

## Acoustic Spectroscopy Investigation of Ion Conductive Glasses of the System $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$

P. Hockicko<sup>a</sup>, P. Bury<sup>a</sup>, S. Jurečka<sup>b</sup>, M. Jamnický<sup>c</sup>, I. Jamnický<sup>a</sup>

<sup>a</sup> *University of Žilina, Department of Physics, 010 26 Žilina, Slovakia,*

<sup>b</sup> *University of Žilina, Department of Fundamental Engineering, 031 01 Liptovský Mikuláš,*

<sup>c</sup> *Slovak Technical University, Department of Ceramic, Glass and Cement, 812 19 Bratislava*

### Abstract

The relaxation and transport mechanisms of ionic glasses that reflect the basic features of the mobile ions can be investigated by acoustic spectroscopy that can have even some advantages comparing to electrical investigation represented by conductivity spectroscopy. In the contribution we present some acoustical and electrical properties of glasses in the system  $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$ . The both acoustical and electrical measurements are utilized to the study of transport mechanisms and relaxation processes occurring in these glasses and some physical parameters characterizing the transport mechanisms are determined. Coherence between the acoustical and electrical properties is discussed, too.

### Introduction

The acoustic spectroscopy investigation of ion conductive glasses can reflect the basic features of the relaxation and transport mechanisms of the mobile ions. The acoustic attenuation measurements seem to be a useful technique for non-destructive investigation of transport mechanisms in conductive glasses and compared to the electrical ones they have even some advantages as high sensitivity, the absence of contact phenomena and so on [1,2].

The experimental study of transport mechanisms in glassy electrolytes with fast ion transport attracts the considerable attention for its important role in a number of modern electrochemical devices such as solid-state batteries, solid-oxide fuel cells, electrochemical sensors, electrochromic displays and oxygen-separation membranes. The fabrication of electrochemical batteries with high energy density and capacity, excellent reversibility, long-time stability and low cost is a necessary part of this development. Other applications, such as portable batteries for heart pacemaker, mobile telephones and laptop computers, have, in recent years, markedly increased the need for solid-state microbatteries with high energy density. Lithium-ion batteries are the

most obvious choice given their low mass and high cell potentials [2].

The general requirements for practical solid electrolytes are high ionic conductivity, negligible electronic conductivity, stability with respect to adjacent phases and to thermal and electrochemical decomposition, suitable mechanical properties, ready availability of chemical constituents, easy of fabrication and reasonable cost.

Phosphate glasses containing  $\text{Cu}^+$  conductive ions are good ionic conductors with room temperature conductivity of the order  $10^{-3} \Omega^{-1}\text{cm}^{-1}$ . The highest conductivity has been recorded in systems containing large fractions of cuprous halides, such as  $\text{CuI}$  or  $\text{CuBr}$  [3].

The investigation of acoustic spectra in ion conductive glasses with different composition can reflect the basic features of the relaxation and transport processes of the mobile ions. It was found that the temperature responses of all acoustic spectra are similar and the relaxation peaks associated with ion transport depend on the glass composition [4].

In the contribution we present both acoustic and conductivity spectra of phosphate glasses containing  $\text{Cu}^+$  conductive ions in the system  $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$  with respect to investigate ion transport

mechanisms and to determine the relation between acoustical and electrical properties considering the various glass compositions with purpose to study ion transport mechanisms in these ion conductive glasses and to find the role of cuprous halides producing  $\text{Cu}^+$  ions.

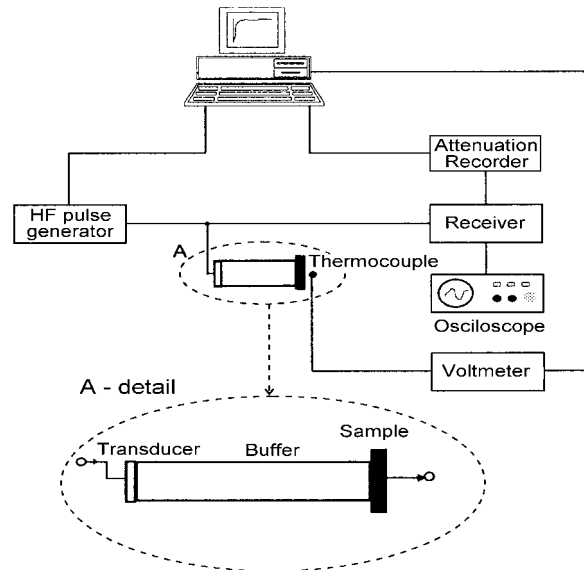
### Experiments

The procedure of glasses preparation in the system  $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$  has been already described [5]. The set of systems of glasses was originally prepared to investigate the role of cuprous halides producing  $\text{Cu}^+$  ion keeping their ratio to the glass forming system constant [4]. The samples for acoustical attenuation measurements were cylindrical in shape (area  $\approx 1 \text{ cm}^2$ , thickness 1.6 - 2.0 mm) and end faces were polished to be flat and parallel. The composition of the complex set of glass presented samples are summarised in Tab. 1.

**Tab. 1** Starting glass compositions (in mol.%) of prepared glasses

Glass sample	Composition (in mol.%)			
	CuI	CuBr	$\text{Cu}_2\text{O}$	$\text{P}_2\text{O}_5$
BIDP1	15,91	2,27	54,55	27,27
BIDP2	13,63	4,55	54,55	27,27
BIDP3	11,36	6,82	54,55	27,27
BIDP5	9,09	9,09	54,55	27,27
BIDP6	6,82	11,36	54,55	27,27
BIDP7	4,55	13,63	54,55	27,27
BIDP8	2,27	15,91	54,55	27,27
BDP	0	18,18	54,55	27,27

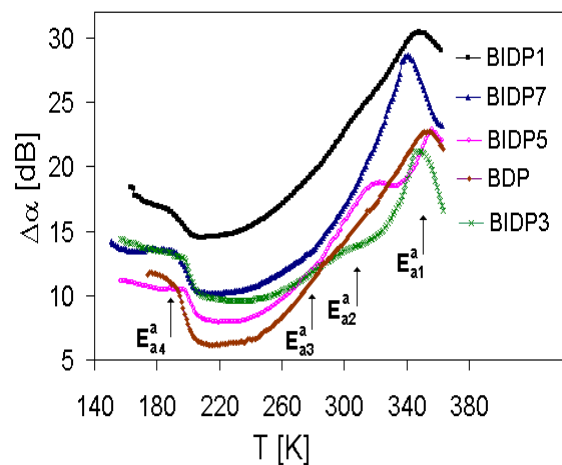
The acoustical attenuation was measured using longitudinal acoustic wave of frequency 13, 18 and 27 MHz generated by quartz transducer in temperature range of 140-380 K. The quartz buffer was used to separate the signal from quite short sample (Fig. 1).



**Fig. 1** Experimental arrangement for acoustic attenuation measurement

The temperature and frequency dependencies of electrical conductivity (dc and ac in the frequency range 50 Hz - 1 MHz) were measured in the same temperature range as acoustical measurements. The measured complex impedance allowed us to obtain the bulk dc and ac conductivity of glass samples by means of the usual impedance analysis. Gold electrodes were sputtered on to the sample surfaces for electrical investigation.

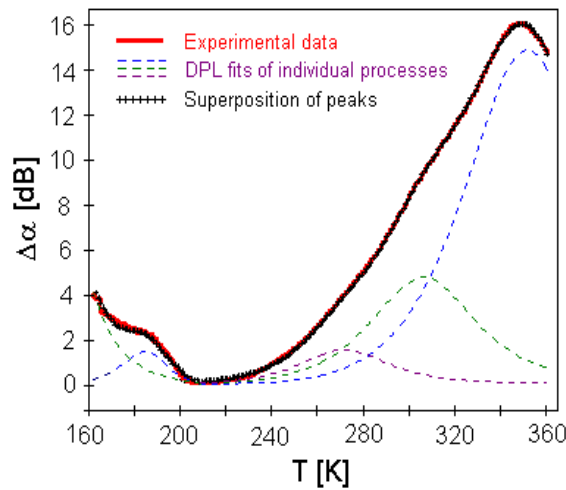
### Results and discussion



**Fig. 2** Acoustic attenuation spectra of ion conductive glasses of the system  $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$

The acoustic attenuation of the most investigated ion conducting glasses is plotted as a function of temperature at a constant frequency  $\nu = 18$  MHz (Fig. 2).

The measurements of the temperature dependence of acoustic attenuation indicate in all investigated samples one broad attenuation peak at higher temperature, in which we initially supposed two separated peaks [6]. But using the theoretical models [7] we fitted the acoustic attenuation spectrum and the superposition of three calculated lines represented by cross-marked line in Fig. 3 gave an excellent agreement with measured spectrum in whole temperature range.



**Fig. 3** Acoustics spectrum of sample BIDP1 (full line). Cross-marked line represents the best fit of superposition at least four relaxation processes.

We tried to use double power law (DPL) model to fit the acoustic attenuation spectra of the investigated glasses. This function has mainly been used to fit mechanical loss data [8]

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

where  $m$  and  $n$  are the power-law exponents and  $\tau$  is the relaxation time.

The distinctive peaks of acoustic attenuation spectra, which are caused by resonant interaction with the mobile ion hopping processes, enable us then to study relaxation and transport mechanisms in the ion

conductive glasses. The attenuation spectra can be explained by the assumption that temperature peaks are caused by the relaxation processes of mobile  $\text{Cu}^+$  ions in connection with different kinds of sites.

The temperature dependence of acoustic attenuation has been analyzed then assuming the existence of four thermally activated relaxation processes of ions in connection with different kinds of sites. The fourth peak, however, was detected at lower temperatures.

All glasses we studied using acoustic spectroscopy exhibit an Arrhenius – type relaxation between the peak temperature and the applied frequency

$$\nu = \nu_0 \exp(-E_a^a / k_B T_{peak}), \quad (2)$$

where  $E_a^a$  is the activation energy,  $k_B$  is Boltzmann constant,  $T_{peak}$  is the temperature of the peak maximum,  $\nu$  is the frequency and  $\nu_0$  is the preexponential factor. The values of  $T_{peak}$  can be easily and directly determined from the theoretical fits.

The existence of four basic possible thermally activated relaxation processes of ions ( $E_{a1}^a, E_{a2}^a, E_{a3}^a$ ) for higher and  $E_{a4}^a$  for lower temperatures) are connected with different kinds of sites for  $\text{Cu}^+$  ions.

Using the values of  $T_{peak}$  for individual peaks and Eq. (2), the activation energies were determined (Tab. 2).

The ion transport properties of ionic conductors can be also directly reflected in the electrical conductivity spectra [7].

The representative results of measured dc conductivity (BIDP1) as a function of temperature are illustrated in Fig. 4. As all of the temperature dependence of dc glass conductivity can be fitted by the equation

$$\sigma = \sigma_0 \exp(-E_a / k_B T). \quad (3)$$

Because the preexponential factor  $\sigma_0$  is a function of temperature, the factor  $\sigma T$  is used in Arrhenius plots of dc conductivity. The temperature dependence of dc conductivity of all samples indicates four transport mechanisms with activation energies  $E_{a1}, E_{a2}, E_{a3}$  and  $E_{a4}$ . The shapes of

experimental Arrhenius plots of dc conductivity indicate also some association and dissociation processes, respectively connected with defects formation [2]. Activation energies calculated from conventional Arrhenius plots of dc conductivity for all glass samples are summarized in Tab. 2, too. As we can see the investigated glasses exhibit a mixed cation effect. All prepared glasses have high ionic conductivity at room temperatures  $10^{-2}$ -  $10^{-4} \Omega^{-1} \text{cm}^{-1}$ .

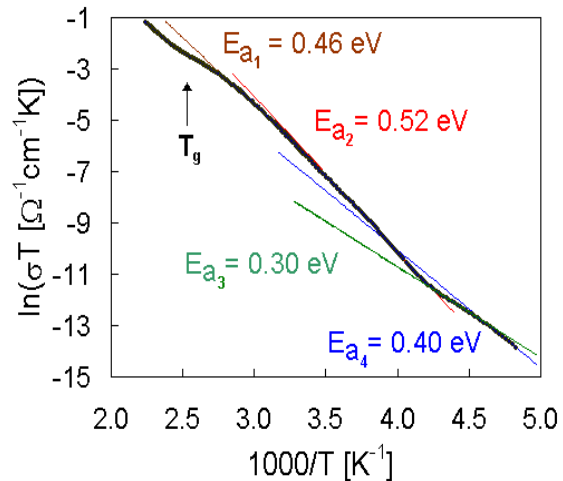


Fig. 4 Arrhenius plot of d.c. conductivity of sample BIDP1.

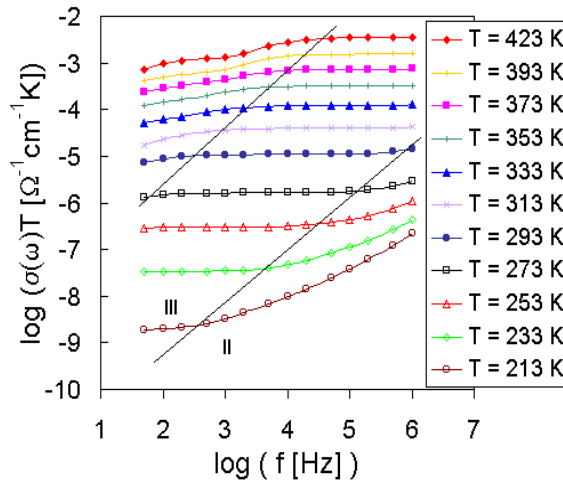
Tab. 2 Activation energies calculated from Arrhenius plots of dc conductivity and acoustic attenuation spectra for all glass samples

Glass Sample	Electrical measurements				Acoustical measurements			
	$E_{a1}$ [eV]	$E_{a2}$ [eV]	$E_{a3}$ [eV]	$E_{a4}$ [eV]	$E_{a1}^a$ [eV]	$E_{a2}^a$ [eV]	$E_{a3}^a$ [eV]	$E_{a4}^a$ [eV]
BIDP1	0.46	0.52	0.30	0.40	0.47	0.41	0.37	0.25
BIDP2	0.44	0.54	0.41	0.44	0.46	0.41	0.36	0.27
BIDP3	0.46	0.58	0.30	0.42	0.46	0.41	0.37	0.26
BIDP5	0.44	0.54	0.32	0.42	0.46	0.42	0.33	0.26
BIDP6	0.39	0.52	0.35	0.43	0.46	0.42	0.35	0.28
BIDP7	0.41	0.50	0.23	0.43	0.45	0.42	0.39	0.25
BIDP8	0.42	0.52	0.26	0.41	0.46	0.43	0.36	0.27
BDP	0.40	0.51	0.15	0.38	0.47	0.43	0.39	0.26

It seems, that some of individual transport mechanisms indicated by acoustical spectra can correspond to the mechanisms indicated by dc measurement and some activation energies are very close to values determined by d.c. electrical measurement, namely  $E_{a1}$  and  $E_{a3}$ .

The set of frequency dependencies of ac conductivity measured at various temperatures (conductivity spectra) is illustrated in Fig. 5 for glass sample BIDP1 as representative of investigated system. The

obtained ac conductivity measurements correspond to the complete conductivity spectra obtained from glassy samples [1]. However, because of limited availability of radio and microwave, representing higher frequencies in our laboratory using lower temperatures we could recognize regimes II and III very well of complete conductivity spectra due to hopping motion, the regime II only at low temperatures yet.



**Fig. 5.** The frequency dependence of ac conductivity at various temperatures for sample BIDP1.

The glass sample BIDP1 similarly as other samples exhibits one slope of brakes on the ac conductivity spectra indicated another transport hopping process. However, the jump from one value of ac conductivity to another characterizing the transition between two kinds of hopping processes or another transport hopping process was registered also at higher temperatures and lower frequencies. Low frequency part in regime III and dispersive regime II are due to the hopping motion of the mobile ions and are obviously explained in terms of jump relaxation model considering several kinds of cation sites [1,10].

### Conclusions

The experimental investigation of ion conductive glasses in system CuI-CuBr-Cu<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> proved that acoustical spectroscopy in like manner as electrical conductivity spectroscopy can be very useful technique for transport mechanisms study and showed some coherence between the acoustical and electrical properties in fast ion conductive glasses.

The acoustical attenuation measurements are also seems even to be very sensitive and can then distinguish between individual transport mechanisms that are connected with relaxation processes of mobile ions.

Several different kinds of sites responsible for ionic hopping motion were discovered. The particular influence of chemical composition on ion transport mechanisms was exhibited and activation energies of individual transport mechanisms were determined using both dc electrical measurement and acoustical attenuation spectra.

Further theoretical analysis of experimental measurements using relaxation models should be done for better understanding of ion transport and relaxation mechanisms in this type of conductive glasses.

### References

- [1] **B. Roling, A. Happe, M. D. Ingram and K. Funke:** *J. Phys. Chem. B* 103 (1999) 4122.
- [2] **P. Knauth, H. L. Tuller:** *J. Am. Ceram. Soc.*, 85 [7] (2002) 1654-80.
- [3] **P. Znášik and M. Jamnický:** *Solid State Ionics* 95 (1997) 207.
- [4] **P. Bury, P. Hockicko, M. Jamnický and I. Jamnický:** *Proceedings of the 18<sup>th</sup> International Congress on Acoustics, Kyoto 2004, Vol. II* 1137-40
- [5] **P. Znášik, M. Jamnický:** *J. Mat Science Letter* 14 (1995) 766.
- [6] **P. Hockicko, P. Bury, M. Jamnický and I. Jamnický:** *Advances in Electrical and Electronics Engineering, Vol.3, No. 2* (2004) 243-46.
- [7] **P. Hockicko, P. Bury, M. Jamnický and I. Jamnický:** *Proceedings of the 9<sup>th</sup> International Workshop on Applied Physics of Condensed Matter, Malá Lučivná 2003*, 174.
- [8] **B. Roling and M. D. Ingram:** *Physical Review B* 57 (1998) 14192.
- [9] **K. Funke:** *Solid State Ionics* 94 (1997) 27-33.
- [10] **P. Bury, P. Hockicko, M. Jamnický and I. Jamnický:** *Advances in Electrical and Electronics Engineering, Vol.2, No. 3-4* (2003) 16-23.

### Acknowledgements

The authors would like to thank Mr. F. Černobila for technical assistance. This work was partly financially supported by Grant 1/9141/02 of the Ministry of Education of the Slovak Republic.