

# ACOUSTIC AND ELECTRICAL BEHAVIOUR OF SOME IONIC PHOSPHATE GLASSES

P. Bury, [bury@fel.utc.sk](mailto:bury@fel.utc.sk), P. Hockicko, I. Jamnický, Department of Physics, FEE, University of Žilina, 010 26 Žilina  
M. Jamnický, Department of Ceramic, Glass and Cement, FChFT, Slovak University of Technology, 812 37 Bratislava, S. Jurečka, Department of Fundamental Engineering, University of Žilina, 031 01 Liptovský Mikuláš

## INTRODUCTION

Dynamic processes in glassy materials with fast ionic conduction are extremely important since the ion transport significantly affects their practical performance. Electrical and mechanical (acoustic) spectroscopy are two of the most common methods for the characterization of dynamic processes [1,2].

Complete conductivity spectra of ionic glassy conductors reflect the essential features of the relaxational and transport dynamics of the mobile ions that encounter different kinds of site and ionic hopping motion connected with charge mobility [3].

Acoustic spectroscopy is another powerful technique for the study of sub- $T_g$  relaxations in glasses due to a strong acousto-ionic interaction [4,5]. Relaxation processes occurring on different time scales can be detected in one experiment since the corresponding acoustic loss peaks are spread out on the temperature scale in an isochronal measurement.

In this contribution the acoustic and electrical relaxation processes are compared on identical ionic phosphate glasses of the system CuI-CuBr-Cu<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> containing Cu<sup>+</sup> ions. Several distinctive peaks in the acoustic attenuation spectra corresponding to different kinds of sites responsible for ionic hopping were exhibited. Electrical conductivity spectra including dc and ac measurements representing at least two conductivity regimes and several transport mechanisms were observed, too. Both the acoustic and electrical measured data were analyzed using suitable model representations.

## EXPERIMENTAL

The procedure of glass preparation of the system (18.18-x) CuI - x CuBr - 54.55 Cu<sub>2</sub>O - 27.27 P<sub>2</sub>O<sub>5</sub> and its complete set consisting of nine samples with equal increasing x (one step is ~2.27 in mol.%) have been already described [6]. The set of glasses was originally prepared to investigate the role of cuprous halides producing Cu<sup>+</sup> ion keeping their ratio to the glass forming system (Cu<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>) constant.

The acoustical attenuation was measured using longitudinal acoustic wave of frequency 13, 18 and 27 MHz in the temperature range 140-380 K [7]. The temperature and frequency dependencies of electrical conductivity (50 Hz – 1 MHz) were also measured in the same temperature range as acoustical ones [7].

## RESULTS AND DISCUSSION

The set of frequency dependences of ac conductivity measured at various temperatures is illustrated in Fig. 1 for glass sample BIDP5 (starting

glass composition in mol.% : 9.09CuI-9.09CuBr-54.55 Cu<sub>2</sub>O-27.27P<sub>2</sub>O<sub>5</sub> ) as representative of investigated system. Because of limited frequency range only two regimes ( II and III ) of complete conductivity spectra [3]

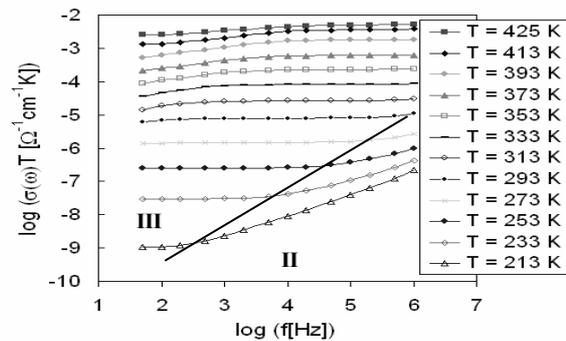


Fig.1. Frequency dependence of ac conductivity measured at various temperatures for sample BIDP5.

could be recognized. However, an additional deviation of conductivity from the flat dc plateau is observed at low frequencies and high temperatures. This dispersion is obviously referred to electrode polarization, but our previous dc measurements [7] indicate at least three transport mechanisms and also some association and/or dissociation process, connected with defects formation. Following these results the shift of the frequency independent component of ac conductivity can represent different hopping centers or different type of ions.

The frequency dependence of electrical conductivity of many solids including glasses consists of a frequency independent and strongly frequency dependent components that can be for a limited frequency region approximated by the simple relation  $\sigma(\omega) = \sigma(0) + A\omega^s$  [8], where  $\sigma(0)$  is the frequency independent dc (or low-frequency) conductivity and the exponent  $s$  lies in the range  $0 < s \leq 1$ ,  $\omega (=2\pi f)$  is angular frequency of measurement. The  $\sigma(0)$  and  $A$  follow Arrhenius type temperature dependencies.

The main ac characteristics of the phosphate conductive glasses determined from our measurements confirm such behaviour. In a fixed frequency range  $s$  increases as temperature decreases, its value is between 0.5 and 0.7 in our investigated temperature range (we can suppose that  $s \rightarrow 1.0$  for  $T \rightarrow 0$ ) and  $s$  is also a function of glass composition. The parameter  $A$  and  $\sigma(0)$  are Arrhenius temperature dependent.

Using these facts we can fit the frequency dependence by the following equation

$$\sigma(\omega) = \sigma_0 \exp\left[-\frac{E_{dc}}{k_B T}\right] + A_0 \exp\left[-\frac{E_{ac}}{k_B T}\right] \omega^s, \quad (1)$$

where  $\sigma_0$  and  $A_0$  are the pre-exponential factors,  $k_B$  is the Boltzmann constant,  $T$  is temperature,  $E_{dc}$  and  $E_{ac}$  are activation energies for dc and ac ion transport.

The acoustic attenuation of some investigated glasses is plotted as a function of temperature at the constant frequency  $\nu = 18$  MHz in Fig. 2. The measurements in all samples indicate one broad

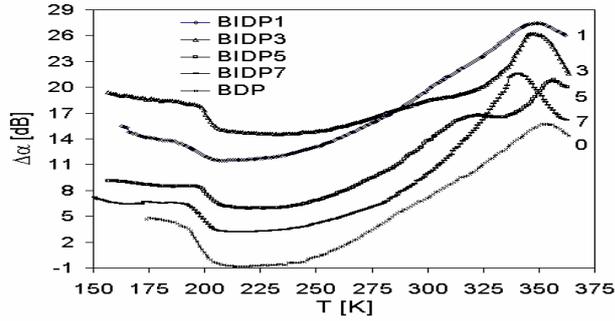


Fig.2. Acoustic attenuation spectra of some glasses of the system CuI-CuBr-Cu<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> [6].

attenuation peak at higher temperature, in which we can distinguish at least two separated peaks. Another peak was detected at lower temperatures.

All the investigated relaxation peaks are much broader than Debye peak corresponding to single relaxation process [4] and can be then interpreted as arising from the existence of a distribution of relaxation times due to random deviations in the local arrangement of the system. The acoustic attenuation will exhibit a maximum when the relaxation time  $\tau$  is comparable to the period ( $1/\omega$ ) of the acoustic perturbation, where  $\tau = \tau_0 \exp(E_a^a / k_B T_{peak})$  is the most probable relaxation time. The relaxation processes described by this Arrhenius equation are characterized by activation energy  $E_a^a$  for jumps over the barrier between two potential minima. Here  $T_{peak}$  is the temperature of peak maximum. The relaxation phenomena observed in a wide variety of glassy materials exhibit a double power-law type of frequency dependence, the relationship to Debye behaviour can be expressed in the form [4]

$$\alpha \approx \left( \frac{1}{(\omega\tau)^{-n} + (\omega\tau)^m} \right), \quad (2)$$

where  $m$  and  $n$  are power-law exponents, which take values between 0 and 1.

The acoustic attenuation spectra of the investigated cuprous halide glasses were then fitted using these theoretical attenuation function and mathematical procedure using the genetic algorithm [6]. The calculated lines gave an excellent agreement with measured spectra for all samples in whole temperature range ( Fig. 3 ). 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. 3) were observed at temperatures below  $T_g$ . The proportion of these peaks intensities depends on the glass composition, namely on the ratio CuI/CuBr (mixing cation effect) and changes between 3.7 and 1.3. 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

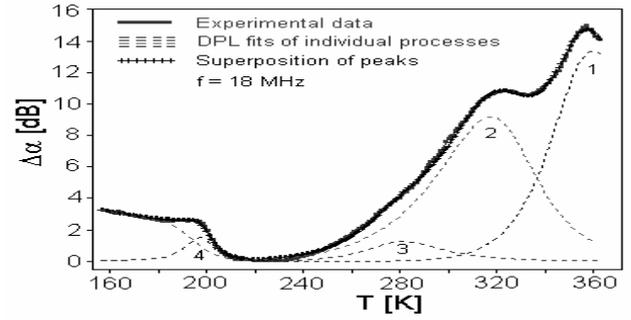


Fig.3. Acoustics spectrum of sample BIDP5 (full line) and the best fit for four relaxation processes (dashed lines).

defects. In this process the oxygen vacancies can be introduced into the system by some reactions associated with an electron representing centers for Cu<sup>+</sup> ions. Another two peaks that can be connected with lower-condensed anions are not affected by halides ratio significantly. Using the values of  $T_{peak}$  for individual peaks,  $E_a^a$  could be determined [6,7].

## CONCLUSIONS

The experimental investigation of ion conductive glasses in system CuI-CuBr-Cu<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> proved that connection of acoustical and electrical conductivity spectroscopy can be very useful for transport mechanisms study

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, frequency response, peak intensity and activation energy of spectra peaks was observed.

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

ACKNOWLEDGEMENT: The authors would like to thank Mr. F. Černobila for technical assistance. This work was supported by Grant 1/2016/05 of the Ministry of Education of the Slovak Republic.

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