

STRUCTURAL RAMAN STUDIES OF $\text{Ge}_x\text{S}_{1-x}$ CHALCOGENIDE GLASSES

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The Raman spectra of binary $\text{Ge}_x\text{S}_{1-x}$ chalcogenide glasses have been measured for various compositions and discussed in terms of the structural units present. High temperature Raman measurements in $\text{Ge}_x\text{S}_{1-x}$ glasses have shown that, above the glass transition temperature T_g , irreversible two step crystallizations occur for the compound GeS_2 ($x=1/3$) and the moderately rich in Ge ($x=0.35$) and S ($x=0.30$) glasses, but in the case of the strongly enriched in S ($x=0.20$) glass, a one step reversible crystallization takes place with the material returning to its starting glassy phase upon slow cooling to room temperature. The evolution of the A_1^c companion Raman band of GeS_2 glass in the crystalline phases provides evidence (in support of predictions) that this controversial band is associated with *symmetric stretching of S atoms in bridges of edge-sharing $\text{Ge}-(\text{S}_{1/2})_4$ tetrahedra*. Raman measurements above melting point have indicated the existence of tetrahedral units in the molten phase of these glasses. High pressure Raman measurements in GeS_2 have shown that the bond lengths decrease substantially with pressure, while the material remains glassy throughout the pressure range of measurements (up to 10.8 GPa). It appears that all pressure induced effects are reversible after pressure relief.

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1. Introduction

Chalcogenide glasses have drawn increasing attention over the past three decades because of their potential in photoresist [1,2], microelectronic [3-5], optoelectronic [6-9] and holographic [10,11] applications. In recent years, Ge-based chalcogenide glasses have been used for manufacturing optical waveguides of high transparency in the infrared window at 1.3 μm and as host materials of rare earth ions for photonic applications [12-14]. Owing to all these applications, knowledge of their electronic and optical properties, as well as their microstructure (local and medium range structure) is very important over the entire glass forming range of compositions of the glass systems. It is generally known [15-19] that Ge-based chalcogenide glasses usually display a photobleaching effect upon illumination with band gap light, an effect which can be reversed after subsequent annealing [17-19] at an appropriate temperature below the glass transition temperature T_g . In fact, these photoinduced and thermally induced changes in their optical properties are often accompanied by structural changes which can be readily detected by Raman spectroscopy.

The structure of $\text{Ge}_x\text{S}_{1-x}$ glasses at ambient conditions has been studied in the past by several groups [20-27] using Raman spectroscopy as the probing technique. It is generally accepted that a phase separation takes place in S-rich $\text{Ge}_x\text{S}_{1-x}$ glasses ($x < 1/3$), with the excess sulphur forming S_8 ring clusters enclosed in the matrix of a, by large, *corner sharing $\text{Ge}-(\text{S}_{1/2})_4$ tetrahedra network*. In contrast, two different models have been proposed for the compound GeS_2 ($x=1/3$) and the Ge-rich ($x > 1/3$) glasses : According to the first [20,21], the structure of these glasses consists of an extended three dimensional and, more or less, chemically ordered network of $\text{Ge}-\text{S}_n\text{Ge}_{4-n}$ ($n=0,1,2,3,4$) tetrahedra centered about Ge atoms which are bonded to S and other Ge atoms, with the parameter n being largely determined by the S and Ge contents. In the second model, introduced [22,28] for the compound GeS_2 and GeSe_2 glasses, a layered structure is proposed similar to the two-dimensional (2D) crystalline phase [29-31] of the respective compound materials; in this model, the glass is built up by fragments of the

2D-phase, with each fragment consisting of *corner-sharing tetrahedra chains bridged by edge-sharing tetrahedra* and being terminated by S-S (Se-Se) dimers which have directions perpendicular to the chains.

It is well known that GeS₂ is a polymorphous material exhibiting, apart from the glassy phase, several crystalline phases having rather complicated low symmetry structures with a large number of molecules in the unit cell [29]. At ambient conditions, GeS₂ can be found in two main crystalline modifications : (i) a three-dimensional structure (3D-GeS₂) in which the crystal lattice is made up by an extended array of *only corner sharing Ge-(S_{1/2})₄ tetrahedra*, and (ii) a layered structure (2D-GeS₂) in which the lattice is built up by *both corner-sharing and edge-sharing tetrahedra*; in the latter structure, chains of corner-sharing tetrahedra are bridged via edge-sharing tetrahedra along a direction perpendicular to the chains. The two crystal phases can be distinguished in Raman experiments by the different frequency of the strongest (main) A₁ mode which has been unambiguously assigned in both phases to symmetric stretching of S atoms in corner-sharing tetrahedra along the direction of chains. This mode was observed at 339 cm⁻¹ in the 3D-phase [30], while there is a disagreement for the 2D-phase with one report [30] claiming a frequency of 356 cm⁻¹ [30] and another at 363 cm⁻¹ [31].

A characteristic feature of the Raman spectrum of the glassy phase of GeS₂ is a polarized band [20-27] for which, it was originally thought, there was no counterpart in the crystal phases. This so-called companion A₁^c mode, with a frequency (374 cm⁻¹) about 10% greater than the normal A₁ mode (342 cm⁻¹) of the glassy phase, exhibits an anomalous dependence of intensity with composition in Ge_xS_{1-x} alloys [20,26]. The existence of this band in the Raman spectra of GeS₂ and GeSe₂ glasses prompted the proposition of the fragmented layered structure model [22,28] for these glasses and the band itself was assigned to symmetric vibrations of S-S dimers [22]. Elsewhere, the A₁^c band was associated with the medium range order (MRO) [23-25]. Finally, in another report [26], bearing in mind the higher frequency of this band compared to the A₁ one, it was predicted that it should be related to *symmetric stretching of S atoms in bridges of edge-sharing tetrahedra*, by virtue of the higher force constant in the bridges in comparison to the chains.

There have not been any studies of structure of Ge-based chalcogenides glasses at high temperatures, although it is generally accepted that they crystallize above T_g. Most part of this work is concerned with the structural changes (as seen by Raman spectroscopy) occurring in glasses of the basic binary alloy system Ge_xS_{1-x} from room temperature, through T_g and T_m (melting point) and up to a temperature of about 130 K above T_m. The main objectives of the present work are : (i) to study the evolution of the Raman spectra with increasing temperature of the glasses and through the observed changes to draw conclusions about certain ambiguous spectral features, such as the controversial A₁^c companion Raman band, and the structure of these glasses as a whole, (ii) the systematic recording of structural changes taking place first with increasing and then with decreasing temperature and (iii) to obtain an idea about the structure of the Ge_xS_{1-x} melts and relate it to the structure of the respective glasses, in an attempt to get an insight on the mechanism of glass formation from the melt (quenching of the melt). In addition, Raman measurements at high hydrostatic pressures have been carried out in GeS₂ glass in order to detect any changes of the structural units with pressure and to study the pressure dependence of the glassy network as a whole.

2. Experimental procedures

Glasses of the Ge_xS_{1-x} system covering a wide glass-forming region (0.17 ≤ x ≤ 0.45) were prepared using the melt quenching technique. Melts of predetermined atomic contents were kept inside a crucible at a temperature of about 100 K above T_m under rocking for about 24 hours, after which period the crucible was transferred quickly to water. The samples for the high temperature measurements were held inside small vacuum tight silica cells to avoid chemical changes of the materials, because GeS₂, and Ge-S alloys in general, decompose [32] and oxidize [33] in open space before they melt. The same samples and cells were used for the measurements of Raman spectra of molten Ge_xS_{1-x} alloys. A vacuum operated optical furnace [34] of low temperature gradients was used for the high temperature experiments. The high pressure experiments were performed using a diamond

anvil cell (DAC) [35] which was loaded with a small size ($\sim 50 \mu\text{m}$) glassy sample for the Raman measurements and ruby chips for monitoring (via the ruby luminescence) the pressure.

Two Raman set-ups were used for recording the spectra of glasses and their melts : One JOBIN YVON model T 64000 triple monochromator equipped with microscope and CCD detector for ambient conditions measurements, and a conventional SPEX model 1403 double monochromator for the high temperature and high pressure experiments. The 488 and 514.5 nm lines of an Ar^+ laser were mainly used, but at very high temperatures (in molten state) the 647 nm line of a Kr^+ laser was also used. The spectral slit width was between 3 and 4 cm^{-1} for either double and triple monochromator set-up. Details regarding experimental procedures have been given elsewhere [36].

3. Results and discussion

3.1. Raman spectra of $\text{Ge}_x\text{S}_{1-x}$ glasses at ambient conditions

In this section we present and discuss briefly our ambient conditions Raman data in connection with previous relevant studies, in order to provide the necessary background for discussing the high temperature and pressure data. Fig. 1 shows the polarized Raman spectra of $\text{Ge}_x\text{S}_{1-x}$ glasses for four compositions: two S-rich glasses ($x=0.20, 0.30$), the stoichiometric (compound) GeS_2 glass ($x=1/3$) and one Ge-rich glass ($x=0.35$). There is good agreement between the Raman spectra of this work and those reported previously [20-27].

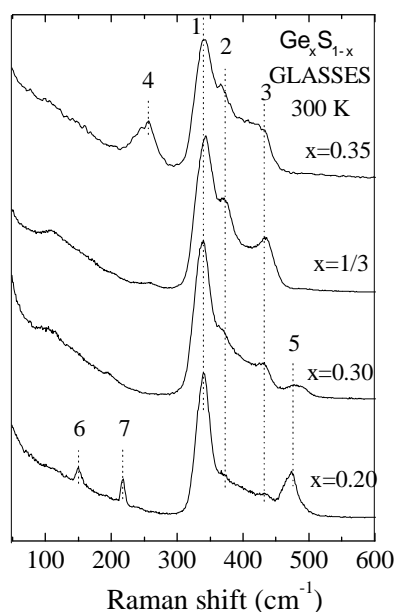


Fig. 1. Raman spectra of $\text{Ge}_x\text{S}_{1-x}$ glasses for the compound ($x=1/3$), one Ge-rich ($x=0.35$) and two S-rich ($x=0.20, 0.30$) compositions.

In the Raman spectrum of the compound GeS_2 glass (Fig. 1), four bands are clearly observed at 110, 342, 374 and 434 cm^{-1} and a fifth one is marginally observed at $\sim 260 \text{ cm}^{-1}$. The band at 110 cm^{-1} has been attributed [27] to bond bending vibrations of S atoms in $\text{Ge}-(\text{S}_{1/2})_4$ tetrahedra, but judging from its low frequency and broad character we suggest that it may be due to intermolecular displacements of whole tetrahedral units. The bands at 342 and 374 cm^{-1} are polarized and correspond to the A_1 (main) and A_1^c (companion) modes mentioned in the introduction; it is generally accepted that the former is due to symmetric stretching of S atoms in the tetrahedra, while the latter has been a matter of controversy in the past and its origin is discussed in the next section 3.2 as is deduced from its temperature dependence. The band at 434 cm^{-1} is relatively depolarized (compared to the A_1 and A_1^c bands) and has been attributed to S-S bond stretching since a similar band has been observed in both fibrous [37] and liquid [38] sulphur which are known to contain sulphur chains. This implies the

existence of either separate small sulphur chains in the network of GeS_2 glass or interconnecting S-S units between tetrahedra. The appearance of homopolar (defective) S-S bonds in the compound glass indicates a deviation from the ideal network of only $\text{Ge}(\text{S}_{1/2})_4$ tetrahedral units. In this situation homopolar Ge-Ge bonds should, also, be present in the network of GeS_2 glass and this is confirmed by the observation of the weak band at 260 cm^{-1} which is attributed to such bonds as a similar band has been observed in amorphous Ge [39]. This argument is, also, supported by the big enhancement of intensity of this band in the Ge-rich $\text{Ge}_x\text{S}_{1-x}$ glasses (Fig. 1). Further increase of the Ge-content ($x > 0.35$) results in the appearance of other broad bands at lower frequencies ($< 250\text{ cm}^{-1}$), an effect combined by a drop of intensity of the 260 cm^{-1} as well the A_1 and A_1^c bands, thus indicating a reduction of the $\text{Ge}(\text{S}_{1/2})_4$ tetrahedral population.

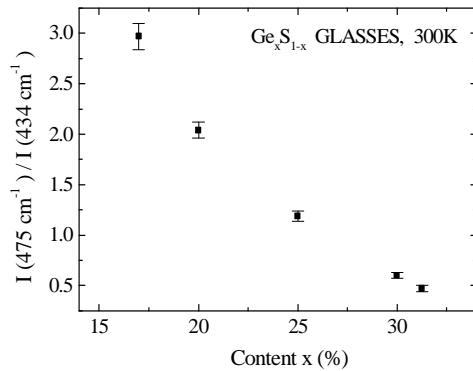


Fig. 2. Ratio of integrated intensities of the 475 to the 434 cm^{-1} bands for $\text{Ge}_x\text{S}_{1-x}$ glasses plotted against Ge content.

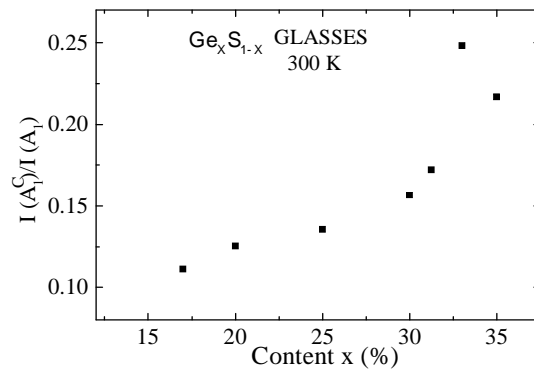


Fig. 3. Ratio of integrated intensities of the $A_1(342\text{ cm}^{-1})$ to the $A_1^c(374\text{ cm}^{-1})$ plotted against Ge content.

Another polarized band at 475 cm^{-1} is observed in the spectra of the S-rich $\text{Ge}_x\text{S}_{1-x}$ glasses (Fig. 1) for which there is general agreement [20-27] that is due to symmetric stretching in S_8 rings. The intensity of this band increases with increasing S-concentration, while that of the 434 cm^{-1} band decreases, showing a relative population increase of S_8 rings against S-S chains. This effect is illustrated in Fig. 2 in which the integrated intensities ratio of the 475 to 434 cm^{-1} bands is plotted against concentration. This ratio increases non-linearly with increasing S- (decreasing Ge-) content. The integrated intensities were deduced by fitting the bands to Gaussian functions.

3.2. High temperature phase transitions of $\text{Ge}_x\text{S}_{1-x}$ glasses

Figs. 4 - 7 show the Raman spectra of four $\text{Ge}_x\text{S}_{1-x}$ glasses at various temperatures from room temperature up to a temperature close to melting point of the respective alloy. Also, in the same Figs. 4 - 7, the Raman spectra of the materials are shown after free (unforced) cooling to room temperature. Specifically, the four compositions include: the compound GeS_2 glass ($x = 1/3$, Fig. 4), one moderately rich in Ge glass ($x = 0.35$, Fig. 5), one moderately rich in S glass ($x = 0.30$, Fig. 6) and a highly enriched in S one ($x = 0.20$, Fig. 7).

From the evolution of the Raman spectrum of GeS_2 glass (Fig. 4), we conclude that two gradual phase transitions take place in this glass at high temperatures. First, at $\sim 750\text{ K}$ the main A_1 band becomes sharper, an effect which is accompanied by a simultaneous appearance of new sharp bands at low frequencies. At $\sim 770\text{ K}$, this band is quite narrow and looks similar (in terms of frequency, intensity and narrowness) to the characteristic A_1 mode of the 3D-crystalline phase [30]. This sharp band is observed at $\sim 337\text{ cm}^{-1}$, that is slightly shifted (compared to the value of 339 cm^{-1} , Ref.30) towards the lower frequencies because the material is at elevated temperature. All these observations indicate that the compound GeS_2 glass undergoes a transition to the 3D-crystalline phase at $\sim 750\text{ K}$. Further increase of temperature to 800 K results in the appearance of a new line at $\sim 352\text{ cm}^{-1}$ which becomes stronger and sharper above this temperature at the expense of the rival A_1 band of

the 3D-phase. This new band is the dominant feature of the spectrum above 900 K and up to melting point T_m (=1123 K), and corresponds to the characteristic A_1 mode of the 2D-crystalline phase [29,31]. This is confirmed by slow cooling of the material to room temperature (Fig. 4), with the 2D-phase being retained throughout the cooling process. This observation also shows that the two step crystallization of GeS_2 glass is irreversible. The first transition to the 3D-phase implies that the network of the GeS_2 glass is, largely, three-dimensional, with the corner-sharing tetrahedra linkages being dominant over the edge-sharing ones. Finally, it should be noted that the 434 cm^{-1} band of GeS_2 diminishes with increasing temperature, well below the crystallization temperature.

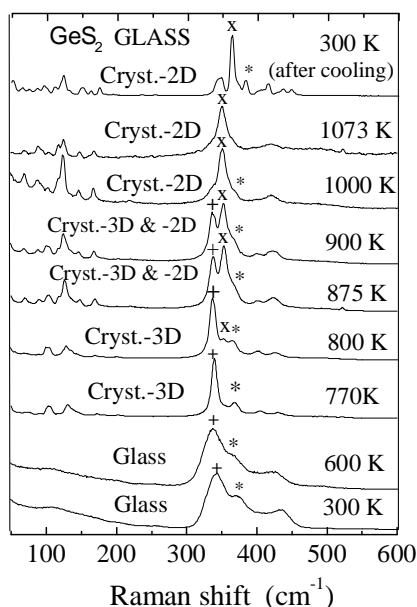


Fig. 4. Evolution of the Raman spectrum of GeS_2 glass showing a two step irreversible crystallization. + main A_1 band of glassy phase; $*A_1^c$ companion band of glassy phase; X main A_1 band of the 2D-crystalline phase.

The evolution of the A_1^c band of GeS_2 glass with temperature reveals that this band has, after all, a counterpart in the crystalline phases and this has been concluded after deconvoluting the high temperature Raman spectra. This band (and its successor in the 3D-phase) is well resolved up to 850 K, while above this temperature is seen (in the unconvoluted spectra) as a shoulder; however, it reappears upon cooling and is clearly resolved below 700 K, with a frequency of 382 cm^{-1} in the room temperature spectrum of the 2D-phase. A similar band has been observed previously [29,31] in the Raman spectrum of the 2D-single crystal of GeS_2 and assigned to symmetric stretching of S atoms in bridges of edge-sharing tetrahedra; hence, a similar assignment is implied for the A_1^c band of GeS_2 glass, in agreement with previous predictions[26].

A similar two-step crystallization is observed at high temperatures in $\text{Ge}_x\text{S}_{1-x}$ glasses having compositions close to that of the compound GeS_2 glass, first to 3D- and then to the 2D-phase (Figs. 5 and 6). The 2D-phase is maintained up to melting point and following a subsequent cooling to room temperature, showing that crystallization of these moderately enriched in Ge and S glasses is also irreversible.

In the $\text{Ge}_x\text{S}_{1-x}$ glass highly enriched in S, though, the structural changes observed at high temperatures are different (Fig. 7). It is reminded that a phase separation takes place in such glasses, with S_8 ring clusters forming in the matrix of predominantly corner-sharing tetrahedra (three-dimensional glassy network, see also Fig. 3). Around 720 K, the A_1 band becomes narrower, indicating that crystallization of the glassy matrix commences to the 3D-phase of GeS_2 , a phase maintained up to melting point. (The exact value of the melting point for this glass is not known, but one can guess it should be around 870 K as the intensity of the spectrum drops substantially at this temperature, Fig. 7). It is significant that after cooling, the spectrum of the material is similar (both with regard to the

lineshape and intensity) to that of the starting glass (Fig. 7), indicating that the one-step crystallization of highly enriched in S glasses is reversible. It has been observed in a previous work [40] that three-dimensional glassy networks of Ge-based chalcogenides favour the appearance of photo- and thermally-induced reversible structural changes because of their larger free volume. Here, the matrix of the highly rich in S glass has a largely three-dimensional structure which, it seems facilitates successive reversible transitions from glass to crystal, but *always retaining its three dimensional character*. The latter should be attributed to the excess sulphur which fills the voids of the glassy matrix, thus preventing the network from becoming two-dimensional as is the case for glasses close to stoichiometry. A more detailed account of the high-temperature transitions is given elsewhere [36].

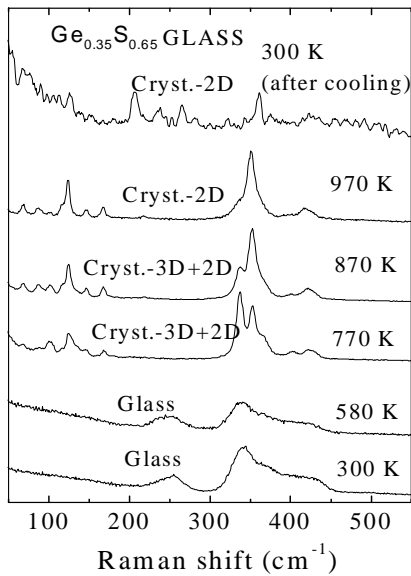


Fig. 5. Temperature dependence of Raman spectrum of $\text{Ge}_{0.35}\text{S}_{0.65}$ glass (slightly rich in Ge) showing a two step irreversible crystallization to the 3D- and 2D-phases of GeS_2 .

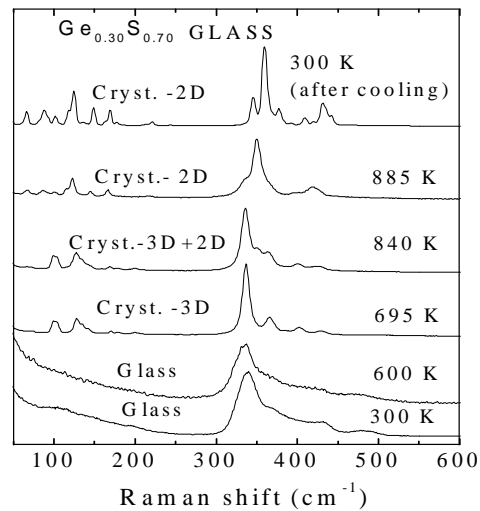


Fig. 6. Temperature dependence of Raman spectrum of $\text{Ge}_{0.30}\text{S}_{0.70}$ glass (moderately rich in S) showing a two stage irreversible crystallization to the 3D- and 2D-phases of GeS_2 .

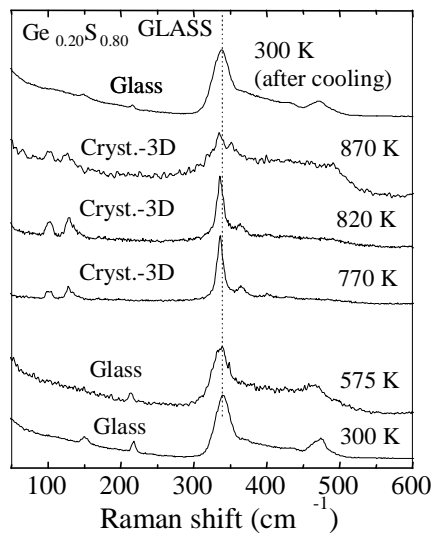


Fig. 7. Temperature dependence of Raman spectrum of the $\text{Ge}_{0.20}\text{S}_{0.80}$ glass (highly rich in S) showing a one stage reversible crystallization to the 3D-phase of GeS_2 .

3.3. Raman spectra of $\text{Ge}_x\text{S}_{1-x}$ melts

The Raman signal from all $\text{Ge}_x\text{S}_{1-x}$ alloys drops abruptly above melting point as the molten samples become almost opaque to any laser line in the visible, that is, they acquire metallic behaviour. As a consequence, the Raman spectrum of the hot silica cell (SiO_2 glass) appears in the recorded spectrum as noise which exceeds the signal from the melt. However, we have succeeded to obtain the Raman spectrum of pure melts by subtracting, in each case, the Raman spectrum of the cell which has been recorded separately (without sample inside it) at a temperature coinciding or close to that of the melt

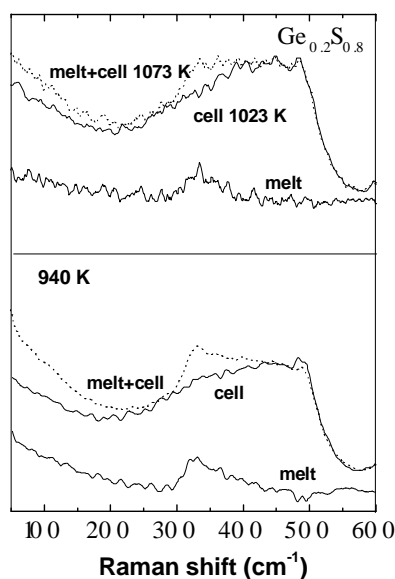


Fig. 8. Raman spectra of molten $\text{Ge}_{0.20}\text{S}_{0.80}$ at two temperatures showing the characteristic band (at $\sim 320 \text{ cm}^{-1}$) due to tetrahedral $\text{Ge}-(\text{S}_{1/2})_4$ units. The Raman spectrum of the silica cell was recorded separately and subtracted from the overall spectrum of melt and cell.

As an example, we present in Fig. 8 the Raman spectrum of the $\text{Ge}_{0.20}\text{S}_{0.80}$ melt at two temperatures as is deduced from the above described procedure. The detection of a weak band at $\sim 330 \text{ cm}^{-1}$ in the spectrum of the pure melt provides evidence that the tetrahedral $\text{Ge}-(\text{S}_{1/2})_4$ units exist in this molten alloy, at least at the lower temperature of 940 K. As the temperature is increased further (1073 K), this Raman band of the melt is only marginally observed (Fig. 8), which can be explained in terms of an increased melt opaqueness or of shorter life-times of the tetrahedral species with temperature. The latter interpretation is compatible with the suggestion that at high temperatures and particularly in the molten phase, the coordination number of Ge changes from 4 to 8 and the element becomes metallic [41,42]. This also explains the opaqueness of $\text{Ge}_x\text{S}_{1-x}$ melts. Similar results have been obtained from other $\text{Ge}_x\text{S}_{1-x}$ melts.

3.4. Raman spectrum of GeS_2 glass at high pressures

The pressure dependence of the Raman spectrum of GeS_2 glass is shown in Fig. 9 for pressures up to 10.8 GPa. Also, in the same figure, the Raman spectrum of the glass is shown after pressure relief. A substantial shift towards the higher frequencies is observed of the whole packet of molecular bands, i.e. the main A_1 band at 342 cm^{-1} , the companion A_1^c band at 374 cm^{-1} and the band due to S-S bonds at 434 cm^{-1} , although only the position of the A_1 band is unambiguously detected at high pressures. These results indicate a substantial densification of the glass and a continuous decrease of the Ge-S and S-S bond lengths with pressure. The band at 260 cm^{-1} is not detected at high pressures.

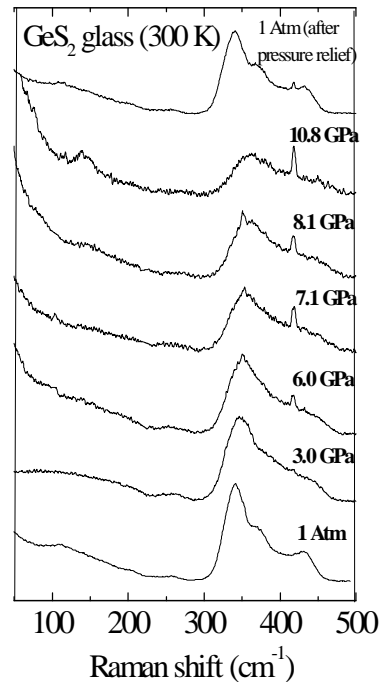


Fig. 9. Pressure dependence of the Raman spectrum of GeS₂ glass showing a strong hardening of the Raman bands.

We have also observed a darkening of the glass at high pressures and a consequent continuous loss of transparency to all laser lines in the visible, which is in agreement with the strong red shift of the absorption edge observed in this glass with pressure [43]. This effect causes a big drop of the Raman intensity from the glass at high pressures and, most likely, results in the emergence of a sharp line at $\sim 420 \text{ cm}^{-1}$ at a pressure of $\sim 5 \text{ GPa}$ which is attributed [44] to Raman scattering from the sapphire (Al₂O₃) window of the DAC or/and the ruby chips. This line emerges in the spectrum at high pressures when the Raman signal of the glass becomes very weak. Above 10 GPa, the glass became almost opaque to visible radiation. After releasing the pressure, the spectrum of GeS₂ glass returns back, more or less, to its initial lineshape and intensity, thus implying no significant hysteresis effects in the glass.

4. Conclusions

The study of the Raman spectra of Ge_xS_{1-x} glasses at high temperatures has shown that all glasses undergo a first-step transition to the 3D-crystalline phase of GeS₂ which confirms that the network of these glasses is, by large, three-dimensional. At higher temperatures, the compound GeS₂ and the moderately rich in Ge or S glasses sustain a second transition to the layered 2D-crystalline phase of GeS₂ which is irreversible upon subsequent cooling to room temperature. In the highly rich in S glass, though, whose glassy matrix is made up almost exclusively of corner-sharing Ge-(S_{1/2})₄ tetrahedra, there is no second transition to the 2D-phase, with the material maintaining the 3D-crystal structure up to melting point and then reversing to its initial glassy state after cooling to room temperature; the reversibility and dimensionality preservation of the matrix of this glass is attributed to the presence of S₈ ring clusters which "fill" the free volume of the three-dimensional matrix.

From the evolution of the A₁^c companion band of GeS₂ glass in the crystalline phases, we have concluded that this band is due to symmetric stretching of S atoms in bridges of edge-sharing tetrahedra, in agreement with previous predictions.

All $\text{Ge}_x\text{S}_{1-x}$ alloys become almost opaque above melting point and this is related to the metallic behaviour of Ge in the molten phase. However, there is evidence that the tetrahedral $\text{Ge}-(\text{S}_{1/2})_4$ units exist in the melts of these alloys, at least up to a certain temperature.

The application of pressure on the GeS_2 glass results in a continuous densification of the glass which is manifested by the substantial hardening of the Raman bands with increasing pressure. The material darkens continuously with pressure because of a strong red shift of its absorption edge, but maintains its glassy phase throughout the pressure range (up to 10.8 GPa). It appears that all pressure induced effects (volume, bond lengths and optical transparency) are reversible after bringing the glass to ambient pressure.

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References

- [1] A. Yoshikawa, O. Ochi, H. Nagai, Y. Mizushima, *Appl. Phys. Lett.* **29**, 677 (1976).
- [2] M. J. Bowden, *Solid State Technology*, June 1981, p. 73.
- [3] D. Adler, *Scientific American* **236**, 36 (1977).
- [4] S. R. Ovshinsky, *J. Non-Cryst. Solids* **141**, 200 (1992).
- [5] V. M. Lyubin, V. K. Tikhomirov, *J. Non-Cryst. Solids* **164-166**, 1211 (1993).
- [6] M. Mitkova, T. Petkova, R. Markovski, V. Mateev, *J. Non-Cryst. Solids* **164-166**, 1247 (1993).
- [7] P. J. S. Ewen, A. Zekak, C. W. Slinger, G. Dale, D. A. Pain, A. E. Owen, *J. Non-Cryst. Solids* **164-166**, 1203 (1993).
- [8] H. Hisakuni, K. Tanaka, *Optics Lett.* **20**, 958 (1995).
- [9] B. G. Aitken, R. S. Quimby, *J. Non-Cryst. Solids* **213&214**, 281 (1997).
- [10] T. Ide, M. Suzuki, M. Okuda, *Japan. J. Appl. Phys, Part II* **34**, L529 (1995).
- [11] K. Tai, E. Ong, R. G. Vadimsky, *Proc. Electrochem. Society* **82-89**, 9 (1995).
- [12] V. Krasteva, D. Machewirth, G. H. Sigel Jr., *J. Non-Cryst. Solids* **213&214**, 304 (1997).
- [13] H. Harada, K. Tanaka, *J. Non-Cryst. Solids* **246**, 189 (1999).
- [14] D. A. Turnbull, B. G. Aitken, S. G. Bishop, *J. Non-Cryst. Solids* **244**, 260 (1999).
- [15] R. A. Street, R. J. Nemanich, G. A. N. Connel, *Phys. Rev.* **B 18**, 6915 (1978).
- [16] A. V. Kolobov, B. T. Kolomiets, V. M. Lyubin, N. Sebastian, M. A. Taguirdzanov, J. Hajto, *Soviet Phys. Solid State* **24**, 603 (1982).
- [17] K. Shimakawa, A. V. Kolobov, S. R. Elliott, *Adv. Phys.* **44**, 475 (1995).
- [18] C. Raptis, Z. G. Ivanova, *J. Appl. Phys.* **64**, 2617 (1988).
- [19] M. Vlcek, C. Raptis, T. Wagner, A. Vidourek, M. Frumar, I. P. Kotsalas, D. Papadimitriou, *J. Non-Cryst. Solids* **192&193**, 669 (1995).
- [20] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, H. A. Six, *Phys. Rev.* **B 10**, 5134 (1974).
- [21] G. Lucovsky, R. J. Nemanich, F. L. Galeener, *Proc. of 7th Intern. Confer. on Amorphous and Liquid Semiconductors*, Edinburgh, 1977 (Ed. W.E. Spear), p. 130.
- [22] P. M. Bridenbaugh, G. P. Espinosa, J. E. Griffiths, J. C. Phillips, J. P. Remeika, *Phys.*

- Rev. **B 20**, 4140(1979).
- [23] K. Murase, K. Yakushiji, T. Fukunaga, *J. Non-Cryst. Solids* **59&60**, 855 (1983).
- [24] K. Arai, *J. Non-Cryst. Solids* **59&60**, 1059 (1983).
- [25] P. Boolchand, J. Grothaus, M. Tenhover, M. A. Hazle, R. K. Grasselli, *Phys. Rev.* **B33**, 5421 (1986).
- [26] S. Sugai, *Phys. Rev.* **B 35**, 1345 (1987).
- [27] Ke. Tanaka, M. Yamaguchi, *J. Non-Cryst. Solids* **227-230**, 757 (1998).
- [28] J. A. Aronovitz, J. R. Banavar, M. A. Marcus, J. C. Phillips, *Phys. Rev.* **B 28**, 4454 (1983).
- [29] Z. V. Popovic, H. J. Stolz, *Phys. Status Solidi* **B 106**, 337 (1981).
- [30] K. Inoue, O. Matsuda, K. Murase, *Solid State Commun.* **79**, 905 (1991).
- [31] Z. V. Popovic, M. Holtz, K. Reiman, K. Syassen, *Phys. Status Solidi* **b 198**, 533 (1996).
- [32] G. J. Janz, *Molten Salts Handbook* (Academic Press, New York, 1967).
- [33] L. Tichy, A. Triska, M. Frumar, H. Ticha, *Philos. Mag.* **54**, 219 (1986).
- [34] C. Raptis, *J. Phys. E* **16**, 749 (1983).
- [35] K. R. Hirsch, W. B. Holzappel, *Rev. Sci. Instrum.* **52**, 149 (1981).
- [36] I. P. Kotsalas, C. Raptis, *Phys. Rev. B*, accepted for publication.
- [37] W. Dultz, H. D. Hochheimer, W. Muler-Lierheim, *Proc. of 5th Intern. Confer. on Amorphous and Liquid Semiconductors*, Vol. **II** (Taylor Francis, London, 1974).
- [38] K. Hattori, H. Kawamura, *J. Non-Cryst. Solids*, **59&60**, 1063 (1983).
- [39] J. C. Lannin, N. Malley, S. T. Kshirsagar, *Solid State Commun.* **53**, 939 (1985).
- [40] I. P. Kotsalas, D. Papadimitriou, C. Raptis, M. Vlcek, M. Frumar, *J. Non-Cryst. Solids* **226**, 85 (1998).
- [41] R. Zallen, *The Physics of amorphous Solids* (John Wiley & Sons, 1983), p. 254.
- [42] A. C. Wright, *NATO ASI Series 3*, Vol. **23**, Ed. M. F. Thorpe and M. I. Mitkova (Kluwer, 1997), p. 83.
- [43] B. A. Weinstein, R. Zallen, M. L. Slade, J. C. Mikkelsen Jr., *Phys. Rev.* **B 25**, 781 (1982).
- [44] S. P. S. Porto, R. S. Krishnan, *J. Chem. Phys.* **47**, 1009 (1967).