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SPECTROSCOPIC STUDIES g-GeSe$_2$ -MATERIAL FOR TELECOMMUNICATION: THEORY AND EXPERIMENT

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1. Introduction

Nowadays a one of the most debated issues in glass science is the origin and the extent of chemical order in disordered networks [1]. In the classic Ge-Se system an addition of Ge to glassy Se imposes an additional length scale on the chemical ordering, associated with Ge–Ge correlations, which is manifested by a so called first sharp diffraction peak (FSDP) that reaches its maximum height at the GeSe$_2$ composition. There is a consensus that the position and width of this feature derive from middle range order [2,3]. This is defined as chemical order extending beyond the nearest-and next-nearest neighbor distances. The FSDP was observed by X-ray and neutron diffraction studies not only for chalcogenide glasses but for oxide, silicate, germanate, borate glasses too [1]. The silica glass network exhibits a broad ring distribution and five-, six-, seven- and eight-membered rings are the most abundant sizes and is made up of a connection of SiO$_4$ tetrahedra sharing oxygen atoms at the corners. Three- and four-membered rings are also found, but none of the known crystalline polymorphs of SiO$_2$ contain such small rings. They were assigned as characteristic of the inorganic glasses, glass-forming liquids and amorphizing solids only. The concentration of these "defect" rings increases on increasing the

cooling rate or the fictive temperature of the glass and also as a result of pressure-induced amorphization of quartz [1]. Except of Ge-Se bonds there was found signatures of the "defects" or homopolar bonds in g-GeSe$_2$. Percentages of Ge and Se homopolar bonds were obtained by using the method of isotopic substitution in neutron diffraction [4]. The benefits of molecular dynamic studies was finding of rings distribution in g- GeSe$_2$ up to 12-fold rings. Ordering on a range extending up to 60 Å has been discovered for several network forming glasses, including a-GeSe$_2$.

The occurrence of a departure from chemical order in GeSe$_2$ has been long-time controversial. We report here the results of extended spectroscopical studies of Ge$_n$Se$_m$ nanoclusters in order to elucidate the medium range structures of g-GeSe$_2$.

2. Experimental and theoretical details

2.1. Sample preparation and experimental details

The bulk germanium diselenide glasses were prepared by the conventional melt-quenching route from a mixture of high purity 99.999 % Ge and Se precursors in evacuated and sealed quartz ampoules. First the ampoules was heated with the rate of 2-3 K/min and kept at 873-900 K for 18-20 h. Then with the rate of 1-2 K/min the temperature was increased and kept constant at 1070 K during 20-30 h. All ingots were quenched in ice water (275-277 K).

High resolution Raman spectra of GeSe$_2$ glasses were measured using a Bruker MULTIRAM FT-Raman spectrometer and a Jasco NRS 3100 Raman spectrometer (1200 lines/mm grating) equipped with CCD detector. Near-IR Nd:YAG ($\lambda_{ex.1} = 1064$ nm, $E_{ex.1} = 1.17$ eV) and a diode ($\lambda_{ex.2} = 785$ nm, $E_{ex.2} = 1.58$ eV) lasers were used as excitation sources. All measurements were performed at room temperature in back-scattering geometry. To yield peak position and intensity the experimental Raman spectra were fitted using a Gauss type functions with prior subtraction of a background and fitting was undertaken until reproducible and converged results were obtained with squared correlations better than r$^2 \sim 0.99998$. The second derivative profile gives valuable information about the position of the

bands and band widths. Thus for the band fitting procedure, the second derivative of the absorption spectrum was used as a guide.

2.2. Modelling and calculations

The first stage of our modelling of the local amorphous structures is based on the structure of corresponding crystals. The $GeSe_4$ tetrahedron in the structure of low temperature (LT) α-form of $GeSe_2$ is mutually connected by their corners and forms the three-dimensional (3D) crystal network. However high temperature (HT) β-form generates two-dimensional (2D) network built up by combination of $GeSe_4$ tetrahedra with corner- and edge-sharing geometries [5]. In this network the parallel endless chains of corner-sharing tetrahedra are linked together by edge-sharing tetrahedra (Figure 1). Thus, the local SRO structure representing α-$GeSe_2$ is corner-sharing tetrahedra and the local SRO structures representing β-form of $GeSe_2$ crystal are corner- and edge-sharing tetrahedra (models I and II). The larger cluster which can be found in the crystal structure of $GeSe_2$ is a six-member ring consisting three $GeSe_4$ tetrahedra connected by their corners (III). Models IV and V represents two six-member rings selected from two directions of 2D network of β-$GeSe_2$ crystal. In the first case the rings are connected by common Ge while in the other model rings are connected via the edge-sharing block. The largest cluster obtained from the β-$GeSe_2$ monolayer (VI) consists of a big 16-member ring.

The *ab initio* methods are very useful to analyse different "defect" configurations. Here we represent few possible models with homopolar Ge-Ge (VII-VIII) and Se-Se (IX-XI) bonds. The simplest model of Ge-Ge bond can be seen in the hypothetical cluster, so called ethane-like geometry (VII). Similar way homopolar Se-Se bond can be realized as a linkage between two $GeSe_4$ tetrahedra (IX). There is also possibility of Se-Se bond formation on the edge of the so-called outrigger raft structure (model XI represents the part of this structure). Recent investigation of the structure of Ge_4Se_9 crystal show that there is another possibility to form Se-Se bond through $Ge_2Se_{3+4/2}$ cluster (X) which substitute edge-sharing blocks in 2D crystalline network of β-$GeSe_2$ [6].
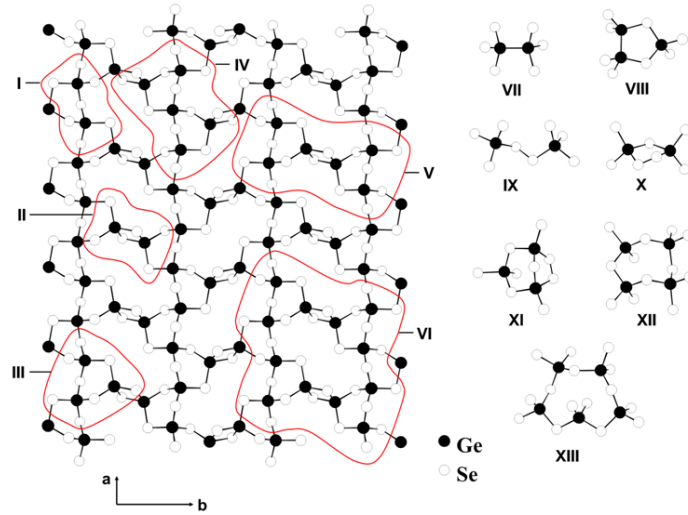
Figure 1. The crystal structure of β-GeSe$_2$ monolayer [5] with the selected Ge$_n$Se$_m$ cluster models (I-VI) (left) and the "defect" Ge$_n$Se$_m$ cluster geometries with homopolar Ge-Ge (VII-VIII) and Se-Se (IX-XI) bonds together with the larger eight- and ten- member rings (right). Saturating hydrogen atoms and corresponding bonds are not shown for clarity.

This cluster together with the model VIII represents five-member rings with incorporated Se-Se and Ge-Ge bonds, respectively. *Ab initio* MD simulations show that in addition to six- and four-member rings the other types of *i*-member rings ($i = 3$-12) in the structure of liquid and glassy GeSe$_2$ can be seen [5]. Therefore in the present study we extend our analysis to larger eight and ten odd-member rings (XII and XIII).

3. Results and discussion

3.1. Experimental Raman spectra of *g*-GeSe$_2$

Figure 2 shows the measured micro-Raman ($E_{ex.2} = 1.58$ eV) spectra of *g*-GeSe$_2$. This spectra and FT-Raman ($E_{ex.1} = 1.17$ eV) spectra (not shown) demonstrates differences only in the low frequency spectral region (< 150 cm^{-1}) caused by the notch filters used. Both spectra in the 150-350 cm^{-1} region show no structural changes that indicates quasi crystallization. In addition to two main bands at ~ 202 and ~ 218 cm^{-1} the bands at ~ 179 and ~ 245 cm^{-1} and two complex broad bands centered at ~ 267 and ~ 312 cm^{-1} were detected. The 202 and 218 cm^{-1} Raman modes are related with the Ge-Se stretching vibrations in so called corner- and edge-sharing tetrahedra, respectively [10]. However, the former mode can also be characteristic

vibration of outrigger raft cluster [11]. The bands at 179 and 245 cm^{-1} may be connected with stretching Ge-Ge vibrations of ethane like cluster and Se-Se stretching vibrations, respectively [10].

Our recent theoretical study of formation energy, stability and electronic properties of different Ge$_n$Se$_m$ clusters indicate that the formation of single ethane like cluster, single corner sharing GeSe$_4$ tetrahedra and cluster based on two GeSe$_4$ tetrahedra connected by Se-Se bridge is energetically not favorable structural motifs [12]. On the other hand we have found that the ring-like structures are most favorable within our Ge$_n$Se$_m$ cluster models.

In one of our previous studies [13] we have found that the vibrational mode at ~ 250 cm^{-1} observed in the Raman spectra of GeS$_2$ glass can be interpreted as existence of GeS microphase rather than ethane-like Ge$_n$S$_m$ cluster with Ge-Ge bond.
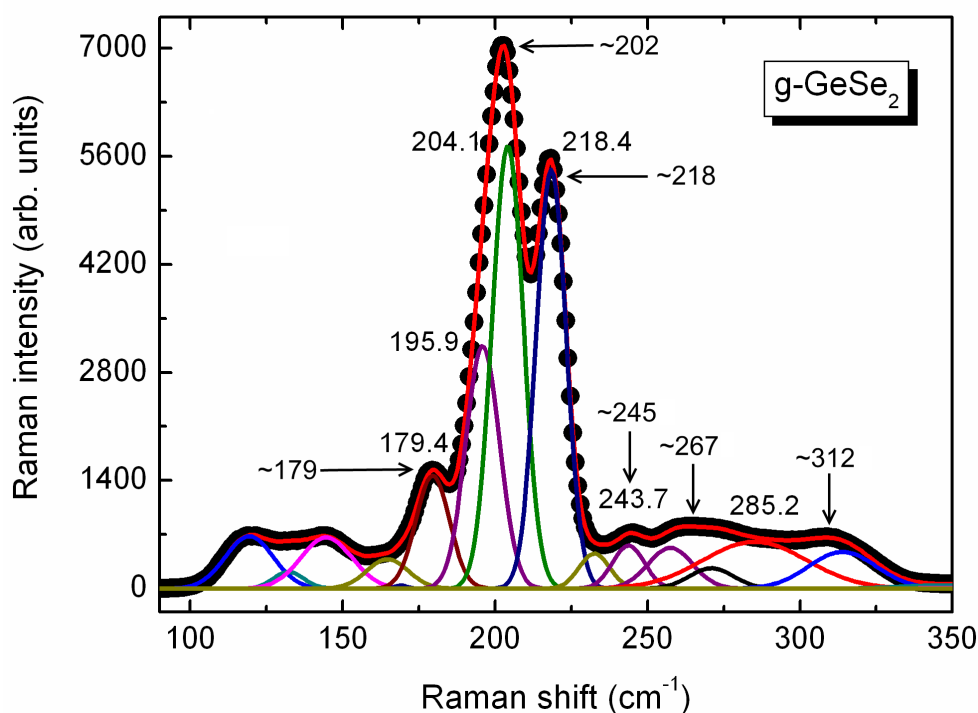

Figure 2. High resolution micro-Raman spectra of *g*-GeSe$_2$ excited with the diode laser (785 nm) together with the results of curve fitting.

3.2. Calculated Raman spectra of Ge-Se cluster models

The calculated Raman spectra of Ge$_n$Se$_m$ nanoclusters are shown in Figure 3. As can be seen from Fig. 3A the main experimental Raman modes observed at 179, 202 and 218 cm^{-1} (see Fig. 2) can be described well using small Ge$_n$Se$_m$ clusters (SRO

regime). The Ge-Ge stretching vibration in ethane-like cluster was calculated at 176 cm^{-1}. The Ge-Se stretching vibrations were calculated at 202 and 219 cm^{-1} for corner- and edge-sharing tetrahedra, respectively. The calculated Se-Se vibration in model IX was found at 287 cm^{-1} which is slightly higher than expected. The small gas phase clusters have deformational vibrations below 150 cm^{-1} and vibrational modes around 300 cm^{-1} that originate from IR active asymmetric Ge-Se stretching vibrations.

With increasing cluster size (Fig. 3B) an additional Raman active mode was found at ~ 250 cm^{-1}. Also, we have observed low energy shift of the Ge-Se stretching vibrations from ~ 203 to 194/191 cm^{-1} with increasing ring size from $i = 6$ to $i = 8/10$ (Fig. 3C).

Observed peculiarities in the calculated Raman spectra of our Ge-Se cluster models were used in order to find the possible signatures of such features in the experiment that will allow distinguishing the different MRO structures in the GeSe$_2$ glass structure. For this purpose we have performed curve fitting procedure on of high resolution Raman spectra of g-GeSe$_2$ using independent Gauss functions. The result of curve fitting is summarized Figure 2. As clearly be seen the main vibrational mode centered at ~202 cm^{-1} in the Raman spectra of g-GeSe$_2$ consists two peaks located at 204.1 and 195.9 cm^{-1}. The former is in very good accordance with the Raman mode at 204/205 cm^{-1} calculated for six-member rings and larger ring-like Ge$_n$Se$_m$ clusters topologically similar with HT-GeSe$_2$ (Fig. 3B). We suppose that the mode at 195.9 cm^{-1} originates from larger rings with $i = 8,10$ (Fig. 3C). The additional signature for the existence of big clusters topologically similar with HT-GeSe$_2$ is the band at 243.7 cm^{-1} observed in the curve fitted Raman spectra of g-GeSe$_2$. Such mode is calculated at 248.8 and 247.4 cm^{-1} for models V and VI, respectively. Thus, it is possible to distinguish between four-, six- and larger (eight-, ten-) member Ge-Se rings in the structure of g-GeSe$_2$: the four- and six-member rings occur in the structure of GeSe$_2$ glass with nearly the same concentration while the concentration of larger eight- and ten- member rings is less but quite significant.

It is not possible to find evidence of five-member rings as energetically more favorable model describing homopolar Ge-Ge and Se-Se bonds [12] using Raman spectroscopy. The calculated Ge-Ge vibration yields the same frequency (175.5 cm^{-1}) for both ethane-like and five-member ring models. Also, the Se-Se stretching vibrations within our Ge-Se clusters calculated at 287.2, 283.3 and 284.5 cm^{-1} for models IX, X and XI, respectively cannot be distinguished due to broadening and overlapping by contribution of asymmetric Ge-Se stretching vibrations.

To analyze the frequency position of the Se-Se stretching vibrations of Ge_nSe_m clusters (models IX-XI) we have calculated Raman spectra of Se_n (n = 12) chain (helical Se) and Se_8 ring using the same method and basis set. The main band of Se-Se stretching vibrations of helical Se and Se_8 ring were calculated at 265 and 271 cm^{-1}, respectively. Although these Raman bands are slightly higher than the main Raman band at 250 cm^{-1} observed in the experimental Raman spectra of *a*-Se they are in good accordance with the observed bands at 259 and 268 cm^{-1} which are characteristic Se-Se symmetric bond stretching of Se chain and Se_8 ring respectively of selenium species confined in zeolite matrix [14]. Therefore the differences between the frequency position of Se-Se stretching vibration of calculated Raman spectra of isolated Se_n chain and Se_8, and the experimental Raman spectra of *a*-Se is mainly due to the intermolecular interaction in the bulk solid.
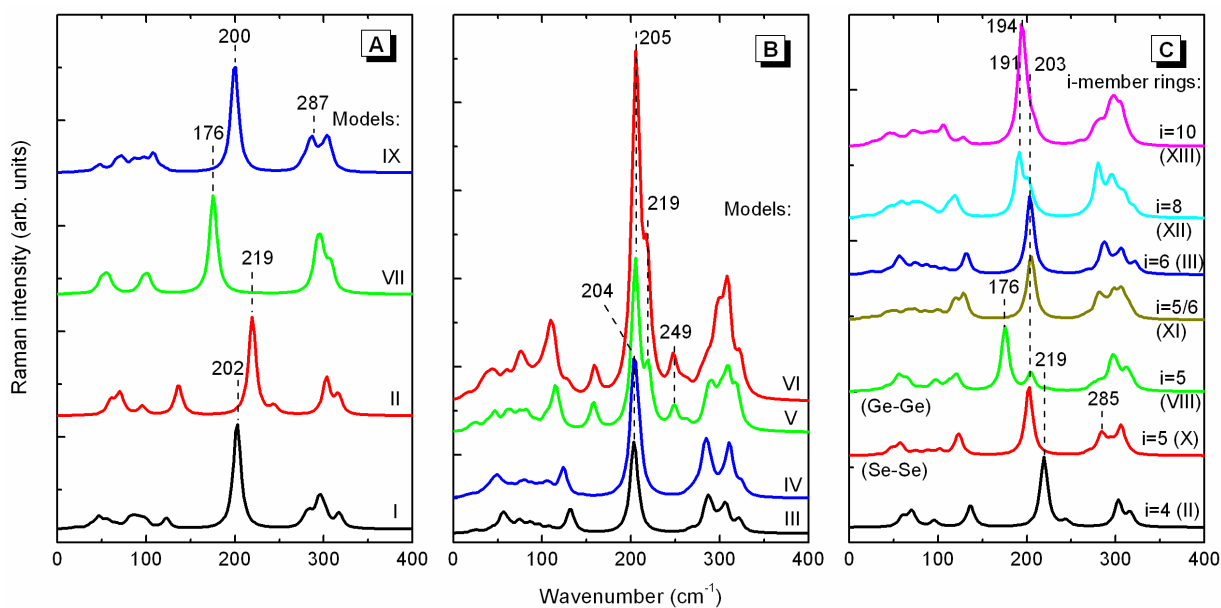

Figure 3. Simulated Raman spectra of Ge_nSe_m

4. Conclusions

The vibrational properties of Ge_nSe_m nanoclusters representing the local and medium range order structures of $GeSe_2$ crystal and "defect" clusters with homopolar Ge-Ge and Se-Se bonds that are thought to be related to the structural inhomogeneity found in $GeSe_2$ glass were studied in detail by using *ab initio* DFT method.

Detailed analysis of the experimental Raman spectra of *g*-$GeSe_2$ using curve fitting procedure showed the presence of nearly the same concentration of four- and six-member rings as well as bigger Ge-Se nanoclusters topologically similar with β-$GeSe_2$ crystal in the glass structure. Significant contributions of larger odd-member rings ($i = 8,10$) were detected.

Acknowledgements

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