

ACOUSTIC PROPERTIES OF ION CONDUCTIVE GLASSES IN THE SYSTEM CuI-CuBr-Cu₂O-(P₂O₅+MoO₃)

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Abstract The technological interest in fast ionic conductivity in solid materials is increased for various solid state electrochemical devices. Apart from some crystalline materials, the high ionic conductivity at room temperature has been observed in some ion conducting glasses. Comparing with the crystalline materials the ion conductive glasses have several advantages the most important of which are: the absence of grain boundaries, the isotropic properties and the composition variability. The acoustical methods have been already proved an effective tool to study the fundamental structural and mechanical properties of the ionic materials and can also significantly contribute to the fundamental experimental knowledge about the mechanical properties of the new kinds of ion conductive glasses and to the determination of their relationship with the electrical ones. In the present contribution we have illustrated the possible relation between the acoustical and electrical properties of ion conductive glasses of the system CuI-CuBr-Cu₂O-(P₂O₅+MoO₃) for different glass composition. The both acoustical and electrical measurements are also utilized to the study of relaxation processes occurring in these fast ion conductive glasses and to the ion activation energy determination.

Introduction A considerable interest is given in experimental study of glassy materials with the fast ion transport because they play an important role in a number of modern electrochemical devices, such as solid-state batteries, electrochromic 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.

It is known that the investigation of conductivity spectra of ionic glasses can reflect 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 with should be meet the fast ion conductive glasses [3,4]. However, the transport mechanisms can be investigated also by acoustic methods, that can have some advantages comparing to electrical ones as the high sensitivity, absence of contact phenomena and so on [4].

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 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 10⁻³Ω⁻¹cm⁻¹ [6,7]. 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 [8], a positive deviation of the electrical conductivity from the additivity rule can be observed (mixed anion effect). In this contribution we present some acoustical and electrical properties of glasses prepared in the systems CuI-CuBr-Cu₂O-M_mO_n where M_mO_n is P₂O₅ and/or MoO₃. The main purpose of the contribution is to investigate ion transport mechanisms and to determine the relation

between acoustical and electrical properties for various glass composition.

Experimental Procedure The preparation of glasses in the system CuI-CuBr-Cu₂O-(P₂O₅+MoO₃) from commercial reagents (Fluka) represented the procedure already described [8]. Batches of 15 g were melted under a dry argon atmosphere to avoid the oxidation of Cu⁺ during melting and mixed in appropriate portion in silica ampoule at 933 K for 90 min. The glass melts were rapidly quenched by pressing 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 originally 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.% [9]. However, for the acoustical attenuation measurements only three samples were chosen (d≈2 mm), the compositions of which is summarized in Table 1.

The samples for acoustical attenuation and electrical conductivity measurements were cylindrical in shape (area ≈ 1 cm², thickness ≈ 2 mm). Gold electrodes were sputtered onto the sample surfaces for electrical investigation. 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. 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.

The acoustical attenuation was measured using MATEC attenuation comparator for longitudinal acoustic wave of frequency 13 MHz generated by quartz

transducer. The quartz buffer was used to separate the signal from quite short sample.

Table 1 Starting glass compositions (in mol.%)

Glass sample	Composition (in mol.%)				
	CuI	CuBr	Cu ₂ O	P ₂ O ₅	MoO ₃
IPM	25.000	-	46.875	9.375	18.750
BPM	-	25.000	46.875	9.375	18.750
IBPM 5	15.625	9.375	46.875	9.375	18.750

Results The measurements of temperature dependence of acoustic attenuation (Fig. 1) indicate one broad attenuation maxima

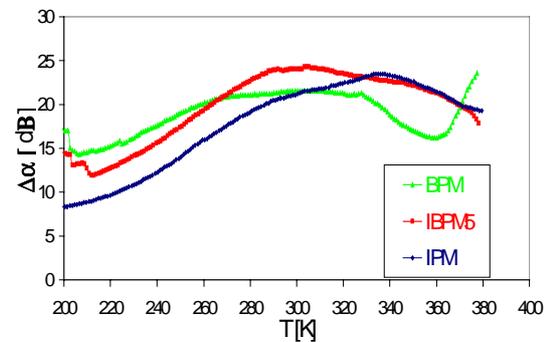


Fig.1 Temperature dependence of acoustic attenuation

in all investigated samples, in which we can distinguish two separated peaks with the different positions for every sample. Except the broad maximum with two peaks the sample BPM exhibits also the rapid attenuation increase at higher temperature indicated another maximum. The measured complex impedance allowed to obtain the bulk d.c. and a.c. conductivity of glass samples given temperature range as all of the temperature dependence of d.c. glass conductivity can be fitted by the equation

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

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 indicate two transport mechanisms with activation energies E_{a1} ,

and E_{a2} for higher and lower temperatures, respectively. Because the pre-exponential factor σ_0 is a function of temperature the factor σT is used in Arrhenius plots of d.c. conductivity. Activation energies calculated from Arrhenius plots of d.c. conductivity for all glass samples are summarised in Table 2.

Table 2 Summary of activation energies calculated from Arrhenius plots of d.c. conductivity

Glass sample	E_{a1} (eV)	E_{a2} (eV)
IPM	0.386	0.402
BPM	0.359	0.382
IBPM5	0.333	0.402

All prepared glasses have high ionic conductivity at room temperature (10^{-2} - $10^{-4} \Omega^{-1} \text{m}^{-1}$). The samples containing the same molar amount of glass-forming components exhibit very close values of activation energies E_{a2} characterising the transport mechanisms at lower temperatures. 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. Two peaks at the broad maxima of acoustical attenuation spectra indicate two possible transport mechanisms with very close activation energies to those determined in d.c. electric measurement.

The set of frequency dependencies of a.c. conductivity measured at various temperatures is illustrated in Fig.2 for glass sample IBPM5 and in Fig.3 for sample IPM.

The obtained a.c. conductivity measurements correspond to the complete conductivity spectra obtained from glassy samples [3,10]. However, because of limited frequency range, only two regimes

(II and III) of [3,10] due to hopping motion separated by slope represented by breaks

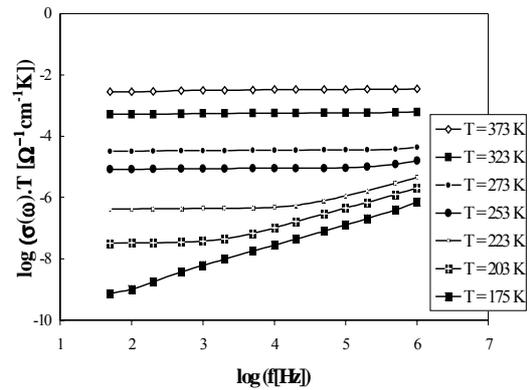


Fig.2 The frequency dependence of a.c. conductivity at various temperatures for sample IBPM 5

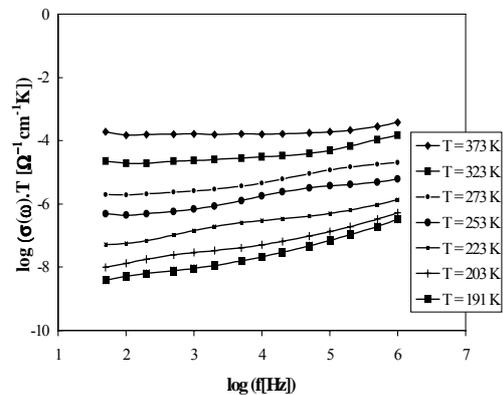


Fig.3 The frequency dependence of a.c. conductivity at various temperatures for sample IPM

on individual curves could be recognised, the regime II only at low temperatures yet. While the glass sample IBPM5 exhibits one slope of breaks, the glass sample IPM exhibits evidently another breaks on the a.c. conductivity spectra indicated another transport hopping process that can be explained by slightly modified jump relaxation model [3].

The study of mechanical losses of mixed cation glasses [11] exhibits an Arrhenius - type relation between peak temperature and applied frequency

$$v = v_0 \exp(-E_a/kT_{\text{peak}}) , \quad (2)$$

where the values for preexponential factor ν_0 are always of order of 10^{14} Hz. Because the acoustic attenuation measurement were performed at the same frequency ν , the activation energy E_a is proportional to the peak temperature T_{peak} . The acoustical spectra show large mechanical loss peaks with activation energies very close to those of d.c. conductivities ($E_{a1} = 0,35$ eV, $E_{a2} = 0,42$ eV for sample BPM, $E_{a1} = 0,38$ eV, $E_{a2} = 0,43$ eV for sample IPM). The attenuation spectra can be then explained by the assumption that temperature peaks are caused by the diffusion processes of various kinds of ions.

Conclusion The experimental investigation of acoustical and electrical properties of ion conductive glasses in system CuI-CuBr-Cu₂O-(P₂O₅+MoO₃) showed the important influence of chemical composition and ion transport mechanisms and indicated more than one transport mechanism. The fact that the activation energies determined from both electrical conductivity measurement and acoustical attenuation spectra have very similar values proved that the same mechanisms can influence electrical and acoustical losses in ion conductive glasses.

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

Acknowledgement The authors would like to thank Mr. F. Černobila for technical assistance. This work was partly financially supported by Grants No 1/8308/01 and No 1/914/02 of the Ministry of Education of the Slovak Republic.

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