Contribution of Acoustic Spectroscopy to Understanding of Transport Mechanisms in Fast Ion Conductive Glasses

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Abstract
The acoustical methods have been proved as an effective tool for studying the fundamental structural and mechanical properties of the ionic materials and can also significantly contribute to finding the fundamental experimental knowledge about the transport mechanisms of the new kinds of ion conductive glasses and determine their relationship with the electrical ones. In this contribution we present results of acoustical investigation of ion conductive glasses of the system CuI-CuBr-Cu_2O-(P_2O_5+M_0O_3) with different composition of glass samples measured at various frequencies and wide temperature range. The possible coherence between the acoustical and electrical properties is illustrated, too.

Introduction

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

The ion transport properties of many ion conducting glasses, melts and crystals are similar. The concept of relaxation is shown to provide a general basis for understanding the spectra in terms of the ion dynamics. In glassy electrolytes, the mobile ions encounter different kinds of site and the jump relaxation model has to be modified accordingly [3]. The most important criterion, which should be met by the fast ion conductive glasses, is the high ion conductivity at room temperature [3,4]. The ion transport properties of conductors are directly reflected in the electrical conductivity spectra [5]. However the transport mechanisms investigated by acoustic methods can have some advantages compared to the electrical ones as high sensitivity, absence of contact phenomena and so on [4,6].

The glasses, which contain Cu^+ conductive ions, have similar electronic configuration and smaller ionic radii in comparison with Ag^+ ion conducting glasses. The conductivity of glasses is affected not only by the type of conductive ions, but also strongly depends on „glass forming" oxide. Phosphate glasses containing Cu^+ conducting ions are good ionic conductors with room temperature conductivity of the order $10^{-3}\ \Omega^{-1}cm^{-1}$. The highest conductivity has been recorded in systems containing large fractions of cuprous halides, such as CuI or CuBr [7,8].

In this contribution we present some acoustical properties of glasses prepared in the system CuI-CuBr-Cu_2O-(P_2O_5+MoO_3). The main purpose of the contribution is to investigate ion transport mechanisms in these fast ion conductive glasses and to determine the relation between acoustical and electrical properties considering the various glass compositions.

Experiments

The procedure of glasses preparation in the system CuI-CuBr-Cu_2O-(P_2O_5+MoO_3) from commercial reagents has been already described [6,9]. The set of systems of glasses was 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.% [10]. However, for the acoustical attenuation measurements only three samples were chosen (d ≈ 2 mm), the compositions of which are summarized in Tab. 1.

Glass sample	Composition (in mol.%)				
	CuI	CuBr	Cu_2O	P_2O_5	MoO_3
IPM	25.000	-	46.875	9.375	18.750
BPM	-	25.000	46.875	9.375	18.750
IBPM5	15.625	9.375	46.875	9.375	18.750

Tab. 1. Starting glass compositions (in mol.%) for acoustical investigation

The samples for acoustical attenuation and electrical conductivity measurements were cylindrical in shape (area ≈ 1 cm^2, thickness ≈ 2 mm).

The acoustical attenuation was measured using MATEC attenuation comparator for longitudinal acoustic wave of frequency 13, 18 and 27 MHz generated by quartz transducer. The quartz buffer was used to separate the signal from quite short sample (Fig. 1).

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 in the temperature range of 140-380 K. Gold electrodes were sputtered onto the sample surfaces for electrical investigation. 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.

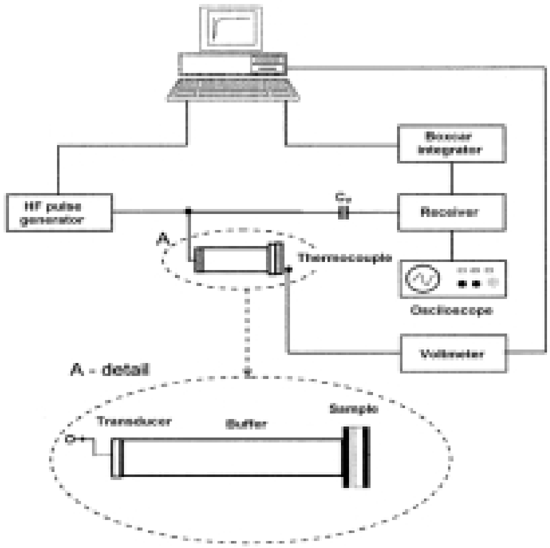

Fig. 1. Experimental arrangement for acoustic attenuation measurement

Results and discussion

The measurements of the temperature dependence of acoustic attenuation at the frequency 13 MHz indicate in all investigated samples one broad attenuation maxima at higher temperature, in which we can distinguish at least two separated peaks. At higher frequency (18 and 27 MHz) the peaks are very well evident and at frequency 27 MHz there are even three peaks (Fig. 2).

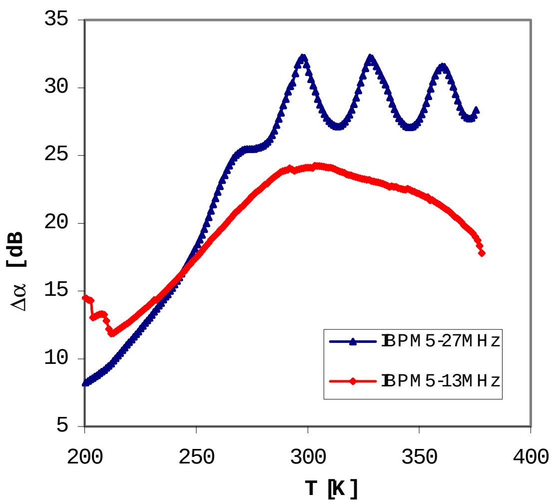

Fig. 2. Temperature dependence of acoustic attenuation measured at frequencies 13 and 27 MHz for sample IBPM5

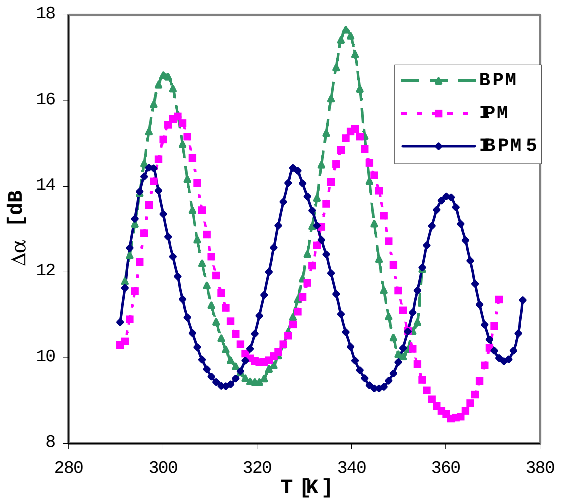

Fig. 3. The separated peaks of broad attenuation maxima measured in all investigated samples at 27 MHz frequency

The positions of separated peaks are different for every sample (Fig. 3) and their shift with increasing frequency is evident.

From the measured complex impedance we obtained the bulk d.c. and a.c. conductivity of glass samples. 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 [10]. Activation energies calculated from Arrhenius plots of d.c. conductivity are summarized in Tab. 2.

Glass sample	E_{a1} (eV)	E_{a2} (eV)
IPM	0.39	0.40
BPM	0.36	0.38
IBPM5	0.33	0.40

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

The values of activation energies E_{a2} that characterise the transport mechanisms at lower temperatures are very close because the samples contain the same molar amount of glass-forming components. The activation energies E_{a1} that characterise ion transport at higher temperatures depend on the ratio of

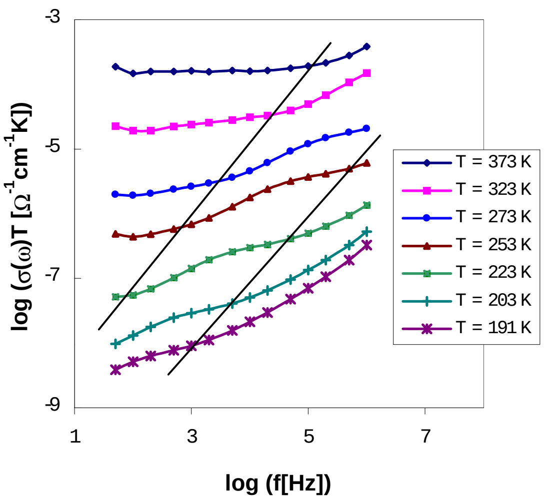

Fig. 4. The frequency dependence of a.c. conductivity at various temperatures for sample IPM

CuI to CuBr responsible for Cu^+ ion concentrations [10].

The a.c. conductivity spectra obtained from the set of frequency dependencies measured at various temperatures are illustrated in Fig. 4. The glass samples exhibits two brakes on the a.c. conductivity spectra and indicated transport hopping processes of Cu^+ ions through various sites that can be explained by jump relaxation models [3]. The brakes in a.c. conductivity slopes corresponding to various transport mechanisms are shown by full lines.

The peaks at the broad maxima of acoustical attenuation spectra (Fig. 2) indicate two possible transport mechanisms with the activation energies very close to those determined in d.c. electric measurement. The attenuation spectra can be explained by the assumption that temperature peaks are caused by the diffusion processes of various kinds of ions. However, another third mechanism is indicated by acoustic measurements comparing with d.c. measurements.

In all glasses we studied an Arrhenius – type relaxation between the peak temperature and the applied frequency,

$$\nu = \nu_0 \exp\,(-E_a / k_B T_{peak})\,, \qquad (1)$$

where E_a is the activation energy, k_B is Boltzmann constant, T_{peak} is the temperature

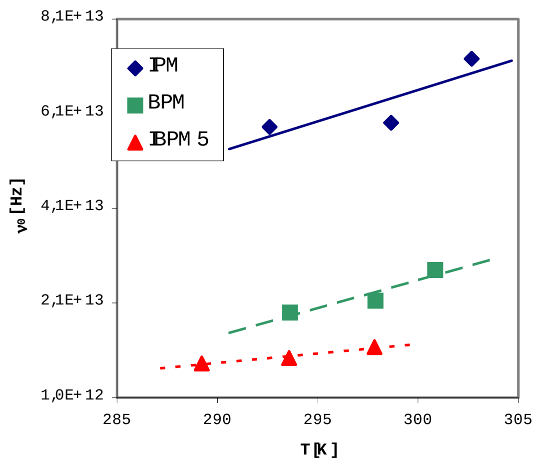

Fig. 5. The temperature dependence of preexponential factor at various frequencies for all samples

of the peak, ν is frequency and ν_0 is preexponential factor. Using the activation energies calculated from the Arrhenius plots of the d.c. conductivity and the temperature values corresponding to the peaks that characterise measurements of acoustical attenuation at various frequencies (13, 18, 27 MHz) (Tab. 3) we found the values for preexponential factor ν_0 (Fig. 5), which depends on temperature.

Glass sample	E^{a}_{a1} (eV)	E^{a}_{a2} (eV)
IPM	0.387	0.402
BPM	0.360	0.382
IBPM5	0.332	0.404

Tab. 3. Summary of activation energies calculated from T_{peak} of acoustic attenuation and preexponential factor ν_0'

We supposed that the temperature dependence of the preexponential factor is a linear function ($\nu_0 = \nu_0' T + const.$). It seems, that the ratio of CuI to CuBr can be responsible for various values of the preexponential factor.

Conclusions

The experimental investigation of ion conductive glasses in system CuI-CuBr-Cu_2O-(P_2O_5+MoO_3) proved that acoustical spectroscopy can be very useful technique for transport mechanisms study and showed the coherence between the acoustical and electrical properties in fast ion conductive glasses. The influence of chemical composition on ion transport mechanisms is important too. It seems, that the same mechanisms can influence electrical and acoustical losses in ion conductive glasses.

Further investigation in wider temperature and frequency ranges of glass samples with different compositions should be done for better understanding of ion transport mechanisms and can help in finding the temperature dependence of the preexponential factor for various types of the investigated ion conducting glasses.

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