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Boson peak and nanostructure of chalcogenide glass-like semiconductors

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ABSTRACT

The structural features of As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$, $As_{33.3}Se_{33.3}S_{33.4}$, $As_{33.3}Se_{33.3}Te_{33.4}$ chalcogenide glasses have been studied by Raman spectroscopy in low-energy region. The results are explained in view of nanostructure of samples, i.e. by presence of heterogeneity in samples at the nanometer scale and with change their size depending on the modification of the chemical composition.

KEYWORDS

Chalcogenide; glass; amorphous semiconductors; Raman scattering; Boson peak

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1. Introduction

In amorphous semiconductors exists the short-range order with small deviations which are characteristic of their crystalline analogues. It leads to disappearance of strict periodicity in atomic arrangement of amorphous materials, i.e. the lack of the long-range order. However, in amorphous semiconductors and chalcogenide glasses also have certain regularity in the arrangement of atoms, the inter-atomic correlations at distances greater than the radius of the second coordination sphere, i.e. outside the short-range order. It's called region of the medium-range order. Nano-heterogeneities in which plays role the medium-range order is as an elementary cell in crystal lattice. Mentioned regions play a significant role in peculiarity formation of vibrational properties mechanisms of electron excitation relaxation and processes of electric charge transfer [1]. Therefore investigation of amorphous and glass-like material structures in nano-metric scale, elucidation of their modification methods allows the electron properties to be controlled and extend application fields. The present paper is devoted to the study of structural features of As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$, $As_{33}Se_{33.3}S_{33.4}$ and $As_{33}Se_{33.3}Te_{33.4}$ compositions using the method of Raman spectroscopy. The advantage of given method by investigating the chalcogenide glasses is that unlike the crystals in given materials is violated of selection rules and all the oscillation modes contributes for the light scattering. Therefore in mentioned materials RS investigations give more information on oscillation spectra than on crystals. Similar investigations in low-energy range allow for obtaining the information of oscillation state density in acoustic frequency ranges. RS spectra of amorphous and glass-like materials are differed from the crystals that in low-frequency range ($\omega<100$ cm^{-1}) the wide band with maximum called boson peak (BP) at the frequency $\omega=(1/3\text{-}1/5)\ \omega_D$ (ω_D -is Debye frequency) has been observed. BP appearance is related to the excessive density of acoustic vibrational states localized in material heterogeneities [1]. According to [2] the structural heterogeneities with characteristic size D must bring about the particular modification of Debye vibrational state density within the frequency range of BP maximum ($\omega\approx\vartheta/D$ where ϑ is the sound velocity). Position of BP in RS spectrum and its intensity depend on the heterogeneity sizes and the degree of disorder. Analysis of reference data shows that there has been lack of perfect theory of BP nature and the influence of chemical composition and impurities hasn't been studied enough. So the pursuance of investigations in this lead promotes to amass new experimental data and enables some considerations about the interrelation of nanostructure with the peculiarities of RS low-frequency spectra to be stated.

2. Experimental

Synthesis of As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$, $As_{33.3}Se_{33.3}S_{33.4}$ and $As_{33.3}Se_{33.3}Te_{33.4}$ materials has been carried out in the following sequence: high pure elementary substances in appropriate atomic percentages are filled into quartz ampoules. After evacuating the air up to pressure 10^{-4} mm Hg for 3 hours they are heated up to 900-950^{0}C and kept for about 12 hours at this temperature. To obtain homogeneous samples synthesis has been conducted in the rotary furnace but, cooling has been made out in the off furnace. The films 10 mkm with thickness used in the investigations have been obtained by thermal evaporation with the rate 0.4-0.5 mkm/min on the glass substrate in vacuum under the pressure 10^{-4} mm Hg. Raman spectra has been investigated on three-dimensional Confocal Laser Micro-spectrograph (Tubitak, Turkey). The excitation has been carried out by He-Ne laser 25 mWt with radiation power and wavelength 632.8 nm. Cross-section radius of falling laser beam on the film is equal to 1 mkm. Exposure time is within 1-90 sec.

3. Results and discussion

Using experimental data from the Raman scattering the reduced intensity (I_R) has been the calculated by the following formula [3-5].

$$I_R=I_m/\{\omega[N(\omega)+1]\} \qquad (1)$$

Where, $N(\omega)=1/[\exp(h\omega/kT-1)]$ is the Bose-Einstein's, $h\omega$-vibrational energy [17-18], I_m is the measured intensity of RS. RS spectra for reduced intensity of As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$, $As_{33.3}Se_{33.3}S_{33.4}$ and $As_{33.3}Se_{33.3}Te_{33.4}$ materials presented in Fig.1

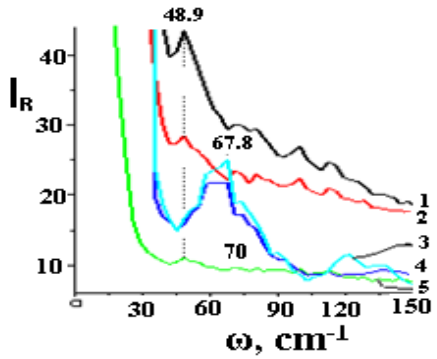

Fig.1. RS spectra for reduced intensity of 1-As_2Se_3, 2-$As_{40}Se_{30}S_{30}$, 3-$As_{33.3}Se_{33.3}Te_{33.4}$ 4-$As_{33.3}Se_{33.3}S_{33.4}$, and 5-$As_{40}Se_{30}Te_{30}$ films 10 mkm in thickness

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According to [6] Raman spectra presented as Fig.1 are identical with shape of the density of vibrational state. As it is seen from Fig.1 spectra of all compositions in frequency ranges $\omega<100$ cm^{-1} show the broad band with maximum of BP intensity, form, position in the spectrum for various chemical compositions are different from each other. BP of non-stoichiometric compositions in width, intensity and also in frequency appropriate to the maximum is considerably higher than for stoichiometric compositions. Such changes in the low-energy Raman spectrum show changes in the size and heterogeneity of concentrations and also of the degree of disorder. In all stoichiometric compositions As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$ BP frequencies coincide (48.5 cm^{-1}) and are rather less than BP frequencies (67.8 cm^{-1}) for non-stoichiometric compositions $As_{33.3}Se_{33.3}S_{33.4}$ and $As_{33.3}Se_{33.3}Te_{33.4}$. It indicates that the sizes of medium-range order in the first case are bigger than in the second case. It is known that for the chalcogenide semiconductors model of chemically ordered network-CON is quite satisfactory. In this model satisfies the rule of 8-N and indicates that strong heterepolar bonds are preferred rather than homopolar. On the other hand, within this model the concentration of homopolar bonds stoichiometric composition does not exceed 1% and they may be considered as structural defects [7]. From these considerations, it turns out that according to the model CON stoichiometric compositions will have a more ordered structure. As a result, sizes of ordered regions will increase. From the comparison of BP stoichiometric compositions (As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$) may notice that more weakly expressed BP in intensity and width are shown in films $As_{40}Se_{30}S_{30}$. It is explained by the fact that, sulfur atoms is high chemically active than selenium and tellurium and participation contributes to the improvement of network-chain structure of the amorphous matrix. If the concentration of chalcogen atoms exceeds the value corresponding to the stoichiometric composition then increases the percentage of homopolar bonds between chalcogen atoms. It leads to formation separate fragments of chalcogen atoms which increase disorder degree and decrease heterogeneity sizes in medium order. In this case one should take into consideration that the chalcogen excess (Se and S) facilitates the appearance of additional degrees of freedom that is also accompanied by growth of disorder degree. As it is seen from Fig.1 BP in RS spectrum of $As_{33,3}Se_{33,3}S_{33,4}$ and $As_{33,3}Se_{33,3}Te_{33,4}$ non-stoichiometric compositions involve several narrow maxima which overlapping forms rather wide peak. It is related to the fact that heterogeneities of various sizes have been existed in materials. As it is known the existence of intrinsic charged defects (D^+ and D^-) [8] appearing due to the breakage of chemical bond is characteristic for CGS (in this case, discontinuity of the chain molecules consisting of chalcogen atoms and covalent bonds between of arsenic and chalcogen atoms). Random distribution of mentioned centers causes fluctuation of electrostatic potential and increase of disorder degree [9]. As it is seen from Fig.1 intensity of BP in $As_{33.3}Se_{33.3}Te_{33.3}$ is more than the $As_{33.3}Se_{33.3}S_{33.4}$ which indicates the high degree of heterogeneity in the first composition. It appears to be due to the fact that presence of Te promotes the decomposition of chain molecules and shortening polymer chains [10] that is why the number of broken bonds and concentration of charged defects have been increased. The latter has been proved by the investigation of charge carrier drift mobility [11]. Studies have been shown that for the investigated glassy materials low-energy excess vibrational density of states associated by nano-inhomogeneities and their geometric dimensions satisfactorily are described with lognormal function presented in [3,6]. In Fig.2 there have been shown the reduced relative Raman spectra of the investigated compounds CGS in the low energy region. Where, I_{Rmax} is intensity at the maximum of boson peak, but ω_B is the frequency corresponding to the same maximum.

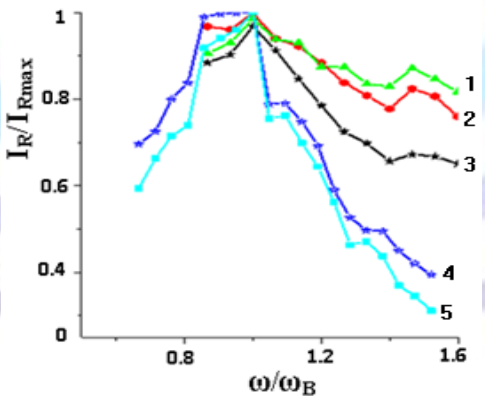

Fig.2 the reduced Raman spectra of 1-$As_{40}Se_{30}Te_{30}$, 2-$As_{40}Se_{30}S_{30}$ 3-As_2Se_3, 4-$As_{33.3}Se_{33.3}S_{33.4}$ and 5-$As_{33.3}Se_{33.3}Te_{33.4}$ films 10 mkm in thickness in low-energy region normalized along the abscissa on ω_B (ω/ω_B) and along the ordinate on I_{Rmax} (I_R/I_{Rmax}).

These graphs clearly show that the chemical composition and the deviation from stoichiometry different influence on the vibrational properties of the materials studied. On the other hand, it is clear that for non-stoichiometric compositions appear bright boson peak and the amplitude is high enough, which again confirms that the non-stoichiometric compositions are more disordered.

4. Conclusion

Raman spectra of all CGS compositions have broad the maximum BP which the intensity, shape and position for different chemical compositions are distinguished from one another. More noticeable difference is observed among the samples of stoichiometric and non-stoichiometric compositions. In all As_2Se_3, $As_{40}Se_{30}S_{30}$, $As_{40}Se_{30}Te_{30}$ stoichiometric compositions BP frequencies are same (48.9cm^{-1}) and significantly less than BP frequencies (67.8cm^{-1}) of $As_{33.3}Se_{33.3}S_{33.4}$ and $As_{33.3}Se_{33.3}Te_{33.4}$ non-stoichiometric compositions. It indicates small sizes of medium order in the first case comparing with the second one. Among of stoichiometric compositions the most slightly expressed BP is observed in $As_{40}Se_{30}S_{30}$ composition. This fact is explained by high chemical activity of sulfur atoms which contributes to the creation of network-chain structure in the amorphous matrix. BP in RS spectrum of $As_{33.3}Se_{33.3}S_{33.4}$ and $As_{33.3}Se_{33.3}Te_{33.4}$ non-stoichiometric compositions involves several narrow maxima which overlap forms a rather wide peak. It's connected with arising some molecular fragments and degrees addition freedom due to chalcogenide atoms, in the result of these reduces the size of in-homogeneities and creates a new structural fragments. Of all CGS compositions BP for $As_{33.3}Se_{33.3}Te_{33.4}$ has the highest intensity. It is attributed to the fact that the presence of tellurium atoms contributes to destruction of chain molecules which increases the number of broken bonds, the concentration of charged defects and degree disorder.

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