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Dielectric properties of Fe-Sb-S-I chalcogenide glasses

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The work presents results of the analysis of dielectric properties of glasses of the type $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ for atomic contents of iron of 0, 0.1, 0.5, 0.8, 1 and 2 %. The glass with the highest Fe content shows metal-type conductivity, with the dielectric properties of orientational type. For the other glasses, the impedances and angles of dielectric losses were measured in the frequency range from 300 Hz to 100 MHz, and from room temperature to temperature close to the glass transition. Frequency dependence of the real dielectric permittivity and factors of dielectric losses suggest the existence of several dielectric phases. The high-frequency composite dielectric component has a characteristic time of dipolar orientation at the frequencies of the order of 10 kHz. Separation of the components was performed on the basis of determining characteristic parameters from the Cole-Cole diagrams for the high-frequency component. The obtained values for standard dielectric permittivity of the high-frequency composite were in the range between 570 and 660 for the different investigated glasses. The dielectric relaxation times and the corresponding activation energies of dielectric orientations were calculated, and it was found that they show an increase with Fe content (0.01-0.05 eV).

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1. Introduction

The investigated glass represents an eutectic composition on the quasi-binary Sb_2S_3-SbI_3 cut, with the different ratios of iron impurity atoms in the glass matrix. Previous investigations showed the limitations in introducing impurity atoms into the glass matrix. Changes in the behaviour of the investigated system are reflected first on the change of electric and magnetic properties (at the concentrations above 1 at % Fe). On the other hand, the mechanical changes and appearance of stable crystalline centres of the iron impurity appears not before the concentration of 3 at % Fe [1]. The implementation of Fe atoms in the chalcogenide glasses is mostly in a sulphide or selenide form [2], whose paramagnetic or ferromagnetic behaviour overrules the diamagnetism of glassy matrix. The obtained glasses have a wide range of transparency in IR spectra up to 20 μm [3] and a high value of the refraction index [4]. The optical band gap decreases linearly with increase of iron concentration up to 1 at % (from 1.83 eV to 1.56 eV), whereas at higher concentrations it remains almost unchanged (increase slowly) [3]. At lower Fe concentrations, the dominant paramagnetism arises from high spin Fe^{2+} (d^6) atoms. Above 1 at % Fe the paramagnetic properties are mostly independent of impurity concentration. At higher temperature (between 490K and 620K) in glass with 1 at % of Fe, permanent ferromagnetic centres of iron sulphide are formed [1]. Up to the concentration of 1 at % Fe, DC conductivity is of semiconductor type with the activation energy about half of the value of the optical band gap [5], which is characteristic of the p-type conductivity [6]. The mechanism of AC conductivity is of hopping type by bipolarons between defect centres near Fermi level ($\Delta E \approx 10^{-2}$ eV) [7]. At the higher Fe concentration DC and AC conductivities are of metallic type.

SbSI monocrystals possess extraordinary ferroelectric properties [8]. In the crystalline environment of SbSI structural units, dielectric permittivity in the dispersion region is in the range between $\varepsilon'_{opt} = 24$ and $\varepsilon'_{st} = 5 \times 10^4$.

Conductive-dielectric properties of chalcogenide glasses can be modelled as a parallel combination of an ideal capacitor and a thermogenic resistor [9]. For the glasses with lower Fe content (up to 1 at %) impedances and dielectric losses angles were measured between 300 Hz and 100 MHz, and from room temperature to the point close to the glass transition temperature (140 °C). Then, components of the relative dielectric permittivity were calculated. Real part of the relative dielectric permittivity ε'_r was calculated from the capacitive resistance of the sample prepared in the form of a parallel-plate capacitor, with the investigated glass as a dielectric between the plates. The losses factor ε''_r for the applied model was calculated from the dielectric losses angle and real dielectric permittivity, using the formula $\varepsilon''_r = \varepsilon'_r \cdot tg\delta$ [9].

In this work are presented the results of measuring dielectric characteristics of the glasses from the investigated series $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ for atomic contents of iron of 0, 0.1, 0.5, 0.8, 1 and 2 %.

2. Experimental

Samples were synthesized from high-purity elementary components in evacuated quartz tubes, applying the previously described regime [1, 3]. Because of the presence of Fe atom, maximal temperature of the synthesis was increased to 800 ^{o}C.

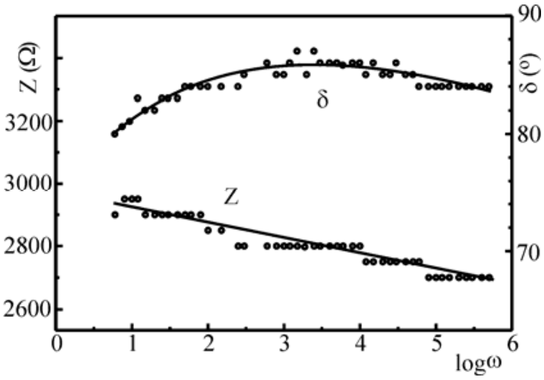

Fig.1. Changes of impedance (Z) and dielectric losses angle (δ) of the sample $Fe_2[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{98}$ at 140 ^{o}C.

Samples were prepared in the form of thin plates (about 1 mm thickness) with round graphite electrodes in a coplanar configuration. Sample impedance and dielectric losses angle were measured on a BM 507 (Tesla) impedance meter in the frequency range between 5 Hz and 500 kHz and on a BM 538 (Tesla) in the range of 0.5-100 MHz. Temperature in the measurement cell was maintained by streaming hot air in the space around the sample. The proof of the existence of dielectric properties of the samples with higher Fe contents was obtained from the measurement of DC resistance of the sample using the resistance bridge R 4060 (Tesla).

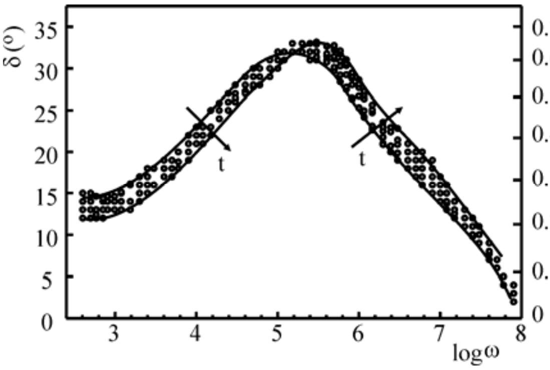

Fig. 2. Dielectric losses angles for the $Fe_{0.8}[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{99.2}$ glass between 20 and 140 ^{o}C (the arrow shows the direction of temperature increase).

3. Results and discussion

The DC conductivity of the sample with 2 at % Fe showed metallic conductivity with the activation energy of about $2 \cdot 10^{-3}\ eV$. Frequency distribution of the impedance and dielectric losses angle of this sample is shown in Fig. 1. Measured values do not practically change in the investigated frequency range. Low-impedance value and large dielectric losses angles confirm the prevailing metallic type of conductivity of these samples. By measuring the time change of resistance on a resistance bridge with constant output voltage, it was possible to monitor the exponential decrease of DC current across the sample. This confirmed the existence of dielectric centres of orientation type [9], with a relaxation time of dipole orientation of about $\tau_{or} = 23 \min \approx 1500\ s$.

Table I. Data of dielectric parameters of the $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ glasses at the temperatures of 20 and 140 ^{o}C.

x at % Fe	t (^{o}C)	ε'_{opt} *	ε'_{std}	β	$\tau_{max\delta}$ (10^{-5}s)	U_δ (eV)	ω_x (kHz)	τ (10^{-5}s)	U (eV)	N (10^{23}m^{-3})
0	20	26.6 (7)	630	0.238	3.2	0.045	26.9	3.7	0.012	7.1
	140	28.0 (7)	660	0.201	1.9		30.9	3.2		
0.1	20	30.7 (6)	620	0.126	3.0	0.043	24.5	4.1	0.016	9.3
	140	31.0 (6)	650	0.112	1.8		29.5	3.4		
0.5	20	23.5 (5)	575	0.269	3.3	0.043	12.3	8.1	0.028	6.6
	140	23.8 (5)	600	0.267	2.0		17.0	5.9		
0.8	20	21.9 (4)	580	0.445	3.4	0.044	5.9	17.0	0.044	3.8
	140	22.2 (5)	600	0.447	2.1		9.8	10.2		
1	20	22.0 (5)	590	0.209	3.4	0.044	12.3	8.1	0.050	7.1
	140	22.4 (5)	605	0.191	2.1		21.9	4.6		

* determined at 10^8 Hz.

Changes of dielectric losses for the glasses up to 1 at % Fe in the measured frequency range (Fig. 2) show that dielectric properties fall completely in the Debye range, with maxima of the order of 10^5 Hz. With increase in temperature, there exists a small displacement of this dependence to higher frequencies. In this concentration range, the glasses show a similar behaviour, so that all their characteristics are shown on the example of the glass with x=0.8 at % Fe. On the basis of the frequency maxima of dielectric losses angles it was possible to calculate the values of relaxation times $\tau_{max\delta}$ (Table I). The relaxation times thus obtained differ insignificantly for the investigated glasses; there is only a decrease in relaxation times with increase in the environment temperature.

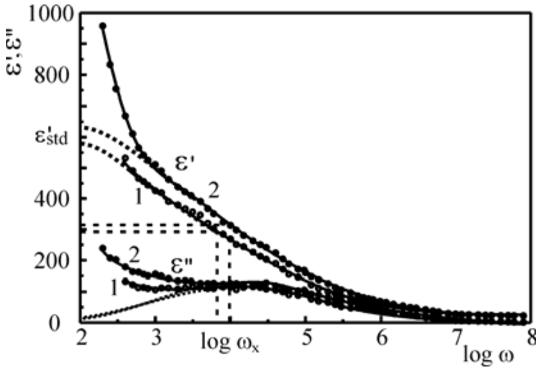

Fig.3. Frequency characteristics of the components of relative dielectric permittivity of the $Fe_{0.8}[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{99.2}$ *glass at 20 °C (1) and 140 °C (2).*

At high frequencies, relative dielectric permittivity becomes practically independent of the frequency and temperature, and tends to the ε'_{opt} value (Fig. 3). At the frequency below 1 kHz, the relative dielectric permittivities of samples show an abrupt rise. Real part of the electric permittivity ε' acquires also values above 500, whereas the imaginary part ε'' does not fall to zero. This deviation of the behaviour from the theoretically expected (dotted lines on Fig. 3) can be explained by the existence of two type of the dielectric centres, with dispersion in the range of about 10 kHz and low-frequency dispersion centres (100 Hz and lower). At increased temperatures, the dispersion shows a mild increase to higher frequencies and higher values of dielectric permittivity.

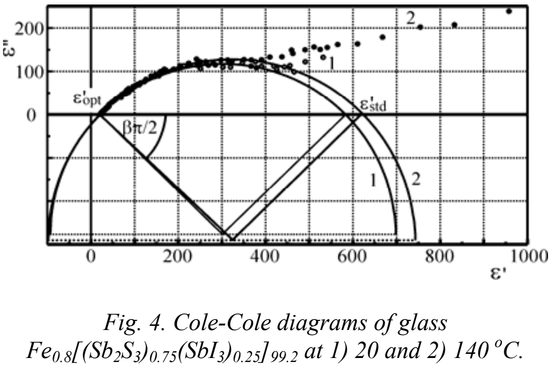

Fig. 4. Cole-Cole diagrams of glass $Fe_{0.8}[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{99.2}$ *at 1) 20 and 2) 140 °C.*

In order to determine high-frequency parameters, Cole-Cole diagrams were drawn at the bordering temperatures (Fig. 4). In the high-frequency range (frequencies for experimental points increase from the right to the left) the dependence can be pretty well fitted by a circle that passes through the ε'_{opt} value (Fig. 5) and covers the majority of points. Centres of half-circles are shifted deep below the coordinate axis, showing that one deals with a composite dielectric, for which at higher frequencies (above 1 kHz) holds Debye theory. Positions of the circle centres shift with increase in temperature to higher values of dielectric permittivity, and the radii of the circumferences become larger. Values of Debye dielectric permittivity (ε'_{std}) (Fig. 6) were determined by graphical extrapolation, from the intersections of the Cole-Cole diagrams. Values of the maxima ε'' were also determined from them. The obtained results served as the basis for drawing dispersion curves in the low-frequency range at the limiting measurement temperatures (Fig. 3, dotted line). The frequencies ω_x, at which ε'' has its maximum and ε' is the mid-way between ε'_{std} and ε'_{opt} (Tab. I), show an increasing tendency with temperature, whereas with increased Fe content in the glass at the same temperature the values mainly show a decrease. The frequency ω_x served to determine relaxation times of dipole orientations τ (Fig. 7, curves 1 and 2). On the basis of the change of relaxation times between the temperature limits, using thermal activation model, it was possible to calculate the activation energies of dipole orientations. They were of the order of magnitude of $10^{-2}\,eV$ and showed a relatively strong dependence on iron concentration (Fig. 8, curve 1). Analytically, the height of potential barrier between two equilibrium positions of the dipole can be described by the relation

$$U\,(eV) = 0.0113 + 0.0388 \cdot x\,(at\,\%\,Fe)$$

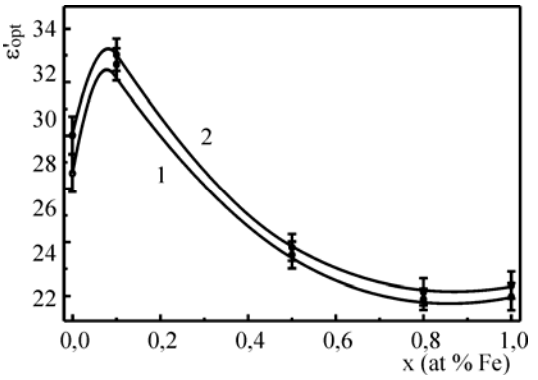

Fig. 5. Dependence of high-frequency relative dielectric permittivity on Fe concentration for the $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ *glasses at 20 °C (1) and 140 °C (2).*

On the other hand, the activation energies of dipole orientation can also be determined on the basis of temperature changes of the relaxation times $\tau_{max\delta}$ (Fig. 8, curve 2). This procedure gave the value of about 0.044 *eV*, irrespective of the iron content in the glasses.

The changes of particular parameters of dielectric properties as a function of Fe concentration in the glass of the eutectic composition $(Sb_2S_3)_{0.75}(SbI_3)_{0.25}$ can be classified into several types of behaviour:

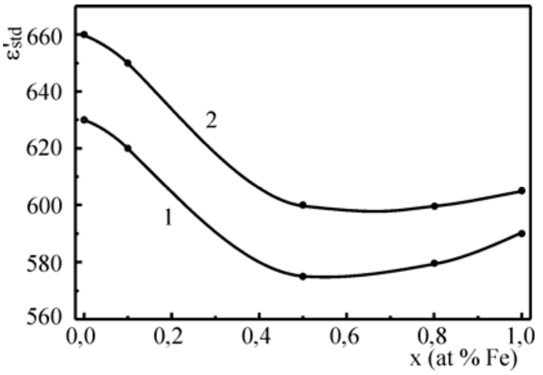

Fig. 6. Changes of graphically determined Debye values of stationary relative dielectric permittivity in the $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ *glasses at 20* ^0C *(1) and 140* ^oC *(2).*

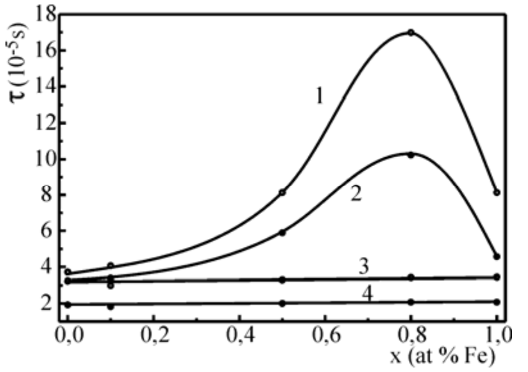

Fig.7. Change of the dipole orientation time in the $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ *glasses at 20* ^0C *(1,3) and 140* ^oC *(2,4) calculated from the temperature dependence (1,2) and maximal angle of dielectric losses (3,4).*

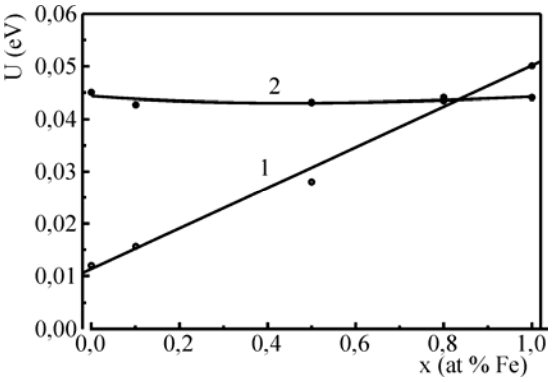

Fig. 8. Change of the activation energy of dipole orientation with Fe concentration in the glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ *determined on the basis of* ω_x *(1) and maximal dielectric losses* $\tau_{max\delta}$ *.(2)*

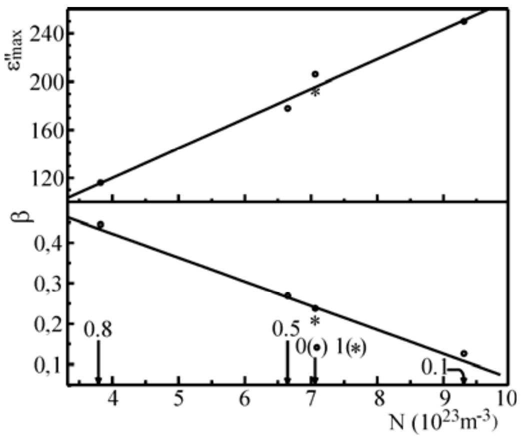

Fig. 9. Dependence of the parameters of dielectric losses on the concentration of defect centers in the $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ *glasses (the arrows show the corresponding x values).*

– The character of the dependence of ε'_{std} and ε'_{opt} is similar to that of some thermal parameters (onset decomposition temperature, crystallization temperature): the introduction of a small amount of Fe into the glass yields an abrupt increase of the parameter, whereas at higher concentrations the values attain a saturation form. Relative dielectric permittivity are probably conditioned by catalytic properties of Fe atoms, with a significant influence at lower concentrations (below 0.5 at % Fe);

– Activation energies of dipole orientation (as well as optical band gap [3], values of magnetic moments) are linear functions of Fe concentration;

– Parameters $\varepsilon''_{\max}$ and the angle of the centre of Cole-Cole diagrams β (as well as the parameters of electric AC conductivity $\ln\sigma_o$ and exponents of AC conductivity s) do not correlate with glass composition. On the basis of Elliott's model of AC conductivity [10, 11] it was possible to determine the concentrations of defect centres in the samples (Tab. I). The calculation showed that the synthesized glasses without Fe and with 1 at % Fe possess the same population of defect centres, and that their number is smallest in the sample with 0.8 at % Fe. As can be seen from Fig. 9, a highly good correlation was obtained for the mentioned parameters with the concentration of defect centres. It can be concluded that these parameters are determined by the regime of glass synthesis.

High-frequency dispersion region can be ascribed to the composite structural units of the type Sb_2S_3 and SbI_3 as the basic composition factors of these glasses. At such high temperatures, apart from the charged D^- and D^+ defect centres, the role of the D^o centres is also pronounced [12,13]. With increasing of sample temperature the jumps of charge carriers between $D^o \rightarrow D^-$ centres (single polaron) become easier due to decreasing the height of potential barrier and increasing the carrier's energy. This yields an increased polarization and enhanced dielectric constant. The presence of iron in the range of 0.1-1.0 at % results in the structural changes of glass matrix which cause an increase in the potential barrier (proportional to the activation energy, Fig 8. curve 1) between *D* defect centres near the Fermi level. The hindered activation of polarons yields thus a decrease in the dielectric constant with increase in the Fe content.

The low-frequency range, which could not be investigated to the end because of the very high impedance of the sample at low frequencies (exceeding the range of measuring instruments), is probably due to the amorphous centres of ferroelectric structural units of the type SbSI, which also exist in the glasses.

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