargeable batteries can provide numerous advantages such as the possibility of miniaturization through thin-film production, longer active life, high reliability, thermal, chemical and mechanical stability. Most of the works have been focused on the ionic conductivity of LiPON thin-films, which is generally given around $2 \times 10^{-4}$ S/cm at 25°C [2] and average activation energy of $E_a = (0.55 \pm 0.02)$ eV [3]. LiPON thin-film electrolytes have been recently studied and their properties and structure compared to those found in lithium phosphate glasses and their oxynitride counterparts [4 and 5]. The structure of a LiPO$_3$ metaphosphate glass is known to be built of long chains or rings of PO$_4$ tetrahedra [6]. Two of the oxygens in each PO$_4$ are bridging oxygens that link together neighbouring groups while the other two are non-bridging oxygens bonded to the modifier cations Li$^+$. On the other hand, the structure of an oxynitride glass will be formed by PO$_4$ and also by new groups, PO$_x$N and PO$_y$N$_z$ tetrahedra, having nitrogen in two different bonding states, as dicoordinated –N= (Nd) or tricoordinated –N< (Nt) nitrogen species. The study of the relaxation processes taking place in these glasses can be important for the future development of all solid-state electrolytes.

The acoustic attenuation spectroscopy in connection with conductivity and dielectric relaxation spectroscopy can be useful techniques for the study of relaxation processes and transport mechanisms in Li$^+$ ion conducting glasses. A theoretical model and mathematical fit of acoustic and conductivity measurements are used for characterization of the ionic hopping motion, relaxation processes and transport mechanisms connected with the mobility of conducting Li$^+$ ions. Results from acoustic measurements are compared with results obtained from electrical conductivity measurements.

**Keywords:** Acoustic spectroscopy, conductivity spectroscopy, dielectric spectroscopy, Li phosphate glasses, relaxation and transport processes.

1. Introduction

The research of lithium conducting glasses has recently seen an increase due to their potential application mainly as solid-state amorphous electrolytes in secondary batteries and the advantages they may offer [1]. In a secondary lithium ion battery, Li metal can be used as the anode material allowing higher energy and power densities than when graphitized anodes are used as anode materials, and one of the most important requirements of the electrolyte material in such a system is to have a high ionic conductivity and being compatible with the electrode materials. The use of solid electrolytes in rechargeable batteries can provide numerous advantages such as the possibility of miniaturization through thin-film production, longer active life, high reliability, thermal, chemical and mechanical stability. Most of the works have been focused on the ionic conductivity of LiPON thin-films, which is generally given around $2 \times 10^{-4}$ S/cm at 25°C [2] and average activation energy of $E_a = (0.55 \pm 0.02)$ eV [3]. LiPON thin-film electrolytes have been recently studied and their properties and structure compared to those found in lithium phosphate glasses and their oxynitride counterparts [4 and 5]. The structure of a LiPO$_3$ metaphosphate glass is known to be built of long chains or rings of PO$_4$ tetrahedra [6]. Two of the oxygens in each PO$_4$ are bridging oxygens that link together neighbouring groups while the other two are non-bridging oxygens bonded to the modifier cations Li$^+$. On the other hand, the structure of an oxynitride glass will be formed by PO$_4$ and also by new groups, PO$_x$N and PO$_y$N$_z$ tetrahedra, having nitrogen in two different bonding states, as dicoordinated –N= (Nd) or tricoordinated –N< (Nt) nitrogen species. The study of the relaxation processes taking place in these glasses can be important for the future development of all solid-state electrolytes.

The acoustic attenuation measurements seem to be a useful technique for investigation of transport mechanisms in conducting glasses and compared to the electrical one it has even some advantages as high sensitivity, the absence of contact phenomena and several others [7]. Acoustical measurements made over a wide range of frequencies and temperatures can characterize different relaxation processes according to corresponding transport mechanisms due to the strong acousto-ionic interaction and it can discover also different kinds of sites and/or ionic hopping motions associated with the charge mobility [8]. The dielectric spectroscopy in principle derived from the same experimental data as electrical conductivity spectroscopy (i.e., real and imaginary components of the sample impedance) is another powerful technique for the study of ion relaxation and transport mechanisms [9 and 10]. The shape of the loss tangent angle $\tan \delta(\omega)$ is actually sensitive to the imaginary part of the permittivity $\varepsilon''(\omega)$ passes through a maximum at a frequency which is temperature dependent and whose inverse is commonly associated with the characteristic time required for dipoles to reorient.

In this contribution we present first results of combined acoustic and electrical investigation of LiPO$_3$ metaphosphate...
glasses. Double Power Law (DPL) model is used for description of experimental results obtained from acoustic spectra of the glasses with the purpose to study ion relaxation processes and transport mechanisms. Electrical measurements characterizing the ion relaxation processes and possible transport mechanisms in investigated ion conducting glasses are presented. The results obtained by different methods are then summarized and compared.

2. Theoretical principles

The acoustic attenuation will exhibit a maximum when the condition \( \tan \delta = 1 \) and

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

is the most probable relaxation time, \( T \) thermodynamic temperature, \( k_B \) the Boltzmann constant, \( \omega = 2\pi f \) and \( f \) is frequency of applied acoustic waves. The relaxation processes, described by an Arrhenius equation (1), are characterized by activation energy \( E_a \) for jumps over the barrier between two potential minima and typical relaxation frequency of ion hopping \( 1/T \approx 10^{11} - 10^{14} \) s\(^{-1} \). An Arrhenius - type relaxation between the temperature of peak maximum \( T_{peak} \) and the applied frequency \( v \) of acoustic waves can be then expressed as

\[
V = V_0 \exp \left( -\frac{E_a}{k_B T_{peak}} \right),
\]

where \( V_0 \) is the preexponential factor [11].

Double Power Law (DPL) function (3) has been mainly used to fit mechanical loss data in investigated glassy materials [11 and 12]

\[
\tilde{\sigma}(\omega, T) = \sigma_0 \frac{1}{\omega^\alpha + (\omega/\tau)^\beta}.
\]

Using this function, we can fit also the acoustic spectrum of the lithium metaphosphate glass.

Determination of the imaginary part of the complex dielectric constant (\( \varepsilon '' \)) compared to the real part (\( \varepsilon ' \)) play a crucial role in the study of fundamental properties of investigated materials [13], where \( \varepsilon ' (\omega) \) and \( \varepsilon '' (\omega) \) characterize the refractive and absorptive properties of the material, respectively. The loss tangent defined by the relation

\[
\tan \delta (\omega) = \frac{\varepsilon '' (\omega)}{\varepsilon ' (\omega)}.
\]

can be also used for the relaxation spectroscopy that reflects the basic features of the relaxation processes of mobile ions. This quantity is related to the attenuation constant (or absorption coefficient) of an electromagnetic wave propagating in a material. The activation energies of the relaxation processes can be estimated from the plots of \( \log f \) vs. \( 1/T_{peak} \) were \( T_{peak} \) can be found using the isochronal peaks of \( \tan \delta (\omega, T) \). These plots are straight lines in accordance with Arrhenius equation

\[
f = f_0 \exp \left( -\frac{E_{ac}}{k_B T} \right),
\]

where \( f \) is the frequency of the applied electrical field, \( f_0 \) is the pre-exponential factor, \( E_{ac} \) is the activation energy associated to the dielectric loss [14].

The electrical conductivity \( \sigma \) of many solids, including glasses, polymers and crystals, has been shown to consist of a frequency independent and a strongly frequency dependent component [15]. Experimental data in a limited frequency region revealed that the overall frequency dependence of \( \sigma \) or the so called “universal dynamic response” (UDR) of ionic conductivity can be approximated by the following simple relation

\[
\tilde{\sigma}(\omega) = \sigma_{dc} + \sigma \omega = \sigma_0 \exp \left( -\frac{E_{ac}}{k_B T} \right) + \sigma \omega',
\]

where \( \omega (=2\pi f) \) is the angular frequency of measurement. Both \( \sigma_{dc} \) and \( \omega' \) follow Arrhenius type strong temperature dependencies. In Eq. 6 \( \sigma_0 \) is the pre-exponential factor, \( E_{ac} \) is the activation energy of the ion transport through hopping processes which can be determined from the DC measurements.

3. Experimental

A lithium metaphosphate glass with composition \( 50Li_2O.50P_2O_5 \) was prepared by conventional melt-quenching procedure. Reagent grade raw materials analytically pure Li_2CO_3 and \((NH_4)_2HPO_4 \) were mixed in stoichiometric amounts and the batch was calcined in a porcelain crucible up to 450 °C, in an electric furnace, then melted during 2 h at 800 °C. The melt was poured onto a brass mould and annealed slightly above its glass transition temperature, previously determined through Differential Thermal Analysis.

Experimental arrangement for acoustic attenuation measurement has been already described in [16]. The longitudinal acoustic waves of frequency 13 MHz were generated by the Pulse Modulator and Receiver - MATEC 7700 and a LiNbO_3 transducer acoustically bonded to a quartz rod buffer. The computer system was used to trigger the apparatus, to record the attenuation changes and to evaluate obtained acoustic spectra. We performed acoustic measurements of the signal going only through the rod buffer without studied sample. So that for the sample investigation we have used only acoustic attenuation on investigated sample.

The electrical conductivity measurements were performed by the FLUKE PM 6306 RCL impedance analyzer at frequencies in the range 50 Hz to 1 MHz. The acoustic and electrical measurements
We have found that activation energy for conduction $E_{a,\text{DC}}$ is very close to activation energy $E_{a1}$ of the main relaxation process calculated from acoustic measurement which can be connected with the same microscopic process. However, the acoustic spectra detected also a second process, which could be related to the appearance of the glass transition with activation energy $E_{a2} = 0.83 \text{ eV}$.

It is known that the conductivity of glasses shows a change in activation energy when passing over the glass transition [17]. Therefore, the second thermally activated process that has been seen through the acoustic measurements, with $E_{a2} = 0.83 \text{ eV}$, could correspond to movement of Li$^+$ ions above $T_g$.

Complex impedance $Z' = Z' - jZ''$ plots at the temperatures from $T = 330 - 390 \text{ K}$ are illustrated in the insert of Fig. 2. The Nyquist plot consists of a depressed semicircle. The $\sigma_{\text{DC}}$ was calculated using the relation $\sigma_{\text{DC}} = \frac{d}{RA}$, where $d$ is the thickness of the bulk glass piece and $A$ is the area of cross section of the glass piece, resistance $R$ was calculated from the Nyquist plot. The DC conductivity was observed above 310 K and is ranged from $6.5 \times 10^{-9} \text{ S/cm}$ at 330 K to $2.1 \times 10^{-4} \text{ S/cm}$ at 550 K. The increase of DC conductivity with the temperature indicates a thermally activated conduction mechanism. The representative Arrhenius plot for investigated sample is illustrated in Fig. 2.

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The real part of the complex relative permittivity versus frequency has been reported in Fig. 5. The behaviour of conductivity and permittivity is divided in two regimes: regime II can be observed only at low temperatures (310 K – 350 K). The conductivity at low temperatures and high frequencies is increased dramatically with the frequency and the permittivity is almost the same in anyway of the frequency and the temperature. Regime III is appeared at higher temperatures. The conductivity is almost constant and corresponds to the $\sigma_{DC}$. The permittivity curve shows a slope. In this frequency range, ions jump from site to site through the bulk of the electrolyte. This corresponds to the random diffusion of Li ions in a disorder matrix [18].

5. Conclusion

Acoustical and conductivity measurements and dielectric relaxation behaviour have been examined over a wide temperature range in the glass with metaphosphate composition LiPO$_3$. Using the theoretical model of Double Power Law function for the simulation of acoustic spectra we have determined the main relaxation process. Comparison the activation energies obtained from acoustic and electric DC measurements showed that the same microscopic phenomena can be responsible for the acoustic and electrical relaxation processes.
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