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SHORT COMMUNICATION

THERMOSTIMULATED RELAXATION OF SbSI GLASS STRUCTURE*

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Dielectric properties and infrared transmission spectra of glassy SbSI are investigated. The anomalies in the temperature dependences of dielectric parameters of SbSI glass are shown to be related to the transition of the glass to the polar state and its subsequent crystallization. The effect of thermal annealing on the structural properties of SbSI is studied.

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The possibility of practical applications attracts the interest to the amorphous materials whose crystalline analogues possess pronounced ferroelectric properties. Disordering of the ferroelectric structure results not only in smearing or suppression of anomalies at the phase transformation temperatures, but also to new effects [1-4], totally determined by structural disorder. For oxide ferroelectric materials of Li(Nb) TaO_3, Ba(Pb)TiO_3-type, obtained in amorphous state by fast cooling, the anomalies at the temperature dependences of dielectric properties are observed, which are not typical for amorphous substances and corresponding crystals.

The present paper is devoted to the studies of far-infrared transmission spectra and dielectric properties (ε and tanδ) of glassy antimony sulphoiodide which in crystalline state is the most prominent representative of A^{V}-B^{VI}-C^{VII} ferroelectric semiconductors.

Glassy SbSI was obtained in the hard quenching mode at the melt cooling rate ~200 $K \cdot s^{-1}$. The high quenching rate is related to the considerable intensity of nucleation ($I_{max} \approx 4.0 \times 10^{21}$ $m^{-3} \cdot s^{-1}$), high linear growth rate of the nucleated crystals ($U_{max} \approx 4.4 \times 10^{7}$ $m \cdot s^{-1}$) as well as small critical nucleus value ($r_c \approx 4.5 \times 10^{-10}$ m). The given parameters are obtained from the built Tamman curves on the basis of the experimental data of differential thermal analysis (DTA) and derivative thermal analysis (DerTA) [5]. The characteristic temperatures of the thermal effects for SbSI glass (Fig. 1, a and b) are the following: T_g = 349 K, T_c = 369 K, T_m = 668 K (T_g, T_c, T_m - the temperatures of glass-forming, crystallization and melting, respectively).

The studies of infrared (IR) transmission spectra were carried out at room temperature in the frequency range 50-400 cm^{-1}. The permittivity, ε, and tangent of dielectric loss angle, tanδ, were investigated in the temperature interval 200-510 K in the frequency range 10^3 - 10^5 Hz.

The measurements of temperature dependences of ε and tanδ for fresh glasses at the frequency 10^5 Hz, their results being given in Fig. 1, c, d, have shown that at the increase of temperature to 345 K the permittivity varies relatively weakly. Heating of samples to $T<T_g$ does not change the character of ε(T) dependence at heating/cooling mode repeated cycling. Heating to higher temperatures results in an irreversible change of ε. The increase of temperature above T_c leads to a sharp growth of ε (Fig. 1, c). In the same range of temperatures an anomaly of tanδ is observed (Fig. 1, d). Such behaviour of dielectric properties of SbSI glass is related to the effect of microcrystallization [6]. This is confirmed by the DTA and DerTA data, the results of microstructural and X-ray phase investigations Microcrystalline inclusions are seen in the cleaved surface photographs, and lines, corresponding to the crystalline phase, are revealed in Debye patterns.

The variation of the field frequency essentially affects the shape of the permittivity temperature dependence. At the frequencies 10^3 and 10^4 Hz a small shoulder is observed at the ε(T) plots in the pre-crystallization range (Fig. 2, curves 1, 2). With the increase of the measuring

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frequency it shifts to higher temperatures and decreases. The presence of the shoulder in the ε(T) dependence is related to the structural relaxation at the glass softening. This is also supported by a weak endothermic anomaly, observed at the DTA curve, being the evidence for the non-equilibrium character of the glassy state, obtained by rapid quenching of the melt. At low temperatures the structural groups, forming the glass matrix, are frozen, and at $T \approx T_g$ they begin to possess some rotation freedom. This favours a more equilibrated configuration of structural elements with high polarizability. Besides, in glassy SbSI in the range of T_g probably, due to the bond switching, chain structural groups are formed where each antimony atom is bound to two sulphur atoms and one iodine atom, and a sulphur atom is bound to two antimony atoms [7]. In this case a polar state of the glass is formed, characterized by high susceptibility to external factors and, hence, an increased ε value.

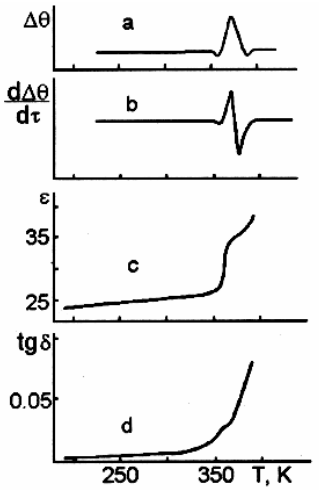

Fig. 1. DTA (a) and DerTA (b) curves, temperature dependences of ε (c) and tanδ (d) for glassy SbSI.

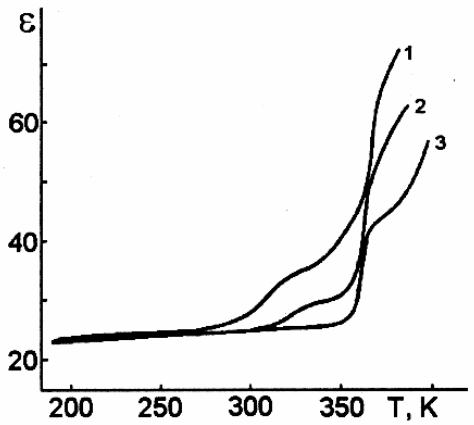

Fig. 2. Temperature dependences of ε for glassy SbSI at the frequencies 10^3 (1), 10^4 (2) and 10^5 (3) Hz.

The dielectric properties of glassy antimony sulphoidide are considerably affected by thermal treatment. The temperature dependences of the dielectric parameters at the frequency of 10^5 Hz are shown in Fig. 3. The permittivity of the crystallized SbSI glass reaches 50-70, and its thermal coefficient in the interval 300-400 K (after isothermic storage at 400 K during 2 h) is $\sim 2\times10^{-2}K^{-1}$. In the range of 270 K a change of the *ε(T)* plot slope is observed (Fig. 3, curve 1). In the same temperature range a maximum in the temperature dependence of tanδ is revealed [6]. Annealing at higher temperatures results in a maximum appearing in the *ε(T)* plot: curves 2 and 3 are obtained as a result of the 3rd and 4th heating cycle after cooling the samples from 470 and 510 K, respectively, to 200 K. The maximal ε value in curve 3 is observed at 287 K, this being close to the phase transition temperature for singlecrystal SbSI (295 K [7]). The temperature dependence of tanδ exhibits a similar behaviour. It should be noted that with the increase of the annealing temperature the anomalies of ε and tanδ become more pronounced and shift to higher temperatures. The permittivity at 200 K of a once heated sample is more than twice higher than that for the fresh one and weakly depends on the annealing temperature.

The effect of thermal treatment on the properties of the obtained antimony sulphoiodide can be interpreted in the framework of the size effect. At the temperatures close to T_c, the size of the crystallites being formed is small and a fine - grain ferroelectric ceramics is obtained. In this case, probably, the grain size is of the order of the correlation length, and hence, the dielectric anomaly at the temperature of the phase transition in SbSI crystal is not revealed (Fig. 3, curve 1). The increase of the annealing temperature results in the grain growth and a typical smeared ferroelectric phase transition.

This conclusion is confirmed by the results of the vibrational spectra studies for the obtained samples. An essential difference in the IR transmission spectra of glassy and crystalline antimony sulphoiodide should be noted (Fig. 4, curves 1 and 4): the IR spectrum of SbSI glass is much more featureless than that of the crystal and consists of two intense absorption bands in the range of 300 and 175 cm^{-1}. Earlier [8] a similar result was obtained at the investigation of vibrational (IR and

Raman) spectra of Sb_2S_3-SbI_3 system glasses with SbI_3 content below 30 mol. %. In the spectra of these glasses bands at 290 and 165 cm^{-1}, corresponding to the vibration of SbS_3 and SbI_3 pyramids, were observed, the increase of antimony triiodide content in the glass composition resulting in the high-frequency band long-wavelength shift. Such behaviour of the spectra is caused by shortening of Sb-S bonds in SbS_3 pyramids [9] due to the influence of SbI_3 groups. Meanwhile, no bands in the spectra were observed which could correspond to the presence of ternary structural groups in the glasses. Low probability of formation of such structural units in the glasses is also confirmed by the monotonous character of compositional behaviour of polarizability for $(Sb_2S_3)_x(SbI_3)_{1-x}$ glasses [8]. The obtained results enable the quasi-eutectic structure of Sb-S-I system glasses to be assumed. The glass matrix is built mostly by SbS_3 and SbI_3 structural groups. The relatively low glass-forming temperatures of the glasses of this system [5] speaks in favour of the molecular character of interaction between the eutectic elements. Even if in these glasses chains can be formed, they should be probably built of alternating SbS_3 and SbI_3 molecules.

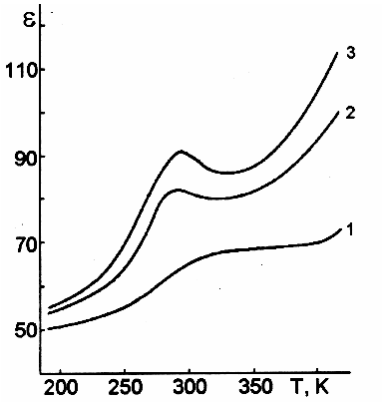

Fig. 3. Temperature dependence of ε for annealed SbSI at the frequency 10^5 Hz. The annealing temperature: 400 (1), 470 (2), 510 (3) K.

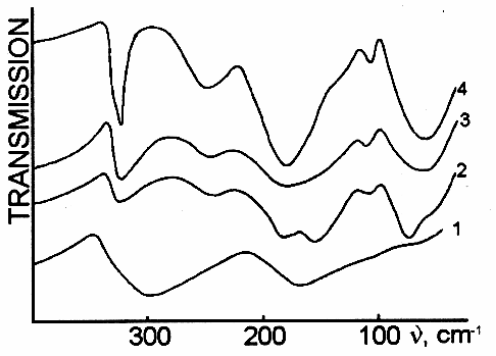

Fig. 4. IR transmission spectra of glassy fresh-prepared (1), glassy - annealed (2,3) and crystalline (4) SbSI. The annealing temperature: 400(2) and 510 (3) K.

In the IR spectrum of SbSI glass the absorption bands are positioned at higher frequencies than in the glasses with smaller content of iodine. This is, probably, related to the strong mutual influence of SbS_3 and SbI_3 structural groups, resulting in their considerable distortion and, possibly, partial destruction. The SbSI glass network is strongly disordered and sensitive to external effects. Therefore, during heating to $T \approx T_g$ a transformation of SbSI glass structure towards formation of ternary structural groups with high polarizability is possible. At $T>T_c$ the crystallization of the glass occurs. The IR spectrum of the crystallized glass is close to that of crystalline antimony sulphoiodide (Fig. 4, curve 2). With the increase of the annealing temperature the spectral pattern is changed towards the crystalline state what is related to the growth of the crystalline grain size.

Thus, the studies of the dielectric properties along with the IR spectroscopy data enabled us to show that the anomalies at the temperature dependences of ε and tanδ in glassy SbSI are related to the transition of the glass to the polar state and its subsequent crystallization. The structure and dielectric properties of antimony sulphoiodide are strongly dependent on the crystallization conditions.

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