

## Analysis of acoustic attenuation spectra due to ion transport processes in glassy electrolytes

P. Bury<sup>\*, 1</sup>, P. Hockicko<sup>1</sup>, S. Jurečka<sup>2</sup>, and M. Jamnický<sup>3</sup>

<sup>1</sup> Department of Physics, Žilina University, 010 26 Žilina, Slovakia

<sup>2</sup> Department of Fundamental Engineering, Žilina University, 031 01 Liptovský Mikuláš, Slovakia

<sup>3</sup> Department of Ceramic, Glass and Cement, Slovak Technical University, 812 37 Bratislava, Slovakia

Received 15 July 2004, revised 3 September 2004, accepted 27 September 2004

Published online 17 November 2004

PACS 43.35.Fj, 61.43.Fs, 66.30.Dn

An acoustic attenuation spectroscopy as a powerful technique is used to study the relaxation processes in phosphate glasses containing  $\text{Cu}^+$  conductive ions of the system  $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$  with respect to ion transport mechanisms. The acoustic attenuation spectra exhibit several distinctive peaks, corresponding to transport mechanisms originating from the different kinds of sites responsible for ionic hopping. The experimental results of acoustic spectra are then analysed in connection with the frequency response, the activation energy at spectra peaks and the peak intensities using theoretical models and suitable mathematical procedure for the simulations to fit the experimental data.

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** It is known that the investigation of acoustic spectra of ionic glasses (glassy electrolytes) can reflect the basic features of the relaxation and transport mechanisms of the mobile ions. Acoustical measurements made over a wide range of frequencies and temperatures can characterize different relaxation processes according to corresponding transport mechanisms due to a strong acousto-ionic interaction [1–3]. In glassy electrolytes, the mobile ions encounter different kinds of sites so that ionic hopping motion and relaxation processes connected with charge mobility can be obviously explained by modified jump relaxation model and suitable response function for transport mechanisms and relaxation processes description, respectively [3, 4].

In this contribution we present experimental results obtained by acoustic investigation of the set of glasses prepared in the system  $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$  and their theoretical description with the purpose to study ion transport mechanisms in these ion conductive glasses and to find the role of cuprous halides producing  $\text{Cu}^+$  ions. An analysis of the acoustical spectra using various theoretical models for the simulations with application of genetic algorithm was provided to fit the experimental data.

**2 Experimental and results** The procedure of glass preparation in the system  $\text{CuI-CuBr-Cu}_2\text{O-P}_2\text{O}_5$  has been already described [5]. The set of glasses was originally prepared to investigate the role of cuprous halides producing  $\text{Cu}^+$  ion keeping their ratio to the glass forming system ( $\text{Cu}_2\text{O-P}_2\text{O}_5$ ) constant. The composition of the complex set of glass samples are summarized in Tab. 1.

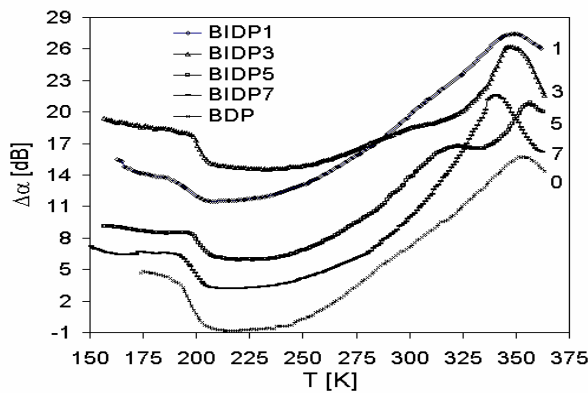
The acoustical attenuation was measured using longitudinal acoustic wave of frequency 13, 18 and 27 MHz in the temperature range 140–380 K [6]. The temperature and frequency dependencies of electrical conductivity (dc and ac in the frequency range 50 Hz - 1 MHz) were also measured in the same temperature range as acoustical measurements [7]. The acoustic attenuation of the most of investigated glasses is plotted as a function of temperature at the constant frequency  $\nu = 18$  MHz in Fig. 1. The measurements

\* Corresponding author: e-mail: bury@fel.utc.sk

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

| Glass<br>Sample | Composition (in mol.%) |       |                   |                               |
|-----------------|------------------------|-------|-------------------|-------------------------------|
|                 | CuI                    | CuBr  | Cu <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> |
| 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                         |

indicate in all samples one broad attenuation peak at higher temperature, in which we can distinguish at least two separated peaks. Another peak was detected at lower temperatures as a part of broader peak.



**Fig. 1** Acoustic attenuation spectra of investigated ion conductive glasses of the system CuI-CuBr-Cu<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> for different glass composition. The individual spectra are shifted for better resolution.

The ion transport properties of these investigated solid electrolytes were also reflected in the electrical conductivity spectra [6, 7]. The temperature dependence of dc conductivity indicates four different transport mechanisms with activation energies  $E_{a1}$ ,  $E_{a2}$ ,  $E_{a3}$  and  $E_{a4}$  including also some association and dissociation processes ( $E_{a2}$ ,  $E_{a3}$ ) connected with some defects formation [7, 8]. All prepared

glasses have high ionic conductivity at room temperatures of the order  $10^{-3} \text{ S m}^{-1}$ . The frequency dependencies of ac conductivity measured at various temperatures (conductivity spectra) exhibit one slope of brakes at higher frequencies and lower temperatures characterizing the transition from dc conductivity to dispersive conductivity indicating thus the transition between two transport hopping processes [2, 7]. Additional jumps from one value of ac conductivity to another characterizing the transition between the similar ion transports but between two kinds of anions was observed at lower frequencies and higher temperatures.

The infrared study confirmed mainly  $\text{P}_2\text{O}_7^{4-}$  phosphate anion groups and also some lower-condensed anions  $\text{PO}_4^{3-}$  and  $\text{P}_3\text{O}_{10}^{5-}$  in small amounts. The cuprous halides as well as their mixtures do not affect significantly the dominant phosphate oxide structural units of glasses.

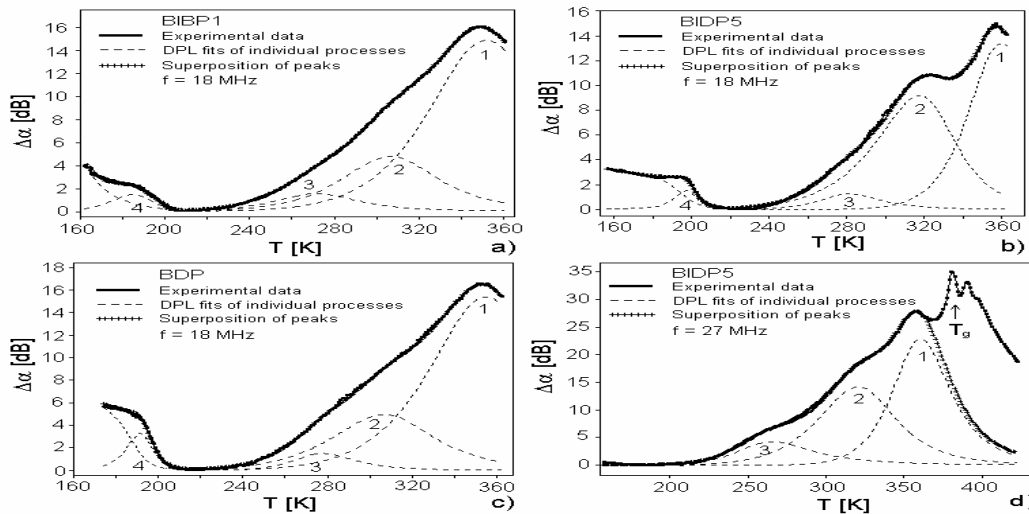
**3 Theoretical analysis of attenuation processes** The ion transport properties and the formal theories of relaxation processes of many ion conducting glasses, melts and crystals are similar [2]. In the case of systems containing a low concentration of mobile ions the attenuation may be described as a superposition of Debye-like, single relaxation time processes in which the individual ion hops occur independently of each other [5]. In fact all the investigated relaxation peaks are much broader than Debye peak that 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. According to this hypothesis when the relaxation losses are not too large one can write for the acoustic attenuation a distribution  $f(\tau)$  of relaxation times [3]. As a consequence, the  $\tau$  distribution can be connected with a distribution of activation energies  $f(E)$ , representing the heights of the barriers that the ions must surmount to go into the near allowed positions. The acoustic attenuation will exhibit a maximum when the relaxation time  $\tau$  is comparable to the period ( $1/\omega$ ) of the

acoustic perturbation, where  $\tau = \tau_0 \exp(E_a / k_B T_{peak})$  is the most probable relaxation time. The relaxation processes described by this Arrhenius equation are characterized by activation energy  $E_a$  for jumps over the barrier between two potential minima and typical values for preexponential factor  $1/\tau_0 = \nu_0 \approx 10^{13} - 10^{14} \text{ s}^{-1}$ . Here  $T_{peak}$  is the temperature of peak maximum and  $k_B$  is the Boltzman constant.

This approach depends on the assumption that ion migration may be treated in terms of a set of non-interacting Debye-like processes. However, 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 a double power-law type of frequency dependence, the relationship to Debye behaviour can be then expressed in the form [3]

$$\alpha \approx \left( \frac{1}{(\omega\tau)^{-n} + (\omega\tau)^m} \right), \quad (1)$$

where  $m$  and  $n$  are power-law exponents, which take values between 0 and 1. When  $m = 1$  and  $n = 1$ , equation (1) reduces to the equation for a single Debye-like process. Another function that can be used to fit acoustic attenuation spectra, is the Kohlrausch-Wiliems-Wats function [9]. The acoustic attenuation spectrum of the investigated cuprous halide glasses can be then fitted using these theoretical attenuation functions and mathematical procedure using the genetic algorithm with binary representation of the theoretical attenuation function variables [10] in connection with the visual construction of the acoustic attenuation model. During the fitting procedure the Debye function, Double Power Law function and modified Double Power Law function were gradually used [11].



**Fig. 2** Acoustics spectra (full lines) of samples BIDP1 (a), BIDP5 (b) and BDP (c) measured at 18 MHz and BIDP5 measured at 27 MHz (d). Cross-marked line represents best fit as superposition of individual peaks (dashed lines).

The representative acoustic spectra and their theoretical simulations are illustrated in Fig. 2(a–c). Using the theoretical model with double power-law function, the calculated lines gave an excellent agreement with measured spectrum in whole temperature range. The temperature dependences of acoustic attenuation were then analyzed assuming the existence of four thermally activated relaxation processes of  $\text{Cu}^+$  ions in connection with different kinds of sites. In spite of the infrared study suggesting only one dominant anion group two strong peaks in acoustic spectra (denoted as 1 and 2 in Fig. 2) were observed at temperatures below the transition temperature. The proportion of these peak intensities de-

depends on the glass composition, namely on the ratio CuI/CuBr (mixing cation effect) and changes from value 3.7 through minimum value 1.3 again to value 3.5 at samples BIDP1, BIDP5 and BDP, respectively. The results of acoustic investigation and the shape of both Arrhenius plots of dc conductivity and conductivity spectra indicate some processes connected with association and/or dissociation of new defects. In these processes the oxygen vacancies can be introduced into the system by some reactions associated with an electron representing then centers for  $\text{Cu}^+$  ions. Another two peaks that can be connected with lower-condensed anions are not affected by halides ratio significantly. Using the values of  $T_{\text{peak}}$  for individual peaks and Eq. (1), the activation energies were determined (Tab. 2). Activation energies calculated from Arrhenius plots of dc conductivity are also summarized in Tab. 2, for comparison.

Comparing the acoustic and electrical measurements, some of the individual transport mechanisms indicated by acoustical spectra can correspond to the mechanisms indicated by electrical measurement, but some can be different because of both different microscopic mechanisms for relaxation processes and the temperature dependence of preexponential factor  $\nu_0$  [6].

**Table 2** Activation energies calculated from Arrhenius plots of dc conductivity and acoustic spectra.

| Glass<br>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            |

**5 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 it seems also even to be very sensitive and can then distinguish between individual transport mechanisms.

Theoretical analysis using double power law function and suitable mathematical model gave the excellent fit of experimental spectra and several different kinds of sites responsible for ionic hopping motion were discovered. The influence of chemical composition on ion transport mechanisms was exhibited and frequency response, peak intensity and activation energy of spectra peaks were observed.

Further experimental study and theoretical analysis of experimental measurements including both new samples and new spectroscopic techniques should be done for better understanding of ion transport and relaxation mechanisms in this type of conductive glasses.

**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.

## References

- [1] E. V. Charnaza, B. F. Borisov, and A. A. Kuleshov, Proc. World Congress on Ultrasonics, Berlin (1995), p. 483.
- [2] B. Roling, A. Happe, M. D. Ingram, and K. Funke, J. Phys. Chem. B **103**, 4122 (1999).
- [3] D. P. Almond and A. R. West, Solid State Ionics **26**, 265 (1988).
- [4] K. Funke, Solid State Ionics **94**, 27 (1997).
- [5] P. Znášik, M. Jamnický, J. Mater. Sci. Lett. **14**, 766 (1995).
- [6] P. Bury, P. Hockicko, M. Jamnický, and I. Jamnický, Adv. EEE **2**, No. 3-4, 16 (2003).
- [7] P. Bury, P. Hockicko, M. Jamnický, and I. Jamnický, Proc. of the 18th International Congress on Acoustics, Kyoto 2004, Vol. II, p. 1137.
- [8] P. Knauth, H. L. Tuller, J. Am. Ceram. Soc. **85** [7], 1654 (2002).
- [9] B. Roling and M. D. Ingram, Phys. Rev. B **57**, 14192 (1998).
- [10] D. E. Goldberg, Genetic Algorithms in Search, Optimization and Machine Learning (Addison-Wesley, 1989).
- [11] P. Hockicko, P. Bury, M. Jamnický, and I. Jamnický, Adv. EEE **3**, No. 2, 243 (2004).