Structural Properties of GeSe₂ at High Pressures

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   Crystalline and glassy GeSe₂ have been subjected to pressures up to 7.7 GPa and temperatures up to 1100°C using a high-pressure belt-type apparatus. Two high-pressure crystalline polymorphs of GeSe₂ have been synthesized. The crystal structure of the tetragonal form of GeSe₂ prepared at 3.0 GPa and 500°C, with space group *I-42d* and *a* = 5.7307(4) and *c* = 9.691(1), was determined by means of powder X-ray diffraction data. The structure consists of GeSe₄ tetrahedra that share corners in a three-dimensional network and has a considerably higher density than the two-dimensional structure of ambient-pressure GeSe₂ consisting of both edge- and corner-sharing tetrahedra. The IR and Raman spectra of tetragonal GeSe₂ are discussed in relation to the structure of GeSe₂ glass. An orthorhombic polymorph of GeSe₂ was formed during quenching from 7.7 GPa and 500°C. Amorphous GeSe₂ compressed at 250–300°C was observed to partly crystallize at 3.0 and 7.7 GPa.   © 1999 Academic Press

INTRODUCTION

GeSe₂ forms a glass when the melt is rapidly cooled below its melting temperature, like some other AB_2 compounds such as SiO₂ and BeF₂. SiO₂, and BeF₂ have crystal structures with low atomic packing density, and the glassy versions of the materials are typical examples of random continuous network of AB_4-tetrahedra (1). AB_2 compounds with significantly higher crystalline densities such as ZnCl₂ also form glasses relatively easily. Crystalline ZnCl₂ has a dense packing of anions with Zn in tetrahedral holes, and glassy ZnCl₂ is not a typical random tetrahedral network but is more ionic in nature (1). GeSe₂, which has a two-dimensional crystal structure at ambient pressure (2), is also a reasonably good glass former (3). Its crystal structure consists also of AB_4 tetrahedra, but the connectivity between the GeSe₂ units is unique, with 50% edge-sharing

and 50% corner-sharing tetrahedra (2). The edge-sharing units reduce the connectivity of the structure, and GeSe₂ therefore has a two-dimensional structure. The ambient pressure GeSe₂ undergoes a second-order phase transition at 147°C that does not change the connectivity of the structure (4). The edge-sharing units and the layer-like structure has also been reported in Ge–Se glasses based on spectroscopy and diffraction measurements (5–9).

   Crystals consisting of AB_4 tetrahedra undergo phase transformations to crystalline states with higher densities under compression. The cristobalite to stishovite transition of SiO₂ where the coordination number of Si transforms from 4 to 6 is a typical example (1). The analogous transition in the glassy state has also been observed as a "first-order"-like transition (10). In analogy with the phenomenon of crystalline polymorphism, this behavior has been termed "amorphous polymorphism" (11). GeSe₂ and GeS₂ have also been observed to undergo phase transitions upon compression (12–14). Prewitt and Young reported a high-pressure tetragonal modification of GeS₂ with only corner-sharing tetrahedra (12). Shimada and Dachille performed high-pressure studies of GeSe₂ and GeS₂ glasses (see Fig. 2) (13). Compression of glasses at 300°C revealed two amorphous phases for which the X-ray diffraction patterns of the recovered samples were significantly different from the X-ray diffraction halo of the ambient-pressure glass. Above 300°C the glasses crystallized during compression. Tetragonal GeSe₂ prepared at 1–5 GPa was indexed with a unit cell $a = 5.69$ and $c = 9.71$ Å and was proposed to correspond to tetragonal GeS₂ reported by Prewitt and Young (12). A hexagonal CdI₂-type structure with $a = 4.03$ and $c = 5.89$ Å was suggested for the third modification of GeSe₂ prepared at 500°C above 6 GPa. In a similar study Shimizu and Kobayashi reported a tetragonal GeSe₂ with HgI₂-type structure ($a = 5.752$, $c = 9.66$ Å) prepared at intermediate pressures (see Fig. 2). The structure of GeSe₂ prepared above 5 GPa and below 800°C was reported to belong to an orthorhombic distorted CdI₂-type structure (14). During compression of crystalline GeSe₂ at ambient,

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no phase transition was observed by X-ray diffraction and Raman spectroscopy until pressure-induced amorphization occurred at 11–14 GPa (15). A similar diamond anvil study using only Raman scattering reported an amorphous phase stable in between two crystalline phases of $GeSe_2$ (16). Finally, electrical resistivity of Ge–Se glasses under compression has been reported (17). All the glasses, including the $GeSe_2$ stoichiometry, showed a discontinuous glassy semiconductor to crystalline metal transition at around 7 GPa. X-ray patterns of the recovered samples could not be identified as any of the above-mentioned crystalline phases.

In the present work crystalline and glassy $GeSe_2$ have been heat treated under pressure using a high-pressure belt-type apparatus. The main purpose of the study was twofold. First, we wanted to establish if $GeSe_2$ is a potential system for showing the polyamorphism as indicated by Shimada and Dachille (13). The second objective was to determine the detailed crystal structure of the high-pressure polymorphs of $GeSe_2$ (13, 14). The new structure data will bring new information on how the tetrahedral network of crystalline and glassy $GeSe_2$ behaves upon compression and are also very useful for understanding the structure of ambient-pressure glassy $GeSe_2$, which is still an open question (5–9). Particularly, the possibility to access glassy and crystalline $GeSe_2$ not containing edge-sharing tetrahedra is very attractive for the ongoing discussion of the structure of glassy $GeSe_2$ (7–9).

EXPERIMENTAL

Amorphous and crystalline $GeSe_2$ were prepared from the pure elements (Goodfellow, England). Stoichiometric amounts of the two elements were transferred to silica tubes, which were sealed under vacuum. The ampules were heat treated at 900°C for 24 h to obtain a homogeneous mixture of the two elements. Crystalline $GeSe_2$ was then formed by cooling the melt at 1°C/h to 600°C. The X-ray diffraction pattern confirmed the ambient pressure $GeSe_2$ to be phase pure and to have the structure reported by Dittmar and Schäfer (2). Glassy $GeSe_2$ was prepared by dropping the ampule with the homogeneous melt from 900°C into a mixture of ice, water, and salt. The glassy nature of the sample was confirmed by X-ray diffraction and Raman spectroscopy.

High-pressure samples were prepared by loading uniaxially pressed disks of powdered crystalline or amorphous $GeSe_2$ (150–160 mg) in a graphite capsule with inner diameter 4.0 mm. The capsule was closed with a graphite cup and finally encapsulated in an outer gold capsule (diameter 6.9 mm, length 7.6 mm), which was mechanically sealed. Sample and capsule were weighed before and after the experiments in order to check for sample weight loss/gain and potential reaction between $GeSe_2$ and graphite/gold.

High-pressure experiments were carried out using a modified belt-type apparatus with a bore diameter of 32 mm (18). The pressure had previously been calibrated at ambient temperature by measuring the phase transition of Bi, Tl, and Ba. The temperature was estimated from a relation between the input power and temperature, which had been obtained in advance. Two different sample assemblies were used for experiments at 3.0 and 7.7 GPa. At 3.0 GPa the height of the sample assembly was 20 mm with a 12 mm inner diameter graphite tube furnace, while at 7.7 GPa a 16 mm height sample assembly was applied (10 mm inner diameter graphite tube furnace). NaCl and NaCl–20 wt% ZrO_2 were used as pressure media between the sample capsule and graphite furnace. Samples were first compressed and then heated to the actual temperatures. All samples were quenched to room temperature by simply turning off the current before the samples were decompressed to ambient pressure.

The $GeSe_2$ samples were examined by powder X-ray diffraction at room temperature (Guiner-Hägg camera, $CuK\alpha_1$ radiation, Si as an internal standard). The X-ray diffraction pattern of the intermediate pressure $GeSe_2$ was indexed by means of the TREOR program (19). Unit cell dimensions were obtained from least squares refinements using the CELLKANT program (20). The power X-ray diffraction pattern of the tetragonal modification of $GeSe_2$ was collected at the Swiss–Norwegian beamline, BM1, at the European Synchrotron Radiation Facility, Grenoble. X-rays of wavelength 0.9963 Å were obtained by reflection from a Si(111) channel cut monochromator. The data were recorded in steps of 0.005° in 2θ between 11.5 and 50° and the counting time was 5 s below $2\theta = 23°$ and 9 s above $2\theta = 23°$. The fine $GeSe_2$ powder was kept in a rotating, 0.3 mm silica glass capillary. Profile refinement was performed with the GSAS program (21).

The infrared spectra were recorded on polypropylene pellets with 1 wt% of the sample using a Bruker IFS 66v Fourier transform spectrometer. Spectra were recorded in the frequency region 50–700 cm^{-1} (resolution 4 cm^{-1}) using a 3.5 mm Mylar film (polyethylene terephthalate) beamsplitter, a DTGS (deuterated triglycine sulfonate) detector with a polyethylene window, and a globar carbon coil light source. Normally 100 scans were collected and averaged for each sample. Raman spectra were obtained using a Spex 1403 double monochromator and a photon counting system. The samples were excited at 54.5 nm by an argon ion laser.

RESULTS

Compression of Crystalline GeSe₂

Two high-pressure polymorphs of $GeSe_2$ were synthesized from ambient-pressure crystalline $GeSe_2$ at 3.0 and 7.7 GPa, 500°C, and a duration of 24 h. Visual observation
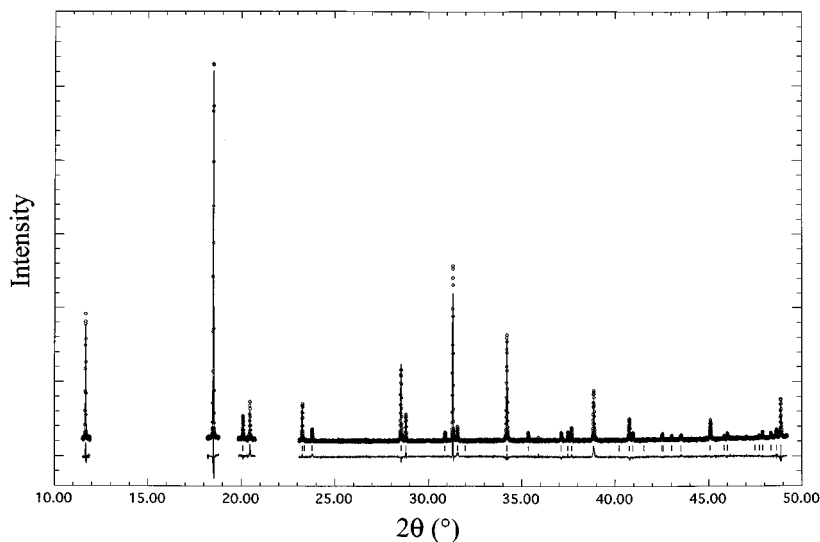
FIG. 1. Observed and difference powder X-ray diffraction pattern for tetragonal GeSe$_2$, space group *I*-42*d*, wavelength $\lambda = 0.9963$ Å.

by light microscopy showed that both phases were homogeneous. The sample prepared at 3.0 GPa was yellow, whereas the sample prepared at 7.7 GPa appeared dark and metallic.

The powder X-ray pattern collected with syncrotron radiation of GeSe$_2$ prepared at 3.0 GPa and 500°C is shown in Fig. 1. The diffraction lines are narrow, which proves that the crystalline modification of GeSe$_2$ stable at 3.0 GPa and 500°C is quenchable to ambient pressure and temperature. The diffraction pattern (Fig. 1 and Table 1) corresponds well with those previously reported for intermediate-pressure modification of GeSe$_2$ (13, 14), except that Shimizu and Kobayashi (14) report two additional diffraction lines due to contamination. The PXD pattern collected by the Guiner–Hägg film technique was indexed by means of the TREOR (19) program on a tetragonal cell with dimensions $a_T = 5.7307(4)$ and $c_T = 9.691(1)$ Å, figure of merit $M(20) = 23$. The occurrence of reflections from the tetragonal GeSe$_2$ obeys the following rules: hkl, $h + k + l = 2n$; hhl, $2h + l = 4n$; $00l$, $l = 4n$; $hh0$, $h = 2n$, giving two possible space groups , $I4_1md$ and I-42d. The correct space group was determined to be I-42d from Rietveld refinements using both space groups. Crystal data and information on the data collection are given in Table 2, and refined atomic coordinates are listed in Table 3. During the profile refinements the x coordinate of Se, the zeropoint, the scalefactor, profile parameters, and isotropic temperature factors for Ge and Se were allowed to vary. The observed and difference PXD patterns are shown in Fig. 1. The Raman and IR spectra of the tetragonal GeSe$_2$ are shown in Fig. 4.

The X-ray diffraction pattern (Guiner–Hägg) for GeSe$_2$ prepared at 7.7 GPa showed very broad diffraction lines. The observed reflections are in agreement with those re-

ported by Shimizu and Kobayashi for a CdI$_2$-like crystal structure (14). Structural refinement of the diffraction data was not performed because of severe broadening of all the diffraction lines.

TABLE 1
Powder X-Ray Diffraction Lines for Tetragonal GeSe$_2$, Miller Indices, *d*-Spacings, and Relative Intensities

h	k	l	d(obs)/Å	d(calc)/Å	Int.
1	0	1	4.934	4.933	35
1	1	2	3.110	3.108	100
2	0	0	2.866	2.865	8
1	0	3	2.815	2.814	10
2	1	1	2.4783	2.4777	10
0	0	4	2.4230	2.4225	4
2	2	0	2.0266	2.0261	20
2	1	3	2.0072	2.0076	7
3	0	1	1.8745	1.8742	3
2	0	4	1.8506	1.8499	45
1	0	5	1.8357	1.8359	4
3	1	2	1.6979	1.6974	30
3	0	3	1.6444	1.6442	2
3	2	1	1.5694	1.5684	3
2	2	4	1.5553	1.5542	3
2	1	5	1.5468	1.5458	4
1	1	6	1.5005	1.5002	14
4	0	0	1.4328	1.4327	8
3	2	3	1.4264	1.4261	2
4	1	1	1.3729	1.3758	2
3	3	2	1.3009	1.3011	6
4	2	0	1.2813	1.2814	1
4	1	3	1.2768	1.2767	2
4	0	4	1.2328	1.2332	1
3	2	5	1.2288	1.2290	2
2	1	7	1.2180	1.2180	2
0	0	8	1.2110	1.2113	3
3	1	6	1.2056	1.2057	10

TABLE 2
Crystal Structure Data for Tetragonal GeSe₂ at 298 K

Formula	GeSe₂
Formula weight (g/cm³)	230.51
Color	Yellow/brown
Space group	*I-42d*
Z	4
λ (Å)	0.9963
2θ range	11.5–50°
Number of reflections	30
Number of structure parameters	3
Profile function	Pseudo_Voigt
a_T (Å)	5.7307(4)
c_T (Å)	9.691(1)
V_T (Å³)	318.26(5)
Density (g/cm³)	4.81
R_{wp}	4.9
R_p	3.4

Compression of Amorphous GeSe₂

Reproduction of the high-pressure forms of amorphous GeSe₂ reported by Shimada and Dachille (13) was attempted via two different pressure–temperature routes. First, amorphous GeSe₂ was compressed for 24 h at 300°C and at 3.0 and 7.7 GPa, respectively. 300°C is well below the glass transition temperature (T_g) of GeSe₂ at ambient pressure (22), and the samples should not crystallize, according to Shimada and Dachille (13). Both samples, however, appeared inhomogeneous in a light microscope, which indicates partial crystallization of the samples. The powder X-ray diffraction pattern of the samples did indeed also show a few weak crystalline reflections in addition to the broad halos typical for amorphous solids. The X-ray pattern of the sample compressed at 7.7 GPa corresponds to that of the orthorhombic GeSe₂ reported by Shimizu and Kobayashi (14). The crystalline reflections observed for the sample compressed at 3.0 GPa did not correspond to any of the previously mentioned crystalline phases. One additional sample prepared at 3.0 GPa and 250°C confirmed the observations at 300°C. The amorphous part of the X-ray patterns to some degree confirmed the results reported by Shimada and Dachille (13).

In addition to the compression of amorphous GeSe₂ below T_g, preparation of glassy GeSe₂ by quenching from the melt has also been tried. The samples quenched from

TABLE 3
Atomic Coordinartes for Tetragonal GeSe₂

Atom	Site	*x*	*y*	*z*
Ge	4*a*	0	0	0
Se	8*d*	0.2495(4)	0.25	0.125

1100°C and 3.0 GPa and 1100°C and 5.5 GPa were both partly crystalline.

DISCUSSION

The Phase Diagram of GeSe₂

A *T–P* phase diagram of GeSe₂ based on previous high-pressure studies (13, 14) and the present experimental results is shown in Fig. 2. The coexistence line between ambient-pressure GeSe₂ and tetragonal GeSe₂ is indicated below 1 GPa according to the results obtained by Shimada and Dachille (13). The volume change of the transition is negative according to the density of the two phases.

The crystal structure of the tetragonal GeSe₂, shown in Fig. 3a, is an isotype of the tetragonal GeS₂ reported by Prewitt and Young (12). A three-dimensional network is formed by corner-sharing (GeSe₄)⁴⁻ tetrahedra. The interatomic distances and bonding angles are given in Table 4. The structure of tetragonal GeSe₂ is quite different from that of the ambient-pressure GeSe₂ although (GeSe₄)⁴⁻ tetrahedra are the principal structural unit in
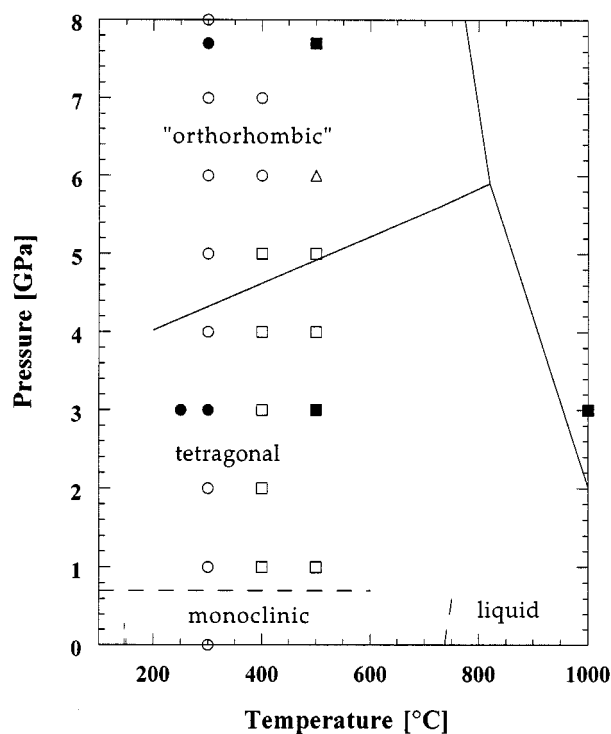

FIG. 2. The *T–P* phase diagram of GeSe₂. The solid coexistence lines are based on experimental observations reported by Shimizu and Kobayashi (14). The experimental data reported by Shimada and Dachille (13) are given by symbols (○ glass, □ tetragonal, △ orthorhombic). The present results are given by filled symbols (● partly crystalline, ■ crystalline). The dotted coexistence line suggested between ambient pressure GeSe₂ and tetragonal GeSe₂ is located below 1 GPa according to Shimada and Dachille (13). The second-order phase transition of ambient-pressure GeSe₂ (4) is indicated by a dotted line.
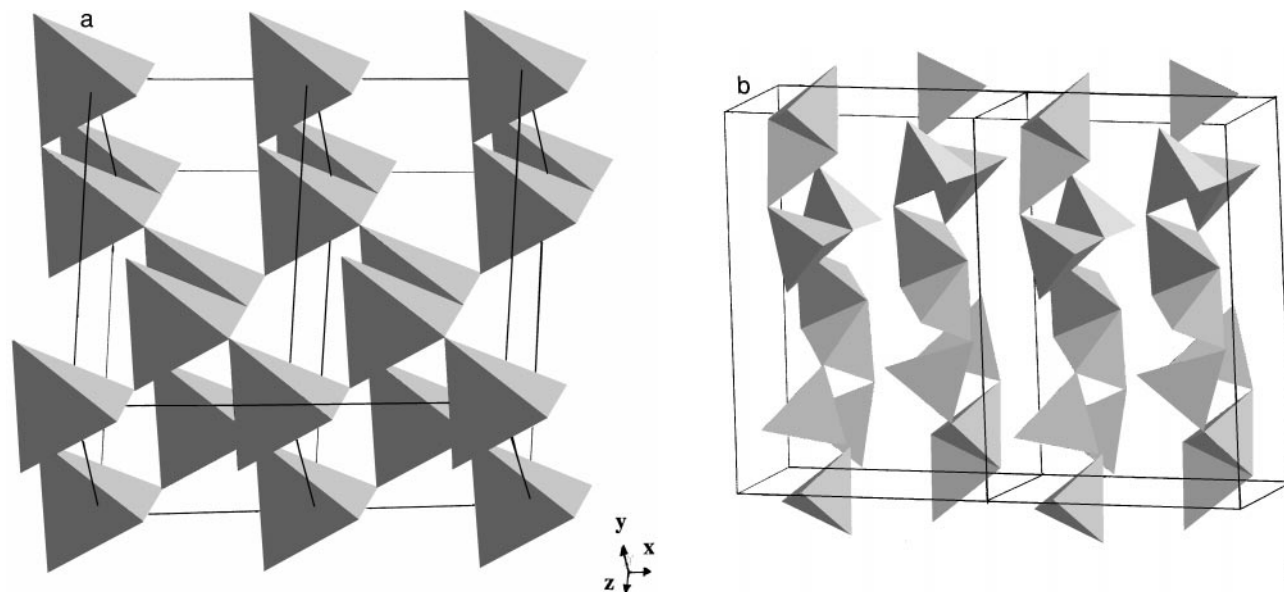
FIG. 3. Comparison of the structure of the intermediate-pressure tetragonal modification of GeSe₂ (a) and ambient-pressure monoclinic GeSe₂ (b).

both phases. The average intratetrahedral Ge–Se distances are almost equal in ambient GeSe₂ and tetragonal GeSe₂, 2.356 and 2.359 Å, respectively, and are in agreement with the sum of Pauling tetrahedral radii for these elements (2.36 Å). The structure of ambient pressure GeSe₂ is two-dimensional with both edge and corner-sharing $(GeSe_4)^{4-}$ tetrahedra as shown in Fig. 3b. The density has increased from 4.39 g/cm³ for the ambient-pressure GeSe₂ to 4.81 g/cm³ for the intermediate-pressure tetragonal GeSe₂. The Ge–Se–Ge bonding angle for tetragonal GeSe₂ (Table 4) is significantly smaller than 180°. The atomic packing is therefore significantly higher compared to SiO₂ and BeF₂, in which the bond angle is near 180° (1).

The diffraction pattern of the crystalline sample prepared at 7.7 GPa and 500°C corresponds to the pattern of the high-pressure GeSe₂ reported by Shimizu and Kobayashi, which was indexed orthorhombically (14). The Bragg reflec-

tions were very broad. We therefore propose that the phase is formed during decompression of a high-pressure modification of GeSe₂ that is not recoverable to ambient pressure. The structure of the stable modification of GeSe₂ above 5–6 GPa probably involves 6 coordination of Ge (13, 14). The border of the stability field of the nonrecoverable GeSe₂ modification (see Fig. 2) is in the same pressure region as the amorphous semiconductor to crystalline metallic transition of glassy GeSe₂ reported by Prasad et al. (17). Compression of GeSe₂ above 6–8 GPa is therefore likely to involve a co-ordination change from 4 to 6 for Ge. The coordination change is accompanied by a semiconducting to metallic transition in accordance with the results reported by Prasad et al. (17).

Vibrational Spectra

The Raman and IR spectra of tetragonal GeSe₂ are shown in Fig. 4. The selection rules for the primitive cell of tetragonal GeSe₂ with space group *I*-42*d* ($z = 4$) are

$$\Gamma = A_1(\text{Raman}) + 2A_2 + 2B_1(\text{Raman})$$
$$+ 2B_2(\text{Raman, IR}) + 4E(\text{Raman, IR})$$

where the optical activity is given in parentheses. Four sharp IR bands are evident while only one strong and several weak Raman bands were observed (see Fig. 4). The four strong IR bonds observed at 300, 280, 264, and 110 cm⁻¹, which clearly are also Raman active, are assigned as the $2B_2$ and $2E$ modes. The strong Raman band at

TABLE 4
Interatomic Distances (Å) and Selected Angles for Tetragonal GeSe₂

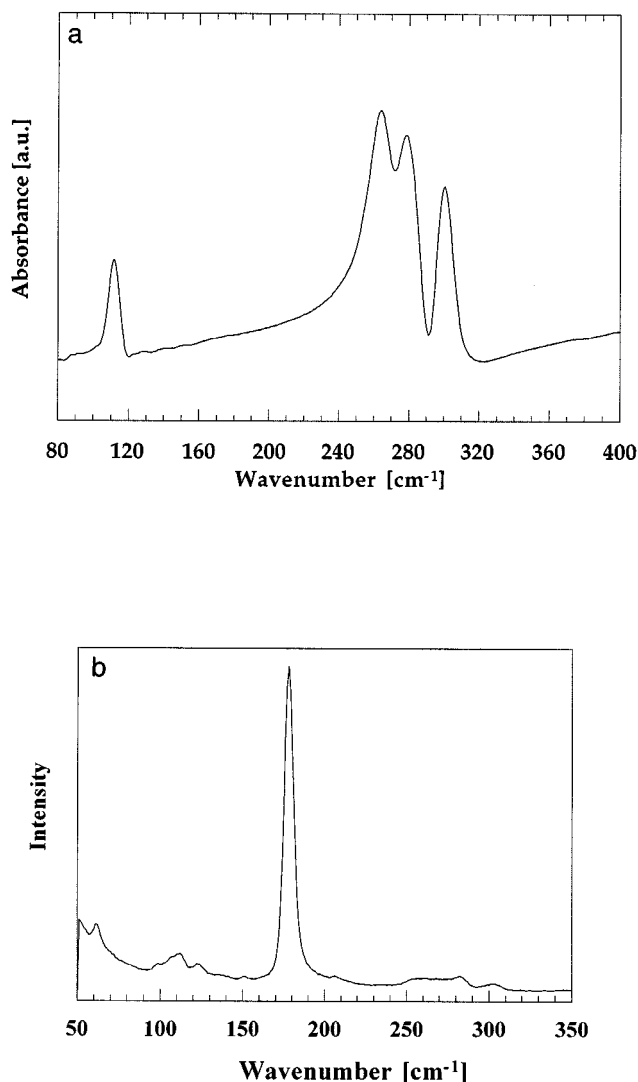|		
Ge–Se	(×4)	2.359
Ge–Ge	(×4)	3.752
Se–Se	(×2)	4.047
Se–Se′	(×4)	3.750
Se–Ge–Se		118.2
Se–Ge–Se′		105.3
Ge–Se–Ge		105.4

FIG. 4. IR (a) and unpolarized Raman (b) spectra of tetragonal GeSe₂ prepared at 500°C and 3.0 GPa.

178 cm^{-1}, which is not IR-active, is clearly an A_1 symmetrical stretching mode of corner-shared GeSe₄ tetrahedra. In ambient-pressure crystalline GeSe₂, this mode has been reported at 210 cm^{-1} with a shoulder at 215 cm^{-1} (the so-called companion peak) that has been assigned to the quasi-localized breathing mode of the edge-sharing Ge₂Se₈ tetrahedra (6). In glassy GeSe₂ the symmetrical stretching band is observed at 198 cm^{-1} together with the companion peak at 212 cm^{-1} and a weak shoulder at 175 cm^{-1} (5, 6). Thus, the Ge–Se symmetrical stretching frequency decreases when the edge-sharing tetrahedra are completely removed from the structure. The reduction of the vibrational frequency of the symmetrical stretching of the Ge–Se bond is mainly due to the reduced Ge–Se–Ge bond angle. Only a weak feature around 206 cm^{-1} (see Fig. 4) is observed in the frequency region of the Raman spectrum

where the so-called companion peak to A_1 has been observed for ambient-pressure crystalline and glassy GeSe₂ (215 and 212 cm^{-1}) (5, 6). The lack of edge-sharing units or four-membered rings in tetragonal GeSe₂ is one possible explanation for this phenomenon. Intermediate order because of larger ring structures is also absent in tetragonal GeSe₂ except for six-membered rings. However, Vashishta *et al.*, have recently estimated phonon density of states of Ge–Se ring structures, and no states corresponding to the companion peak could be resolved for six-membered rings (8). It seems therefore that the shift in the A_1 frequency and the disappearance of the companion peak to A_1 are due to the removal of edge-sharing tetrahedra and larger ring structures. Compared with the Raman spectra of Ge–Se glasses, the A_1 frequency observed for tetragonal GeSe₂ coincides with the frequency of a Raman band observed when the Ge content exceed 33.3 mol% (5). In this composition region the so-called companion peak was also observed to rapidly disappear with increasing Ge content (5). We therefore suggest that tetrahedra with only corner-sharing Ge–Se–Ge bonds are present in Ge–Se glasses above 33.3 mol% Ge. At lower content of Ge the GeSe₄ tetrahedra are bonded by both edge- and corner-sharing Ge–Se–Ge bonds.

CONCLUSIONS

The crystal structure tetragonal GeSe₂, prepared at 3.0 GPa and 500°C, was refined from powder X-ray diffraction data. The tetragonal space group was *I*-42*d* and $a = 5.7307(4)$ and $c = 9.691(1)$. The structure consists of GeSe₄ tetrahedra that share corners in a three-dimensional network and has a considerably higher density than the two-dimensional structure of ambient pressure GeSe₂ consisting of both edge- and corner-sharing tetrahedra. The IR and Raman spectra of tetragonal GeSe₂ are discussed in relation to the structure of GeSe₂ glass. Amorphous GeSe₂ compressed at 250–300°C was observed to partly crystallize at 3.0 and 7.7 GPa.

ACKNOWLEDGMENT

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