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## Structural properties of $\text{Sb}_2\text{S}_3$ under pressure: evidence of an electronic topological transition

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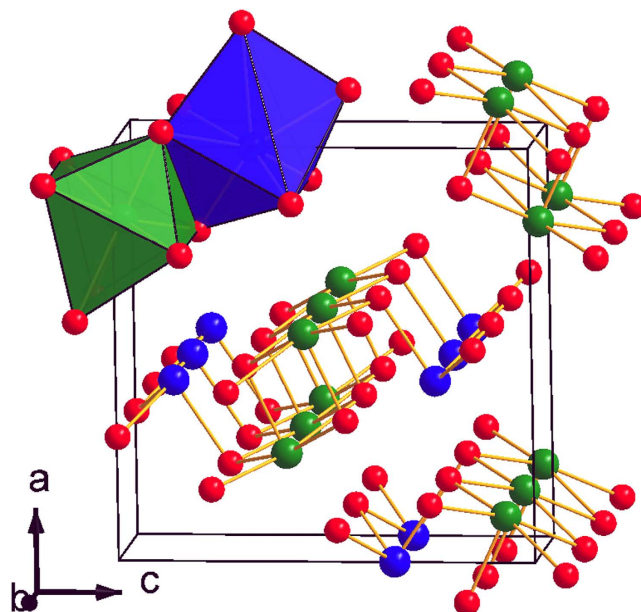
High-pressure Raman spectroscopy and x-ray diffraction of  $\text{Sb}_2\text{S}_3$  up to 53 GPa reveals two phase transitions at 5 GPa and 15 GPa. The first transition is evidenced by noticeable compressibility changes in distinct Raman-active modes, in the lattice parameter axial ratios, the unit cell volume, as well as in specific interatomic bond lengths and bond angles. By taking into account relevant results from the literature, we assign these effects to a second-order isostructural transition arising from an electronic topological transition in  $\text{Sb}_2\text{S}_3$  near 5 GPa. Close comparison between  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  up to 10 GPa reveals a slightly diverse structural behavior for these two compounds after the isostructural transition pressure. This structural diversity appears to account for the different pressure-induced electronic behavior of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  up to 10 GPa, i.e. the absence of an insulator-metal transition in  $\text{Sb}_2\text{S}_3$  up to that pressure. Finally, the second high-pressure modification appearing above 15 GPa appears to trigger a structural disorder at ~20 GPa; full decompression from 53 GPa leads to the recovery of an amorphous state.

The  $\text{Sb}_2\text{S}_3$  material (stibnite) is a well-known binary semiconductor with an optical band gap  $E_g \sim 1.7$  eV<sup>1</sup>. This material constitutes a promising candidate for solar energy conversion<sup>2</sup> and optoelectronic applications<sup>3</sup>. At ambient conditions,  $\text{Sb}_2\text{S}_3$  crystallizes in a complex orthorhombic structure (SG  $Pnma$ ,  $Z = 4$ ,  $\text{U}_2\text{S}_3$ -type)<sup>4</sup>. This  $Pnma$  phase can be described as a layered structure, consisting of parallel molecular  $(\text{Sb}_4\text{S}_6)_n$  ribbon-like chains along the short  $b$ -axis held together by weak intermolecular forces. The  $\text{Sb}^{3+}$  ions are located at two different sites in this phase, and their coordination environment can be described as sevenfold for the Sb(1) ion and eightfold ( $7 + 1$ ) for the Sb(2) ion, respectively (Fig. 1). The same structure is adopted by  $\text{Sb}_2\text{Se}_3$ <sup>5</sup>, whereas  $\text{Sb}_2\text{Te}_3$  adopts a rhombohedral structure (SG  $R\bar{3}m$ ,  $Z = 3$ ) made up of  $\text{SbTe}_6$  octahedral layers piled up along  $c$ -axis<sup>6</sup> due to the absence of the  $\text{Sb}^{3+}$  lone electron pair stereochemical activity<sup>7</sup>.

Very recently,  $\text{Sb}_2\text{Se}_3$  was shown also to undergo an electronic topological transition (ETT) near 3 GPa<sup>8</sup>, with theoretical works corroborating such behavior<sup>9,10</sup>. This ETT, which appears to be a common trend for these systems<sup>11</sup>, was manifested as a second-order isostructural transition via compressibility changes in several structural parameters<sup>11,12</sup>. We remind here that an ETT occurs when a band extremum, which is associated to a Van Hove singularity, crosses the Fermi energy ( $E_F$ ) and leads to a strong redistribution of the electronic density of states (EDOS) near  $E_F$ . This EDOS redistribution induces a second-order isostructural transition, i.e. a transition without any volume discontinuity at the transition point or changes in the crystalline symmetry. The elastic constants are affected by the ETT, however, hence leading to distinct compressibility changes of the material under study<sup>13,14</sup>. In addition, high-pressure resistivity measurements of  $\text{Sb}_2\text{Se}_3$  revealed also an insulator-metal transition near 3 GPa, whereas pressure-induced superconductivity was observed above 10 GPa<sup>12</sup>. The superconducting state persisted up to 40 GPa, with further compression leading to the transformation of the  $Pnma$  structure into a disordered body-centered cubic (bcc) phase above 55 GPa<sup>15</sup>.

A similar ETT was recently observed for  $\text{Sb}_2\text{S}_3$  by means of Raman spectroscopic and resistivity probes near 5 GPa, with a second phase transition following at 20 GPa<sup>16</sup>. Even though a x-ray diffraction (XRD) study of  $\text{Sb}_2\text{S}_3$  up to 10 GPa showed the persistence of the  $Pnma$  phase up to that pressure<sup>17</sup>, the mechanism of ETT at 5 GPa, the detection of the second transition at 20 GPa, as well as the possibility of additional structural modifications

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**Figure 1.** Unit cell of  $\text{Sb}_2\text{S}_3$  at ambient conditions (SG  $Pnma$ ,  $Z=4$ ). The blue, green, and red spheres correspond to the Sb(1), Sb(2), and S ions, respectively. The blue Sb(1) $\text{S}_7$  and green Sb(2) $\text{S}_{7+1}$  polyhedra are also displayed.

upon further compression<sup>15,18–20</sup>, calls for an updated structural investigation of  $\text{Sb}_2\text{S}_3$  in a more extended pressure range.

We present here our combined high-pressure Raman and XRD studies on  $\text{Sb}_2\text{S}_3$  up to 25 GPa and 53 GPa, respectively. Overall, we have detected two phase transitions at 5 GPa and 15 GPa. The first transition is manifested via compressibility changes in several structural parameters, an observation which correlates strongly with the reported ETT<sup>16</sup>. As for the second transition at 15 GPa, this new phase could not be identified due to the onset of structural disorder above 20 GPa. Full decompression of  $\text{Sb}_2\text{S}_3$  from 53 GPa leads to the recovery of an amorphous state.

## Results

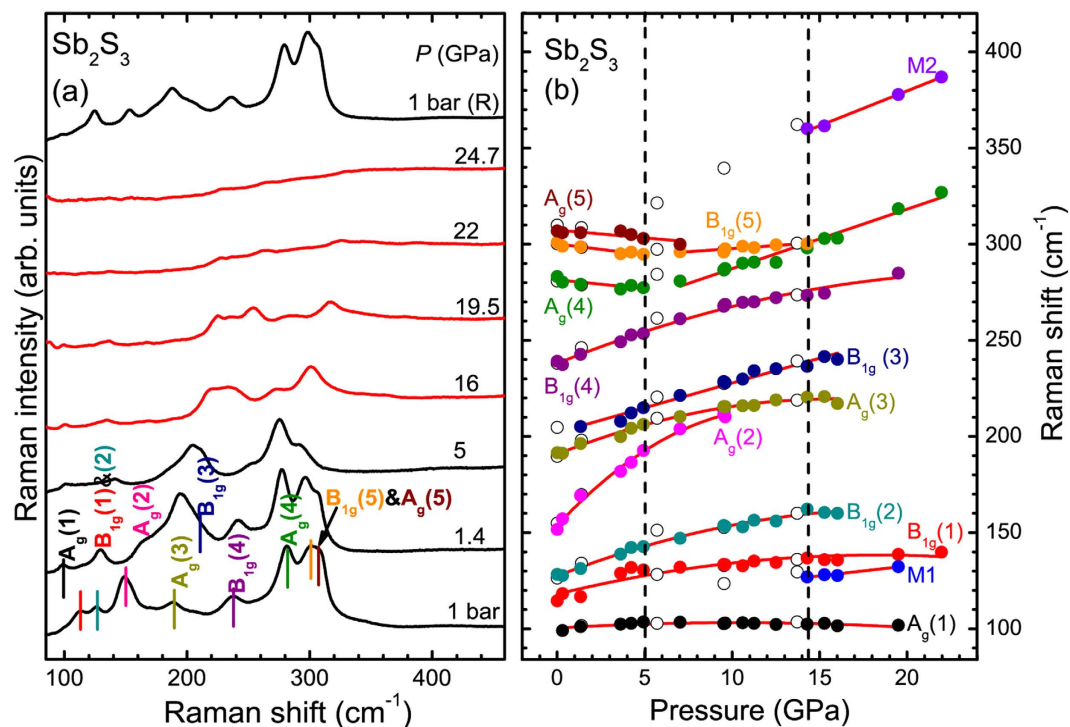
Given that Raman spectroscopy is a more sensitive probe for isostructural transitions<sup>11</sup>, we present first our high-pressure Raman spectroscopic investigation on  $\text{Sb}_2\text{S}_3$ . According to group theory, a sum of thirty Raman-active modes are expected for the  $Pnma$  phase of  $\text{Sb}_2\text{S}_3$ <sup>21</sup>:

$$\Gamma = 10A_g + 5B_{1g} + 10B_{2g} + 5B_{3g} \quad (1)$$

We can resolve ten broad bands in our Raman spectra (Fig. 2), which is consistent with the reported literature<sup>16,22,23</sup>. The mode assignment is adopted from the polarization studies of Sereni *et al.*<sup>23</sup> (Table 1). Upon increasing pressure, most of the Raman modes upshift in frequency; on the contrary, the high-frequency  $A_g(4)$ ,  $A_g(5)$ , and  $B_{1g}(5)$  modes downshift in energy up to 5 GPa. Beyond that pressure, the  $A_g(4)$  and  $B_{1g}(5)$  features display a compressibility change, with the  $A_g(4)$  mode exhibiting a completely different pressure-induced behavior after 5 GPa with a positive pressure slope [Fig. 2(b) and Table 1]. In addition, the pressure slope of the  $B_{1g}(5)$  mode reduces substantially beyond 5 GPa. As for the  $A_g(5)$  mode, it merges with its neighboring  $B_{1g}(5)$  mode at 7 GPa, and could not be followed above that pressure. Since these modes correspond to the stretching vibrations of the shorter Sb-S distances<sup>22</sup>, the observed compressibility changes should reflect the pressure-induced behavior of the corresponding bond lengths. Overall, our observations are in excellent agreement with the recent study of Sorb *et al.*<sup>16</sup>.

Further compression of  $\text{Sb}_2\text{S}_3$  results in the appearance of two new low-intensity features beyond 15 GPa [denoted as M1 and M2 in Fig. 2(b), see also supplementary Fig. S1]. Since the strongest Raman features of elemental Sb<sup>24</sup> and S<sup>25–27</sup> do not reside in these frequencies, we can safely exclude any decomposition and attribute the appearance of the M1 and M2 features to a pressure-induced phase transition. The M2 feature was also detected in the study of Sorb *et al.* above 20 GPa<sup>16</sup>. Beyond 15 GPa, however, the Raman modes exhibit pronounced broadening; consequently, the Raman spectra become rather featureless at 22 GPa [Fig. 2(a)]. Full decompression from 25 GPa leads to the recovery of the original  $\text{Sb}_2\text{S}_3$  Raman spectrum, indicating the reversibility of the pressure-induced Raman changes.

Having documented the pressure-induced changes from our Raman investigation, we now focus on the structural properties of  $\text{Sb}_2\text{S}_3$  under pressure. Selected XRD patterns are presented in Fig. 3. As we can observe, the Bragg peaks of the  $Pnma$  phase could be detected up to the highest pressure, i.e. 53 GPa. The Bragg peaks, however, exhibit significant broadening beyond 20 GPa, indicating the onset of structural disorder above that pressure. This pressure-induced structural disorder is most likely responsible for the featureless Raman spectra at

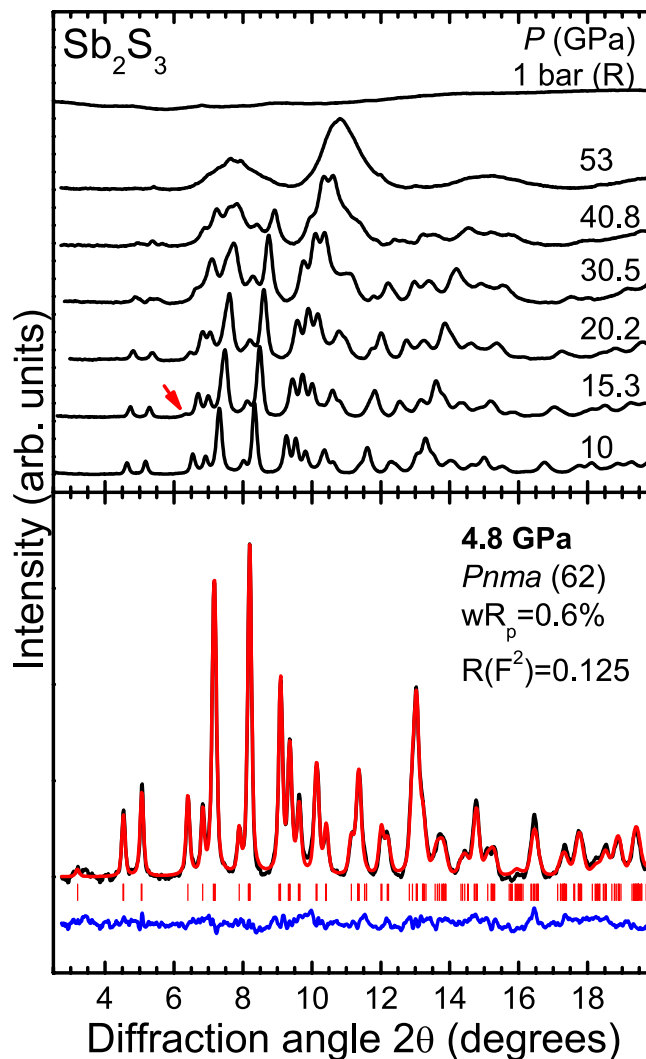


**Figure 2.** High-pressure Raman spectroscopic results of  $\text{Sb}_2\text{S}_3$ . (a) Raman spectra of  $\text{Sb}_2\text{S}_3$  at selected pressures ( $\lambda = 532$  nm,  $T = 300$  K). Vertical lines indicate the  $\text{Sb}_2\text{S}_3$  Raman-active modes. (b) Raman mode frequency evolution of  $\text{Sb}_2\text{S}_3$  against pressure. Solid and open circles correspond to data collected upon compression and decompression, respectively. Solid lines represent least square fits. The dashed lines mark the onset of phase transitions (see text).

Mode symmetry	$P_R$ (GPa)	$\omega_R$ ( $\text{cm}^{-1}$ )	$\partial\omega/\partial P$ ( $\text{cm}^{-1}/\text{GPa}$ )	$\partial^2\omega/\partial P^2$ ( $\text{cm}^{-1}/\text{GPa}^2$ )	$\gamma$
$A_g(1)$	$10^{-4}$	100.4	0.6	-0.03	0.16
$B_{1g}(1)$	$10^{-4}$	108	2.2	-0.06	0.55
$B_{1g}(2)$	$10^{-4}$	127.5	3.5	-0.09	0.75
$A_g(2)$	$10^{-4}$	153.8	9.7	-0.4	1.72
$A_g(3)$	$10^{-4}$	190.8	3.6	-0.11	0.51
$B_{1g}(3)$	$10^{-4}$	202	2.6	-	0.35
$B_{1g}(4)$	$10^{-4}$	238	3.7	-0.07	0.42
$A_g(4)$	$10^{-4}$	281.5	-0.9	-	-0.09
	5	271	3.1	-	0.74
$B_{1g}(5)$	$10^{-4}$	300.1	-1.1	-	-0.1
	5	295	-0.6	-	-0.13
$A_g(5)$		307	-0.8	-	0.07
M1	15	127	1	-	-
M2	15	361	3.6	-	-

**Table 1.** Mode assignment<sup>23</sup>, Raman mode frequencies, pressure coefficients, and the mode Gruneisen parameters  $\gamma$  of the Raman features of  $\text{Sb}_2\text{S}_3$  calculated at a reference pressure  $P_R$ . The pressure dependence of the Raman-active modes is described by the relation:  $\omega(P) = \omega_R + \alpha P + bP^2$ . Mode Gruneisen parameters  $\gamma$  are determined from the relation:  $\gamma = (B_0/\omega_R) \times (\partial\omega/\partial P)$ ; the bulk modulus  $B_0 = 27.2$  GPa (or  $B = 65$  GPa at 5 GPa) was employed.

22 GPa [Fig. 2(a)]. Further compression leads to the substantial broadening of the  $Pnma$  Bragg peaks in our XRD patterns. Upon decompression from 53 GPa we obtain an amorphous-like state, in apparent contradiction with our Raman study where the original phase is recovered upon decompression from 25 GPa [Fig. 2(a)]. It appears that unloading from a significantly larger pressure favors the quenching of an amorphous state instead of the original structure.

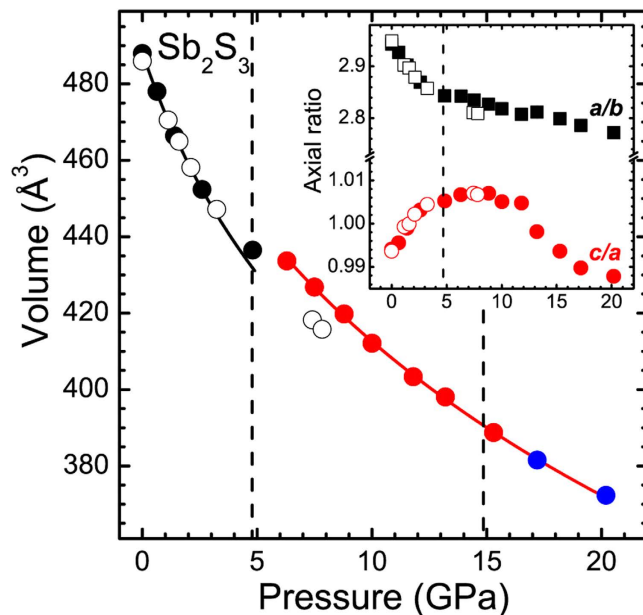


**Figure 3.** Selected XRD patterns of  $\text{Sb}_2\text{S}_3$  at various pressures ( $\lambda = 0.4246 \text{ \AA}$ ,  $T = 300 \text{ K}$ ). The red arrow marks the new Bragg feature. An example of a Rietveld refinement at 4.8 GPa is also provided. The black and red solid lines correspond to the measured and the fitted spectra, whereas their difference is depicted as a blue line. Vertical ticks mark the Bragg peak positions for the  $Pnma$  phase.

In addition, a new Bragg peak could be detected at  $2\theta \approx 6.6^\circ$  near 15 GPa (Fig. 3 and supplementary Fig. S2). This feature could not be assigned either to the  $Pnma$  or any “contaminating” phase such as rhenium (gasket material), helium, or ruby. Therefore, the appearance of this extra Bragg peak signals a structural transition of  $\text{Sb}_2\text{S}_3$  at 15 GPa, in excellent agreement with our Raman study (Fig. 2). Attempts to fit the XRD patterns with any of the reported high-pressure phases of related  $\text{A}_2\text{B}_3$  compounds<sup>18–20,28</sup> proved unsuccessful. A possible elemental decomposition into  $\text{Sb}^{29}$  and  $\text{S}^{30}$  could also not account for this novel peak. Therefore, we speculate that the  $\text{Sb}_2\text{S}_3$  XRD patterns consist of a mixture of two phases above 15 GPa, i.e. the  $Pnma$  structure and a high-pressure modification. Due to the pronounced Bragg peak broadening and the fact that this high-pressure phase is characterized by a single Bragg feature, however, its identification becomes unattainable at this point.

Given the aforementioned Bragg peak overlap and broadening upon pressure increase, the interatomic and lattice parameters of the  $Pnma$  phase could be obtained reliably up to 9 GPa and 20 GPa, respectively. All of these structural data are provided in supplementary Tables S1 and S2, whereas the extracted  $P$ - $V$  data are shown in Fig. 4. As we can observe, there is a clear compressibility change in the volume and in the orthorhombic axial ratios near 5 GPa, in excellent agreement with the compressibility changes observed in our Raman spectra (Fig. 2). By taking into account the pressure-induced behavior of isostructural  $\text{Sb}_2\text{Se}_3$ <sup>8,12</sup> and  $\text{Bi}_2\text{S}_3$ <sup>31</sup> compounds, and in close comparison with the related  $\text{Bi}_2\text{Te}_3$ <sup>32,33</sup>, we attribute these compressibility changes to an *isostructural* transition of  $\text{Sb}_2\text{S}_3$  near 5 GPa. This isostructural transition is most likely the signature of the reported ETT in  $\text{Sb}_2\text{S}_3$ <sup>16</sup>, reflecting a change in the topology of the Fermi surface<sup>8,10,11,13</sup>.

The fitting of the  $P$ - $V$  data to a Birch-Murnaghan Equation of State (B-M EoS) yielded volumes and bulk moduli values of  $V_0 = 488.2(4) \text{ \AA}^3$  and  $B_0 = 27.2(6) \text{ GPa}$ , and  $V = 434.2(7) \text{ \AA}^3$  and  $B = 65(2) \text{ GPa}$  (calculated at  $P = 5 \text{ GPa}$ ) before and after the isostructural transition, with fixed bulk moduli derivatives of  $B'_0 = 6$  and  $B' = 4$ ,



**Figure 4.** Plot of the unit cell volume as a function of pressure for the *Pnma* phase of  $\text{Sb}_2\text{S}_3$ . The solid lines represent the fitted Birch-Murnaghan Equation of State. The orthorhombic axial ratios are shown in the inset. The vertical dashed lines mark the onset of phase transitions (see text). The open symbols correspond to data from Lundegaard *et al.*<sup>17</sup>.

respectively. The  $B_0$  value of  $\text{Sb}_2\text{S}_3$  prior to the transition is consistent with that of Lundegaard *et al.*<sup>17</sup> and in line with the  $B_0$  value of  $\text{Sb}_2\text{Se}_3$ <sup>12,15</sup>.

Except from these compressibility changes in the lattice parameters and the bulk volume, inspection of the interatomic parameters also reveals distinct changes above 4 GPa (Fig. 5). For example, we can observe that the Sb(1)-S(3) short bond distance *elongates* up to 4 GPa, whereas a reduction is evidenced above that pressure. Actually, this pressure-induced trend is in excellent agreement with the behavior of the stretching  $A_g(4)$  Raman-active mode [Fig. 2(b)]. A similar trend applies for the S(3)-Sb(2)-S(3) bond angle (Fig. 5), which reflects the tiltings and distortions of the Sb(1) $\text{S}_7$  polyhedra<sup>12</sup>. Overall, the isostructural transition can be readily witnessed from the behavior of the interatomic parameters, a common trend for these systems<sup>12,15,31</sup>.

## Discussion

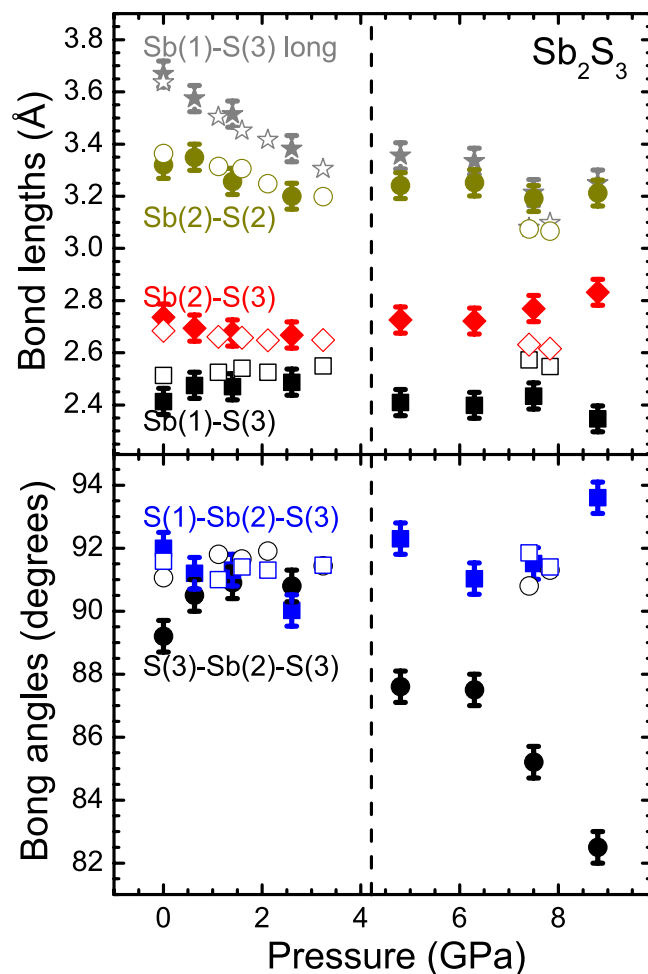
Having resolved the structural evolution of  $\text{Sb}_2\text{S}_3$  under pressure, a comparison between the pressure-induced behavior of  $\text{Sb}_2\text{S}_3$  and the isostructural  $\text{Sb}_2\text{Se}_3$  is in order. Both of these compounds exhibit isostructural transitions at the same pressure, i.e. close to 5 GPa<sup>12,15</sup>. In both cases, an electronic topological transition was put forward in order to account for the structural and vibrational changes beyond that pressure<sup>8,12,16</sup>. Interestingly, the high-pressure resistivity studies of these compounds reveal diverse behavior<sup>12,16</sup>. In particular, the room temperature resistivity of  $\text{Sb}_2\text{S}_3$  was found to *increase* up to 5 GPa, where it reached saturation; two anomalies were also detected at 1.4 GPa and 2.4 GPa<sup>16</sup>. For  $\text{Sb}_2\text{Se}_3$  on the other hand, a reduction of resistivity was observed up to 3.5 GPa, where an *insulator-metal* transition takes place; further compression leads to the induction of superconductivity at 10 GPa ( $T_c = 2$  K)<sup>12</sup>. This pressure-induced behavior of  $\text{Sb}_2\text{Se}_3$  resembles the transport properties of  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ , and  $\text{Sb}_2\text{Te}_3$  compounds<sup>34–39</sup>. Given the fact that  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  exhibit almost identical electronic band structures<sup>7,40</sup>, this diverse behavior in resistivity is puzzling.

A direct comparison between the pressure-induced behavior of the  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  structural parameters provides some hints. Generally, the compression mechanism for both compounds is practically identical up to 5 GPa<sup>15</sup>. As expected, the *b*-axis is the least compressible direction, since it contains the  $\text{Sb}_4\text{S}(\text{Se})_6$  molecular ribbons comprising the *Pnma* structure (Fig. 1). On the other hand, the *a*-axis and *c*-axis reduce much faster compared to *b*-axis under compression, with *a*-axis being more compressible than *c*-axis up to 5 GPa. This is easily evidenced from the increasing rate of the *c/a* axial ratio up to that pressure [Fig. 6(a)].

Beyond 5 GPa, however,  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  exhibit slightly diverse compressibility trends. In particular, the orthorhombic *c*-axis becomes more compressible and the *b*-axis less compressible in  $\text{Sb}_2\text{S}_3$  than  $\text{Sb}_2\text{Se}_3$  above 5 GPa; the *a*-axis exhibits similar compressibility for both compounds. As a result, the axial ratios of  $\text{Sb}_2\text{S}_3$  behave differently than those of  $\text{Sb}_2\text{Se}_3$  above 5 GPa, e.g. the  $\text{Sb}_2\text{S}_3$  *c/a* axial ratio shows a more prominent decreasing trend beyond 5 GPa compared to the  $\text{Sb}_2\text{Se}_3$  *c/a* axial ratio [Fig. 6(a)].

A closer look at the microscopic structural behavior reveals additional information. In Fig. 6(b,c) we plot the pressure-induced evolution of the X(3)-Sb(2)-X(3) bond angle, the volume of the Sb(1) $\text{X}_7$  polyhedra ( $\text{X} = \text{S}, \text{Se}$ ), and the Sb(1) cation eccentricity for both  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  compounds. We note that the X(3)-Sb(2)-X(3) bond angle reflects the tiltings of the Sb(1) $\text{X}_7$  polyhedra parallel to the *ac* plane<sup>12</sup>, whereas the cation eccentricity is a quantitative measure of the stereochemical activity of the  $\text{Sb}^{3+}$  lone electron pair (LEP); the larger the eccentricity



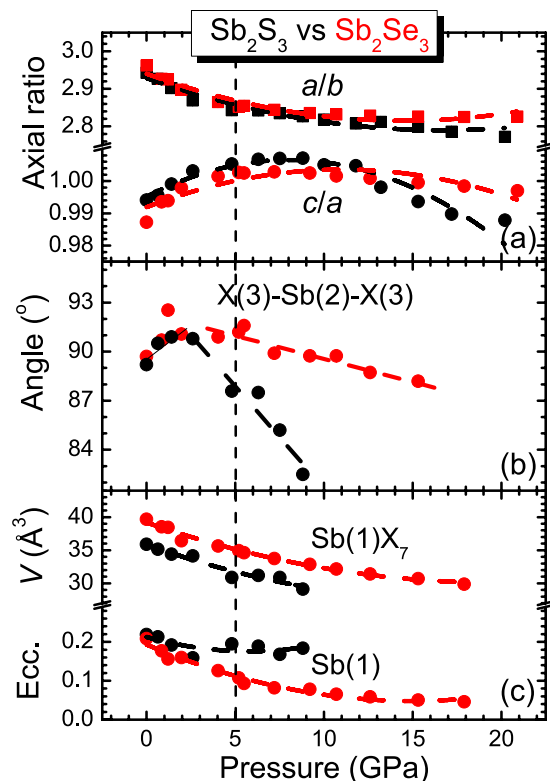


**Figure 5. Distinct interatomic  $\text{Sb}_2\text{S}_3$  parameters as a function of pressure.** (a) Selected Sb-S bond lengths and (b) S-Sb-S bond angles up to 9 GPa. The vertical dashed line marks the onset of the isostructural transition. The nomenclature of the Sb and S ions is provided in supplementary Fig. S3. The open symbols correspond to data from Lundegaard *et al.*<sup>17</sup>.

value, the more active the LEP<sup>17,41</sup>. As we can observe, the X(3)-Sb(2)-X3 bond angles behave similarly for both  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  up to 5 GPa, i.e. up to the isostructural transition [Fig. 6(b)]. Further compression, however, leads to the reduction of the S(3)-Sb(2)-S(3) bond angle in  $\text{Sb}_2\text{S}_3$  in a more pronounced rate compared to the Se(3)-Sb(2)-Se(3) bond angle of  $\text{Sb}_2\text{Se}_3$ . Given that the LEPs are located at the *ac* plane<sup>42,43</sup>, this diverse bond angle changes mirror different  $\text{Sb}^{3+}$  LEP behaviors in these materials.

Indeed, in Fig. 6(c) we can observe that the Sb(1) cation eccentricities of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  display different behavior beyond 5 GPa. More precisely, the larger Sb(1) eccentricity value for  $\text{Sb}_2\text{S}_3$  compared to  $\text{Sb}_2\text{Se}_3$  indicates a larger stereochemical activity for the former after the isostructural transition. In other words, the Sb(1) LEP of  $\text{Sb}_2\text{S}_3$  does not hybridize strongly with its neighboring S-p orbitals up to 10 GPa, as opposed to  $\text{Sb}_2\text{Se}_3$  where the Sb(1) cation eccentricity value approaches an almost zero value after 5 GPa (almost complete orbital overlap). We speculate that this lack of LEP hybridization in  $\text{Sb}_2\text{S}_3$  up to 10 GPa is the reason behind the different pressure-induced behavior in the electronic properties of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$ , i.e. the reason why an insulator-metal transition is observed for  $\text{Sb}_2\text{Se}_3$ <sup>12</sup> and not in  $\text{Sb}_2\text{S}_3$  (at least up to 10 GPa)<sup>16</sup>. Theoretical calculations are required, however, to verify this scenario.

Finally, we would like to briefly address the structural disorder in  $\text{Sb}_2\text{S}_3$  initiating beyond 20 GPa (Fig. 3). Interestingly, the onset of this structural disorder lies at much lower pressures compared to  $\text{Sb}_2\text{Se}_3$ <sup>15</sup> and  $\text{Bi}_2\text{S}_3$ <sup>31</sup>, but close with that of  $\alpha\text{-Sb}_2\text{O}_3$ <sup>44</sup>. Such disorder can generally be accounted for by two mechanisms<sup>45</sup>: (a) the disordered phase may be a precursor of a structural transformation into another crystalline phase, which cannot be formed due to kinetic barriers, or (b) the tendency of the material to decompose into its constituents. Given the pressure-induced trends of  $\text{Bi}_2\text{Te}_3$ <sup>19,35,46</sup>,  $\text{Sb}_2\text{Te}_3$ <sup>18,28</sup>,  $\text{Bi}_2\text{Se}_3$ <sup>20,37,47-49</sup>, and  $\text{Sb}_2\text{Se}_3$ <sup>15</sup> towards high-pressure disordered phases instead of elemental decomposition, however, the scenario of a kinetically-hindered structural transition in  $\text{Sb}_2\text{S}_3$  appears more plausible. Actually, the appearance of the high-pressure modification above 15 GPa might be exactly that, i.e. the onset of a structural transformation of the *Pnma* phase towards another crystalline state, which is obstructed due to kinetic effects; a combined high-pressure and high-temperature structural study will



**Figure 6.** Structural comparison between  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$ . Plot of (a) orthorhombic axial ratios, (b) the  $\text{X}(3)\text{-Sb}(2)\text{-X}(3)$  bond angle, (c)  $\text{Sb}(1)\text{X}_7$  polyhedral volumes, and the  $\text{Sb}(1)$  cation eccentricity as a function of pressure for both  $\text{Sb}_2\text{S}_3$  (black) and  $\text{Sb}_2\text{Se}_3$  (red, data from ref. 15). Dashed lines are guides to the eye. The vertical dashed line marks the isostructural transition.

be needed in order to resolve this matter. Considering nevertheless the structural trends of the  $\text{A}_2\text{B}_3$  series under pressure, we can expect that this new structure will exhibit higher cationic coordinations.

In conclusion, our combined high-pressure Raman and XRD investigations revealed two phase transitions in  $\text{Sb}_2\text{S}_3$  at 5 GPa and 15 GPa. The first transition is manifested via noticeable compressibility changes in several structural parameters. By taking into account an earlier report<sup>16</sup>, we assign these changes to a *second-order isostructural transition* arising from changes in the electronic structure of  $\text{Sb}_2\text{S}_3$ . Close comparison between the  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  compounds up to 10 GPa reveals a slightly diverse pressure-induced behavior in the  $\text{Sb}^{3+}$  LEP activity after the isostructural transition, a plausible reason behind their different high-pressure electronic behavior above 5 GPa<sup>12,16</sup>. As for the second transition of  $\text{Sb}_2\text{S}_3$  at 15 GPa, the new phase could not be identified due to the onset of structural disorder above 20 GPa. We speculate that the structural disorder is a transient state of this new high-pressure phase, which cannot be completed due to kinetic effects. Finally, an amorphous state is recovered upon full decompression from 53 GPa.

## Materials and Methods

**Sample and high-pressure technique details.** Polycrystalline  $\text{Sb}_2\text{S}_3$  powder was purchased commercially (Alfa-Aesar, 99.999% purity). The XRD measurements at ambient conditions did not detect any impurity phases. Pressure was generated with a gasketed symmetric diamond anvil cell, equipped with a set of diamonds with 300  $\mu\text{m}$  culet diameter. The ruby luminescence method was employed for pressure calibration<sup>50</sup>.

**High-pressure Raman spectroscopy.** The high-pressure Raman measurements were conducted with a solid-state laser ( $\lambda = 532 \text{ nm}$ ) coupled to a single-stage spectrometer and a charge-coupled device. The spectral resolution was  $2 \text{ cm}^{-1}$  and the lowest resolvable frequency was  $\sim 90 \text{ cm}^{-1}$ . Given the photo-sensitivity of the material<sup>51</sup>, the incident laser power was kept below 2 mW outside the DAC, whereas the size of the laser spot on the sample was approximately 30  $\mu\text{m}$ . Mixtures of methanol-ethanol 4:1 and methanol-ethanol-water 16:3:1 served as pressure transmitting media (PTM) in separate experimental runs.

**High-pressure angle-dispersive powder x-ray diffraction.** The monochromatic angle-dispersive powder x-ray diffraction (XRD) measurements under pressure were performed at the 16BM-D beamline of the High Pressure Collaborative Access Team's facility, at the Advanced Photon Source of Argonne National Laboratory (APS-ANL). The x-ray beam wavelength was  $\lambda = 0.4246 \text{ \AA}$  and the sample-detector distance about 320 mm. The XRD patterns were collected with a MAR345 Image Plate detector. The geometrical parameters were calibrated with a  $\text{CeO}_2$  standard from NIST. The intensity versus  $2\theta$  spectra were processed with the FIT2D software<sup>52</sup>.



Refinements were performed with the GSAS + EXPGUI software packages<sup>53</sup>, whereas crystal-chemical calculations with the IVTON software<sup>54</sup>. The *P*-*V* data were fitted with a Birch-Murnaghan equation of state (B-M EoS)<sup>55</sup>. Helium was employed as PTM; the compressed gas loading took place at the gas-loading system of GeoSoilEnviroCARS<sup>56</sup> (Sector 13, APS-ANL).

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## Author Contributions

I.E. and Y.W. designed the project. I.E., C.B. and Y.W. did the experiments. I.E. and Y.W. analyzed the data and wrote the manuscript. All authors reviewed the manuscript.

## Additional Information

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