

MODELING OF ACOUSTIC ATTENUATION SPECTRA OF ION CONDUCTIVE GLASSES

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INTRODUCTION

Ion conductive glasses have attracted attention during last few decades due to their potential usage in a number of modern electrochemical devices such as solid-state batteries (mobile telephones and laptop, portable batteries for heart pacemaker), electrochemical sensors, solid-oxide fuel cells and oxygen-separation membranes. Phosphate glasses containing Cu^+ conductive ions as one of the possible perspective ionic materials 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 glass forming systems were prepared in various compositions for the study of basic features of the relaxation and transport processes in these materials, especially mixed anion effect and effect of mixing glass forming oxide.

Acoustic spectroscopy is a powerful technique for the study of sub- T_g relaxations in glasses due to a strong acousto-ionic interaction. The investigated glasses can be classified as glasses which contain one type of cation Cu^+ and various kinds of phosphate structural units, from discrete to polymeric anions. Several relaxation peaks in the acoustic attenuation spectra corresponding transport mechanisms connected with several structural units were observed. The measured acoustic spectra are analyzed using Double Power Law function which gave the best agreement in comparison with Debye or Kohlrausch-Williams-Watts functions [2].

EXPERIMENTAL

The set of glasses of the system $\text{CuI} - \text{CuBr} - \text{Cu}_2\text{O} - \text{P}_2\text{O}_5$ 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 compositions of the set of glass samples are summarized in Table 1. The preparation of glasses in the investigated system has been already described [3].

TAB. 1. Starting composition of prepared glasses investigated by acoustic measurements

Glass samples	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

The samples for acoustical attenuation measurements were cylindrical in shape (area $\approx 1 \text{ cm}^2$, thickness 1.5 - 2.0 mm). The acoustic attenuation spectra were measured using MATEC attenuation comparator for longitudinal acoustic waves 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.

THEORETICAL DESCRIPTION

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

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

is the most probable relaxation time. The relaxation processes are characterized by activation energy E_a^a for jumps over the barrier between two potential minima and typical relaxation frequency of ion hopping $1/\tau_0 \approx 10^{13} - 10^{14} \text{ s}^{-1}$. 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 form of Arrhenius type equation between the peak temperature T_{peak} and the applied frequency

$$\nu = \nu_0 \exp(-E_a^a / k_B T_{peak}) \quad (2)$$

where ν_0 is the pre-exponential factor (the value is always of the order of 10^{14} Hz), we can determine the value of activation energy of the ion hopping process.

The relaxation phenomena observed in a wide variety of materials exhibit a power-law type of frequency dependence. The acoustic attenuation spectrum of the investigated cuprous halide glasses can be then fitted using Double Power Law (DPL) function

$$\alpha(\omega, T) \approx 1 / ((\omega\tau)^n + (\omega\tau)^m) \quad (3)$$

which gave an excellent agreement with the measured acoustic spectrum in the whole temperature range. Here m and n are power-law exponents.

RESULTS AND DISCUSSION

The acoustic attenuation spectra for all investigated samples indicate one broad attenuation peak at higher temperature in which we can distinguish at least two separated peaks. Another peak was detected at lower temperatures.

The representative acoustic attenuation spectra plotted as a function of temperature at constant frequency $\nu = 18 \text{ MHz}$ is illustrated in Figure 1. The individual spectra are shifted for better distinction.

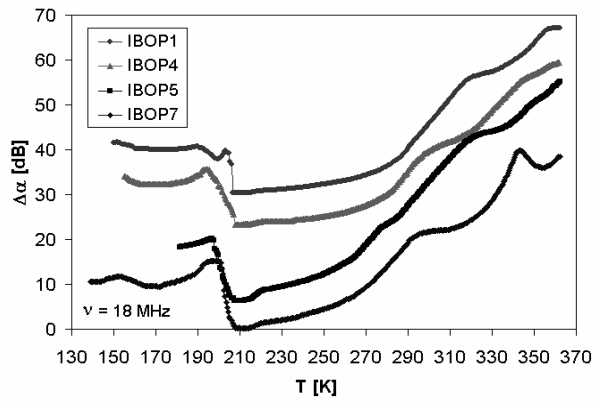


Fig. 1. Acoustic attenuation spectra of the samples measured at the frequency $\nu = 18$ MHz

Using Arrhenius equation (2) between the peak temperature T_{peak} and the applied frequency $\nu = 13, 18, 27$ MHz for sample IBOP7 (Fig. 2) we found the pre-exponential factor $\nu_0 = 1.48 \times 10^{14}$ Hz.

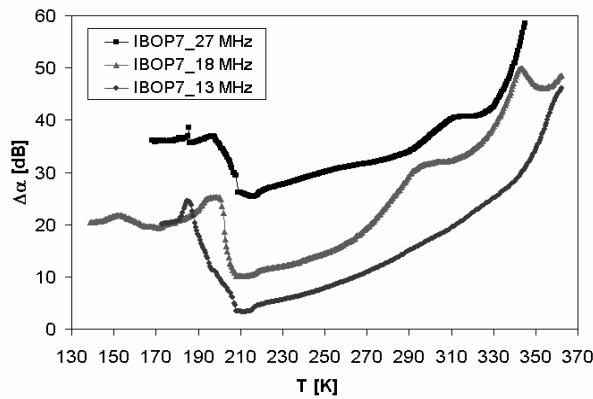


Fig. 2. Acoustic attenuation spectra of sample IBOP7 measured at the frequency $\nu = 13, 18, 27$ MHz. The individual spectra are shifted for better distinction.

Applying DPL function (3) we tried to simulate measured data from acoustic attenuation spectra (Fig. 3) and determined the values of activation energies (Tab. 2) of the individual relaxation and transport processes connected with ion hopping process.

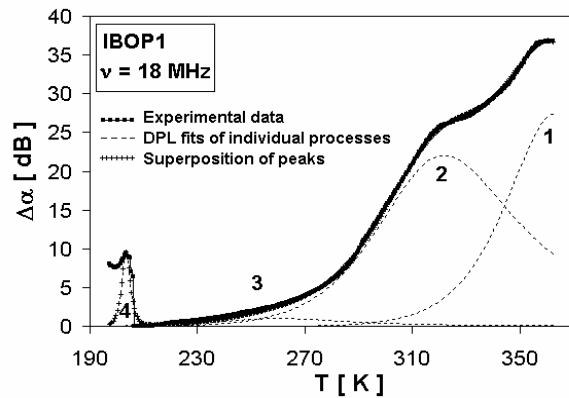


Fig. 3. Modeling of acoustic attenuation spectra of sample IBOP1 measured at the frequency $\nu = 18$ MHz using DPL functions. The temperatures $T_{peak1} - T_{peak4}$ represent the temperatures of peak maxima (denoted as peaks 1 – 4).

TAB. 2. Activation energies calculated using DPL model and corresponding Arrhenius equation

Glass samples	E_{a1}^a [eV]	E_{a2}^a [eV]	E_{a3}^a [eV]	E_{a4}^a [eV]
IBOP1	0.50	0.44	0.36	0.28
IBOP4	0.49	0.42	0.36	0.27
IBOP5	0.49	0.44	0.38	0.27
IBOP7	0.48	0.42	0.36	0.27

Comparing the acoustic and electrical measurements [4] we can suppose that some relaxation mechanisms indicated by acoustic spectra correspond to the relaxation and transport mechanisms indicated by electrical measurements. The fact that some of activation energies determined from conductivity and acoustic spectroscopy have very close values proved that the same mechanisms can influence electrical and acoustical losses in investigated ion conductive glasses.

Using the results from infrared (IR) spectroscopy we can suppose, that the finding activation energies of the thermal activated processes can be associated with different structural units - orthophosphate PO_4^{3-} oxoanions, diphosphate oxoanions $P_2O_7^{4-}$, triphosphate $P_3O_{10}^{5-}$ anions and possible other polymeric chains. Because of stronger electrostatic interactions between the mobile Cu^+ ions and orthophosphate anions than those between Cu^+ ions and diphosphate or triphosphate anions we can suppose that the relaxation processes with bigger activation energies can be connected with orthophosphate anions and the processes with smaller energies can be connected with low-condensed anions identified by IR spectroscopy.

CONCLUSIONS

We have studied acoustic properties of the set of ion conductive glasses of composition $CuI - CuBr - Cu_2O - P_2O_5$ to obtain the fundamental properties of investigated materials.

Theoretical analysis using Double Power Law function gave the excellent fit of experimental spectra and several different kinds of sites responsible for ionic hopping motion were discovered and described.

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REFERENCES

1. P. Knauth, H. L. Tuller: J. Am. Ceram. Soc., **85** [7], 1654 (2002).
2. P. Hockicko, P. Bury, M. Jamnický, I. Jamnický: Advances in EEE, No. **2**, Vol. 3, 243 (2004).
3. P. Znášik, M. Jamnický: J. Mat. Science Letter **14**, 766 (1995).
4. P. Bury, P. Hockicko, S. Jurečka, M. Jamnický: Physica Status Solidi (c), No. **11**, 2888 (2004).