

Acoustic Investigation of Ion Conductive Glasses

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A considerable attention is given to materials with the fast ion transport called solid electrolytes because of the possibility of their application in modern electromechanical devices. While many known crystalline materials with the ability of fast ion transport have the limiting factor of their application in the achievement of requested structural parameters ensuring the high ion conductivity, the ion conductive glasses have several advantages the most important of which are: the absence of grain boundaries, the isotropic properties and the composition variability. The acoustical methods have been proved an effective tool to study the fundamental structural and mechanical properties of the ionic materials and can also significantly contribute to find the fundamental experimental knowledge's about the mechanical properties of the new kinds of ion conductive glasses and determine their relationship with the electrical ones. In the present contribution we have illustrated the coherence between the acoustical and electrical properties of ion conductive glasses of the system CuI-Cu₂O-(P₂O₅+M₀O₃). The both acoustic and electrical measurements are also utilised to the study of relaxation processes occurring in these ion conductive glasses and to the ion activation energies determination.

INTRODUCTION

In recent years, the technological interest in fast ionic conductivity in solid materials is increased for various solid state electrochemical devices. Apart from some crystalline materials, the high ionic conductivity at room temperature has been observed in some ion conducting glasses. Glass materials are particularly interesting for application because of their easy preparation, their stability and the large available composition ranges.

Ionic conductive glasses have common structural characteristic, that includes a highly ordered, immobile framework complemented by a highly disordered interstitial sublattice in which carriers are randomly distributed and in which the number of equivalent sites is greater than the number of available ions to fill them. These low potential sites comprising the carrier sublattice must be sufficiently interlined to provide continuous transport paths necessary for optimal movement of ions [1].

The most important criterion which should be meet the fast ionic conductive glasses is high ionic conductivity at room temperature. The highest ionic conductivity ($\sigma_{25} \sim 10^{-2} \Omega^{-1} \text{cm}^{-1}$) were obtained in Ag⁺ containing glasses. Because of a shortage of silver it is necessary to find new chemical composition of glasses, with conductivity comparable to the Ag⁺ containing glasses. Here is a good opportunity for glasses containing Cu⁺ conductive ions that have similar electronic configuration and smaller ionic radii in comparison with Ag⁺ ion. From a theoretical point of view, this is a good chance to achieve conductivity comparable with the best Ag⁺ conductive glasses [2].

The conductivity of glasses is affected not only by the type of conductive ions, but also strongly depends on „glass forming“ oxide. The glass formation of many systems containing Cu⁺ conductive ions was investigated [3], but glasses were prepared only in systems containing either P₂O₅ or M₀O₃ as a „glass forming oxide“. It has been found that the mixing of two glass formers yields glasses with higher electrical conductivity. Such glasses were also prepared in systems with mixed „glass forming“ oxides P₂O₅-MoO₃ [3,4].

In the present contribution the ion conducting glass of the system 0,3CuI – 0,4375Cu₂O – 0,0875P₂O₅ – 0,1750MoO₃ was chased for the experimental investigation, its electrical and acoustical properties were studied and some relations between electrical conductivity and acoustical attenuation is discussed.

EXPERIMENTAL AND RESULTS

The preparation procedure of glasses in the system CuI – Cu₂O – P₂O₅ – MoO₃ has been already described [5]. The glasses investigated here were prepared in a similar manner to the previously described method. The glass melt was rapidly quenched by its pressing between two brass plates to a final thickness of $\approx 1,5$ mm. The resulting disc was kept between the plates until the temperature decreased to room temperature. The chemical compositions of glasses are given in previous part.

The samples for both the electrical conductivity and acoustical attenuation measurements were cylindrical in shape (area $\approx 1 \text{ cm}^2$, thickness $\approx 1,5$ mm). Gold electrodes were sputtered onto the sample surfaces. The frequency and temperature dependencies

of electrical conductivity were measured in the frequency range from 50 Hz to 1 MHz using FLUKE PM 6306 impedance bridge from temperature up to $\sim 100^\circ\text{C}$. 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. All of the temperature dependencies of glass conductivity fitted the equation

$$\sigma = \sigma_0 \exp(-E_a/kT), \quad (1)$$

where E_a is the activation energy, k is the Boltzman constant and T is the thermodynamic temperature. The pre-exponential term σ_0 , however, can be the function of temperature T .

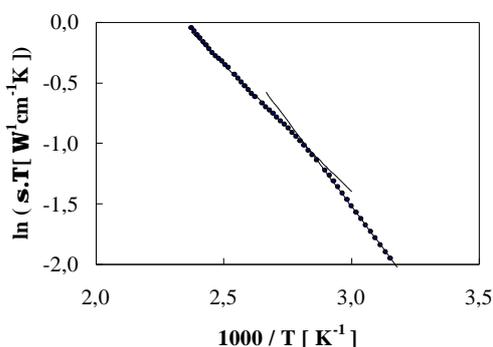


FIGURE 1. Arrhenius plot of d.c. conductivity

The d.c. electrical conductivity against the temperature is plotted in Fig. 1. The Arrhenius plots enables both the E_a and pre-exponential factor calculation. The temperature dependence of conductivity (Fig.1) indicates two conductivity mechanisms with activation energy 0,18 eV or/and 0,24 eV, respectively. The frequency dependence of a.c. conductivity confirmed the supposition about not very significant influence of hopping processes up to 1 MHz [6]. The temperature dependence of a.c. conductivity is showed in Fig. 2

The acoustical attenuation was measured

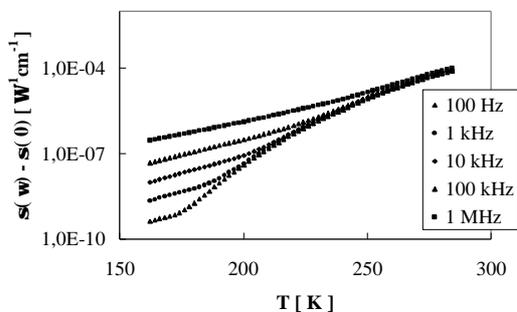


FIGURE 2. Temperature dependence of a.c. conductivity

using MATEC attenuation comparator for longitudinal acoustic wave of frequency 13 MHz generated by quartz transducer. The quartz buffer was used to separate the signal from quite short sample.

The first experimental investigation of electrical and acoustical properties of ion conductive glasses in system $\text{CuI} - \text{Cu}_2\text{O} - (\text{P}_2\text{O}_5 - \text{MoO}_3)$ indicate the important fact that the same mechanism can probably influence the electrical and acoustical losses in the ion conducting glasses and showed the coherence of chemical composition and electrical conductivity and indicated also more than one possible conductivity mechanism. However, the further investigations in wider temperature and frequency ranges of samples with different compositions and combined with some different measurements should be done for better understanding of ion conductivity mechanism.

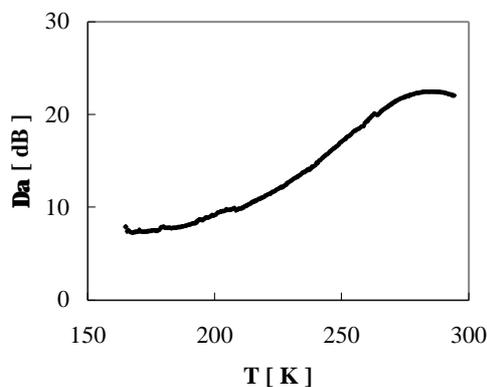


FIGURE 3. Temperature dependence of acoustic wave attenuation

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