Selected members of the A₂B₃ (A = Sb, Bi; B = Se, Te) family are topological insulators. The Sb₂Se₃ compound does not exhibit any topological properties at ambient conditions; a recent high-pressure study, however, indicated that pressure transforms Sb₂Se₃ from a band insulator into a topological insulator above ~2 GPa; in addition, three structural transitions were proposed to occur up to 25 GPa. Partly motivated by these results, we have performed x-ray diffraction and Raman spectroscopy investigations on Sb₂Se₃ under pressure up to 65 GPa. We have identified only one reversible structural transition: the initial Pnma structure transforms into a disordered cubic bcc alloy above 51 GPa. On the other hand, our high-pressure Raman study did not reproduce the previous results; we attribute the discrepancies to the effects of the different pressure transmitting media used in the high-pressure experiments. We discuss the structural behavior of Sb₂Se₃ within the A₂B₃ (A = Sb, Bi; B = Se, Te) series.

The A₂B₃ (A = Sb, Bi; B = S, Se, Te) series consists of layered chalcogenide semiconductors that have attracted considerable interest, mainly due to their exceptional thermoelectric properties. More recently, three members of this series, namely the Bi₂Te₃, Sb₂Te₃, and Bi₂Se₃ compounds, were shown to exhibit topological properties. This discovery has revitalized the scientific interest in these materials.

At ambient conditions, the A₂B₃ (A = Sb, Bi; B = S, Se, Te) family is divided into two structural classes: the heavier Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃ compounds adopt a rhombohedral structure (SG R-3m, Z = 3), which is composed of layers of AB₆ octahedra stacked perpendicular to the long c-axis; the lighter Bi₂S₃, Sb₂S₃, and Sb₂Se₃ materials on the other hand, crystallize in an orthorhombic phase (SG Pnma, Z = 4, U₃S₃-type), made up of AB and AB₇+,₈ polyhedra (Fig. 1 and Supplementary Fig. S1 online).

Pressure provides a means for “tuning” the physical properties of these compounds. As an example, their thermoelectric properties are enhanced by application of external pressure, a feature attributed to an electronic topological transition. More recent and detailed high-pressure investigations on Bi₂Te₃,²⁹⁻⁻¹³, Bi₂Se₃,¹⁴⁻⁻¹⁸, and Sb₂Te₃⁶⁻⁻¹³ have revealed a plethora of phase transitions. In particular, novel structures with higher cationic coordinations,¹⁷⁻⁻¹⁵,¹⁸⁻⁻²¹ insulator-to-metal transitions,¹⁶⁻⁻¹⁵, and even superconductivity,¹²⁻⁻¹³,¹²⁻⁻¹³ have been observed upon increasing pressure. Quite surprisingly, the compounds crystallizing in the R-3m structure do not adopt the denser Pnma phase upon compression. The only known exception is Bi₂Se₃, which can adopt the Pnma structure at combined high-pressure and high-temperature conditions or, as recently shown, at ambient conditions after high-pressure treatment.

The present study focuses on the effect of pressure on the structural and vibrational properties of Sb₂Se₃, which is an insulator with a ~1 eV band gap. Even though it does not exhibit the topological properties of the Sb₂Te₃, Bi₂Te₃, and Bi₂Se₃ compounds, Sb₂Se₃ has attracted significant interest over the years as a potential candidate for optical storage devices, as well as in photovoltaic and thermoelectric applications. Two recent studies on Sb₂Se₃ have indicated the possibility of a pressure-induced electronic topological transition, thus transforming the material from a normal band insulator into a topological insulator upon pressure application. These investigations, however, considered the R-3m structure (isostructural to Bi₂Te₃) as an ambient-pressure phase for Sb₂Se₃, a modification which has not been observed experimentally. In addition, a most recent high-pressure Raman study on Sb₂Se₃ indicated several phase transitions taking place up to ~25 GPa. Therefore, a detailed structural investigation of Sb₂Se₃ is necessary in order to clarify any potential pressure-induced phase transitions. The key findings of this work can be summarized as follows:

1. A novel binary alloy between Sb and Se atoms was observed. In particular, the ambient-pressure Pnma phase of Sb₂Se₃ persists up to ~51 GPa; beyond that pressure, Sb₂Se₃ begins to transform into a disordered cubic bcc phase (SG Im-3m, Z = 2), similar to the Bi₂Te₃ and Sb₂Te₃ compounds. The transition, which is reversible, is not fully completed up to the highest pressure reached here, i.e. 65 GPa.
(II) To our knowledge, a direct structural transition from the \textit{Pnma} phase into any other structure type has not previously been observed for any \textit{A}_2\textit{B}_3 materials. Therefore, this study adds a new structural “path” to the \textit{P}-\textit{T} phase diagrams of \textit{A}_2\textit{B}_3 compounds.

(III) The high-pressure Raman study on \textit{Sb}_2\textit{Se}_3 could not reproduce the recently reported results\cite{29}. This discrepancy prompted a more detailed investigation of the Raman response of \textit{Sb}_2\textit{Se}_3 from our side, under both ambient- and high-pressure conditions. Considering the available literature, we offer a thorough discussion on the vibrational properties of \textit{Sb}_2\textit{Se}_3.

**Results**

At ambient conditions, \textit{Sb}_2\textit{Se}_3 adopts an orthorhombic \textit{Pnma} structure (\textit{U}_2\textit{S}_3-type, Fig. 1). There are two non-equivalent \textit{Sb} cation sites in this phase, denoted as \textit{Sb}(1) and \textit{Sb}(2) in Fig. 1. The \textit{Sb}(1) cation is coordinated by seven \textit{Se} anions; on the other hand, the coordination around the \textit{Sb}(2) site can be described as of (7 + 1) with respect to the \textit{Se} ions. A more detailed description of the \textit{Pnma} structure is provided in the Supplementary Information online.

Overall, \textit{Sb}_2\textit{Se}_3 undergoes one structural transition under pressure (Fig. 2): the initial \textit{Pnma} phase begins to transform into a disordered bcc structure (\textit{SG Im}-3\textit{m}, \textit{Z} = 2) above 51 GPa. The transition to the bcc phase is almost complete at 65 GPa. Upon pressure release, the bcc phase persists down to 35 GPa; below that pressure, \textit{Sb}_2\textit{Se}_3 reverts to the ambient-pressure \textit{Pnma} phase (see Supplementary Fig. S2 online), thus hindering any reliable refinement. The reversibility of the ambient-pressure \textit{Pnma} structure is verified by our Transmission Electron Microscopy (TEM) study on the recovered \textit{Sb}_2\textit{Se}_3 sample (see Supplementary Figs. S4&S5 online).

For the initial \textit{Pnma} phase, Rietveld refinements were possible up to \textasciitilde 35 GPa; both the unit cell constants, as well as the interatomic parameter evolution as a function pressure could be obtained (Fig. 3). An example of a refined XRD pattern is displayed in Fig. 2(b), whereas the extracted crystallographic parameters are listed in Table 1. The Bragg peaks corresponding to the \textit{Pnma} phase broaden significantly above 40 GPa [Fig. 2(a)]; therefore, only the lattice parameters could be obtained beyond that pressure.

The pressure dependence of the lattice parameters for the \textit{Pnma} structure is plotted in Fig. 3(a). The long orthorhombic \textit{a} - and \textit{c} -axes, which lie very close in values throughout the investigated pressure range, exhibit a similar non-linear pressure-induced behavior, with a change in their slopes at about 20 GPa. We should note here that a structural transition has been claimed to take place at about 20 GPa for \textit{Sb}_2\textit{Se}_3 from a recent Raman investigation\cite{29}. Since we do not detect any changes in our XRD patterns, and considering that our Raman spectra do not reproduce the pressure-induced Raman response of \textit{Sb}_2\textit{Se}_3 reported in Ref. 29 as we discuss in more detail below, we attribute this change in the pressure dependence of both the \textit{a} - and \textit{c} -axes to a decrease in the compressibility of \textit{Sb}_2\textit{Se}_3 along these two directions beyond 20 GPa. On the other hand, the short \textit{b}-axis exhibits an almost linear (within error) pressure-change up to 48 GPa.

The \textit{P}-\textit{V} data for the \textit{Pnma} phase of \textit{Sb}_2\textit{Se}_3 are shown in Fig. 3(b). By employing the measured zero-pressure volume per formula unit \textit{V}_0/\textit{Z} = 136.4 Å³, the Birch-Murnaghan EOS fitting yields a bulk modulus \textit{B}_0 = 30(±1) GPa and its pressure derivative \textit{B}'_0 = 6.1(±0.2). The obtained \textit{B}_0 and \textit{B}'_0 values are consistent with those of isostructural \textit{Sb}_2\textit{S}_3\textsuperscript{17} and \textit{Bi}_2\textit{S}_3\textsuperscript{18} compounds.

The effect of pressure on the interatomic \textit{Sb}-\textit{Se} bond lengths for both \textit{Sb}(1) and \textit{Sb}(2) cations within the \textit{Sb}(1)\textit{Se}_7 and \textit{Sb}(2)\textit{Se}_7\textsuperscript{+} polyhedral cages is displayed in Figs. 3(c,d). In the low-pressure regime, the \textit{Se}-coordination environment around both \textit{Sb}(1) and \textit{Sb}(2) cations is highly asymmetric, as indicated by the large dispersion of the \textit{Sb}-\textit{Se} bond length values within the respective polyhedral. The effect of pressure is more pronounced for the longer \textit{Sb}-\textit{Se} bonds; the shorter \textit{Sb}-\textit{Se} bonds on the other hand, remain almost unaffected upon increasing pressure [Figs. 3 (c, d)]. The second observation is that pressure “forces” the various \textit{Sb}-\textit{Se} bond lengths of the \textit{Sb}(1)\textit{Se}_7 polyhedra to adopt similar values at \textasciitilde 35 GPa [Fig. 3(d)]. This effect can be translated into a pressure-induced “symmetrization” of the \textit{Sb}(1)\textit{Se}_7 polyhedral units. Actually, the distortions of the coordination polyhedra around the \textit{Sb}\textsuperscript{3+} cations reflect the stereochemical activity of the lone electron pairs of \textit{Sb}\textsuperscript{3+}, as discussed in more detail in the Supplementary Information.

Above 51 GPa, new Bragg peaks appear in the XRD patterns at about 11, 15, and 19’ (Fig. 2). Upon further pressure increase, these new peaks gain in intensity, indicative of a pressure-induced structural transition. The high-pressure phase can be assigned to a simple, yet disordered, bcc structure (\textit{Im}-3\textit{m}, \textit{Z} = 2). Within the \textit{Im}-3\textit{m} phase, the \textit{Sb} and \textit{Se} atoms are randomly distributed on the bcc lattice sites, forming a \textit{Sb}-\textit{Se} substitutional alloy. A similar phase transition has been observed for the \textit{Bi}_2\textit{Te}_3\textsuperscript{39} and \textit{Sb}_2\textit{Te}_3\textsuperscript{19,20} compounds above \textasciitilde 15 GPa and \textasciitilde 22 GPa, respectively.

The only high-pressure studies conducted on \textit{U}_2\textit{S}_3-type compounds up to now are those on \textit{Sb}_2\textit{S}_3\textsuperscript{17} and \textit{Bi}_2\textit{S}_3\textsuperscript{18} up to 10 GPa, and on the \textit{Bi}_2\textit{Se}_3-II phase up to 26 GPa\cite{32}. In all of these studies, no structural transition was observed under pressure. Therefore, a \textit{direct} pressure-induced structural transition from the \textit{U}_2\textit{S}_3-type phase to another structure type (\textit{Im}-3\textit{m}) has been observed here for the first time.

**Figure 1** (Left) The unit cell of \textit{Sb}_2\textit{Se}_3 at ambient conditions (\textit{SG Pnma}, \textit{Z} = 4). The blue, green, and red spheres correspond to \textit{Sb}(1), \textit{Sb}(2), and \textit{Se} ions, respectively. The \textit{Sb(1)Se}_7 (blue) and \textit{Sb(2)Se}_7\textsuperscript{+} (green) polyhedra are also displayed. (Right) Sketch of the coordination environment around the \textit{Sb(1)} and \textit{Sb(2)} cations. The various \textit{Sb}-\textit{Se} bonds are depicted by different colors.
time in the case of Sb$_2$Se$_3$. This result supplements further the already rich P-T phase diagrams of A$_2$B$_3$ compounds.

The transition into the bcc phase is not fully completed at 65 GPa for Sb$_2$Se$_3$, the highest pressure reached in this study, as some remnant Pnma phase can still be observed in the XRD patterns [Fig. 2(b)]. The fitting of the P-V data for the bcc phase with a Birch-Murnaghan EOS form [Fig. 3(b)] yields the following values for the elastic parameters: $V_{\text{Tr}}/Z = 87.25(\pm 0.1)$ Å$^3$ and $B_{\text{Tr}} = 217(\pm 11)$ GPa, with $B_{\text{Tr}} = 4$ (fixed value) and $Z = 0.4^{39}$. It should be also noted here that the P-V data employed for the bcc EOS fitting correspond to both compression [filled symbols in Fig. 3(b)] and decompression [open symbols in Fig. 3(b)] cycles. Therefore, the transition pressure point $P_{\text{Tr}}$ for the Pnma-Im-3m transition, where the obtained elastic parameters are evaluated, is assumed to occur at 36.2 GPa for the EOS fitting purposes.

In addition, we have probed the high-pressure vibrational features of Sb$_2$Se$_3$ by employing Raman spectroscopy. For the starting Pnma phase, a sum of thirty first-order Raman-active modes are expected $^{33}$:

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

At ambient conditions [bottom spectra in Fig. 4(a)], the Raman spectrum of Sb$_2$Se$_3$ consists of eight relatively sharp peaks (labeled 1–8) and some broad Raman features, such as the low-intensity “wings” of peak 3. Upon pressure application, these broad bands become more prominent and can be clearly resolved (D1–D3, Fig. 4). Given the distinct width differences between the sharp and broad Raman features in the Sb$_2$Se$_3$ Raman spectra, we speculate that the scattering mechanism and, therefore, the origin of these Raman bands are different. We assign the sharp Raman features to first-order Raman-active modes of Sb$_2$Se$_3$ (except for mode 8), whereas the broad bands to defect-induced Raman scattering. Our arguments are the following:

(a) Structural defects are known to affect the Raman response of crystalline materials, by introducing broad bands in the measured Raman spectra $^{34,35}$. This kind of defect-induced Raman scattering mechanism has been explored in detail for several binary semiconductors $^{34}$.

(b) Most of the reported ambient-pressure Sb$_2$Se$_3$ Raman spectra exhibit only sharp Raman features $^{36–38}$, which are consistent with our observed (1–7) Raman peaks. In addition, additional TEM measurements performed on these Sb$_2$Se$_3$ materials $^{36–38}$ established their high crystalline quality. On the other hand, the Raman spectra of Sb$_2$Se$_3$ reported in Refs. 29, 39 are quite different. The main feature in both of these studies is a broad Raman band located at $\sim 190$ cm$^{-1}$; since no other microstructural studies were provided in those investigations, the crystalline quality of the measured samples is unclear and questionable. Nevertheless, this apparent discrepancy prompted us to conduct additional Raman measurements on Sb$_2$Se$_3$ (see Supplementary Information).

(c) As part of these detailed Raman investigations, we have studied the effect of laser annealing on the Raman response of Sb$_2$Se$_3$ at ambient pressure. After the laser annealing process, the background in the Sb$_2$Se$_3$ Raman spectrum becomes completely flat, whereas the broad features are eliminated completely [see Supplementary Fig. S6(a) online]. Given that such laser-annealing/high-temperature treatment induces analogous effects, i.e. improves the quality of the 3C-SiC Raman spectra due to the suppression of microstructural disorder $^{38}$, we can
Table 1 | Refined crystallographic data for the starting Pnma structure and the high-pressure Im-3m modification of Sb2Se3 [Fig. 2(b)]

| Space Group | Pnma (62) | Im-3m (229) |
|-------------|-----------|-------------|
| Pressure (GPa) | 9.2 | 65 |
| a (Å) | 10.8837(1) | 3.1538(2) |
| b (Å) | 3.8378(1) | 3.1538(2) |
| c (Å) | 10.9118(1) | 3.1538(2) |
| c/a | 1.003 | 1 |
| c/b | 2.843 | 1 |
| a/b | 2.836 | 1 |
| V (Å³) | 455.8 | 31.4 |
| Z | 4 | 2 |
| wR(F²) | 0.017, 0.124 | 0.038, 0.245 |
| Atomic coordinates | Sb(1): 4c [-0.000291(1), 0.25, 0.67724(3)] | Sb/Se: 2a [0, 0, 0] |
| | Sb(2): 4c [0.3432(1), 0.25, 0.4559(2)] | |
| | Se(1): 4c [0.05968(2), 0.25, 0.13273(3)] | |
| | Se(2): 4c [0.36755(3), 0.25, 0.06293(2)] | |
| | Se(3): 4c [0.21616(2), 0.25, 0.78949(3)] | |

Figure 3 | (a) Lattice constants and (b) unit cell volume per formula unit as a function of pressure for the two phases of Sb2Se3. The closed and open symbols correspond to data collected upon compression and decompression cycles, respectively. The dashed rectangle marks the transition regime for the Pnma-Im-3m structural transition. The red solid lines represent the fitted Birch-Murnaghan EOS functions to the measured P-V data. (c, d) Pressure-induced changes of the Sb(2)-Se and the Sb(1)-Se bond lengths within the Sb(2)Se711 and Sb(1)Se7 polyhedra, respectively, for the Pnma phase of Sb2Se3. The various Sb-Se bond distances are displayed in Fig. 1 for clarity.
reasonably assume that a similar effect is taking place in the case of Sb\textsubscript{2}Se\textsubscript{3} as well.

The measured zero-pressure frequencies \(v_0\) for the first-order Raman modes of Sb\textsubscript{2}Se\textsubscript{3} (Supplementary Table S1 online) are in good agreement with the reported values \(^{36–38}\). The Raman mode assignment (1–7) is achieved by comparing the (almost identical) Raman spectra of isostructural Sb\textsubscript{2}Se\textsubscript{3} and Sb\textsubscript{2}S\textsubscript{3} compounds (see Supplementary Fig. S7 online). All of the observed sharp Raman peaks (1–7) are thus identified as first-order Raman modes. The only notable exception is mode 8 located at \(705\) cm\(^{-1}\); interestingly, this mode is present in both Sb\textsubscript{2}Se\textsubscript{3} and Sb\textsubscript{2}S\textsubscript{3} compounds, as well as in the cubic Sb\textsubscript{2}O\textsubscript{3} (see Supplementary Fig. S7 online). Although such a mode is expected in the case of Sb\textsubscript{2}O\textsubscript{3} due to the presence of the light oxygen anion\(^{41}\), it is not anticipated for the heavier S- and Se-bearing compounds. By taking also into account its (almost) identical pressure dependence with the respective \(F_2g\) mode of Sb\textsubscript{2}O\textsubscript{3}\(^{41}\), we attribute mode 8 to an impurity Raman band.

Upon compression, most of the first-order Raman-active modes of Sb\textsubscript{2}Se\textsubscript{3} (1–7) exhibit “normal” behavior, i.e. their frequencies shift to higher values with increasing pressure (Fig. 4). The effect of pressure is more pronounced for the 1, 3, 6, and 7 Raman modes, implying that the respective force constants are more sensitive against pressure application. This larger pressure dependence results in the merging of both 1 and 3 modes with their neighboring 2 and 4 bands above \(10\) and \(20\) GPa, respectively. On the contrary, mode 5 exhibits pressure-induced softening (even though marginal) up to \(32\) GPa. Since this mode is assigned to a Sb-Se stretching motion, it most likely reflects the pressure-induced behavior of the shorter (and almost incompressible) Sb-Se bonds [Figs. 3 (c, d)].

As for the disorder-induced D\textsubscript{1}, D\textsubscript{2}, and D\textsubscript{3} modes, their frequencies increase with increasing pressure. Mode D\textsubscript{3} broadens significantly above \(7.5\) GPa; two bands (D\textsubscript{4} and D\textsubscript{5} in Fig. 4) are employed for the fitting of this feature beyond this pressure point. Upon further compression, an additional broad band (D\textsubscript{6}) appears in our Raman spectra above \(29\) GPa. Coincidentally, the strongest sharp peak of Sb\textsubscript{2}Se\textsubscript{3} (mode 4) starts to decline in intensity, whereas the broad Raman features (D\textsubscript{1}, D\textsubscript{3}, and D\textsubscript{5}) enhance above that pressure intensity-wise. Mode 4 can be resolved up to \(40\) GPa; the Raman spectra are dominated by the four D\textsubscript{1}, D\textsubscript{3}, D\textsubscript{5}, and D\textsubscript{6} broad bands beyond that pressure (Fig. 4).

The total loss of the sharp Raman peaks above \(40\) GPa coincides roughly with the broadening of the Bragg peaks evidenced in the XRD patterns (Fig. 2). Since the \(Pnma\rightarrow\text{Im}3m\) structural transition initiates at a higher pressure, i.e. above \(51\) GPa, the loss of the sharp peaks in the Raman spectra arises probably due to pressure-induced structural disorder rather than a structural transition. However, and since the high-pressure \(Im\text{-}3m\) structure is both a disordered and a Raman-inactive phase, this utter loss of the sharp Raman features above \(40\) GPa might also be a signature for the \(Pnma\rightarrow\text{Im}3m\) structural transition. The original phase/Raman spectrum of Sb\textsubscript{2}Se\textsubscript{3} is recovered upon decompression (Fig. 4), but only after full pressure release.

Before finishing this Section, a direct comparison between our high-pressure Raman study and that of Bera \textit{et al.}\(^{29}\) is in order. As mentioned before, our Sb\textsubscript{2}Se\textsubscript{3} Raman spectra are quite different from those reported in Ref. 29, where the main feature of the Raman spectra is a broad band located at \(190\) cm\(^{-1}\). In order to resolve this discrepancy, we have probed the Raman activity of Sb\textsubscript{2}Se\textsubscript{3} in different environments and experimental conditions [see Supplementary Fig. S6(b) online]. In particular, the form of the sample (single-crystalline or grounded powder) does not influence the Raman response at ambient conditions. On the contrary, the choice of the pressure transmitting medium (PTM) employed for the high-pressure measurements affects the Raman signal of Sb\textsubscript{2}Se\textsubscript{3} significantly. More precisely, the Raman spectrum of Sb\textsubscript{2}Se\textsubscript{3}, measured with

![Figure 4](https://www.nature.com/scientificreports/)
helium as PTM (the PTM employed for this study) is consistent with the Raman spectra obtained from the sample at ambient conditions. Employing mixtures of methanol-ethanol-water (M/E/W) 16:3:1 and methanol-ethanol (M/E) 4:1 as PTM, however, alters the Raman response of Sb$_2$Se$_3$ drastically: the strongest Raman band is now located at ~190 cm$^{-1}$, whereas the intense Raman peak at ~250 cm$^{-1}$ is absent from the Raman spectra in both cases. The Raman spectra obtained in this case resemble that of Ref. 29. It should be noted, however, that the Raman spectra obtained with M/E/W and M/E exhibit also distinct differences between each other, e.g. completely different relative intensities of the Raman peaks [Supplemental Fig. S6(b) online]. Therefore, it becomes clear that the choice of PTM affects the Raman response of Sb$_2$Se$_3$.

Given the disordered nature of the high-pressure Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Sb$_2$Se$_3$ bcc phases, we speculate that these modifications will most likely transform into ordered crystalline structures upon sufficient heating (unless decomposition occurs). A plausible structural candidate after such high-temperature treatment might be the defect cubic Th$_3$P$_4$-type phase (SG $I-4d$, $Z = 4$), with eightfold cationic coordination. This structure is a common polymorph for rare-earth based A$_2$B$_3$ chalcogenides ($\gamma$-phase) at high-temperature and/or high-pressure conditions. Furthermore, this cubic modification is structurally resilient against pressure increase. The disordered high-pressure bcc modifications of the heavier Bi$_2$Te$_3$ and Bi$_2$Se$_3$ compounds are more suitable candidates for testing this suggestion, mainly due to their lower transition pressures.

Finally, we would like to add some thoughts on the electronic properties of Sb$_2$Se$_3$ in the high-pressure bcc modification. At ambient conditions, Sb$_2$Se$_3$ is an insulator with a band gap of ~1 eV. Given that (a) the high-pressure bcc phases of both Bi$_2$Te$_3$ and Bi$_2$Se$_3$ are metallic and superconducting and (b) the respective high-pressure CsCl-type/bcc modifications for several binary compounds are also metallic and superconducting, it is reasonable to assume that the high-pressure bcc phase of Sb$_2$Se$_3$ will also exhibit metallic, and possibly superconducting behavior. This assumption, however, needs to be checked by appropriate high-pressure electrical transport measurements.

Methods

Sample and high-pressure technique details. The Sb$_2$Se$_3$ compound was available in single-crystalline form (Alfa-Aesar, 99.999% purity). Both the XRD and TEM measurements at ambient conditions did not detect any impurity phases. For the x-ray measurements, the single crystals were grinded into fine powder. Pressure was generated by a symmetric diamond anvil cell (DAC) with 300 $\mu$m diamond cuvet diameter. A 150 $\mu$m diameter hole was drilled in the middle of a pretreated rhenium gasket of 40 $\mu$m thickness and served as the sample chamber.

XRD measurements were conducted at the 16BM-D beamline of the High Pressure Collaborative Access Team, at APS-ANL. The x-ray beam size was ~8 $\mu$m x 12 $\mu$m and the x-ray wavelength was 0.4246 Å. The XRD patterns were collected with a MAR 345 Image Plate detector. The intensity vs. 2$\theta$ patterns were obtained using the FIT2D software. Refinements of the measured XRD patterns were performed using the GSAS & EXPGUI software packages. The measured P-V data for both the ambient-pressure Pnma and high-pressure Im-3m phases were fitted with a Birch-Murnaghan equation of state (EOS).

Angle-dispersive powder x-ray diffraction. The monochromatic angle-dispersive powder XRD measurements under pressure were performed at the 16BM-D beamline of the High Pressure Collaborative Access Team, at APS-ANL. The x-ray beam size was ~8 $\mu$m x 12 $\mu$m and the x-ray wavelength was 0.4246 Å. The XRD patterns were collected with a MAR 345 Image Plate detector. The intensity vs. 2$\theta$ patterns were obtained using the FIT2D software. Refinements of the measured XRD patterns were performed using the GSAS & EXPGUI software packages. The measured P-V data for both the ambient-pressure Pnma and high-pressure Im-3m phases were fitted with a Birch-Murnaghan equation of state (EOS).
chemical calculations were performed with the IVTON software. We should emphasize here that there exist several available settings for SQ Pnma; here we choose to employ the same Pnma setting as in isostructural Sb$_2$S$_3$ and Bi$_2$S$_3$ compounds.

**Transmission electron microscopy.** In order to verify the reversibility of the original phase of Sb$_2$Se$_3$ from the XRD study, we have performed transmission electron microscopy (TEM) studies on the starting Sb$_2$Se$_3$ sample (crushed powder) and the quenched Sb$_2$Se$_3$ powder, i.e. the Sb$_2$Se$_3$ sample recovered after full decomposition from the aforementioned XRD study. For this purpose, the samples were dispersed onto holey-carbon TEM grids and were analyzed using a JEOL 3011 microscope by means of high-resolution TEM images (HRTEM) and selected area electron diffraction (SAED) patterns.

**High-pressure Raman spectroscopy.** The high-pressure Raman experiments were conducted on single-crystalline Sb$_2$Se$_3$ samples with a solid-state laser ($\lambda = 532$ nm) coupled to a single-stage Raman spectrometer (Andor iD500) and a charge-coupled device. The spectral resolution was 2 cm$^{-1}$ and the lowest resolvable frequency was $\sim$75 cm$^{-1}$. The size of the laser spot on the sample surface was approximately 30 µm, whereas the laser power was 2 mW outside the DAC (unless specified otherwise). In order to investigate the effect of PTM, as well as the effect of the incident laser power on the sample, additional Raman measurements on Sb$_2$Se$_3$ were conducted. These extra Raman studies are presented in the Supporting Information (SI).

1. Ovsyannikov, S. V. & Schchenikov, V. V. High-Pressure Routes in the Thermoelectricity or How One Can Improve a Performance of Thermoelectrics. Chem. Mater. 22, 635 (2010).
2. Chen, Y. L. et al. Experimental Realization of a Three-Dimensional Topological Insulator, Bi$_2$Te$_3$. Science 325, 178 (2009).
3. Zhang, H. L. et al. Topological insulators in Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ with a single Dirac cone on the surface. Nat. Phys. 5, 438 (2009).
4. Qi, X. L. & Zhang, S.-C. Topological insulators and superconductors. Rev. Mod. Phys. 83, 1057 (2011).
5. Yan, B. & Zhang, S.-C. Topological materials. Rep. Prog. Phys. 75, 96501 (2012).
6. Zhu, L. et al. Substitutional Alloy of Bi and Te at High Pressure. Phys. Rev. Lett. 106, 145501 (2011).
7. Einaga, M. et al. Pressure-induced phase transition of Bi$_2$Te$_3$ to a bcc structure. Phys. Rev. B 83, 92102 (2011).
8. Einaga, M., Tanabe, Y., Ohmura, A. N. A., Ishikawa, F. & Yamada, Y. New superconducting phase of Bi$_2$Te$_3$ under pressure above 11 GPa. J. Phys.: Conf. Ser. 215, 12036 (2010).
9. Jacobsen, M. K., Sinogeikin, S. V., Kumar, R. S. & Cornelius, A. L. High pressure transport characteristics of Bi$_2$Te$_3$, Sb$_2$Te$_3$, and BiSbTe$_3$. J. Phys. Chem. Sol. 73, 1154 (2012).
10. Pradhan, G. K., Bera, A., Kumar, P., Muthu, D. V. S. & Sood, A. K. Raman signatures of pressure induced electronic topological and structural transitions in Bi$_2$Te$_3$. J. Phys.: Condens. Matter 24, 284 (2012).
11. Vilaplana, R. et al. High-pressure vibrational and optical study of Bi$_2$Te$_3$. Phys. Rev. B 84, 104112 (2011).
12. Zhang, J. L. et al. Pressure-induced superconductivity in topological parent compound Bi$_2$Te$_3$. PNAS 108, 24 (2011).
13. Zhang, J. S. et al. The comprehensive phase evolution for Bi$_2$Te$_3$ topological compound as function of pressure. J. Phys. Appl. Phys. 41, 112630 (2012).
14. Liu, G. T., Zhu, L., Ma, Y. M., Lin, C. L. & Liu, J. Stabilization of 9/10-Fold Pnma Structure in Bismuth Selenide at High Pressures. J. Phys. Chem. C 117, 10045 (2013).
15. Zhao, J. et al. High-pressure phase transitions, amorphization, and crystallization behaviors in Bi$_2$Se$_3$. J. Phys. Cond. Matt. 25, 125602 (2013).
16. Hanlin, J. et al. High pressure transport properties of the topological insulator Bi$_2$Se$_3$. J. Phys. Cond. Matt. 24, 35602 (2012).
17. Segura, A. et al. Trapping of three-dimensional electrons and transition to twodimensional transport in the three-dimensional topological insulator Bi$_2$Se$_3$ under high pressure. Phys. Rev. B 85, 195139 (2012).
18. Vilaplana, R. et al. Structural and vibrational study of Bi$_2$Se$_3$ under high pressure. Phys. Rev. B 84, 184110 (2011).
19. Zhao, J. et al. Pressure-Induced Disordered Substitution Alloy in Sb$_2$Te$_3$, Inorg. Chem. 50, 11291 (2011).
20. Ma, Y. et al. Determinations of the high-pressure crystal structures of Sb$_2$Te$_3$. J. Phys.: Condens. Matter 24, 475403 (2012).
21. Souza, S. M. et al. High pressure monochromatic phases of Sb$_2$Te$_3$. Phys. Rev. B 40, 3761 (1989).
22. Comis, O. et al. Lattice dynamics of Sb$_2$Te$_3$ at high pressures. Phys. Rev. B 84, 174305 (2011).
23. Zhu, J. et al. Superconductivity in Topological Insulator Sb$_2$Te$_3$ Induced by Pressure. Sci. Rep. 3, 168 (2013).
24. Atabaeva, E. Y., Maskalov, S. A. & Popova, S. V. Die Kristallstruktur der neuen Modifikation von Bi2Se3 II. Kristallogr. A 18, 173 (1973).
25. Koc, H., Mamedov, A. M., Deligoz, E. & Oziisk, H. First principles prediction of the elastic, electronic, and optical properties of Sb$_2$S$_3$ and Sb$_2$Se$_3$ compounds. Sol. St. Sci. 14, 1211 (2012).
26. Arun, P., Vedejswar, A. G. & Mehra, N. C. Laser-induced crystallization in amorphous films of Sb$_2$C$_3$ (C = S, Se, Te), potential optical storage media. J. Phys. D: Appl. Phys. 32, 183 (1999).
27. Fernandez, A. M. & Merino, M. G. Preparation and characterization of Sb$_2$Se$_3$ thin films prepared by electrodeposition for photovoltaic applications. Th. Sol. Films 366, 202 (2000).
28. Minnich, A. J., Dresselhaus, M. S., Ren, Z. F. & Chen, G. Bulk nanostructured thermoelectric materials: current research and future prospects. Energy Environ. Sci. 2, 466 (2009).
29. Beni, A. et al. Sharp Raman anomalies and broken adiabaticity at a pressure induced transition from band to topological insulator in Sb$_2$Se$_3$. Phys. Rev. Lett. 27, 2013.
30. Liu, W. et al. Anisotropic interactions and strain-induced topological phase transition in Sb$_2$Se$_3$ and Bi$_2$Se$_3$. Phys. Rev. B 84, 245105 (2011).
31. Lunegarde, L. F., Miletich, R., Balic-Zunic, T. & Makovicky, E. Equation of state and crystal structure of Sb$_2$Se$_3$ between 0 and 10 GPa. Phys Chem Miner. 30, 465 (2003).
32. Lunegarde, L. F., Makovicky, E., Boffa-Ballaran, T. & Balic-Zunic, T. Crystal structure and cation lone electron pair activity of Bi$_2$Se$_3$ between 0 and 10 GPa. Phys Chem Miner. 32, 578 (2005).
33. Sereni, P., Musso, M., Knoll, P., amid, K., Schwarz, P. B. & Schmidt, G. Phonon-Dependent Raman Characterization of Stibnite (Sb$_2$S$_3$). AIP Conf. Proc. 1267, 1131 (2010).
34. Falkovsky, L. A. Investigation of semiconductors with defects using Raman scattering. Phys. Usp. 47, 249 (2004).
35. Wielgórski, M., Wang, Y. & Zerda, T. W. Raman spectra of silicon carbide small particles and nanowires. J. Phys. Cond. Matt. 17, 2387 (2005).
36. Ma, X. et al. Large-scale growth of wire-like Sb$_2$Se$_3$ microcrystallines via PEG-400 polymer-assisted route. J. Cryst. Growth 263, 491 (2004).
37. Wang, J., Deng, Z. & Li, Y. Synthesis and characterization of Sb$_2$Se$_3$ nanorods. Mater. Res. Bull. 37, 495 (2002).
38. Zhu, T. et al. Single-Crystalline Sb$_2$Te$_3$ Nanowires for High-Performance Field Emitters and Photodetectors. Adv. Mater. 22, 4530 (2010).
39. Rohrfield, S., Hundhausen, M. & Ley, L. Influence of Stacking Disorder on the Raman Spectrum of 3C-SiC. Phys. Stat. Sol. (b) 215, 119 (1995).
40. Pereira, A. L. J. et al. Structural and vibrational study of cubic Sb$_2$O$_3$ under high pressure. Phys. Rev. B 85, 174108 (2012).
41. Ovsyannikov, S. V. et al. Giant improvement of thermoelectric power factor of Bi$_2$Te$_3$ under pressure. Appl. Phys. Lett. 104, 53713 (2012).
assistance during the XRD measurements. We are grateful to Prof. A. K. Sood for providing
the manuscript of Ref. 29 prior to publication, and Dr. A. L. J. Pereira for the
ambient-conditions XRD and Raman data of Sb₂O₃. Finally, we would like to thank Prof.
Balic-Zunic Momma for providing the IVTON software.

Author contributions
I.E. and Y.W. conceived and designed the research, I.E., M.K., C.P. and Y.W. conducted the
high pressure experiments, J.Z. carried out the TEM measurements and provided the
related images and text, I.E. and Y.W. wrote the manuscript, R.E. revised and commented
the manuscript.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/
scientificreports
Competing financial interests: The authors declare no competing financial interests.
How to cite this article: Efthimiopoulos, I. et al. Sb₂Se₃ under pressure. Sci. Rep. 3, 2665;
DOI:10.1038/srep02665 (2013).

This work is licensed under a Creative Commons Attribution-
NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license,
visit http://creativecommons.org/licenses/by-nc-nd/3.0