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 PCMs. The system is 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. However, neither the local structure of material nor the change in the structure during the phase transition is well established. Several details of the GST electronic structure, supposed to control the transport properties and the switching mechanism, are still a matter of debate. In some reports, the strong optical and electronic contrast between the amorphous and crystalline phases GST system is attributed to a change in the coordination numbers [4], and in others, to a change of bonding upon crystallization [5] or to a

high concentration of defects [6] and Peierls-distortion in an octahedral environment of Ge atoms [7].

At present, the most advanced techniques, such as the extended x-ray absorption fine structure (EXAFS) spectroscopy and spectroscopy of neutron scattering and Raman scattering (RS) are employedin studies of the local atomic structure and dynamics of GST. Interestingly, the infrared (IR) spectroscopy is rarely used [8], and no IR absorption spectra of GST system are available for the frequency range of RS-spectrum, on which conclusions about the molecular mechanism of the phase transition in this system is based.

The IR absorption in solids can provide useful information about the lattice vibration density and structure of solids. The vibrations that contribute to IR absorption yield the most direct structural information because their frequencies are determined primarily by the nearest interactions, and thus,the relative IR activity are governed by local molecular symmetry. IR spectroscopy is one of the most frequently used spectroscopic tools for the study of the crystals and amorphous materials (including chalcogenide) [9]. Its application for studying the structure of short- range order and the dynamics of individual structural units of GST would be quite natural. This is especially so 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 terminology of RS-spectroscopy [10]) is manifested.

However, it is only known about the optical properties of the GST system that thesematerialshave high transparency in the infrared range, from the electronicabsorption edge up to the multiphonon edge near 20 micrometers.However, spectrophotometry has been recently used in the mid-IR region

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 GSTsystem. This is also evidenced by the results of the comparative study and analysis of the terahertz (THz) time-domain spectra of four different GST compounds, in whose spectra a phonon mode and a contribution of free charge carriers at range of 10-80 cm^{-1} [12] are observed.

The aim of the present study was to obtain IR transmission spectra of polycrystalline and glassy material of a GST system containing 15 at % germanium, 15 at % antimony, and 70 at % tellurium (henceforth $Ge_{15}Sb_{15}Te_{70}$) in the region 20-400 cm^{-1}, to analyze these spectra on the basis of calculation and published data, and to find the relationship between the parameters of the far-IR spectra and the molecular characteristics of $Ge_{15}Sb_{15}Te_{70}$. The results are interpreted in terms of vibrations of isolated molecular units of the alloy under study. A detailed comparison of the spectra demonstrated that glassy $Ge_{15}Sb_{15}Te_{70}$ exhibits characteristic extreme far-IR absorption as result of phonon coupling to modes which are not active in the corresponding crystalline material. The vibrational assignments of various absorption bands and the differences revealed in the spectra will make it possible tomore confidently specify the possible molecular mechanism of the crystal-to-amorphous transition in GST alloys.

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS /

The melt-quench technique with elemental Ge, Sb and Te of 5N purity was used to prepare$Ge_{15}Sb_{15}Te_{70}$ glassy samples [13]. The materials were weighed according to their atomic weight percentages and sealed in evacuated (~10^{-3} Pa) quartz ampoules. The ampoules were kept in a furnace the temperature of which was raised up to 950 °C at a heating rate of 3-4 °C min^{-1}. The ampoules were frequently rocked for 20 h to make the melt homogeneous. Then the melts were rapidly quenched outside the furnace by dropping the ampoules in liquid nitrogen for fast cooling and to ensure the amorphization of the alloy.The alloys so obtained were crushed to the powder form for analysis.The nature of the thus prepared sampleswas confirmed by the X-ray diffraction patterns obtained with an Rigaku –D/MAX diffractometer with Cu Kα radiation (λ = 0.15406 nm). Figure 1 shows the XRD patterns for rapidly quenched and thermally annealed at 200 ^{0}C alloys. XRD pattern of rapidly quenched samples reveals the amorphous nature of the alloy as she do not show any spectacular peak while XRD pattern of samples annealed at 200 ^{0}C show the polycrystalline nature of the alloy.

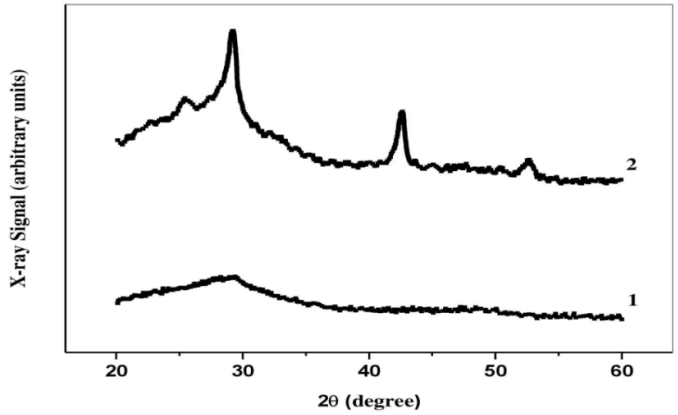


Figure.1. X-ray diffraction spectra of GST alloy composition $Ge_{15}Sb_{15}Te_{70}$.
1. X-ray scan of alloy quenched in liquid nitrogen.
2. X-ray scan of thermally annealed alloy at 200^{0}C.

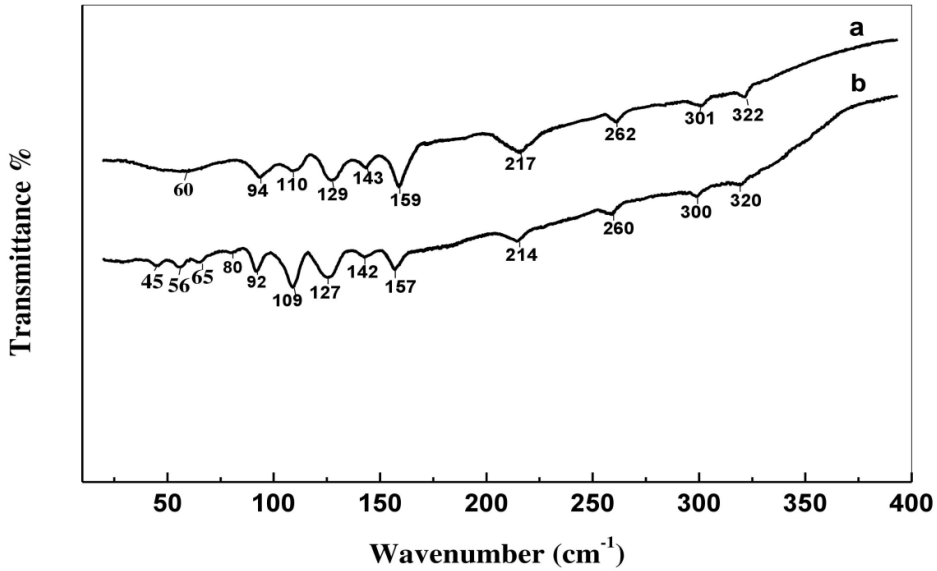
Bulk samples were characterized using energy dispersive X-ray spectroscopy (EDAX)(Zeiss EVO 40 EP with EDAX attachment operated at 20 kV) for theanalysis of compositions.EDAX results indicate

that the atomic percentages of $Ge_{15}Sb_{15}Te_{70}$ compositions are close to starting elements (Ge-15.2, Sb- 15.1, Te - 70.3 at. %, with accuracy of ±5%.To obtain polycrystalline samples, the bulk samples were annealed in inert atmosphere for 120 min at temperature about 20^{0}C above the temperature of amorphous - *fcc* phase transition determined by differential scanning calorimetry. Differential scanning calorimetry (DSC-50, Shimadzu) at heating rate of 5°C/min in a nitrogen flow was used toexamine the thermal properties of investigated materials. Polycrystalline samples were crushed and pressed into Al pans. The temperature range studied was 20 to 630°C. The necessary amount of amorphous material (about 2–4 mg).

The far-IR absorption measurements were made in spectral range 20-400 cm^{-1} at room temperature. Far-IR spectra were obtained on two spectrometers. A spectrometer designed at the Leningrad State University [14]and then modified with an OAP-7 and a new filtration system was used in the frequency range from 20 to 150 cm^{-1}. The spectra in the range 150 to 400 cm^{-1} were recorded with Hitachi FIS-21 (Japan) spectrometer. The resolution at a signal-to-noise ratio of the order of 100 was 1 to 2 cm^{-1}. The peak positions of the spectral bands were determined to within 1 - 2 cm^{-1}. All the measurements were madeby using the polyethylene pellet method. The glassy and polycrystalline samples were thoroughly ground to an average size of 10-15 µm in dry argon to preclude surface oxidation. The pellets were made by mixing 2-mg portion of a sample with 200 mg of spectroscopic grade polyethylene.The mixture was compacted into pellets with a hydraulic press (10 tons cm^{-2} for 5 min under vacuum). To take into account the absorption of polyethylene, it was used as reference. The spectrum of a sample was divided by the reference spectrum to eliminate the absorption of polyethylene.

3. RESULTS AND DISCUSSION

The figure2 shows the far-IR transmission spectra of polycrystalline and glassy GST material of composition $Ge_{15}Sb_{15}Te_{70}$ in the region 20 - 400 cm^{-1}. The recorded spectra have the form of an almost structureless plateau, with several peaks of the overlapping absorption bands seen on its background. The most distinct of these are the bands 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}, 157cm^{-1}, and 214 cm^{-1} in the spectrum of polycrystalline material.



. Figure 2. Far-infrared spectra of GST system composition $Ge_{15}Sb_{15}Te_{70}$ in the amorphous (a) and the crystalline (b) state.

Thesebands were tentative assigned on the basis of calculations in which the GTS alloy is regarded as a 3D polymer. Its structure was expressed in the form of the two covalently bound structural units:

tetrahedral “molecules” of germanium tetratelluride ($GeTe_4$) in regions with a short-range order and pyramidal “molecules” of antimony tritelluride$SbTe_3$. The validity of this approach follows from the close relationship between the vibrational spectra of molecules or molecular ions and those of glass-like solids containing the same or analogous structural groups in the form of regionswith a 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 [15]:

$$\Gamma(T_d) = A1 + E + F_1 + 3F_2 ,$$

where F_1 corresponds to a pure rotation (noted as R in the literature), and one of the F_2 is a pure translation (designated 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 v1, v2, v3 and v4, respectively, and are regarded as internal modes of the $GeTe_4$ tetrahedra in $Ge_{15}Sb_{15}Te_{70}$.

The modes which predicts a group theory for a tetrahedral symmetry and the calculated phonon frequencies at the $\Gamma(T_d)$-point are listed in Table 1. They are attributed as shown in Table 1 below in accordance with the assignments of the germanium tetraiodide (GeI_4)molecular vibrations [16, 17].

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

From the spectrum of a Ge-Sb-Te alloy composition $Ge_{15}Sb_{15}Te_{70}$.

substance	Normal vibrational mode (cm^{-1}) *					
	v1	**v2**	**v3**	**v4**	**vR**	**vT**
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

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

The analogy between the modes of the $GeTe_4$ and the GeI_4 tetrahedra can be used because the mass ratio of germanium tetraiodide is very similar to germanium tetratelluride,and, therefore, a correspondence in the respective frequencies can be expected.

Although only the v3 and v4 modes are IR-active in tetrahedral GeX_4 molecules, it is expected that all the fundamental modes appear in IR absorption spectra because of the violation of the selection rules in polycrystalline and glassy materials. In addition, the structure of crystalline GST is only “rock salt like” [1].

The $SbTe_3$ molecule crystallizes in a structure with symmetry C_{3v}. There are four atoms per unit cell, and, consequently, $SbTe_3$ exhibits 12 phonon modes, including external R and T modes for each wavevector K. A group-theoretical analysis yields for K = 0 the following reduction: Γ_{tot} (C_{3v}) = $2A_{1g}$ $+2A_{1u}$ + $2E_g$ + $2E_u$, which splits into acoustical modes and IR- orRaman-active optical modes as follows: $\Gamma_{acoustical} = A_{1u}+E_u$,$\Gamma_{Raman}= 2A_{1g}+ 2E_g$ and $\Gamma_{IR}= A_{1u} + E_u$, where one of the A_{1u} corresponds to a pure rotation(designated as vR here) and one of the E_u is a pure translation(designated as vT here). Following the spectroscopic notation, the stretching modes are designated by v1 and v3 for the totally symmetric and the antisymmetric (double-degenerate) vibrations, respectively. Analogously, the bending modes correspond to v2 (A_1) and v_4 (E). All four vibrations are both infrared- and Raman-active.

The modes predicted by the group theory for a pyramidal symmetry and the calculated phonon frequencies at the Γ_{tot} (C_{3v})-point are listed in Table 2. They are attributed as shown in Table 2 below

in accordance with the assignments of the of the antimony triiodide (SbI_3) molecular vibrations [18]. The IR band assignments given here can be further substantiated by comparing the ratios between

Table 2.Normal vibrational modes of the SbI_3 and $SbTe_3$ pyramids.

From the spectrum of a Ge-Sb-Te alloy composition $Ge_{15}Sb_{15}Te_{70}$.

	Normal vibrational mode (cm^{-1})*							
substance	**v1**	**v2**	**v3**	**v4**	**vR**	**vT**	**v3/v1**	**v4/v2**
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

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

the experimental frequencies of the stretching modes (v3/v1) and of the bending (v4/v2) 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 ratios v3/v1 and v4/v2 are essentially the same for the SbI_3 and $SbTe_3$.

The calculated assignments of the IR bands in the spectrum of the crystalline Ge_{15} Sb_{15} $Te_{70,}$ presented in the Tables 1 and 2 are qualitatively comparable with assignment of Raman frequencies of GST materials, reported in literature [19, 20]. So, main Raman bands peaked at 127 cm^{-1} and 157 cm^{-1} in cubic $Ge_{22}Sb_{22}Te_{56}$ were also associated with stretching modes of $GeTe_4$ tetrahedra and $SbTe_3$ pyramids, respectively. The theoretical calculations made in the study show that bands peaked at 127 cm^{-1} and 157 cm^{-1} have also a contribution of v2(A_{1u}) and v1(E_u) modes of $SbTe_3$, respectively. The lower frequency band, covering 85-115 cm^{-1} frequency region of the far-IR spectrum of $Ge_{15}Sb_{15}Te_{70}$ is comparable in intensity with the peaks of stretching modes $GeTe_4$ and $SbTe_3$ and is formed by at least two overlapping bands at 92 cm^{-1} and 110 cm^{-1}. According to the calculations,these can be attributed to bending modes v2 (E) and v4 (E_u) of the $GeTe_4$ tetrahedra and $SbTe_3$ pyramids, respectively. In the frequency range 180 - 330 cm^{-1},at least four small bands peaked at ~214, 260, 300, and 320 cm^{-1} can be distinguished in the far-IR spectrum of crystalline $Ge_{15}Sb_{15}Te_{70}$ (see Figure 2). The first of these, lying at 214 cm^{-1}, can apparently be assigned to v3 (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 $Ge_{22}Sb_{22}Te_{56}$ [21]. The weak bands at 260 and 320 cm^{-1} are quite probably due to the so-called 2 - phonon vibrational absorption arising from excitations of fundamental molecular stretching modes of $GeTe_4$ (at 127cm^{-1}) and $SbTe_3$ (at 157cm^{-1}), respectively; while absorption band near 300 cm^{-1} can be attributed to vibrations of Ge-Ge ethane-like clusters [22].The absorption bands at the frequencies 95 cm^{-1} and 143 cm^{-1}, which were assigned to the modes v2(E) and v3(E) of the $GeTe_4$ and $SbTe_3$, respectively, in the far-IR spectrum of the Te-rich $Ge_{15}Sb_{15}Te_{70}$ might also contain the contribution of the fragments consisting only of tellurium atoms [23].

The proposed interpretation of the IR-spectrum of polycrystalline $Ge_{15}Sb_{15}Te_{70}$ can be used for the attribution of the absorption bands at v > 80 cm^{-1} of the IR-spectrum of the samealloy in amorphous (glassy) state. This is so because experimental spectra of these states practically do not differ from each other in range in which intramolecular modes of the structural units of $Ge_{15}Sb_{15}Te_{70}$, are manifested, except for a negligible red shift and changes in the shape of bands in the IR-spectrum of polycrystalline $Ge_{15}Sb_{15}Te_{70}$ with respect to that of the amorphous state. Because, as a rule, the crystalline phase is more ordered than the amorphous one, this fact shows unusual similarity of the amorphous and crystalline structures Ge_{15} Sb_{15} Te_{70} of short range order and leads to an assumption

of rather similar degree of topological 'disordering' between these two forms. This means that thelocal structure of the building blocks (tetrahedra and pyramids) of $Ge_{15}Sb_{15}Te_{70}$ remains basically unchanged upon the phase transition from the crystalline to the amorphous phase.
At the same time, an analysis of Figure 2 readilyshows thatthe amorphous to crystal transition appear in the IR- spectra of $Ge_{15}Sb_{15}Te_{70}$ as drastic changes at $v < 80$ cm^{-1}, where the lattice absorption due to external librational and translational degrees of freedom of the structural units of crystal is manifested.
The presence of absorption peaks at 65, 56, and 45 cm^{-1} (modes vR(F1), vT(F2) and vT(E), respectively) in the IR spectrum of polycrystalline $Ge_{15}Sb_{15}Te_{70}$ is due, according to the calculations, to the manifestation of the intermolecular librations and translations of tetrahedra and pyramids as a whole.The IR spectrum glassy $Ge_{15}Sb_{15}Te_{70}$contains in the same frequency range only a single abnormally broad band peaked at ~ 60 cm^{-1}, which can be readily assigned as the well-known band ubiquitously present in amorphous solids, 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 [24]. 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 in which only limited (on a scale of medium-range order) correlation between the intermolecular vibrational motions is preserved [25]. So, the boson peak is occasionally assigned to cooperative orientational motion (librations) of several molecular groups [26, 27].
That is, when IR-spectra of polycrystalline and glassy materials are compared in range in which *intramolecular modes* of the structural units of $Ge_{15}Sb_{15}Te_{70}$are manifested, there is no evidence about the contrasting local structure between the amorphous and the crystalline phases, so the appearance of the boson peak at frequencies of *intermolecular modes* suggests that the medium-range crystalline order is also preserved in glassy $Ge_{15}Sb_{15}Te_{70}$. These data clearly reflect the local ordering of the atoms in the amorphous state which is similar to that in the crystalline $Ge_{15}Sb_{15}Te_{70}$ but lacks long-range ordering.

The spectral changes at low optical frequencies suggest the following scenario of a phase transition in the system $Ge_{15}Sb_{15}Te_{70}$. Local distortions inherent "tetrahedral" and "pyramidal" structural units of glassy $Ge_{15}Sb_{15}Te_{70}$, which facilitate the formation of Ge-Ge and Ge-Sb bonds [28], and also correlated torsional oscillations (librations) of these structures with a noticeable share of vacancy form medium-range (chain-like) order in the system. This is evidenced of this is the presence of the boson peak in the spectrum. For the transition to occur, such a system in a metastable ordered state not require a restructuring of local structures, but rather reorientation of existing clusters (the chains). In essence, the order-disordertransition is in this case a relaxation transition by the fast β-relaxation Johari-Goldstein mechanism [29]. Such a transition requires the minimuminput of power and has a nanosecond relaxation time.

4. CONCLUSION

In the present study the far-IR transmission spectra of polycrystalline and glassy materials of the GST system of composition $Ge_{15}Sb_{15}Te_{70}$were measuredin 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.

The results, by the example of the composition $Ge_{15}Sb_{15}Te_{70}$, demonstrate, that the use of far-IR spectroscopy has a clear potential to characterize of the local atomic structure and dynamics of the GST alloys. Further studies on the new GST materials will give possibility to improve the parameters of the already developed memory elements and will provide additional information about the nature of the switching effect.

REFERENCES

1. Kolobov AV, Tominaga J. Chalcogenides: Metastability and Phase Change Phenomena; Press: Springer-Verlag, Berlin; 2012.

2. Meinders ER, Mijiritskii AV, van Pieterson L, Wuttig M. Optical Data Storage Phase-Change Media and Recording; Philips Research Book Series, V. 4. Press: Springer- Verlag, Berlin; 2006.

3. Burr GF, Breitwisch MJ, Franceschini M. et al. Phase change memory technology. J. Vac. Sci. Technology B 2010; 28:223-262.

4. Kolobov AV, Fons P, Frenkel AI, Ankudinov AL, Tominaga J, and Uruga T. Understanding the phase-change mechanism of rewritable optical media. Nature Materials. 2004;3(10): 703-708.

5. Shportko K, Kremers S, Woda M, Lencer D, Robertson J. Wuttig M. Resonant bonding in crystalline phase-change materials.Nature Materials. 2008;7(8):653-658.

6. Wuttig M, Lusebrink D, Wamwangi D, Welnic W, Gilleben M, Dronskowski R. The role of vacancies and local distortions in the design of new phase-change materials.Nature Materials. 2007; 6(2):122-128.

7. Raty JY, Godlevsky V, Ghosez P, Bichara C, Gaspard JP, and Chelikowsky JR. Evidence of a Reentrant Peierls Distortion in Liquid GeTe. Phys. Rev. Lett. 2000; 85:1950 - 1953.

8. Cai YF, P. Zhou P, Lin YY, Tang TA, Chen LY, Li J et al. Nitrogen and Silicon Co-Doping of $Ge_2Sb_2Te_5$ Thin Films for Improving Phase Change Memory Performance. Chin. Phys. Lett. 2007; 24(3):781 - 783.

9. Moller K, Rothshild W. Far Infrared Spectroscopy. Press: Wiley, New York; 1971.

10. Martin AJ, and Brenig W. Model for Brillouin Scattering in Amorphous Solids. Phys. Status Solidi B 1974; 64(1):163-172.

11. Mendoza-Galvan A, and Gonzalez-Hernandez J. Drude-like behavior of Ge:Sb:Te alloys in the infrared. J. Appl. Physics. 2000; 87:760-765.

12. Kadlec F, Kadlec C, Kuzel P. Contrast in terahertz conductivity of phase-change materials. Solid State Communications. 2012;152(10):852-855.

13. Dzhurkov V, Fefelov S, Arsova, Nesheva D, and Kazakova L. Electrical conductivity and optical properties of tellurium-rich Ge-Sb-Te films. Journal of Physics: Conference Series. 2014;558:012046 - 1 - 6.

14. Ryzhov VA, Tonkov MV. Technique of far-IR spectroscopy. In: Denisov GS (ed) Molecular spectroscopy; Press: University Press, Leningrad; 1973.

15. Herzberg G. Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules; Press: D. Van Nostrand, London; 1945.

16. Stammreich H, Forneris Roberto, and Tavares Yara. Raman Spectra and Force Constants of GeI4 and SnI4.J. Chem. Phys. 1956;25:1278-1279.

17. Delwaulle ML. Mise en evidence par l'effet Raman de la formation de chlorobromoiodures de germanium lorsqu'onmelange les tetrachlorure, tetrabromure et tetraiodure de germanium. C. R. Acad. Sci. 1954; 238:84-87.French.

18. Kiefer W. Raman-Spektreneines AsJ3-Einkristalls und von SbJ_3 - und BiJ_3 - Kristallpulvern. Z. Naturforsch. 1970; 25a:1101-1107. Germany.

19. Nemec P, Nazabal V, Moreac A, Gutwirth J, Bene L, Frumar M. Amorphous and crystallized Ge-Sb-Te thin films deposited by pulsed laser: Local structure using Raman scattering spectroscopy. Materials Chemistry and Physics.2012; 136:935-941.

20.Kozyukhin S, Veres M, Nguyen HP, Ingramd A, Kudoyarova V. Structural changes in doped $Ge_2Sb_2Te_5$ thin films studied by Raman spectroscopy.Physics Procedia.2013; 44:82- 90.

21. Upadhyay M, Murugavel S, Anbarasu M, and Ravindran TR. Structural study on amorphous and crystalline state of phase change material. J. Appl. Phys. 2011;110:083711 - 1 - 6.

22. Koblar J, Arlin B, Shau G, Porezag DV, and Pederson MR. Raman-active modes of a-$GeSe_2$ and a-GeS_2 : A first-principles study. Phys. Rev. B 1999; 60:R14985 - R14989.

23. Grosse, P. and Richter, W. Physics of Non-tetrahedrally BondedElements and Binary Compounds. In: Madelung O (ed) Landolt–Bornstein -Group III Condensed Matter; Press: Springer, Berlin; 1998.
24. Grigera TS, Martin-Mayor V, Parisi G. & Verrocchio P. Phonon interpretation of the 'boson peak' in supercooled liquids. Nature.2003; 422:289-292.
25. Johari GP. Molecular inertial effects in liquids: Poley absorption, collision-induced absorption, low-frequency Raman spectrum and Boson peaks. J. Non-Crystalline Solids. 2000; 307-310:114-127.
26. Bembenek SD, Laird BB. Instantaneous normal modes analysis of amorphous and supercooled silica.J. Chem. Phys. 2001; 114: 2340-2344.
27. Baran J, Davydova NA, Pietraszko A. Spectroscopic study of the formation of molecular glasses. J. Molec. Structure. 2005; 744-747:301-305.
28. Kolobov AV, Krbal M, Fons P, Tominaga J, Uruga T. Distortion-triggered loss of long-range order in solids with bonding energy hierarchy. Nature Chemistry.2011; 3:311 - 316.
29. Johari GP. Localized molecular motions of β-relaxation and its energy landscape. J. Non-Crystalline Solids. 2002; 307-310:317-325.