Study of Mixed Cation Effect in Ion Conductivity Glasses Using Electrical Conductivity Spectra

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Abstract The acoustical and electrical methods have been already proved to be an effective tool for studying the fundamental structural, mechanical and also transport of the ionic materials. Thus we can determine the relationship between mechanical and electrical properties of the new kinds of ion conductive glasses. In the contribution we present both the data obtained by electrical measurement (d.c. and a.c. conductivity) and acoustical measurement (acoustical attenuation) of ion conductive glasses of the system CuI-CuBr-Cu_2O-P_2O_5 for different glass composition and outline the possible relation between its acoustical and electrical properties. The expected mixed cation effect in the electrical conductivity and acoustical attenuation spectra of several systems of CuI-CuBr-Cu_2O-P_2O_5 that differ by the concentration of its components ion conductivity glasses is identified and their interrelation is analyzed. We observe characteristic effects in frequency response of the complex electrical conductivity and in the magnitudes of acoustic attenuation.

INTRODUCTION There is a considerable interest in the experimental study of glassy materials with the fast ion transport, particularly in their ion transport mechanisms, because they can play an important role in a number of modern electrochemical devices, such as solid-state batteries, electrochronic displays, and sensors [1,2]. The ion conductive glasses have several advantages comparing with crystalline materials because of their easy preparation, their stability composition ranges, the absence of grain boundaries, the isotropic properties and the large available composition variability.

Ion conductive glasses have common structural characteristic, that includes a highly ordered, immobile framework complemented by a highly disordered interstitial sublattice in which carriers are randomly distributed and in which the number of equivalent sites is greater than the number of available ions to fill them. These low potential sites comprising the carrier sublattice must be sufficiently interlined to provide continuous transport paths necessary for optimal movement of ions [3].

The investigation of conductivity spectra of ionic glasses reflects the basic features of the relaxation and transport mechanisms of the mobile ions [4]. The high ion conductivity at room temperature is the most important criterion, which should be met by the fast ion conductive glasses [5,6]. 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 [6,7].

The glasses, which contain Cu^+ conductive ions, have similar electronic configuration and smaller ionic radii in comparison with Ag^+ ion conducting glasses in various glass-forming systems. The conductivity of glasses is affected not only by the type of conductive ions, but also strongly depends on „glass forming“ oxide, but Cu^+ ion conducting glasses are only known in very limited glass-forming systems. Phosphate glasses containing Cu^+ conducting ions are good ionic and the highest conductivity has been recorded in systems containing large fractions of cuprous halides, such as CuI or CuBr [8,9]. Moreover, if two different kinds of halide anions are mixed into cation conducting glasses [9], a positive deviation of the electrical conductivity from the additivity rule can be observed (mixed anion effect).

In this contribution we present some electrical and acoustical properties of glasses prepared in the systems CuI-CuBr-Cu_2O-P_2O_5. The main purpose of the contribution is to investigate ion transport mechanisms and to determine the relation between acoustical and electrical properties considering the various glass compositions.

EXPERIMENTAL PROCEDURE The procedure of glasses preparation in the system CuI-CuBr-Cu_2O-P_2O_5 from commercial reagents (Fluka) represented the procedure already described [10]. The compositions of glass samples are summarized in Table 1. The samples for acoustical attenuation and electrical conductivity measurementswere cylindrical in shape (area ≈ 1 cm^2, thickness ≈ 1.6 - 2.0 mm). Gold electrodes were sputtered onto the sample surfaces for electrical investigation. The frequency and temperature dependencies of electrical conductivity (d.c. and a.c. in the frequency range from 50 Hz up to 1 MHz) were measured using FLUKE PM 6306 impedance analyser and in the temperature range of 140-365 K. The

Glass sample	Composition (in mol.%)			
	CuBr	CuI	Cu_2O	P_2O_5
BIDP1	2.27	15.91	54.55	27.27
BIDP3	6.82	11.36	54.55	27.27
BIDP5	9.09	9.09	54.55	27.27
BIDP7	13.63	4.54	54.55	27.27
BDP	18.18	-	54.55	27.27

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

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 18 MHz generated by quartz transducer. The quartz buffer was used to separate the signal from quite short sample.

RESULS The representative result of d.c. conductivity measurement (sample BIDP7) as a function of temperature is illustrated in Fig. 1. Four different slopes (denoted 1 - 4) of measured can be recognized. However, very interesting feature, not observed before [7], is jump in the curve indicated as slope (3). All of the temperature dependencies of d.c. glass conductivity can be fitted by the equation:

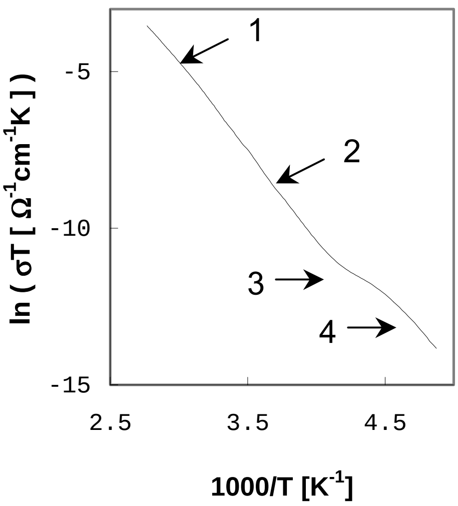

Fig. 1 *Arrhenius plot of d.c. conductivity of sample BIDP7*

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \quad , \qquad (1)$$

where E_a is the activation energy, k_B is the Boltzman constant and T is the thermodynamic temperature. The pre-exponential factor σ_0 is a function of temperature, too. Because of that the factor σT is used in Arrhenius plots of d.c. conductivity. The plots of the temperature dependencies of d.c. conductivity indicate more then two transport mechanisms with activation energies E_{a1}, E_{a2}, maybe E_{a3} and E_{a4} from higher to lower temperatures. Activation energies calculated from Arhenius plots of d.c. conductivity are summarized in Table 2 for all glass samples.

Glass sample	E_{a1} [eV]	E_{a2} [eV]	E_{a4} [eV]
BIDP1	0,47	0,54	0,36
BIDP3	0,46	0,58	0,42
BIDP5	0,44	0,54	0,42
BIDP7	0,43	0,49	0,41
BDP	0,40	0,51	0,38

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

All of the prepared glasses have high ionic conductivity at room temperature (10^{-2} - $10^{-4}\Omega^{-1}m^{-1}$). The samples containing the same molar amount of glass-forming components exhibit very close values of activation energies E_{a4} characterising the transport mechanisms at lower temperatures. However, the activation energy E_{a1} that characterises the 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 that govern the conductivity. A.c. conductivity measured at various temperatures is illustrated in Fig. 2 for glass sample BIDP1.

The obtained a.c. conductivity measurements correspond to the complete conductivity spectra obtained from glassy samples [5,10]. However, because of the limited frequency range, only two regimes (II and III) of [5,10] which are due to hopping motion are differed by breaks on individual curves could be recognized. The transport hopping process can be explained by slightly modified jump relaxation model [5]. Similarly as d.c. measurements a.c. spectra show jump, that can be recognized at lover frequencies and higher temperatures.

The measurements of temperature dependence of acoustic attenuation (Fig. 3) indicate one broad attenuation maximum in all investigated samples, in which we can distinguish two or three separated peaks with a different position for every sample. The another peak can be seen at lover temperature range.

The peaks at the broad maxima of acoustical attenuation spectra indicate transport mechanisms with activation energies very close to that determined in d.c.

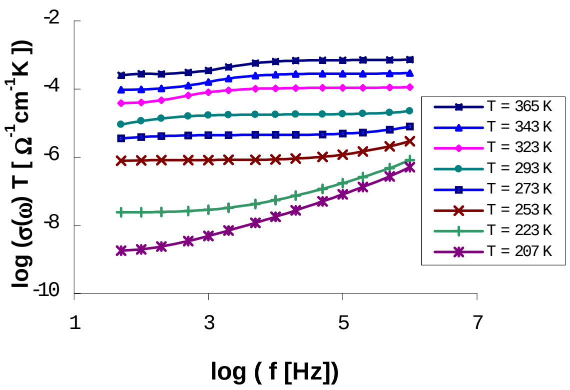

Fig. 2 *The frequency dependence of a.c. conductivity at various temperatures for sample BIDP1*

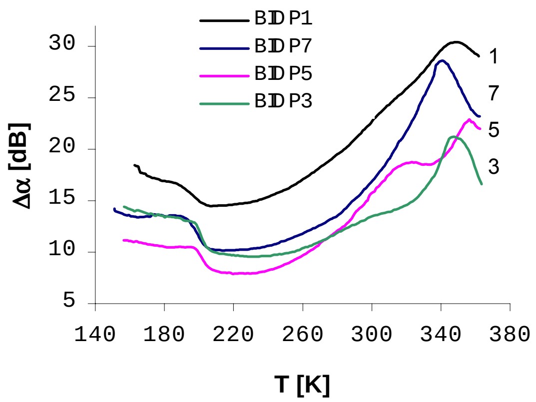

Fig. 3 *Temperature dependence of acoustic attenuation*

electric measurements. The study of acoustical attenuation results in an Arrhenius – type relation between peak temperature and applied frequency [10]:

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

where the values for preexponential factor ν_0 are of order of 10^{14} Hz, but they are again depended on temperature. The activation energies calculated from the peak temperatures T_{peak} are summarized in Table 3 for four glass samples.

Glass sample	E^a_{a1} [eV]	E^a_{a2} [eV]	E^a_{a3} [eV]
BIDP1	0,47	0,41	0,21
BIDP3	0,46	0,41	0,26
BIDP5	0,48	0,40	0,27
BIDP7	0,46	0,39	0,26

Table 3 *Summary of activation energies calculated from T_{peak} of acoustic attenuation*

CONCLUSION We have studied the mixed cation effect using the conductivity spectra and in the acoustical attenuation spectra of ion conductive glasses in the system CuI-CuBr-Cu_2O-P_2O_5. The experimental investigation of acoustical and electrical properties of ion conductive glasses showed the important influence of chemical composition and ion transport mechanisms and indicated also more than two transport mechanisms. The fact that the activation energies determined from both electrical conductivity measurements and acoustical attenuation spectra have very similar values proved that the same mechanisms can influence both electrical and acoustical losses in ion conductive glasses.

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