

Original Research Article**Far-Infrared Spectra of the Alloy of
Germanium-Antimony-Tellurium
in the Glassy and Crystalline State****ABSTRACT**

Far-infrared spectra of a germanium-antimony-tellurium alloy in the glassy and crystalline states have been measured and analyzed in the frequency range 20–400 cm^{-1} at room temperature. The absorption in this range is due to the phonon modes of the structural units of crystalline and correlated librational vibrations (boson peak) of glassy alloy, which precede the appearance of relaxation dynamics. The vibrational assignments of various absorption bands and the differences revealed in the spectra will make it possible to more confidently elucidate the possible molecular mechanism of the crystal-to-amorphous transition in other chalcogenide alloys. New details of the crystal-to-amorphous transition scenario are suggested.

Keywords: far-infrared spectra, phonons, boson peak, chalcogenide, phase transition.

1. INTRODUCTION

Phase-change materials (PCMs) based on chalcogenide alloys are of great technological importance due to their ability to undergo on being heated a fast and reversible transition between the amorphous and crystalline phases [1, 2]. This property is exploited in rewritable optical media and electronic nonvolatile memory, which are based on the strong optical and electronic contrast between the two phases [3].

Te-containing chalcogenides such as the Ge-Sb-Te ternary alloy system usually abbreviated as GST has been known to satisfy material requirements for PCM. However, although GSTs are already in use for the rewritable compact discs and digital versatile discs and their commercial application in electronic non-volatile memory devices is expected in the near future as well; neither the local structure of material nor the change in the structure during the phase transition is well established. Several details of the electronic structure GST, which are supposed to control the transport properties and the switching mechanism, are still a matter of debate. One suggests that the strong optical and electronic contrast between the amorphous and crystalline phases GST system relate with a change in the coordination numbers [4], others with a change of bonding upon crystallization [5] or with a

high concentration of defects [6] and Peierls-distortion in an octahedral environment of Ge atoms [7]. In studies of the local atomic structure and dynamics of GST now uses the most advanced techniques such as the extended x-ray absorption fine structure (EXAFS) spectroscopy and spectroscopy of neutron scattering and Raman scattering (RS). Interestingly, the infrared (IR) spectroscopy is rarely used [8], and we do not know the IR absorption spectra of GST in the frequency range of RS-spectrum, which is based on conclusions about the molecular mechanism of the phase transition in this system.

Infrared absorption of solids can provide useful information about the lattice vibrational density of solids and structure of solids. The vibrations that contribute to IR absorption yield the most direct structural information since their frequencies are determined primarily by nearest interactions and thus relative IR activity by local molecular symmetry. The IR spectroscopy is one of the most often used spectroscopic tools for the study of the crystals and amorphous materials (including chalcogenide) [9]. Its use for studying the structure of short-range order and of the dynamics of individual structural units of GST would be quite natural. Especially at low frequencies, where manifest multiphonon absorption in groups of the short-range order, lattice absorption in the crystal and disorder-induced absorption in glasses ("boson peak" by RS-spectroscopy terminology [10]).

However, out of the optical properties of the GST system is known only that they have a high transparency in the infrared range from edge of the electronic absorption up to the multiphonon edge near 20 microns. But recently in the mid-infrared region spectrophotometry was used to measure the transmittance of selected materials from this system [11]. The experimental data were successfully

interpreted in terms of Drude-type plasma of free carriers and it was found that the main increase of optical constants occurs in the far-infrared domain. Consequently, the far-infrared spectroscopy appears to be convenient experimental method to study directly the structure and dynamics of the system GST. This is also evidenced by the results of the comparative study and analysis of the time-domain terahertz (THz) spectra of four different GST compounds in whose spectra observed a phonon mode and a contribution of free charge carriers at range of 10-80 cm^{-1} [12].

The aim of the present study was to obtain the IR transmission spectra of polycrystalline and glassy material of the GST system containing 15 at % germanium, 15 at % antimony and 70 at % tellurium (further $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$) in the region 20-400 cm^{-1} , to analyze them on the basis of calculation and of the literature data, and to find the relationship between the parameters of the far-infrared spectra and the molecular characteristics of $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$. The results are interpreted in terms of the vibrations of the isolated molecular units of investigated alloy. Detailed comparisons of obtained spectra has shown that glassy $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ exhibits a characteristic extreme far-infrared absorption as result of phonon coupling to modes which are not active in the corresponding crystalline counterpart material. The made vibrational assignments of various absorption bands and the revealed differences in the spectra will allow more confidently specify the possible molecular mechanism of the crystal-to-amorphous transition in GST alloys.

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS /

Melt quench technique using elemental Ge, Sb and Te with 5N purity has been used for alloy preparation of $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ glassy samples. The materials were weighed according to their atomic weight percentages and sealed in evacuated ($\sim 10^{-3}$ Pa) quartz ampoules. The sealed ampoules were kept inside a furnace, where the temperature was increased up to 950 $^{\circ}\text{C}$ at a heating rate of 3-4 $^{\circ}\text{C min}^{-1}$. The ampoules were frequently rocked for 20 h to make the melt homogeneous. The melts were rapidly cooled inside the furnace. The amorphous nature of the obtained glasses was confirmed by the X-ray powder diffraction method [13]. The bulk samples were characterized using energy dispersive X-ray spectroscopy for the analysis of compositions. To obtain polycrystalline samples, the bulk samples were annealed in inert atmosphere for 120 min at temperature about 20 $^{\circ}\text{C}$ above the temperature of amorphous - fcc phase transition determined by differential scanning calorimetry.

The far-IR absorption measurements were carried out in spectral range 20-400 cm^{-1} at room temperature. Far-infrared spectra were obtained on two spectrometers. A spectrometer designed at the Leningrad State University was used in the frequency range from 20 to 150 cm^{-1} . The spectra in the range 150 to 400 cm^{-1} were recorded using Hitachi FIS-21 (Japan) spectrometer. The resolution at a signal-to-noise ratio of the order of 100 was equal to 1 to 2 cm^{-1} . The location of the spectral bands at their maxima was determined to within 1 - 2 cm^{-1} . All the measurements were carried out using the polyethylene pellet method. The glassy and polycrystalline samples were thoroughly ground to an average size of 10-15 μm ; grinding was performed in dry argon to exclude surface oxidation. The pellets were made by mixing 2 mg sample with 200 mg of spectroscopic grade polyethylene and pressed into pellets using hydraulic press (10 tons cm^{-2} for 5 min under vacuum). To take account of polyethylene absorption, the spectrum of polyethylene was used as reference spectrum. The sample spectrum was divided by the reference spectrum to nullify the polyethylene absorption.

3. RESULTS AND DISCUSSION

Figure shows the far-IR transmission spectra of polycrystalline and glassy material of GST of the composition $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ in the region 20 - 400 cm^{-1} . The recorded spectra have the form of the almost structureless plateau on which background can pick out several peaks of the overlapping absorption bands. The most notable ones are at 60 cm^{-1} , 94 cm^{-1} , 110 cm^{-1} , 129 cm^{-1} , 159 cm^{-1} and 217 cm^{-1} in the spectrum of glassy and at 45 cm^{-1} , 56 cm^{-1} , 65 cm^{-1} , 92 cm^{-1} , 109 cm^{-1} , 127 cm^{-1} , 157 cm^{-1} and 214 cm^{-1} in the spectrum of polycrystalline material.

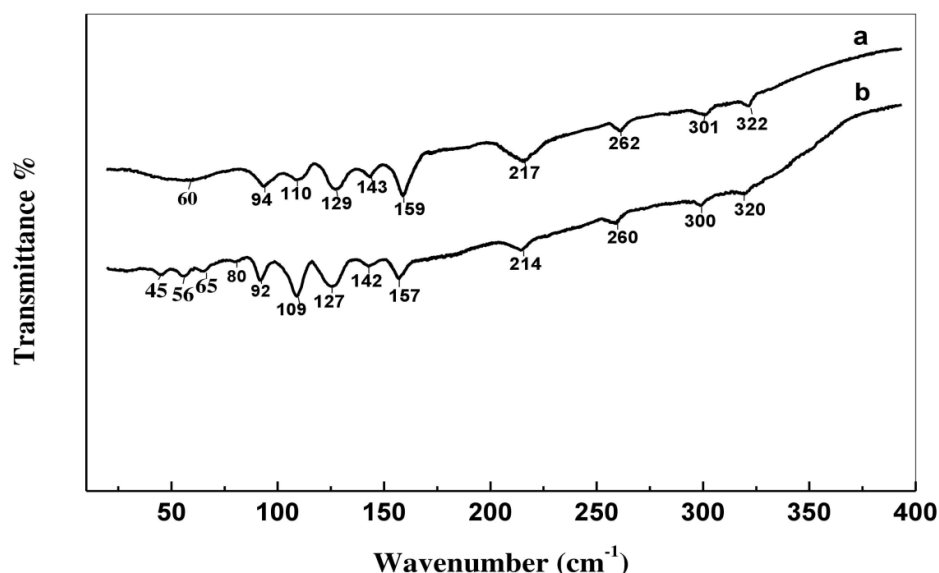


Figure 1. Far-infrared spectra of GST material of composition $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ in the amorphous (a) and the crystalline (b) state.

The tentative assignments of these bands were carried out on the basis of calculations in which the GST alloy is considered as a spatial three-dimensional polymer. Its structure has been expressed in the form of the two covalently constructed structural units - of areas of short-range order- tetrahedral “molecules” of GeTe_4 and pyramidal “molecules” of SbTe_3 . The validity of this approach follows from the close relationship between the vibrational spectra of molecules or molecular ions and the vibrational spectra of glass-like solids containing the same or analogous structural groups in the form of areas of short-range order.

The GeTe_4 molecule has 5 atoms and thus supports 15 modes of motion, including 3 pure rotations and 3 pure translations. The T_d symmetry of the GeTe_4 molecule leads to 6 zone- center modes following the decomposition in standard notation [14]:

$$\Gamma(T_d) = A_1 + E + F_1 + 3F_2,$$

where F_1 corresponds to a pure rotation (noted as R in the literature), and one of the F_2 is a pure translation (noted as T). R and T modes are related to the external modes. The modes derived from the tetrahedral A_1 , E and $2F_2$ modes are usually named as ν_1 , ν_2 , ν_3 and ν_4 , respectively, and are considered as internal modes of the GeTe_4 tetrahedra in $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$.

The modes which predicts a group theory for a tetrahedral symmetry and the calculated phonon frequencies at the $\Gamma(T_d)$ -point are reported in Table 1. They are attributed as shown in Table 1 below in accordance with the assignments of the GeI_4 molecular vibrations [15, 16].

Table 1. Normal vibrational modes of the GeI_4 and GeTe_4 tetrahedra.

From the spectrum of a Ge-Sb-Te alloy composition $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$.

substance	Normal vibrational mode (cm^{-1}) [*]					
	ν_1	ν_2	ν_3	ν_4	ν_R	ν_T
GeI_4	159	60	264	80	56 [19]	-

GeTe ₄	125	87	209	78	60	55
Ge ₁₅ Sb ₁₅ Te ₇₀	127	92	214	80	65	60

124 v1 and v3 – the stretching modes for symmetric and antisymmetric vibrations,
 125 respectively;
 126 v2 and v4 – bending modes for symmetric and antisymmetric vibrations,
 127 respectively;
 128 vR and vT- external modes for pure rotation and pure translation, respectively.

129 We can use the analogy between modes of the GeTe₄ and the GeI₄ tetrahedra since the mass ratio of
 130 germanium tetraiodide is very similar to germanium tetratelluride and therefore can expect a
 131 correspondence in the respective frequencies.
 132 Although only the v3 and v4 modes are infrared active in tetrahedral GeX₄ molecules, it is expected
 133 that all the fundamental modes appear in infrared absorption spectra because of breakdown of
 134 selection rules in polycrystalline and glassy materials. In addition the structure of crystalline GST is
 135 only “rock salt like” [1].
 136 The SbTe₃ molecule crystallizes in a structure with symmetry C_{3v}. There are four atoms per unit cell
 137 and consequently SbTe₃ exhibits 12 phonon modes, including external R and T modes for each
 138 wavevector K. Group theoretical analysis yields for K = 0 the following reduction: $\Gamma_{\text{tot}}(C_{3v}) = 2A_{1g}$
 139 $+2A_{1u} + 2E_g + 2E_u$, which splits into acoustical modes and IR- or
 140 Raman-active optical modes as follows: $\Gamma_{\text{acoustical}} = A_{1u} + E_u$, $\Gamma_{\text{Raman}} = 2A_{1g} + 2E_g$ and $\Gamma_{\text{IR}} = A_{1u} + E_u$, where
 141 one of the A_{1u} corresponds to a pure rotation and one of the E_u is a pure translation. Following the
 142 spectroscopic notation, the stretching modes are designated by v1 and v3 for the totally symmetric
 143 and the antisymmetric (double-degenerate) vibrations, respectively. Analogously, the bending modes
 144 correspond to v2 (A₁) and v₄ (E). All four vibrations are both infrared- and Raman-active.
 145 The mode which predicts a group theory for a pyramidal symmetry and the calculated phonon
 146 frequencies at the $\Gamma_{\text{tot}}(C_{3v})$ -point are reported in Table 2. They are attributed as shown in Table 2
 147 below in accordance with the assignments of the SbI₃ molecular vibrations [17]. The IR band
 148 attributions given here can be further substantiated by comparing of the
 149

150 **Table 2. Normal vibrational modes of the SbI₃ and SbTe₃ pyramids.**

151 **From the spectrum of a Ge-Sb-Te alloy composition Ge₁₅Sb₁₅Te₇₀.**

substance	Normal vibrational mode (cm ⁻¹) [*]						v3/v1	v4/v2
	v1	v2	v3	v4	vR	vT		
SbI ₃	177	89	147	71	67,5	45,5	0.83	0.80
SbTe ₃	164	122	145	106	53	46	0.88	0.86
Ge ₁₅ Sb ₁₅ Te ₇₀	157	127	142	109	56	45	0.90	0.87

152 v1 and v3 – the stretching modes for symmetric and antisymmetric vibrations,
 153 respectively;
 154 v2 and v4 – bending modes for symmetric and antisymmetric vibrations,
 155 respectively;
 156 vR and vT- external modes for pure rotation and pure translation, respectively.

ratio of the experimental frequencies of the stretching modes (ν_3/ν_1) and of the bending (ν_4/ν_2) modes for SbI_3 with similar values obtained in calculating the phonon modes for SbTe_3 . The important aspect of this comparison is that the frequency ratio ν_3/ν_1 and ν_4/ν_2 is essentially the same for the SbI_3 and for the SbTe_3 .

The calculated assignments of the IR bands in the spectrum of the crystalline $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ presented in the Tables 1 and 2 are qualitatively comparable with assignment Raman frequencies of GST materials, reported in literature [18, 19]. So, main Raman bands peaking at 127 cm^{-1} and 157 cm^{-1} in cubic $\text{Ge}_{22}\text{Sb}_{22}\text{Te}_{56}$ were also connected with stretch modes of GeTe_4 tetrahedra and SbTe_3 pyramids, respectively. Our theoretical calculations show that bands peaking at 127 cm^{-1} and 157 cm^{-1} have also a contribution of $\nu_2(\text{A}_{1u})$ and $\nu_3(\text{E}_u)$ modes of SbTe_3 , respectively. More low-frequency band, covering $85\text{--}115\text{ cm}^{-1}$ frequency region of the far-IR spectrum of $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$, comparable on intensity with the peaks of stretching modes GeTe_4 and SbTe_3 and is formed at least from two overlapping bands at 92 cm^{-1} and 110 cm^{-1} . These peaks according to the calculations can be attributed to bending modes $\nu_2(\text{E})$ and $\nu_4(\text{E}_u)$ of the GeTe_4 tetrahedra and SbTe_3 pyramids, respectively. In the frequency range $180\text{--}330\text{ cm}^{-1}$ far-IR spectrum of crystalline $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ one can recognize at least four small bands with maxima at ~ 214 , 260 , 300 , and 320 cm^{-1} (see Figure). The first of them near 214 cm^{-1} apparently can be assigned to $\nu_3(\text{F}_2)$ asymmetric stretching modes of GeTe_4 tetrahedra. An analogous feature was observed in Raman spectra of bulk crystalline GeTe , which are isostructural to $\text{Ge}_{22}\text{Sb}_{22}\text{Te}_{56}$ [20]. The weak bands at 260 and 320 cm^{-1} are quite probably due to the so-called 2 - phonon vibrational absorption arisen from excitations of fundamental molecular stretching modes of GeTe_4 (at 127 cm^{-1}) and SbTe_3 (at 157 cm^{-1}), respectively; while absorption band near 300 cm^{-1} can be related to vibrations of Ge-Ge ethane-like clusters [21].

The proposed interpretation of the IR-spectrum of polycrystalline $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ can be used for the attribution of the absorption bands at $\nu > 80\text{ cm}^{-1}$ of the IR-spectrum of the same alloy in amorphous (glassy) state. Because experimental spectra of these states in range, where are manifested intramolecular modes of the structural units of $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$, practically do not differ from each other. Except of the negligible red shift and changes in bands shape of the IR-spectrum polycrystalline $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ with respect to that of the amorphous state. Since, as a rule, the crystalline phase is more ordered than the amorphous one, this fact shows unusual similarity of the amorphous and crystalline structures $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ of short range order, assuming a rather similar degree of topological 'disordering' between these two forms. This means, at the phase transition from the crystal to the amorphous phase, basically the local structure of the building blocks (tetrahedra and pyramids) of $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ remains unchanged.

The same time, by inspection of Figure 1, it is easily seen that the amorphous to crystal transition is displayed in the IR- spectra of $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ through drastic changes at $\nu < 80\text{ cm}^{-1}$, where is manifested lattice absorption due to external librational and translational degrees of freedom of the structural units of crystal. In the IR-spectrum of polycrystalline $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ with the manifestation of the intermolecular librations and translations of tetrahedra and pyramids as a whole, is connected, according to the calculations, the presence of absorption peaks at 65 , 56 , and 45 cm^{-1} (modes $\nu\text{R}(\text{F}_1)$, $\nu\text{T}(\text{F}_2)$ and $\nu\text{T}(\text{E})$, respectively). In the IR-spectrum glassy $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ in the same frequency range is only one of abnormally broad band with a maximum at $\sim 60\text{ cm}^{-1}$, in which not difficult to discern the well-known, and ubiquitously present for amorphous solids, band, i.e. the boson peak.

Boson peak is attributed to the disorder-induced absorption, which is a manifestation of a low energy vibrational excitations emerging from cancellation of the selection rules in an amorphous medium. The peak observed in the low-frequency spectra of glasses appeared to correspond to the peaks observed at low frequencies in region of acoustic phonons of corresponding crystals [22]. Its appearance in the low-frequency spectra of glasses at the phase transition indicates that in the absence of a long-range order a system of coupled harmonic oscillators of crystal became a system of disoriented oscillators which preserve only limited (on a scale of medium-range order) correlation of the intermolecular vibrational motions [23]. So, in some works boson peak is assigned to cooperative orientational motion (librations) of several molecular groups [24, 25].

That is, as upon comparison IR-spectra of polycrystalline and glassy materials in range, where are manifested *intramolecular modes* of the structural units of $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$, we had no hint concerning the contrasting local structure between the amorphous and the crystalline phases, so and the appearance of the boson peak at frequencies of *intermolecular modes* allow suggest that and the medium-range crystalline order in glassy $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ are also stored. This data reflects clearly the local ordering of the atoms in the amorphous state which is similar to that in the crystalline $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ but lacks long-range ordering.

The spectral changes at low optical frequencies allow suggest the following scenario of a phase transition in the system $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$. Local distortions inherent "tetrahedral" and "pyramidal" structural units of glassy $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$, facilitating the formation of Ge-Ge and Ge-Sb bonds [26], and also correlated torsional oscillations (librations) of these structures, at the essential share of vacancy, form medium-range (chain-like) order in the system. The evidence of this is the presence of the boson peak in the spectrum. For the transition such a system in a metastable ordered not require restructuring of local structures, but rather reorientation of existing clusters (the chains). In essence, the transition of the order-disorder in this case is the relaxation transition on the mechanism of fast β -relaxation Johari-Goldstein [27]. Such a transition requires minimal power inputs and has a nanosecond time of relaxation.

4. CONCLUSION

In the present work the far-infrared transmission spectra of polycrystalline and glassy materials of the GST system of composition $\text{Ge}_{15}\text{Sb}_{15}\text{Te}_{70}$ have been obtained in the spectral range 20 - 400 cm^{-1} at room temperature and also analyzed on the basis of theoretical calculation and of the literature data. Although the made vibrational assignments of various absorption bands given here could be considered as tentative and alternative interpretations may be proposed, these assignments and the revealed differences in the spectra is allow suggest the following possible molecular mechanism for unusual amorphization- crystallization process in GST alloys.

According to the majority of existing models, the presence of the boson peak, as an indication of a medium-range order existing in the structure of glasses, in the low-frequency spectra is associated with the correlative orientational motion (librations) of fragments a crystalline structure of glass. These fragments of a crystalline structure can play the role of crystallization centers on the nanometer scale and their correlative librational vibrations can be viewed as precursors of phonons due to short-range ordering. Then according to this model, the recrystallization from the amorphous phase may be achieved easily by reorientation of the randomly oriented fragments of a crystalline structure back to the original well-aligned structure of the crystalline phase. We emphasize that in this case crystallization of GST does not involve relaxation of the complete covalent network but is more like the so- called β -relaxation, where only fragments of the network relax. This process requires very small atomic displacements and hence can be extremely fast.

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