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MICRO-RAMAN SPECTRA OF BULK $Ge_xAs_xSe_{1-2x}$ CHALCOGENIDE GLASSES

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Abstract. In this work are reported the Micro-Raman spectra of $Ge_xAs_xSe_{1-2x}$ (x = 0.05÷0.30). The Micro-Raman spectra consist of three main peaks located around $\nu = 193$ cm^{-1}, $\nu = 213$ cm^{-1}, and $\nu = 255$ cm^{-1}. The peaks around $\nu = 193$ cm^{-1} and $\nu = 213$ cm^{-1} could be attributed to the vibration of GeSe bonds. The presence of the Raman peak at $\nu = 255$ cm^{-1} is due to the bond-stretching vibration of the disordered Se chains and rings. With the increase of the Ge concentration this peak shifts to a higher wavenumber due to the shortening of Se chains. The peak around $\nu = 300$ cm^{-1} is characteristic to Ge-Ge vibration mode. The Ge concentration slightly changes the shape of Micro-Raman spectra, mainly its ratio of the intensity.

Key words: chalcogenide glasses, Micro-Raman spectra, coordination number.

1. INTRODUCTION

In the last decade the interest in chalcogenide glasses has increased due to the fact that these materials are promising candidates for photonic and optoelectronic applications. Chalcogenide glasses $Ge_xAs_xSe_{1-2x}$ (with average coordination number $Z = 2.1.5÷2.90$), which contain elements of IV group of the Periodic Table, such as Ge, are important for a wide range of technical applications, such as infrared optical elements, acousto-optic and all-optical switching devices, holographic recording media, diffractive optics, photonic crystals, etc. [1, 2]. The Raman spectroscopy is an efficient method for obtaining information on the local structure of the disordered material, especially when the composition is varied. The glasses of the ternary system Ge-As-Se exhibit high chemical stability, good transmission in the IR region, high refractive index, excellent linear and non-linear properties, low phonon energy, and photo-induced effects [1–4]. Recently Ge-As-Se chalcogenide glasses are used as core materials for high-efficiency fiber amplifiers, Raman-parametric laser and wavelength converter [5, 6]. It was established that the physical properties of covalently-bonded glasses are determined by the mean coordination number Z (average number of covalent bonds per atom) [7]. Recently it was established, that in the disordered network of glassy system $Ge_xAs_xSe_{1-2x}$ there exist three distinct phases: *floppy, intermediate* and *stressed rigid,* and the dependence of physical properties of the average coordination number Z [8–10]. It was, demonstrated that some chalcogenide glasses from the $Ge_xAs_xSe_{1-2x}$ system, namely $Ge_{0.18}As_{0.18}Se_{0.64}$ system, which exists in the *stressed rigid* phase are stable to the action of temperature and can successfully by used as temperature sensors [11]. Besides that, according to Mössbauer spectroscopy of ^{119}Sn in the As_2Se_3:Sn_x glassy system [12] and X-ray photoelectron spectroscopy study [7], by introduction of the elements of IV group of the Periodic Table (Sn or Ge) in arsenic selenide base glass, new tetrahedral $Sn(Se_{1/2})_4$ and quasi-octahedral SnSe, and $GeSe_4$ structural units can be formed, respectively. Besides that, formation of metal-metal bonds and phase separation in the investigated $Ge_xAs_xSe_{1-2x}$ and $(As_4S_3Se_3)_{1-x}Sn_x$ glasses can explain some physical-chemical properties [7]. Optical investigations such as infrared reflectance and Raman spectroscopy are efficient tools for obtaining information on the local structure of the disordered material, especially when the composition is varied. The analysis of Raman spectra of binary chalcogenide glasses As_xS_{100-x} has been evidenced the presence of phase separation effects for $x \leq 25$ [13]. It was shown that doping of chalcogenide glasses with metal impurities shifts the main bands to the high frequency region and leads to the appearance of the additional vibration bands in the low frequency spectral range [14–16]. It was demonstrated that doping of As_2Se_3 with 0.5 at. %Dy leads to appearance in the Raman spectra of a new additional band located at $\nu = 185$ cm^{-1}, which can be attributed to the formation of new structural units like DySe/$DySe_2$ [17]. In addition, the Raman spectroscopy was successfully used for the investigation of the photo-induced transformation and structural changes during the heat treatment in amorphous As-based thin films. Some results on bulk glasses (optically polished plates) and amorphous thin films of $Ge_xAs_xSe_{1-2x}$ were reported [18]. It was shown that the Micro-Raman spectra of bulk glasses and thermally deposited amorphous $Ge_xAs_xSe_{1-2x}$ thin films consist of one main vibration band located at around $\nu = 246$ cm^{-1} for lower concentration of Ge and As, and is attributed to $(AsSe_{1/2})_3$ pyramidal units. With increasing of Ge and As concentrations this band shifts to higher frequency region up to $\nu = 236$ cm^{-1} for $x = 0.30$. The vibration band situated around $\nu = 205$ cm^{-1} is attributed to $Ge(Se_{1/2})_4$ tetrahedral units and increases in the intensity with increasing of Ge and As concentrations. Some shoulders in high frequency regions at $\nu = 365$–390 cm^{-1} and $\nu = 500$–530 cm^{-1}, caused by the presence of As-Se bands and Se-Se chains were also observed. Thermal properties, refractive index (n), optical band gap, Raman gain, and femtosecond laser damage of Ge-As-S glasses were also examined [19]. These results revealed that the n and density (ρ) of the studied glasses decreased as Ge concentration increased, whereas the band gap and glass transition temperature (Tg) increased. The Raman gain coefficients (g_R) of the samples were calculated on the basis of spontaneous Raman scattering spectra.

In the present work we report the experimental results of Raman spectra of powder samples of $Ge_xAs_xSe_{1-2x}$ glasses ($x = 0.05 \div 0.30$, $Z = 2.15 \div 2.90$).

2. EXPERIMENTAL

The bulk chalcogenide glasses $Ge_xAs_xSe_{1-2x}$ ($x = 0.05 \div 0.30$) were prepared from the elements of *6N* purity (Ge, As, Se,) by conventional melt quenching method. The starting components were mixed in quartz ampoules and then evacuated to pressure of $P \sim 10^{-5}$ torr, sealed and heated to temperature $T = 900$ °C at the rate of 1 °C/min. The quartz tubes were held at this temperature for 48 hours for the homogenization and then slowly quenched in the furnace.

The Raman studies of the CG samples were carried out at room temperature by Confocal Micro-Raman Spectroscopy, using a LabRam HR800 system. All the Raman spectra were generated by exposing the specimens during 300 s to a 0.03 mW, 532 nm wavelength green excitation laser and dispersing the emitted signal onto the CCD detector using a 600 lines/mm grating. The spectral resolution is around 0.6 cm^{-1}. The CG samples were optically examined using an Axio Observer Inverted Microscope (Zeiss). All the micrographs were captured in reflection mode at different magnifications (5×, 10×, 20×, and 50×).

3. RESULTS AND DISCUSSIONS

Figures 1 and 2 represent the Micro-Raman spectra of powder $Ge_{0.05}As_{0.05}Se_{0.90}$ glasses with the mean coordination number $Z = 2.15$. This composition with low concentration of Ge is situated in the floppy region [9]. The Micro-Raman spectra of glass powder consist of four main vibration bands located around $\nu = 193$ cm^{-1}, $\nu = 236$ cm^{-1}, $\nu = 255$ cm^{-1} and $\nu = 475$ cm^{-1}. The peak around $\nu = 193$ cm^{-1} could be attributed to the vibration of GeSe bonds (structural units $Ge(Se_{1/2})_4$). The peak $\nu = 236$ cm^{-1} shows modes of $As(Se_{1/2})_3$ pyramids [9,19]. The presence of the Raman peak at $\nu = 255$ cm^{-1} is due to the bond-stretching vibration of the disordered Se chains and rings. The peak located in high frequency region at $\nu = 475$ cm^{-1} can be caused by the presence of As-Se bands and Se-Se chains.

Figures 3 and 4 show the Micro-Raman spectra of powder $Ge_{0.14}As_{0.14}Se_{0.72}$ glasses with the mean coordination number $Z = 2.42$. The composition with concentration of 14 at. % of Ge is situated in the intermediate region. The Micro-Raman spectra of powder glasses consist of five main vibration band located around $\nu = 194$ cm^{-1}, $\nu = 230$ cm^{-1}, $\nu = 260$ cm^{-1} $\nu = 300$ cm^{-1}, and $\nu = 475$ cm^{-1}. As in the case of $Ge_{0.14}As_{0.14}Se_{0.72}$ glasses, the peak around $\nu = 194$ cm^{-1} has high intensity and could be attributed to the more amount of vibration of GeSe bonds (structural units $Ge(Se_{1/2})_4$). The peak $\nu = 230$ cm^{-1} shows modes of $As(Se_{1/2})_3$ pyramids.

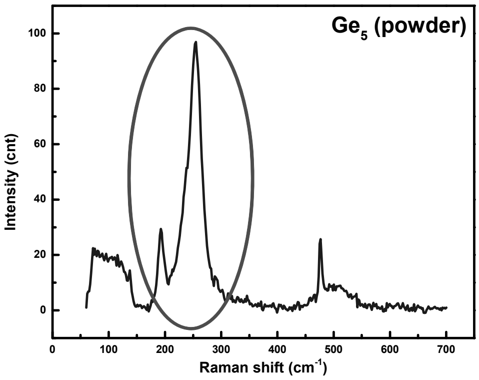

Fig. 1 – Raman spectra of $Ge_{0.05}As_{0.05}Se_{0.90}$ powder samples.

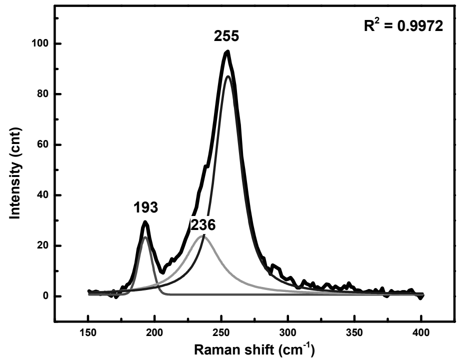

Fig. 2 – Deconvolution of the spectral region marked in Fig. 1.

The presence of the Raman peak at $\nu = 260$ cm^{-1} is due to the bond-stretching vibration of the disordered Se chains and rings. The peak located in high frequency region at $\nu = 475$ cm^{-1} can be caused by the presence of As-Se bands and Se-Se chains.

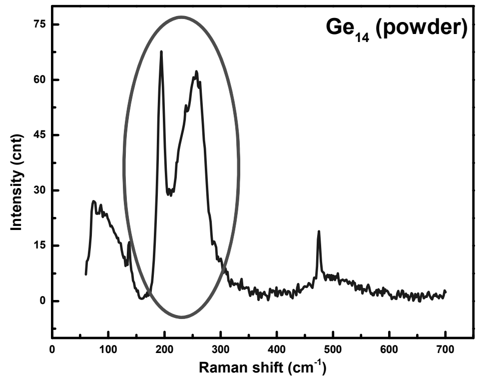

Fig. 3 – Raman spectra of $Ge_{0.14}As_{0.14}Se_{0.72}$ powder samples.

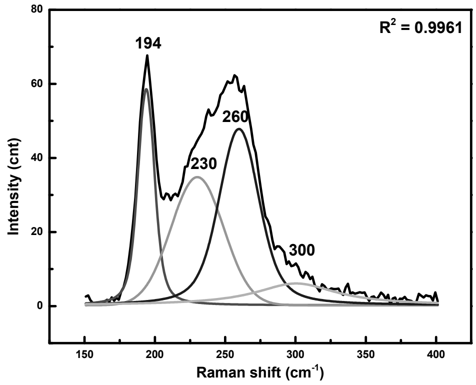

Fig. 4 – Deconvolution of the spectral region marked in Fig. 3.

Figures 5 and 6 represent the Micro-Raman spectra of powder $Ge_{0.30}As_{0.30}Se_{0.40}$ glasses with the mean coordination number $Z = 2.90$. This composition is situated in the stressed-rigid region. The Micro-Raman spectra of $Ge_{0.30}As_{0.30}Se_{0.40}$ powder glasses consist of one wide maximum centered at $\nu = 260$ cm^{-1}, and one less intensively peak in the low frequency region at ν=130 cm^{-1}, and two peaks in high frequency region at $\nu = 370$ cm^{-1} and $\nu = 475$ cm^{-1}. The Gaussian deconvolution of the main peak gives the positions of the vibration modes located at $\nu = 188$ cm^{-1}, $\nu = 213$ cm^{-1}, $\nu = 240$ cm^{-1} $\nu = 262$ cm^{-1}, and $\nu = 290$ cm^{-1}.

The Raman spectra of $Ge_xAs_xSe_{1-2x}$ powder samples show that with increasing of Ge concentration, the vibration mode $\nu = 194$ cm^{-1} described by the vibration of GeSe bonds becomes more intense, while the peak $\nu = 230$ cm^{-1} attributed to modes of $As(Se_{1/2})_3$ pyramids decreases in intensity. This is illustrated in Fig.7, where are summarized the Micro-Raman spectra for all samples of the $Ge_xAs_xSe_{1-2x}$ glass system. It seems that with increasing of Ge concentration up to $x = 0.18$ ($Z = 2.54$) the intensity of the mode $\nu = 195$ cm^{-1} attributed to the vibration of GeSe bonds increases. According to other measurements [20], the investigation of Raman spectra of Ge-Se compounds establishes the reduction in scattering strength of the chain mode of Se near $\nu = 260$ cm^{-1} and the enhancement in scattering strength of the vibration mode around $\nu = 216$ cm^{-1}, which indicate on some phase separation in these materials.

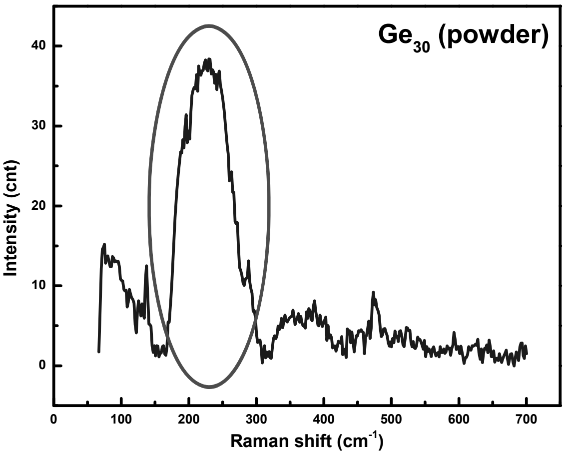

Fig. 5 – Raman spectra of $Ge_{0.30}As_{0.30}Se_{0.40}$ powder samples.

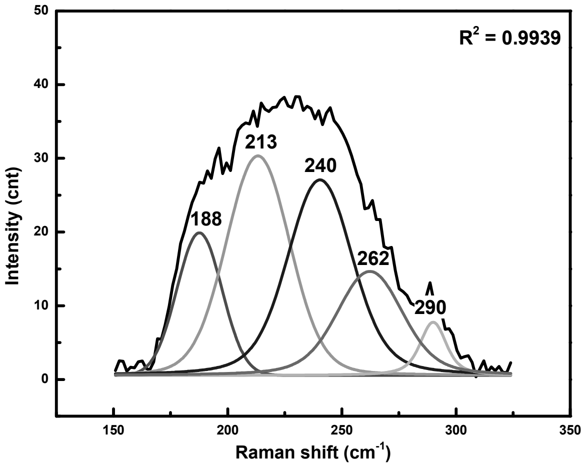

Fig. 6 – Deconvolution of the spectral region marked in Fig. 7.

Figure 8 represents the dependence of wavenumbers position of the vibration modes located around $\nu = 193$ cm^{-1}, $\nu = 236$ cm^{-1}, and $\nu = 255$ cm^{-1} on the mean coordination number Z. In Fig. 8 are also indicated the *floppy, intermediate*, and *stressed-rigid* phases, and these dependences for each regions. The same dependences of peak position of vibration modes on mean coordination number Z were obtained for the glassy system $Ge_xAs_ySe_{1-x-y}$ [21]. It was shown that the corner-sharing $\nu = 190$ cm^{-1} vibration mode of tetrahedral units $GeSe_{4/2}$ is almost constant when the mean coordination number Z is less than 2.5, but slightly decreases to low wavenumbers when $Z > 2.5$, as in our case (Fig. 8, black curve). The $\nu = 236$ cm^{-1} $AsSe_{3/2}$ pyramidal and $\nu = 255$ cm^{-1} of Se-Se vibration modes can be seen in the range of the mean coordination number Z. For the values of the mean coordination number $Z \geq 2.6$ all vibration modes mix and transform into a broad band with the extinction between 160 and 300 cm^{-1}. The disappearance of vibration modes at $\nu = 255$ cm^{-1} means the complete replacement of Se by Ge and As in $Ge_xAs_xSe_{1-2x}$ chalcogenide glasses. The Full Width at Half Maximum (FWHM) of the vibration band located at $\nu = 193$ cm^{-1} increases with increasing of Ge concentration from 14 cm^{-1} for $x = 0.05$ up to 27 cm^{-1} for $x = 0.30$.

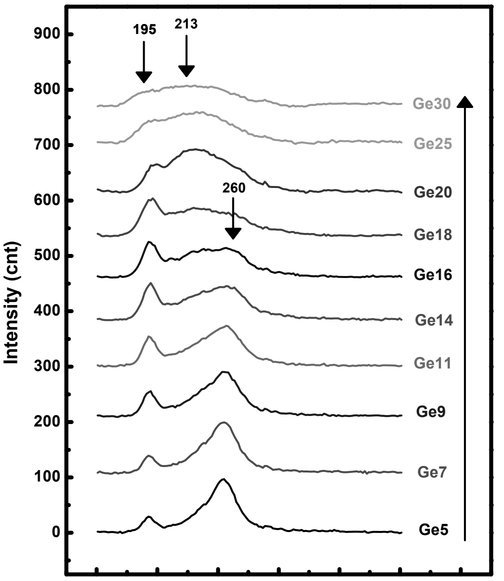

Fig. 7 – Raman spectra of $Ge_xAs_xSe_{1-2x}$ powder samples. The content of Ge is indicated in percenters.

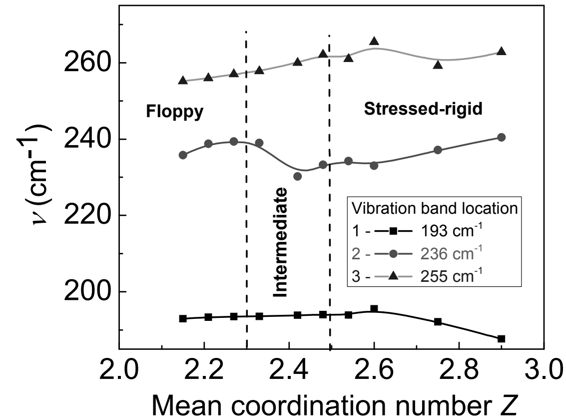

Fig. 8 – Dependence of the position of the peaks of main vibration bands ($\nu = 193$ cm^{-1}, $\nu = 213$ cm^{-1}, and $\nu = 255$ cm^{-1}) in the Raman spectra of $Ge_xAs_xSe_{1-2x}$ powder samples.

The area of $Ge_xAs_xSe_{1-2x}$ chalcogenide glass samples where the Micro-Raman spectrum was recorded was optically examined using an Axio Observer Inverted Microscope (Zeiss). The micrographs were captured in reflection mode at different magnifications (5×, 10×, 20×, and 50×). Figure 9 shows fragments of the morphology of the examined portions of some investigated glass samples.

The pictures in Fig. 9 clearly show fragments of phase separation in the examined portions of bulk $Ge_xAs_xSe_{1-2x}$ glass samples.

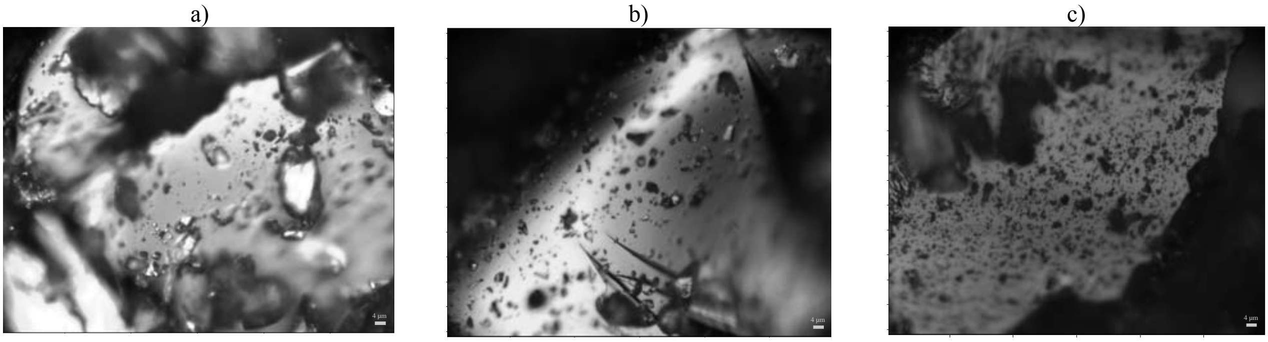

Fig. 9 – a) The area where the Raman spectrum of $Ge_xAs_xSe_{1-2x}$ samples was recorded (magnification – 50×). Composition x: $x = 0.05$; b) $x = 0.16$ (b); c) $x = 0.30$.

4. SUMMARY

Micro-Raman spectra were investigated for characterization of bulk (powder) glasses of $Ge_xAs_xSe_{1-2x}$ ($x = 0.05 \div 0.30$) system with average coordination number $Z = 2.15 \div 2.90$. It was shown that the Micro-Raman spectra consist of three main peaks located around $\nu = 193$ cm^{-1}, $\nu = 213$ cm^{-1}, and $\nu = 255$ cm^{-1}. The peaks around $\nu = 193$ cm^{-1} and $\nu = 213$ cm^{-1} could be attributed to the vibration of Ge-Se bonds. The presence of the Raman peak at $\nu = 255$ cm^{-1} is due to the bond-stretching vibration of the disordered Se chains and rings. It was found that the vibration features of the Micro-Raman spectra changes with increasing of the mean coordination number Z. With the increase of the Ge concentration, the vibration peak $\nu = 255$ cm^{-1} shifts to a higher wavenumbers due to the shortening of Se chains. The Ge concentration in the glassy system also changes the intensity of the vibration modes in the Micro-Raman spectra.

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