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DIELECTRIC RELAXATION SPECTROSCOPY OF THERMAL ACTIVATED PROCESSES IN ION CONDUCTIVE GLASSES

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Analyzing the temperature and frequency dependences of real and imaginary part of the dielectric permittivities we can study ionic hopping motion and the transport mechanisms connected with the charge mobility in ion conductive glasses. The experimental results getting from electric measurements are analyzed, discussed and compared with acoustic measurements. Coherence between the results from distinctive peaks of loss tangent and acoustic attenuation spectra which are caused by resonant interaction of acoustic waves with the mobile ions enable us to suppose that the same mechanisms can influence electrical and acoustical losses in ion conductive glasses.

Keywords: Ion conductive glasses, relaxation and transport processes, dielectric relaxation spectroscopy, acoustic attenuation measurements

1 Introduction

Phosphate glasses containing Cu^+ conductive ions as one of the possible perspective ionic materials which can be used in a number of modern electrochemical devices are good ionic conductors with the conductivity of 10^{-5} to 10^{-3} Scm^{-1} at room temperature [1]. Modified phosphate glasses with different cuprous halides and constant glass forming systems were prepared in various compositions for the study of mixed anion effect and effect of mixing glass forming oxide. Using dielectric relaxation and conductivity spectroscopy in comparison with acoustic attenuation spectroscopy we investigated prepared glass samples for purpose to study relaxation and transport processes in these materials.

The investigated materials can be classified as glasses which contain one type of cation Cu^+ and various kinds of phosphate structural units. Using infrared (IR) spectroscopy [2] it has been found several different kinds of sites responsible for ionic hopping motion.

2 Theoretical principles

Dielectric relaxation spectroscopy is a powerful technique for the study of ion transport processes in fast ion conductive glasses. In general, using this spectroscopy, we can study molecular and ionic dynamics of charge carriers and dipoles, we can observe different systems from gases to solid substance. It has been observed that the determining the imaginary part of the complex dielectric constant (ε'') compared to the real part (ε') (which

characterize the absorptive and reflective properties of material) play a crucial role in the study of fundamental properties of investigated materials. Using the functions

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad (1)$$

for presenting dielectric relaxation data for materials in which the motion of charges is dominated, the position of a peak ($\omega_0 = 1/\tau_0$) in the loss component $\varepsilon''(\omega)$ outlines a characteristic time scale of the orientational molecular mobility. For ionically conducting glasses no equivalent feature in $\varepsilon''(\omega)$ was found which immediately sets a time scale for ionic mobility [3]. For that reason is used so-called loss tangent of the material

$$\tan \delta(\omega) = \varepsilon''(\omega) / \varepsilon'(\omega) , \quad (2)$$

which is related to the attenuation constant of electromagnetic wave propagating in material.

The activation energies of the relaxation processes can be than estimated using the isothermal or isochronal peaks of tan δ (ω, T) from the plots of log f_{max} vs. 1/T (isothermal plots) or log f vs. $1/T_{max}$ (isochronal plots) (f_{max} is the frequency corresponding to the maximum of tan δ(ω), T_{max} is the temperature corresponding to the maximum of tan δ(T)). These plots are straight lines in accordance with Arrhenius equation

$$f = f_0 \exp (-E_a^{tg\delta} / k_B T_{max}) , \quad (3)$$

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

The dc electrical measurements can be fitted by the equation

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

where σ(0) represents the dc conductivity, σ_0 is the preexponential factor and E_a^{dc} is the activation energy of ion transport processes.

The form of Arrhenius type equation between the peak temperature T_{peak} of temperature dependence of acoustic attenuation and the applied frequency ν can be expressed

$$\nu = \nu_0 \exp (-E_a^{a} / k_B T_{max}) , \quad (5)$$

where ν is the applied frequency, ν_0 is the preexponential factor. Using Arrhenius equations (3), (4) and (5) we can determine the value of activation energies of the ion hopping process.

3 Experimental and Results

The preparation of the glasses in investigated system CuI – CuBr – Cu_2O – P_2O_5 has been already described [4]. The several sets of glasses from commercial reagents was originally prepared to investigate the role of cuprous halides producing Cu^+ ions keeping their ratio to the glass forming system constant. The initial composition of investigated set of glass samples are summarized in Tab. 1.

Glass Sample	Starting composition (in mol. %)			
	CuI	CuBr	Cu_2O	P_2O_5
IBOP1	21.88	3.12	56.25	18.75
IBOP4	14.06	10.94	56.25	18.75
IBOP5	12.50	12.50	56.25	18.75
IBOP7	6.25	18.75	56.25	18.75

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

The temperature and frequency dependencies of electrical conductivity (dc and ac in the frequency range 50 Hz - 1 MHz) were measured using FLUKE PM 6306 impedance analyzer in the temperature range 140-380 K. Gold electrodes were sputtered on to the sample surfaces for electrical investigation. The measured complex impedance allowed us to obtain the bulk conductivity of glass samples by means of the usual impedance analysis. Using the values obtained from ac measurements we calculated the real and imaginary parts of the complex dielectric permittivities (ε', ε'') and the loss tangent (tan δ).

The acoustical attenuation was measured using MATEC attenuation comparator for longitudinal acoustic wave of frequency 13, 18 and 27 MHz in the same temperature range as electrical measurements. Representative results from measurements of investigated set of glasses can be seen in Fig. (1), Fig. (2) for sample IBOP4.

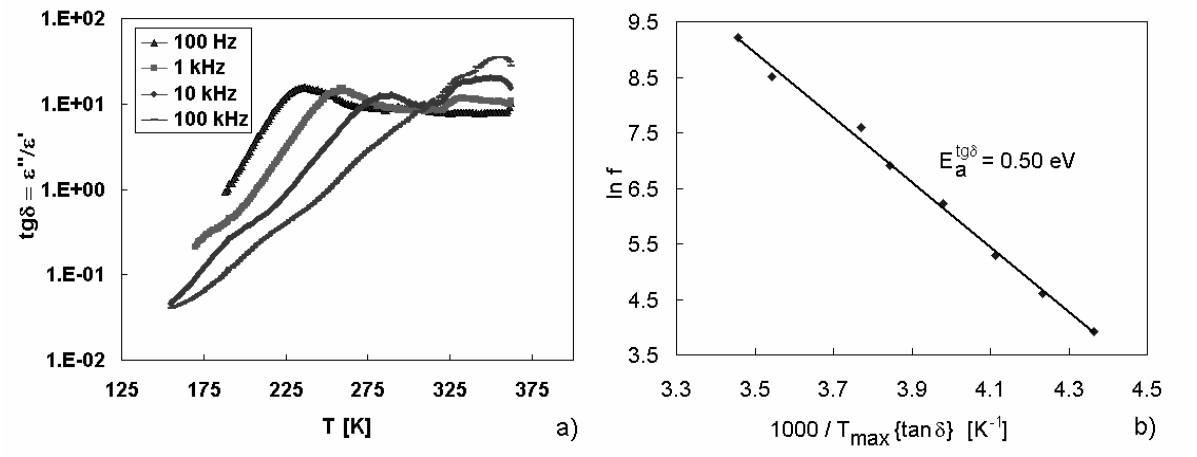

Fig. 1. (a) Temperature dependence of the dielectric loss tangent for the sample IBOP4. One broad peak for every frequency was observed and its maximum position was shifted to higher temperatures with increasing frequency. (b) Arrhenius plot between the temperature T_{max} of peak corresponding to the maximum of tan δ(T) and applied frequency.

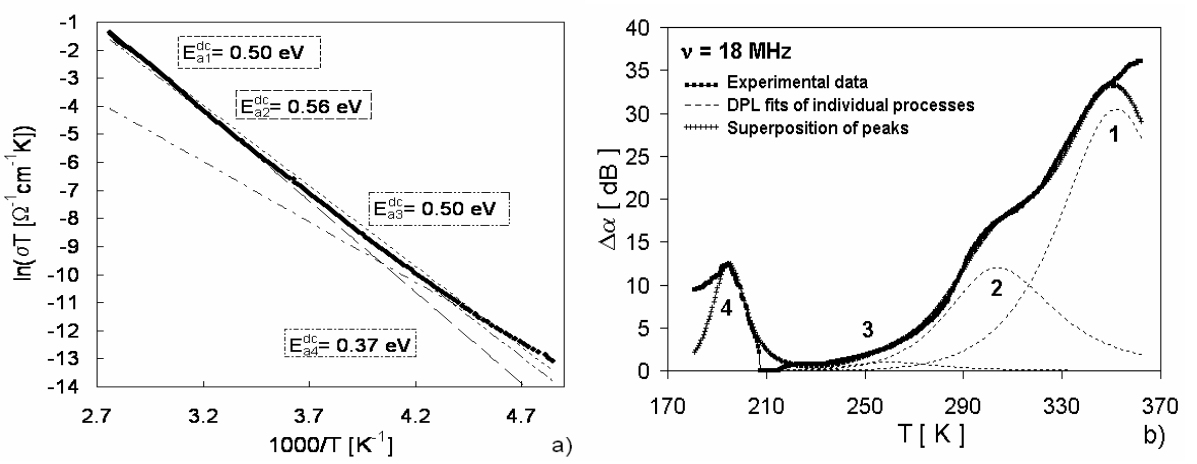

Fig. 2. (a) Arrhenius plot of dc conductivity of sample IBOP4. (b) Acoustics spectrum of sample IBOP4 (full line). Cross-marked line represents the best fit of superposition of four relaxation processes. The maxima of peaks of individual processes are denoted as peaks 1 – 4.

Using Eq. (3-5) and Double Power Law model [5] for acoustic measurements we determined some relaxation and transport processes and the activation energies of the barriers between equilibrium positions of ions. Calculated energies from electrical and acoustic measurements are summarized in Tab.2.

Glass Sample	Electrical measurements					Acoustical measurements			
	$E_a^{tg\delta}$ [eV]	E_{a1}^{dc} [eV]	E_{a2}^{dc} [eV]	E_{a3}^{dc} [eV]	E_{a4}^{dc} [eV]	E_{a1}^{a} [eV]	E_{a2}^{a} [eV]	E_{a3}^{a} [eV]	E_{a4}^{a} [eV]
IBOP1	0.48	0.48	0.51	0.46	-	0.50	0.44	0.36	0.28
IBOP4	0.50	0.50	0.56	0.50	0.37	0.49	0.42	0.36	0.27
IBOP5	0.49	0.47	0.49	0.45	-	0.49	0.44	0.38	0.27
IBOP7	0.48	0.43	0.44	0.41	0.37	0.48	0.42	0.36	0.27

Tab. 2. Activation energies calculated from Arrhenius plots of dielectric and dc conductivity measurements and acoustic spectra. Some of E_{a4}^{dc} we could not determine because of limited temperature range. The supposed same mechanisms have the identical shaded background.

4 Conclusions

We have studied correlation between dielectric, conductivity and acoustic spectroscopy in the set of ion conductive glasses of composition CuI–CuBr–Cu_2O–P_2O_5 to obtain the transport and relaxation properties of investigated materials. Comparing the electrical and acoustic measurements, we can suppose that some relaxation mechanisms indicated by electrical measurements correspond to the relaxation mechanisms indicated by acoustic measurements.

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 very close values of activation energy proved that the same mechanisms can influence electrical and acoustical losses in investigated ion conductive glasses.

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