RAMAN SPECTRA OF $\text{As}_x\text{Se}_{100-x}$, $\text{As}_{40}\text{Se}_{60}$ AND $\text{As}_{50}\text{Se}_{50}$ GLASSES DOPED WITH METALS

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Abstract

The Raman spectra of chalcogenide glasses in the system $\text{As}_x\text{Se}_{100-x}$, $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{50}\text{Se}_{50}$ doped with metals (Bi, Ge, Cd, Ag, Sn, Mn, Dy and Sm) were investigated for characterizing the structure in the short-range order. The Raman spectra of $\text{As}_x\text{Se}_{100-x}$ ($x<40$) consist of one broad band located in the 200-300 cm$^{-1}$ region, while for $x\geq 50$ some narrow and strong bands in the region 100-200 cm$^{-1}$ appear, and which indicate higher degree of the structure ordering. Raman spectra of $\text{As}_{50}\text{Se}_{50}$ doped with 0.1 at. %Me are more complicated. Two vibrational modes at 237 and 252 cm$^{-1}$ correspond to $\underline{\text{Se}}\text{Se} \underline{\text{Se}}\text{Se}$ chains and of Se$_8$ rings. For $\text{As}_{50}\text{Se}_{50}+7.5$ at.% Sn a strong band located at 186 cm$^{-1}$ gives evidence of formation of the new Me-based structural units, such as tetrahedral Sn(Se$_{1/2}$)$_4$ and quasi-octahedral SnSe. The experimental results are discussed in frame of the molecular structure model of chalcogenide glasses and are compared with the existing data from literature.

1. Introduction

Chalcogenide glasses are important for a wide range of technical applications, such as infrared optical elements, acousto-optic and all-optical switching devices, holography recording media etc. Optical investigation such as IR reflectance and Raman scattering are useful in obtaining information on the local structure of the disordered material, especially when the composition is varied [1,2]. Recently measurements of Raman spectra in binary arsenic chalcogenide glasses ($\text{As}_x\text{S}_{100-x}$) have been established a phase separation and a clustering of the amorphous material [3]. Using Raman scattering technique the phase separation in the network glass of the chalcogenide systems of $\text{As}_x\text{S}_{100-x}$ and $\text{As}_x\text{Se}_{100-x}$ was established [4,5]. In our previous work [6] it was shown that doping of $\text{As}_2\text{S}_3$ with 0.5 at.% Mn leads to the appearance of a number of narrow bands in Raman spectra located in the frequency region 130 and 220 cm$^{-1}$, and which are associated with the formation of new sulphur-containing structural units, like the MnS clusters.

In this paper, the experimental results on Raman spectra of chalcogenide glasses in the system $\text{As}_x\text{Se}_{100-x}$, $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{50}\text{Se}_{50}$ doped with metals (Bi, Ge, Cd, Ag, Sn, Mn, Dy and Sm) are presented. The obtaining results are discussed in frame of the molecular structure model of chalcogenide glasses and are compared with the existing data from literature.
2. Experimental
Chalcogenide glasses $\text{As}_x\text{Se}_{100-x}$ ($x=0, 5, 10, 40, 50, 60$) were synthesised using elements of 6N (As, Se) purity using the conventional melting in evacuated ($p\sim10^{-5}$ Torr) and sealed silica ampoules at $800\div850$ °C for 8 hours followed by quenching in cold water. The bulk glasses were cut into plates of 2±3 mm in thickness using a low speed diamond saw, and then polished to yield samples with high quality flat surfaces suitable for optical measurements. Raman spectra were measured on a Fourier-transform spectrometer (Bruker RFS100) in a back-scattering geometry and resolution of 2 cm$^{-1}$. The 1064.4 nm line of a Nd-Y laser was used for excitation and this leads to Raman spectra free of luminescence background.

3. Results and discussion
3.1. Raman spectra of $\text{As}_x\text{Se}_{100-x}$ Glasses
The Raman spectra of $\text{As}_x\text{Se}_{100-x}$ bulk glasses are presented In Fig.1 and Fig.2. For the elementary selenium and for selenium rich samples there are distinct two very sharp bands located at 236 and 253 cm$^{-1}$ and which correspond to $\text{Se}--\text{Se}$—$\text{Se}$—$\text{Se}$— chains and of Se$_8$ rings. According to [7] the amorphous selenium is composed of a mixture of chains ($\text{Se}_n$) and rings ($\text{Se}_8$) with the covalence bonding of the atoms in the rings and Van der Waals weak bonding between the chains. The average inter-atomic distance is about 2.37 Å.

Increasing the concentration of arsenic in $\text{As}_x\text{Se}_{100-x}$ bulk glasses changes the Raman spectra (Fig.2). Besides the broad band characteristic of $\text{As}_{40}\text{Se}_{60}$ glass located at 225 cm$^{-1}$ and which is attributed to stretching vibrational mode of AsSe$_{3/2}$ pyramids, for the concentrations of arsenic more than 40 at.% As new absorption bands appear in the Raman spectra. The new bands...
with maximum at about 204 and 237 cm\(^{-1}\) arise from the presence of As\(_4\)Se\(_4\) (204 cm\(^{-1}\)) and As\(_4\)Se\(_3\) (237 cm\(^{-1}\)) structural units [2].

The new narrow bands situated in the 100-200 cm\(^{-1}\) region confirm the presence of structural units containing As—As bonds. The presence of —Se—Se—Se— chains and of Se\(_8\) rings in the structure of the glass is confirmed by the Raman bands located at 237 and 252 cm\(^{-1}\). The narrow band at 280 cm\(^{-1}\) which appears as a shoulder in the Raman spectra of As\(_{60}\)Se\(_{40}\) sample according to [2] is due to the presence of —Se—Se— bridges between AsSe\(_3\) pyramidal units and As\(_4\)Se\(_4\) or As\(_4\)Se\(_3\) cages.

3.2. Raman spectra of As\(_{50}\)Se\(_{50}\) and As\(_{40}\)Se\(_{60}\) doped with metals and rare-earth ions

The Raman spectra of As\(_{50}\)Se\(_{50}\) glasses doped with metals of the I-V groups of the periodic table of elements (Ag, Cd, Ge, Sn, Bi) are presented in Fig.3. It is seen that the more intensively absorption band located at about 220 cm\(^{-1}\), and in As\(_{40}\)Se\(_{60}\) glass attributed to stretching vibrational mode of AsSe\(_3\) pyramids is presented in all the samples. Besides, the bands at 237, 252 and 282 cm\(^{-1}\) due to the presence of —Se—Se—Se— chains, Se\(_8\) rings and of —Se—Se— bridges between AsSe\(_3\) pyramidal units and As\(_4\)Se\(_4\) or As\(_4\)Se\(_3\) cages also are presented.

A small concentrations of metals introduced in As\(_{50}\)Se\(_{50}\) glass did not change essentially the Raman spectra. Only at higher concentrations of metal impurities (7.5 at.% Sn, curve 7) an intensive band located at 186 cm\(^{-1}\) appears in the Raman spectra. This band can be attributed to new tetrahedral structural units (Sn(Se\(_{1/2}\))\(_4\)) which appear at such concentrations of tin added into
As$_{50}$Se$_{50}$ glass. Introduction of Sn additives in As$_{50}$Se$_{50}$ base glass promotes growth of Sn(Se$_{1/2}$)$_4$ structural units and leads to the base glass becoming As-rich by forming of monomeric As$_4$Se$_4$ cages based on Realgar structure [8].

The Raman spectra of As$_{40}$Se$_{60}$ glasses doped with different concentrations of rare-earth ions (0.1 and 0.5 at.% of Dy and Sm) and transition metal Mn are presented in Fig. 4. As in the case of As$_2$S$_3$, doping of base glass with small concentrations of rare-earth ions did not change the Raman spectra [6]. In our case the exception is only for As$_{40}$Se$_{60}$+0.5 at.% Dy, for which in the Raman spectra an additional band located around 185 cm$^{-1}$ is observed. This band, according to X-ray diffraction experiments, electrical and photoelectrical measurements carried out on As$_{40}$Se$_{60}$ glass doped with rare-earth ions can be attributed to the appearance of new structural units like DySe or DySe$_2$ [9]. For the glass As$_{40}$Se$_{60}$ doped with 0.1 at.% Dy a broad fluorescence band between 900-300 cm$^{-1}$ with the maximum at 600 cm$^{-1}$ was observed. These results suggest that rare-earth doped chalcogenide glasses, especially optical fibers may be used as Raman amplifiers with Raman gain with a value of 340 times greater than the coefficient of silica [10,11].

4. Summary

The Raman spectra of chalcogenide glasses in the system As$_x$Se$_{100-x}$, As$_{50}$Se$_{50}$ doped with metals (Bi, Ge, Cd, Ag, Sn), and As$_{40}$Se$_{60}$ doped with rare-earth ions (Dy and Sm) and transition metal Mn were investigated. The experimental results are compared with the published data and discussed in frame of the molecular structure model of chalcogenide glasses.

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References