CORRELATION BETWEEN ACOUSTIC AND DIELECTRIC SPECTROSCOPY IN ION CONDUCTIVE GLASSES

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Abstract: An acoustic attenuation spectroscopy is known as a powerful technique to study the relaxation processes in condensed matter. The correlation between the acoustic and dielectric spectra of ion conductive glasses of the system CuI-$CuBr$-Cu_2O-P_2O_5 is studied here to investigate the basic features of the relaxation and transport processes in phosphate glasses containing Cu^+ conductive ions. The temperature responses of acoustic attenuation, electrical conductivity and dielectric permittivity are associated with ion transport and depend on the glass composition. Experimental aspects of acoustic and dielectric spectroscopy in ion conductive glasses are reviewed, too. Results obtained from acoustic attenuation and electrical (both dc and ac) conductivity measurements are then compared each other. The coupling between individual relaxation processes identified by different methods in investigated glasses can have important theoretical and practical implications.

1. Introduction

In recent years, ion conductive glasses have attracted extensive attention due to their potential usage in a number of modern electrochemical devices such as solid-state batteries (portable batteries for heart pacemaker, mobile telephones and laptop), solid-oxide fuel cells, electrochemical sensors and oxygen-separation membranes [1]. Phosphate glasses containing Cu^+ conductive ions are good ionic conductors with room temperature conductivity of the order of $10^{-3} \, \Omega^{-1} cm^{-1}$.

Acoustic spectroscopy is a powerful technique for the study of sub-Tg relaxations in glasses due to a strong acousto-ionic interaction [2]. 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. The distinctive peaks of acoustic attenuation spectra, which are caused by resonant interaction with the mobile ion hopping processes, enable us then to study relaxation and transport mechanisms in the ion conductive glasses.

Dielectric relaxation spectroscopy is another useful technique for the study of ion transport processes in fast ion conductive glasses [3]. In general, using this spectroscopy we can study molecular and ionic dynamics of charge carriers and dipoles, in different systems from gases to solid substance.

Acoustic measurements compared to the electrical ones (dc, ac) can have even some advantages as high sensitivity, absence of contact phenomena and

so on. Simultaneous investigation of ion conductive glasses by acoustic attenuation and electrical measurements can get additional information about transport and relaxation processes in investigated materials [4, 5].

In this contribution the acoustic and electrical relaxation processes are studied on identical ionic phosphate glasses of the system CuI-$CuBr$-Cu_2O-P_2O_5 containing Cu^+ ions. Several distinctive peaks in the acoustic attenuation spectra corresponding to different kinds of sites responsible for ionic hopping can be observed. Electrical dc conductivity measurements exhibit several transport processes as well. Experimental results obtained by ac electric measurements were additionally analyzed using the both method of dielectric relaxation and conductivity spectroscopy and confirmed several possible transport and relaxation mechanisms, too. Data measured by acoustic and electrical methods were analyzed using suitable model representations and compared.

2. Theoretical principles

The acoustic attenuation will exhibit a maximum when the relaxation time τ is comparable to the period $(1/\omega)$ of the acoustic perturbation $(\omega\tau = 1)$, where ω is angular frequency and [6]

$$\tau = \tau_0 \exp (E_a^{\ a} / k_B T_{peak}) \qquad (1)$$

is the most probable relaxation time. The relaxation processes, described by an Arrhenius equation (1), are characterized by activation energy $E_a^{\ a}$ for jumps over the barrier between two

potential minima and typical relaxation frequency of ion hopping $1/\tau_0 \approx 10^{13} - 10^{14}$ s^{-1}. Here k_B is the Boltzmann constant and T_{peak} is the temperature of the attenuation maxima, which corresponds to the most frequent relaxation process detected by the acoustic spectroscopy. Using another form of Arrhenius type equation between the peak temperature T_{peak} and the applied frequency ν

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

where ν_0 is the preexponential factor, we can determine the value of activation energy of the ion hopping process.

The electrical conductivity spectra can be fitted by the equation [7]

$$\sigma(\omega) = \sigma(0) + A\omega^s , \qquad (3)$$

where $\sigma(0)$ is the frequency independent conductivity (dc or low-frequency ac) and the exponent s lies in the range $0 < s \le 1$. The both $\sigma(0)$ and A follow Arrhenius type strong temperature dependencies by the equations

$$\sigma(0) = \sigma_0 \exp\left(-E_a^{dc} / k_B T \right) , \qquad (4)$$

$$A = A_0 \exp\left(-E_a^{ac} / k_B T \right) , \qquad (5)$$

where σ_0 and A_0 are the preexponential factors, E_a^{dc} and E_a^{ac} are the activation energies of the ions transport and hopping processes determined from dc and ac measurements, respectively.

The complex permittivity ε^* can be expressed by equation as [3]

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) , \qquad (6)$$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts of the complex permittivity which characterize the *refractive* and *absorptive* properties of the material, respectively. The imaginary and real part of $\varepsilon^*(\omega)$ defines the so-called *loss tangent* of the material

$$\tan \delta(\omega) = \varepsilon''(\omega) / \varepsilon'(\omega) \qquad (7)$$

that is related to the attenuation constant (or absorption coefficient) of an electromagnetic wave propagating in the material.

The activation energies of the relaxation processes can be than estimated using the isothermal or isochronal peaks of $\tan \delta(\omega, T)$ from the plots of $\log f_{max}$ vs. $1/T$ (isothermal plots) or $\log f$ vs. $1/T_{max}$ (isochronal plots). These plots are straight lines in accordance with another Arrhenius equation

$$f = f_0 \exp\left(-E_a^{tg\delta} / k_B T_{max} \right) , \qquad (8)$$

where f is the frequency of applied electrical field, f_0 is the preexponential factor and $E_a^{tg\delta}$ is the value of activation energy of the ion hopping process determined using dielectric relaxation spectroscopy.

3. Experimental

The set of glasses of the system (18.18-x) CuI – x CuBr – 54.55 Cu$_2$O – 27.27 P$_2$O$_5$ from commercial reagents with different and increasing x (one step is $\sim$ 2.27 in mol.%) was originally prepared to investigate the role of cuprous halides producing Cu$^+$ ions keeping their ratio to the glass forming system constant. The initial compositions of the complex set of glass samples are summarized in Table 1. The preparation of glasses in the investigated system has been already described [8].

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

Glass samples	Composition (in mol.%)			
	CuI	CuBr	Cu$_2$O	P$_2$O$_5$
IDP	18.18	0	54.55	27.27
BIDP1	15.91	2.27	54.55	27.27
BIDP2	13.63	4.55	54.55	27.27
BIDP3	11.36	6.82	54.55	27.27
BIDP5	9.09	9.09	54.55	27.27
BIDP6	6.82	11.36	54.55	27.27
BIDP7	4.55	13.63	54.55	27.27
BIDP8	2.27	15.91	54.55	27.27
BDP	0	18.18	54.55	27.27

The acoustical attenuation was measured using MATEC attenuation comparator for longitudinal acoustic wave of frequency 13, 18 and 27 MHz generated by quartz transducer in the temperature range of 140-380 K. The quartz buffer was used to separate signal from quite short sample (Figure 1).
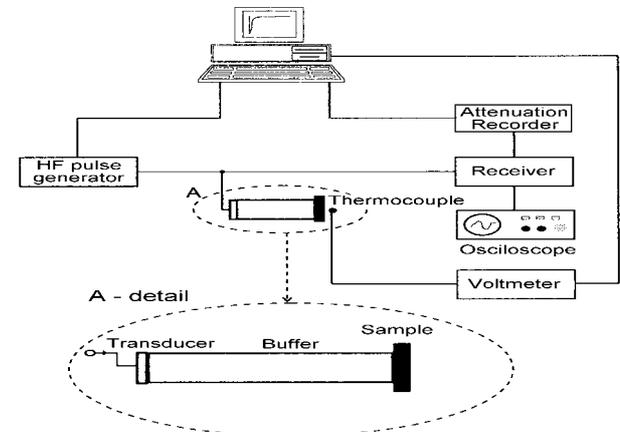
Figure 1. Experimental arrangement for acoustic attenuation measurement.

The temperature and frequency dependencies of both dc and ac electrical conductivity were measured using FLUKE PM 6306 impedance analyser in the same temperature range as acoustic measurements. The measured complex impedance allowed us to obtain the bulk conductivity of glass samples by means of the usual impedance analysis. Gold electrodes were sputtered on to the sample surfaces for electrical investigation.

The real and imaginary parts of the complex dielectric permittivities (ε', ε'') and the loss tangent (tan δ) were calculated using the values obtained from measurements in the frequency range from 50 Hz to 1 MHz and in the same temperature range as we used in the dc electrical and acoustic measurements.

4. Results and Discussion

The acoustic attenuation measured at the constant frequency ν = 18 MHz in all samples of investigated set indicate one broad attenuation peak at higher temperature in which we can distinguish three separated peaks (Figure 2). Another peak was detected at lower temperatures.
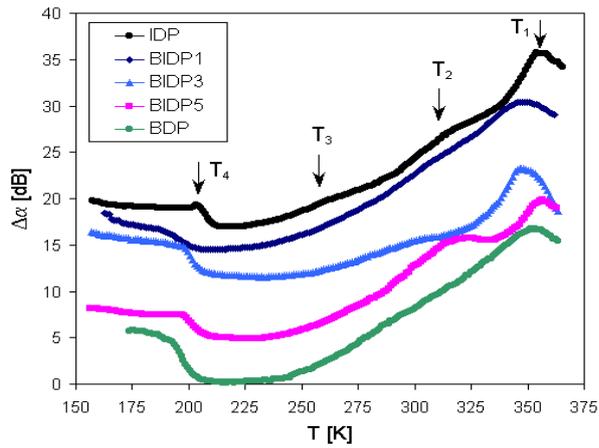
Figure 2. Acoustics attenuation spectra of selected samples of investigated system of glasses. The individual spectra are shifted for better distinction.

The acoustic attenuation spectra of the investigated cuprous halide glasses were fitted using suitable theoretical attenuation functions and mathematical procedure using the genetic algorithm with binary representation of the theoretical attenuation function variables [5] in connection with the visual construction of the acoustic attenuation model. During the fitting procedure the Debye function, Kohlrausch-Wiliems-Wats function and Double Power Law function were gradually used [9].

Using the theoretical model with Double Power Law function [5],

$$\alpha = \approx 1/((\omega\tau)^{-n} + (\omega\tau)^m) , \qquad (7)$$

where m and n are power-law exponents, which take values between 0 and 1, the calculated lines gave an excellent agreement with the measured acoustic spectrum in the whole temperature range.

The representative acoustic attenuation and its theoretical simulation is illustrated in Figure 3 for sample IDP. The temperature dependencies of the acoustic attenuation were analyzed assuming the existence of at least four thermally activated relaxation processes of Cu^+ ions in connection with different kinds of sites. The temperatures T_{1-4} represent the temperatures of simulated peaks. The proportion of the peak intensities (mainly first two peaks (T_1, T_2)) depends on the glass composition, namely on the ratio CuI/CuBr. Using Equation (2) and values of T_{peak} for individual peaks, the activation energies E_a^a were determined (Table 2).
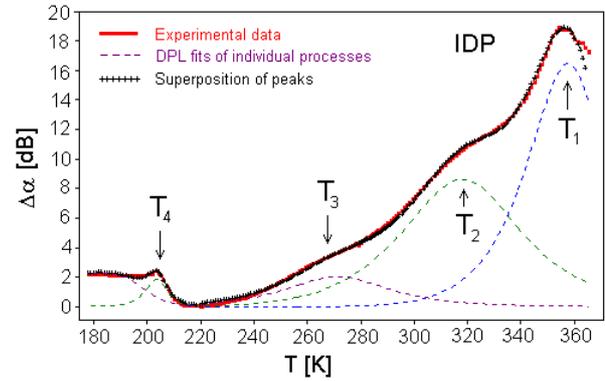
Figure 3. Acoustics spectrum of sample IDP (full line). Cross-marked line represents the best fit of superposition of four relaxation processes.

The temperature dependencies of the dc conductivity for all samples indicate four different transport mechanisms with activation energies E_{a1}^{dc}, E_{a2}^{dc}, E_{a3}^{dc} and E_{a4}^{dc} (Figure 4) including also some dissociation and association processes connected with defect formation [1, 4].
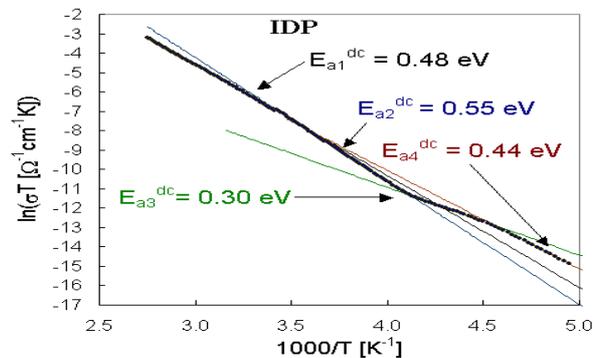
Figure 4. Arrhenius plot of dc conductivity of sample IDP.

Table 2. Activation energies calculated from acoustic and dielectric spectra, as well as dc and ac measurements using corresponding Arrhenius plots. The supposed same mechanisms have the identical shaded background.

Glass Sample	Acoustic measurements				Electrical measurements					
	$E_{a1}{}^{a}$[eV]	$E_{a2}{}^{a}$[eV]	$E_{a3}{}^{a}$[eV]	$E_{a4}{}^{a}$[eV]	$E_{a1}{}^{dc}$[eV]	$E_{a2}{}^{dc}$[eV]	$E_{a3}{}^{dc}$[eV]	$E_{a4}{}^{dc}$[eV]	$E_{a}{}^{tg\delta}$[eV]	$E_{a}{}^{ac}$[eV]
IDP	0.48	0.43	0.36	0.27	0.48	0.55	0.30	0.44	0.48	0.28
BIDP1	0.47	0.41	0.37	0.25	0.46	0.52	0.30	0.40	0.46	0.30
BIDP2	0.46	0.41	0.36	0.27	0.46	0.54	0.35	0.44	0.47	0.27
BIDP3	0.46	0.41	0.37	0.26	0.46	0.55	0.30	0.42	0.48	0.27
BIDP5	0.46	0.42	0.33	0.26	0.46	0.54	0.33	0.42	0.47	0.27
BIDP6	0.46	0.42	0.35	0.28	0.45	0.52	0.35	0.43	0.48	0.29
BIDP7	0.45	0.42	0.39	0.25	0.45	0.50	0.23	0.43	0.47	0.26
BIDP8	0.46	0.43	0.36	0.27	0.42	0.52	0.26	0.41	0.50	0.27
BDP	0.47	0.43	0.39	0.26	0.43	0.51	0.18	0.41	0.47	0.27

The temperature dependences of the loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) in the frequency region 50Hz to 1MHz for representative sample IDP can be see in Figure 5.
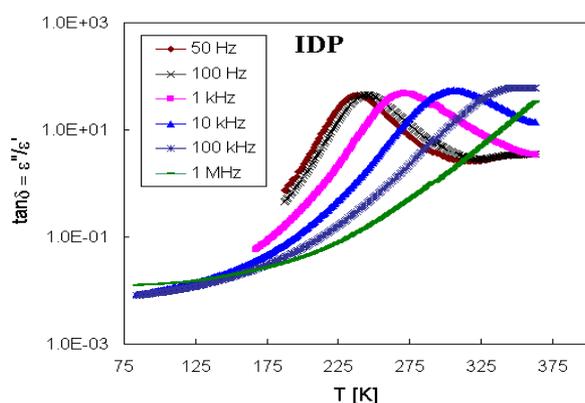
Figure 5. Temperature dependence of the dielectric loss tangent in the sample IDP.

The picture shows that only one broad peak for every frequency was observed and its maximum position ($\tan\delta\,(T_{max})$) is shifted to higher temperatures with increasing frequency. Plotting the frequency f of ac electric field in logarithmic scale as a function of corresponding inverse temperature of maximum of loss tangent (Equation 8), we can than obtain the values of activation energies of the dielectric losses.

Calculated activation energies of the barriers between equilibrium positions of ions using acoustic and electrical measurement are summarized in Table 2 for comparison.

5. Conclusions

We have studied correlation between acoustic, conductivity and dielectric spectroscopy results in the set of ion conductive glasses of composition (18.18-x) CuI – x CuBr – 54.55 Cu$_2$O – 27.27 P$_2$O$_5$ to obtain the fundamental properties of investigated materials. Comparing the acoustic and electrical measurements, we can suppose that some relaxation mechanisms indicated by acoustical spectra correspond to the relaxation mechanisms indicated by electrical ones.

The fact that some of activation energies determined from dielectric and conductivity spectroscopy on the one side and acoustic attenuation spectroscopy on the other side have the same values of activation energy proved that the same mechanisms can influence electrical and acoustical losses in ion conductive glasses.

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