SPECTROSCOPIC STUDIES OF MEDIUM RANGE ORDERING IN g-GeSe$_2$: THEORY AND EXPERIMENT

High resolution Raman spectra of GeSe$_2$ glass were measured and fitted using individual components. The structural origin of the components were interpreted using the results of ab initio DFT calculations which were performed on Ge$_n$Se$_m$ nanoclusters (n=2-6,12; m=6-9,12,14-16,30) that represent the local structure of GeSe$_2$ glass and on some “defect” Ge$_n$Se$_m$ clusters that are thought to be related to the inhomogeneity of the structure at the nanoscale. The calculated vibrational properties of Ge$_n$Se$_m$ nanoclusters and their couplings with the local and medium range order structure formations in GeSe$_2$ glass are analysed and discussed.

Key words: Ge$_n$Se$_m$ nanoclusters, DFT calculations, GeSe$_2$ glass, Raman spectra.

1. Introduction

Nowadays 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 controversal. 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\textsubscript{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 (\(\lambda_{\text{ex,1}} = 1064\) nm, \(E_{\text{ex,1}} = 1.17\) eV) and a diode (\(\lambda_{\text{ex,2}} = 785\) nm, \(E_{\text{ex,2}} = 1.58\) 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\textsubscript{4} tetrahedron in the structure of low temperature (LT) \(\alpha\)-form of GeSe\textsubscript{2} is mutually connected by their corners and forms the three-dimensional (3D) crystal network. However high temperature (HT) \(\beta\)-form generates two-dimensional (2D) network built up by combination of GeSe\textsubscript{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 \(\alpha\)-GeSe\textsubscript{2} is corner-sharing tetrahedra and the local SRO structures representing \(\beta\)-form of GeSe\textsubscript{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\textsubscript{2} is a six-member ring consisting three GeSe\textsubscript{4} tetrahedra connected by their corners (III). Models IV and V represents two six-member rings selected from two directions of 2D network of \(\beta\)-GeSe\textsubscript{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 \(\beta\)-GeSe\textsubscript{2} monolayer (VI) consists of a big 16-member ring.

The \textit{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\textsubscript{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\textsubscript{3}Se\textsubscript{8} crystal show that there is another possibility to form Se-Se bond through Ge\textsubscript{2}Se\textsubscript{4+4/2} cluster (X) which substitute edge-sharing blocks in 2D crystalline network of \(\beta\)-GeSe\textsubscript{2} [6]. This cluster together with the model VIII represents five-member rings with incorporated Se-Se and Ge-Ge bonds, respectively. \textit{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\textsubscript{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).

The dangling bonds of the surface atoms of the selected finite Ge\textsubscript{n}Se\textsubscript{m} models were saturated by hydrogen atoms for a better representation of the cluster boundaries and H-terminated Ge\textsubscript{n}Se\textsubscript{m} nanoclusters used for further calculations. The computational part consists of \textit{ab initio} DFT calculations performed using the Gaussian-03 quantum-chemical program package [7]. The self-consistent DFT field method was applied for geometry optimizations of the clusters using the Berny optimization procedure. The LANL2DZdp ECP basis set of Hay and Wadt [8] with polarization function was used for the Ge, Se and H atoms together with the full Heyd-Scuseria-Ernzerhof hybrid functional based on a screened Coulomb potential (HSE06) [9]. Subsequent second derivative calculations verified the obtained structures as true energy minimum geometries.
3. Results and discussion

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

Figure 2 shows the measured micro-Raman ($E_{\text{ex,2}} = 1.58$ eV) spectra of g-GeSe$_2$. This spectra and FT-Raman ($E_{\text{ex,1}} = 1.17$ 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.

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 \(\sim 250\) cm\(^{-1}\). Also, we have observed low energy shift of the Ge-Se stretching vibrations from \(\sim 203\) 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 \(\sim 202\) 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 \(195.9\) cm\(^{-1}\) observed in the curve fitted Raman spectra of \(g\)-GeSe\(_2\). Such mode is calculated at 243.7 cm\(^{-1}\) observed in the experiment 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

![Fig. 3. Simulated Raman spectra of Ge\(_n\)Se\(_m\) clusters calculated at HSE06/LANL2DZ ECP polarized (p,d) level of theory: spectra of Ge\(_n\)Se\(_m\) clusters at SRO regime (A), evolution of spectra of Ge\(_n\)Se\(_m\) clusters topologically similar with HT-GeSe\(_2\) (B), spectra of \(i\)-member ring Ge\(_n\)Se\(_m\) clusters (C).]
spectra of isolated Se₈ chain and Se₈, and the experimental Raman spectra of α-Se is mainly due to the intermolecular interaction in the bulk solid.

4. Conclusions

The vibrational properties of GeₙSeₘ nanoclusters representing the local and medium range order structures of GeSe₂ crystal and “defect” clusters with homopolar Ge-Ge and Se-Se bonds that are thought to be related to the structural inhomogeneity found in GeSe₂ glass were studied in detail by using ab initio DFT method.

Acknowledgements

This work was performed within Ukrainian-Turkish collaboration in Science and Technology (Project Numbers M85-2010 and TUBITAK-109T643).

REFERENCES

Ужгородський національний університет, 88000 Ужгород, Україна, e-mail: holomb@ukr.net

Р. Голомб¹, В. Міца¹, Е. Акалін², С. Акуз³, М. Січка¹
¹ Інститут фізики і хімії твердого тіла, Ужгородський національний університет, 88000 Ужгород, Україна
² Фізичний факультет, Стамбульський університет, Везнецілер 34134, Стамбул, Туреччина
³ Фізичний факультет, Стамбульський культурний університет, Бакіркій 34156, Стамбул, Туреччина

**СПЕКТРОСКОПІЧНІ ДОСЛІДЖЕННЯ СЕРЕДНЬОГО ПОРЯДКУ В c-GeSe₂: ТЕОРІЯ ТА ЕКСПЕРИМЕНТ**

Високороздільні Рaman спектри стекол GeSe₂ були виміряні і апроксимовані використовуючи окремі компоненти. Структурна природа компонент була інтерпретована використовуючи результати первопримінних розрахунків методом функціоналу густини (DFT), проведених на нанокластерах GeₙSeₘ (n=2-6,12; m=6-9,12,14-16,30), які представляють локальну структуру стекол GeSe₂ і на деяких “дефектних” кластерах GeₙSeₘ, які можуть бути пов’язані з негомогеністю структури в наномасштабі. Розраховані коливні властивості нанокластерів GeₙSeₘ і їх взаємозв’язок з утворенням локальної структури та структури середнього порядку в стеклах GeSe₂ проаналізовані і обговорені.

**Ключові слова:** нанокластери GeₙSeₘ, DFT розрахунки, стекла GeSe₂, Raman спектри.

Р. Голомб¹, В. Міца¹, Е. Акалін², С. Акуз³, М. Січка¹
¹ Інститут фізики і хімії твердого тіла, Ужгородський національний університет, 88000 Ужгород, Україна, e-mail: holomb@ukr.net
² Фізичний факультет, Стамбульський університет, Везнецілер 34134, Стамбул, Туреччина
³ Фізичний факультет, Стамбульський культурний університет, Бакіркій 34156, Стамбул, Туреччина

**СПЕКТРОСКОПІЧНІ ІССЛЕДОВАНИЯ СРЕДНЕГО УПОРЯДОЧЕНИЯ В C-GeSe₂: ТЕОРІЯ І ЕКСПЕРИМЕНТ**

Високоразрешенные Рaman спектры стекол GeSe₂ были измерены и аппроксимированы, используя отдельные компоненты. Структурная природа компонент была интерпретирована, используя результаты первопримитивных расчетов методом функционала плотности (DFT), проведенных на нанокластерах GeₙSeₘ (n=2-6,12; m=6-9,12,14-16,30), которые представляют локальную структуру стекол GeSe₂, и на некоторых “дефектных” кластерах GeₙSeₘ, которые могут быть связаны с неномогенностю структуры в наномасштабе. Рассчитанные колебательные свойства нанокластеров GeₙSeₘ и их взаимосвязь с образованием локальной структуры, а также структуры среднего порядка стекол GeSe₂ проанализированы и обсуждены.

**Ключевые слова:** нанокластеры GeₙSeₘ, DFT расчеты, стекла GeSe₂, Рaman спектры.