

DIELECTRIC SPECTROSCOPY OF IONIC GLASSES OF THE SYSTEM CuI-CuBr-Cu₂O-P₂O₅

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Summary We have used dielectric relaxation spectroscopy to measure frequency and temperature dependence of complex dielectric functions $\varepsilon^*(\omega)$, $\varepsilon^*(T)$ of ion conductive glasses of the system CuI-CuBr-Cu₂O-P₂O₅. The observation, analysis and interpretation of the temperature and frequency dependences of real and imaginary part of the dielectric permittivities can reflect the basic features of the relaxation and transport processes of the mobile ions. The experimental results are analyzed, discussed and compared with both acoustic and conductivity spectra measurements.

1. INTRODUCTION

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.

The central quantities in this context are the dielectric displacement \mathbf{D} and the electric field \mathbf{E} , with the dielectric permittivity ε_r using the SI system being defined by

$$\mathbf{D} = \varepsilon_r \varepsilon_0 \mathbf{E} = \varepsilon_0 \mathbf{E} + \chi \varepsilon_0 \mathbf{E} = \varepsilon_0 \mathbf{E} + \mathbf{P}, \quad (1)$$

where $\varepsilon_0 = 8.854 \cdot 10^{-12} \text{ AsV}^{-1} \text{ m}^{-1}$ is the permittivity of vacuum, $\chi = \varepsilon_r - 1$ is the susceptibility and \mathbf{P} is the polarization. It has been observed that the determining the imaginary part of the complex dielectric constant (ε'') compared to the real part (ε') play a crucial role in the study of fundamental properties of investigated materials [1]. Using the functions $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ or $\varepsilon(t)$ is common in practice for presenting dielectric relaxation data for materials in which the motion of charges is dominated, where the position $\omega_0 = 1/\tau_0$ of a peak in the loss component $\varepsilon''(\omega)$ outlines a characteristic time scale of the orientational molecular mobility. For ionically conducting glasses no equivalent feature in $\varepsilon''(\omega)$ is found which immediately sets a time scale for ionic mobility [2].

In this contribution the method of dielectric spectroscopy is used to analyze the experimental results obtained by ac electric measurements of the ion conductive glasses of the system CuI-CuBr-Cu₂O-P₂O₅. The obtained results are then compared with the results of acoustic and conductivity spectroscopy to understand better ion transport and relaxation mechanisms in these ionic glasses.

2. EXPERIMENTAL DETAILS

The detailed procedure of glasses preparation of the system (18.18-x) CuI - x CuBr - 54.55 Cu₂O - 27.27 P₂O₅ from commercial reagents and its

complete set consisting of nine samples with different and increasing x (one step is ~ 2.27 in mol.%) have been already described [3, 4]. 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 them between two brass plates to a final thickness of ≈ 2 mm. The resulting discs of 20 mm in diameter (area $\approx 1 \text{ cm}^2$) were kept between the plates until their temperature decreased to room temperature.

The real and imaginary parts of the complex dielectric permittivities (ε' , ε'') and loss tangent ($\text{tg } \delta$) were calculated from the values obtained from the measurements in frequency ranges 50Hz – 1MHz by FLUKE PM 6306 impedance analyzer.

For experimental investigation by dielectric relaxation spectroscopy the sample IDP (x = 0) was chosen as representative of investigated glass system. We were investigated and analyzed temperature dependences of complex dielectric function $\varepsilon^*(T)$ for sample IDP.

3. RESULTS AND DISCUSSION

The Figures 1 and 2 represent the real and imaginary parts of complex permittivity ε^* as a

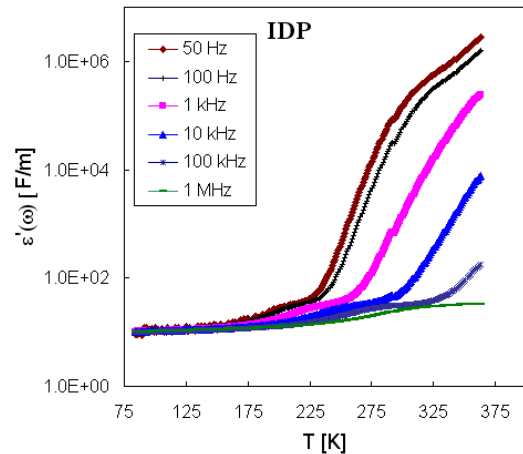


Fig. 1. Temperature dependence of real part of complex dielectric permittivity

function of temperature, respectively.

The temperature dependences of loss tangent angle ($tg\delta = \epsilon''/\epsilon'$) in the same frequency region

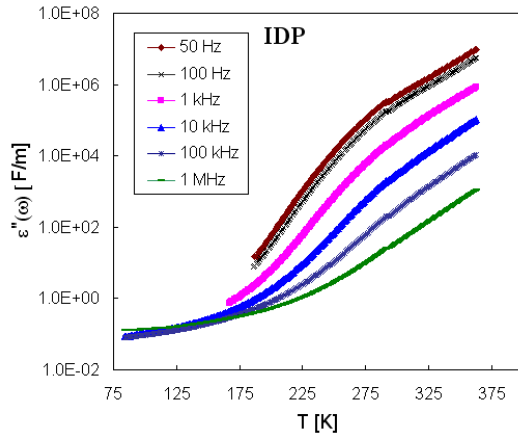


Fig. 2. Temperature dependence of loss component complex dielectric function

we can see on the Figure 3. It is seen that the only one broad peak was observed and its maximum position ($tg\delta(T_{max})$) is shifted to higher temperatures with increasing frequency.

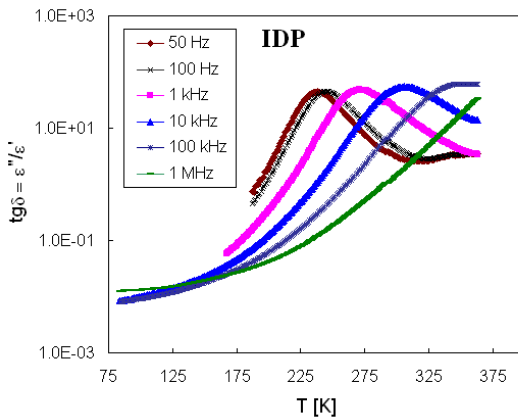


Fig. 3. Temperature dependence of dielectric loss angle tangent in the sample IDP

It is an established fact that the condition for observing a maxima in the dielectric losses is given by the relation

$$\omega_0 \tau_0 = 1, \quad (2)$$

where $\omega_0 = 2\pi f_{max}$ (f_{max} is the frequency corresponding to the maximum of $tg\delta(f)$) and τ_0 is the relaxation time. Now the relaxation time is related to the jumping probability per unit time, p , by equation $\tau = 1/2p$ or $f_{max} \sim p$ [5]. Therefore, a maximum can be observed when hopping or jumping frequency of ions becomes approximately equal to the frequency of applied field. The shift of maxima in temperature dependencies of the dielectric loss tangent towards to high-frequency side could be due to high values of hopping probability (p) per unit time in the sample.

Plotting the frequency of ac electric field in logarithmic scale as a function of corresponding inverse temperature of maximum of loss tangent angle ($tg\delta(T_{max})$) (Arrhenius plot, Figure 4), we can then obtain a value of $E_a^{tg\delta} = 0.48$ eV for activation energy of the dielectric losses.

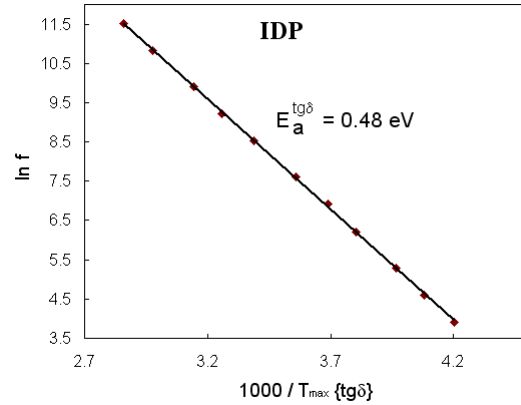


Fig. 4. Temperature dependence of dielectric loss angle tangent maxima and frequency

4. COMPARISON WITH ACOUSTICAL AND ELECTRICAL MEASUREMENTS

In Figures 5 and 6, we present for comparison dc electrical conductivity and acoustic attenuation spectra measurements, respectively, allowing to obtain the values of activation energy E_a of the relaxation and transport processes in investigated sample IDP by different techniques.

The logarithm of real part of dc electrical conductivity is shown in Figure 5 as a function of inverse temperature. The value of $E_a^{dc} = 0.48$ eV was obtained from this conventional Arrhenius plot for high temperature region.

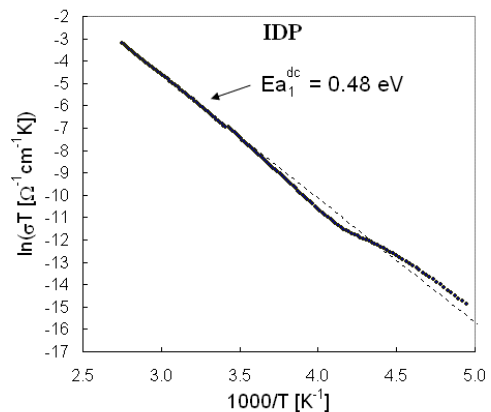


Fig. 5. Arrhenius plot of dc conductivity of sample IDP

The acoustic attenuation was measured using longitudinal acoustic wave of frequency 18 MHz in the temperature range 140-380 K [3]. The relaxation processes are also described by Arrhenius type

relaxation between the peak temperature and the applied frequency

$$\nu = \nu_0 \exp(-E_a^a / k_B T_{max}), \quad (3)$$

where k_B is Boltzmann constant, T_{peak} is the temperature of the peak maximum, ν is the frequency, ν_0 is the preexponential factor and E_a^a is activation energy for jump over the barrier between two potential minima. Using the value of T_{Ipeak} of attenuation maxima, of the peak corresponding to the most impacted relaxation process detected by acoustic spectroscopy, the value of activation energy $E_{a1}^a = 0.48 \text{ eV}$ was determined.

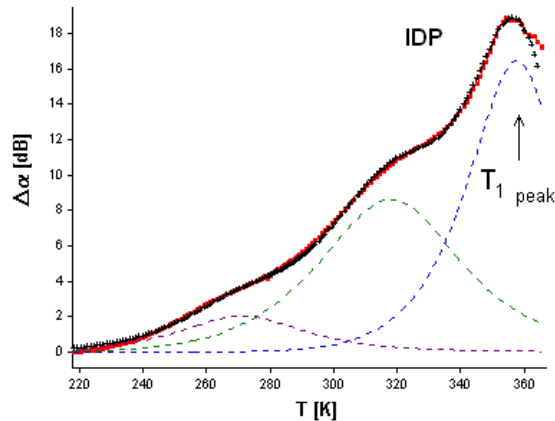


Fig. 6. Acoustic attenuation spectrum of sample IDP (full line). Cross-marked line represents the best fit of superposition at the smallest three relaxation processes.

5. CONCLUSION

We have studied temperature dependence of dielectric loss angle tangent in the sample IDP, one of the system $(18.18-x) \text{ CuI} - x \text{ CuBr} - 54.55 \text{ Cu}_2\text{O} - 27.27 \text{ P}_2\text{O}_5$ using imaginary part of the complex dielectric constant (ϵ'') compared to the real part (ϵ') for the obtain of fundamental properties of investigated materials of composition $\text{CuI}-\text{CuBr}-\text{Cu}_2\text{O}-\text{P}_2\text{O}_5$.

We have found, that the activation energy of dielectric losses $E_a^{tg\delta} = 0.48 \text{ eV}$ is in good agreement with the both activation energy for hopping or jumping of ions calculated using acoustic attenuation measurement and dc measurement. Similar results can be observed from measurements of other samples of the investigated system $\text{CuI}-\text{CuBr}-\text{Cu}_2\text{O}-\text{P}_2\text{O}_5$.

Comparing the electrical and acoustic measurements, we can suppose that some relaxation mechanisms indicated by acoustical spectra can correspond to the relaxation mechanisms indicated by electrical ones. However, it was observed [6, 7], that the electrical conductivity spectra including dc and ac measurements similarly as acoustic spectra represent several relaxation processes or conductivity regimes corresponding to several transport mechanisms.

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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