# Study of Mechanisms of Ion Transport in Ion Conducting Glasses

P. Bury [a], P. Hockicko [a], M. Jamnický [b] and I. Jamnický [a]

[a] *Department of Physics, Žilina University, 010 26 Žilina, Slovakia* (bury@fel.utc.sk)
[b] *Department of Ceramic, Glass and Cement, Slovak Technical University, 812 37 Bratislava*

**Abstract** In the past twenty years, there has been an increase of interest in ion conductive glasses and their possible future practical application. Comparing with the crystalline materials the ionic glasses has several advantages the most important of which are: the absence of grain boundaries, the isotropic properties and the composition variability. The electrical methods have been already proved an effective tool to study the fundamental transport properties of the ionic materials and the conductivity measurements made over a wide range of frequencies and temperatures can characterise different types of transport mechanisms. The purpose of present work is to compare data obtained by electrical measurement (dc and ac conductivity) of ion conductive glasses of the system CuI-CuBr-$Cu_2O$-($P_2O_5$+$M_0O_3$) for different glass composition and study the ionic hopping motion and relaxation processes connected with the charge mobility. Partial attention is paid also to the problem of the role of composition in this system.

**I. Introduction** A considerable attention is given in recent years to glassy materials with the fast ion transport called solid state electrolytes because of the possibility of their application in modern electrochemical devices, such as solid-state batteries, electrochronic displays, and sensors as well as for fundamental interest in their ion transport mechanisms [1,2]. The ion conductive glasses have several advantages comparing with crystalline materials because of their easy preparation, their stability and the large available composition ranges.

The investigation of conductivity spectra of ionic glasses can reflects the basic features of the relaxation and transport mechanisms of the mobile ions and the high ion conductivity at room temperature is the most important criterion witch should be meet the fast ion conductive glasses. Here is a good opportunity for glasses containing $Cu^+$ conductive ions that have similar electronic configuration and smaller ionic radii in comparison with $Ag^+$ ion and could achieve comparable conductivity [3].

While there are many papers on $Ag^+$-ion conducting glasses in various glass-forming systems, $Cu^+$-ion conducting glasses are only known in very limited glass-forming systems. Phosphate glasses containing $Cu^+$ conducting ions are good ionic conductors with room temperature conductivity of the order $10^{-3}\Omega^{-1}cm^{-1}$ [4,5]. The highest conductivity has been recorded in systems containing large more fractions of cuprous halides, such as CuI or CuBr. Moreover, if two different kinds of halide anions are mixed into cation conducting glasses [6], a positive deviation of the electrical conductivity from the additivity rule can be observed (mixed anion effect). In this contribution we present some electrical (transport) properties of glasses prepared in the systems $CuI$-$CuBr$-$Cu_2O$-$M_mO_n$ where $M_mO_n$ is $P_2O_5$ and/or $MoO_3$. The main purpose of the contribution is to investigate ion transport mechanisms and to determine the relation between glass composition and electrical conductivity.

**II. Experimental** The preparation of glasses in the system $CuI$-$CuBr$-$Cu_2O$-($P_2O_5$+$MoO_3$) from commercial reagents (Fluka) represented the procedure already described [6]. Batches of 15 g were melted under a dry argon atmosphere to avoid the oxidation of $Cu^+$ during melting and mixed in appropriate portion (see Tables 1 and 2) in silica ampoule at 933 K for 90 min. The glass melts were rapidly quenched by pressing them between two brass plates to a final thickness of ≈ 1.5 mm. The resulting discs of 20 mm in diameter were kept between the plates until their temperature decreased to room temperature. Losses in weight during melting were < 1 %. To check the reproducibility of the results, all glasses were prepared three times. Two systems of glasses were prepared to investigate both the role of glass-forming system and the role of cuprous halides produced $Cu^+$ ions keeping their ratio 60 mol. % to 40 mol. %.

The samples for electrical conductivity measurements were cylindrical in shape (area ≈ 1 $cm^2$, thickness ≈ 1-2 mm). Gold electrodes were sputtered onto the sample surfaces. The frequency and temperature dependencies of electrical conductivity were measured (d.c. and a.c. in the frequency range from 50 Hz up to 1 MHz using FLUKE PM 6306 impedance analyser and in the temperature range of 140-380 K temperature range ~ 100°C. The measured complex impedance allowed us to obtain the bulk d.c. and a.c. conductivity of glass samples by means of the usual impedance analysis.

Table 1 Starting compositions (in mol.%) of glasses prepared in the System I

| Glass sample | Composition (in mol.%) | | | | |
|---|---|---|---|---|---|
| | CuI | CuBr | $Cu_2O$ | $P_2O_5$ | $MoO_3$ |
| IP | 25.000 | - | 56.250 | 18.750 | - |
| IPM | 25.000 | - | 46.875 | 9.375 | 18.750 |
| BPM | - | 25.000 | 46.875 | 9.375 | 18.750 |
| IM | 25.000 | - | 37.500 | - | 37.500 |

Table 2 Starting compositions (in mol.%) of glasses prepared in the System II

| Glass sample | Composition (in mol.%) | | | | |
|---|---|---|---|---|---|
| | CuI | CuBr | $Cu_2O$ | $P_2O_5$ | $MoO_3$ |
| IBPM 2 | 21.875 | 3.125 | 46.875 | 9.375 | 18.750 |
| IBPM 3 | 18.750 | 6.250 | 46.875 | 9.375 | 18.750 |
| IBPM 5 | 15.625 | 9.375 | 46.875 | 9.375 | 18.750 |
| IBPM 1 | 12.500 | 12.500 | 46.875 | 9.375 | 18.750 |
| IBPM 4 | 6.250 | 18.750 | 46.875 | 9.375 | 18.750 |

**III. Results** The measured complex impedance allowed to obtain the bulk d.c. and a.c. conductivity of glass samples of both systems at given temperature range.

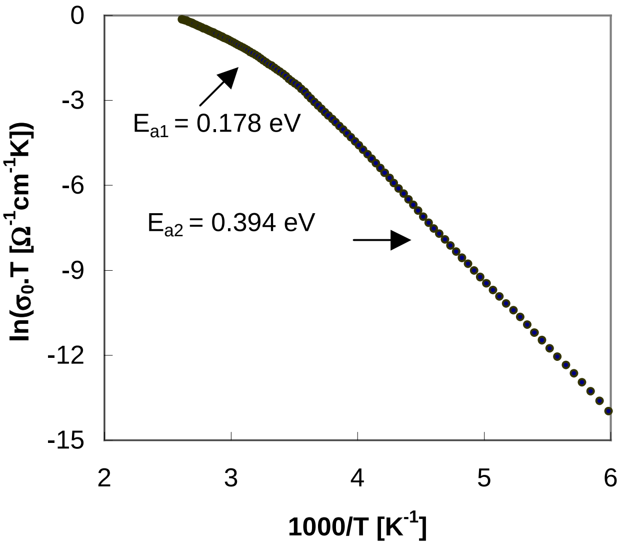

Fig. 1.

The representative results of d.c. conductivity measurement (sample IBPM 2) as a function of temperature are illustrated in Fig. 1. As all of the temperature dependence of d.c. glass conductivity can be fitted by the equation

$$\sigma = \sigma_0 \exp(-E_a/kT), \qquad (1)$$

where $E_a$ is the activation energy, $k$ is the Boltzman constant and $T$ is the absolute temperature, the temperature dependencies of d.c. conductivity indicates two transport mechanisms with activation energies $E_{a1}$, and $E_{a2}$ for higher and lower temperatures, respectively. Because the pre-exponential factor $\sigma_0$ is a function of temperature the factor $\sigma T$ is used in Arrhenius plots of d.c. conductivity. Activation energies calculated from Arhenius plots of d.c. conductivity for all glass samples are summarised in Table 3.

Table 3. Summary of activation energies calculated from Arrhenius plots of d.c. conductivity for glasses of both systems

| Glass sample | $E_{a1}$ (eV) | $E_{a2}$ (eV) | Glass sample | $E_{a1}$ (eV) | $E_{a2}$ (eV) |
|---|---|---|---|---|---|
| IP | 0.295 | 0.500 | IBPM 2 | 0.178 | 0.394 |
| IPM | 0.386 | 0.402 | IBPM 3 | 0.274 | 0.405 |
| BPM | 0.359 | 0.382 | IBPM 5 | 0.333 | 0.402 |
| IM | 0.240 | 0.320 | IBPM 1 | 0.341 | 0.399 |
|  |  |  | IBPM 4 | 0.247 | 0.383 |

All the prepared glasses have high ionic conductivity at room temperatures ($10^{-2}$ -$10^{-4}$ $\Omega^{-1}m^{-1}$). The samples of system II. that contain always the same molar amount of glass-forming components exhibit very close values of activation energies $E_{a2}$ characterising the transport mechanisms at lower temperatures. The same activation energy $E_{a2}$ have also samples IPM and BPM from system I. but containing the same concentrations of $Cu_2O$-$P_2O_5$-$MoO_3$ components. However, the activation energies $E_{a1}$ characterising ion transport at higher temperatures depends on the ratio of CuI to CuBr responsible for $Cu^+$ ion concentrations and indicates similar role of both components in the process of $Cu^+$ mobile ion governing the conductivity.

The set of frequency dependencies of a.c. conductivity measured at various temperatures is illustrated in Fig. 2 for glass sample IBPM 3 and in Fig. 3 for sample

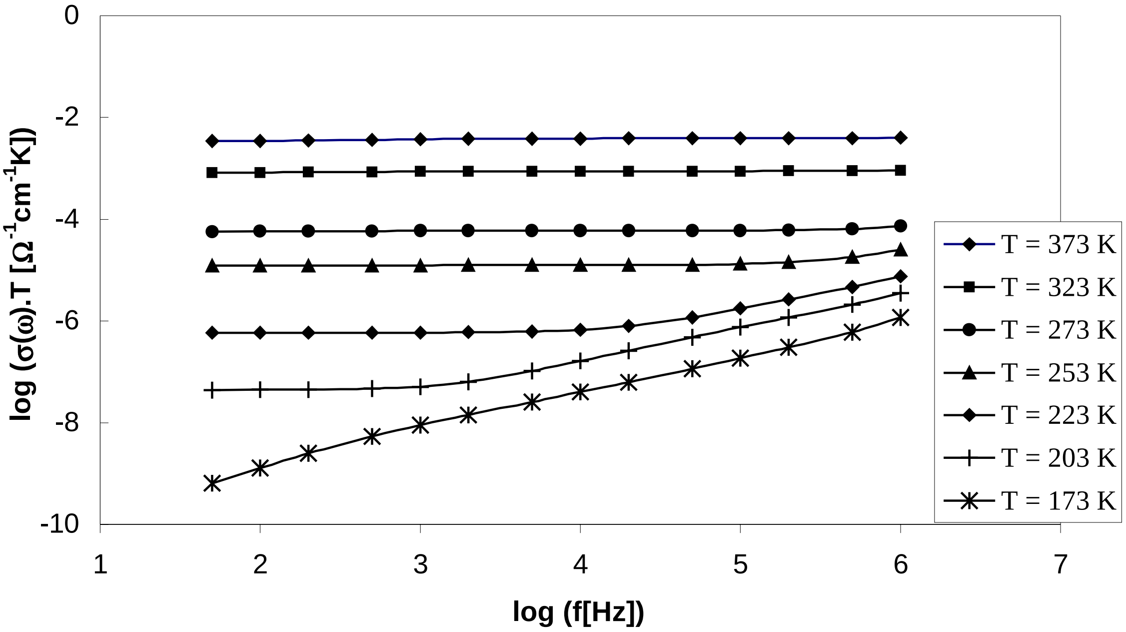

Fig. 2.

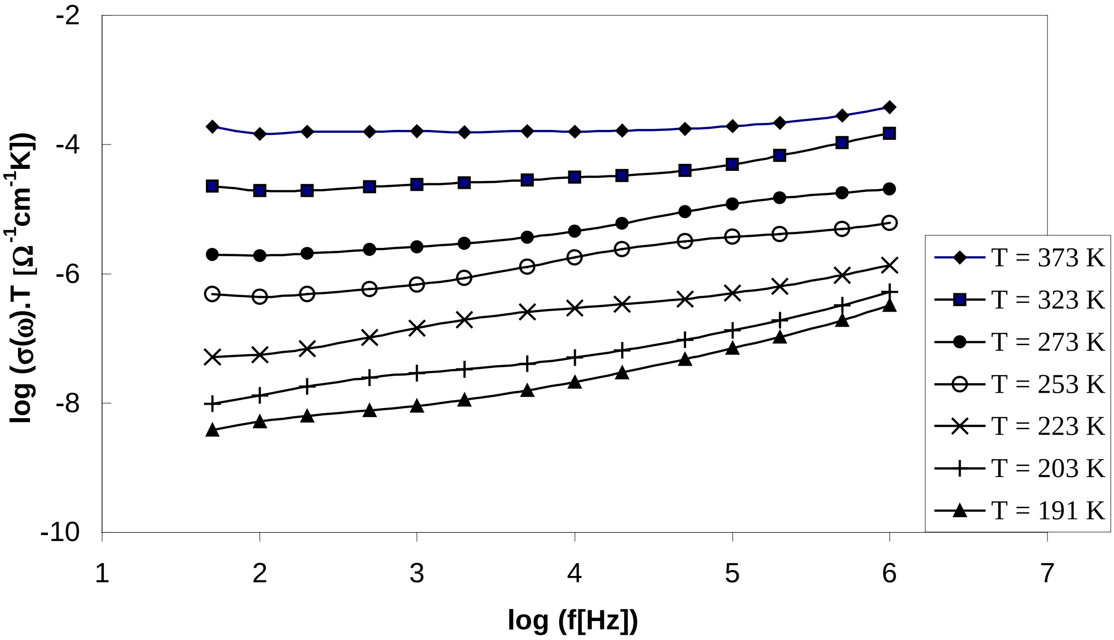

Fig. 3.

IPM. The obtained a.c. conductivity measurements correspond to the complete conductivity spectra obtained from glassy samples [7,8]. However, because of limited frequency range, only two regimes (II and III) of [7, 8] due to hopping motion separated by slope represented by breaks on individual curves could be recognised, the regime II only at low temperatures yet. While the glass samples of system II. exhibits one slope of brakes, the glass sample IPM exhibits evidently another brakes on the a.c. conductivity spectra indicated another transport hopping process that can be explained by slightly modified jump relaxation model [7].

**IV. Conclusion** The first experimental investigation of electrical properties both d.c. and a.c. conductivity of ion conductive glasses in system CuI-CuBr-$Cu_2O$-($P_2O_5$+$MoO_3$) showed the important influence of chemical composition an ion transport mechanisms and indicated more than one possible conductivity mechanism.

However, the further investigation in wider temperature and frequency ranges of glass samples with different compositions and comparing with the results some different measurements should be done for better understanding of ion transport mechanisms in investigated ion conducting glasses.

**Acknowledgement** This work was partly financially supported by Grants No 1/8308/01 and No 1/9141/02 of the Ministry of Education of the Slovak Republic

## References

[1] M. D. Ingram, Phil. Mag. **60** (1989) 729.

[2] S. W. Martin, J. Amer. Ceram. Soc. **74** (1991), 1767.

[3] T. Minami, J. Non-Cryst. Solids **119** (1990) 95.

[4] P. Znášik and M. Jamnický, Solid St. Ionics **95** (1997) 207.

[5] Ch. Lin and C.A. Angel, Solid St. Ionics **13** (1984) 105-

[6] T. Minami and N. Machida, Mater. Chem. Phys. **23** (1989) 63.

[7] K. Funke, Sol. State Ionics 94 **94** (1997) 27.

[8] K. Funke, B. Roling, M. Lange, Sol. State Ionics **105** (1998) 195.