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**Structural properties of Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ alloys**

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In the present paper the amorphous Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ alloys have been studied by X-ray diffraction and Raman spectroscopy. The experimental X-ray diffraction patterns were used for calculations of radial distribution functions which have given the positions of the nearest-neighbour bond length $r_1$ - 2.67 Å and second-neighbour bond length $r_2$ - 4.27 Å. Similar $r_1$ values were observed for Ga-Ge-Te glasses of other compositions. Observed bands in the Raman spectra of Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ samples show that such glass contains different nanophases and can be explained in the terms of vibrational modes of Ga-Te and Ge-Te glasses and films. Investigations of compositional dependencies of characteristic constituent Raman bands intensities whose concentration is changing with the composition are necessary in order to obtained better assignment of Raman bands.

**Keywords:** chalcogenide glasses, X-ray diffraction, radial distribution function, Raman spectroscopy, nanophases.

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**Introduction**

Chalcogenide thin films and composites on their base are used as the recording medium for fabrication of optical elements, in holography and phase change-type optical memory discs, integrated and fiber optics, sensors, etc. [1-19] This is due to their possession of unique characteristics such as wide range of optical transparency, high refractive index and photo structural transformations, accompanied by the change of optical and chemical properties [2-5]. Among the number of different photo-induced effects are photo-darkening and bleaching, local expansion or contraction, changes of the refractive index, polarization-dependent structural changes, photoinduced dichroism [1-2, 4-5]. In recent times, studies of nanocomposite materials based on chalcogenide glasses have been actively conducted [6, 11, 13-14]. Such nanocomposite materials provide possibility of the direct recording of surface reliefs (without step of selective etching), recording process depends on the polarization of the recording beams.

Family of GaGeTe alloys is interesting due to versatile far-IR optics [7-10], phase change-type optical memory [15-16] and sensor [17] applications. The structural features of chalcogenide glasses and films are important for various characteristics and processes, including photoinduced ones. The addition of Ga to GeTe alloys can influence crystallization timings and room-temperature stability [20]. Accordingly, better understanding of the structural properties can help in the optimization of the sensitivity and relief formation processes of composite nanomultilayer structures based on chalcogenide glasses, which are promising for the direct recording of optical elements.

The better understanding of the correlations between their structural and macroscopic properties and the information on the short-range order structure of chalcogenide glasses is needed. This was the main motivation to study Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ alloys.

**I. Experimental**

Studied bulk Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ alloys were prepared by the conventional melt quenching technique. Proper quantities of high-purity (99.999%) elements, vacuum sealed into a quartz ampoule, were kept in a furnace at ~1000 °C for about 30 h, shaken for homogeneous mixing and then quenched in cold water.

X-ray diffraction patterns samples were recorded with
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use of the X-ray diffractometer with Bragg–Brentano geometry, using Cu K\textsubscript{α} radiation 1.54178 Å and mounted graphite monochromator for a diffracted beam. The diffraction data were collected in the range of scattering vector magnitudes \( Q \) between 0.4 and 8 Å

\[
Q = \frac{4\pi \sin \theta}{\lambda}
\]

All samples were examined in transmission geometry. All the X-ray experiments were performed at ambient temperature. The diffraction intensities were corrected for the background, incoherent (polarization and absorption) and multiple scattering in the usual ways in order to eliminate the part of radiation which does not carry structural information. The spectra were measured at a constant rate. The Compton scattering was corrected using the values given by Balyuzi and Faber-Ziman [21-22], total structure factor \( S(Q) \) was calculated from the scattering intensity as

\[
S(Q) = \frac{Q^2}{<f^2(Q)> - <f(Q)^2>}
\]

with \(<f^2(Q)> = \sum c_i f_i^2(Q), <f(Q)> = \sum c_i f_i(Q)\) where \(c_i\) is the molar fraction and \(f_i\) is the total atomic scattering factor of the \(i\)-th component of the glass.

After Fourier transformation the reduced radial distribution functions \(G(r)\) (RDF) were determined, the measured \(S(Q)\) using the fast Fourier transform technique [23-26] as follows:

\[
G(r) = \frac{2}{\pi} \int_0^{\infty} (S(Q) - 1))Q \sin(Qr)dQ
\]

In reality, the data should be multiplied by a modification factor in order to reduce the ripples inevitably introduced due to the finite accessible upper \(K\) value \((K_{\text{max}})\) in the measurements. Eq.(1) therefore becomes

\[
G(r) = \frac{2}{\pi} \int_0^{\infty} (S(Q) - 1))Q M(Q) \sin(Qr)dQ
\]

where \(M(K)\) is called the damping factor [25-26] and is given by

\[
M(Q) = \frac{\sin\left(\frac{\pi Q}{Q_{\text{max}}}\right)}{\frac{\pi Q}{Q_{\text{max}}}} Q \leq Q_{\text{max}},
\]

\[
M(Q) = 0, Q > Q_{\text{max}}
\]

\(G(r)\) may also be expressed directly in real space coordinates to emphasize its relationship with the local atomic density, \(\rho(r)\) at a distance \(r\) and the bulk atomic density, \(\rho_0\); as follows

\[
G(r) = 4\pi r(\rho(r) - \rho_0)
\]

where \(\rho(r)\) is the density function, which represents an atomic pair correlation function, and is equal to zero at values of \(r\) less than the average nearest neighbor interatomic separation and equal to the average value of density \(\rho_0\) at very large value of \(r\), where the material becomes homogenous. In between these two limits, \(\rho_0\) for an amorphous solid will exhibit an oscillatory behavior, with peaks in the probability function representing the average interatomic separations. At short distances \((r \leq 2\text{Å})\), see Eq.(3), \(G(r)\) should follow the density line \((-4\pi r\rho_0)\) which is used as a quality check of the data [25-26].

The radial distribution function, RDF(r), is defined as the number of atoms lying at distances between \(r, r + dr\) from center of an arbitrary origin atom and written as

\[
\text{RDF}(r) = rG(r) + 4\pi r^2 \rho_0 = 4\pi r^2 \rho(r)
\]

The function that is used in the determination of atomic distances and co-ordination numbers is the total distribution function, \(T(r)\)

\[
T(r) = \frac{\text{RDF}(r)}{r} = 4\pi \rho(r).
\]

The average coordination number, \(N\), in a spherical shell between radius \(r_1\) and \(r_2\) around any given atom, can be calculated as the number of atoms in the area between \(r_1\) and \(r_2\) where \(r_1\) is a lower limit of \(r\), below which \(\rho(r)\) is zero, and \(r_2\) is the first minimum of \(4\pi r^2 \rho(r)\).

The position of the first peak gives a value for the nearest-neighbour bond length, \(r_1\), and similarly, the position of the second peak gives the next neighbour distance, \(r_2\). The RDF yields only a limited amount of information, restricted essentially to the local structure around a given atom, i.e. bond lengths and bond angles. A knowledge of both bond length \(r_1\) and \(r_2\) yield the value of the bond angle \(\theta\) given by [27]:

\[
\theta = 2 \cdot \sin^{-1}\left(\frac{r_2}{2r_1}\right)
\]

Raman spectra of Ga\textsubscript{11.7}Ge\textsubscript{14.1}Te\textsubscript{74.2} samples were measured in the spectral range from 50 to 400 cm\(^{-1}\) at room temperature using a FRA-106 Raman attachment to Bruker IFS 88 applying the diode pump Nd:YAG laser of ca. 100 mW power and using the liquid nitrogen-cooled Ge detector with the resolution set to 1 cm\(^{-1}\) with 256 scans collected in each experiment.

II. Results and Discussion.

Radial Distribution Functions

The X-ray diffractograms of Ga\textsubscript{11.7}Ge\textsubscript{14.1}Te\textsubscript{74.2} alloys were used for calculation of radial distribution functions (RDF). RDF for studied alloys were obtained using program the RAD GTK+ [28] and are presented in Fig.1. The positions of the nearest-neighbour bond length \(r_1\) was 2.67 Å and \(r_2\) 4.27 Å. Similar \(r_1\) values were observed for Ga–Ge–Te glasses of other compositions. The values of the \(r_2/r_1\) ratio are close to 1.63 which is a typical value for a regular tetrahedron structure. EXAFS studies of a-GeTe [29] have shown that the Ge–Te distance is about 2.65 Å. For GaGeTe systems according to [30] Te–Ga bonds lengths were estimated as 2.67 Å. Similar values for Ga–Te bonds in GaTe (2.64–2.69 Å) were obtained in [31] and 2.67 Å for Ga\textsubscript{2}Te\textsubscript{5} in [15].

The bond angle values \(\theta\) = 106° calculated using eq. (5) for Ga\textsubscript{11.7}Ge\textsubscript{14.1}Te\textsubscript{74.2} alloys is in good agreement with other published data on GaGeTe alloys [32].
The Raman spectra of Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ samples can be explained in the terms of vibrational modes of Ga-Te and Ge-Te glasses [33-47]. The band at 88 cm$^{-1}$ in spectrum, is ascribed to GeTe vibration modes (bending modes of GeTe$_4$ (GaTe$_4$) tetrahedral) [34-39] or trigonal Te [40]. The band at 104 cm$^{-1}$ is characteristic to the trigonal Te [40]. Raman spectra for the annealed GeTe$_2$ films have two broad Raman bands from 110-135 cm$^{-1}$ and 135-145 cm$^{-1}$ with a maximum at 121 cm$^{-1}$ and 141 cm$^{-1}$ and an additional Raman band is noticed at 156 cm$^{-1}$ [33]. The Raman band obtained at 121 cm$^{-1}$ is assigned to A1 mode of GeTe$_4$ tetrahedral unit [41]. Raman data for bulk Ga−Te glasses [15] assign 109 cm$^{-1}$ band to symmetric Ga−Te breathing mode, 124–135 cm$^{-1}$ range - corner-sharing (CS) or edge-sharing (ES)GaTe$_4$ tetrahedrabreathing modes, 156 cm$^{-1}$ mode to Te−Te stretching modes. Raman spectra of the as-deposited and annealed Ge-Ga-Te films covering the region 100–200 cm$^{-1}$ consist of the following features: two main bands located at 1 to 25 cm$^{-1}$ (peak A) and 150 to 155 cm$^{-1}$ (peak B) and for annealed films peak C (141 cm$^{-1}$) [42]. Peak A can be assigned to stretching mode of [GeTe$_4$], eventually [GeTe$_4$] tetrahedral [42-43] or Te-Te vibrations bonds [36, 42, 44], peak C at 141 cm$^{-1}$ can be assigned to crystalline Te phase [42, 44-46].

In Raman spectra of GeTe films deposited at different temperatures [34] peaks at 88, 120, 139, and 160 cm$^{-1}$ are found. The broad peaks found at 88 and 160 cm$^{-1}$ are contributed by GeTe vibration modes [35-37]. Two distinct peaks were also observed at 120 and 139 cm$^{-1}$. It is known that crystalline Tellurium has strongest peaks at 120.4±0.5 and 140.7±0.5 cm$^{-1}$ [47]. The close proximity of the observed peaks suggests the presence of homopolar Te−Te bonds in the as-deposited GeTe films. In the Raman spectra of a-GeTe four main bands appear in the frequency range 50–250 cm$^{-1}$ (with approximate wavenumber positions of these bands are as follows: band A, ~83 cm$^{-1}$; band B, ~125 cm$^{-1}$; band C, ~162 cm$^{-1}$; band D, ~218 cm$^{-1}$) [35]. It was noted, that bands A, B and C are certainly combinations of at least two individual peaks each.

The frequency assignments of known structural units in glasses were used to perform the peak-fitting analyses and to compare the relative contribution of each structural unit in the spectrum of amorphous Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ alloys. It is necessary to note that a larger number of vibrational modes contribute to the overall spectrum. We allowed upon fitting the Raman spectra a maximum 2-3 cm$^{-1}$ displacement of the peak from the position of the peaks known from the reference literature. Tentative Gaussian decomposition of Raman spectra of Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ alloy is shown in Fig.2. Assignments of particular bands detected in Raman spectra of Ga$_{11.7}$Ge$_{14.1}$Te$_{74.2}$ samples are summarized in Table 1.
Table 1
Assignment of particular bands detected in Raman spectra of Ga-Ge-Te, Ge-Te, Ga-Te, Te samples.

<table>
<thead>
<tr>
<th>Wave number, cm⁻¹</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>88 cm⁻¹</td>
<td>GeTe vibration modes</td>
<td>[34-38]</td>
</tr>
<tr>
<td>92 cm⁻¹</td>
<td>Trigonal Te</td>
<td>[40]</td>
</tr>
<tr>
<td>104 cm⁻¹</td>
<td>bending modes of GeTe₄ (GaTe₄) tetrahedral</td>
<td>[38-39]</td>
</tr>
<tr>
<td>109 cm⁻¹</td>
<td>Te modes</td>
<td>[40]</td>
</tr>
<tr>
<td>115-125 cm⁻¹</td>
<td>symmetric Ga–Te breathing mode</td>
<td>[15]</td>
</tr>
<tr>
<td>120.4±0.5 cm⁻¹</td>
<td>(peak A) stretching mode of [GeTe₄], [GaTe₄] tetrahedral units</td>
<td>[42, 43]</td>
</tr>
<tr>
<td>121 cm⁻¹</td>
<td>Te–Te bonds</td>
<td>[47]</td>
</tr>
<tr>
<td>124–135 cm⁻¹</td>
<td>A1 mode of GeTe₄ tetrahedral unit</td>
<td>[41]</td>
</tr>
<tr>
<td>141 cm⁻¹</td>
<td>(peak C) crystalline Te phase</td>
<td>[42, 44-46]</td>
</tr>
<tr>
<td>140.7±0.5 cm⁻¹</td>
<td>Te–Te bonds</td>
<td>[47]</td>
</tr>
<tr>
<td>150-155 cm⁻¹</td>
<td>(peak B) Te-Te vibrations bonds</td>
<td>[36, 44]</td>
</tr>
<tr>
<td>156 cm⁻¹</td>
<td>(peak B) Te–Te stretching modes</td>
<td>[15]</td>
</tr>
<tr>
<td>160 cm⁻¹</td>
<td>(peak B) GeTe vibration modes</td>
<td>[34-37]</td>
</tr>
</tbody>
</table>

Conclusions

In the present paper the amorphous Ga₁₁₀Ge₁₄₁Te₇₄.2 alloys have been studied by X-ray diffraction and Raman spectroscopy. The experimental X-ray diffraction pattern were used for calculations of radial distribution functions which have given the positions of the nearest-neighbour bond length $r_1 = 2.67$ Å and $r_2 = 4.27$ Å. Obtained $r_1$ values are in good agreement with known from reference literature Ge-Te and Ga-Te bonds lengths, similar $r_1$ values were observed for Ga-Ge-Te glasses of other compositions. Observed bands in the Raman spectra of Ga₁₁₀Ge₁₄₁Te₇₄.2 samples show that such glass contain different nanophases and can be explained in the terms of vibrational modes of Ga-Te and Ge-Te glasses and films. Investigations of compositional dependencies of characteristic constituent Raman bands intensities whose concentration is changing with the composition are necessary in order to obtained better assignment of Raman bands.

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У цій роботі аморфні сплави Ga_{11.7}Ge_{14.1}Te_{74.2} досліджено методами рентгенівської дифракції та раманівської спектроскопії. Експериментальні рентгенівські дифрактограми були використані для розрахунку функцій радіального розподілу, які вказують положення довжин зв'язку найближчого сусіда $r_1 = 2.67$ Å і довжин зв'язку другого сусіда $r_2 = 4.27$ Å. Подібні значення $r_1$ спостерігаються для стекол Ga-Ge-Te інших складів. Смуги, які спостерігаються в спектрах комбінаційного розсіювання зразків Ga_{11.7}Ge_{14.1}Te_{74.2} показують, що це скло містить різні нанофази, що можна пояснити за допомогою режимів коливань, властивих склам Ga, Ge і Te інших складів.

**Ключові слова:** халькогенідні стекла; рентгенісоструктурний аналіз; функція радіального розподілу; Раманівська спектроскопія; нанофази.