# Structural and Electrical Properties of LiPO₃ Glasses

*Peter HOCKICKO[1], Jozef KUDELCIK[1], Francisco MUNOZ[1],
Laura MUNOZ-SENOVILLA[2]*

[1]Department of Physics, Faculty of Electrical Engineering, University of Zilina, Univerzitna 1,
010 26 Zilina, Slovakia
[2]Ceramics and Glass Institute (CSIC), Kelsen 5, 280 49 Madrid, Spain

hockicko@fyzika.uniza.sk, kudelcik@fyzika.uniza.sk, fmunoz@icv.csic.es, lmsenovilla@icv.csic.es

**Abstract.** *This paper reports on the structural and electrical properties of LiPO₃ glass over a wide range of frequencies (10 Hz–2 MHz) and temperatures (290 K–627 K). The temperature dependence of a.c. conductivity is studied at different frequencies. The d.c. conductivity is due to the hopping of lithium ions. A theoretical model and mathematical fit of conductivity measurements are used for characterization of the ionic hopping motion connected with the mobility of conducting Li⁺ ions. The acoustic attenuation spectroscopy can be useful technique for the study of relaxation processes in ion conducting glasses too. Raman experiments showed the rings and chains configuration at the medium range.*

## Keywords

*Conductivity spectroscopy, dielectric spectroscopy, Li phosphate glasses, relaxation and transport processes.*

## 1. Introduction

Lithium-ion conducting glasses have been widely studied due to their potential application as solid-state amorphous electrolytes in secondary batteries [1]. Lithium-ion batteries are the major power source for portable electronic devices such as cellular phones, laptops, cameras, camcorders, etc. [2]. 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. 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.

Many works have been focused on the ionic conductivity of LiPON thin-film electrolytes and their properties and structure compared to those found in lithium phosphate glasses and their oxynitride counterparts [3], [4].

The structure of a LiPO₃ metaphosphate glass is known to be built of long chains or rings of PO₄ tetrahedra (Fig. 1) [5]. Two of the oxygens in each PO₄ are bridging oxygens that link together neighbouring groups while the other two are non-bridging oxygens bonded to the modifier cations Li⁺. The study of the transport and relaxation processes taking place in these glasses can be important for the future development of amorphous solid-state electrolytes.

The conductivity and dielectric relaxation spectroscopies are powerful techniques for the study of ion relaxation and transport mechanisms [6].

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 also discover different kinds of sites and/or ionic hopping motions associated with the charge mobility [8].

In this contribution we present the results of an electrical and structural investigation of a LiPO₃ metaphosphate glass. Electrical and acoustic measurements characterizing the ion relaxation processes and
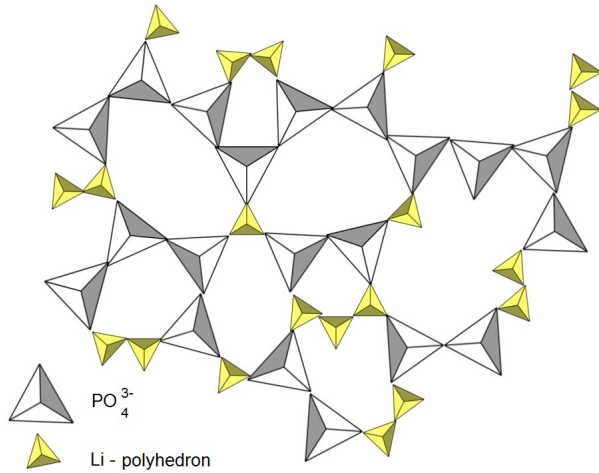
**Fig. 1:** Structure of LiPO$_3$.

possible transport mechanisms in investigated ion conducting glasses are presented.

## 2. Theoretical Principles

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 [9]. 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 Jonscher's power law equation

$$\sigma(\omega) = \sigma_{DC} + A\omega^s, \qquad (1)$$

where $\omega = 2\pi f$ is the angular frequency of measurement and $s$ is the frequency exponent in the range $0 < s < 1$. Both $\sigma_{DC}$ and $A$ follow Arrhenian type temperature dependencies and

$$\sigma_{DC} = \sigma_0 \exp\left(-\frac{E_a^{DC}}{k_B T}\right), \qquad (2)$$

where $\sigma_0$ is the pre-exponential factor, $k_B$ is the Boltzmann constant, $E_a^{DC}$ is the activation energy of the conduction process, which can be determined from the $DC$ measurements. The frequency-independent conductivity at low frequencies indicated the long-range transport of activated charges in response to the applied electric field. The power law feature ($\sigma \sim A\omega^s$) is usually observed at higher frequencies. Electrical conductivities of investigated materials are calculated using the following equation

$$\sigma = \frac{h}{RS}, \qquad (3)$$

where $h$ is thickness of sample, $S$ is area of sample (electrode), $R$ is resistance read from the Nyquist plots (imaginary part of complex impedance $Z''$ versus real part $Z'$), where complex impedance of material is given by equation

$$Z^* = Z' - jZ''. \qquad (4)$$

The complex permittivity of materials is given by

$$\varepsilon^* = \frac{1}{j\omega C Z^*} = \varepsilon' - j\varepsilon, \qquad (5)$$

where $\varepsilon'$ is the dielectric constant, $\varepsilon''$ the dielectric loss, $C = \varepsilon_0 S/h$, $\varepsilon_0$ is free space permittivity. The determination of the imaginary part ($\varepsilon''$) of the complex dielectric constant compared to the real part ($\varepsilon'$) plays a crucial role in the study of the fundamental properties of the investigated materials [10], where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ characterize the refractive and absorptive properties of the material, respectively. The loss tangent (dissipation factor) defined by the relation

$$\tan\delta(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}, \qquad (6)$$

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 complex electric modulus of a material is given by

$$M^* = \frac{1}{\varepsilon^*} = j\omega C Z^* = M' + jM''. \qquad (7)$$

The imaginary part of the electric modulus ($M''$) vs frequency at constant temperature increases with frequencies and reach a maximum peak value. The activation energies of the relaxation processes can be estimated from the plots of $\ln f$ vs $1/T_{max}$ were $T_{max}$ can be found using the isochronal peaks of $M''$ or $\ln f_{max}$ vs $1/T$ (from isothermal plots). These plots are straight lines in accordance with Arrhenius equation

$$f = f_0 \exp\left(-\frac{E_a^M}{k_B T}\right), \qquad (8)$$

where $f$ is the frequency of the applied electrical field, $f_0$ is the pre-exponential factor and $E_a^M$ is the activation energy associated to the dielectric loss [11]. It is an established fact that the condition for observing a maximum in the dielectric losses is given by the relation [12], [13]

$$\omega_m \tau_m = 1, \qquad (9)$$

where $\omega_m = 2\pi f_{max}$ ($f_{max}$ being the frequency corresponding to the maximum of $M''(f)$) and $\tau_m$ is the

relaxation time. A maximum can be observed when hopping or jumping frequency of ions becomes approximately equal to the frequency of the applied field.

The acoustic attenuation will exhibit a maximum when the condition $\omega\tau$ is equal to 1 and

$$\tau = \tau_0 \, \exp\left(\frac{E_a^a}{k_B T_{peak}}\right), \qquad (10)$$

is the most probable relaxation time, $T_{peak}$ is thermodynamic temperature, $\omega = 2\pi\nu$ and $\nu$ is frequency of applied acoustic waves. The relaxation processes, described by an Arrhenius equation Eq. (10), are characterized by activation energy $E_a^a$ for jumps over the barrier between two potential minima and typical relaxation frequency of ion hopping $1/\tau_0 \approx 10^{13}$–$10^{14}$ s$^{-1}$. An Arrhenius – type relaxation between the temperature of peak maximum $T_{peak}$ and the applied frequency $\nu$ of acoustic waves can be then expressed as

$$\nu = \nu_0 \, \exp\left(\frac{E_a^a}{k_B T_{peak}}\right), \qquad (11)$$

where $\nu_0$ is the preexponential factor [14].

Double Power Law (DPL) function Eq. (12) has been mainly used to fit mechanical loss data in investigated glassy materials [14]

$$\alpha(\omega, T) \propto \frac{1}{(\omega\tau)^{-n} + (\omega\tau)^m}. \qquad (12)$$

# 3. Experimental

A lithium metaphosphate glass with composition $50Li_2O. \ 50P_2O_5$ was prepared by conventional melt-quenching procedure. Reagent grade raw materials $Li_2CO_3$ and $(NH_4)_2HPO_4$ were mixed in stoichiometric amount 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.

The electrical conductivity measurements were performed by the FLUKE PM 6306 RCL impedance analyzer at frequencies in the range 0 Hz to 1 MHz and the LCR Meter OT 7600 Plus at frequencies in the range 10 Hz to 2 MHz (200 measurements at constant temperature). The electrical measurements were carried out by FLUKE at temperatures ranging from 290 K to 540 K at a heating rate of 0.5 K/min. Using LCR Meter we carried out measurements at chosen temperatures (5 minutes per measurement, 30 minutes for stabilization of measured system), some of them were above Tg point of investigated sample up to 627 K.

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 sample. The computer system was used to trigger the apparatus, to record the attenuation changes and to evaluate obtained acoustic spectra.

The sample for electrical and acoustic measurements was square in shape (thickness $\approx 1.82$ mm and area $= 10.1 \times 10.1$ mm$^2$) and end faces were polished to be flat.

# 4. Results and Discussion

The Nyquist plots of investigated sample LiPO$_3$ are shown in Fig. 2. As it can be seen, the Nyquist plots consist of semicircle. The semicircles are due to parallel combination of resistive and capacitive properties of the investigated material. The equivalent circuit for the observed impedance spectra can be seen in Fig. 2. The resistance $R$ has been calculated from the low-frequency interception of the real axis of $Z''$ vs $Z'$ graphs.
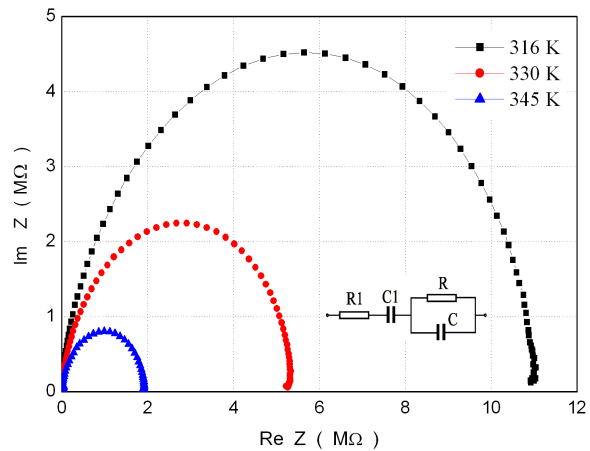


**Fig. 2:** Nyquist plots of LiPO$_3$ glass sample.

Figure 3 and Fig. 4 describe frequency dependencies of real and imaginary part complex impedance.

The equivalent circuit is divided in 2 parts in the series: series and parallel connection of $R$ and $C$. The circuit elements $R1$ and $R$ are related to d.c. conductivity and the ionic a.c. conductivity of the glass, respectively. $C$ is the a.c. conductivity of the LiPO$_3$ into the bulk capacitance. Capacitance $C1$ causes decrease of imaginary part of complex impedance to zero at low frequencies.

Using symbolic-complex method of circuit analysis the equivalent circuit can be written in the form Eq. (4)
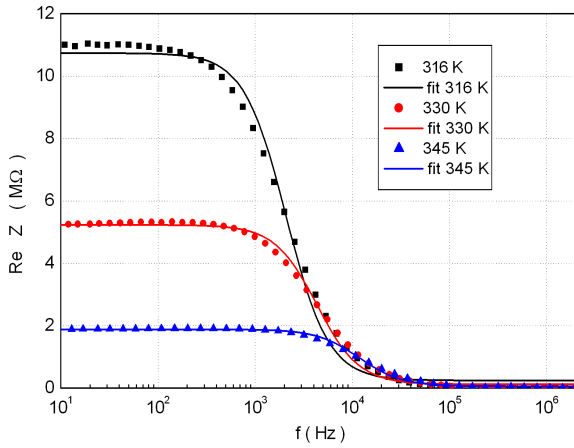
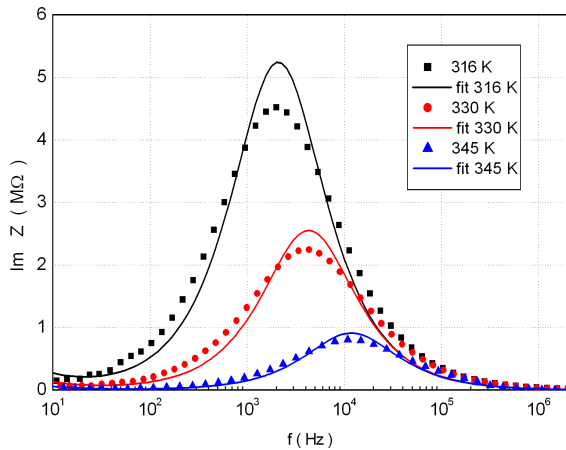**Fig. 3:** Frequency dependence of the real part of complex impedance.



**Fig. 4:** Frequency dependence of the imaginary part of complex impedance.

where real and imaginary parts are

$$Z' = R1 + \frac{R}{1 + \omega^2 R^2 C^2}, \tag{13}$$

$$Z'' = -\frac{1}{\omega C1} + \frac{\omega R^2 C}{1 + \omega^2 R^2 C^2}, \tag{14}$$

where values of $R$, $C$, $R1$ and $C1$ are summarized in Tab. 1. The real and imaginary parts of measured data were fitted simultaneously by previous functions in program Microcal Origin. The observed differences of constructed peaks indicates the non-Debye behavior of investigated materials.

The temperature dependence of d.c. conductivity indicates one main transport mechanism with activation energy $E_a^{DC}$. We measured conductivity parameters two times, first using FLUKE by constant heating rate (0.5 K/min.) (blue squares), second time by LCR Meter at constant temperature (30 min. for stabilization and 5 min. for measurement) (black circles) especially

**Tab. 1:** Fitted parameters in complex impedance for various temperatures.

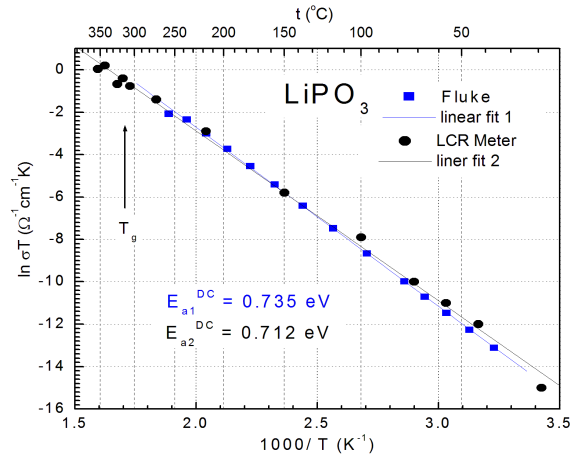| T [K] | 345 | 330 | 316 |
|---|---|---|---|
| **R1 [ kΩ ]** | 65.8 | 128.5 | 252.6 |
| **C1 [ nF ]** | 276.5 | 129.3 | 70.3 |
| **R [ MΩ ]** | 1.8 | 5.1 | 10.5 |
| **C [ pF ]** | 7.40 | 7.22 | 7.26 |



**Fig. 5:** Arrhenius plots constructed from temperature dependences of d.c. conductivity calculated from Nyquist diagrams.

above $Tg$ point ($Tg = 589$ K). As it can be seen, the calculated values of d. c. conducitvities are very close.

In Fig. 6, the imaginary part of the modulus is plotted against frequency at different temperatures. As it can be seen the imaginary part displays a peaked function. The electric modulus $M''$ increases with frequency and reaches a maximum $M''_{max}$, which is moving to higher frequencies with increasing temperature.
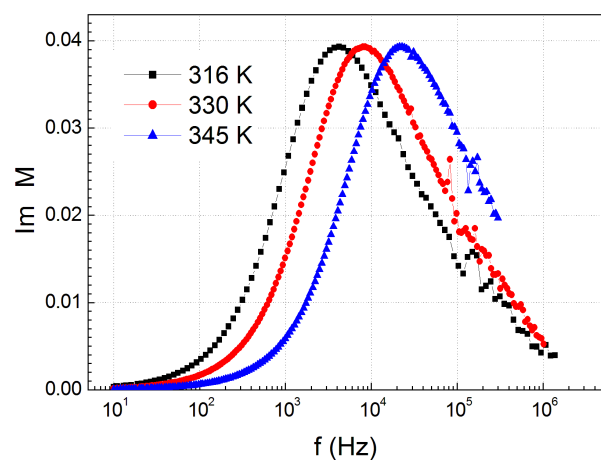


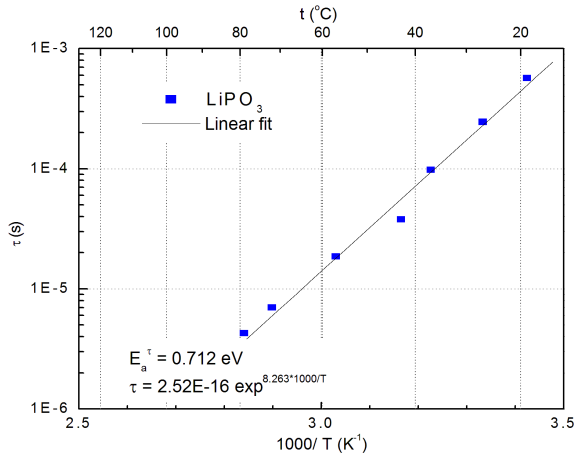**Fig. 6:** Frequency dependence of the imaginary part of electric modulus.

**Fig. 7:** Arrhenius plots constructed from temperature dependences of relaxation times.
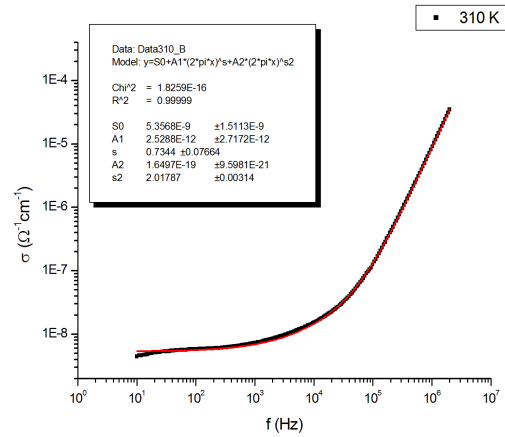


**Fig. 8:** Modelled electrical conductivity.

The relaxation time obtained from the positions of the peaks of the imaginary part of the electric modulus (the position of the characteristic relaxation frequency $f_{max}$) calculated by means of Eq. (9) has been plotted as a function of inverse temperature in Fig. 7. It is seen that the relaxation time follows the Arrhenius behaviour

$$\tau = \tau_0 \exp\frac{E_a^\tau}{k_B T}. \tag{15}$$

It can be seen, that the values of $E_a^\tau$ and $E_a^{DC}$ obtained from the slopes of straight lines (Fig. 5 and Fig. 7) are comparable (the same). This can be explained because that the ionic motion responsible for difusion of independent electrical relaxation and difussive translation motion are the same [12].

Next Fig. 8 shows modelled a.c. conductivity using equation

$$\sigma(\omega) = \sigma_0 + A_1\omega^s + A_2\omega^{s_2}. \tag{16}$$

Parameters $A_1$, $A_2$, $s$, $s_2$, $\sigma_0$ were calculated by program Microcal Origin.

From Fig. 9 the temperature and frequency dependences of loss tangent of $LiPO_3$ structure in 3D presentation can be seen.

The acoustic attenuation spectrum (Fig. 10) indicates one broad attenuation peak with a maximum at a temperature about 530 K. Applying DPL function Eq. (12) we could simulate acoustic attenuation spectra at constant frequency as a superposition of individual peaks and determined the values of activation energies of the individual relaxation processes connected with ion hopping. The other peak occurring at the temperature higher than 590 K are connected with the processes appearance above the glass transition temperature, $T_g$ (for investigated sample $T_g = 587$ K). The broad attenuation peak with a maximum at a temperature about 530 K could not be modelled only by one
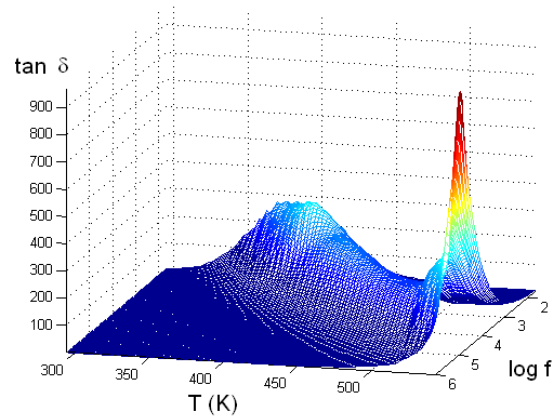


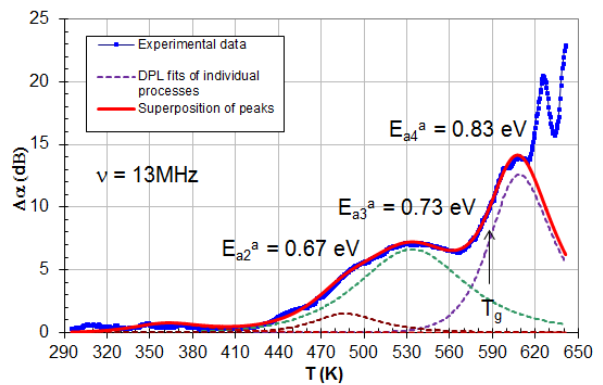**Fig. 9:** Temperature and frequency dependence of loss tangent in 3D.



**Fig. 10:** Analysis of acoustics attenuation measurement.

peak, another small peak with a maximum at a temperature about 485 K was necessary.

The whole temperature dependence of acoustic attenuation has been analyzed assuming the existence of a thermally activated relaxation process associate to $Li^+$ ions. Using the theoretical DPL model Eq. (12),

and Arrhenius equation Eq. (11), we calculated the energy of the main relaxation process, $E_{a2}^a = 0.73$ eV from acoustic attenuation measurement. This value is very close to the activation energy for conduction found from DC measurements $E_a^{DC} = 0.735$ eV (Fig. 5). Using AC measurements and electric modulus the activation energy of the $E_a^\tau = 0.712$ eV was obtained (Fig. 7).

Figure 11 and Fig. 12 show the Raman spectra collected for the metaphosphate LiPO$_3$. The spectra were decomposed into Gaussian contributions from 600 cm$^{-1}$ to 1400 cm$^{-1}$. The spectra are dominated by two main bands appearing at about 650–750 cm$^{-1}$ and 1150–1250 cm$^{-1}$ and attributed to the symmetric stretching modes of P–O–P and NBO–P–NBO bonds, respectively [15]. The P–O bond bending mode of Q$^2$ units appears as a broad shape in the range of 200 cm$^{-1}$ to 400 cm$^{-1}$. The band attributed to the asymmetric stretching mode of the NBO–P–NBO bonds in Q$^2$ groups is located around 1280 cm$^{-1}$.
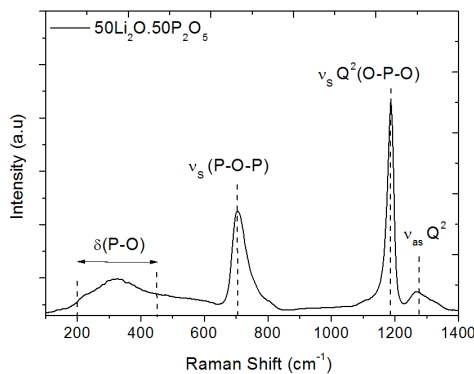


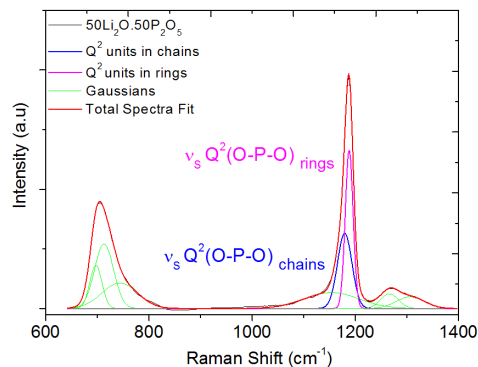**Fig. 11:** Raman spectra of LiPO$_3$ glass.



**Fig. 12:** Modelled Raman spectra of LiPO$_3$ glass.

## 5. Conclusions

The electrical, dielectric and structural properties of LiPO$_3$ glass sample have been investigated and described. The theoretical model has been used for better characterization the measured data. The broadness of the peaks and differences with measured data show non-Debye behavior, what corresponds to the relaxation of hopping charges.

The modulus study, especially the shift of maxima in temperature dependencies towards to high-frequency side could be due to the high values of hopping probability per unit time in the sample.

Using the theoretical model of Double Power Law function for the simulation of acoustic spectra we have determined the several relaxation processes.

## Acknowledgment

## References

[1] MOREAU, F., A. DURAN and F. MUNOZ. Structure and properties of high Li$_2$O-containing aluminophosphate glasses. *Journal of the European Ceramic Society*. 2009, vol. 29, iss. 10, pp. 1895–1902. ISSN 0955-2219. DOI: 10.1016/j.jeurceramsoc.2008.12.016.

[2] LIU, J.-R., M. WANG, X. LIN, D.-C. YIN and W.-D. HUANG. Citric acid complex method of preparing inverse spinel LiNiVO$_4$ cathode material for lithium batteries. *Journal of Power Sources*. 2002, vol. 108, iss. 1–2, pp. 113–116. ISSN 0378-7753. DOI: 10.1016/S0378-7753(02)00010-1.

[3] MUNOZ, F., A. DURAN, L. PASCUAL, L. MONTAGNE, B. REVEL and A. RODRIGUES. Increased electrical conductivity of LiPON glasses produced by ammonolysis. *Solid State Ionics*.

2008, vol. 179, iss. 15–16, pp. 574–579. ISSN 0167-2738. DOI: 10.1016/j.ssi.2008.04.004.

[4] MASCARAQUE, N., J. L. G. FIERRO, A. DURAN and F. MUNOZ. An interpretation for the increase of ionic conductivity by nitrogen incorporation in LiPON oxynitride glasses. *Solid State Ionics*. 2013, vol. 233, iss. 1, pp. 73–79. ISSN 0167-2738. DOI: 10.1016/j.ssi.2012.12.017.

[5] BROW, R. K. Review: the structure of simple phosphate glasses. *Journal of Non-Crystalline Solids*. 2000, vol. 263–264, iss. 1, pp. 1–28. ISSN 0022-3093. DOI: 10.1016/S0022-3093(99)00620-1.

[6] HOCKICKO, P., P. BURY and F. MUNOZ. Investigation of relaxation and transport processes in LiPO(N) glasses. *Journal of Non-Crystalline Solids*. 2013, vol. 363, iss. 1, pp. 140–146. ISSN 0022-3093. DOI: 10.1016/j.jnoncrysol.2012.12.027.

[7] ROLING, B., A. HAPPE, M. D. INGRAM and K. FUNKE. Interrelation between Different Mixed Cation Effects in the Electrical Conductivity and Mechanical Loss Spectra of Ion Conducting Glasses. *The Journal of Physical Chemistry B*. 1999, vol. 103, iss. 20, pp. 4122–4127. ISSN 1520-6106. DOI: 10.1021/jp9839652.

[8] FUNKE, K. Ion transport in fast ion conductors — spectra and models. *Solid State Ionics*. 1997, vol. 94, iss. 1, pp. 27–33. ISSN 0167-2738.

[9] JONSCHER, A. K. The 'universal' dielectric response. *Nature*. 1977, vol. 267, iss. 5613, pp. 673–679. ISSN 0028-0836. DOI: 10.1038/267673a0.

[10] VENKATESH, J., V. SIVASUBRAMANIAN, V. SUBRAMANIAN and V. R. K. MURTHYA. Far-IR reflectance study on B-site disordered Ba $(Zn_{1/3}Ta_{2/3})O3$ dielectric resonator. *Materials Research Bulletin*. 2000, vol. 35, iss. 8, pp. 1325–1332. ISSN 0025-5408. DOI: 10.1016/S0025-5408(00)00335-4.

[11] PEVZNER, B., A. F. HEBARD and M. S. DRESSELHAUS. Role of molecular oxygen and other impurities in the electrical transport and dielectric properties of $C_{60}$ films. *Physical Review B*. 1997, vol. 55, iss. 24, pp. 16439–16449. ISSN 0163-1829.

[12] KARAN, N., B. NATESAN and R. KATIYAR. Structural and lithium ion transport studies in borophosphate glasses. *Solid State Ionics*. 2006, vol. 177, iss. 17–18, pp. 1429–1436. ISSN 0167-2738. DOI: 10.1016/j.ssi.2006.07.032.

[13] SOARES, B. G., M. E. LEYVA, G. M. O. BARRA and D. KHASTGIR. Dielectric behavior of polyaniline synthesized by different techniques. *European Polymer Journal*. 2006, vol. 42, iss. 3, pp. 676–686. ISSN 0014-3057. DOI: 10.1016/j.eurpolymj.2005.08.013.

[14] BURY, P., P. HOCKICKO, M. JAMNICKY. Transport and Relaxation Study of Ionic Phosphate Glasses. *Advanced Materials Research*. 2008, vol. 39–40, iss. 1, pp. 111–116. ISSN 1022-6680.

[15] MUNOZ-SENOVILLA, L. and F. MUNOZ. Behaviour of viscosity in metaphosphate glasses. *Journal of Non-Crystalline Solids*. 2014, vol. 385, iss. 1, pp. 9–16. ISSN 0022-3093. DOI: 10.1016/j.jnoncrysol.2013.10.021.

[16] KOLTUNOWICZ, T. N., P. ZHUKOWSKI, A. K. FEDOTOV, A. V. LARKIN, A. PATRYN, B. ANDRYEVSKYY, A. SAAD, J. A. FEDOTOVA and V. V. FEDOTOVA. Influence of Matrix Type on Negative Capacitance Effect in Nanogranular Composite Films FeCoZr-Insulator. *Elektronika ir Elektrotechnika*. 2013, vol. 19, iss. 4, pp. 37–40. ISSN 1392-1215. DOI: 10.5755/j01.eee.19.4.1693.

# About Authors

**Peter HOCKICKO** was born in 1973, in Levoca, Slovakia. In 1996 he graduated (M.Sc.) at the Faculty of Mathematics, Physics and Informatics at the Comenius University in Bratislava. He defended his Ph.D. thesis in the field of physics of condensed matter and acoustics in 2008 at the University of Zilina. Since 2012 he has been working an associate professor of Electro-technology and materials at the Faculty of Electrical Engineering at the University of Zilina (Slovakia), where he delivers courses of fundamental physics. He has active research interests in investigation new perspective materials, especially ion conductive glasses by acoustic spectroscopy.

**Jozef KUDELCIK** was born in January 1975, in Ruzomberok, Slovakia. In 1998; he graduated (M.Sc.) at the Department of Plasma physics of the Faculty of Mathematics and Physics at Comenius University in Bratislava. He defended his Ph.D. (2003) in the field of stage of breakdown in the mixtures with SF6. In 2011 (associate professor), he habilitated in Electro-technology and materials. Since 1998; he has been working as a researcher at the Department of Physics at the University of Zilina. His scientific research is focused on discharge mechanism in gases and in dielectric, as water or oil. In present he is interested about process in magnetic fluid in the external magnetic field studied by acoustic spectroscopy.

**Francisco MUNOZ** was born in Barcelona (Spain) in 1974. He obtained his B.Sc. in Chemistry in the University of Alicante in 1997, and the Ph.D. in the University Autonoma de Madrid in 2003. He has worked as a postdoctoral in the Universities of Rennes and Lille (France) and the Friedrich-Schiller University of Jena (Germany), under a Marie-Curie fellowship. He currently holds a Tenured Scientist position at the Ceramics and Glass Institute of the Spanish Research Council (CSIC) in Madrid. His main research lines are devoted to the study of conducting glasses, the transport properties and atomic structure of glasses, glass-ceramics and the development of oxynitride glasses. He participates in the TC03 technical committee of the International Commission on Glass dedicated to the structure and properties relationship in glasses, in which he has served as Chairman between 2011 and 2013.

**Laura MUNOZ-SENOVILLA** was born in Madrid (Spain) in 1986. She obtained her M.Sc. in Applied Chemistry, Universidad Autonoma de Madrid (UAM), Spain in 2011. Her interests are: Materials Science, Inorganic Chemistry, Glass, Characterization of properties and structure.