

Pressure-Induced Amorphization of GeSe₂

Andrzej Grzechnik,* Tor Grande,† and Svein Stølen‡

**École Normale Supérieure de Lyon, 46 allée d'Italie, F-69364 Lyon Cedex 07, France;* †*Department of Inorganic Chemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway;* and ‡*Department of Chemistry, University of Oslo, N-0315 Oslo, Norway*

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The high-pressure room temperature behavior of crystalline GeSe₂ is investigated with Raman scattering and energy-dispersive X-ray diffraction in a diamond anvil cell. No evidence for phase transitions to known polymorphs of GeSe₂ is observed during compression up to 11 GPa. Pressure-induced amorphization, associated with the sample becoming opaque, occurs between 11 and 14 GPa. The sample recovered to ambient conditions from 14 GPa is amorphous by X-ray diffraction. The Raman spectrum of the sample decompressed from the 11- to 14-GPa range is significantly different from the Raman spectra of glassy GeSe₂ prepared by melt quenching at atmospheric pressure. These results are discussed in relation to the possible transition from the 2:4 to 3:6 coordination during compression of AB₂ compounds with structures related to the random tetrahedral network model of amorphous GeSe₂. © 1998 Academic Press

INTRODUCTION

Amorphous and crystalline semiconductors based on chalcogenide phases of germanium and silicon have many interesting properties as well as many potential applications such as optoelectronic and IR optical devices, optical storage and photosensitive materials, and solar cells. etc. Among them, compounds with the GeSe₂ composition are a subject of numerous studies, utilizing both experimental and theoretical approaches (1–9). Most of the efforts have been concentrated on better understanding the tetrahedral framework and properties of the GeSe₂ glasses and disordered thin films. The medium- to short-range order in these materials is believed to resemble the structure of their crystalline counterparts. For this reason, crystal chemistry investigations of tetrahedral chalcogenide Ge systems at ambient and extreme conditions are important to understand the structural network in the amorphous materials. At elevated pressures, four-to-six coordination phase transformations and/or changes in dimensionality of the structures can be expected in the crystalline phases. Such structural transitions would most likely be associated with the changes in electronic properties. Pressure-induced coordination transitions could also be envisioned in related

melts, supercooled liquids, and glasses, with the possibility of synthesizing different amorphous polymorphs. Another method for the preparation of amorphous or disordered phases is pressure-induced solid-state amorphization of crystalline materials. Under pressure, a metastable crystalline phase tends to convert to a denser stable one. Such a structural reaction can be kinetically slow and the intermediate disorder can be frozen, yielding an amorphous state. These phenomena associated with a four-to-six coordination change have been reported for several geological and technological materials (10). The amorphization induced at high pressure is not a thermodynamic phase transition but rather a disruption of the crystal lattice due to its mechanical instability. Recently, it has been shown that the *P–T* kinetic lines for amorphization can be extrapolated to the ordinary crystal-to-crystal hysteresis lines at high temperatures (11). In consequence, one finds that the *P–T* diagrams of amorphous phases are similar to the phase diagrams of the corresponding crystalline counterparts (12). This in turn emphasizes the necessity of precisely knowing the high-pressure behavior of crystalline materials to better understand possible polymorphic transitions in related amorphous phases.

There are three ambient-pressure forms of GeSe₂ reported in the literature. Orthorhombic α -GeSe₂ (*Pmnm* or *Pmn*) has a distorted layered structure of CdI₂ (*P* $\bar{3}$ *m1*), where the cations are octahedrally coordinated (13, 14). Layered β -GeSe₂ (*P2₁/c*) is isotopic with the high-temperature modification of GeS₂ (HT-GeS₂), with GeSe₄ tetrahedra connected via corners into chains along the *a* axis and by edge-sharing Ge₂Se₈ double tetrahedra along the *b* axis (15–19). Recently, a second-order phase transition of β -GeSe₂ has been reported by Stølen *et al.* (20). The enthalpy of the transition is small and the structural origin of this transformation could not be resolved with X-ray diffraction. The structure of γ -GeS₂ is related to hexagonal SnSe₂ of the CdI₂ type (21). Reported melting temperatures of the α , β , and γ modifications of GeSe₂ are $T_m = 1013(\pm 3)$ K, $T_m = 1016(\pm 5)$ K, and $T_m = 1123(\pm 3)$ K, respectively (13, 21). The stability of different polymorphs of GeSe₂ has been discussed by Stølen *et al.* (20). There are

only two reports on α -GeSe₂ (13,14) and one on γ -GeSe₂ (21). In all other synthesis reports only β -GeSe₂, the stable ambient-pressure modification (20), has been obtained (15–19). The occurrence of α -GeSe₂ and six-coordinated Ge atoms at ambient pressure has been questioned by Dittmar and Schäfer (18). Moreover, in their report on γ -GeSe₂ Bletska *et al.* (21) neither have confirmed the composition of their product (synthesis by vapor deposition in a sealed silica tube) nor have presented their X-ray diffraction data.

General structural variations in the dichalcogenide materials of silicon and germanium at ambient and extreme conditions have been summarized and discussed by Shimizu and Kobayashi (22). At ambient pressure, low-dimensional chain (SiS₂) or layered (β -GeSe₂) tetrahedral structures are preferred for disulfide and diselenide materials. At high pressure and high temperature, there is a tendency for disulfides and diselenides to attain the three-dimensional tetrahedral cristobalite (a high-temperature, low-pressure form of silica) or the layered octahedral CdI₂ and tetrahedral HgI₂ (*P4₂/nmc*) structures.

In this study we are interested in the high-pressure behavior of β -GeSe₂ investigated with X-ray diffraction and Raman spectroscopy in a diamond anvil cell at room temperature. All previous reports on GeSe₂ at extreme conditions are based on investigations of the decompressed samples recovered from high-pressure synthesis (22–26). To some extent, contradicting results of these studies, as seen above, could be rationalized by indicating that several metastable high-pressure, high-temperature crystalline and amorphous polymorphs of GeSe₂ may be prepared depending on the nature of the starting materials, including the heat treatment of melt-quenched glasses and pressure-temperature compression and/or decompression routes. Since the recovered phases to ambient conditions from high-pressure synthesis do not necessarily represent the actual high-pressure equilibrium, an *in situ* study of pressure-induced transformations is desirable to provide more information on how the crystalline structure behaves upon compressing and decompressing and whether there are other phases of crystalline and/or amorphous GeSe₂ that have not been recovered to ambient conditions yet.

less, the pressure in which the GeSe₂ glass metallizes ($P_T \approx 7$ GPa) (26) corresponds to the formation of the CdI₂ type structure (25). β -GeSe₂ has been studied with Raman spectroscopy under pressure to 8 GPa at 10 K (27). At 6.2 GPa the sample amorphized and upon further compression to 7 GPa it transformed to a modification isotypic with the low-temperature polymorph of GeS₂. At 8 GPa this polymorph transformed back to the disordered phase.

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EXPERIMENTAL

The sample of GeSe₂ was synthesized from pure elements (Goodfellow, England) weighed in stoichiometric proportions and sealed in silica ampoules under vacuum. The ampoules were slowly heated to 1173 K and kept at this temperature for 24 h. The crystalline product, obtained by cooling the melt at 1 K/h to 873 K, was phase pure and had the β -GeSe₂ structure reported by Dittmar and Schäfer (18).

High-pressure X-ray diffraction patterns were recorded using an energy-dispersive configuration on the wiggler line of the DCI storage ring at the Laboratoire pour l'Utilisation du Rayonnement Électromagnétique (LURE) in Orsay (France). The polychromatic X-ray beam was collimated to a 100 × 100 μ m sized spot at the pressurized sample. The diffracted beam was collected between 5 and 60 keV ($E_d = 50.27 \pm 0.03$ keV \AA) using a Canberra planar germanium detector. The powder sample, with nitrogen as a pressure-transmitting medium, was loaded into a membrane diamond cell with type I diamonds, brilliant cut with 500- μ m culets, and a sample chamber diameter of 250 μ m.

Raman spectra were collected with an XY Dilor Raman spectrometer (1800 groove/mm gratings) in backscattering geometry with CCD signal detection. Raman scattering was

excited using an Ar^+ laser at a wavelength of 514.5 nm. A single crystal of $\beta\text{-GeSe}_2$, about 100 μm in diameter and 10 μm thick, and CsI, as a pressure-transmitting medium, were loaded into a Mao-Bell type diamond cell with type II-a diamonds, brilliant cut with 600- μm culets, and a sample chamber diameter of 250 μm . The laser power at the sample was minimal to avoid sample heating by the laser irradiation (the actual sample heating by laser irradiation was not measured in this study). Pressures during both X-ray diffraction and Raman spectroscopy experiments were determined from the R_1 ruby fluorescence line (28).

RESULTS

Vibrational spectra of $\beta\text{-GeSe}_2$ ($P2_1/c$, $Z = 16$) at ambient conditions have been reported and discussed in detail previously (1–4, 6, 7, 29, 30). Normal modes at the Γ point of a Brillouin zone are distributed as $\Gamma = 36A_g + 36B_g + 35A_u + 34B_u$, where the A_g and B_g modes are Raman active and the A_u and B_u modes are infrared active. Various models of vibrational force fields have been used for precise assignment of the observed infrared and Raman bands to optically allowed modes (6, 29). Especially, the two Raman bands at 211 and 216 cm^{-1} (Fig. 1) have attracted much of the effort, as they are closely related to the bands observed in the Raman spectrum of amorphous GeSe_2 (1–4, 6, 7). The very

intense 211- cm^{-1} band is assigned to the symmetric breathing vibrational mode of the corner-shared GeSe_4 tetrahedra, whereas the weak band at 216 cm^{-1} is due to the quasi-localized breathing mode on the edge-sharing Ge_2Se_8 tetrahedra, strongly coupled to the exciton observed in the absorption spectra at about 2.7 eV (1).

Changes in the Raman spectra of $\beta\text{-GeSe}_2$ upon compression to 9.8 GPa can be followed in Fig. 1. All the Raman features, better resolved at high pressures, are accounted for by comparison with the single-crystal data at ambient conditions reported by Popovic and Stolz (29). The observed bands shift monotonously with pressure toward higher wavenumbers without mode softening. There is no change in our Raman spectra indicating a phase transition into either the three-dimensional cristobalite-like (22–25) or layered HgI_2 (22) structures in the entire pressure region studied here. Any transformation into these two polymorphs would be associated with a drastic change of the selection rules for normal optical modes at the Γ point of a Brillouin zone and the number of the observed bands. For the three-dimensional cristobalite-like structure ($I\bar{4}2d$, $Z = 4$), in which all the GeSe_4 tetrahedra share corners only, the selection rules in the primitive cell are $\Gamma = A_1(\text{Raman}) + 2A_2 + 2B_1(\text{Raman}) + 2B_2(\text{IR} + \text{Raman}) + 4E(\text{IR} + \text{Raman})$, where optical activity is indicated in parentheses. In the case of the HgI_2 type structure ($P4_2/nmc$,

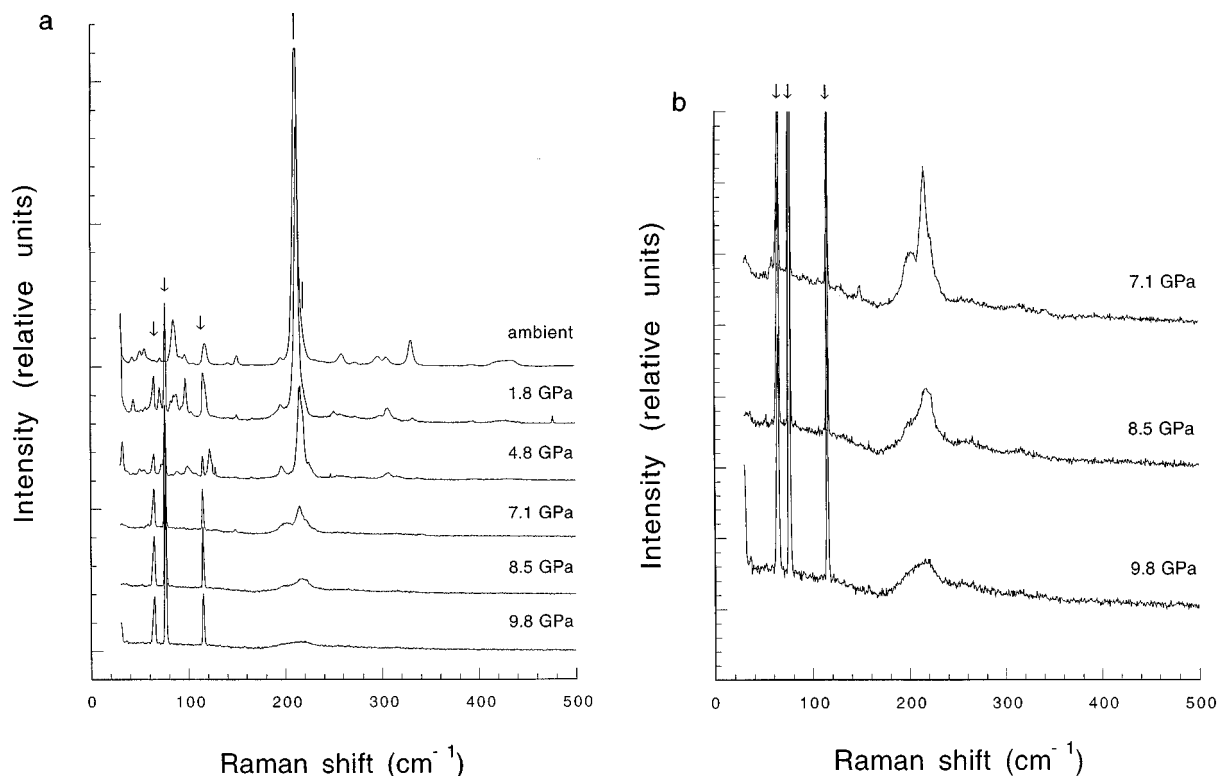


FIG. 1. Raman spectra of $\beta\text{-GeSe}_2$ upon compression in the 0.0001- to 9.8-GPa (a) and 7.1- to 9.8-GPa (b) pressure ranges. Arrows indicate the positions of Ar^+ plasma lines. Ticks show the positions of the 211- and 216- cm^{-1} bands.

$Z = 2$), in which the corner-sharing GeSe₄ tetrahedra form layers, the respective selection rules are $\Gamma = A_{1g} + B_{1g} + B_{2g} + 3E_g + A_{2u} + B_{2u} + 2E_u$, where the A_{1g} , B_{1g} , B_{2g} and E_g modes are Raman active, and the A_{2u} and E_u modes are infrared active. In the lattice of β -GeSe₂ ($P2_1/c$, $Z = 16$), 141 modes are optically active, whereas in both the $I\bar{4}2d$ ($Z = 4$) and $P4_2/nmc$ ($Z = 2$) lattices, the number of the active modes is reduced to 13 and 14, respectively. The Raman spectrum recorded at 9.8 GPa still shows the spectral features that can be related to β -GeSe₂, although all the bands are considerably less intense and broader than the corresponding ones at lower pressures. There is also no indication for the existence of phases with sixfold-coordinated Ge atoms in any of the Raman spectra measured at this pressure. The most remarkable change in the Raman spectra upon compression is a significant intensity decrease of the band at 211 cm⁻¹. As seen in Fig. 1, the two features at 211 and 216 cm⁻¹, due to the symmetric breathing vibrational mode of the corner-shared GeSe₄ tetrahedra and the quasi-localized breathing mode on the edge-sharing Ge₂Se₈ tetrahedra, respectively, are resolved up to about 7 GPa. Above this pressure, these two bands are largely overlapping, partly due to their pressure-induced broadening. Additionally, at about 7 GPa the sample starts to be opaque, eventually leading to a vanishing of the Raman spectra

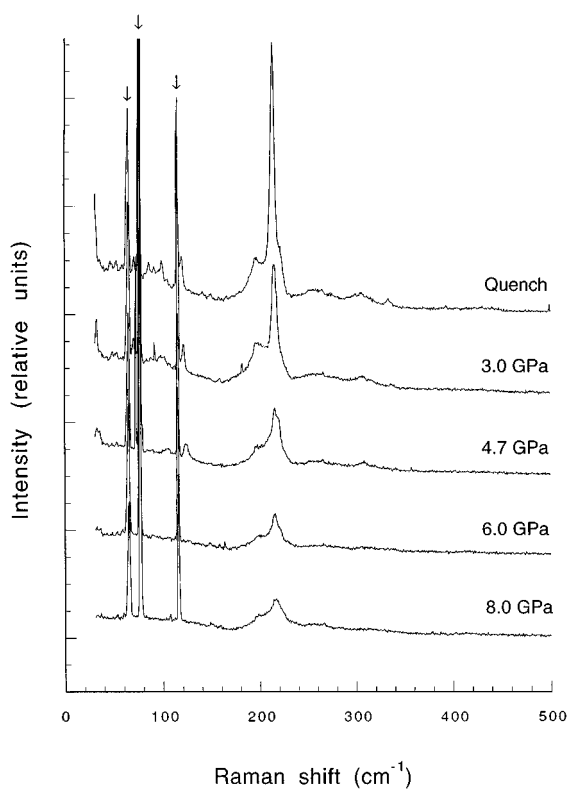


FIG. 2. Raman spectra of β -GeSe₂ upon decompression from 9.8 GPa. Arrows indicate the positions of Ar⁺ plasma lines.

above approximately 10 GPa. Upon decompression from 9.8 GPa, there is progressive sharpening of all the observed Raman bands and an increase of the 211-cm⁻¹ band intensity (Fig. 2). However, the intensity ratio of the 211-cm⁻¹ band to the intensities of other bands is much smaller in the decompressed sample than in the noncompressed one. The two bands at about 211 and 216 cm⁻¹ can already be resolved at 6 GPa.

The energy-dispersive X-ray diffraction patterns of β -GeSe₂ as a function of pressure are shown in Fig. 3. The expected X-ray diffraction patterns for possible crystalite-like ($I\bar{4}2d$), HgI₂ ($P4_2/nmc$), and CdI₂ ($P\bar{3}m1$) high-pressure phases of GeSe₂ (22–25) are not compatible with the observed ones to about 11 GPa. Although the relative intensities of the energy-dispersive X-ray diffraction peaks vary from one data collection to another (32), all of the peaks can be indexed with $P2_1/c$ symmetry (18), indicating that there is no phase transition in β -GeSe₂ at that pressure range, in agreement with the Raman data. At higher pressures, the X-ray diffraction peaks broaden, decrease in intensity, and entirely vanish at 14.0 GPa, signaling the appearance of the pressure-amorphized material. Upon decompression, only broad X-ray diffraction diffuse peaks,

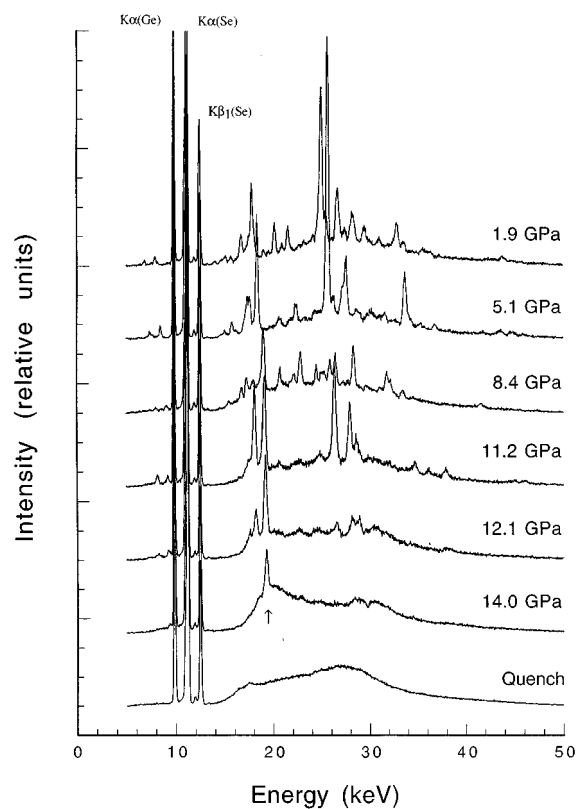


FIG. 3. Energy-dispersive X-ray diffraction patterns of β -GeSe₂ as a function of pressure. $K\alpha$ (Ge), $K\alpha$ (Se), and $K\beta_1$ (Se) are the X-ray emission lines of Ge and Se, respectively. The arrow indicates the (210) X-ray reflection of the δ phase of solid nitrogen [31].

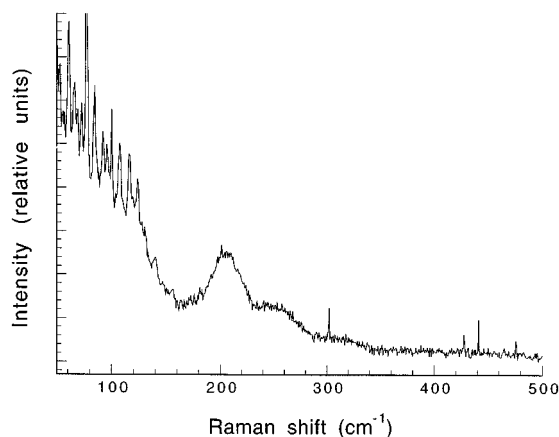


FIG. 4. Raman spectrum of GeSe₂ decompressed from 12.8 GPa. The sharp bands at low wavenumbers are due to the rotational–vibrational spectrum of the air.

due to the amorphous material, are visible. The diffuse features, with no peaks from crystalline phases, are also observed in the X-ray pattern of the sample decompressed from 14.0 GPa to ambient pressure. This stands in contrast to the high-pressure behavior of isostructural HT-GeS₂, in which the ordered-to-disordered phase transformation at about 15 GPa, associated with sample becoming opaque, is reversible (33).

Figure 4 shows a Raman spectrum of the sample decompressed from 12.8 GPa. This spectrum differs from the ones reported previously for the noncompressed melt quenched amorphous material at ambient conditions (1–4, 6, 7). The very broad bands in the 150- to 300-cm⁻¹ region are well separated and there is no low-wavenumber shoulder feature in the 150- to 200-cm⁻¹ region that can be associated with the stretching vibration of the Ge–Ge bonds (3).

DISCUSSION

There are two structural models for the amorphous GeSe₂ material prepared at ambient conditions to explain the results of studies using several different experimental techniques (1–8). According to the first one, randomly bonded GeSe₄ tetrahedra are linked together into a three-dimensional covalent framework that is chemically ordered (5). The second model considers the network in which GeSe₄ tetrahedra are covalently bonded in layer fragments having a two-dimensional atomic arrangement similar to the one in the crystalline material; i.e., a medium-range structure of the amorphous material is topologically similar to the structure of β-GeSe₂ (1–7). As a consequence, the like-atom bonds are intrinsic to the amorphous material, and both breaking of the chemical order and phase separation lead to Se- and

Ge-enriched regions. The *ab initio* molecular dynamics study of the structural and electronic properties of amorphous GeSe₂ demonstrates that this material has a structure with *n*-order rings, in which there are both corner- and edge-shared GeSe₄ tetrahedra (8). Additionally, the *ab initio* calculations suggest that there are no states in the fundamental band gap at ambient conditions, despite all the topological defects.

The results of our Raman spectroscopy and X-ray diffraction experiments at room temperature suggest that with increasing pressure the crystal lattice of β-GeSe₂ becomes disordered and eventually amorphous. From our observations, we infer that pressure-induced amorphization in this material differs significantly from disordering that occurs at ambient conditions. The Raman spectra of various samples of GeSe₂ prepared at atmospheric pressure, varying from β-GeSe₂ single crystals through small crystallites to amorphous films, reveal that with increasing disorder the intensity ratio of the 216-cm⁻¹ band to the 211-cm⁻¹ band becomes progressively larger but the two bands remain resolved even in the amorphous samples (1–4, 6, 7). Hence, the medium-range structure of the amorphous framework is topologically similar to that in the crystalline β-GeSe₂, in which both corner- and edge-sharing tetrahedra occur. The pressure-induced disordering of β-GeSe₂ follows a different path. Initially, both GeSe₄ and Ge₂Se₈ units are present in the crystal lattice upon compression, as can be seen from the two resolved bands at about 216 and 211 cm⁻¹ (Fig. 1). However, at about 7 GPa, i.e., the pressure at which the melt-quenched amorphous material metalizes (26), the two bands, broadened and largely overlapped, cannot be resolved. This could be explained by the onset of local breaking of the double edge-shared Ge₂Se₈ tetrahedra and vanishing of large ring structures. This would not be associated with disordering or amorphization on the length scale probed with X-ray diffraction up to about 11 GPa. As seen from Fig. 2, there is a small hysteresis in backtransformations in the pressure-disordered material, as the two bands at about 211 and 216 cm⁻¹ can already be distinguished at 6 GPa. When sample is compressed to higher pressures, it becomes completely opaque and irreversibly amorphous, as probed with Raman spectroscopy and X-ray diffraction (Fig. 3), respectively. This indicates that at room temperature the breaking of the edge-shared units and large-ring motifs is complete at pressures above about 11 GPa. The Raman spectrum for the decompressed sample from 12.8 GPa does not show the presence of the vibrational feature at about 180 cm⁻¹ that is assigned to the Ge–Ge stretching modes in the amorphous material prepared at ambient pressure (1–4, 6, 7). This could mean that whereas high pressure tends to structurally disorder crystalline β-GeSe₂, it also suppresses the occurrence of the chemical disorder, i.e., “wrong” bonds and Se- and Ge-enriched regions.

Although, the precise high-pressure, high-temperature phase diagram of crystalline GeSe₂ is not known (24), it could be shown that the layered structure of HgI₂ (*P4₂/nmc*), in which the tetrahedra share corners only, is an intermediate between the β -GeSe₂ (*P2₁/c*) and cristobalite-like (*I4₂d*) structures (34). Both the HgI₂ and cristobalite-like polymorphs of GeSe₂ have a common Ge₄Se₁₀ unit, consisting of four corner-sharing tetrahedra. Linking this unit can give either the two-dimensional HgI₂ or three-dimensional cristobalite-like networks. Such a transformation path, β -GeSe₂ \rightarrow HgI₂ \rightarrow cristobalite, possible at high pressure and high temperature for the crystalline material (34), could also occur in its amorphous analogue. It is interesting to point out that the three-dimensional chemically ordered framework of amorphous GeSe₂ prepared at ambient pressure (5) would be a randomly distorted and disordered variant of the cristobalite-like structure of GeSe₂ at high pressure and high temperature. The hexagonal layered CdI₂ structure (*P3 \bar{m} 1*), with octahedral coordination of the Ge atoms, could also be derived from the layered HgI₂ type. The change of the coordination around the cations can be induced by a shear translation of the anion layers perpendicular to the *c* axis. It would be a displacive type of a transition, requiring some energy to overcome the activation barrier. In the case of GeSe₂, it means that the CdI₂ type phase would occur at relatively higher pressures than the cristobalite-like one, with the HgI₂ type structure as an intermediate between β -GeSe₂ and both cristobalite-like and CdI₂ structures. Such structural considerations are supported by the combined results of high-pressure studies at 573–1173 K (22, 24). The transition into the tetrahedral structures of the HgI₂ or cristobalite-like types occurs at about 3 GPa, whereas the one due to four-to-six coordination changes of the Ge atoms is observed at about 7 GPa. The two sequences of the phase transitions, β -GeSe₂ \rightarrow HgI₂ \rightarrow cristobalite and β -GeSe₂ \rightarrow HgI₂ \rightarrow CdI₂, can also be inferred from the high-pressure, high-temperature phase diagram of HT-GeS₂ (22), isostructural with β -GeSe₂ (15–19). Our *in situ* high-pressure data obtained at room temperature do not show any direct evidence for the presence of the phase transition between β -GeSe₂ and any of the high-pressure phases with the tetrahedral coordination of the Ge atoms. However, the onset of disordering at about 7 GPa; i.e., local distortions of the crystal lattice and breaking of the double Ge₂Se₈ tetrahedra, could be interpreted as due to the local occurrence of the intermediate HgI₂ type structure. The pressure-induced amorphization at about 11 GPa is then related to the tendency of the crystalline material to undergo the room temperature inhibited phase transition (25), in which the coordination of the Ge atoms changes from four to six to attain higher density. The amorphization is observed in the pressure region in which β -GeSe₂ is no longer stable mechanically (i.e., crossing the spinodal of β -GeSe₂).

The inferred β -GeSe₂ \rightarrow HgI₂ \rightarrow cristobalite and β -GeSe₂ \rightarrow HgI₂ \rightarrow CdI₂ transformation paths result from the observation that these phases are synthesized in different pressure and temperature conditions (22–25). Accordingly, the latter path would occur at relatively higher pressures. Our *in situ* experiments at room temperature would then most probably correspond to the β -GeSe₂ \rightarrow HgI₂ \rightarrow CdI₂ transformation path. On the other hand, the quenching experiments do not necessarily probe the high-pressure, high-temperature equilibrium (35). Upon thermal evolution at constant pressure, a metastable system follows a transformation path determined by relative free energies of all possible polymorphs and the least stable polymorph crystallizes first. In analogy, it cannot be ruled out that there is only one pressure-induced structural transition in β -GeSe₂ due to the four-to-six coordination change around the Ge atoms, and the cristobalite-like and HgI₂ type compounds (22–25) are obtained as metastable polymorphs upon decompression to ambient conditions, in which β -GeSe₂ is the most stable phase (21).

In a previous report on electrical resistivity measurements in Ge_xSe_{100-x} ($0 \leq x \leq 40$) glasses at pressures up to 14 GPa and temperatures 77–298 K (26), it was shown that a discontinuous glassy semiconductor-to-crystalline metallic phase transition for the GeSe₂ composition occurs at about 7 GPa. The electronic states in amorphous GeSe₂ can be explained with a model assuming the existence of two Ge–Se bonding and Se lone pair valence bands and a lower conduction (Ge–Se antibonding) band (8, 9). In β -GeSe₂, with a similar electronic structure, the lone pair electrons at the edge-sharing Ge₂Se₈ tetrahedra will have higher energy than those at the corner-sharing GeSe₄ tetrahedra, because the Se bonds at the first ones are under strain (1). Our observation that the sample of β -GeSe₂ starts to be opaque at 7 GPa is consistent with the report by Prasad *et al.* (26). Breaking of the double Ge₂Se₈ tetrahedra would directly influence and modify the electronic states of the material. The Raman spectra measured in this study eventually vanish above 10 GPa when the sample becomes entirely amorphized and devoid of edge-sharing polyhedra. We then conclude that the pressure-induced opaqueness of the sample or metalization of GeSe₂ is related to the changes in the electronic structure of the GeSe₂ material rather than to the formation of gap states at the preserved fundamental band gap in the pressure-amorphized material (7, 8, 33). The topological defects responsible for the gap states should rather be suppressed by external pressure, as discussed earlier. Although it is not possible to infer the electronic structure of the high-pressure GeSe₂ modifications from our Raman spectroscopy and X-ray diffraction data, we conclude that the pressure-induced metalization of β -GeSe₂ is associated with a structural phase transition into the CdI₂ type.

CONCLUSIONS

The thermodynamic driving force for pressure-induced phase transitions is a tendency to achieve a higher density state relative to that at ambient conditions. For instance, it can be accomplished by increasing the coordination of the atoms in the compressed material. Our consideration of the phase transitions in β -GeSe₂ is an illustration of a mechanism in which the equilibrium four-to-six coordination change in the crystalline material is kinetically inhibited at room temperature and instead largely disordered and eventually amorphous phases form in the broad (7–14 GPa) pressure range, when β -GeSe₂ is no longer stable mechanically (10) (i.e., crossing the spinodal of β -GeSe₂). Similarly, isostructural HT-GeS₂ undergoes the ordered-to-disordered phase transformation at about 15 GPa (33). It is interesting at this point to recall the pressure-induced phenomena in chemically related SiO₂ and GeO₂, with structures similar to the random tetrahedral network model of amorphous GeSe₂ (5). When α -quartz, the ambient-pressure, room-temperature, three-dimensional tetrahedral form of silica, is pressurized at 300 K, it gradually transforms to an amorphous state at about 25–35 GPa, bypassing the phase transformation to stishovite with the three-dimensional TiO₂ rutile structure in which the cations are sixfold coordinated (36). An analogous behavior occurs in GeO₂ quartz in the 7- to 9-GPa pressure range, where amorphization is also associated with the four-to-six coordination change (37). Thus, it can be seen that pressure-induced amorphization in the AB₂ (A = Si, Ge; B = O, S, Se) compounds results from the tendency for these materials to attain higher coordinated phases at pressures dependent on the parent structure as well as on the cation and anion present.

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