

Spectroscopic evidence of coexistence of clusters based on low (α) and high temperature (β) GeS₂ crystalline phases in glassy germanium disulfide matrix

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Abstract – Technologically modified g-GeS₂(T_iV_j) glasses prepared by melt quenching from different temperatures (T_i) and with different cooling rates (V_j) were studied using Raman spectroscopy and model calculations. Differential Raman spectra {I_RGeS₂(T_iV₁)-I_RGeS₂(T₂V₁)} showed the splitting of the main, most intensive wide-band, centered at 340 cm⁻¹. The position of the peaks found in the differential Raman spectra near 340 and 360 cm⁻¹ and position of the main vibrational modes in the ordinary Raman spectra of low- and high-temperature crystalline phases (α -, β -GeS₂) were found to be in good agreement. Vibrational spectra of 4- and 6-member ring fragments selected from crystalline structure of β -GeS₂ were also determined using model calculations. Based on rings composed of GeS₄ tetrahedrons connected by corners and edges the structural interpretation of the vibrational bands of g-GeS₂(T_iV_j) at 360, 370 and 433 cm⁻¹ in their Raman spectra was performed. The existence of homopolar Ge-Ge and S-S “defect” bonds in the structure of germanium disulfide glasses was proved by formation of 5-member rings. Formation of fragments of both low- and high-temperature α -, β -GeS₂ crystalline phases in the structure of g-GeS₂(T_iV_j) glasses indicates the existence of mixed medium-range ordering in g-GeS₂.

I. INTRODUCTION

Glassy germanium disulfide is among chalcogenide glasses attracting much attention and widely studied for many years. Thanks to the large infrared optical transmission window it found usage as material for night vision, acusto-optical modulators, chemical sensors, mid-infrared light delivery, thermal imaging, environmental monitoring, integrated optics and also in the area of fast ion conducting glasses for battery applications [1-6]. One of the promising new ways of its mid-IR application is to prepare glass-ceramics with controlled crystallization [7]. Due to their specific optical properties transparent glassy ceramics are considered as perspective materials for photonics [7]. A number of structural studies were performed on this material and it was concluded that the medium-range order existing in g-GeS₂ is connected with clustering of GeS₄ tetrahedral units by edges or corners

and the two kinds of linkages produce both six- and four-member rings in a 2:1 ratio, like in layered β -GeS₂ crystalline structure [8-13]. In the low temperature α -GeS₂ crystalline phase the corner-sharing GeS_{4/2} tetrahedra form a three-dimensional (3D) structure [14,15]. The density of α -GeS₂ is only about 0.055 g/cm³ higher than that of β -GeS₂ [14]. The structure of α -GeS₂ crystal was used as starting configuration in a Reverse Monte Carlo (RMC) calculations [16]. In contrast to the common conclusions [8-13] about layered structure of g-GeS₂, the RMC simulation revealed that the structure of g-GeS₂ is somewhere between the structure of α -GeS₂ and β -GeS₂ crystals [16]. This conclusion was also confirmed by studies of g-GeS₂ performed at high pressures [17], where short-range structures of densified g-GeS₂ transformed from a mixed α -GeS₂ and β -GeS₂ type arrangement into an α -GeS₂-like structure [17]. Comparison of the Raman spectra of g-GeS₂ and α - and β -GeS₂ crystals in [18] showed that the middle-range structural order of g-GeS₂ is controlled by a corner-shared three-dimensional network which is topologically similar to that in the α -GeS₂ crystal. Similarity of medium-range ordering of g-GeS₂ and α -GeS₂ was also confirmed by the study of GeS₂ microcrystals grown in g-GeS₂ during annealing at 497 °C, below the glass transition temperature [18]. Linear crystal growth kinetics of both α -GeS₂ and β -GeS₂ polymorphs has also been observed in g-Ge₄₂S₅₈ over a relatively broad range of temperatures, *i.e.* 420 < T < 494 °C that correspond to viscosity of supercooled melt: 3 x 10⁹ > η > 8 x 10⁵ Pa s [19].

In spite of the findings described above, the structural information about medium-range ordering in g-GeS₂ is controversial. It is still debated whether the structure of g-GeS₂-type glass is a continuous or a broken network of Ge-(S_{1/2})₄ tetrahedra [20]. The new potential applications, however, compel a need for thorough structural characterization of these glasses prepared in different technological regimes, including the utilization

of both experimental techniques and atomic scale modeling.

II. MATERIALS AND METHODS

The g-GeS₂ samples were synthesized by melt quenching from different temperatures: 1173 K (T₁), 1273 K (T₂), 1373 K (T₃) and 1473 K (T₄) and cooling rates of 100 K/s (V₁) and 150 K/s (V₂). The four different g-GeS₂ samples will hereafter be denoted as (T₁V₁), (T₂V₂), (T₃V₂) and (T₄V₂). DFT calculations were performed on Ge_nS_m (n=2,3,5,6,12; m=6–9,14,16,30) units that represent the local structure of g-GeS₂ and some ‘defect’ Ge_nS_m clusters (Fig.1). The local short-range order structural units representing the beta form of GeS₂ crystal are corner- and edge-sharing tetrahedra (models I and II). Further extension of the length scale to the larger coordination spheres leads to an increase in the degree of freedom in the formation of amorphous structures. In this case, the structure formation may be studied in detail by *ab initio* method using a gas-phase cluster approach. The largest cluster which can be found in the crystal structure of GeS₂ is a six-member ring consisting of three GeSe₄ tetrahedra connected by their corners (III). It should be noted here that two edge-sharing tetrahedra can also be classified as a four-member ring. Models IV and V represent two six-member rings selected from two directions of 2D of β-GeS₂ crystal. In the first case the rings are connected by common Ge atom while in the other model rings are connected via the edge-sharing block. The largest cluster obtained from the crystal structure of GeS₂ monolayer (VI) consists of a big 16-member ring. Here, we represent few possible models with homopolar Ge–Ge (VII–VIII) and S–S (IX–XI) bonds. The simplest model of Ge–Ge bond being present in the hypothetical cluster is the so-called ethane-like geometry (VII). There is also possibility of S–S bond formation on the edge of the so-called ‘outrigger raft’ structure (model XI represents a part of this structure) [8]. In α-GeS₂ the GeS_{4/2} tetrahedra pack to form a dense three-dimensional network with large hollows surrounded by twenty four-member rings together with six-member rings (Fig. 2).

Raman spectra of g-GeS₂ and β-GeS₂ were measured using Dilor–Labram and Renishaw system 1000 Raman spectrometers equipped with CCD detectors. Excitation was performed with lasers operating at 1064 and 785 nm.

III. RESULTS AND DISCUSSION

Fig. 3 shows the Raman spectra of g-GeS₂ glasses measured using excitation photon energy of 1.17 eV (1064 nm), being less than the Tauc optical gap of GeS₂ glasses (E_g=3.2 eV) [21]. All these spectra are very similar to those measured with shorter excitation wavelengths (632.8 and 785 nm) and they can be treated as non-resonant Raman spectra. All spectra are normalized to their 340 cm⁻¹ peak. A pronounced difference between the samples is that both the (T₁V₁)

and the (T₃V₂) samples show similar small increases in the intensity of 370 and 433 cm⁻¹ vibrational modes, as compared to (T₂V₂). For the (T₄V₂) sample these peaks broadened and merge with the main peak at 340 cm⁻¹. A very weak c-GeS-like Raman mode at ~200 cm⁻¹ is observed for all samples while a weak S–S mode at 490 cm⁻¹ is detected only for (T₂V₂) showing evidence of c-GeS type clusters (Fig.4) and S-rich clusters (IX–XI) respectively (Fig.1).

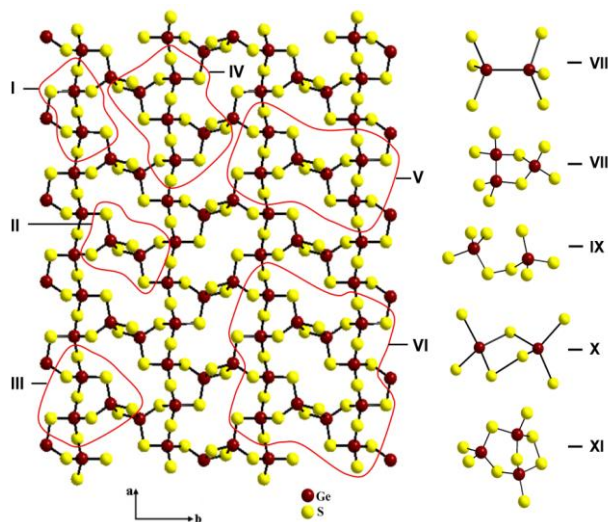


Figure 1. The crystal structure of high- temperature (β) GeS₂ monolayer [15] with the selected Ge_nS_m cluster models (I–VI) (left) and the ‘defect’ Ge_nS_m cluster geometries with homopolar Ge–Ge (VII–VIII) and S–S (IX–XI) bonds (right). Saturating hydrogen atoms and corresponding bonds are not shown for clarity.

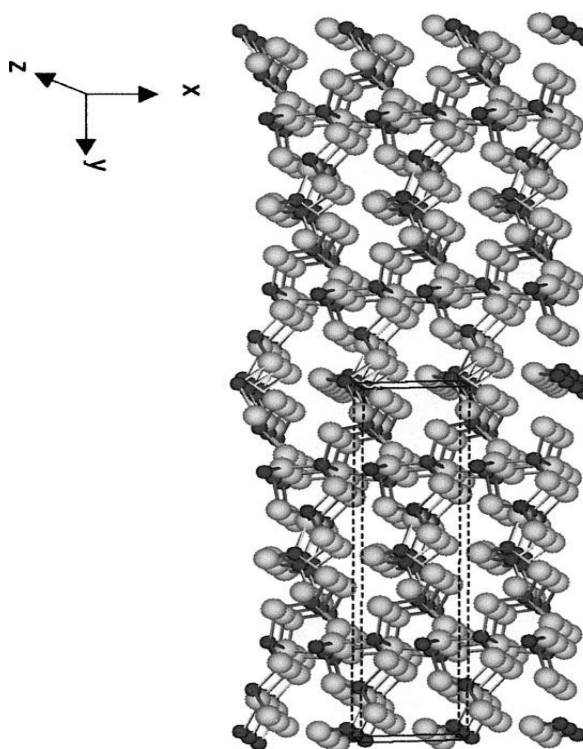


Figure 2. Crystal structure of α-GeS₂ (low-temperature modification) [14].

The Raman spectrum of $g\text{-GeS}_2(\text{T}_2\text{V}_2)$ didn't show band near 255 cm^{-1} being characteristic for Ge-Ge bonds in (VII-VIII) type of clusters (Fig.1). The Raman spectrum of this (T_2V_2) technological regime contains only minority of 'defect' clusters and was chosen as reference spectrum for the extraction of other differential Raman spectra of $g\text{-GeS}_2(\text{T}_i\text{V}_j)$ samples. The Raman modes at 360 and 370 cm^{-1} are related to the Ge-S stretching vibrations in so called corner- and edge-sharing tetrahedra, respectively [21]. However, the former modes can also be characteristic for an 'outrigger raft' cluster [8]. Our recent theoretical study on formation energy, stability and electronic properties of different Ge_nS_m clusters indicates that the formation of single ethane-like cluster, single corner sharing GeS_4 tetrahedra and cluster based on two GeS_4 tetrahedra connected by an S-S bridge are energetically not favorable structural motifs [22]. On the other hand, we have found that the ring-like structures were most favorable within our Ge_nS_m cluster models. One of our previous studies [21] showed that the vibrational mode at $\sim 250\text{ cm}^{-1}$ observed in the Raman spectra of GeS_2 glass can be interpreted as the existence of GeS microphase rather than ethane-like Ge_nS_m cluster with Ge-Ge bond.

The differential Raman spectra $\{I^R\text{GeS}_2(\text{T}_i\text{V}_2) - I^R\text{GeS}_2(\text{T}_2\text{V}_2)\}$, ($i=1, 3$ and 4) clearly show two bands centered at 339 and 360 cm^{-1} (Fig.5) which are typical for Raman spectra of $\alpha\text{-GeS}_2$ and $\beta\text{-GeS}_2$, respectively [23,24]. These two bands are more distinct in the differential Raman spectra $\{I^R\text{GeS}_2(\text{T}_i\text{V}_1) - I^R\beta\text{-GeS}_2\}$ (Fig.6). Differential Raman spectrum $\{I^R\text{GeS}_2(\text{T}_1\text{V}_1) - I^R\beta\text{-GeS}_2(\text{T}_2\text{V}_1)\}$ is mainly $\beta\text{-GeS}_2$ like (Fig.5). For this (T_1V_1) technological regime the fraction of edge-sharing tetrahedra in the glassy structure increases. By increasing temperature from T_2 to T_3 and T_4 the concentration of 5-member rings with Ge-Ge bonds and GeS-like clusters

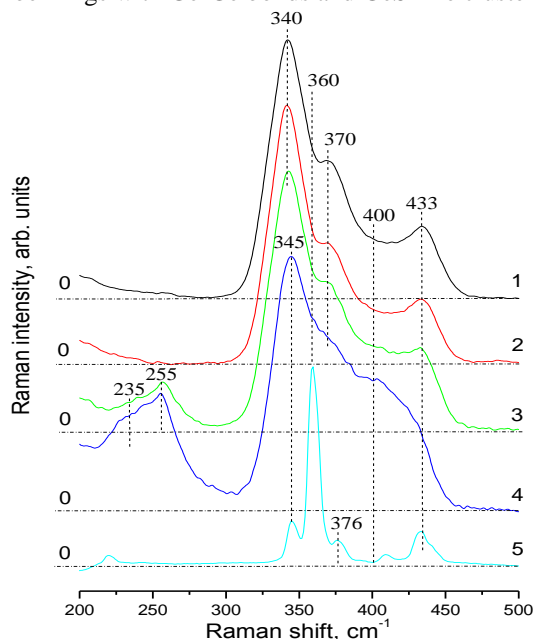


Figure 3. Raman spectra of GeS_2 glasses: 1- T_1V_1 ; 2- T_2V_2 ; 3- T_3V_2 ; 4- T_4V_2 ; 5- Raman spectrum of $\beta\text{-GeS}_2$.

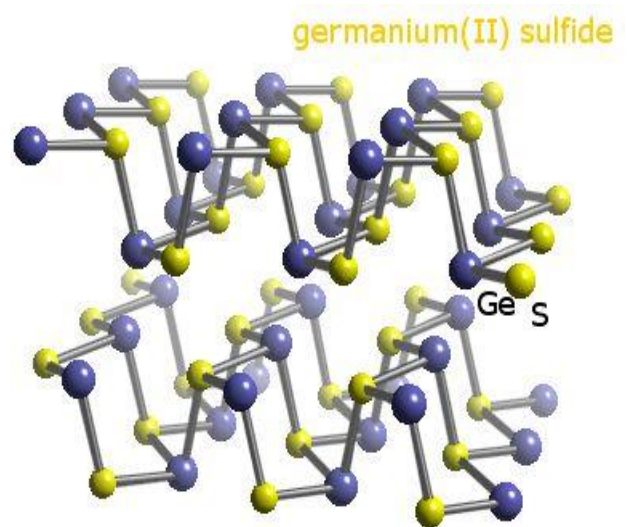


Figure 4. Crystal structure of $c\text{-GeS}$ [14]

increases and concentration of 4-member rings with edge-sharing tetrahedra in the structure decreases. Therefore, in structural aspect, nucleates with medium-range ordering based on $\alpha\text{-GeS}_2$ and $\beta\text{-GeS}_2$ crystal type clusters coexist in the structure of $g\text{-GeS}_2(\text{T}_i\text{V}_1)$ during nucleation of the melt by quenching from different temperatures.

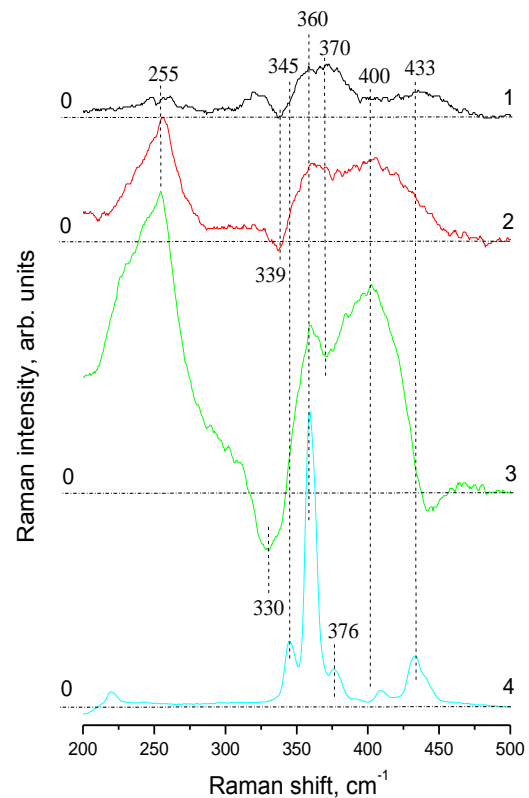


Figure 5. Differential Raman spectra $\{I^R\text{GeS}_2(\text{T}_i\text{V}_1) - I^R\text{GeS}_2(\text{T}_2\text{V}_2)\}$: 1- T_1V_1 ; 2- T_3V_2 ; 3- T_4V_2 ; 4 - Raman spectrum of $\beta\text{-GeS}_2$.

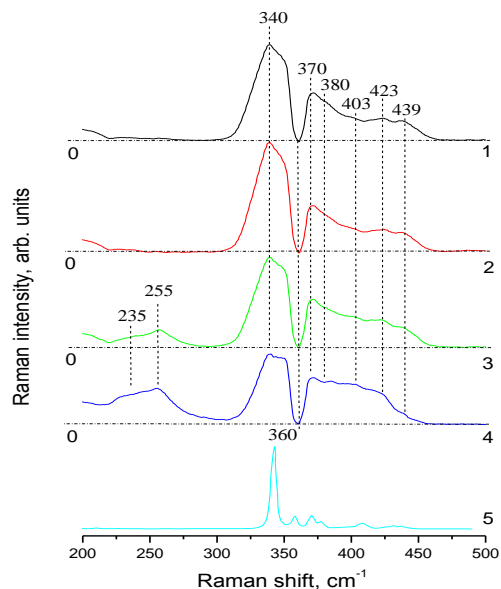


Figure 6. Differential Raman spectra $\{I^R \text{GeS}_2(T_i V_1) - I^R \beta\text{-GeS}_2\}$: 1 - $T_1 V_1$; 2 - $T_2 V_2$; 3 - $T_3 V_2$; 4 - $T_4 V_2$; 5 - Raman spectrum of $\alpha\text{-GeS}_2$ [18].

IV. CONCLUSION

Two bands, centered at 339 and 360 cm^{-1} were observed in the differential Raman spectra $\{I^R \text{GeS}_2(T_i V_1) - I^R \text{GeS}_2(T_j V_2)\}$, ($i=1,3,4$), which are typical for most intense bands in Raman spectrum of $\alpha\text{-GeS}_2$ and $\beta\text{-GeS}_2$ crystals, respectively. These two peaks appear more clearly in the differential spectra $\{I^R \text{GeS}_2(T_i V_1) - I^R \beta\text{-GeS}_2\}$, $i=1-4$. In structural aspect, during the melt clustering by quenching a middle-range structural ordering is created in g- GeS_2 as mixture of corner-shared three-dimensional clusters being topologically similar to those in $\alpha\text{-GeS}_2$ crystal and middle range order which is topological similar to the two-dimensional $\beta\text{-GeS}_2$ crystal type.

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REFERENCES

- [1] W.H. Zachariasen, "The crystal structure of germanium disulfide", J. Chem. Phys, vol.4, pp. 618-619, 1936.
- [2] A.F. Ioffe, A.R. Regel, "Non-crystalline, amorphous and liquid electronic semiconductors", Progress in semiconductors. London. vol.4, №20, pp. 25-30, 1960.
- [3] J. Savage, S.Nilsen, "Chalcogenide glasses transmitting in the infrared between 1 and 20 μm - a state of the art review", J.Infrared Phys, vol. 5, pp. 195-204, 1965.
- [4] V. Mitsa, R. Holomb, M. Veres, A. Marton, I. Rosola, I. Fekeshgazi, M. Koós, "Non-linear optical properties and structure of wide band gap non-crystalline semiconductors", Phys. Stat. Sol. C., vol.8, №9, pp. 2696-2700, 2011.
- [5] Inseok Seo and Steve W. Martin. New Developments in Solid Electrolytes for Thin-Film Lithium Batteries, Lithium Ion Batteries - New Developments, Dr. Ilias Belharouak (Ed.), (2012). ISBN: 978-953-51-0077-5.
- [6] V. Mitsa, M. Ivanda, O. Gamulin, R. Holomb, O. Kondrat, N. Popovych, N. Tsud, V. Matolín, K.C. Prince, G. Lovas, S.

- Petrecky, "Visible luminescence and synchrotron XPS spectra of amorphous Ge_2S_3 based films", 2013 MIPRO Proceedings of the 36th International Convention, pp. 34-39, 2013.
- [7] Changgui Lin, Haizheng Tao, Xiaolin Zheng, Ruikun Pan, Haochun Zang, and Xiujian Zhao, "Second-harmonic generation in IR-transparent- GeS_2 crystallized glasses", Optics Letters, vol. 34, No. 4, pp. 437-439, 2009.
- [8] P.M. Bridenbaugh, G.P. Espinosa, J.E. Griffiths, J.C. Phillips, and J.P. Remeika, "Microscopic origin of the companion A_1 Raman line in glassy $\text{Ge}(\text{S,Se})_2$ ", Phys. Rev. B., vol.20, №10, pp. 4140-4144, 1979.
- [9] R.J. Nemanich, F.L. Galeener, I.C. Mikkelsen G.A.N. Connel, "Configuration of chemically ordered continuous random network to describe the structure of GeSe_2 glass," Physica B., vol.117-118, pp. 959-961, 1983.
- [10] G. Lucovsky, C.K. Wong, W.B. Pollard, "Vibrational properties of glasses: intermediate range order", J. Non-Cryst. Sol, vol. 59-60, №2, pp. 839-846, 1983.
- [11] P. Boolchand, J. Grothaus, M. Tenhaver, M. Halze, R.K. Grassli. "Structure of GeS_2 glass: spectroscopic evidence for broken chemical order", Phys. Rev. B., vol. 33, pp. 5421-5434, 1986.
- [12] P.S. Salmon, R.A. Martin, P.E. Mason. "Topological versus chemical ordering in network glasses at intermediate and extended length scales", Nature, vol.435, pp. 75-78,2005.
- [13] P. Armand, A. Ibanez, H. Dexpert, D. Bittencourt, D. Raoux, E. Philippot, "Structural approach of Ge-X, GeX_2 - Ag_2X (X= S,Se) glassy systems", Journal de physique IVColloque C2, vol. 2, pp. c2-189-c2-194, 1992.
- [14] C.T. Crewitt, H.S. Young, "Germanium and silicon disulfides: structure and synthesis", Science, vol. 149, pp. 535-537- 1965.
- [15] G. Dittmar and H. Schäfer, "Die Kristallstruktur von Germaniumdiselenid", Acta Cryst. B., vol. B32, pp. 2726-2728, 1976.
- [16] X. Zhao, H. Higuchi, Y. Kawamoto, "Structural analysis of GeS_2 glass by means of reverse Monte Carlo simulation", Physics and Chemistry of Glasses - European Journal of Glass Science and Technology Part B , vol. 39, pp. 98-100, 1998.
- [17] K. Miyauchi, J. Qiu, M. Shojiya, Y. Kawamoto, N. Kitamura, "Structural study of GeS_2 glasses permanently densified under high pressures up to 9 GPa", Journal of Non-Crystalline Solids, vol. 279, pp. 186-195, 2001.
- [18] Z. Černošek, E. Černošková, L. Beneš, "Raman scattering in GeS_2 glass and its crystalline polymorphs compared", Journal of Molecular Structure, vol. 435, pp. 193-198, 1997.
- [19] J. Shanelova, J. Malek, M. Alcalá, J.Criado, "Kinetics of crystal growth of germanium disulfide in $\text{Ge}_{42}\text{S}_{58}$ chalcogenide glass", Journal of Non-Crystalline Solids, vol. 351, pp. 557-567, 2005.
- [20] V. Petkov, D. Le Messurier, "Atomic-scale structure of GeSe_2 glass revisited: a continuous or broken network of $\text{Ge}-(\text{Se}_{1/2})_4$ tetrahedra?", J. Phys.: Condens. Matter., vol. 22, pp.115402-115408, 2010.
- [21] R. Holomb, P. Johansson, V. Mitsa and I. Rosola, "Local structure of technologically modified g- GeS_2 : resonant Raman and absorption edge spectroscopy combined with ab initio calculations", Phil. Mag., vol. 85, pp. 2947-2960, 2005.
- [22] R. Holomb, V. Mitsa, S. Akyuz, E. Akalin, "New ring-like models and *ab initio* DFT study of the medium-range structures, energy and electronic properties of GeSe_2 glass", Phil. Mag., vol. 93, pp. 2549-2562, 2013.
- [23] K. Inoue, O. Matsuda, K. Murase, "Raman spectra of tetrahedral vibrations in crystalline germanium dichalcogenides, GeS_2 and GeSe_2 , in high and low temperature forms", Solid State Commun., vol. 79, pp. 905-910, 1991.
- [24] I.P. Kotsalas, C. Raptis, "Structural Raman studies of $\text{Ge}_x\text{S}_{1-x}$ chalcogenide glasses", Journal of Optoelectronics and Advanced Materials, vol. 3, pp. 675-684, 2001.