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Phase transformations and volume of the IV–VI GeTe semiconductor under high pressure

J M Leger and A M Redon

CNRS, ER 060211, GEMAP, 1 Place A Briand, 92195 Meudon Cédex, France

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Abstract. The properties of the ferroelectric IV–VI semiconductor GeTe have been studied as a function of pressure up to 25 GPa at room temperature, by powder x-ray diffraction in a diamond anvil cell. In a truly hydrostatic medium, the transition from the rhombohedral to cubic NaCl-type structure was not observed up to 8 GPa while it occurred below 5 GPa in a solid pressure transmitting medium. In both cases, no discontinuity could be observed in the lattice parameter. However, the transformation probably remains of the first order, as at normal pressure, but with a very small volume discontinuity. The presence of small anisotropic stress components has a large effect on the equilibrium pressure of the transition and possibly on its mechanism. In addition, a transition to an orthorhombic structure takes place in the same pressure range; no cubic CsCl-type structure was evident below 25 GPa.

1. Introduction

The IV–VI monochalcogenides MX (M = Ge, Sn, Pb and X = S, Se, Te) are iso-electronic with the elements of group V and have structures, in the ambient conditions of pressure and temperature, which may be considered as the binary derivatives of those observed for the pure elements. These compounds often present one or two structural transitions with increasing temperature or pressure.

Under high temperature, the rhombohedral compounds GeTe and SnTe transform into the cubic NaCl-type structure by a first-order transition for GeTe [1, 2] and a second order transition for SnTe [3–5]. All the remaining Ge and Sn monochalcogenides have an orthorhombic (B16) type structure but exhibit different types of phase transformations: GeS [6] has no transformation up to its melting point, GeSe transforms into a cubic NaCl-type phase [6] by a first-order transition while SnS and SnSe [6–8] transform into another orthorhombic structure (B33) by second-order transitions (table 1).

GeTe, a ferroelectric IV–VI narrow band gap semiconductor has been studied by neutron diffraction at normal pressure in the temperature range 295 K–716 K [2]. Accurate positional and thermal parameters of the Ge and Te atoms were determined around the ferroelectric transition ($T_c = 705$ K) from the rhombohedral (B13, R3m, C_{3v}^5) to the cubic NaCl-type structure (B1, Fm3m, O_h^5). As the transitional group remains the same in both phases, the transition could be a second-order one, according to the Landau–Lifshitz type symmetry criterion. However, when examining the order parameters which are the shift Δx of the relative positions of the Ge and Te substructures and the angle difference $\Delta\alpha$ of the rhombohedral cell to 90° , the two following processes were observed:

Table 1. The structures and phase transitions in the IV–VI monochalcogenides MX (M = Ge, Sn, Pb; X = S, Se, Te) at normal pressure as a function of temperature.

	Structure at room temperature	First transition temperature (K) and order	Structure
GeS [6]	Orthorhombic B16 $Pbnm (D_{2h}^{16})$	melts at 931 K	
SnS [6–8]	Orthorhombic B16 $Pbnm (D_{2h}^{16})$	878 K 2nd order	Orthorhombic B33
GeSe [6]	Orthorhombic B16 $Pbnm (D_{2h}^{16})$	924 K 1st order	Cubic NaCl-type B1
SnSe [6–8]	Orthorhombic B16 $Pbnm (D_{2h}^{16})$	807 K 2nd order	Orthorhombic B33
GeTe	Rhombohedral B13	705 K 1st order	Cubic NaCl-type B1
SnTe [3–5]	Rhombohedral B13 $R_{3m} (C_{3v}^5)$	75 K 2nd order	Cubic NaCl-type B1

(i) a continuous decrease of Δx from $\Delta x = \frac{1}{4} - x = 0.0124$ at 295 K to $\Delta x = 0$ at the critical temperature (displacive phase transition);

(ii) a continuous decrease of $\Delta\alpha$ from $\Delta\alpha = 90^\circ - \alpha = 1.8^\circ$ at 295 K to $\Delta\alpha = 0$ at $T_c = 705$ K.

However, at the transition temperature T_c , there is a weak discontinuity on both Δx and $\Delta\alpha$ which are respectively the primary and secondary order parameters. In addition, there is also a small jump in the lattice cell constant, and the volume decreases by approximately 0.7%. Therefore, the transition appears to be of the first order with a small volume discontinuity. Similar phase changes have been observed in SnTe, but the transition is then continuous at the critical temperature $T_c = 75$ K. It is now well established that on mixed crystals $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ [9, 10], the order of the transition depends on the value of x , with a tri-critical point at $x = 0.72$, the transition being of second order for $x < 0.72$.

Under pressure and at room temperature, the orthorhombic B16 phases of the compounds, GeS, GeSe, SnS or SnSe do not undergo transformations up to $P = 36$ GPa [11]. The cubic NaCl-type phases of PbS, PbSe, PbTe and SnTe [12] are transformed into orthorhombic structures (B16 or B33) by first order transitions and then into cubic CsCl-type structures at higher pressures (table 2).

Rhombohedral GeTe was previously studied at room temperature up to 6 GPa [13]: a strong first-order transition to the cubic NaCl-type structure occurred at $P = 3.5$ GPa and was accompanied by a sudden volume decrease of 3%, much larger than at normal pressure; no other phase transition was detected.

From the above results and according to the well known trend that under pressure the phases which exist at lower pressures with larger cations are found, it can be expected that GeTe would show the following sequence of phase transformations with increasing pressure: rhombohedral \rightarrow cubic NaCl \rightarrow orthorhombic B16 or B33 \rightarrow cubic CsCl.

Powder x-ray diffraction experiments were performed on GeTe up to 25 GPa, a much larger pressure range than previously investigated, in order to resolve the apparent

Table 2. The structures and phase transitions in the IV–VI monochalcogenides MX (M = Ge, Sn, Pb; X = S, Se, Te) at room temperature as a function of pressure.

	Structure at normal pressure	First transition pressure and order	Space group	Second transition pressure and order	Space group
GeS	Orthorhombic B16 $Pbnm$ (D_{2h}^{16})	no transition up to $P = 36$ GPa			
SnS	Orthorhombic B16 $Pbnm$	no transition up to $P = 36$ GPa			
PbS	Cubic NaCl B1	2.2 GPa 1st order	Orthorhombic B16 or B33	21.5 GPa 1st order	CsCl B2
GeSe	Orthorhombic B16 $Pbnm$	no transition up to $P = 36$ GPa			
SnSe	Orthorhombic B16 $Pbnm$	no transition up to $P = 36$ GPa			
PbSe [18]	Cubic NaCl B1	4.5 GPa 1st order	Orthorhombic B16 or B33	16 GPa 1st order	CsCl B2
GeTe this work	Rhombohedral B13 R_{3m} (C_{3v}^5)	6.5 GPa 1st order	Cubic NaCl B1		
SnTe	Cubic NaCl B1	1.8 GPa 1st order	Orthorhombic B16		
PbTe [18]	Cubic NaCl B1	6 GPa 1st order	Orthorhombic B16 or B33	13 GPa 1st order	CsCl B2

discrepancy of the nature of the rhombohedral–cubic transition [13] and detect possible further transitions to the cubic CsCl-type structure.

2. Experimental procedures

High pressures were generated within a gasketed diamond anvil cell. The sample was placed in a 0.2 mm hole made in an Inconel X750 gasket. It was mixed with a pressure marker and a pressure transmitting medium; different media were used to study their influence. A finely collimated x-ray beam 0.15 mm in diameter of zirconium-filtered molybdenum radiation was directed onto the sample along the load axis. The maximum angular dispersion was $2\theta = 40^\circ$, and the diffraction patterns were recorded on flat films which were located 24 mm away from the samples. They were analysed with a low magnification microscope. The exposures usually lasted about 24 h [14].

The samples were obtained by crushing a single crystal of GeTe, grown from the gas phase. At normal pressure, the lattice constant values obtained for these samples, $l = 5.986$ Å, and $\alpha = 88.59^\circ$, were in very good agreement with published results [2]. No additional phase was detected.

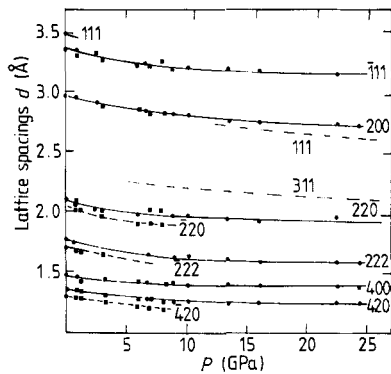


Figure 1. Interplanar spacings of GeTe compounds as a function of pressure (■ 4:1 methanol-ethanol liquid medium; ● solid silicone grease).

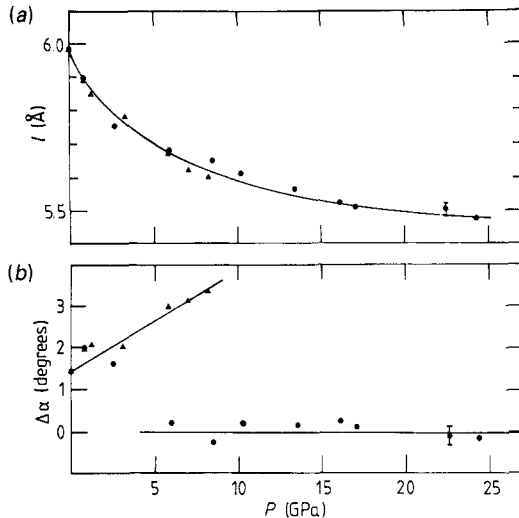


Figure 2. (a) Cell parameter l of the rhombohedral cell of GeTe as a function of pressure. (b) Angle difference between the rhombohedral and the cubic face centred structure, $\Delta\alpha = 90^\circ - \alpha$, for GeTe as a function of pressure (▲ 4:1 methanol-ethanol liquid medium; ● solid silicone grease).

Experiments were performed in two different pressure transmitting media: the usual liquid 4:1 methanol-ethanol mixture which ensures a truly hydrostatic environment up to its solidification at 10–12 GPa, and silicone grease which becomes a solid well below 3 GPa. The pressure was calculated from the lattice parameter of a pressure marker mixed with the sample, CsCl and silver metal in the liquid and solid media respectively. The diffraction lines for silver were the (111), (200) and (220) lines when separated from those of the sample and for CsCl the lines were (100), (110), (111), (200), (210) and (211).

2.1. Behaviour of GeTe under pressure

The indexing of the diffraction patterns was made assuming a rhombohedral cell. In the experiment in the liquid medium, all the more intense lines ($\bar{1}11$), (200), ($\bar{2}20$), (220), ($\bar{2}22$), (400), (420) and ($\bar{4}20$) from the rhombohedral structure were observed except the weak (111) and (222) lines. In the solid pressure transmitting medium, ($\bar{2}20$) and ($\bar{2}22$) were not detected but a much higher pressure could be reached.

2.1.1. Experiment in silicone grease. In this pressure transmitting medium, the observations could be performed up to a pressure of 25 GPa.

(i) The lattice spacings (figure 1) decreased smoothly with pressure and did not show any apparent discontinuity.

(ii) The lattice parameter l of the rhombohedral cell decreased continuously up to $P = 25$ GPa but the rhombohedral angle increased: the angle difference to 90° , $\Delta\alpha = 90^\circ - \alpha$, markedly decreased from its value $\Delta\alpha = 1.4^\circ$ at normal pressure to zero around $P = 4$ GPa (figure 2) and then remained constant.

(iii) The volume presented no detectable discontinuity as a function of pressure. A volume jump of 1% should have been detected (figure 3).

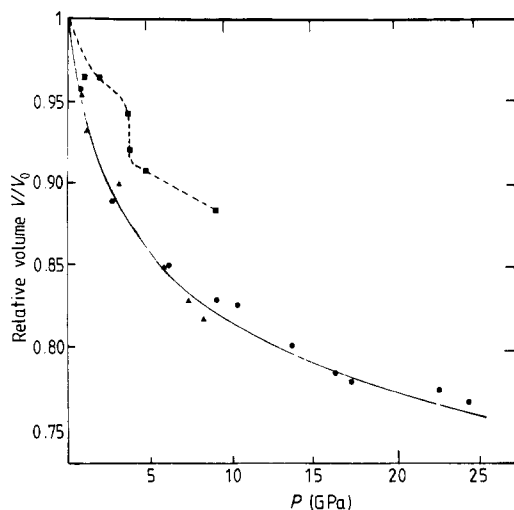


Figure 3. Relative volume V/V_0 of GeTe as a function of pressure. Pressure transmitting media: \blacktriangle 4:1 methanol-ethanol liquid medium; \bullet solid silicone grease; \blacksquare and dashed line [13].

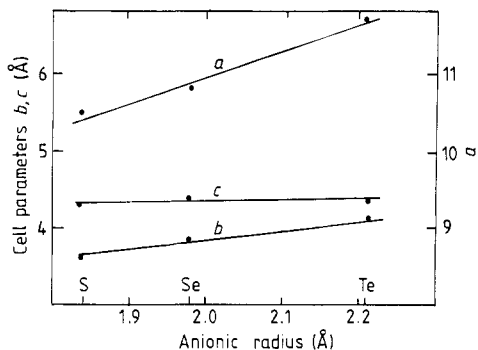


Figure 4. Cell parameters of the orthorhombic GeX (X = S, Se, Te) compounds as a function of the anionic radius [19–21].

(iv) Two new diffracted lines appeared under high pressure; the first one above 5 GPa and the second one, only above 12 GPa. Their intensities increased with pressure.

(v) No diffraction line which could have been attributed to a cubic CsCl-type structure appeared up to 25 GPa.

2.1.2. Experiment in the liquid 4:1 methanol-ethanol medium. The rhombohedral phase persisted at least up to 8 GPa, the maximum pressure investigated in this case. Furthermore, the doublets were always clearly observed and did not progressively merge under pressure (figure 1). This indicated that the rhombohedral angle did not increase in this pressure range but rather decreased and conversely, as shown in figure 2, the difference in the angle from 90° , $\Delta\alpha$, increased. However, the cell parameter l and the volume behaviours in the liquid methanol-ethanol mixture were similar to those observed in silicone grease which solidified well below 3 GPa (figures 2 and 3).

3. Discussion

With silicone grease as the pressure transmitting medium, the rhombohedral phase only existed up to about $P = 4$ GPa. Above this pressure, only singlet lines were observed, and the diffraction pattern was well indexed with a face centred cubic structure. In this solid medium, we did not observe any dependence of the cubic cell parameter on the hkl values [14]. This would have been a clear indication of uniaxial stresses acting on the sample. This cubic phase remained observable up to the maximum investigated pressure, 25 GPa. However, the intensities of corresponding lines decreased, mainly above 20 GPa.

In the liquid medium, the rhombohedral-cubic transformation was not detected up to 8 GPa. In addition, in this last medium, the angle difference to 90° , $\Delta\alpha$, did not decrease, but rather slightly increased as it probably does in the solid medium at the

lowest pressures (see figure 2). The transition would then probably take place at higher pressure, and would probably occur with a rather large discontinuity of the rhombohedral angle but without any noticeable volume change. Actually, if the transition were discontinuous and only due to the variation of $\Delta\alpha$, the variation of the volume would then be very small, about 0.15%, since the volume depends only on $\Delta\alpha$ to the second order when $\Delta\alpha$, the angle difference to 90° , is small: $V = V_0(1 - \frac{3}{2}\Delta\alpha^2)$. This would be below the accuracy of the measurements.

The lower pressure transition observed in silicone grease could be attributed to some anisotropic stress components acting in a solid pressure transmitting medium although we have not been able to evidence their existence from an hkl dependence of the lattice parameter of the cubic phase. It is well known that such stresses may considerably decrease the transition pressures; in particular, shear deformations alter the stability of phases and change the mechanism of phase transitions in InTe [15]. In addition, continuous transitions in truly hydrostatic media have been shown to occur discontinuously when anisotropic stress components were present in solid pressure transmitting media. For example, such behaviour has been previously observed for CeS or CeAl₂ [16–17]: in these two cases, no discontinuous transition occurs in truly hydrostatic pressure but isomorphous and discontinuous volume transitions with $\Delta V/V$ of about 3% were detected when using solid pressure transmitting media. In addition the compression at lower pressures was then reduced, thus leading to an apparently too high bulk modulus.

This phenomenon is probably responsible for the smaller compression and the discontinuous transition, $\Delta V/V = 3\%$, at $P = 3.5$ GPa reported by Kabalkina *et al* [13]. The GeTe sample was mixed in this case with pure boron which is very hard so that very high anisotropic components could then be introduced. In addition, the bulk modulus is higher at lower pressures, as expected when uniaxial stress components are acting. Using the hexagonal description of a rhombohedral cell, both the a and c parameters suddenly decreased at the transition; the c/a ratio dropped from 1.27 to 1.225, the ideal value for a cubic system. These variations of the volume of GeTe with pressure as previously reported are typical of the presence of strong anisotropic stress components which have been neglected. However, it should be noticed that the raw experimental data of [13] indicated a very large compression at the lowest pressures, as we observed in the present work over a much larger pressure range. The volume variations of GeTe that we determined, are very large in the lower pressure range, below 3 GPa in both pressure transmitting media. It follows that the bulk modulus of this phase is exceptionally low. This could indicate that the rhombohedral phase is close to instability.

Indeed, the volume compression of GeTe, which has a B13 structure analogous to the A7 structure of Sb is, below 8 GPa, more rapid than the compression of this element which undergoes a phase transition to a tetragonal structure at 9 GPa. A similar structure change is not observed in GeTe; but above 9 GPa, the volume variations are nearly equal. At 25 GPa, the compression of GeTe is slightly less than for elemental Sb, but slightly more than for pure As. The relative volume measured at 25 GPa compares well with the values obtained for the pure elements As and Sb [18] while the volume of GeTe previously reported up to 9 GPa [13] extrapolates to a markedly higher value.

No equation of state has been associated with the experimental data for GeTe (figure 3), as the change from the rhombohedral to cubic structure induces a change of the bulk modulus. In addition the initial volume of this high pressure phase is unknown, which adds a third parameter to the initial bulk modulus and its first pressure derivative in the data fitting procedure.

In the alloys $\text{Sn}_{1-x}\text{Ge}_x\text{Te}$ [9], the temperature of the rhombohedral–cubic transition decreases from 705 K for GeTe to 230 K for SnTe. With pressure, the transition temperature of GeTe is lowered to 300 K at 5 GPa. The effect of pressure on the transition temperature is equivalent to replacing germanium by tin (chemical pressure). However, the mechanisms are different, probably because the carrier concentrations or couplings of the soft transverse optical mode with acoustical modes vary differently. With increasing tin content, $\Delta\alpha$ decreases while with increasing pressure on pure GeTe, $\Delta\alpha$ remains approximately constant or increases in the hydrostatic environment. The rhombohedral–cubic transition in GeTe under pressure at room temperature is very similar to the one observed in black phosphorus at 10 GPa: the diffraction lines from its rhombohedral structure merge abruptly at 473 K but progressively so at higher temperatures.

The two additional diffraction lines observed in the patterns above 5 GPa were tentatively attributed to an orthorhombic structure as was found in SnTe, PbSe and PbTe under high pressure at room temperature [12] or in GeS, SnS, GeSe, SnSe at normal pressure [6–8].

The cell parameters obtained by extrapolation of the lattice parameters of B16 or B33 orthorhombic GeS and GeSe [20, 21] as a function of the anionic radius (figure 4) are: $a = 11.76 \text{ \AA}$, $b = 4.14 \text{ \AA}$, $c = 4.36 \text{ \AA}$. The two observed lines in our pressure experiments could then be attributed to the (111) and (311) interplanar distances (assuming a compression similar to the one observed for the cubic phase). Intensity calculations showed that the (111) line should be the strongest, and thus it should show up first. This was not the case because it overlapped with the strong (200) line from the rhombohedral structure. It became completely separated from the latter at 12 GPa and was then clearly recorded. The (311) line, the next strongest line, appeared at pressures as low as 6 GPa because it did not overlap with any other. The weaker (400) and (511) lines could not be observed because of overlapping with other lines from the rhombohedral structure. The intensities of the two new lines increased with pressure relative to the lines of the cubic NaCl-type structure. The intensity calculations did not allow for choosing an orthorhombic B16 or B33 structures.

The existence of an orthorhombic phase of GeTe at normal pressure was previously reported [19], but the cell parameters b and c obtained then were precisely four times larger than the above lattice constants. However, most of the reported d spacings can be attributed to the above orthorhombic structure, and it is possible that the remaining weak lines came from impurities: the sample (52 at.% Te) was kept at 350 °C for 2000–4000 h and lines of the rhombohedral structure of GeTe were removed. Another possibility would be the existence of a superstructure. Therefore, it seems that the orthorhombic phase of GeTe can be obtained at normal pressure and at about 350 °C or at room temperature, under a pressure of about 5 GPa. The appearance of the orthorhombic and cubic phases at approximately the same pressure leads to the conclusion that the triple point between the rhombohedral, orthorhombic and cubic phases is close to these conditions. The volumes of these three phases do not differ by more than 0.3% in normal conditions.

In GeTe the orthorhombic structure appeared at the same pressure as the cubic one, around 5 GPa. In SnTe, it appeared at 1.8 GPa although recent experiments [22] cast some doubts about its exact structure. In PbTe, it only appears at 6 GPa [12]. It is difficult to compare these pressure transitions as the experiments have been performed in different types of high pressure apparatus and the uniaxial components may, therefore, be very different.

4. Conclusions

The ferroelectric narrow band gap semiconductor GeTe has been studied by powder x-ray diffraction at room temperature in a diamond anvil cell at pressures up to 25 GPa in two different pressure transmitting media.

In a truly hydrostatic medium, the rhombohedral to cubic transition could not be observed below 8 GPa and the rhombohedral angle did not increase towards 90° in this pressure range. In a solid pressure transmitting medium, silicone grease, the rhombohedral angle reached 90° below 5 GPa but no discontinuity in the lattice parameter could then be observed. No volume discontinuity at the rhombohedral–cubic transition was detected which is to be expected as it should be very small, of the order of 0.15%. However, the transition probably remains of the first order as the lines from the rhombohedral structure did not progressively merge. The volume variations of GeTe are very similar to those of the pure elements As or Sb of group V. In GeTe, the transition from the rhombohedral to the cubic NaCl-type structure was accompanied by a simultaneous transition to an orthorhombic structure, B16 or B33. No transition to a cubic CsCl-type structure could be evidenced up to 25 GPa.

The exact behaviour of the lattice cell was modified by the presence of anisotropic stress components, although they were certainly small in the gasketed configuration we used. These stress components seem to have a large effect on narrow band gap semiconductors. They produced changes not only in the hysteresis of a transition but also in the phase transformation process. For these compounds, it is absolutely essential to carefully control the exact nature of the applied stresses. This should also be considered in the pressure studies of the elements of group V whose structures are analogous and where different results have been reported.

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