

Structural, Vibrational, and Electronic Study of α -As₂Te₃ under Compression

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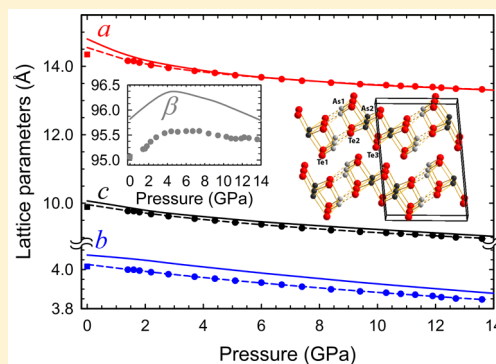
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Supporting Information

ABSTRACT: We report a study of the structural, vibrational, and electronic properties of layered monoclinic arsenic telluride (α -As₂Te₃) at high pressures. Powder X-ray diffraction and Raman scattering measurements up to 17 GPa have been complemented with *ab initio* total-energy, lattice dynamics, and electronic band structure calculations. Our measurements, which include previously unreported Raman scattering measurements for crystalline α -As₂Te₃, show that this compound undergoes a reversible phase transition above 14 GPa at room temperature. The monoclinic crystalline structure of α -As₂Te₃ and its behavior under compression are analyzed by means of the compressibility tensor. Major structural and vibrational changes are observed in the range between 2 and 4 GPa and can be ascribed to the strengthening of interlayer bonds. No evidence of any isostructural phase transition has been observed in α -As₂Te₃. A comparison with other group 15 sesquichalcogenides allows understanding the structure of α -As₂Te₃ and its behavior under compression based on the activity of the cation lone electron pair in these compounds. Finally, our electronic band structure calculations show that α -As₂Te₃ is a semiconductor at 1 atm, which undergoes a trivial semiconducting–metal transition above 4 GPa. The absence of a pressure-induced electronic topological transition in α -As₂Te₃ is discussed.



INTRODUCTION

Arsenic telluride (As₂Te₃) and other group 15 sesquichalcogenides with generic formula A₂X₃ (A = As, Sb, Bi; X = S, Se, Te) have been widely studied because of their outstanding thermoelectric properties.^{1–3} In this regard, the most stable phase of arsenic telluride at ambient conditions (α -As₂Te₃) is a quasi-layered structure with monoclinic C2/m symmetry^{4–6} and a smaller figure of merit than Sb- and Bi-based tellurides;⁷ however, the metastable β -As₂Te₃ polymorph, known for many years^{8–11} and with layered tetradymite-like rhombohedral R $\bar{3}m$ symmetry, exhibits notable thermoelectric properties.^{12,13} Additionally, As₂Te₃ glasses have also been extensively studied due to their interesting applications as IR devices, electric and optical switches, memory devices, high-resolution displays, acousto-optic devices, optical fibers, and amplifiers.^{14–19}

The recent discovery of 3D topological insulators (TIs) among group 15 sesquichalcogenides^{20–22} has stimulated in the

last years the study of these materials, which crystallize in a number of polymorphs depending on the activity of the cation lone electron pair (LEP). Many of the group 15 sesquichalcogenides that behave as 3D TIs crystallize in the layered tetradymite R $\bar{3}m$ structure, like α -Sb₂Te₃, α -Bi₂Se₃, and α -Bi₂Te₃. Since this phase has been found in several sesquichalcogenides at high pressures (HP) and/or high temperatures (HT), HP studies of these materials are extremely interesting in order to search for new 3D TIs. Consequently, a number of HP experimental and theoretical studies have been conducted in recent years in group 15 sesquichalcogenides looking for an improvement of thermoelectrical properties or for the discovery

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of topological properties^{23–43} (see ref 23 for studies prior to 2013).

Despite the interest in group 15 sesquichalcogenides from both fundamental and technological points of view, many properties of crystalline As_2Te_3 are unknown. In particular, there is no report on the vibrational properties of crystalline phases of As_2Te_3 even at room conditions, to our knowledge, and only a few HP studies have been devoted to crystalline As_2Te_3 . In this respect, synthesis at HP/HT conditions explored the phase boundary between the α and β phases up to 2 GPa three decades ago,^{8,9} and much later, changes in the thermoelectric power of α - As_2Te_3 were reported above 2 and 6 GPa and a structural transformation to β - As_2Te_3 between 6 and 8 GPa was claimed without reporting full structural details of the high-pressure phase.⁷ Finally, two recent studies of α - As_2Te_3 up to 40 and 47 GPa have been reported. In these two works, two isostructural phase transitions (IPTs) of α - As_2Te_3 and a progressive first-order phase transition to the γ - Bi_2Te_3 phase above 13–15 GPa have been reported.^{42,43} In this regard, it must be noted that a new monoclinic $P2_1/m$ (named β') has also been recently found at low temperatures.⁴⁴

As regards the electronic structure, recent *ab initio* calculations have reported that uniaxially strained β - As_2Te_3 should undergo a pressure-induced electronic topological transition (ETT) leading from a trivial insulator to a Weyl semimetal and then to a topological insulator.⁴⁵ While there is still no experimental result on β - As_2Te_3 under pressure, a recent work has reported electrical measurements at HP combined with theoretical *ab initio* calculations and observed the metallization of α - As_2Te_3 above 5 GPa;⁴² however, another recent work has suggested on the basis of theoretical calculations that there is no metallization of α - As_2Te_3 on increasing pressure but there are two second-order electronic transitions.⁴³ These recent studies contrast with previous studies of amorphous and liquid semiconductors As_2S_3 , As_2Se_3 , and As_2Te_3 at HP that suggested a decrease of the optical and electronic bandgap with increasing pressure, leading to a common semiconductor–metal transition and glass transitions.^{46–52}

In light of the cited works and the interesting properties found in other group 15 sesquioxides and sesquichalcogenides, it is interesting to study the properties of α - As_2Te_3 at HP in order to (i) understand the stability of their different polymorphs; (ii) check if there is any IPT or ETT in α - As_2Te_3 ; (iii) verify if α - As_2Te_3 undergoes metallization under compression; and (iv) explore if α - As_2Te_3 can behave as a 3D-TI at HP. For those reasons, here we report a HP study of structural, vibrational, and electronic properties of α - As_2Te_3 at room temperature by means of powder X-ray diffraction (XRD) and Raman scattering (RS) measurements up to 17 GPa, which are complemented with *ab initio* total energy, lattice dynamics, and electronic structure calculations. We will show that our measurements reveal a reversible phase transition above 14 GPa to the γ phase in good agreement with recent reports,^{42,43} but no IPTs are found in α - As_2Te_3 contrary to the same recent reports.^{42,43} The crystalline structure and compressibility of α - As_2Te_3 is analyzed by calculating the compressibility tensor at HP and explained in light of its comparison to that of other group 15 sesquichalcogenides by taking into account the activity of the cation LEP. The RS spectrum of α - As_2Te_3 at room conditions is reported for the first time, and its HP behavior has been discussed. Finally, our electronic band structure calculations suggest that there is a progressive closing of the bandgap of α - As_2Te_3 with increasing pressure leading from a trivial semiconductor to a trivial metal

above 4 GPa with no evidence for a pressure-induced ETT. Taking into account that the calculated bandgap is slightly underestimated in our calculations, we suggest the closing of the experimental bandgap above 6–7 GPa in good agreement with a recent work,⁴² but in disagreement with another recent study.⁴³ Therefore, our results are consistent with the changes in resistivity and thermopower measurements previously reported.^{7,42}

■ EXPERIMENTAL DETAILS

Commercially available polycrystalline As_2Te_3 powder (Alfa-Aesar, 99.999%) was used in the present study. XRD measurements at ambient pressure performed with a Rigaku Ultima IV diffractometer showed that samples correspond to the α phase with no presence of other phases or impurities. HP angle-dispersive powder XRD experiments at room temperature up to 17 GPa were conducted in a membrane-type diamond anvil cell (DAC) at the BL04-MSPD beamline of ALBA synchrotron. Incident monochromatic beam with wavelength of 0.4246 Å was focused to $20 \times 20 \mu\text{m}$ using a pinhole of $50 \mu\text{m}$ to cut the X-ray beam tail.⁵³ Images covering a 2θ range up to 18° were collected using a SX165 CCD located at 240 mm from sample. One-dimensional diffraction profiles of intensity as a function of 2θ were obtained by integration of the observed intensities with the Fit2D software.⁵⁴ Rietveld refinement of the experimental diffraction patterns gave reliable correlation factors up to 6 GPa. Above this pressure, the atomic positions have not been included in the fit and the lattice parameters were extracted through a Le Bail analysis of the experimental diffraction patterns. Rietveld and Le Bail refinements were carried out with GSAS package software for synchrotron measurements.^{55,56} Interatomic distances were extracted with VESTA software.⁵⁷ The equation of state (EoS) of copper,⁵⁸ whose powder was mixed with the sample powder, was used for pressure calibration.

Room-temperature unpolarized RS measurements up to 12 GPa were carried out with a Horiba Jobin Yvon LabRAM HR spectrometer equipped with a thermoelectrically cooled multi-channel CCD detector that enables a spectral resolution better than 2 cm^{-1} . RS measurements were excited using the 6328 Å line of a He:Ne laser with an output power below 0.3 mW in order to avoid laser heating since these samples are very prone to laser damage both outside and inside the DAC. This fact could explain why RS measurements even at ambient conditions have not been previously reported for this compound to our knowledge. Pressure was determined with the ruby fluorescence method.⁵⁹ In both HP-XRD and HP-RS measurements, a methanol–ethanol (4:1 ratio) mixture was used as a pressure-transmitting medium with hydrostatic conditions up to 10 GPa and quasi-hydrostatic conditions up to 17 GPa.^{60,61}

■ THEORETICAL DETAILS

Ab initio total-energy calculations were performed for α - As_2Te_3 and β - As_2Te_3 within the density functional theory (DFT)⁶² using the plane-wave method and the pseudopotential theory with the Vienna *Ab initio* Simulation Package (VASP)⁶³ including scalar relativistic effects and spin–orbit interaction (SOI). The projector-augmented wave scheme (PAW)^{64–67} was used as implemented in this package and the basis set of plane waves extended up to an energy cutoff of 440 eV in order to achieve highly converged results and accurate description of the electronic properties. The exchange–correlation energy was described in the generalized gradient approximation (GGA)

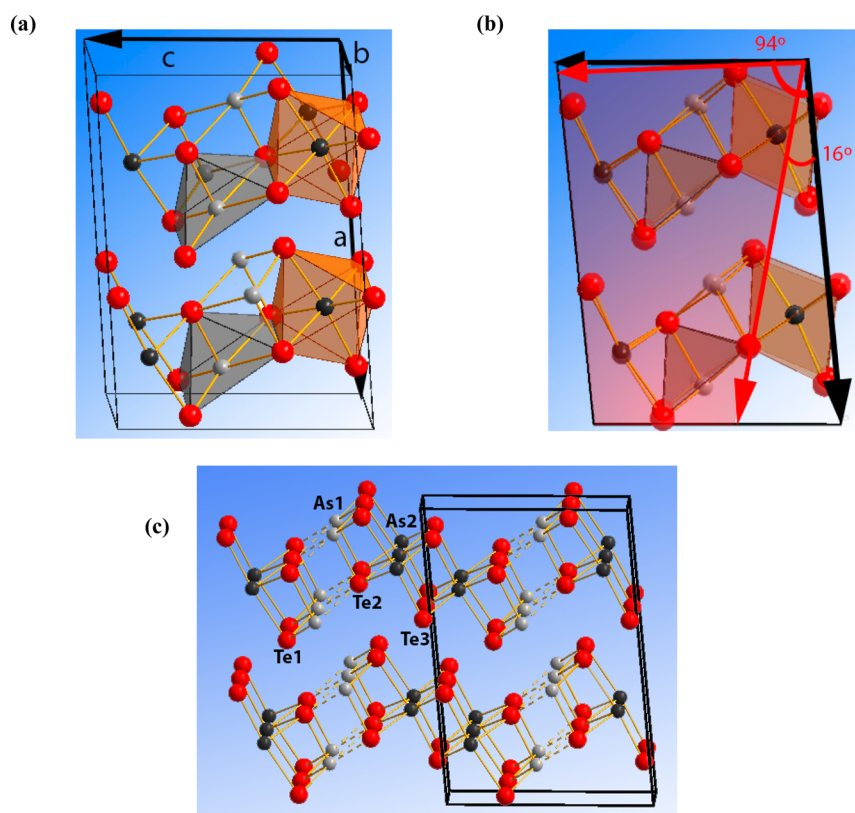


Figure 1. (a) Unit cell of α -As₂Te₃ structure at room pressure. Coordination polyhedral of As1 (3 + 2) and As2 (6) atoms are shown. (b) Representation of the effect of pressure in the α -As₂Te₃ structure at 1 atm (base scheme) and 14 GPa (scaled and superimposed, transparent scheme). Atoms at 14 GPa seem greater than at 1 atm due to rescaling of cell axes to match the values at 1 atm. Light gray, dark gray, and red colors correspond to As1, As2, and Te atoms, respectively. Red arrow indicates the direction of maximum compressibility of the compound at room and high pressure. (c) Layer and rod layout. Dashed As–Te bonds divide the layers into rods and indicate the long As–Te bond distances leading to 3 + 2 coordination of As1 atoms.

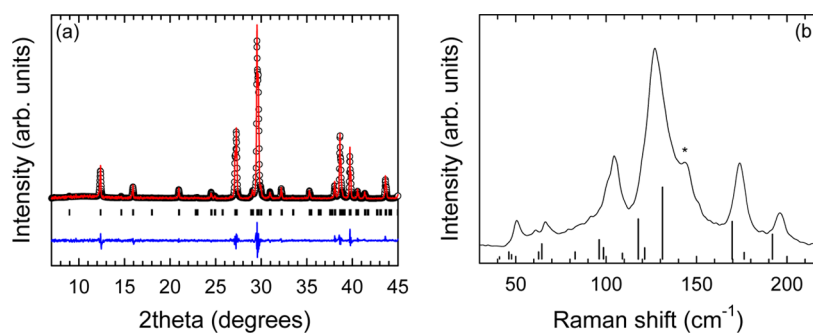


Figure 2. Structural and vibrational characterization of α -As₂Te₃ at room conditions: (a) Powder XRD pattern. Rietveld refinement and residuals are also plotted. (b) RS spectrum. Bottom marks show theoretical Raman-active mode frequencies whose length scales indicate the calculated intensity for each mode. The asterisk indicates a peak from crystalline Te.

with the PBE prescription.⁶⁸ In order to obtain very well converged energies and forces, the integration over the Brillouin zone (BZ) was performed using dense meshes of special k -points. At selected volumes, the structures were fully relaxed to their optimized configuration through the calculation of the forces on atoms and the stress tensor. In the optimized configurations, the forces on the atoms are less than 0.002 eV/Å and the deviations of the stress tensor from a diagonal hydrostatic form are less than 1 kbar (0.1 GPa).

Electronic band-structure calculations were carried out at different pressures along selected paths on the first BZ. In turn, lattice-dynamics calculations were performed at the zone center (Γ point) and along high-symmetry directions of the BZ as a

function of pressure using the direct-force constant approach.⁶⁹ The construction of the dynamical matrix at the Γ point of the BZ involves separate calculations of the forces that result from a fixed displacement away from equilibrium of the atoms in the primitive cell. The diagonalization of the dynamical matrix provides the normal-mode frequencies. Moreover, these calculations allow identifying the irreducible representations and the character of the vibrational phonon modes at the Γ point.

RESULTS AND DISCUSSION

Structural and Vibrational Characterization of α -As₂Te₃ at Room Conditions. As₂Te₃ usually crystallizes in the α polymorph with monoclinic $C2/m$ space group. The

crystalline structure of the α phase (Figure 1) is composed of zigzag layers piled up mainly along the a axis, which are linked by very weak van der Waals forces. In turn, zigzag layers are formed by rods extending along the b axis, which are linked by weak ionic–covalent As–Te forces mainly along the c axis. This zigzag layered structure is similar to that recently described for Sb_2S_3 , Sb_2Se_3 , and Bi_2S_3 .⁴¹ In $\alpha\text{-As}_2\text{Te}_3$, there are five atoms occupying independent 4i Wyckoff sites (As1, As2, Te1, Te2, and Te3); i.e., all atoms are located in the planes $y = 0$ and $y = 1/2$. The two independent As1 and As2 atoms have 5-fold and 6-fold coordination, respectively. In particular, Te atoms around As2 form a distorted octahedron with As–Te distances around 2.8 Å, while Te atoms around As1 form a square-based pyramid in a 3 + 2 coordination with three As–Te distances around 2.7 Å and two distances around 3.2 Å. This 5-fold and 6-fold coordination of As atoms in $\alpha\text{-As}_2\text{Te}_3$ contrasts with the pure 6-fold coordination of As atoms in $\beta\text{-As}_2\text{Te}_3$. In this regard, we must note that a higher 5 + 2 coordination has been proposed for As1 in $\alpha\text{-As}_2\text{Te}_3$ (with two long (>4 Å) As–Te distances between As1 atoms and Te atoms corresponding to the adjacent layer).⁶ We will show later in the discussion of HP-XRD results that the right coordination of As1 in $\alpha\text{-As}_2\text{Te}_3$ at room conditions is five.

The experimental XRD pattern of our sample at ambient conditions (Figure 2a) can be refined with a Gd_2Cl_3 -type structure ($C2/m$ space group), with small residuals and a correlation factor R_{wp} of 10%, yielding the following lattice parameters: $a = 14.3441(4)$ Å, $b = 4.01627(19)$ Å, $c = 9.8895(4)$ Å, and $\beta = 95.053(3)^\circ$ with $V_0 = 567.52(3)$ Å³. These values show good agreement with our theoretical lattice parameters (see Table 1) and with previously reported experimental val-

Table 1. Experimental and Theoretical Fractional Coordinates Corresponding to the $C2/m$ Phase of $\alpha\text{-As}_2\text{Te}_3$ at Ambient Conditions^a

atoms	site	character	x	y	z
As1	4i	exptl	0.6117(4)	0	0.4436(9)
		theor	0.6218		0.4408
As2	4i	exptl	0.7917(7)	0	0.8608(13)
		theor	0.7962		0.8593
Te1	4i	exptl	0.972(3)	0	0.7143(6)
		theor	0.9619		0.7137
Te2	4i	exptl	0.778(3)	0	0.3391(7)
		theor	0.7812		0.3371
Te3	4i	exptl	0.623(3)	0	0.9682(6)
		theor	0.6284		0.9664

^aExperimental (exptl) lattice parameters and volume are $a = 14.3441(4)$ Å, $b = 4.01627(19)$ Å, $c = 9.8895(4)$ Å, $\beta = 95.053(3)^\circ$, and $V_0 = 567.52(3)$ Å³. Theoretical (theor) lattice parameters and volume are $a = 14.7995$ Å, $b = 4.0744$ Å, $c = 10.0667$ Å, $\beta = 95.8181^\circ$, and $V_0 = 603.88$ Å³.

ues.^{4–6,42,43} Furthermore, our theoretical values at room pressure compare also well to those of recently reported *ab initio* calculations including SOI.⁷⁰ Therefore, our XRD analysis at room conditions shows that our sample corresponds to pure $\alpha\text{-As}_2\text{Te}_3$. No traces of crystalline Te have been observed in our samples.

As regards the vibrational properties of $\alpha\text{-As}_2\text{Te}_3$, group theory predicts 30 zone-center vibrational modes at the BZ center with mechanical representation:⁷¹

$$\Gamma_{30} = 10(A_g + B_u) + 5(A_u + B_g) \quad (1)$$

where g (gerade) modes are Raman active and u (ungerade) modes are infrared (IR) active, except one A_u and two B_u modes, which are acoustic modes. Therefore, $\alpha\text{-As}_2\text{Te}_3$ has 15 Raman-active modes and 12 IR-active modes. A_u and B_g modes correspond to atom vibrations along the b axis while A_g and B_u modes correspond to vibrations of atoms in the a – c plane.

Figure 2b shows an unpolarized RS spectrum of $\alpha\text{-As}_2\text{Te}_3$ at room conditions together with the theoretically predicted frequencies (bottom marks) scaled in intensity according to theoretical calculations of the Raman scattering cross section. The values of the experimental and theoretical frequencies of the Raman-active modes of $\alpha\text{-As}_2\text{Te}_3$ at room pressure are summarized in Table 2. It can be observed that our RS spectrum clearly shows 10 out of the 15 Raman-active modes with a rather good agreement between our experimental and theoretical frequencies and intensities. However, the large number of Raman-active modes in a small frequency region of the RS spectrum at room pressure and the broadening of experimental peaks make their identification, using only the RS spectrum at room pressure with the help of *ab initio* calculations, almost impossible. Therefore, a tentative assignment of experimental peaks has been performed on the basis of HP-RS measurements and calculations commented in a posterior section.

The RS spectrum of $\alpha\text{-As}_2\text{Te}_3$ is dominated by a mode close to 120 cm^{−1} and two characteristic high-frequency modes between 170 and 200 cm^{−1}. Unfortunately, our RS spectrum of crystalline $\alpha\text{-As}_2\text{Te}_3$ cannot be compared to previous measurements since this is the first time this RS spectrum is reported to the best of our knowledge. However, we must note that our RS spectrum is consistent with RS spectra reported in glasses containing As and Te (see discussion in the Supporting Information), which show vibrational frequencies^{72–78} below 200 cm^{−1}. In this regard, it must be stressed that the RS spectrum of $\alpha\text{-As}_2\text{Te}_3$ resembles that of crystalline Te since the most intense mode of the RS spectrum of $\alpha\text{-As}_2\text{Te}_3$ (the A_g^7 mode around 120 cm^{−1}) occurs at similar frequency as the most intense mode (A_1 mode) of crystalline Te.⁷⁹ We will show later in our HP-RS study that the RS spectrum of $\alpha\text{-As}_2\text{Te}_3$ at several pressures shows two Raman-active modes of crystalline Te: the A_1 mode of Te which is overlapped with the A_g^7 mode near 120 cm^{−1} and the E'' mode of Te around 140 cm^{−1} (marked with an asterisk in Figure 2b). Since XRD peaks of crystalline Te do not appear in our XRD pattern at ambient conditions, laser heating appears to be responsible for the presence of these Te-related modes, even at the small powers used in this work for exciting RS measurements. Further discussion of the vibrational properties of $\alpha\text{-As}_2\text{Te}_3$ is given in the Supporting Information, where four characteristic Raman-active modes have been discussed and visualized and with the J-ICE software (see Figure S1)⁸⁰ in the same way as was previously reported for monoclinic $\alpha\text{-Bi}_2\text{O}_3$.⁸¹

HP-XRD Measurements. Figure 3 shows powder HP-XRD patterns of $\alpha\text{-As}_2\text{Te}_3$ at selected pressures up to 17.2 GPa. It can be observed that the low-pressure monoclinic $C2/m$ structure is stable up to 14 GPa. Above this pressure, a reversible structural transition to a HP phase is evidenced by new peaks (marked by asterisks in Figure 3) in the pattern of 17.2 GPa and by the recovery of the XRD pattern of $\alpha\text{-As}_2\text{Te}_3$ on releasing pressure to room pressure (see pattern at the top of Figure 3). This result is in agreement with two recent works,^{42,43} but contrasts with a previous work that reported a phase transition to $\beta\text{-As}_2\text{Te}_3$ between 6 and 8 GPa under non-hydrostatic conditions.⁷ None of the peaks of the new phase can be assigned to either $\beta\text{-As}_2\text{Te}_3$ or $\beta'\text{-As}_2\text{Te}_3$. Our XRD pattern at 17.2 GPa matches with the γ -

Table 2. Theoretical and Experimental Raman Mode Frequencies and Their Pressure Coefficients in α -As₂Te₃ at Room Temperature As Fitted with the Equation $\omega(P) = \omega_0 + \alpha P + \beta P^2$

mode	<i>ab initio</i> calculations			experiment		
	ω_0 (cm ⁻¹)	α (cm ⁻¹ /GPa)	β (cm ⁻¹ /GPa ²)	ω_0 (cm ⁻¹)	α (cm ⁻¹ /GPa)	β (cm ⁻¹ /GPa ²)
Ag ¹	43.0(6)	1.2(5)	−0.10(4)	49.0(2)	2.5(5)	−0.19(5)
Ag ²	47.4(5)	3.4(3)	−0.070(17)	67.0(4)	4.3(2)	−0.15(3)
Bg ¹	48.3(7)	1.5(2)	−0.077(19)	66.0(4)	0.15(6)	−0.014(4)
Bg ²	62.4(2)	2.0(1)	−0.011(5)			
Ag ³	63.8(1)	3.8(2)	−0.08(1)			
Ag ⁴	83.0(5)	2.9(1)	−0.08(1)	90.6(3)	1.8(1)	−0.037(9)
Bg ³	95.6(3)	4.5(3)	−0.15(2)	99.0(8)	6.0(8)	−0.7(2)
Ag ⁵	99.1(4)	2.6(1)	−0.068(9)			
Bg ⁴	107.9(2)	3.2(2)	−0.04(1)	119.2(2)	2.2(1)	−0.045(9)
A ₁ (Te)				123.1(4)	−3.4(3)	0.13(5)
Ag ⁶	117.7(2)	1.9(3)	−0.005(2)			
Ag ⁷	121.0(3)	2.8(3)	−0.018(3)	128.0(8)	2.3(4)	−0.02(3)
Bg ⁵	130.9(4)	1.5(1)	0.05(1)	137.0(9)	−0.8(4)	0.16(2)
E''(Te)				142.0(3)	−0.6(2)	0.11(4)
Ag ⁸	170.2(4)	−1.3(2)	0.17(2)	171.4(3)	−0.3(1)	0.13(3)
Ag ⁹	177.3(2)	0.22(6)	0.074(5)			
Ag ¹⁰	192.0(1)	−1.3(3)	0.14(2)	193.2(3)	0.13(5)	0.066(8)

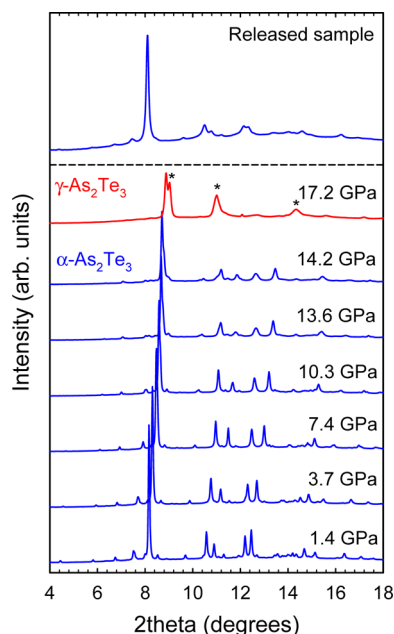


Figure 3. Powder HP-XRD patterns of α -As₂Te₃ at selected pressures up to 17.2 GPa where the sample has already undergone a transition to γ -As₂Te₃. Patterns are shifted in vertical for comparison.

Bi₂Te₃ and γ -Bi₂Se₃ phases (monoclinic C2/c), in good agreement with the two recent works.^{42,43} The study of the HP phase of α -As₂Te₃ is out of the scope of this work.

Rietveld refinements performed up to 6 GPa and Le Bail analysis at higher pressures (see examples in Figure S2) allowed us to get the structural parameters of α -As₂Te₃ at different pressures. A monotonous decrease of the unit cell volume of α -As₂Te₃ up to 14 GPa is observed (Figure 4a). Fit of pressure vs experimental volume to a third-order Birch–Murnaghan equation of state (BM-EoS)⁸² yields a zero-pressure volume, bulk modulus, and pressure derivative of the bulk modulus of $V_0 = 579(4)$ Å³, $B_0 = 24(3)$ GPa, and $B_0' = 7.9(9)$, respectively. The volume at zero pressure, V_0 , obtained from the BM-EoS fit is similar, but slightly different from the value measured outside the

DAC. This is a common fact noted in many experimental works when XRD measurements outside the DAC are performed with commercial equipment by using the $K\alpha_1$ and $K\alpha_2$ lines of Cu, whereas HP-XRD patterns are measured using synchrotron radiation.⁸³ In any case, both results are comparable with those of literature.^{4–6,42,43} On the other hand, our bulk modulus and pressure derivative under hydrostatic conditions are similar to those recently reported ($B_0 = 26$ GPa, $B_0' = 9.0$) under quasi-hydrostatic conditions,⁴² but different from those recently reported ($B_0 = 38.4$ GPa, $B_0' = 4.0$ fixed) under hydrostatic conditions.⁴³ In this respect, we must note that all these results are comparable since fixing B_0' leads to an increase of B_0 . In fact, it seems to be unreliable to fix the bulk modulus pressure derivative to 4 in order to fit the volume vs pressure in highly compressible noncovalent compounds with a large cation LEP activity, as it has been observed for structurally related sesquichalcogenides Sb₂S₃, Sb₂Se₃, and Bi₂S₃ characterized by bulk modulus pressure derivatives⁴¹ larger than 4.

It must be also stressed that results from our experimental BM-EoS are in good agreement with those from our theoretical BM-EoS: $V_0 = 603.2(6)$ Å³, $B_0 = 19.7(3)$ GPa, and $B_0' = 8.1(4)$. The theoretical bulk modulus is slightly smaller than the experimental one, which can be explained by the overestimation of the theoretical volume at zero pressure in the GGA-PBE approximation. As expected, our experimental and theoretical values for the bulk modulus of the α phase are larger than those deduced for As₂Te₃ glass (~ 15 GPa) from ultrasonic measurements.⁴⁸ However, it must be noted that our bulk modulus is much smaller than the value recently reported (42.7 GPa) from elastic constant calculations based on GGA-PBE calculations.⁷⁰

The lattice parameters of α -As₂Te₃ up to 16 GPa also show a monotonous and smooth decrease as pressure increases (Figure 4b). The nice agreement of the theoretical behavior of volume and lattice parameters with experimental results gives support to the absence of a first-order phase transition between 6 and 8 GPa at room temperature under hydrostatic conditions, unlike assumed in a previous work⁷ and in agreement with recent works.^{42,43} Furthermore, the pressure dependence of our lattice parameters does not show evidence of anomalies in the region close to 13 GPa which could be indicative of any IPT as recently

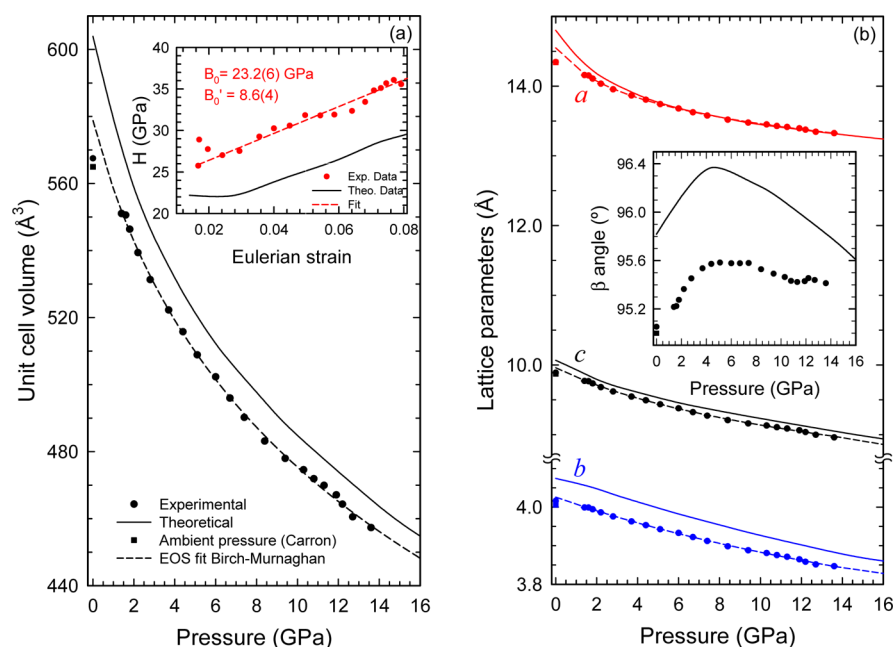


Figure 4. Experimental (symbols) and theoretical (solid lines) pressure dependence of the unit-cell volume (a) and lattice parameters (b) in α -As₂Te₃. Experimental data are fit to a BM-EoS (dashed lines) and compared to theoretical data. Inset of panel (a) shows the reduced pressure vs Eulerian strain plot for both experimental and theoretical data. Inset of panel b shows the pressure dependence of the monoclinic β angle. Squares correspond to data at ambient pressure taken from ref 32.

suggested.⁴³ In this regard, it is possible that the anomalous changes of correlated a and c parameters observed in literature⁴³ could be due to mistakes in the fit due to the mixture of the low- and high-pressure phases coexisting above 13 GPa.

For completeness, the experimental and theoretical pressure dependence of the axial ratios of α -As₂Te₃ is shown in Figure S3. As can be observed, there is a monotonous behavior of the experimental c/b axial ratio, which is well reproduced by our calculations. On the other hand, the theoretical a/b and a/c axial ratios display a non-monotonic dependence showing changes in the region between 2 and 4 GPa. Our axial ratios are similar to those recently reported,^{42,43} but we have not observed the anomalies found at some pressures in these two last works. In some recent works, changes in the pressure dependence of the axial ratios of several group 15 sesquichalcogenides have been considered as a proof for the occurrence of a pressure-induced ETT^{29,39,40} because a minimum of the c/a ratio was previously observed to be coincident with the occurrence of a pressure-induced ETT in α -Bi₂Se₃, α -Sb₂Te₃, and α -Bi₂Te₃.²³ However, this fact has been put into question in recent works^{41,84} because the minimum of the c/a ratio can be originated by a change in the ratio of interlayer/intralayer forces, and it cannot be taken for granted that this change should be necessarily translated into a change in the electronic density of states near the Fermi level.

The inset of Figure 4b shows a change of the slope of the β monoclinic angle (always perpendicular to the b axis) above 4 GPa. This result implies that in α -As₂Te₃ the direction of the a axis changes with pressure, i.e., assuming that the directions of both b and c axes remain constant. The departure of β from 90° indicates that the direction of maximum compressibility at room pressure is not exactly that of the a axis, i.e., the main direction in which layers are piled up (see Figure 1). The change in the slope of the β angle together with the change of the compressibility of the a axis (correlated with a change in the a/b ratio) near 4–5 GPa has been interpreted in a recent work as a proof of the occurrence of a second-order IPT.⁴² Similarly, changes of the β

angle together with the changes in the electronic band structure near 3 and 6 GPa have been interpreted in a recent work as a proof of the occurrence of two second-order IPTs.⁴³ In the following we will demonstrate that no pressure-induced IPT occurs in α -As₂Te₃ up to the first-order phase transition above 14 GPa; however, we will first analyze the compressibility tensor of our monoclinic material.

In order to evaluate the change in the direction of maximum compressibility as a function of pressure we have calculated and diagonalized the experimental and theoretical isothermal compressibility tensor, β_{ij} , at different pressures (details are given in the Supporting Information). This tensor is a symmetric second rank tensor which relates the state of strain of a crystal to the change in pressure that induced it,⁸⁵ and it has been obtained with the finite Eulerian approximation as implemented in the Win_Strain package.⁸⁶ Diagonalization of the β_{ij} tensor at room pressure yields for our experiments the maximum, intermediate, and minimum compressibilities $27.3(21) \times 10^{-3}$, $14.0(11) \times 10^{-3}$, and $4.7(4) \times 10^{-3}$ GPa⁻¹, respectively; whereas for the case of our calculations the obtained values for the compressibilities are $38(3) \times 10^{-3}$, $14.6(11) \times 10^{-3}$, and $4.3(5) \times 10^{-3}$ GPa⁻¹. As observed, the a axis is the most compressible one, the b axis is by far the less compressible axis, and the compressibility of the c axis is intermediate between that of the a and b axes. The experimental (theoretical) axial compressibilities indicate that around 59% (67%) of the total compression at room pressure is being accommodated along the direction of maximum compressibility. The major compression direction at room pressure occurs in the (010) plane at the given angle ψ (see Tables S1 and S2) relative to the c axis (from c to a) or equivalently at an angle θ relative to the a axis (from a to c). In particular, the experimental major compression direction at room pressure is at $\theta = 16.0(1.4)^\circ$ from the a axis whereas our calculations predict that it is at $5.5(7)^\circ$ from the a axis (see red arrow in Figure 1b).

As regards the behavior of the compressibility tensor at HP, the evolution under pressure of the β_{xx} tensor coefficients (related to the axial compressibilities) is shown in Figure S4. Note that the evolution of the experimental and theoretical compressibility tensors at HP is very similar. The most notable feature is that the experimental compressibility of the a axis is higher than that of the c axis ($\beta_{11} > \beta_{33}$) below 2.0 GPa; however, both compressibilities are similar at 2 GPa and $\beta_{11} < \beta_{33}$ beyond 3 GPa within experimental uncertainties. Moreover, the decrease of the compressibility of the a axis with increasing pressure is so large that the compressibilities of the a and b axes become equal around 13 GPa ($\beta_{11} = \beta_{22}$). These results imply that the c axis becomes more compressible than the a axis above 3 GPa. In this way, the direction of maximum compressibility moves away from the a axis and approaches the c axis with increasing pressure; i.e., the θ angle increases. At 3 GPa the direction of maximum compressibility is closer to the c axis than to the a axis, and at pressures beyond 5 GPa the direction of maximum compressibility is already very close to the c axis.

From the experimental and theoretical compressibility tensors at different pressures we can obtain the experimental and theoretical volume compressibility (trace of the tensor) at each pressure, which is plotted in Figure S5. As observed, there is a continuous evolution of the compressibility as a function of pressure so no one can infer the presence of any pressure-induced second-order IPT. This result contrasts with the pressure-induced second-order IPTs suggested in recent works.^{42,43} In this respect, an IPT near 5 GPa based on a change of the β angle, a change in the slope of the compressibility at HP, and a change in the reduced pressure vs the Eulerian strain ($F-f$) plot has been suggested.⁴² We plot in the inset of Figure 4a the $F-f$ plot of our experiments and calculations. As observed, no change of the slope is observed when using the unit cell volume obtained from our fitted EoS. Therefore, our measurements and calculations do not support the existence of any IPT up to 14 GPa. In any case, we have to note that the results of the $F-f$ plot are not completely reliable because they are very sensitive to errors in the volume at room pressure and the dispersion of data measured at HP, as already discussed regarding the structural behavior of α -Bi₂Se₃, a compound which shows a pressure-induced second-order phase transition.⁸⁷ Further support to the absence of pressure-induced second-order IPTs in α -As₂Te₃ is provided below.

In order to better understand the HP behavior of the structural parameters in α -As₂Te₃ previously described, we have studied the experimental and theoretical pressure dependence of the x and z atomic parameters of the Wyckoff positions for the five nonequivalent As (As1 and As2) and Te (Te1, Te2, and Te3) atoms (see Figure S6) and the main interatomic distances (see Figures S7 to S10). As can be seen in Figure S6, all atomic parameters evolve in a monotonous way between ambient pressure and 14 GPa. This result means that all atomic positions are located at planes $b = 0$ and $1/2$ ($y = 0$ or $y = 1/2$ atomic coordinate) at all pressures up to 14 GPa and that the changes of the atomic parameters do not show evidence for any phase transition up to 14 GPa. No increase or decrease of the symmetry of our theoretical atomic positions is observed in the whole pressure range studied unlike in the case of β -Bi₂O₃ where an increase of symmetry has been observed along the β - β' IPT.⁸⁸ Therefore, our theoretical calculations do not support the existence of any IPT in α -As₂Te₃.

Similarly, Figures S7 to S10 show an overall monotonous decrease of the experimental and theoretical As–Te, As–As, and

Te–Te distances as pressure increases. In general, there is a good agreement between the behavior of experimental and theoretical interatomic distances. Note that the values of the refined distances are of the same order as those theoretically calculated, which indicates that the refinement is correct; however, errors in Rietveld refinement positions propagate when calculating interatomic distances, especially with increasing pressure, which accounts for the differences between experimental and theoretical data. Therefore, in the following the discussion of the evolution of interatomic distances with pressure is going to be based on the evolution of the theoretical distances, which have been calculated in the whole range of pressure from 1 atm to 14 GPa.

Regarding the coordination of As1 atoms in α -As₂Te₃, Figure S7 shows that As1 is 5-fold ($3 + 2$) coordinated at room pressure if one considers all intralayer As–Te bonds, i.e., intralayer As–Te bonds below 3.0 Å and interlayer bonds above 3.2 Å. At pressures above 6 GPa, As1 atoms can be considered to become truly 5-fold coordinated (all intralayer As–Te bonds below 3.0 Å). On the other hand, As1 polyhedral units only tend toward a $5 + 2$ coordination at pressures far from the stability range of the low-pressure phase if interlayer As1–Te1 distances (>3.5 Å at 14 GPa) are considered. Regarding the coordination of As2 atoms, Figure S8 shows that As2 is 6-fold coordinated at room pressure and all six As2–Te distances tend to similar values above 6–7 GPa, thus indicating a regularization of the distorted As2 octahedron on increasing pressure. Finally, Figures S9 and S10 show that intralayer and interlayer As–As and Te–Te distances show different behaviors under pressure. Intralayer distances show a small compression, while interlayer distances show a large contraction up to around 3–4 GPa and a considerable saturation above this pressure range. Figures S7 to S10 allow us to understand the different compressibilities of a , b , and c axes at HP. At room pressure, the a axis is considerably more compressible than b and c axes at room pressure, as it was expected from the strong initial compression of the weak van der Waals forces present in the space between adjacent layers that are piled up mainly along the a axis (Figure 1a). This strong compression of the a axis below 3 GPa is related to the strong compressibility of interlayer Te–Te distances in this pressure range. On the contrary, the b axis is the less compressible axis at any pressure because of strong intralayer As–Te covalent bonds (<3.0 Å) which extend along the b axis. Finally, the compressibility of the c axis is intermediate between that of the a and b axes because of the presence of long As1–Te2 distances (>3.2 Å) at room pressure. On the other hand, interlayer Te–Te distances at pressures above 3–4 GPa decrease at a similar rate as intralayer Te–Te distances with the exception of Te2–Te2 distances which extend mainly along the c axis. This result evidences the hardening of interlayer bonds and explains why the a axis is no more the most compressible axis above this pressure range and why the most compressible axis approaches the c axis as pressure increases as evidenced from the analysis of the compressibility tensor.

To finish this section regarding the structural properties of α -As₂Te₃, it is interesting to compare the structure of α -As₂Te₃ and its pressure behavior with that of other group 15 sesquichalcogenides. This family of compounds crystallize in a number of distorted crystalline structures due to the activity of the cation LEP, which increases in the series Bi–Sb–As.⁸⁹ Therefore, the study of the behavior of the As LEP in α -As₂Te₃ at HP is crucial in order to understand the properties of this compound and other group 15 sesquichalcogenides under compression. Figures S11a

and S12a show the decrease of the volume of the different Te polyhedra around As1 and As2 atoms, respectively. As observed, a good agreement is obtained between experiment and theoretically simulated evolution of these polyhedral units. The decrease of the distortion index (Figures S11b and S12b) shows that these polyhedra become more regular with increasing pressure and evidences a decrease of the As LEP activity with increasing pressure, in good agreement with previous results in a number of Sb- and Bi-related materials.^{29,41,88,90,91} A comparison of the structure of α -As₂Te₃ with that of α -Sb₂Te₃, α -Bi₂Te₃ and orthorhombic Sb₂Se₃ (isostructural to Sb₂S₃ and Bi₂S₃) and their pressure dependences is provided in the Supporting Information taking into account the cation LEP activity. We can conclude that the structure of α -As₂Te₃ and its pressure behavior can be understood as intermediate between that of α -Sb₂Te₃ and Sb₂Se₃ in good agreement with what is expected from the activity of cation LEP in group 15 sesquichalcogenides. In this way, the nonobservation of a pressure-induced second-order IPT in α -As₂Te₃ is consistent with the fact that no IPT has also been found in Sb₂Se₃,²⁸ Bi₂S₃,²⁹ or Sb₂S₃⁴¹ with a similar zigzag layered structure. We speculate that the reason for the lack of pressure-induced IPTs in these compounds is due to the large structural flexibility of orthorhombic and monoclinic structures (with many free atomic parameters) to accommodate changes in the cation LEP activity due to pressure, as compared to cubic, tetragonal, and rhombohedral structures of α -Sb₂O₃, β -Bi₂O₃, and α -Sb₂Te₃, respectively, which already show pressure-induced second-order IPTs.^{88,92,93}

In summary, the effect of pressure in the structure of α -As₂Te₃ is a progressive contraction of the interlayer space and a slight rotation of polyhedral units (see the main difference between the structure of α -As₂Te₃ at 1 atm and 14 GPa in Figure 1b) that leads to an increase of the average coordination of As ions and to a decrease of the distortion of the polyhedral units around As ions (due to the decrease of the cation LEP), but without modifying the γ parameter of the initial Wyckoff sites of the five nonequivalent atoms of the unit cell. No evidence for a pressure-induced IPT has been found in α -As₂Te₃.

HP-RS Measurements. As already discussed, HP-XRD measurements at room temperature under quasi-hydrostatic conditions show no phase transition to the β phase either above 8 or above 14 GPa, unlike expected from previous results.⁷ In order to clarify the stability of both α -As₂Te₃ and β -As₂Te₃ phases, we have performed *ab initio* calculations of the enthalpy vs pressure for both phases (Figure S13). Unlike previous calculations,⁴² our calculations suggest that the α -to- β phase transition in As₂Te₃ could occur at relatively small pressures (>1 GPa). This means that, perhaps, the α -to- β phase transition in As₂Te₃ is kinetically hindered at room temperature and at quasi-hydrostatic conditions by a high energy barrier. Therefore, some additional thermal energy is needed in order to overcome this energy barrier. This result is in agreement with experiments reporting the existence of β -As₂Te₃ at relatively low pressures and high temperatures.^{8–11} In this regard, a possible transition above 6 GPa, as previously suggested from thermopower measurements⁷ and expected from extrapolation of experimental HP/HT data at relatively low pressures,^{8,9} could correspond to the non-hydrostatic conditions in ref 7 or to thermal activation at HP derived from the increase in temperature inherent to thermopower measurements. Additionally, it can be observed from Figure S13 that the enthalpy of the β phase is higher than that of the α phase above 15 GPa; therefore, our calculations show that the β phase is not a competitive phase at very HP as it was

previously assumed. This may explain why we have observed a new phase above 14 GPa different from that of the β phase in good agreement with two recent works.^{42,43}

In order to study the possible effect of hydrostaticity on the appearance of the α -to- β phase transition we have conducted HP-RS measurements at both hydrostatic and non-hydrostatic conditions, which have been compared to lattice-dynamical calculations in order to better understand the HP behavior of α -As₂Te₃. Figure 5 shows room-temperature RS spectra of α -

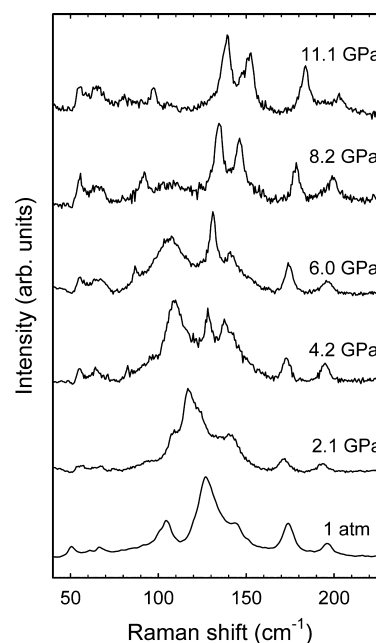


Figure 5. Room-temperature Raman scattering spectra of α -As₂Te₃ at selected pressures.

As₂Te₃ at selected pressures under hydrostatic conditions up to 12 GPa. It can be observed that RS spectra clearly correspond to α -As₂Te₃ in this pressure range.

As already mentioned, it is very difficult to assign the features that show up in the room-pressure RS spectrum of α -As₂Te₃. However, it is possible to perform a tentative peak assignment by studying the behavior of the Raman-active peaks at HP in combination with the results of lattice-dynamical calculations. Figure 6 shows the pressure dependence of the experimental and theoretical Raman-active mode frequencies of α -As₂Te₃ measured up to 12 GPa under hydrostatic conditions. In general, theoretical frequencies of Raman-active modes do not show a simple monotonic behavior with increasing pressure. In fact, they show a complex behavior with crossings and anticrossings of modes with different and equal symmetries, respectively. This complex behavior is caused by the presence of 15 Raman-active modes in a small region between 50 and 200 cm^{−1} similar to that found in orthorhombic Sb₂S₃, Sb₂Se₃, and Bi₂S₃.⁴¹ Apart from crossings and anticrossings already observed in related orthorhombic compounds Sb₂S₃, Sb₂Se₃, and Bi₂S₃,⁴¹ small changes in the pressure coefficient of some theoretical Raman-active modes have been observed in the range between 2 and 4 GPa in α -As₂Te₃, which could be attributed to the strong changes in the interatomic distances around these pressures already mentioned in the previous section.

Despite the complex behavior observed in theoretical Raman-active modes, several experimental modes are found to show a

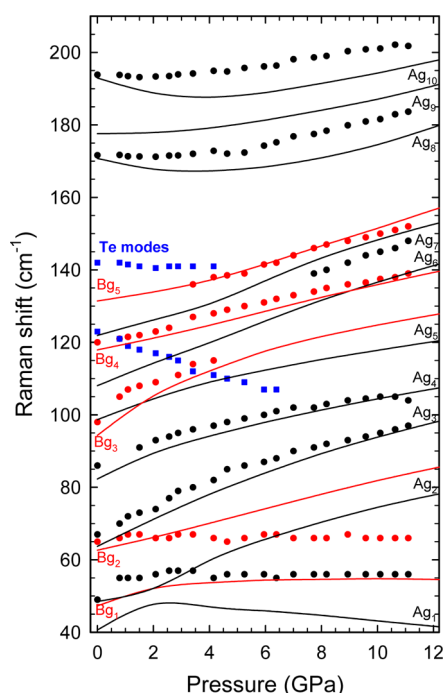


Figure 6. Experimental (symbols) and theoretical (lines) pressure dependence of the Raman-mode frequencies of α -As₂Te₃. Different colors represent Raman-active modes of different symmetries. Blue squares represent the modes corresponding to crystalline Te.

behavior consistent with the theoretical ones. In particular, the two high-frequency theoretical Raman modes above 160 cm⁻¹ show small negative pressure coefficients at room pressure in rather good agreement with the almost negligible pressure coefficient of our two highest-frequency modes. These small negative or even negligible pressure coefficients are consistent with the small or even negligible increase of the shorter intralayer As1–Te distances (Figure S7) at low pressures. Therefore, tentative assignments of the experimental Raman-active modes of α -As₂Te₃ reported in Figure 6 have been made by comparing the experimental and theoretical values of frequencies and pressure coefficients. The tentative assignments are summarized in Table 2.

As can be seen in Figure 6, we have additionally observed two experimental Raman modes in the range from 120 to 145 cm⁻¹ (see blue symbols in Figure 6) whose frequency decreases with increasing pressure. The frequencies of these two modes are close to those previously reported for crystalline Te,⁷⁹ as already mentioned. Furthermore, the negative pressure coefficients shown by these two modes are in agreement with those reported for crystalline Te.^{91,92,94,95} Consequently, we have attributed the modes near 120 cm⁻¹ and near 140 cm⁻¹ to the A₁ and E'' (marked with an asterisk in Figure 2b) modes of crystalline Te. In this regard, we have to note that Raman-active modes associated with Te have been already observed in nonstoichiometric samples of Bi₂Te₃ nanowires and were assigned to Te clusters in Te-rich regions in nanowires.⁹⁶ Furthermore, segregation of Se nano-clusters caused by laser-induced damage during HP-RS measurements has also been observed in several chalcogenides.^{97,98} In our experiments, it is highly difficult to avoid such damage when performing experimental RS measurements, at least with the red He:Ne laser. These modes are no longer observed at pressures beyond 4–5 GPa likely because of the improvement in the thermal conductivity inside the DAC with increasing pressure in

part due to the metallization of α -As₂Te₃ as discussed in the next section.

Room-temperature HP-RS spectra and the pressure dependence of the Raman-active modes under non-hydrostatic conditions (without pressure transmitting medium) are shown in Figures S14 and S15, respectively. As observed, no phase transition near 6–8 GPa is observed either under hydrostatic or under non-hydrostatic conditions, thus supporting the hypothesis that thermal activation at HP is needed in order to force the α -to- β phase transition in α -As₂Te₃ at relatively low pressures.^{8,9}

In order to check if there could be any pressure-induced second-order IPT in α -As₂Te₃, we have also studied the phonon dispersion curves theoretically calculated at different pressures up to 14 GPa (see Figure S16) since second-order IPTs must be related to the presence of a soft phonon mode according to Landau theory. As observed, there is no soft mode along the whole BZ at any pressure either in the range from 3 to 5 GPa or in the range from 6 to 13 GPa, unlike in β -Bi₂O₃.⁸⁸ Therefore, we can safely conclude that there is no pressure-induced IPT in α -As₂Te₃ up to 14 GPa, unlike recently reported.^{42,43}

Finally, we must mention that in order to check if there could be a possible occurrence of a pressure-induced ETT in α -As₂Te₃, we have also studied the pressure dependence of the line width for the most intense Raman-active modes in both HP-RS experiments under hydrostatic and non-hydrostatic conditions. We have found no major change on increasing pressure which could be indicative of a pressure-induced ETT in this compound. Only a small increase of the RS background is observed above 4 GPa which could be indicative of the progressive metallization of the material above this pressure as will be discussed in the next section.

Electronic Band Structure Calculations. Taking into account that ETTs are very subtle transitions (they are 2^{1/2} transitions in Ehrenfest notation) whose occurrence could be difficult to evidence by XRD or RS measurements, we have performed *ab initio* band-structure calculations in α -As₂Te₃ at HP in order to identify possible changes of the band extrema that could be related to a pressure-induced ETT. We show in Figure 7 the electronic band structure at different pressures. As can be seen, the electronic structure at 0 GPa exhibits an indirect bandgap (theoretical value around 0.7 eV) with the conduction band minimum (CBM) located close to the L point of the BZ and three almost degenerate valence band maxima (VBM) located in different directions close to the A point of the BZ in good agreement with recent calculations,⁴² but in disagreement with other calculations.^{43,70} In any case, all reported theoretical DFT results for α -As₂Te₃ at 0 GPa underestimate the experimental bandgap value at room pressure, which is estimated to be experimentally between 0.82 and 0.92 eV.^{99,100}

The indirect bandgap progressively closes at HP in good agreement with recent results.^{42,43} Around 1 GPa, our calculations show that the bandgap remains indirect with a value above 0.4 eV and that the CBM changes from the L point to the V point. No major changes occur in the electronic band structure above this pressure. Our calculations indicate that the indirect bandgap of α -As₂Te₃ closes completely around 4 GPa undergoing a pressure-induced trivial semiconductor–metal transition and no other major change occurs at higher pressures. Therefore, due to the underestimation of the theoretical bandgap in DFT calculations, it is reasonable to assume that the actual closing of the bandgap takes place at a slightly larger pressure (around 6–7 GPa). This closing could explain the anomalies observed in thermopower measurements in this pressure range⁷

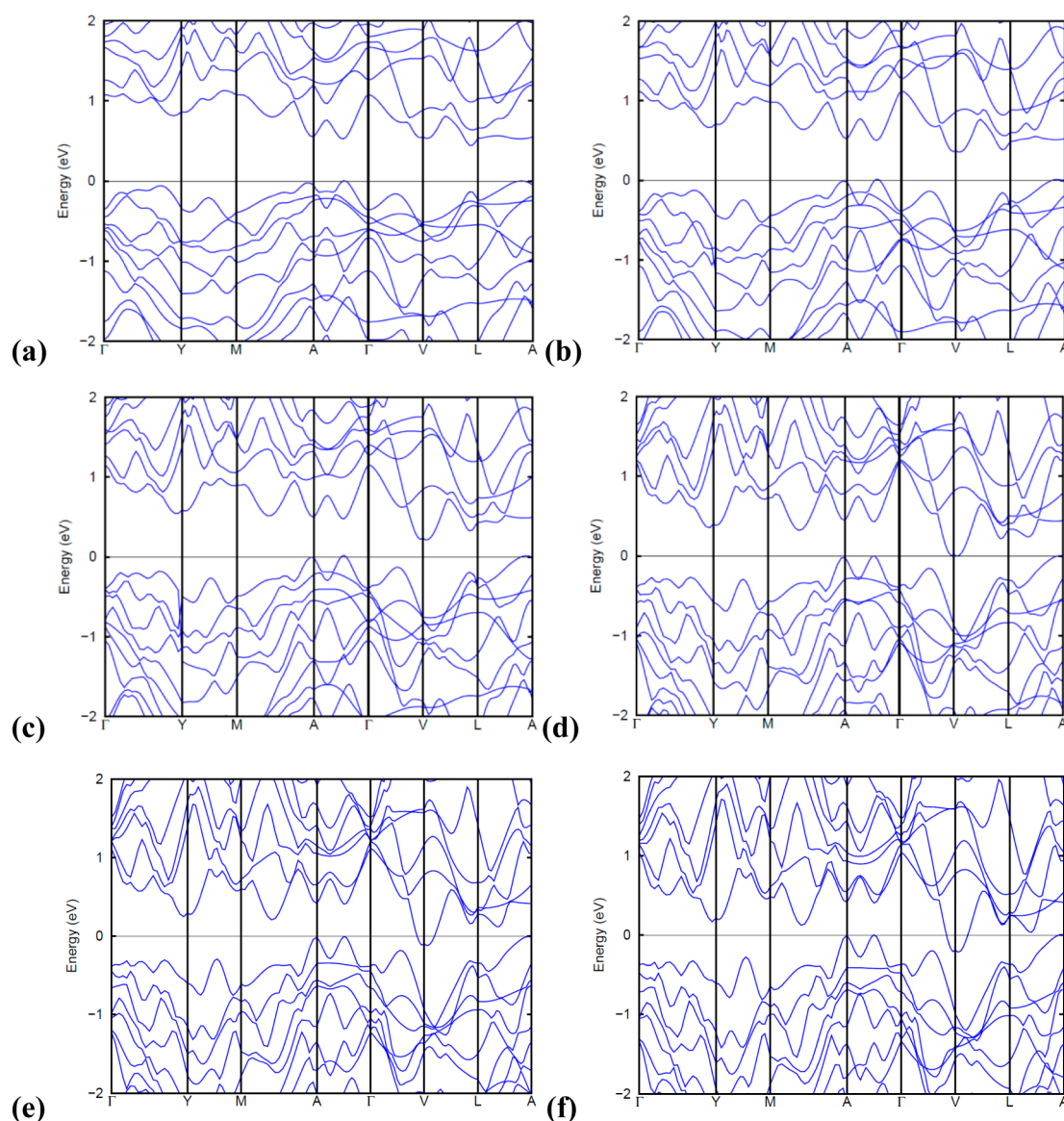


Figure 7. Calculated band structure of α -As₂Te₃ at different pressures: (a) 0 GPa, (b) 1 GPa, (c) 2 GPa, (d) 4 GPa, (e) 6 GPa, and (f) 8 GPa.

and is in good agreement with the recent electric measurements and theoretical calculations of a recent report.⁴² However, our results are in disagreement with another recent report that suggests two indirect-to-direct crossovers that have been incorrectly interpreted as IPTs⁴³ and whose calculations do not allow explanation of the electrical results recently obtained.⁴²

In summary, our theoretical electronic band structure calculations show that α -As₂Te₃ is a semiconductor with an indirect bandgap above 0.7 eV at room pressure, whose energy decreases with increasing pressure until it becomes a semimetal above 4–6 GPa. Only a change in the location of the CBM in the BZ is observed around 1 GPa which could lead to a pressure-induced ETT; however, the bandgap at this pressure is too high (probably above 0.5 eV) to result in a strong modification of the electronic density of states near the Fermi level. Therefore, we conclude that there is no evidence for a pressure-induced ETT in α -As₂Te₃ and that changes in the resistance of α -As₂Te₃ measured by Scheidemantel et al.⁷ between 1 and 2 GPa and above 6 GPa match with the changes in the electronic band structure here reported. However, in light of the present results and the discrepancies observed among the different calculations,

we must say that more precise calculations including SOI should be performed to shed further light on the pressure dependence of the electronic band structure of α -As₂Te₃.

CONCLUSIONS

We have studied the structural, vibrational, and electronic properties of α -As₂Te₃ at room temperature and high pressure. We have observed that there is a stronger interlayer compressibility in α -As₂Te₃ than in α -Sb₂Te₃ and α -Bi₂Te₃, which can be explained due to the larger lone electron pair effect of As than Sb and Bi. In fact, we have shown that the structure of α -As₂Te₃ can be understood as an intermediate structure between that of Sb₂Se₃ and α -Sb₂Te₃. Strong changes in the monoclinic β angle and in the axial compressibilities are observed in the region between 2 and 4 GPa, which are related to the strengthening of the interlayer van der Waals bonds in this pressure range. This feature was demonstrated by the change of the direction of the maximum compressibility given by the analysis of the compressibility tensor. Furthermore, we have observed that polyhedral units around As cations in α -As₂Te₃ become more regular with increasing pressure and show a small

rotation in order to accommodate pressure in a clear tendency to increase the coordination with increasing pressure of both nonequivalent As atoms. Our *ab initio* theoretical simulations predict that the β phase, where As atoms are in true 6-fold coordination, is thermodynamically more stable than the α phase above 1 GPa. However, no phase transition to the β phase has been observed at ambient temperature even above 17 GPa; however, a phase transition to the γ phase has been observed. The lack of observation of the phase transition from α -As₂Te₃ to β -As₂Te₃ at ambient temperature is likely because it is a highly reconstructive first-order phase transition, which can be frustrated due to the presence of a high kinetic energy barrier and lately hidden by the phase transition toward a γ polymorph.

Our Raman scattering measurements and lattice dynamics calculations support the stability of the α phase up to 12 GPa and show small changes in the region between 2 and 4 GPa, consistent with the progressive changes of the interatomic distances with increasing pressure. Phonon dispersion curves at different pressures do not show any soft mode which evidences a pressure-induced second-order IPT. Additionally, changes in the RS spectrum which could be indicative of a pressure-induced ETT have not been observed. This is in agreement with theoretical calculations of the electronic band structure, which show that α -As₂Te₃ is an indirect semiconductor with a bandgap above 0.7 eV which shows a change of the conduction band minimum close to 1 GPa. A closing of the indirect bandgap occurs with increasing pressure, which suggests experimentally a semiconductor-to-metal transition above 6 GPa.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b06049.

Analysis of the vibrational properties of α -As₂Te₃, structural evolution of compressed α -As₂Te₃, and description of the experimental and theoretical isothermal compressibility tensor (PDF)

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Notes

The authors declare no competing financial interest.

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