

ANALYSIS OF SOME DIELECTRIC PROPERTIES IN MULTI-COMPONENT CHALCOGENIDE As-S-Se-Te-I GLASSY SYSTEM

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In this paper we present results of complex dielectric function measurements, obtained for chalcogenide glassy system $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$. Frequency and temperature dependence of the real ϵ' and imaginary part ϵ'' of dielectric permittivity ϵ have been studied in the frequency range 20 Hz – 1 MHz and temperature range from room temperature to the glass transition temperature. Dielectric function parameters showed decreasing trend at higher frequencies and lower temperatures. Also, the presented results indicated the dependence of ϵ' values on $(AsSe_{0.5}Te_{0.5}I)$ concentration. Small values of ϵ'' indicated that these materials have a small energy absorption and are among the materials with low dielectric losses. The participation of two mechanisms (electronic and dipole) in total polarization has been found. Analysis of Cole-Cole diagram showed that investigated glasses can be considered as composite dielectrics. Some significant parameters, such as static dielectric constant (ϵ'_{st}), optical dielectric constant (ϵ'_{opt}) and the dipole relaxation time τ , has been also determined.

(Received October 24, 2017; Accepted February 13, 2018)

Keywords: Chalcogenides; Melt quenching; Dielectric properties; Impedance spectroscopy

1. Introduction

Chalcogenide glasses are a special group of amorphous semiconductors, which include one or more chalcogenide elements from the VI group of the periodic table (S, Se or Te elements). The common features of chalcogenide glasses are the presence of localized states in the mobility gap due to the absence of long-range order [1,2]. The chemical bonding of their matrix is usually directional and covalent [3]. They have been studied for almost half of the century [4] and today are used in many applications in technological field [5,6]. In recent years great attention has been given to chalcogenide glasses mainly due to their wide range of application in solid state devices. These glasses exhibit unique IR transmission, photosensitivity and electrical properties that make them useful for threshold switching, memory switching, inorganic photoreceptors, IR transmission and detection through lenses and optical wave guides [7,8]. Further, they possess higher value of refractive indices [9,10], low acoustic losses of ultrasonic waves [11].

The mode of bonding of the elements in the structural network of amorphous materials is not strictly defined as in long-range ordered systems (crystals), so that the transport processes in glasses are largely dependent on the nature and degree of short-range order [12]. Of special significance is the relationship between the structure and properties of glasses and conditions of their preparation. The effect of structural-technological modifications, i.e. the possibility of adjusting the physico-chemical parameters on the basis of specially selected compositions and technological procedures of their preparation open up new possibilities in the area of practical application of glassy materials.

Results presented in this paper refers to investigation of influence of tellurium introduction in arsenic-sulphide matrix via a structural element $AsSe_{0.5}Te_{0.5}I$, in order to optimize primarily electrical and dielectrical properties of this chalcogenide system. Previous measurement of DC conductivity of this system showed that the increase in the concentration of tellurium yielded a

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significant increase in the conductivity and lowering of the activation energy [13]. It was established that dominant conduction mechanisms are the transfer of charge carriers between the localized states at the band edges and hopping between the localized states near the Fermi level. The low values of the activation energies (10^{-2} – 10^{-1} eV) obtained in the AC regime indicate that conduction in these materials at higher frequencies takes place by hopping of charge carriers between the charge defect states near the Fermi level [13].

The study of dielectric behavior of chalcogenide glasses is expected to reveal structural information which, in effect, can be useful for the understanding of conduction mechanism as well. The total polarization of dielectrics has four components: electronic, ionic, orientational and space charge polarization. Electronic polarization occurs due to displacement of electron cloud of each atom relative to nucleus, which exist in all dielectrics at the frequencies up to 10^{16} Hz. Ionic polarization occurs due to the displacement of negative and positive ions with respect to each other which exist in ionic crystals at 10^{13} Hz. Orientational polarization occurs due to the presence of molecules with permanent electric dipole moments that can change its direction of rotation into that of the applied electric field exist in polar substance at frequencies up to about 10^{10} Hz. Space charge polarization can take place due to accumulation of charges in the interfaces between the component layers of dielectrics at frequencies ranged between 1 Hz and 10^3 Hz. Total polarization of a dielectric material is related to the dielectric permittivity under the effect of AC field [14,15]. Chalcogenide glasses usually possess permanent dipoles, therefore along with electronic, the orientation (dipole) polarization is also typical for these materials.

In alternating electric field, for the cases when the period of oscillation is approximate in size with the relaxation time of dipole orientation, polarization in chalcogenide glasses is established with a certain delay for electric field change. The consequence of this delay is a power loss in the material, that is dielectric loss. Hence, in the description of the dielectric behavior of these glasses complex relative permittivity is used, $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, where $\varepsilon'(\omega)$ refers to the real part of the relative dielectric permeability and $\varepsilon''(\omega)$ is the imaginary part or loss factor. Parameter $\varepsilon'(\omega)$ defines the maximum energy that can be stored in the material. Loss factor $\varepsilon''(\omega)$ represents the absorbed energy of alternative electric field in the observed glass [16]. In that sense, frequency dependence of polarization can be used to identify present and dominant transport mechanisms.

The aim of this study is to investigate the temperature and frequency dependence of the real and imaginary part of dielectric permittivity for bulk samples of $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ glassy system and the influence of content of structural element $AsSe_{0.5}Te_{0.5}I$ on these parameters.

2. Experimental

The set of investigated glassy samples from series $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ ($x=0, 5, 10, 15, 20, 25, 30, 35, 50, 70$ and 90 mol %) were prepared from very high purity (99.999 %) elementary components using standard melt-quenching method. According to their atomic percentage, starting elements were weighted and sealed in quartz ampoules under vacuum of $\sim 10^{-4}$ Torr. The content of sealed ampoules was heated in the furnace with automatic temperature control at a rate 0.8 °C/min in cascade regime of raising temperature. In order to carry out homogenization, melts were kept at maximal temperature (750 °C) for 18 h. The all fivecomponent melts were quenched in a alumina (Al_2O_3) powder, while the sample $AsSe_{0.5}Te_{0.5}I$ has been cooled by putting the ampoule in cold water. Amorphous character of the samples was verified by X-ray diffraction and polarization microscopy [17].

Samples for measurements of dielectric quantities were prepared in the form of small flat-plates of dimensions $(4 \times 3 \times 2)$ mm³, previously polished with carborundum powder. To ensure good ohmic contacts, electrodes were formed with high purity silver paste deposited on the opposite sides of the prepared samples and connected by flexible metal conductors to the measuring instrument.

The dielectric permittivity ε was determined for the samples with $x=5, 10, 20, 30$ i 35 mol % $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ in a frequency range of 20 Hz to 1 MHz using a device HP4284A Precision LCR Meter. The real ε' and imaginary part ε'' of dielectric permittivity were calculated using the experimentally measured parallel values of the resistance R and the capacitance C according to relations:

$$\varepsilon' = \frac{d C(\omega)}{A \varepsilon_0} \quad \varepsilon'' = \frac{1}{R(\omega) \omega C_0} \quad (1)$$

where d is the sample thickness, A is the cross-sectional area, ω is the angular frequency, ε_0 is the free space permittivity.

For the samples with $x=10$ and 30 mol % in addition to frequency dependence, ε' and ε'' were examined as a function of temperature in the range from room temperature to glass transition temperature.

3. Results and discussion

Fig. 1 shows frequency dependence of the real part of dielectric permittivity ε' for the samples with $x=5, 20$ and 35 mol % $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ at room temperature. For the compounds with $x=10$ and 30 mol % $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ this dependence is illustrated on different temperatures on Fig. 2 and 3 (from the room temperature to the glass transition value of the investigated glasses).

A slight decrease of ε' with increase in frequency of the applied electric field is observed for all samples at room temperature. The ε' values at room temperature and at a field frequency of 10 kHz range from 8.1 ($x=5$ mol %) up to 9.4 ($x=35$ mol %). These values are in the interval of those characteristic for chalcogenide glassy systems [16,18].

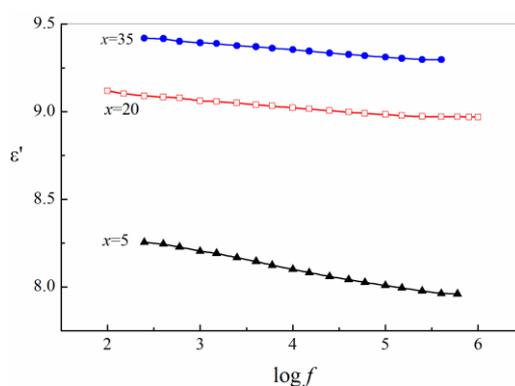


Fig. 1. Frequency dependence of ε' for the glass $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$ at room temperature

On the other hand, experimental values of ε' also increase with introduction of structural element $\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I}$ in glassy matrix As_2S_3 and with increase of its content x . Namely, the replacement of lighter atoms of S with heavier atoms of Se, Te effects on increase in electron density of the glass network. Although selenium have the same valence as well as sulfur, its atom is larger so the valence electrons are poorly bonded to the core. Generally speaking, the larger atoms and those with d- and f-electrons in the outer shells tend to be more polarized and have a higher refractive index [16]. Therefore, the share of electronic polarization in the overall polarization of the system $(\text{As}_2\text{S}_3)_{100-x}(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_x$ increases and values of parameter ε' have a growing tendency.

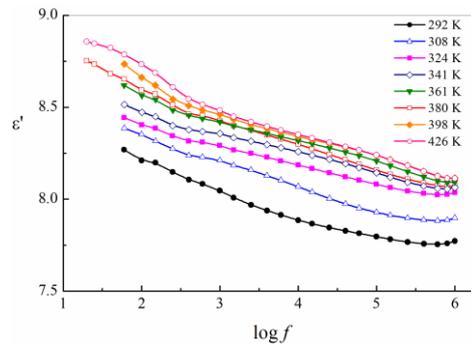


Fig. 2. Frequency dependence of ϵ' for the glass $(As_2S_3)_{90}(AsSe_{0.5}Te_{0.5}I)_{10}$ at different temperatures

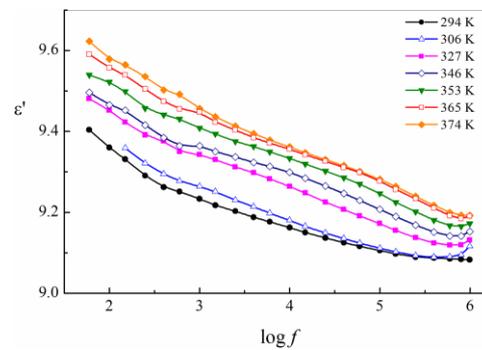


Fig. 3. Frequency dependence of ϵ' for the glass $(As_2S_3)_{70}(AsSe_{0.5}Te_{0.5}I)_{30}$ at different temperatures

The mechanism of electron polarization includes the widest part of the frequency interval and therefore always participates in the overall polarization in the dielectric material. It is the only present polarization type at the frequencies from the visible part of spectrum. In the optical range of frequencies the following relation holds $\epsilon' = n^2$, where n is the refractive index of material [16].

Substituting the measured values of the refractive index of investigated glasses [19] in the expression $\epsilon' = n^2$ and comparing the values obtained in this way with experimental one for the real part of the dielectric permittivity of given samples, it is possible to conclude that, depending on the content $AsSe_{0.5}Te_{0.5}I$, electronic mechanism in a given frequency interval participates with 66–72 % of the share in total polarization. Since the refractive index increases with increasing content of dopant structural element [19], the electronic share of the polarization is increased and therefore ϵ' has a growing trend.

In the investigated frequency range spatial polarization by electric charge can not be expected since there is no boundary surfaces or grain boundaries in amorphous glassy network which would create a spatial charge. Ionic polarization share is also negligible because the character of bonds in chalcogenide glasses is mainly covalent. It is therefore possible to conclude that in the observed materials two mechanisms participate in polarization: the electronic and the dipole one, whereby the electronic polarization is dominant.

Figures 4 and 5 show the temperature dependence of quantity ϵ' at selected frequencies of 1 kHz, 10 kHz and 100 kHz for the samples with $x=10$ and 30 mol % $AsSe_{0.5}Te_{0.5}I$. It can be noticed that at a given frequency parameter ϵ' increase with temperature while at the same temperature the real part of permittivity decreases as a function of frequency. This behavior is common in chalcogenide glasses i.e. in systems in which the dipole polarization is present. In that case, the increase of ϵ' with temperature can be attributed to the fact that the orientational

polarization is connected with the thermal motion of molecules. Dipoles cannot orient themselves at low temperatures. As the temperature increases, the orientation of dipoles is facilitated and this increases the value of orientational polarization; therefore, ϵ' increases with increasing temperature.

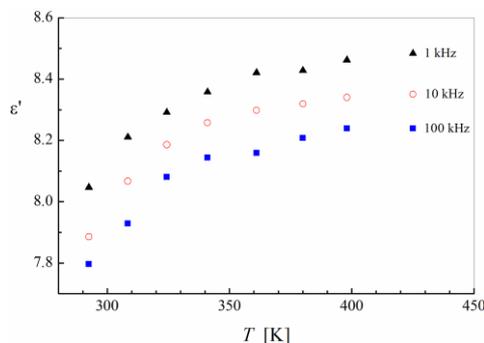


Fig. 4. Temperature dependence of ϵ' for the glass $(As_2S_3)_{90}(AsSe_{0.5}Te_{0.5}I)_{10}$ at different frequencies.

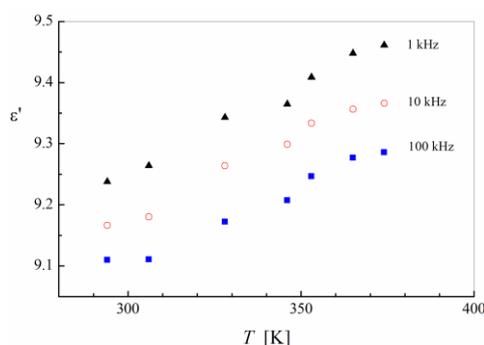


Fig. 5. Temperature dependence of ϵ' for the glass $(As_2S_3)_{70}(AsSe_{0.5}Te_{0.5}I)_{30}$ at different frequencies.

Figure 6 shows the frequency dependency of the imaginary part of the permittivity ϵ'' at room temperature for the samples with $x=5$ and 35 mol % $AsSe_{0.5}Te_{0.5}I$. For the samples with $x=10$ and 30 mol % of dopant structural unit this dependence is shown at different temperatures on Figures 7 and 8. From the Figure 6 it is possible to observe that the values of the parameter ϵ'' at frequency of 10 kHz are not significantly different for the samples with the minimum ($\epsilon'' \approx 0.03$) and maximum content of $AsSe_{0.5}Te_{0.5}I$ ($\epsilon'' \approx 0.07$). Also, for all other samples there is no any significant change in the loss factor value at room temperature with increase of frequency (Figures 7 and 8). On the other hand, at lower frequencies, there is a significant change of ϵ'' as a function of temperature.

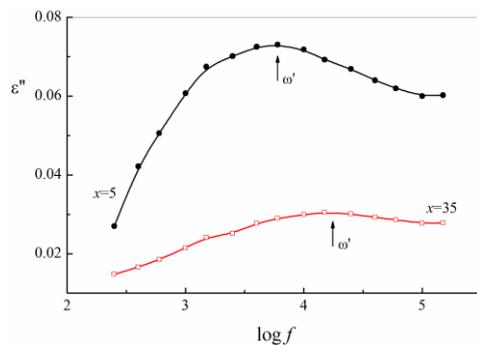


Fig. 6. Frequency dependence of dielectric loss ε'' for the glass $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ at room temperature

In the temperature range from room temperature to 425 K (at a field frequency of 100 Hz) for the glass with $x=10$ mol % of doping element, the ε'' value changes for an order of magnitude (from 0.08 to 0.8), and for the sample with $x=30$ mol % $AsSe_{0.5}Te_{0.5}I$ loss factor increases from 0.11 to 8. At higher frequencies change of ε'' with temperature is much less pronounced. However, the investigated compounds are characterized by relatively low values of ε'' in the whole frequency-temperature interval suggesting that these materials have a low absorption of electric power and that can be classified into glasses with low dielectric losses.

On the graph of frequency dependence of ε'' (Figures 7 and 8), the low frequency area illustrates the losses due to electrical resistance of material, while the other area (area of high frequency) so called area of Debye power losses, corresponds to relaxation polarization of the dielectric.

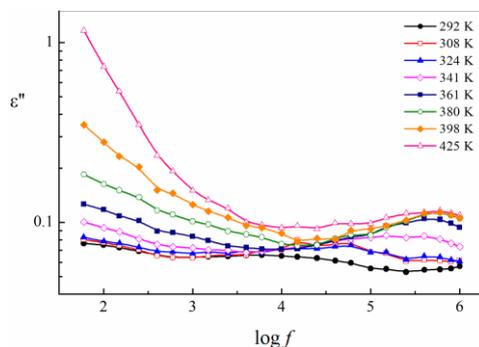


Fig. 7. Frequency dependence of dielectric loss ε'' for $(As_2S_3)_{90}(AsSe_{0.5}Te_{0.5}I)_{10}$ at different temperatures

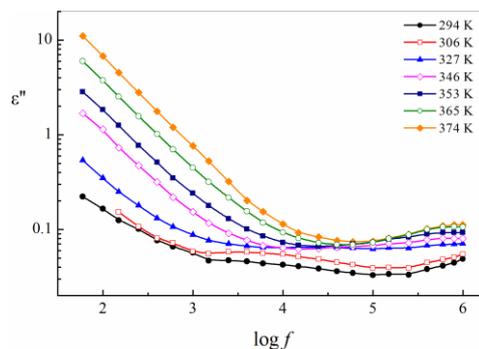


Fig. 8. Frequency dependence of dielectric loss ε'' for $(As_2S_3)_{70}(AsSe_{0.5}Te_{0.5}I)_{30}$ at different temperatures

In accordance with the Debye theory [20], dipole losses exhibit a maximum at a certain frequency. The frequency ω' that corresponds to the maximum of losses at the given temperature (Figure 7 and 8) represents the resonance frequency at which the period of the external electric field coincides with the dipole relaxation time needed to overcome the resistance of the viscous medium. From the approximate condition ($\omega' \tau = 1$), which holds for polar dielectrics it is easy to calculate the numerical values for dipole relaxation times at the given temperature (Table 1).

By analyzing the Debye theory, Cole and Cole [20] found that the values of real and imaginary parts of the dielectric permittivity for different frequencies in the dispersion area lie on a semi-circle with the center on ϵ' axis, i.e. the relation between these two parameters can be expressed as:

$$\left(\epsilon' - \frac{\epsilon'_{st} + \epsilon'_{opt}}{2} \right)^2 + (\epsilon'')^2 = \left(\frac{\epsilon'_{st} - \epsilon'_{opt}}{2} \right)^2 \quad (2)$$

where ϵ'_{st} and ϵ'_{opt} are the static and optical dielectric constants, respectively. Radius of the circle is defined as:

$$r = \frac{\epsilon'_{st} - \epsilon'_{opt}}{2} \quad (3)$$

In the cases when experimental results deviate from the Debye theory, Cole-Cole diagram does not describe the dependence through semicircle with its center on the ϵ' axis but with the point below it. In this way, the radius drawn to the points ϵ'_{opt} and ϵ'_{st} makes an angle of $\alpha\pi/2$ with an abscissa. The parameter of macroscopic relaxation time distribution α is equal to zero when the dielectric has only one value of relaxation time, while for distribution of relaxation times α varies between 0 and 1. The higher values of α , the wider distribution of relaxation times. This behavior is typical for composite dielectrics and materials containing multiple types of molecules (structural units) and whose relaxation time are quite close.

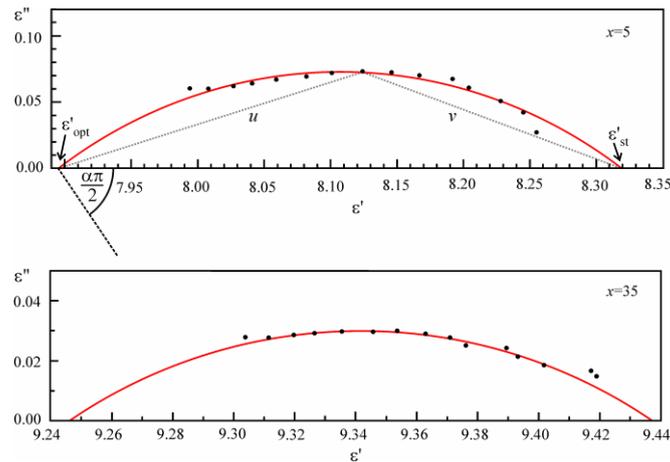


Fig. 9. Cole-Cole diagrams for the glassy system $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ at room temperature.

Fig. 9 presents the Cole-Cole plots of investigated glasses with $x=5$ and $x=35$ mol % $AsSe_{0.5}Te_{0.5}I$. For both compositions, the dependence $\epsilon'' = f(\epsilon')$ can be described with unique semicircle passing through the greatest number of experimental points with satisfactory accuracy. Since the center of the semicircle lies below the coordinate axis, it can be concluded that these materials are composite dielectrics that can be described with Debye theory at higher frequencies.

Table 1. Dielectric parameters of the glassy system $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ at room temperature.

x [mol %]	ε'_{opt}	ε'_{st}	α	τ_0 [10^{-6} s]	τ_{01} [10^{-6} s] for $f=6$ kHz	τ_{02} [10^{-6} s]	τ_m [10^{-6} s] eq. (5)
5	7.897	8.320	0.578	18.1	19.3	28.3	17.8
35	9.248	9.436	0.602	8.8	9.5	9.7	8.7

The values of quantities ε'_{st} and ε'_{opt} are determined from the Cole-Cole diagrams. On the basis of graphically estimated values, it was also possible to determine frequencies ω' at which the relative permittivity ε falls to half of the value between ε'_{st} and ε'_{opt} . Based on the relation between ω' and dipole relaxation time ($\omega'\tau = 1$), macroscopic dipole relaxation time τ_0 could be assessed. Values of parameter τ_0 obtained for the investigated glasses are given in Table 1. Moreover, knowing the parameter α , one can determine τ_0 by using relation [21]:

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \quad (4)$$

where u is the distance on Cole-Cole plot between ε'_{opt} and the experimental point, v is the distance between that point and ε'_{st} and ω is the angular frequency for this experimental point (Table 1, parameter τ_{01}). Finally, the relaxation time values determined on the basis of the maximum of the curve $\varepsilon'' = f(\omega)$ and according to relation $\omega'\tau = 1$ are also given in Table 1 (parameter τ_{02}) and are in good agreement with those defined from the Cole-Cole diagrams. All values obtained relaxation times are in agreement with the expected for this type of materials (order of $\sim 10^{-6}$ s).

Based on macroscopic relaxation time values τ_0 , one can also estimate molecular relaxation time τ_m by using the relation [22,23]:

$$\tau_m = \tau_0 \frac{2\varepsilon'_{st} + \varepsilon'_{opt}}{3\varepsilon'_{st}} \quad (5)$$

Analysis of the τ_m values, also shown in Table 1, indicated very small deviation of the molecular relaxation times from the values determined from the Cole-Cole plots, and from the values τ_0 , calculated in different ways. This was expected, since all the methods are related to most probable value of spread of relaxation time τ .

4. Conclusions

The real ε' and imaginary part ε'' of dielectric permittivity ε for compounds of $(As_2S_3)_{100-x}(AsSe_{0.5}Te_{0.5}I)_x$ glassy system are measured as a function of temperature and frequency. Results of measurements showed that these parameters decrease with frequency and increase with temperature.

Introduction of the structural element $AsSe_{0.5}Te_{0.5}I$ in a glassy matrix As_2S_3 and increase of its content influence on increase of experimental values of parameter ε' . Replacement of the lighter sulfur atoms with heavier atoms of Se, Te and I caused an increase of the electron density in a glass network and also the share of electronic polarization, resulting in higher values of ε' .

On the basis of the refractive index values for investigated glasses it was concluded that, depending on dopant structural element content, the mechanism of electron polarization contributes with 66–72 % and the dipole one with 28–34 % in total polarization.

Relatively small values of ε'' indicated that these glasses have a small absorption of electrical energy and are among the materials with small dielectric losses. Analysis of Cole-Cole diagrams of selected samples showed that these composite dielectrics can be described with Debye theory at higher frequencies. It was also found that parameters such as static and optical dielectric constants, as well as the dipole relaxation time (macroscopic and molecular relaxation times) are order of magnitude 10^{-6} s.

Acknowledgements

The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. III 45021).

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