

High-temperature structural phase transitions of $\text{Ge}_x\text{S}_{1-x}$ alloys studied by Raman spectroscopy

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(Received 27 December 2000; revised manuscript received 6 June 2001; published 11 September 2001)

A high-temperature Raman study of $\text{Ge}_x\text{S}_{1-x}$ alloys is reported up to a temperature close to the melting point, including both Ge-rich ($x=0.35$) and S-rich ($x=0.20, 0.30$) glasses, as well as the compound glass ($g\text{-GeS}_2$; $x=\frac{1}{3}$). The variation in the Raman spectra indicates that above certain temperatures $g\text{-GeS}_2$ gradually crystallizes, first to the three-dimensional (3D) phase and then to the layered two-dimensional (2D) phase, with the latter being maintained up to melting point and upon subsequent cooling to room temperature. There is evidence that the controversial A_1^c companion band of $g\text{-GeS}_2$ evolves to a counterpart band of the 2D crystalline phase, implying that this band is due to symmetric stretch vibrations of S atoms in *bridges of edge-sharing $\text{Ge}(\text{S}_{1/2})_4$ tetrahedra*, in agreement with a previous prediction. Similar two step irreversible crystallization to the 3D and 2D phases of GeS_2 have been observed above T_g for the moderately rich in Ge ($x=0.35$) or in S ($x=0.30$) $\text{Ge}_x\text{S}_{1-x}$ glasses, but at lower thresholds of crystallization temperature. In the strongly enriched in S ($x=0.20$) glass, though, crystallization takes place only to the 3D phase of GeS_2 , a process which is reversible after cooling the alloy to room temperature, i.e., the material returns to its initial amorphous phase. This reversible crystallization is explained in terms of the three-dimensional network of S-rich $\text{Ge}_x\text{S}_{1-x}$ glasses which evolves only to the respective 3D crystalline phase lattice at high temperatures. It is pointed out that all $\text{Ge}_x\text{S}_{1-x}$ glasses studied undergo a first-step transition to the 3D crystalline phase, which shows that the *network of these glasses is, by large, three dimensional*.

DOI: 10.1103/PhysRevB.64.125210

PACS number(s): 78.30.Ly; 61.43.Dq; 64.70.Kb

I. INTRODUCTION

Raman spectroscopy has been a valuable probing technique for the study of structure of stoichiometric ($x=\frac{1}{3}$) and nonstoichiometric $\text{Ge}_x\text{S}_{1-x}$ glasses.¹⁻⁸ Unambiguous assignment of the broad and (often) overlapping Raman bands of these glasses has not always been possible, though, thus leading to diverse structural interpretations. One undisputed result concerning the S-rich ($x<\frac{1}{3}$) alloys is that a molecular phase separation occurs in these glasses, namely, the excess sulphur forms S_8 ring clusters situated like islands in the glassy matrix of $\text{Ge}(\text{S}_{1/2})_4$ tetrahedra which are linked by one (common) or two (in chain) S atoms; this was reported by Lucovsky *et al.*¹ in their early Raman (and IR) work and confirmed later in similar studies by other groups.^{4,6} It is therefore expected that in S-rich glasses there exist Ge-S and S-S bonds, but not Ge-Ge ones. For the stoichiometric GeS_2 and the Ge-rich ($x>\frac{1}{3}$) $\text{Ge}_x\text{S}_{1-x}$ glasses, Lucovsky *et al.*^{1,2} proposed an extended three-dimensional and, by large, chemically ordered network of $\text{Ge-S}_n\text{Ge}_{4-n}$ ($n=0,1,2,3,4$) tetrahedra centered about Ge atoms which are bonded to S and Ge neighboring atoms at a (macroscopically average) ratio determined by the S and Ge contents. As such, this model for Ge-rich glasses excludes S-S bonds.

A considerably different structural model was introduced for the stoichiometric GeS_2 (and its isomorphous GeSe_2) glass by Bridenbaugh *et al.*³ and advanced by Aronovitz *et al.*⁹ based on Raman measurements and calculations of density of states in large clusters, respectively. Bridenbaugh *et al.*³ were led to their proposition by the observation in both GeS_2 and GeSe_2 of a polarized Raman line (for which, it was believed, there was no counterpart in the crystal) with

a frequency of about 10% greater than the normal A_1 mode. In contrast to the A_1 mode, the intensity of this so-called companion A_1^c mode displays an anomalous composition dependence^{7,10} in $\text{Ge}_x\text{S}_{1-x}$ and $\text{Ge}_x\text{Se}_{1-x}$ alloys. Bearing in mind its polarized spectral features, it was pointed out^{3,9} that the A_1^c mode is most likely associated with symmetric motions of S atoms (different from the symmetric breathing motions assigned to the A_1 mode) and that the structure of $\text{GeS}_2(\text{Se}_2)$ glasses could not be described by a highly disordered three-dimensional network of corner sharing $\text{GeS}_4(\text{Se}_4)$ tetrahedra; instead, they proposed^{3,9,11} a model of clusters having a layered structure similar to the high-temperature two-dimensional (2D) crystal phase. In this model, each cluster is regarded as a fragment of the 2D crystal phase and consists of corner-sharing tetrahedra chains linked to each other via bridges of edge-sharing tetrahedra; unlike the crystal, however, each cluster is terminated by S-S(Se-Se) dimers along a direction perpendicular to the chain axis. The A_1^c mode was then attributed to symmetrical vibrations of the S-S dimers. Similar or modified terminating cluster models were adopted later by other groups^{4,5} which generally associate the A_1^c companion mode with the medium-range order (MRO).

A third model proposed by Boolchand *et al.*⁶ suggests a broken heterogeneous network consisting of two types of molecular clusters: the first type is similar to the layered structure fragments described in the previous paragraph,^{3,9} while the second involves chains of ethane-like $\text{S}_3\text{Ge-GeS}_3$ structural units.

At ambient conditions GeS_2 displays two crystalline modifications, both having complicated low symmetry (most likely monoclinic) structures with several molecules in the

unit cell.^{12,13} It is generally considered^{12,14} that in the three-dimensional structure (3D-GeS₂), often mentioned in the literature as the low-temperature phase, the GeS₄ tetrahedral units are linked via common corners only (one common S atom in the tetrahedra corners). The other modification is a layered structure (2D-GeS₂), known as the high-temperature phase, in which both corner-sharing and edge-sharing tetrahedral linkages exist;^{13–16} in this structure, chains of corner sharing tetrahedra are bridged via edge-sharing tetrahedra in a direction perpendicular to the chains. It must be said that the terms low- and high-temperature phase are associated with the method of growth of the respective crystal polymorphs rather than the temperature region of phase stability. Room-temperature Raman studies of both crystalline phases of GeS₂ have been reported^{14–16} showing in either case a spectrum of about 70 Raman active modes, most of them in close proximity with each other. A complete, unambiguous mode assignment has not been possible, though, because of the complexity of crystal structures. However, the two phases can be distinguished in Raman measurements by the different frequency of the most intense A_1 mode which has been unambiguously attributed^{14,16} in either phase to symmetric stretch vibrations of S atoms along the direction of chains of corner-sharing tetrahedra. This mode is observed at 339 cm⁻¹ for the 3D phase,¹⁴ but there is a discrepancy regarding its frequency for the 2D phase: Inoue *et al.*¹⁴ have reported it at 356 cm⁻¹, while Popovic *et al.*¹⁶ at 363 cm⁻¹. In *g*-GeS₂ the two characteristic A_1 and A_1^c Raman modes have been observed^{1–8} at 342 and 374 cm⁻¹, respectively. These modes are also observed in the Raman spectra of non-stoichiometric Ge_xS_{1-x} glasses,^{1,2,4,7} with an intensity ratio $I(A_1^c)/I(A_1)$ varying nonlinearly with composition.^{1,7}

The main objective of this work is to study the Raman spectra of Ge_xS_{1-x} glasses at high temperatures and register systematically any spectral changes taking place in them up to a temperature close to melting point, which can be used as evidence for structural changes. Both Ge- and S-rich glasses, as well as the stoichiometric *g*-GeS₂ have been investigated. It is generally known that chalcogenide glasses crystallize above their T_g , but in the case of the Ge_xS_{1-x} alloys, there have been no relevant publications reporting high-temperature phase transitions of these glasses. In addition, the temperature dependence of Raman spectra provides an appropriate opportunity to study the evolution of the controversial A_1^c mode in the crystal phase(s) and thus draw evidence about its origin.

II. EXPERIMENT

Samples of Ge_xS_{1-x} glasses of various compositions ($0.17 \leq x \leq 0.45$) and of good optical quality were prepared by quenching the respective melts to water from a temperature of about 100 K above melting point. The melts were kept in the crucible for 24 h, under rocking in order to maximize their homogeneity. The highest melting point (1125 K) corresponds to the stoichiometric GeS₂ material.^{15,17} The Raman spectra of several glasses with compositions varying from a strongly rich in S ($x=0.17$), through the stoichiometric ($x=\frac{1}{2}$) and up to one with an excessive Ge content

($x=0.45$) were measured at room temperature.

For the high-temperature Raman measurements four glasses were chosen: Ge_{0.20}S_{0.80}, Ge_{0.30}S_{0.70}, GeS₂, and Ge_{0.35}S_{0.65}. It was not possible to study at high temperatures glasses near the end of the Ge-rich side of the composition spectrum ($x \sim 0.45$) because such glasses absorb strongly the laser lines, resulting in very weak Raman signals. The samples for the temperature-dependence measurements were held in vacuum inside small sealed silica cells in order to avoid material degradation as it is known that GeS₂ (and the related Ge_xS_{1-x} alloys) decomposes¹⁷ in free space before it melts, and also oxidizes¹⁸ in atmospheric air. The silica cell was positioned centrally inside a vacuum operated furnace¹⁹ of low-temperature gradients.

Raman spectra of glasses at room temperature were recorded using mainly a JOBIN-YVON model T 64 000 triple monochromator in a backscattering geometry and in micro-Raman operation, and equipped with charge-coupled device (CCD) detector. The 488- and 514.5-nm lines of an Ar⁺ laser at a power of about 0.3 mW were used for the excitation of spectra in the triple monochromator system. In addition, a conventional Raman system was employed for measurements at room and high temperatures which comprised a SPEX model 1403 double monochromator, a cooled photomultiplier, and a photon counter. Both polarized and depolarized spectra were recorded separately at room temperature corresponding to parallel and crossed polarizations of incident and scattered beams, respectively. All spectra recorded at high temperatures were unpolarized, i.e., both polarized and depolarized components were recorded simultaneously in the same spectrum by removing the analyzer from the entrance slit of the spectrometer. Nearly backscattering and 90° geometries were used for the high-temperature measurements in which various blue and green lines of the Ar⁺ laser, as well as the 647-nm line of a Kr⁺ laser were employed for exciting the spectra at powers of 50 (lower temperatures) to 100 mW (higher temperatures). The spectral resolution for both double and triple monochromator set-ups was varied between 3 and 4 cm⁻¹.

III. RESULTS AND DISCUSSION

A. Raman spectra of Ge_xS_{1-x} glasses at room temperature

In this section we discuss briefly and compare our room-temperature data to those of previous relevant works. Figure 1 shows the polarized Raman spectra of Ge_xS_{1-x} glasses at room temperature for several values of x covering the entire range of available compositions ($0.17 \leq x \leq 0.45$); these spectra were recorded at identical experimental conditions using the 488-nm line of the Ar⁺ laser and the triple monochromator setup. For completeness, we have also measured the room-temperature spectra of the glasses using the double monochromator setup and the results are, as expected, identical with those obtained by the triple monochromator setup. In general, the Raman spectra presented in this work are in good agreement with previously reported ones^{1–8} on these glasses.

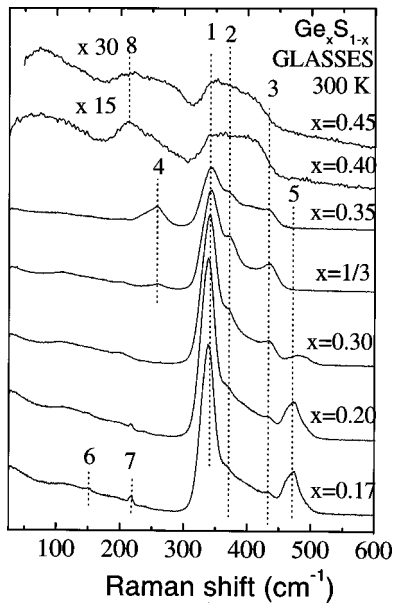


FIG. 1. Raman spectra of $\text{Ge}_x\text{S}_{1-x}$ glasses comprising the compound GeS_2 glass ($x = \frac{1}{3}$) and several S-rich ($x < \frac{1}{3}$) and Ge-rich ($x > \frac{1}{3}$) glasses recorded with the triple spectrometer. 1: main A_1 band at 342 cm^{-1} ; 2: companion A_1^c band at 374 cm^{-1} ; 3: band due to short S-S chains between GeS_4 tetrahedra (434 cm^{-1}); 4: band attributed to ethanelike $\text{S}_3\text{Ge}-\text{GeS}_3$ units (260 cm^{-1}); 5, 6, 7: bands due to symmetric stretching (475 cm^{-1}) and bending ($150, 220 \text{ cm}^{-1}$) vibrations in S_8 rings; 8: broad band due to stretching vibrations of Ge-Ge bonds in tetrahedra containing more than two Ge atoms (210 cm^{-1}). See text for details.

1. Compound GeS_2 glass

We start commenting on the spectra from the compound GeS_2 glass ($x = \frac{1}{3}$). Four bands are clearly observed in this glass at $110, 342(A_1), 374(A_1^c)$, and 434 cm^{-1} . A fifth band, marginally observed at about 260 cm^{-1} , is discussed below in detail as it appears strongly in the spectra of Ge-enriched glasses (see, for example, the spectrum of $\text{Ge}_{0.35}\text{S}_{0.65}$ in Fig. 1). The broad band at 110 cm^{-1} , superimposed on the high-frequency tail of the boson peak, has also been observed in previous works,^{1,2,6-8} but there has been only one brief comment⁸ attributing its origin to bond bending motions of S atoms in GeS_4 tetrahedra, presumably by analogy to the two regime behavior proposed^{14,15} for the crystalline phases of GeS_2 , i.e., bond-bending modes up to 250 cm^{-1} and bond-stretching ones between 340 and 460 cm^{-1} . Bearing in mind its broad features and low frequency, we suggest that considerable contribution to this band may arise from intermolecular displacements of whole GeS_4 structural units. In this respect, this band should be associated with the medium range order (MRO) of the glass in a way similar to that suggested for the boson peak.^{20,21}

The bands at 342 and 374 cm^{-1} are strongly polarized and it is generally accepted that the former (referred to as the main band) corresponds to A_1 symmetric stretch vibrations of S atoms in GeS_4 units, while the latter (designated as the companion A_1^c band) has been a matter of controversy in the past and its origin (as deduced from the data of this work) is discussed in the next section. The band at 434 cm^{-1} is rela-

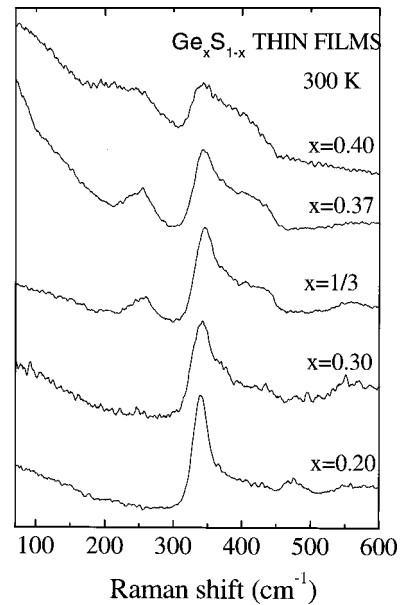


FIG. 2. Raman spectra of $\text{Ge}_x\text{S}_{1-x}$ thin films for two S-rich compositions ($x = 0.20, 0.30$), two Ge-rich compositions ($x = 0.37, 0.40$) and the compound GeS_2 compositions ($x = \frac{1}{3}$) recorded with the double spectrometer. The thickness of the films was $\sim 1 \mu\text{m}$.

tively (to the A_1 and A_1^c bands) depolarized and generally recognized to be due to S-S bonds. In density of states calculations⁴ based on the model of layered clusters,^{3,9,11} this band has been attributed to stretch vibrations of cluster edge S-S dimers. On the other hand, a similar band has been observed at a nearby frequency (425 cm^{-1}) in the Raman spectrum of fibrous sulphur²² which consists mainly of long S-S chains. In addition, the band at 434 cm^{-1} has been observed in the Raman spectrum of liquid sulphur²³ for which it is known that contains S-S chains. This evidence indicates a probable existence of small S-S chains in $g\text{-GeS}_2$ either as separate molecular units (inhomogeneities) or as interconnecting units between GeS_4 tetrahedra. Hence, the existence of S-S bonds in connection with the observation of the very weak Raman band at 260 cm^{-1} (attributed to Ge-Ge bonds; see the next section) indicates that the structure of stoichiometric GeS_2 glass does not consist only of GeS_4 units. It is pointed out that the band at 260 cm^{-1} has also been observed in previous Raman works^{4,6} of $g\text{-GeS}_2$.

The deviation from the ideal extended array of tetrahedra in the stoichiometric glass and the existence of such structural defects (inhomogeneities) should be attributed to fluctuations of local atomic concentrations in the melt, a situation which is inherited by the glass upon quenching. It seems that such fluctuations cannot be entirely eliminated in the melt, no matter how long the latter is kept in the crucible or to what treatments (rocking, steering) it is subjected. The band at 260 cm^{-1} is much stronger in the Raman spectra of the respective amorphous thin films of GeS_2 (Fig. 2), indicating an anticipated higher level of structural defects in the films compared to the bulk glasses; this should be attributed to the method of preparation of the former (thermal evaporation) which favors the appearance of inhomogeneities.

2. Ge-rich glasses ($x > \frac{1}{3}$)

In the moderately enriched in Ge glass ($x=0.35$), the band at 260 cm^{-1} becomes very pronounced (Fig. 1), while the other bands (A_1 , A_1^c , and S-S at 434 cm^{-1}), maintain, more or less, their relative intensities. The band at 260 cm^{-1} has been attributed^{1,2} to Ge-Ge bonds as the excessive Ge atoms start occupying corner sites in the tetrahedra. It is known²⁴ that the main Raman band of amorphous Ge appears at about 270 cm^{-1} and this supports the view that the band at 260 cm^{-1} in our spectra has its origin in Ge-Ge bond vibrations, with the small shift towards the lower frequencies being justified by the different environments around the Ge-Ge bond in each case. Alternatively, the 260-cm^{-1} band has been assigned⁶ as the breathing mode of crystalline GeS_2 which, is believed, forms in Ge-rich compositions.

Further increase of the Ge content ($x > 0.35$) in the $\text{Ge}_x\text{Si}_{1-x}$ alloys results in the appearance of another strong band at 220 cm^{-1} which obscures clear observation of the band at 260 cm^{-1} and is maintained up to the richest in Ge composition ($x=0.45$) of the series. At the same time, a considerable drop of intensity of the A_1 and A_1^c bands is observed with increasing Ge content, indicating a reduction of tetrahedral population. In general, scattering from Ge-rich $\text{Ge}_x\text{Si}_{1-x}$ alloys in the region $200\text{--}300\text{ cm}^{-1}$ has been related^{1,2} with structural units containing more than one Ge atoms, such as the ethanelike $\text{S}_3\text{Ge-GeS}_3$ or $\text{S}_3\text{Ge-S}_2\text{Ge-GeS}_3$ units. It has been argued⁶ that, even in the compound GeS_2 glass, these units could form one-dimensional chains lying between fragments of a layered network of tetrahedra. A broad feature at about 75 cm^{-1} in the spectra of highly enriched in Ge glasses taken with the triple monochromator setup (Fig. 1) is most likely an art effect as it does not appear in respective spectra recorded with the double monochromator. As expected, the intensity of the 434-cm^{-1} band (S-S bond vibrations) diminishes at high-Ge contents ($x \geq 0.40$).

3. S-rich glasses ($x < \frac{1}{3}$)

The interesting feature in the Raman spectra of the S-rich $\text{Ge}_x\text{Si}_{1-x}$ alloys (Figs. 1 and 2) is the polarized band at about 475 cm^{-1} which is generally recognized^{1-8,22,23} to be due to symmetric stretch vibrations in S_8 rings. As the S content increases, this band becomes stronger, while the band at 434 cm^{-1} decreases in intensity. In the case of the compound GeS_2 glass, we have suggested that the 434-cm^{-1} band may be connected with the existence of small S-S chains in the glassy network. In such an event, the population of S_8 rings increases rapidly with increasing S content at the expense of the chain population. This effect has been verified by comparing the integrated intensities of the 475- and 434-cm^{-1} bands (as they are deduced by fitting them to Gaussian functions) and plotting the ratio of the intensities against S (or Ge) content. At very high S contents ($x \leq 0.20$), two rather narrow bands are observed in the spectra at 150 and 220 cm^{-1} (Figs. 1 and 2) which have been assigned^{1,7,22,23} previously to bond-bending vibrations in S_8 rings.

Furthermore, in the S-rich glasses, the resolution and intensity of the A_1^c companion band decreases with increasing S content, while the A_1 main band becomes clearer and

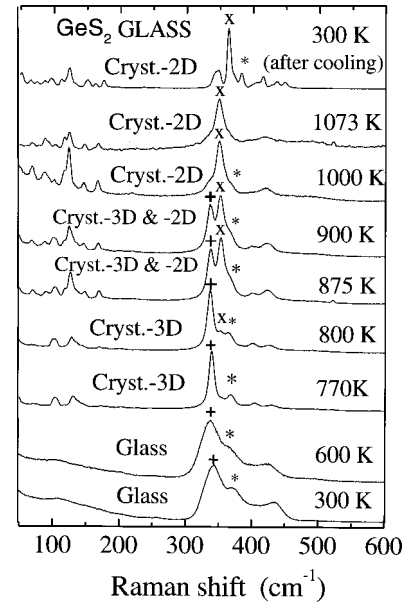


FIG. 3. Evolution of the Raman spectrum of the GeS_2 glass with temperature showing a two stage irreversible crystallization, first to the 3D phase and then to the 2D phase, with the latter being retained upon subsequent cooling of the glass to room temperature; +: main A_1 band of GeS_2 glass (symmetric stretching vibrations of S atoms in chains of corner sharing tetrahedra) and its successor in the 3D crystalline phase; *: companion A_1^c band of GeS_2 glass and its counterpart in the crystalline phases attributed to symmetric stretching vibrations of S atoms in bridges of edge sharing tetrahedra; X: main A_1 band of the 2D crystalline phase due to symmetric stretching vibrations of S atoms in chains of corner sharing tetrahedra.

stronger. If we accept (see Sec. III B) that the intensities of the A_1 and A_1^c bands represent measures of the populations of corner-sharing tetrahedra and of edge-sharing tetrahedra bridges, respectively, it is concluded that the fraction of corner-sharing tetrahedra linkages increases with increasing S content at the expense of edge-sharing bridge linkages. This result has also been demonstrated by fitting the two bands to Gaussians and plotting the ratio of the integrated intensities against composition.

B. Raman spectra and phase transitions of $\text{Ge}_x\text{Si}_{1-x}$ glasses at high temperatures

Figures 3–6 show the evolution of Raman spectra of four $\text{Ge}_x\text{Si}_{1-x}$ glasses with temperature from room temperature up to a temperature close to the melting point of the respective alloy. Also, in Figs. 3–6, the Raman spectrum of each alloy is shown after free (unforced) cooling of the sample to room temperature. The four compositions involved are: the stoichiometric GeS_2 ($x = \frac{1}{3}$, Fig. 3), a moderately enriched in Ge ($x=0.35$, Fig. 4), a moderately enriched in S ($x=0.30$, Fig. 5), and a highly rich in S one ($x=0.20$, Fig. 6).

1. Structural phase transitions of $g\text{-GeS}_2$

The sequence of Raman spectra of $g\text{-GeS}_2$ (Fig. 3) implies the occurrence of two gradual structural changes with

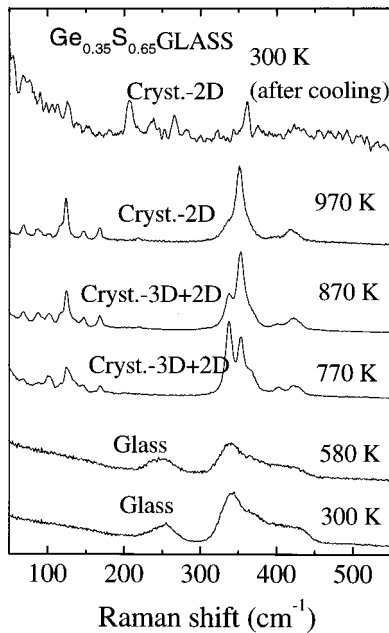


FIG. 4. Temperature dependence of the Raman spectrum of the $\text{Ge}_{0.35}\text{S}_{0.65}$ glass (moderately rich in Ge) showing irreversible phase transitions to the 3D and 2D crystalline phases of GeS_2 .

temperature, first to a structure which appears to be dominated by the 3D crystalline phase and then to the 2D crystalline phase. Specifically, the main A_1 band at 342 cm^{-1} starts to become sharper at about 750 K , with a simultaneous appearance (at the same temperature) of additional sharp bands in the low-frequency region of the spectrum. These effects denote the onset of crystallization to the 3D phase. At 770 K , the dominant feature of the spectrum is the (by now) narrow band at 337 cm^{-1} which corresponds to the charac-

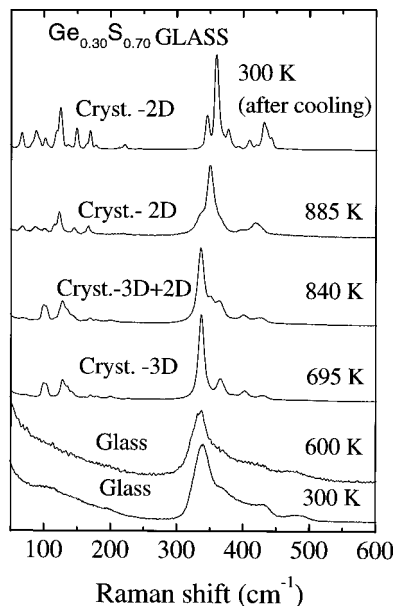


FIG. 5. Temperature dependence of the Raman spectrum of the $\text{Ge}_{0.30}\text{S}_{0.70}$ glass (moderately rich in S) displaying irreversible phase transitions to the 3D and 2D crystalline phases of GeS_2 .

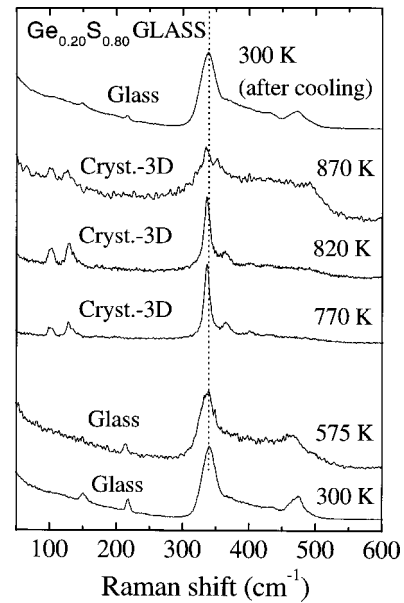


FIG. 6. Temperature dependence of the Raman spectrum of the $\text{Ge}_{0.20}\text{S}_{0.80}$ glass (highly enriched in S) showing a one stage reversible crystallization only to the 3D phase of crystalline GeS_2 .

teristic A_1 mode of the 3D crystalline phase¹⁴ (see introduction) slightly shifted towards the lower frequencies at elevated temperatures. It seems that crystallization of $g\text{-GeS}_2$ commences slightly below its normal glass transition temperature (a value of 780 K was measured²⁵ for the T_g of this glass). It is reminded that the sample is held in the cell under vacuum which should cause a lowering of T_g . Also, some extra heating by the laser beam may raise the sample temperature locally above that measured by the sensor at the edge of the sample. At 800 K (Fig. 3), a new line is resolved in the spectrum at 352 cm^{-1} whose intensity and sharpness increase rapidly above this temperature at the expense of the rival A_1 band of the 3D phase. This new band, which dominates the spectrum above 900 K and up to a temperature just below melting point T_m ($=1123\text{ K}$), is the characteristic A_1 mode of the 2D crystalline phase^{15,16} and this is confirmed by cooling the sample to room temperature. In the cooling process, the new sharp band is retained in the spectrum as the dominant feature with a frequency of 363 cm^{-1} at 300 K (Fig. 3), while the overall spectrum resembles that of the 2D phase.^{15,16} All these observations show that the two-step crystallization to the 2D phase is irreversible after cooling the material. It is pointed out that in the heating process, the two crystalline phases co-exist over a wide temperature range ($800\text{--}1000\text{ K}$). The first transition of $g\text{-GeS}_2$ to a structure dominated by the 3D crystalline phase provides strong evidence that the network of this compound glass is, by large, three dimensional in which the population of corner-sharing tetrahedra linkages is much greater than that of the edge-sharing bridges. The temperature dependences of the A_1 and A_1^c modes of the amorphous phase and their successors in the crystalline phases are shown in the plots of Fig. 7 for both heating and cooling stages.

The evolution of the A_1 mode with temperature is discussed below in detail. The third band in this high-frequency

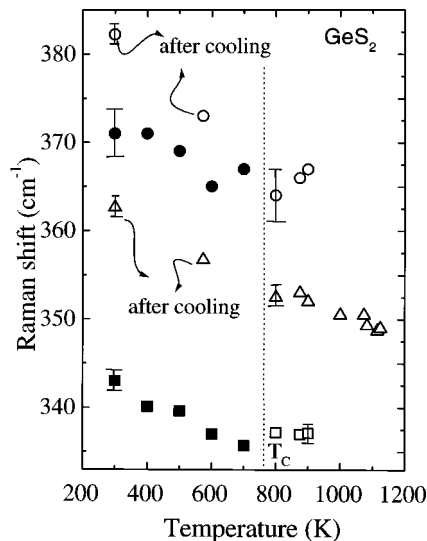


FIG. 7. Frequency versus temperature plot for the main A_1 (■) and companion A_1^c (●) bands of GeS_2 glass and their successors (□, ○) in the crystalline phases; ■ (□): symmetric stretching vibrations of S atoms in chains of corner sharing tetrahedra of GeS_2 glass (3D crystalline phase); ● (○): symmetric stretching vibrations of S atoms in bridges of edge sharing tetrahedra of GeS_2 glass (2D crystalline phase); Δ : symmetric stretching vibrations of S atoms in chains of corner sharing tetrahedra of the 2D crystalline phase of GeS_2 .

molecular spectrum of $g\text{-GeS}_2$ at 434 cm^{-1} decreases in intensity with increasing temperature, even before the material crystallizes, indicating that the S-S bonds in the glassy network start breaking considerably below T_g . Finally, the very broad band of $g\text{-GeS}_2$ peaking at 110 cm^{-1} splits into a large number of intermolecular (external) phonon peaks in the crystalline phases which is justified by the big size of the unit cell of these phases.

2. Evolution of the A_1^c mode of $g\text{-GeS}_2$ in the crystalline phases

By deconvoluting the Raman spectra of GeS_2 of both the amorphous and crystalline phases (Fig. 3), we have determined the temperature dependence of the A_1^c band of $g\text{-GeS}_2$ and the band which appears to succeed it in the crystalline phases. The A_1^c mode is clearly resolved up to 850 K, but above this temperature and up to 1000 K, its successor is seen only as a shoulder because it is masked by the rapidly growing in strength A_1 mode (at 352 cm^{-1}) of the 2D phase; above 1000 K, it is not detected, but it reappears during the cooling process and is well resolved below 700 K as its spectral distance from the A_1 mode increases. Hence, following its temperature dependence during cooling, this counterpart mode is observed at 382 cm^{-1} in the room-temperature spectrum of the 2D phase. Since a similar peak has been observed previously^{15,16} at this frequency in the 2D crystalline phase of GeS_2 and attributed to symmetric stretch vibrations of S atoms in bridges of edge-sharing tetrahedra, we suggest a likewise assignment for the corresponding A_1^c mode of $g\text{-GeS}_2$. This assignment is in agreement with a previous empirical predictions.⁷

3. Structural changes of moderately rich in Ge or in S $\text{Ge}_x\text{S}_{1-x}$ glasses at high temperatures

As in the stoichiometric GeS_2 glass, a similar two-step crystallization is observed with temperature in glasses having compositions close to stoichiometry, first to 3D GeS_2 and then to 2D GeS_2 (Figs 4 and 5). The 2D phase is maintained up to temperatures close to the respective melting points and upon subsequent cooling of the alloys to room temperature. Hence the crystallization of these alloys ($x=0.35, 0.30$) is also irreversible. The only difference, with respect to the stoichiometric glass, is their slightly lower crystallization threshold which is a consequence of their lower glass transition temperatures T_g (680 K for $x=0.35$ and 543 K for $x=0.30$).²⁵

As anticipated, the 260-cm^{-1} band of the Ge-rich glass, disappears in the crystalline phases (Fig. 4) as Ge-Ge bonds are not expected in the crystal which always has stoichiometric composition. In this situation, phase separation occurs upon crystallization, with the material becoming a solid solution of atomic Ge in $c\text{-GeS}_2$. The presence of atomic Ge probably explains the dark color of the material after cooling and the low quality of its Raman spectrum at room temperature. The evolution of the A_1^c mode is similar to that observed in the compound glass.

In the moderately rich in S glass (Fig. 5), the sequence of structural changes are similar, although the temperature range within which the material transforms from the 3D to the 2D phase is relatively narrow (840–880 K). Phase separation should also occur in this glass, but the small amount of excess atomic S does not appear to affect the quality of the Raman spectrum in both heating and cooling processes, most likely because it evaporates and then condenses (during cooling) in the upper parts of the silica cell.

4. Reversible crystallization of the highly enriched in S glass

The situation is considerably different in the case of the highly enriched in S ($x=0.2$) glass. It is reminded that such glasses consist of S_8 ring clusters in the matrix of GeS_4 tetrahedra with the latter being linked mainly through their corners (three-dimensional glassy network, Figs. 1 and 2). At about 720 K, a narrowing of the A_1 main band (Fig. 6) indicates the beginning of crystallization of the glassy matrix to the 3D crystalline phase of GeS_2 , a phase maintained up to a temperature of about 850 K. Above this temperature, the spectrum becomes broad and decreases in intensity indicating that the melting point is approached. The precise value of the melting point is not known for this alloy, but, judging from the substantial drop of intensity of the spectrum at about 870 K (Fig. 6), we conclude that it should be around this temperature. Spectroscopic measurements from various $\text{Ge}_x\text{S}_{1-x}$ alloys close to and above the melting point have shown²⁶ that these materials become almost opaque in the liquid phase, thus resulting in a very small penetration depth of the sample by the probing laser beam and a very weak Raman-scattering signal. As a consequence of this intensity decrease, the broad Raman bands of the silica cell (SiO_2 glass) which contains the sample emerge in an overall Raman spectrum. These features are evident in the Raman spec-

trum at 870 K of Fig. 6. It is significant that after subsequent cooling, the spectrum of the alloy resembles (both in line shape and intensity) that of the starting glass (Fig. 6), implying that the one-step crystallization of this glass to the 3D phase is reversible.

It is interesting that the 475-cm^{-1} band disappears from the spectrum of the S-rich glass (Fig. 6) upon crystallization of the matrix at high temperatures, indicating that the S_8 rings break. However, the rings reform during the cooling process as the characteristic band at 475 cm^{-1} reappears in the spectrum, showing that all thermally induced structural changes are reversible in this alloy.

As has been found out in a previous work²⁷ on the ternary $\text{Ge}_x\text{Sb}_y\text{S}_{1-x-y}$ glassy system, a three-dimensional structure in Ge-based chalcogenides favors the appearance of photo- and thermally induced reversible structural changes because of the large free volume shown by such a structure. Similarly, in the present work, the matrix of the highly rich in S glass is dominated by corner-sharing tetrahedra giving a largely three-dimensional structure which, it appears, can be successively interchanged from amorphous to crystalline by alternatively heating and cooling the sample; however, the *three-dimensional character of the matrix structure is retained over these changes* and this should be attributed to the excess sulphur which occupies the structural voids (free volume) of the matrix. All these results indicate that this alloy displays a kind of “memory” concerning the original structures of its two constituent phases (S_8 rings and glassy matrix of GeS_4 tetrahedra).

In contrast, as has been discussed in previous sections, $\text{Ge}_x\text{S}_{1-x}$ glasses close to stoichiometry ($x=0.30, \frac{1}{3}, 0.35$) with considerable fraction of edge-sharing tetrahedral bridges in their network give as an end-product at high temperatures the 2D crystalline phase. In general, 2D networks are not as flexible as the 3D ones²⁷ (largely because of the smaller free volume of the former), thus preventing further structural changes of these alloys in the opposite direction upon cooling.

IV. CONCLUSIONS

Systematic measurements of Raman spectra of several $\text{Ge}_x\text{S}_{1-x}$ glasses ($0.17 \leq x \leq 0.45$) at room temperature have

provided the means for a comparative study of their vibrational and structural properties.

The stoichiometric $g\text{-GeS}_2$ undergoes a two-step gradual crystallization at high temperatures, first to the 3D phase and then to the 2D phase, with both transitions being irreversible upon subsequent cooling. The first transition indicates that the structure of $g\text{-GeS}_2$ is predominantly three dimensional in which the population of corner-sharing tetrahedra is much greater than that of edge-sharing tetrahedra. By monitoring the evolution of the A_1^c companion band of $g\text{-GeS}_2$ in the crystalline phases, we have obtained experimental evidence that this band is associated with *symmetric stretch vibrations of S atoms in edge-sharing tetrahedral units*. Also, $\text{Ge}_x\text{S}_{1-x}$ glasses having compositions close to the stoichiometric one show a similar sequence of two step irreversible crystallization at high temperatures.

In the highly enriched in S glass, though, a one step reversible crystallization to the 3D phase is observed at high temperatures, with the network of the glassy matrix of tetrahedra maintaining its dimensionality (3D) over both heating and cooling stages. It appears that the S_8 ring clusters play a significant role in the reversibility of structural effects and the preservation of dimensionality of the glassy matrix.

The most important aspect of the high-temperature structural changes is that all $\text{Ge}_x\text{S}_{1-x}$ glasses undergo a first-stage transition to the 3D crystalline phase, which implies that *their structure is, by large, three dimensional*.

ACKNOWLEDGMENTS

We are grateful to Professor G. Papatheodorou and Dr. E. A. Pavlatou at the Institute of Chemical Engineering and High Temperature Chemical Processes of the Foundation of Research and Technology-Hellas, Patras, for providing the special silica sample holders and for helping in some high-temperature experiments on $g\text{-GeS}_2$. Many thanks are also due to Professor M. Frumar and Dr. M. Vlcek at the Department of General and Inorganic Chemistry, University of Pardubice, Czech Republic, for their assistance in the preparation of $\text{Ge}_x\text{S}_{1-x}$ glasses during the scientific visit of one of us (I.P.K.) to the University of Pardubice.

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