













Cite this: *Phys. Chem. Chem. Phys.*,
2021, 23, 23625

Pressure-induced order–disorder transitions in β - In_2S_3 : an experimental and theoretical study of structural and vibrational properties†

Samuel Gallego-Parra, ^a Óscar Gomis, ^{a,b} Rosario Vilaplana, ^b
Vanesa Paula Cuenca-Gotor, ^a Domingo Martínez-García,^c
Plácida Rodríguez-Hernández, ^d Alfonso Muñoz, ^d Aldo Romero,^e
Arnab Majumdar, ^{fg} Rajeev Ahuja, ^{fh} Catalin Popescu ⁱ and
Francisco Javier Manjón ^a

This joint experimental and theoretical study of the structural and vibrational properties of β - In_2S_3 upon compression shows that this tetragonal defect spinel undergoes two reversible pressure-induced order–disorder transitions up to 20 GPa. We propose that the first high-pressure phase above 5.0 GPa has the cubic defect spinel structure of α - In_2S_3 and the second high-pressure phase (ϕ - In_2S_3) above 10.5 GPa has a defect α - NaFeO_2 -type ($R\bar{3}m$) structure. This phase, related to the NaCl structure, has not been previously observed in spinels under compression and is related to both the tetradymite structure of topological insulators and to the defect LiTiO_2 phase observed at high pressure in other thiospinels. Structural characterization of the three phases shows that α - In_2S_3 is softer than β - In_2S_3 while ϕ - In_2S_3 is harder than β - In_2S_3 . Vibrational characterization of the three phases is also provided, and their Raman-active modes are tentatively assigned. Our work shows that the metastable α phase of In_2S_3 can be accessed not only by high temperature or varying composition, but also by high pressure. On top of that, the pressure-induced β – α – ϕ sequence of phase transitions evidences that β - In_2S_3 , a $\text{B}_2^{\text{III}}\text{X}_3^{\text{V}}$ compound with an intriguing structure typical of $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ compounds (intermediate between thiospinels and ordered-vacancy compounds) undergoes: (i) a first phase transition at ambient pressure to a disordered spinel-type structure (α - In_2S_3), isostructural with those found at high pressure and high temperature in other $\text{B}_2^{\text{III}}\text{X}_3^{\text{V}}$ compounds; and (ii) a second phase transition to the defect α - NaFeO_2 -type structure (ϕ - In_2S_3), a distorted NaCl-type structure that is related to the defect NaCl phase found at high pressure in $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ ordered-vacancy compounds and to the defect LiTiO_2 -type phase found at high pressure in $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ thiospinels. This result shows that In_2S_3 (with its intrinsic vacancies) has a similar pressure behaviour to thiospinels and ordered-vacancy compounds of the $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ family, making β - In_2S_3 the union link between such families of compounds and showing that group-13 thiospinels have more in common with ordered-vacancy compounds than with oxospinel and thiospinels with transition metals.

Received 30th June 2021,
Accepted 11th October 2021

DOI: 10.1039/d1cp02969j

rs.c.li/pccp

^a Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain. E-mail: sagalpar@doctor.upv.es

^b Centro de Tecnologías Físicas, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain. E-mail: osgohi@fis.upv.es

^c Departamento de Física Aplicada-ICMUV-MALTA Consolider Team, Universitat de València, c/Dr. Moliner 50, 46100 Burjassot (València), Spain

^d Departamento de Física, Instituto de Materiales y Nanotecnología, MALTA Consolider Team, Universidad de La Laguna, 38207 San Cristóbal de La Laguna, Spain

^e Physics Department, West Virginia University, Morgantown, 26505, USA

^f Department of Physics and Astronomy, Uppsala University, Box 516, Uppsala, SE-75120, Sweden

^g Département de Physique and Regroupement Québécois sur les Matériaux de Pointe, Université de Montréal, C. P. 6128, Succursale Centre-Ville, Montréal, Québec H3C 3J7, Canada

^h Department of Physics, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India

ⁱ ALBA-CELLS, MALTA Consolider Team, 08290 Cerdanyola del Valles (Barcelona), Catalonia, Spain

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1cp02969j

Introduction

Spinel s constitute a class of technologically important materials used in a wide range of applications, such as in dielectrics, sensors, solar cells, and energy materials. High-performance In-based nontoxic (Cd free) semiconductors are under the attentive watch of the industry to implement reliable and eco-friendly devices due to the environmental and biological issues concerning the use of toxic semiconductors in an ever-increasing demand for solar cells. In this context, In-based semiconductors, like spinel-type In_2S_3 , have drawn relevant interest for buffer layers to replace CdS. More specifically, several works have evaluated In_2S_3 -buffered thin films in solar cells, achieving efficiencies between 12.9 and 16.4% by various deposition techniques.^{1–3} These results make In_2S_3 a worthy competitor of CdS in solar cells. Moreover, as an n-type semiconductor, In_2S_3 exhibits a bandgap around 2.2 eV (depending on the growth conditions),^{4–6} a high optical transmission in the visible region,⁷ modest electrical transport properties,⁸ a low lattice thermal conductivity,⁹ and excellent chemical stability.

Due to the above properties, different In_2S_3 phases have been exploited not only in buffer layers, but also in other devices and applications, such as photodetectors, lithium-ion batteries, oxygen sensors, as well as in thermoelectric, luminescent, and photocatalytic applications.^{10–16} Up to three phases of In_2S_3 have been described at ambient pressure and different temperatures: (i) the β phase, with tetragonal defect spinel structure (space group (S.G.) $I4_1/amd$, $Z = 16$, Fig. 1a)) at ambient temperature; (ii) the α phase, with cubic defect spinel structure (S.G. $Fd\bar{3}m$, $Z = 10.67$, Fig. 1(b)) above 749 K; and (iii) the γ phase, with trigonal structure (S.G. $P\bar{3}m1$, $Z = 1$) above 1100 K.

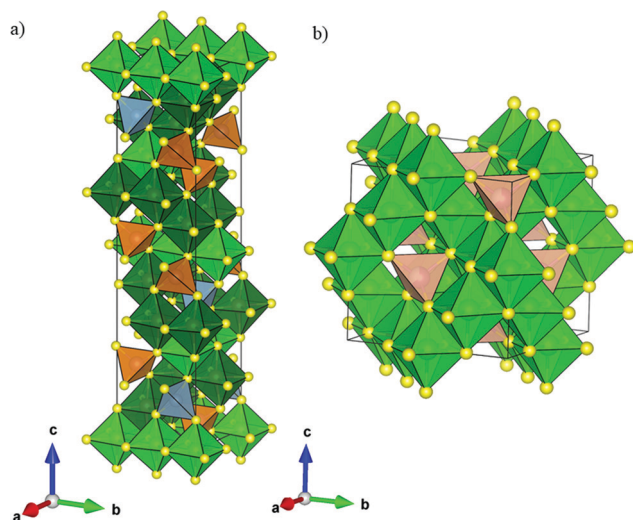


Fig. 1 (a) Crystal structure of $\beta\text{-In}_2\text{S}_3$. Ordered cation vacancies are located in Td(4a) sites (blue tetrahedra). In atoms are placed in Td(8e), Oh(8c), and Oh(16c) sites (orange tetrahedra, green and dark green octahedra). (b) Crystal structure of $\alpha\text{-In}_2\text{S}_3$. Fractional occupation of In atoms occurs in Td(8a) sites (light orange tetrahedra) coming from Td(8e) and Td(4a) sites of the β phase. Oh(8a) sites are fully occupied by In atoms.

The stable phase at ambient conditions, $\beta\text{-In}_2\text{S}_3$, features In cations occupying 2/3 of tetrahedral (Td) positions, the Td(8e) sites, and totally occupying octahedral positions (Oh), the Oh(16h), and Oh(8c) sites. Curiously, 1/3 of the Td positions, the Td(4a) sites, are empty.^{17–21} No other $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ compound shows the defect spinel structure at ambient pressure to our knowledge and only Al_2S_3 and Al_2Se_3 are known to show this phase at high pressure (HP) and high temperature (HT).^{22,23} Indeed, the empty Td(4a) sites can be treated as ordered vacancies, so $\beta\text{-In}_2\text{S}_3$ is in fact the only In-based ordered-vacancy compound (OVC). In this context, $\beta\text{-In}_2\text{S}_3$ can be considered a defective $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ compound (it can be reformulated as $\text{In}_{0.66}\text{In}_2\text{S}_4$ and found at the ICSD database). This material is located between $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ compounds with cubic spinel structure and those with defect chalcopyrite and defect stannite (or famatinite) structures.

On the other hand, $\alpha\text{-In}_2\text{S}_3$ is a phase characterized by a single Td site, the Td(8a) site, which is shared by vacancies and In atoms as a consequence of the order–disorder transition taking place in In_2S_3 above 749 K. In other words, above that temperature vacancies spread over all Td(4a) and Td(8e) sites of the β phase and the structure changes from tetragonal to cubic with a single Td site in the structure.^{18,24–26} The cubic defect spinel phase has also been observed in Al_2S_3 when Al is partially substituted by a 2% As²⁷ and in Al_2S_3 and Al_2Se_3 at HP-HT conditions (4 GPa and 673 K).²³ The HT β – α phase transition (PT) in In_2S_3 has been revisited quite recently.²⁸ In addition, several recent studies have studied the β – α PT at ambient conditions.^{29,30} Aluminium substitution in $\beta\text{-In}_2\text{S}_3$ at relatively high concentration leads to chemical disordering between In and Al cations in the Td(8e) and Td(4a) sites and thus inducing the β – α PT.²⁹ On the other hand, an extensive study on the β – α PT has been carried out by playing with the composition, X, in $\text{In}_{1-x}\text{Vac}_x\text{In}_2\text{S}_4$, where Vac stands for the vacancy.³⁰ This β – α PT has been induced by Se(Te)-for-S substitution as well.³¹ Therefore, in view of these studies, the β – α PT can be triggered by HT or by composition.

Above 1100 K, another order–disorder transition occurs with vacancies being randomly distributed over both Td and Oh cation sites. This additional disorder thus leads to the γ phase,^{24–26} that was refined by Pistor *et al.* during a reinvestigation of the HT-PTs.²⁶ A few studies have considered the possibility of stabilizing $\gamma\text{-In}_2\text{S}_3$ at ambient conditions by adding a 5% of As, Sb, or Bi.^{32,33} The γ -phase of In_2S_3 is similar to the trigonal A-type phase of rare-earth sesquioxides, typical of La_2O_3 ; however, In atoms at the La 2d sites ($z \sim 0.25$) of the La_2O_3 structure are splitted into two 2d sites of $z \sim 0.19$ and 0.35 with fractional occupations in $\gamma\text{-In}_2\text{S}_3$. Noteworthy, the A-type phase of rare-earth sesquioxides was observed in In_2Se_3 at HT with a $z \sim 0.19$,³⁴ so it is possible that the same phase is observed in $\gamma\text{-In}_2\text{S}_3$ and that problems with Rietveld refinement had yielded an additional 2d site with an abnormally high value of z ($z \sim 0.35$).

HP studies in $\beta\text{-In}_2\text{S}_3$ have raised even more controversies than HT studies. The ϵ phase, with a corundum-like structure (S.G. $R\bar{3}c$, $Z = 6$), was quenched from HP-HT studies

(3.5 GPa and 800 K),³⁵ and this phase was also observed in Al_2S_3 .³⁶ As regards HP studies carried out at ambient temperature, several X-ray diffraction (XRD) measurements have addressed the structural properties of the β phase under compression.^{37–39} Three HP-PTs near 6.6, 11, and 35.6 GPa (the last one aided by laser heating) were reported by Lai *et al.*³⁷ The structure of the first two HP phases could not be determined, but the third one (hereafter named $\delta\text{-In}_2\text{S}_3$) was identified as a defect Th_3P_4 -like structure (S.G. $I\bar{4}3d$, $Z = 5.33$).³⁷ In agreement with Lai *et al.*, Yao *et al.* observed a HP-PT at 7.1 and 4.3 GPa in undoped and Ce-doped $\beta\text{-In}_2\text{S}_3$, respectively.³⁸ Concerning the 1st HP phase, they indexed it to a cubic structure, but no more details about the structure were given. Curiously, no HP-PT was found in a more recent HP-XRD work that studied $\beta\text{-In}_2\text{S}_3$ up to 41.3 GPa.³⁹ Despite this result, the same authors observed a pressure-induced metallization of In_2S_3 around 6.8 GPa in a later study;⁴⁰ a result that is in agreement with the 1st HP-PT seen in the two first HP-XRD studies. Finally, we must stress that the 1st HP-PT in $\beta\text{-In}_2\text{S}_3$ has been also recently evidenced by HP-Raman scattering (RS) and impedance spectroscopy measurements around 7 GPa.⁴¹ Moreover, a semiconductor–metal PT at 41.2 GPa has been also reported.⁴¹

Despite the recent HP studies on $\beta\text{-In}_2\text{S}_3$, many questions are still open, being the most important ones related to the nature of the 1st and 2nd HP phases that remain unknown. On the other hand, no *ab initio* simulations of structural and vibrational properties of the β phase at HP have been conducted yet, to our knowledge, to help us to understand the obtained experimental results. Finally, neither of the already mentioned HP studies has explored if the β – α PT could be induced by pressure.

In this work, we present the results of a joint experimental and theoretical study on $\beta\text{-In}_2\text{S}_3$ under compression. HP-XRD and HP-RS measurements up to 15.0 and 21.2 GPa, respectively, are complemented with *ab initio* simulations to shed light on the above commented issues. We will show that there are two HP-PTs whose onset is around 4.9 and 10.2 GPa. We will propose that the 1st HP phase has the cubic defect spinel structure ($\alpha\text{-In}_2\text{S}_3$) and that the 2nd HP phase (hereafter named $\phi\text{-In}_2\text{S}_3$) has a defect $\alpha\text{-NaFeO}_2$ -type structure. This is the first time, to our knowledge, that the defect $\alpha\text{-NaFeO}_2$ -type structure has been proposed as a post-spinel phase and the first time that it is commented on the possibility that the β – α PT on $\beta\text{-In}_2\text{S}_3$ could be induced by pressure. Moreover, we will show that the defect $\alpha\text{-NaFeO}_2$ -type structure bears a relation to the tetradymite-type structure, which is a typical structure of group-15 $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ compounds with topological insulating properties.⁴² We will also provide an experimental and theoretical characterization of the structural and vibrational properties of the three phases (β , α , and ϕ). For this purpose, and due to the difficulty in simulating disordered structures, like $\alpha\text{-In}_2\text{S}_3$ and $\phi\text{-In}_2\text{S}_3$, we will discuss the properties of these two phases by comparison with isostructural compounds CdIn_2S_4 and Na(Ag)InS_2 , respectively.

Most importantly, we will finally show in this work that thiospinels (either with $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ or $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ composition)

undergo pressure-induced order–disorder transitions similar to those of ordered–vacancy compounds. In other words, they tend to HP phases related to the NaCl structure, typical of AX or ABX_2 compounds (with the same number of cations and anions) as if vacancies could be counted as additional cations. Consequently, we will show that thiospinels at HP behave more similarly to ordered–vacancy compounds than to oxospinel and propose new experiments to verify it.

Experimental and theoretical details

$\beta\text{-In}_2\text{S}_3$ powders of high purity (99.999%) used in the present study were commercially acquired from Alfa Aesar company. Additionally, $\alpha\text{-In}_2\text{S}_3$ powders of high purity (99.99%) were commercially acquired from Sigma Aldrich company. Powders were characterized at ambient conditions to verify the presence of either the β or the α phase. HP measurements on $\beta\text{-In}_2\text{S}_3$ at 300 K were performed using a membrane-type diamond–anvil cell (DAC) with 400 μm diameter culet. Powder samples were placed in a 150 μm diameter hole performed in a 40 μm -thick stainless-steel gasket and pressurized by a pressure-transmitting medium (PTM), like 4 : 1 methanol–ethanol mixture (M–E), that remains quasi-hydrostatic up to 10 GPa.^{43,44}

Angle dispersive powder HP-XRD measurements were carried out up to 15 GPa in BL04-MSPD beamline at ALBA synchrotron using a monochromatic X-ray beam with $\lambda = 0.4246$ Å and a Rayonix MARCCD detector located at 240 mm from the sample.⁴⁵ Copper was placed inside the pressure cavity and used as the pressure sensor through copper EoS.⁴⁶ A pinhole placed before the sample position was used as a cleanup aperture for filtering out the tail of the X-ray beam, which was focused down to $20 \times 20 \mu\text{m}^2$ using Kickpatrick–Baez mirrors. Powder XRD patterns were integrated as a function of 2θ using Dioptas software in order to obtain conventional, one-dimensional, diffraction profiles⁴⁷ that were refined using GSAS-II program package.⁴⁸

Unpolarized HP-RS measurements were carried out up to 21 GPa using a Horiba Jobin Yvon LabRAM UV HR microspectrometer equipped with a thermoelectrically cooled multichannel charge coupled device detector that allows a spectral resolution better than 2 cm^{-1} . The Raman signal was excited with a HeNe laser (632.8 nm line) with a power of less than 10 mW and collected in backscattering geometry using an edge filter working in perpendicular configuration and cutting around 100 cm^{-1} . Raman signals down to 50 cm^{-1} or even less can eventually be detected by adjusting the angle between the edge filter and the light containing the Raman signal. The pressure was determined by the ruby luminescence method.⁴⁹ The frequencies of the Raman-active phonons were experimentally obtained by fitting Raman peaks with Voigt profiles of fixed Gaussian line width to the experimental setup resolution (1.6 cm^{-1}).^{50,51}

First-principles density-functional theory (DFT)⁵² calculations at 0 K for $\beta\text{-In}_2\text{S}_3$, cubic spinel CdIn_2S_4 , and AgInS_2 and NaInS_2 (both with $\alpha\text{-NaFeO}_2$ -type structure) were carried out with the Vienna *ab initio* Simulation Package (VASP),⁵³ using

the projected augmented wave (PAW) scheme.^{54,55} Calculations were performed with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzenhof revised for solids (PBEsol).⁵⁶ The basis set of plane waves was extended up to a cutoff 530, 600, and 530 eV for the β - In_2S_3 , thiospinel CdIn_2S_4 , and AgInS_2 and NaInS_2 , respectively, in order to achieve highly converged results. For each relaxed structure, calculations were performed with the automatic k -point generation method included in the VASP package (Monkhorst–Pack scheme⁵⁷) with Hellman–Feynman forces smaller than $0.004 \text{ eV } \text{\AA}^{-1}$ per atom and deviations of the stress tensor from the diagonal hydrostatic form smaller than 0.1 GPa.

Lattice dynamics calculations were performed at the zone center (Γ -point) of the Brillouin zone. The supercell method with the primitive cell was employed for the calculation of the dynamical matrix at the Γ -point.^{53,58} In order to obtain the phonon density of states at 0 GPa, a $2 \times 2 \times 2$ supercell was used for β - In_2S_3 and CdIn_2S_4 .

Structural search by theoretical means were employed to try to identify the 2nd HP crystalline structure phase of β - In_2S_3 . The potential energy surface was systematically explored with the help of the minima hopping and evolutionary genetic methods. The first was employed in the multidimensional potential energy landscape of In_2S_3 with 5, 10, 15, 20, and 40 atoms in the unit cell. We have used the minima hopping method to identify the lower energy configurations at ambient pressure,^{59,60} and at least ninety symmetrically different local minima energy structures were identified for each cell size. The evolutionary genetic method was used as it is implemented in the USPEX code.^{61–63} Initially, the first generation of prediction consisted of 300 structures by considering 1 to 10 formula units for fixed composition search in the unit cell. From the second generation onwards, structures were obtained by applying the 40% heredity (of each generation), 20% soft-mutation, and 20% transmutation operators. The remaining 20% of each generation was generated by using random⁶⁴ and topological generators.⁶⁵ This procedure was performed for 6 and 10 GPa pressure points, near those experimental transition observed. The structures predicted for both methods were kept according to their high symmetry, *i.e.*, those with the least inequivalent atomic positions and a high number of symmetry operations. The study of partially occupied structures has been conducted with the Supercell program⁶⁶ to explore the different supercell configurations describing the analyzed structure. Each one of the selected structures was reoptimized with VASP and symmetrized by using similar convergence criteria than in the case of the vibrational analysis. Only those structures with the smallest energies, with few XRD peaks and few Raman-active modes, like the ones obtained experimentally, were considered for further analysis.

Results and discussion

A. Structural properties under high pressure

Fig. 2 shows the evolution of the XRD patterns of β - In_2S_3 upon compression and decompression. For the sake of clarity, we

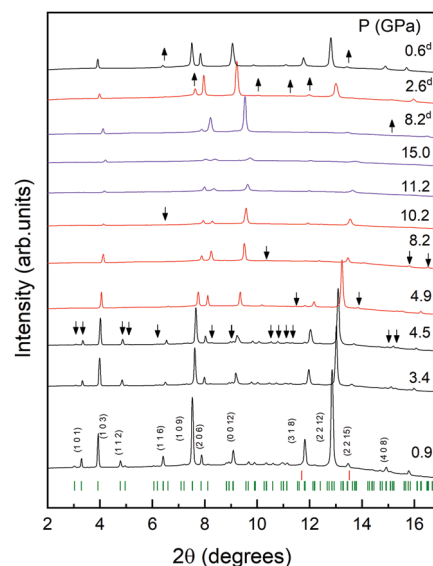


Fig. 2 HP-XRD patterns of β - In_2S_3 on compression up to 15.0 GPa and decompression (d) down to 0.6 GPa. Labels for the most representative ($h k l$) indices for β - In_2S_3 are given. Green ticks represent the β - In_2S_3 reflections at the lowest pressure on upstroke. Black, red, and magenta colors represent the three β , α , and ϕ phases, respectively.

have included the Miller indices ($h k l$) of the most intense reflections of the β phase at 0.9 GPa. An example of Le Bail refinement of the β phase at 0.9 GPa is shown in Fig. 3. At 4.9 GPa, most reflections of β phase occur. Only the most intense peaks of the β phase, namely, (1 0 3), (1 0 9), (2 0 6), (0 0 12), (3 1 8), (2 2 12), (2 2 15) and (4 0 8) reflections remain. Above 4.9 GPa, the β phase cannot be refined anymore; therefore, we consider that this is the onset transition pressure of the 1st HP-PT. Despite the PT, the Miller indices ($h k l$) of the β

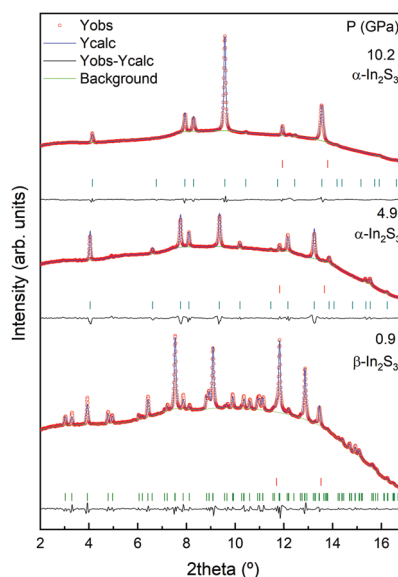


Fig. 3 Le Bail refinement of selected XRD patterns of β - In_2S_3 at 0.9 GPa and of α - In_2S_3 at 4.9 and 10.2 GPa. Copper, β - and α - In_2S_3 reflections are marked with red, green and blue ticks, respectively.

phase are used above 4.9 GPa to refer to the relevant reflections from the HP phases. Above 8.2 GPa, several weak reflections disappear (Fig. 2). At 10.2 GPa, the (1 1 6) reflection disappears and the relative intensities between the (1 0 9) and (2 0 6) reflections changes. Therefore, we consider that a 2nd HP-PT occurs above 10.2 GPa. On decompression down to 0.6 GPa, most of the reflections that disappeared during compression emerge again, thus pointing out the reversibility of the effect exerted by pressure on β - In_2S_3 .

Analysis of the structural parameters of β - In_2S_3 under compression has been obtained by Le Bail refinement (see Fig. 4) and compared to those provided by theoretical calculations. A rather good agreement is found between the experimental and theoretical lattice parameters a and c and their evolution with pressure (Fig. 4(a)). In fact, there is a better agreement of theoretical calculations with the a lattice parameter than with the c lattice parameter (that is slightly overestimated). Consequently, the theoretical volumes are slightly overestimated in comparison to experimental ones (Fig. 4(b)). To evaluate the effect of pressure on the lattice parameters a and c , we have calculated the experimental (theoretical) zero-pressure axial compressibilities, defined as $\kappa_x = -\frac{1}{x} \frac{\partial x}{\partial P}$, which are: $\kappa_a = 5.2 \times 10^{-3}$ (6.2×10^{-3}) GPa and $\kappa_c = 6.4 \times 10^{-3}$ (6.7×10^{-3}) GPa. Our results show that the theoretical and experimental values for κ_c are closer than those for κ_a , unlike the case for the lattice

parameters. Additionally, it is found that the long lattice parameter c is more compressible than the short lattice parameter a . This result can be understood if we consider that ordered vacancies are placed along a 4_1 screw axis parallel to the c axis.

To evaluate the experimental and theoretical pressure dependence of the unit-cell volume of the β phase, we have used both a 2nd and 3rd-order Birch–Murnaghan equation of state (BM2- and BM3-EoS). A good agreement between experimental and theoretical data and the corresponding BM3-EoS can be seen in Fig. 4(b). Our experimental and theoretical zero-pressure volume (V_0), bulk modulus (B_0), and first pressure derivative (B'_0) show a good agreement, as can also be seen in Table 1. Our B_0 values for β - In_2S_3 are very close to that reported for In_2S_3 :Ce nanoparticles,³⁸ slightly smaller than those reported for In_2S_3 nanoparticles³⁸ and for bulk In_2S_3 in ref. 31 and larger than those reported for bulk In_2S_3 in ref. 39. Again, the use of different PTMs and their associated hydrostatic limits⁴³ yield different values for B_0 . In particular, our B_0 values are smaller than those of works using less hydrostatic PTM, like solid powders or silicon oil,^{37,38} and larger than those of works using equal or more hydrostatic PTM, like M–E and Ne.³⁹ In fact, we think that our results and those of ref. 39 are not so different. The main differences between the two works stem from the pressure range used to fit the EoS. In this work, the EoS was fitted up to 4.5 GPa, while in ref. 39 it was fitted up to 41.3 and 21.4 GPa, with M–E and Ne, respectively. It must be mentioned that the bulk modulus of β - In_2S_3 is similar to those of some OVCs, like α' - Ga_2S_3 ⁶⁷ and Ga_2Se_3 ,⁶⁸ and also similar to that of layered α - In_2Se_3 and β' - In_2Se_3 .⁶⁹ In particular, the similar bulk modulus of an OVC, like β - In_2S_3 , and of a layered material, like α - In_2Se_3 , could

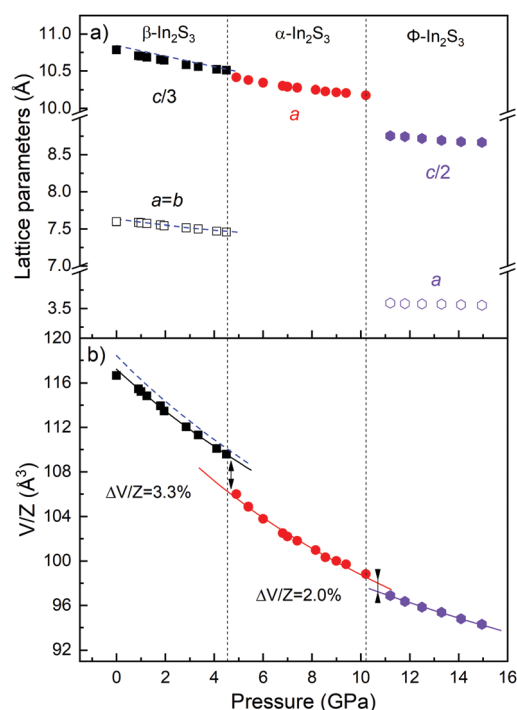


Fig. 4 Pressure dependence of the lattice parameters (a) and volume per formula unit, V/Z (b), in β -, α -, and ϕ - In_2S_3 . The theoretical pressure dependence of the lattice parameters (dash lines) in β - In_2S_3 is plotted in (a). Experimental (solid lines) and theoretical (dash lines) BM3-EoS for β - In_2S_3 are shown in (b). Only experimental BM3-EoS (solid lines) are shown for α -, and ϕ - In_2S_3 in (b).

Table 1 Experimental (exp.) and theoretical (th.) unit-cell volume at zero pressure (V_0 , in Å³), bulk modulus (B_0 , in GPa), and first pressure derivative (B'_0) for β - In_2S_3 . PTM used and transition pressure (TP, in GPa) are also indicated. Results of previous HP works have been added for comparison.^{37–39} The volume per formula unit (V/Z , in Å³) for β - In_2S_3 ($Z = 16$) is shown as well

		V_0	B_0	B'_0	V/Z	TP	PTM
β - In_2S_3	exp. ^b	1876(2)	57(4)	4.5(7)	117(1)	4.9	M–E ^a
		1875(1)	58.2(7)	4.0, fixed	117(1)		
	th. ^b	1895.0(6)	53.1(9)	4.1(4)	118(1)		
		1895.0(4)	53.5(3)	4.0, fixed	118(1)		
	exp. ^c	1880.4 ^d	37.8(2)	4.4(1)	118(1)	No TP	M–E ^a
		1882(1)	39.7(2)	4.0, fixed	118(1)		
		1880.4 ^d	42.8(3)	4.1(1)	118(1)	No TP	Ne
		1883(1)	42.7(2)	4.0, fixed	118(1)		
	exp. ^e	1875(3)	63(3)	4.0, fixed	117(1)	6.6	S ^a
						6.8	LiF ^f
	exp. ^g	1880.7(1)	87(4)	4.0, fixed	118(1)	7.1	S ^a
		1918.1(1)	56(4)	4.0, fixed	120(1)	4.3 ^h	
	exp. ⁱ					6.8	No PTM
	exp. ^j					~7.2	He
						6.8	No PTM

^a M–E: 4 : 1 methanol–ethanol, S: silicone oil. ^b Present work. ^c Ref. 39. ^d Authors in ref. 39 fix V_0 to 1880.4 Å³ for the BM3-EoS for the different PTMs used. ^e Ref. 37. ^f No EoS is given in ref. 37. ^g Ref. 38. ^h In_2S_3 :Ce nanoparticles. ⁱ Ref. 40. 1st PT observed by electrical measurements. ^j Ref. 41. 1st PT observed by Raman and electrical measurements.

be surprising since this last compound is a van der Waals compound that does not present vacancies in its structure; however, the gap between layers in van der Waals materials can be considered to be formed by intrinsic vacancies, as recently suggested,⁷⁰ and this justifies the similarities of both bulk moduli.

A deep analysis of the decrease of the relative volume of the different polyhedral units in β - In_2S_3 , as provided by our theoretical calculations (Fig. S1 in the ESI†), shows that the small bulk modulus of β - In_2S_3 is mainly given by the compression of the polyhedral volume associated to the vacancy (Vac); *i.e.* the VacS_4 tetrahedron (centered at 4a sites). The In-based polyhedral units, InS_4 tetrahedra (centered at 8e sites) and InS_6 octahedra (centered at 8c and 16h sites), compress at a much smaller rate than the tetrahedron around the vacancy. BM2-EoS fit of polyhedral volumes yield a low bulk modulus (9.1 GPa) for the VacS_4 tetrahedron, which is much smaller than those for the InS_4 tetrahedron and InS_6 octahedra (8c and 16h sites), whose values are 54.8, 99.7, and 84.7 GPa, respectively. Therefore, the soft bulk modulus of β - In_2S_3 (~ 57 GPa) can be explained by the strong compression of the polyhedral unit around the vacancy. In fact, if one considers the polyhedral bulk moduli obtained from theoretical calculations and the multiplicity of each site in the tetragonal defect spinel structure, one can calculate a bulk modulus of ~ 65.5 GPa for β - In_2S_3 , which is in relatively good agreement with the theoretical values for the bulk modulus obtained from the unit-cell volume (see Table 1).

A significant larger compression of the tetrahedron around the vacancy than of In-based polyhedra is noticed when comparing the theoretical Vac-S and In-S distances (Fig. S2 in the ESI†). For the sake of completeness, we have also provided in Fig. S3 in the ESI† the pressure dependence of the distortion index (D), quadratic elongation (λ), bond angle variance (σ^2), and effective coordination number (ECoN) corresponding to InS_4 and VacS_4 tetrahedra and both InS_6 octahedra in β - In_2S_3 . Our calculations show a gradual change of all parameters with increasing pressure and, apparently, there is no abrupt change or singular value that could suggest the onset of the order-disorder PT taking place in β - In_2S_3 above 4.9 GPa.

We will now discuss the 1st HP phase observed above 4.9 GPa. The 1st PT is characterized by the disappearance of most reflections of the tetragonal defect spinel phase and the lack of appearance of new peaks; *i.e.* the β phase seems to be a superstructure of the 1st HP phase. Considering the group-supergroup relation between the α and β phases of In_2S_3 , we considered the α phase with cubic spinel structure as a potential candidate for the 1st HP phase of the tetragonal β phase. In fact, we have successfully performed a Le Bail refinement of XRD pattern of the 1st HP phase with the α phase from 4.9 to 10.2 GPa (see Fig. 3). For this purpose, we have used the structural data of the α phase from Pistor *et al.*²⁶ Above 10.2 GPa, the α phase does not fit the experimental XRD patterns anymore.

It is interesting to mention that the cubic spinel structure has also been observed in Al_2S_3 , Al_2Se_3 , CdAl_2S_4 , HgAl_2S_4 , CdAl_2Se_4 , and HgAl_2Se_4 at HP-HT conditions (around 4–7 GPa

and 673–873 K).^{23,71} Therefore, we consider that we have identified the nature of 1st HP phase of β - In_2S_3 and it corresponds to the cubic spinel structure. This phase is isostructural to α - In_2S_3 , observed also at HT and under varying composition.

It must be stressed that in previous HP studies of β - In_2S_3 the nature of the 1st and 2nd HP phases was not provided. Our assignment of the 1st HP phase to the cubic α phase agrees with the cubic symmetry found for the 1st HP phase in a previous work (the S.G. was not provided).³⁸ The main difference between our work and ref. 38 is that our HP-XRD measurements at 4.9 GPa do not show the emergence of new peaks, unlike in ref. 38. In this sense, we want to comment that the XRD patterns from ref. 38 do not exhibit a good peak resolution, likely due to the non-uniform nanoparticle size used in that study, so the appearance of new peaks close to those of the original phase must be considered with caution. It must also be noted that the disappearance of most of the weak reflections of the β phase was also observed in ref. 39, despite the fact that no PT was claimed to occur in that study.

For the sake of comparison with the β phase, we have plotted the lattice parameter a (Fig. 4(a)) and the volume per formula unit, V/Z , (Fig. 4(b)) of α - In_2S_3 as a function of pressure. We must note that Z is 8 for a typical AB_2X_4 spinel; however, we must reformulate Z in terms of the B_2X_3 stoichiometry, like β - In_2S_3 , to compare the V/Z of the different phases studied. For this purpose, we have to consider the Td(8a) fractional occupation of 2/3 and the multiplicity of both In and S atoms. In this way, a renormalized $Z = 10.67$ for the cubic spinel phase of α - In_2S_3 is obtained. By looking at the pressure dependence of V/Z for the β and α phases, we have observed a relative decrease of 3.3% at the 1st PT in β - In_2S_3 . Curiously, this value is similar to the volume changes reported between the low pressure (LP) and HP phases of the AlIn_2S_4 thiospinels.⁷² This means that this small relative volume change seems to be typical of pressure-induced order-disorder PTs in both $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ and $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ thiospinels.

The a lattice parameter compressibility, κ_a , of the α phase (7.9×10^{-3} GPa) is larger than those of the a and c axes of the β phase. On top of that, the bulk modulus, B_0 , of the α phase (obtained either with BM2- or BM3-EoS, see Table 2) is smaller than that of the β phase (Table 1). The softer pressure behaviour of the α phase, reflected in its κ_a and B_0 , is justified by the fractional occupation of the Td(8a) sites in the α phase, coming from ordered Td(8e) and empty Td(4a) sites in the β phase. An estimation of the unit-cell volume fraction associated with vacancies at 0 GPa yields a 1.54 and 3.22% for the β and α phases, respectively. These values reflect the larger fraction of the unit-cell volume occupied by vacancies in the α phase than in the β phase that supports the softer pressure behavior of the α phase compared to the β phase. In this context, the disorder of cations and vacancies in the Td(8a) sites of the defect cubic spinel phase of α - In_2S_3 also explains its smaller B_0 in comparison with the cubic spinel phase of AlIn_2S_4 compounds, that do not present vacancies in their occupied atomic positions (see Table 2).

It must be noted that a smaller B_0 value of the 1st HP phase of the AlIn_2S_4 (A = Cd, Mn, Mg) thiospinels, with defect LiTiO_2

Table 2 Experimental (exp.) unit-cell volume at zero pressure (V_0 , in \AA^3), bulk modulus (B_0 , in GPa), and first pressure derivative (B'_0) obtained for $\alpha\text{-In}_2\text{S}_3$. Experimental and theoretical (th.) data for the low-pressure (LP) and high-pressure (HP) defect- LiTiO_2 -type phases of the AlIn_2S_4 thiospinels (A = Cd, Mg, Mn) are given for comparison.⁷² The volume per formula unit (V/Z , in \AA^3) for $\alpha\text{-In}_2\text{S}_3$ ($Z = 10.67$), as well as for the spinel ($Z = 8$) and defect- LiTiO_2 -type ($Z = 8$) phases of the AlIn_2S_4 thiospinels are also shown. Note that the Z value of the defect- LiTiO_2 structure is renormalized to that of the typical AB_2X_4 composition of spinels. PTM used and transition pressure (TP, in GPa) are indicated

		V_0	B_0	B'_0	V/Z	TP	PTM
$\alpha\text{-In}_2\text{S}_3$	exp. ^b	1245(9)	39(3)	4.5(8)	117(1)	8.2	M-E ^a
		1240(9)	42(3)	4.0, fixed	116(1)		
CdIn_2S_4	LP exp. ^c	1274(2)	78(4)	3.1(8)	159(1)	9.5	M-E ^a
	LP th. ^c	1241.45(2)	79.8(2)	4.65(6)	155(1)	11.5	
MgIn_2S_4	HP exp. ^c	1206(6)	74(4)	4.0, fixed	151(1)		
	HP th. ^c	1174.6(8)	71.6(4)	4.0, fixed	147(1)	8.3	M-E ^a
	LP exp. ^c	1227(1)	76.3(3)	2.8(7)	154(1)	6.0	
	LP th. ^c	1211.9(4)	75.4(9)	4.3(3)	152(1)		
MnIn_2S_4	HP exp. ^c	1222(6)	55(2)	4.0, fixed	153(1)		
	HP th. ^c	1124.8(6)	68.8(4)	4.0, fixed	141(1)	6.8	M-E ^a
	LP exp. ^c	1230(1)	78(4)	3.2(1)	154(1)	6.9	
	LP th. ^c	1200.7(5)	80(2)	3.9(3)	150(1)		
	HP exp. ^c	1187(2)	62(1)	4.0, fixed	148(1)		
	HP th. ^c	1121.0(4)	70.1(3)	4.0, fixed	140(1)		

^a M-E: 4 : 1 methanol-ethanol, S: silicone oil. ^b Present work. ^c Ref. 72.

structure, than that of the cubic spinel phase has also been observed (Table 2).⁷² Again, this is a result of the pressure-induced order-disorder PTs. In the cubic spinel phase of AlIn_2S_4 thiospinels, all cations are mainly ordered with A cations occupying Td(8b) sites and In cations occupying Oh(16c) sites. However, in the defect LiTiO_2 structure, vacancies and A and In cations are disordered in the Oh(16c) sites, resulting in a larger compressibility than that of the cubic spinel phase.

Further support to the assignment of the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ to the α phase comes from the value of the lattice parameter a of the α phase extrapolated to 0 GPa: $a = 10.758 \text{ \AA}$ (10.745 \AA) from our BM3-EoS (BM2-EoS). This value compares well with the lattice parameter a of 10.736 \AA obtained from the commercial sample powders of $\alpha\text{-In}_2\text{S}_3$ at ambient pressure (see Fig. S4(a) in the ESI†). These values can be nicely compared with data reported in the literature for the α phase. In fact, a value of $a = 10.774 \text{ \AA}$ was reported many years ago at ambient conditions,¹⁸ and a little bit longer lattice parameter a of 10.832 \AA was refined at 749 K.²⁶ Moreover, the α phase was observed with a lattice parameter a of 10.769 and 10.758 \AA in $\text{In}_{1-x}\text{Vac}_x\text{In}_2\text{S}_4$ with In contents of 40.5 and 41.0%, respectively.³⁰ As observed, these values of the lattice parameter a for the α phase match quite well with our experimental values, thus confirming the nature of the 1st HP phase of $\beta\text{-In}_2\text{S}_3$.

As already commented, the β - α PT that is induced by HT or varying composition yields the mixing of the ordered Td(8e) and empty Td(4a) sites in the β phase within a unique disordered Td(8a) site in the α phase. Considering that 2/3 of Td positions in the β phase (the Td(8e) sites) are occupied when these sites mix with the empty Td(4a) sites, the occupation fraction in Td(8a) sites in the α phase must be 2/3. This is confirmed in the studies of HT²⁴⁻²⁶ and it is also expected for

HP since no change of composition is expected in either HT or HP studies. Unfortunately, we cannot provide the occupation fraction of Td(8a) sites in the α phase obtained at HP due to the impossibility to perform Rietveld refinements of our HP-XRD patterns. In this context, it must be noted that the α phase obtained by introducing a high In content exhibit an occupation fraction in the Td(8a) site that is higher than 2/3,³⁰ in opposition with what is observed at HT and is expected at HP. This reasoning allows us to predict that a slightly higher bulk modulus of the α phase should be observed in $\text{In}_{1-x}\text{Vac}_x\text{In}_2\text{S}_4$ samples with a high content of In than in stoichiometric $\alpha\text{-In}_2\text{S}_3$. In fact, this hypothesis is indirectly supported by the smaller values of the lattice parameter a found in $\text{In}_{1-x}\text{Vac}_x\text{In}_2\text{S}_4$ samples with a high content of In³⁰ with respect to samples of almost stoichiometric $\alpha\text{-In}_2\text{S}_3$,¹⁸ if one considers the typical inverse relation between volume and bulk modulus. Therefore, the results on $\text{In}_{1-x}\text{Vac}_x\text{In}_2\text{S}_4$ samples give support to our assignment of the nature of the 1st HP phase in $\beta\text{-In}_2\text{S}_3$.

Now, we will focus on the 2nd HP phase observed above 10.2 GPa. First of all, we want to remember that a 2nd PT was reported above 11 GPa in ref. 37. In that work, the 2nd PT was identified by the emerging of new peaks at about 2.6 and 3.0 \AA of d spacing, but the nature of the 2nd HP phase was not identified perhaps due to the lack of an enough number of diffraction peaks and because of the weakness of the few peaks observed.³⁷ It must be noted that the new peaks observed in ref. 37 should be located around 8 and 9 degrees in our XRD patterns, near the (2 0 6) and (0 0 12) reflections of the previous β phase, respectively. Curiously, no new peaks appear near these reflections appear in our HP-XRD measurements. On the other hand, the HP-XRD patterns of ref. 39 show the disappearance of the (1 1 6) reflection as well as the change in the relative intensity of (1 0 9) and (2 0 6) reflections of the previous β phase, as occurs in our HP-XRD patterns (Fig. 2 and 3). Therefore, we can conclude that the results of ref. 39 provide evidence of the 2nd PT, despite the authors of ref. 39 said that no PTs were observed in their HP-XRD measurements.

To identify the 2nd HP phase of $\beta\text{-In}_2\text{S}_3$, several approaches were undertaken. First, we tried with several polymorphs observed on In_2S_3 either at HP, at HT, or at HP-HT. They include the ϵ phase, the γ phase, and the δ phase.³⁷ Moreover, LP and HP phases seen in other compounds with AX (NaCl, CrB, LuS, TiS, CoO and NiO), ABX_2 (LiTiO_2 , LiFeO_2 and NaFeO_2), A_2X_3 (Gd_2S_3 , U_2S_3 , Th_2S_3 , Os_2Al_3 and In_2Se_3), ABX_3 (perovskite, post-perovskite), and AB_2X_4 (post-spinel CaMn_2O_4 , CaTi_2O_4 and CaFe_2O_4) compositions were tested. Further to this, we decided to use structure prediction methods to help us obtain the crystalline structure of the 2nd HP phase of $\beta\text{-In}_2\text{S}_3$. After all this challenging task, we found that the rhombohedral $\alpha\text{-NaFeO}_2$ -type (S.G. $R\bar{3}m$, $Z = 3$) structure, a layered distorted variant of the NaCl-type structure⁷³ observed in ABX_2 compounds,⁷⁴⁻⁷⁸ was the only one compatible with our XRD patterns. Le Bail refinements of the 2nd HP phase with a defect $\alpha\text{-NaFeO}_2$ -type structure at two pressures (11.2 and 15 GPa) are plotted in Fig. 5. This 2nd HP phase ($\phi\text{-In}_2\text{S}_3$) is also a defective phase with vacancies and cations mixed at the same Wyckoff

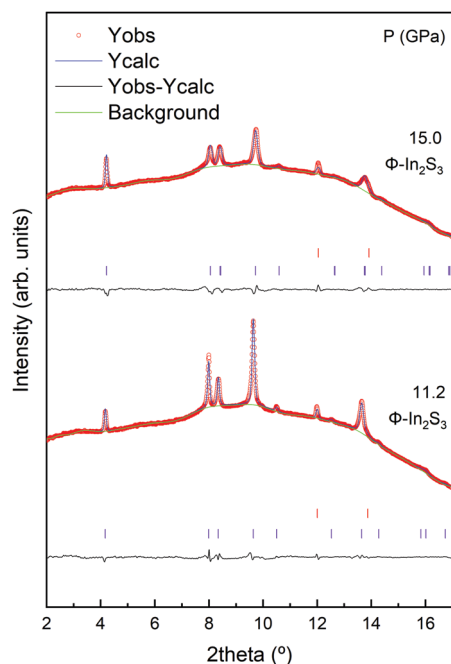


Fig. 5 Le Bail refinement of selected XRD patterns of ϕ - In_2S_3 at 11.2 and 15.0 GPa. Copper and ϕ - In_2S_3 reflections are marked with red and purple ticks, respectively.

sites and has a smaller number of reflections than those in α - In_2S_3 . In particular, the peak located around 6.8 degrees in α - In_2S_3 (Fig. 3) disappears in ϕ - In_2S_3 (Fig. 5). Furthermore, the notable widening of the peaks located around 8.5 and 13.8 degrees around 15 GPa (Fig. 5) comes from the splitting of many reflections of ϕ - In_2S_3 .

We must stress that this is the first time, to our knowledge, that a post-spinel phase with defect α - NaFeO_2 -type structure has been proposed. Noteworthy, this phase has been obtained by chemical lithiation of spinel LiTi_2O_4 ⁷⁹ and in spinel LiCoO_2 at HT.⁸⁰ Additionally, the spinel structure is also found in high-energy irradiated α - NaFeO_2 .⁸¹ These are clear examples of the relation between the rhombohedral $R\bar{3}m$ α - NaFeO_2 -type structure of ABX_2 compounds and the cubic $Fd\bar{3}m$ spinel structure of AB_2X_4 compounds. On top of that, the α - NaFeO_2 -type structure has been found at ambient conditions in several $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ compounds, like Sc_2S_3 ,⁸² Ti_2S_3 ,⁸³ and Zr_2Se_3 .⁸⁴ These last compounds have 2 equal octahedra in 3a and 3b sites for the B cation and an occupation fraction of 1/3 in the 3b sites. Due to the lack of Rietveld refinements, we propose for ϕ - In_2S_3 the same occupation observed in the above mentioned $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ compounds with this α - NaFeO_2 -type structure (see Fig. 6(a)); i.e., a full occupation of 3a sites by In atoms and a 1/3 occupation of 3b sites by In atoms. For the sake of comparison, we have included the structure of NaInS_2 (Fig. 6(b)), where Na cations are in those sites where the ϕ - In_2S_3 has 1/3 of occupation fraction. In conclusion, we propose the defect α - NaFeO_2 -type structure as the 2nd HP phase of ϕ - In_2S_3 at ambient temperature.

Curiously enough, if we remove 1 of every 3 cation layers (from partially occupied 3b sites) of the defect α - NaFeO_2 -type

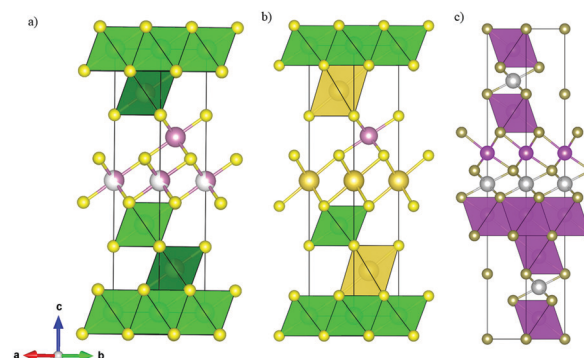


Fig. 6 Comparison of ϕ - In_2S_3 (a), α - NaFeO_2 (b), and α - Bi_2Te_3 (c) structures. Note that vacancies (grey balls) have been added at 3b sites (those between the layers) in the tetradymite structure of α - Bi_2Te_3 to highlight the similarities the α - NaFeO_2 -type and tetradymite-type structures.

structure (S.G. $R\bar{3}m$), we can obtain the tetradymite-like structure (also S.G. $R\bar{3}m$) observed in many $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ compounds, like Bi_2Se_3 (Fig. 6(c)). In this way, the structural relation between the defect NaFeO_2 -type structure and tetradymite structure is emphasized. In a recent work, it has been proposed that the array of intrinsic vacancies forming the gap between the layers in van der Waals materials, like those having a tetradymite structure, should be considered as part of the crystalline structure.⁷⁰ If we apply this rule, both structures are even more connected. In this way, it seems that for $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ compounds with B cations in octahedral coordination, like in the NaCl-type structure, some cations that mix well with vacancies can lead to the defect α - NaFeO_2 -type structure, like in Sc_2S_3 , while other cations that do not mix well with vacancies can lead to the tetradymite-like structure, like in Bi_2Se_3 , where atoms and vacancies group into separate planes leading to quintuple layers.

For the sake of comparison with the previous phases, we have plotted the lattice parameters a and c (Fig. 4(a)) and the volume per formula unit, V/Z , (Fig. 4(b)) of ϕ - In_2S_3 as a function of pressure. Again, reformulating Z for ϕ - In_2S_3 we got $Z = 2$ by considering the occupation fraction of 1/3 in the 3b sites and the multiplicity of both In and S atoms. Attending to the pressure dependence of V/Z for the α and ϕ phases, a relative volume decrease of 2.0% at the 2nd PT in β - In_2S_3 is obtained. Again, this value is similar to the volume changes reported between the LP and HP phases of the AlIn_2S_4 thiospinels,⁷² so this result confirms that this small relative volume change seems to be typical of pressure-induced order-disorder PTs in both $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ and $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ thiospinels.

The a and c lattice parameter compressibilities, κ_a and κ_c , of the ϕ phase (3.1×10^{-3} and 5.4×10^{-3} GPa, respectively) are smaller than those of the a and c axes of the β phase and than that of the a axis of the α phase. On top of that, the bulk modulus, B_0 , of the ϕ phase (obtained either with BM2- or BM3-EoS, see Table 3) is larger than those of the β and α -phases. Note that the unit-cell volume fraction associated with vacancies in the ϕ phase is $\sim 11.11\%$; i.e. larger than those in the β and α phases, but this does not result in a softer pressure

Table 3 Experimental (exp.) unit-cell volume at zero pressure (V_0 , in \AA^3), bulk modulus (B_0 , in GPa), and first pressure derivative (B'_0) obtained for ϕ - In_2S_3 . Theoretical (th.) data for NaInS_2 and AgInS_2 are given for comparison. The volume per formula unit (V/Z , in \AA^3) for ϕ - In_2S_3 ($Z = 2$) and Na(Ag)InS_2 ($Z = 3$) are shown as well

		V_0	B_0	B'_0	V/Z
ϕ - In_2S_3	Exp.	217(3)	78(3)	4.4(4)	109(1)
		216(3)	82(4)	4.0, fixed	108(1)
NaInS_2	th.	248.9(1)	51(5)	4.6(7)	83(1)
		247.8(4)	56(2)	4.0, fixed	83(2)
AgInS_2	th.	229.6(2)	86(2)	4.8(2)	77(1)
		229.2(3)	93(2)	4.0, fixed	76(1)

behaviour of the ϕ phase than the other two phases. The harder pressure behaviour of the ϕ phase is not justified by its fractional occupation of 1/3 in the octahedral cation 3b sites, but for the smaller compressibility of octahedra than of tetrahedra in all spinel-related structures. In addition to this, the low V/Z of the ϕ phase (109 \AA^3 ($Z = 2$)) in comparison to those of β and α phases (117.25 ($Z = 16$) and 116.68 ($Z = 10.67$) \AA^3 , respectively) support the largest incompressibility of the ϕ phase. It must be stressed that the experimental bulk modulus found for ϕ - In_2S_3 is like the theoretical ones predicted for isostructural AgInS_2 , with a similar V value, and larger than NaInS_2 , with a larger V value (see Table 3). This result is in good agreement with the already mentioned inverse relation between volume and bulk modulus.

B. Vibrational properties under high pressure

For β - In_2S_3 , containing 16 molecules in the unit cell, group theory predicts the 120 vibrational modes at the Brillouin zone center:

$$\Gamma = 9A_{1g} + 5A_{1u} + 4A_{2g} + 11A_{2u} + 9B_{1g} + 5B_{1u} + 4B_{2g} + 11B_{2u} + 17E_u + 14E_g$$

From these modes, there are 3 acoustic modes ($A_{2u} + E_u$) and 117 optical modes that correspond to 42 infrared-active modes ($10A_{2u} + 16E_u$), 50 Raman-active modes ($9A_{1g} + 9B_{1g} + 4B_{2g} + 14E_g$), and 25 silent modes ($5A_{1u} + 4A_{2g} + 5B_{1u} + 11B_{2u}$) that are all hyper-Raman-active except for the $4A_{2g}$ modes. Therefore, 36 Raman-active and 26 IR-active peaks are expected since E_g modes (as well as E_u modes) are doubly degenerated. A super-index has been added to the symmetry of the vibrational modes of the different phases to classify them as a function of increasing frequency.

Fig. 7(a) shows a selection of HP-RS spectra of β - In_2S_3 under compression up to 21.2 GPa and decompression down to ambient pressure. The Raman modes of the β phase disappear above 4.5 GPa; *i.e.* at the onset of the 1st PT in good agreement with our HP-XRD measurements. When this PT occurs, the relatively narrow Raman peaks of the β phase disappear, and eight broad bands appear that are consistent with the disorder of cations and vacancies in tetrahedral sites, as expected for the α phase. Moreover, the Raman intensity of most peaks lowers noticeably (at about a 25% of the β phase's signal). For that reason, selected normalized Raman spectra from 5.6 to 21.2 GPa

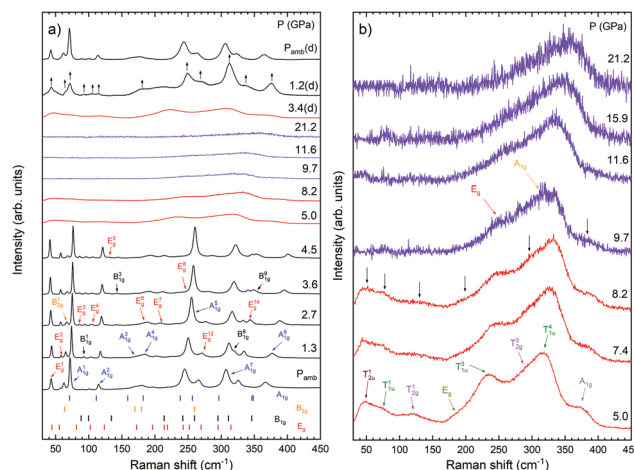


Fig. 7 (a) Stacked Raman spectra of β - In_2S_3 under compression up to 21.2 GPa and under decompression (d) down to ambient pressure. (b) Normalized Raman spectra under compression in the range of 5.0 and 21.2 GPa, where HP phases α - In_2S_3 and ϕ - In_2S_3 are seen. Up and down arrows in both panels show the Raman peaks that disappear/emerge under both compression and decompression.

are shown in Fig. 7(b). Above 8.6 GPa, the Raman signal becomes even worse (at about a 10% of the β phase's signal), and only two broad bands can be distinguished. This marks the onset of the 2nd PT that is in good agreement with our HP-XRD measurements. Finally, upon decompression from 21.2 GPa, we observed several broad bands, as during upstroke, and the appearance of the main Raman modes of the β phase below 1.2 GPa; thus supporting the partial reversibility of the two observed PTs. This result is again in good agreement with our HP-XRD measurements.

The Raman spectrum of β - In_2S_3 at ambient conditions (see the bottom Raman spectrum of Fig. 7(a)) is similar to that published in previous works.^{30,41,85–87} The Raman spectrum covers a wide frequency range (between 40 and 400 cm^{-1}) and shows similar features to those reported by Kambas *et al.*⁸⁵ Moreover, our Raman spectra at different pressures are in agreement with those already found in previous HP-RS measurements.⁴¹ However, unlike in ref. 41, we have measured a considerable frequency shift of the Raman-active modes of β - In_2S_3 (see Fig. 8 and Table 4), especially for the high-frequency modes. These Raman shifts do not agree with the almost negligible Raman shifts reported in ref. 41 for both hydrostatic and non-hydrostatic HP-RS measurements. The experimental and theoretical pressure dependence of the frequencies corresponding to the Raman-active modes of the β phase are plotted in Fig. 8. The good agreement between the experimental and theoretical zero-pressure Raman frequencies and their pressure coefficients has allowed us to tentatively assign the symmetry of the 22 observed Raman-active modes of the β phase (see Fig. 7 and Table 4). With the exception of the B_{1g}^2 mode, we have assigned all the predicted modes to every observed peak below 120 cm^{-1} . At higher frequencies, the assignment is more doubtful due to the large number of Raman-active modes of the β phase and the lack of clear observation of a number of them. It can be noticed that, in

Table 5 Experimental (exp.) zero-pressure frequencies (ω_0 , in cm^{-1}), pressure coefficients (a_1 , in $\text{cm}^{-1} \text{GPa}^{-1}$; a_2 , in $10^{-2} \text{cm}^{-1} \text{GPa}^{-2}$) and Grüneisen parameters, $\gamma = B_0 a_1 / \omega_0$ (ω_0 at 0 GPa), of the observed modes in $\alpha\text{-In}_2\text{S}_3$ as obtained from fits of Raman data to $\omega_0 + a_1(P - P_0)$, with $P_0 = 5.0$ GPa. Frequencies of $\alpha\text{-In}_2\text{S}_3$ from commercial powders and from extrapolations of HP data are also given for comparison. Also summarized are theoretical (th.) and experimental zero-pressure frequencies, pressure coefficients, and reduced slopes of Raman-, IR- and silent-active modes in CdIn_2S_4 . The theoretical data of CdIn_2S_4 have been fitted to $\omega_0 + a_1P$. To calculate γ , we have used $B_0 = 39$ GPa for $\alpha\text{-In}_2\text{S}_3$ and 79.8 GPa for CdIn_2S_4 as well as the frequencies measured at 0 GPa

Mode	$\alpha\text{-In}_2\text{S}_3$ (exp.) ^a					CdIn_2S_4 (th.) ^a			CdIn_2S_4 (exp.) ^b		
	ω_0^c	a_1	γ	ω_0^d	ω_0^e	ω_0	a_1	γ	ω_0	a_1	γ
$\text{T}_{2u}^1(\text{S})$	48(2)	−0.5(2)	−0.4(2)	49(3)	43(1)	49.5(3)	−0.9(1)	−1.5(2)			
$\text{T}_{1u}^1(\text{IR})$	74(2)	−1.0(1)	−0.5(2)	79(3)	70(1)	69.4(3)	−1.1(1)	−1.2(2)	70(1)	0.7(2)	0.8(3)
$\text{T}_{2g}^1(\text{R})$	119(2) ^f	1.1(2)	0.4(3)	113(1)	110(1)	92(1)	0.7(1)	0.6(1)	93(1)	0.5(2)	0.4(3)
$\text{T}_{1u}^2(\text{IR})$						169.7(2)	2.6(1)	1.0(2)			
$\text{A}_{2u}^1(\text{S})$						185.0(2)	1.6(1)	0.7(1)			
$\text{E}_g(\text{IR})$	198(3)	1.9(3)	0.4(1)	187(2)	185(1)	189.1(2)	2.3(1)	1.0(1)	188(1)	2.7(2)	1.1(1)
$\text{T}_{1u}^3(\text{IR})$	236(3)	4.5(1)	0.8(1)	210(3)	217(1)	216.4(3)	3.5(4)	1.3(1)	207(1)	2.6(2)	1.0(1)
$\text{T}_{2u}^2(\text{S})$						227.7(3)	3.8(1)	1.3(1)			
$\text{T}_{2g}^2(\text{R})$						241.5(4)	3.7(1)	1.2(1)	249(1)	4.4(2)	1.4(1)
$\text{T}_{2g}^3(\text{R})$	291(3)	5(1)	0.7(2)	270(2)	264(1)	299.7(4)	6.0(1)	1.6(2)	315(1)	5(2)	1.2(1)
$\text{T}_{1u}^4(\text{IR})$	323(3)	4.4(3)	0.6(2)	298(2)	305(1)	301.2(1)	3.5(2)	1.7(1)	301(1)	3.3(2)	0.9(1)
$\text{A}_{2u}^2(\text{S})$					341(1)	354(1)	6.2(1)	1.4(1)			
$\text{A}_{1g}(\text{R})$	378(3)	5(1)	0.6(2)	354(3)	370(1)	357(1)	5.8(1)	1.3(1)	360(1) ^g	6.1(2) ^g	1.3(1) ^g
									367(1) ^h	6.1(2) ^h	1.3(1) ^h

^a Present work. ^b Ref. 98. ^c Frequencies of $\alpha\text{-In}_2\text{S}_3$ at 5.0 GPa (from data fitting). ^d Frequencies of $\alpha\text{-In}_2\text{S}_3$ at 0 GPa (extrapolated from fits to HP data). ^e Frequencies of $\alpha\text{-In}_2\text{S}_3$ at 0 GPa (experimental data from commercial $\alpha\text{-In}_2\text{S}_3$). ^f This mode can be assigned either the T_{2g}^1 symmetry or as a second order (SO) mode. Further details in the text. ^g A_{1g} mode associated with the vibration of InS_4 tetrahedral units, according to ref. 98. ^h A_{1g} mode associated with the vibration of CdS_4 tetrahedral units, according to ref. 98.

thiospinels; *i.e.* disorder between 4-fold coordinated A cations and 6-fold coordinated In atoms, a partial breakdown of the Raman selection rules occurs due to the loss of translation symmetry, and IR-active and silent modes could be observed in the Raman spectrum.⁹⁷ Therefore, a total of 13 modes could be observed in the Raman spectrum of $\alpha\text{-In}_2\text{S}_3$. We have measured 8 modes in the Raman spectrum of the 1st HP phase (see Fig. 7(b)). The frequencies and pressure coefficients of the 8 modes measured and assigned to $\alpha\text{-In}_2\text{S}_3$ are summarized in Table 5. The pressure coefficients were obtained from the experimental data fitting to the equation $\omega_0 + a_1(P - P_0)$, with $P_0 = 5.0$ GPa.

The fractional occupation in the $\text{Td}(8a)$ sites of $\alpha\text{-In}_2\text{S}_3$ complicates the simulation of its structural and vibrational properties. Therefore, in order to help assigning the symmetry of the experimentally observed modes of the α phase, we have tabulated in Table 5 the theoretical and experimental⁹⁸ modes of CdIn_2S_4 thiospinel, as an approach to the observed modes of $\alpha\text{-In}_2\text{S}_3$. That approximation is justified by the similarity of Cd and In masses and by the proximity of the molecular masses of both compounds per unit cell: 3763 and 3474 for CdIn_2S_4 ($Z = 8$) and $\alpha\text{-In}_2\text{S}_3$ ($Z = 10.66$), respectively. Therefore, similar vibrational frequencies would be expected for both compounds at similar pressures. With this information, we have tentatively assigned the modes observed in the Raman spectrum obtained from the commercial sample powders of $\alpha\text{-In}_2\text{S}_3$ at ambient pressure (Fig. S4(b), ESI†) and at HP in Fig. 7(b). For a better comparison, the Grüneisen parameter for each vibrational mode, $\gamma = B_0 a_1 / \omega_0$, is used to normalize the pressure coefficients of the modes observed in both $\alpha\text{-In}_2\text{S}_3$ and CdIn_2S_4 (see Table 5). Since the value of B_0 for CdIn_2S_4 is almost twice that for $\alpha\text{-In}_2\text{S}_3$ (see Table 2), γ' values for CdIn_2S_4 are almost twice those for $\alpha\text{-In}_2\text{S}_3$ (see Table 4).

According to our experimental results on $\alpha\text{-In}_2\text{S}_3$ and the comparison with isostructural CdIn_2S_4 , the bands observed in the Raman spectrum of $\alpha\text{-In}_2\text{S}_3$ at ambient pressure (Fig. S4(b), ESI†) can be explained as follows (see Table 5). The first band located at 43 cm^{-1} should correspond to a silent T_{2u}^1 mode that is calculated to be around 49.5 cm^{-1} in CdIn_2S_4 . A negative value of γ is observed for this mode in $\alpha\text{-In}_2\text{S}_3$ and also predicted in CdIn_2S_4 . This T_{2u}^1 mode is neither Raman- nor IR-active and becomes Raman-active due to the cation-vacancy disorder in the $\text{Td}(8a)$ sites of the α phase. Concerning the T_{2u}^2 and A_{2u}^1 modes, their theoretical ω_0 do not compare well with those observed experimentally in our HP-RS measurements (Table 5). On top of that, they cannot be assigned properly in the Raman spectra of the commercial $\alpha\text{-In}_2\text{S}_3$ powders of Sigma Aldrich at ambient pressure, because of the broad band between 150 and 250 cm^{-1} (Fig. S4(b), ESI†). However, we have tentatively assigned the A_{2u}^1 mode, the highest-frequency silent mode, to the right shoulder of that peak located at about 300 cm^{-1} (Fig. S4(b), ESI†). The band at about 70 cm^{-1} can be assigned to the IR-active T_{1u}^1 mode, with a_1 quite close to that calculated for CdIn_2S_4 and both with negative γ . Curiously, the experimental pressure coefficient of this mode in CdIn_2S_4 was found to be of opposite sign to that of calculations.⁶⁶ This soft mode was also observed in MgIn_2S_4 ,⁹⁸ while in MnIn_2S_4 , the T_{1u}^1 mode was not observed. The T_{1u}^2 mode, not observed either in $\alpha\text{-In}_2\text{S}_3$ or in CdIn_2S_4 , should be located around 170 cm^{-1} , in accordance with our calculations for CdIn_2S_4 . The T_{1u}^3 and T_{1u}^4 modes in $\alpha\text{-In}_2\text{S}_3$ have been assigned to the broad peaks located in our Raman spectra around 217 and 305 cm^{-1} (236 and 323 cm^{-1} near 5 GPa in Fig. 7(b)), by means of the agreement among the a_1 and ω_0 of our $\alpha\text{-In}_2\text{S}_3$ (those extrapolated at 0 GPa, see Table 5) and both experimental and

theoretical ones for CdIn_2S_4 . Furthermore, these T_{1u}^3 and T_{1u}^4 modes can be likely associated with the peaks observed around 237 and 306 cm^{-1} near 6.6 GPa in ref. 41, but the a_1 reported in ref. 41 for these modes do not match with those collected in our Table 5. The γ values for the T_{1u}^3 mode in $\alpha\text{-In}_2\text{S}_3$ and CdIn_2S_4 are the highest below 230 cm^{-1} . Regarding the T_{1u}^4 mode, the experimental and theoretical γ values in $\alpha\text{-In}_2\text{S}_3$ and CdIn_2S_4 , respectively, are the highest above 230 cm^{-1} .

The rest of the broad bands seen in the Raman spectra of the commercial $\alpha\text{-In}_2\text{S}_3$ sample at ambient pressure and in the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ are tentatively attributed to Raman-active modes of $\alpha\text{-In}_2\text{S}_3$. The broad bands located around 110 and 264 cm^{-1} at ambient pressure (119 and 291 cm^{-1} near 5 GPa in Fig. 7b) can be assigned to the T_{2g}^1 and T_{2g}^3 modes. It must be stressed that the T_{2g}^1 could also be assigned as a second-order mode, as Ursaki *et al.* assigned for the mode observed with a zero-pressure frequency around 110 cm^{-1} in CdIn_2S_4 .⁹⁸ On the other hand, we consider that the T_{2g}^2 mode is not observed in our Raman spectra of $\alpha\text{-In}_2\text{S}_3$. This mode should be placed between 249 and 285 cm^{-1} , where the ω_0 of CdIn_2S_4 , MgIn_2S_4 , and MnIn_2S_4 thiospinels are placed for this mode.⁹⁸ On the other hand, we have assigned the broad peak located around 185 cm^{-1} at ambient pressure (198 cm^{-1} around 5 GPa in Fig. 7b) to the E_g mode on the basis of the close values of the experimental and theoretical a_1 and ω_0 in CdIn_2S_4 , which are also in agreement with those experimental a_1 values reported for MgIn_2S_4 and MnIn_2S_4 thiospinels.⁹⁸ In addition, positive γ values are observed in $\alpha\text{-In}_2\text{S}_3$ for this E_g mode, as well as in AlIn_2S_4 thiospinels.⁹⁸ Last but not least, we have tentatively assigned the highest-frequency broad peak placed around 370 cm^{-1} at ambient pressure (378 cm^{-1} around 5 GPa in Fig. 7b) to the A_{1g} mode, according to the experimental and theoretical a_1 and ω_0 in CdIn_2S_4 . This A_{1g} mode can also be assigned to the broad band observed near 373 cm^{-1} around 7 GPa in ref. 41. As was stressed by Ursaki *et al.*,⁹⁸ the A_{1g} mode refers to the breathing mode (In–S symmetric stretching of InS_4); *i.e.* the vibration of S atoms towards the centre of the tetrahedron. This mode splits into two bands in inverse AlIn_2S_4 thiospinels, associated with the S motion in AS_4 and InS_4 tetrahedra due to cation disorder. The pressure evolution of these two bands has been experimentally seen in the HP-RS measurements of AlIn_2S_4 thiospinels, and this mode was found to have one of the highest values of the pressure coefficients,⁹⁸ in good agreement with our HP-RS measurements in $\alpha\text{-In}_2\text{S}_3$. Similarly, the A_{1g} mode must also split in $\alpha\text{-In}_2\text{S}_3$, due to the cation-vacancy disorder at Td(8a) sites, between the S motions of VacS_4 and InS_4 . Unfortunately, we do not presently know the location of the local vibrational mode around the vacancy (if it exists).

A final comment can be added regarding the pressure coefficients of the β and α phases. It can be observed that the Raman modes with the smallest frequencies in both phases show negative pressure coefficients, unlike in $\phi\text{-In}_2\text{S}_3$ (see Fig. 7(a)). The negative pressure coefficients of the low-frequency modes in both phases are due to the softening of zone-edge TA phonons in tetrahedrally bonded solids that is

not present in octahedrally bonded solids.⁹⁹ Some of these zone-edge phonons become Raman active due to zone folding of cubic structures in more complex structures with a smaller group symmetry, like in $\beta\text{-In}_2\text{S}_3$, or with a large number of atoms in the unit cell, like in $\alpha\text{-In}_2\text{S}_3$. Therefore, the negative pressure coefficient of the lowest frequency mode in the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ is a direct proof that tetrahedral coordination is still present in that phase, and thus gives support to our assignment of the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ to the cubic spinel structure of $\alpha\text{-In}_2\text{S}_3$ where In cations are both tetrahedrally and octahedrally coordinated as in $\beta\text{-In}_2\text{S}_3$.

Support for the identification of the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ with $\alpha\text{-In}_2\text{S}_3$ also comes from the matching between the Raman- and IR-active modes observed in the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ and those seen in $\alpha\text{-In}_2\text{S}_3$ thin films deposited on different substrates,^{41–43} as well as in quenched $\alpha\text{-In}_2\text{S}_3$ samples with high In contents.³⁰ For example, the lowest-frequency IR-active T_{1u}^1 mode has been observed weakly on cubic In_2S_3 thin films deposited on InAs substrates¹⁰⁰ and in quenched $\alpha\text{-In}_2\text{S}_3$ samples with higher In contents.³⁰ The modes found in several works around 126, 240, and 266 cm^{-1} at ambient pressure can be tentatively assigned to T_{2g}^1 , T_{1u}^3 , and T_{2g}^2 modes (the last one not observed in our HP-RS measurements). These frequencies have been traditionally attributed to the presence of $\alpha\text{-In}_2\text{S}_3$ on annealed In_2S_3 thin films deposited on glass substrates.^{101,102} A broad band observed near 166 cm^{-1} on In_2S_3 thin films¹⁰⁰ could be attributed to the T_{1u}^2 mode (not seen in our Raman spectra), which could also be consistent with the modes reported around 170 and 178 cm^{-1} in quenched $\alpha\text{-In}_2\text{S}_3$ samples with In content of 41.0 and 41.5%, respectively.³⁰ In these quenched samples, the modes around 206 and 211 cm^{-1} found in samples with In content of 41.0 and 41.5%, respectively, could be related to the E_g mode at 200 cm^{-1} in our $\alpha\text{-In}_2\text{S}_3$ sample at ambient pressure. Finally, the high-frequency modes T_{2g}^3 , T_{1u}^4 , and A_{1g} mode can be seen in In_2S_3 thin films and in quenched $\alpha\text{-In}_2\text{S}_3$ samples with a high In contents above 295 cm^{-1} .^{30,100–103} All in all, the vibrational information provided in this work for the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ gives support to its $\alpha\text{-In}_2\text{S}_3$ nature.

Finally, we have included the theoretical PDOS of CdIn_2S_4 at 0 GPa in Fig. S5(b) in the ESI,[†] as an approach to that of $\alpha\text{-In}_2\text{S}_3$, in order to compare the vibrational properties of $\alpha\text{-In}_2\text{S}_3$ and $\beta\text{-In}_2\text{S}_3$. As observed, the narrow phonon gap of $\beta\text{-In}_2\text{S}_3$ located at 280 cm^{-1} (Fig. S5a, ESI[†]) becomes wider in the α phase (Fig. S5(b), ESI[†]). Furthermore, a second-wide phonon gap appears around 340 cm^{-1} . Curiously, the Raman spectra of the α phase under compression (Fig. 7(b)) and that measured from the commercial powders of $\alpha\text{-In}_2\text{S}_3$ (Fig. S4b, ESI[†]) do not seem to show those two phonon gaps. In this context, we can speculate that perhaps the cation-vacancy disorder in Td(8a) sites in the α phase results in broad Raman bands that prevent the observation of such phonon gaps in the Raman spectrum.

As regards the 2nd HP phase of $\beta\text{-In}_2\text{S}_3$, we have already commented that above 8.2 GPa most Raman modes of the α phase disappear, and only three broad bands are observed (see Fig. 7). In fact, one of these modes corresponds to the A_{1g} mode

of the α phase that persists up to 9.7 GPa. Therefore, only two broad bands between 200 and 350 cm^{-1} can be ascribed to the 2nd HP phase above 8.2 GPa (see Fig. 7(b)). According to group theory, the rhombohedral α -NaFeO₂-type phase has 12 vibrational modes at the Γ point with irreducible representations:

$$\Gamma = 1A_{1g}(\text{R}) + 2A_{2u}(\text{IR}) + 1E_g(\text{R}) + 2E_u(\text{IR}) + 1A_{2u} + 1E_u$$

where R and IR indicate the Raman- and IR-active modes. Therefore, there are 2 Raman-active modes (E_g and A_{1g}), 4 IR-active modes ($2A_{2u}$ and $2E_u$), and 3 acoustic modes. The two Raman-active modes correspond to anion movements in the stretching and bending modes of the cation-anions bonds.⁷⁴ The frequency shifts of the two bands of ϕ -In₂S₃ upon compression up to 21.2 GPa are plotted in Fig. 8. Of these two peaks, the smallest (highest) in frequency was previously followed under pressure up to 23 (43) GPa.⁴¹ In this respect, our HP-RS measurements agree with those already published.⁴¹ The main difference between both HP-RS studies is that the previous work does not consider that there is a PT above 8.6 GPa, despite there are clear changes in the Raman spectra supporting this 2nd PT in β -In₂S₃.

To verify that the two observed Raman bands of the 2nd HP phase of β -In₂S₃ correspond to the $R\bar{3}m$ structure of defect α -NaFeO₂, we have simulated the pressure dependence of the Raman-active frequencies of isostructural NaInS₂ as an approach to the observed modes of ϕ -In₂S₃ (see Fig. 8 and Table 6). That approximation is justified by the proximity of the molecular masses of both compounds per unit cell: 620 and 656 for NaInS₂ ($Z = 3$) and ϕ -In₂S₃ ($Z = 2$), respectively. Therefore, similar vibrational frequencies are expected for both compounds at similar pressures. With this information, we have tentatively assigned the modes observed in the Raman spectrum of ϕ -In₂S₃ above 8.2 GPa in Fig. 7(b), whose pressure dependence of the vibrational frequencies are plotted in Fig. 8.

For a better comparison of ϕ -In₂S₃ and NaInS₂, the Grüneisen parameter for each vibrational mode, $\gamma = B_0 a_1 / \omega_0$, is used to normalize the pressure coefficients in both compounds (see Table 6). A good agreement between the extrapolated experimental frequencies of ϕ -In₂S₃ at ambient pressure and the experimental⁷⁴ and theoretical frequencies of NaInS₂ at ambient pressure can be observed. Moreover, both compounds show similar a_1 and γ values (see Table 6). This result gives support to the assignment of the 2nd HP phase of β -In₂S₃ to the defect α -NaFeO₂-type structure.

Therefore, we can conclude that our HP-RS measurements provide clear support for the existence of two pressure-induced order-disorder PTs in tetragonal β -In₂S₃ up to 20 GPa. Besides, Raman spectra of the 1st and 2nd HP phases are consistent with the cubic spinel (α -In₂S₃) and the defect α -NaFeO₂-type (ϕ -In₂S₃) structures, respectively, as suggested by Le Bail refinements of our HP-XRD measurements.

To finish this section, we want to stress that the defect α -NaFeO₂ structure bears a close relation with the defect LiTiO₂ structure found as a HP phase in AlIn₂S₄ ($A = \text{Cd, Mg, Mn}$) thiospinels. It must be noted that two broad Raman peaks were also observed in the HP phase of AlIn₂S₄ ($A = \text{Cd, Mg, Mn}$) thiospinels,⁹⁸ as it occurs in the 2nd HP phase of β -In₂S₃. In both kinds of thiospinels, a drastic decrease of the Raman signal was observed at the PT (Fig. 1(a), 2(a) and 3(a) of ref. 98). In the case of AlIn₂S₄ thiospinels, a defect NaCl-type structure (typical HP phase of A^{II}B^{III}X₄^{VI} OVCs), later observed in CdAl₂S₄,⁹³ was first proposed as a HP phase from HP-RS measurements.⁹⁸ However, subsequent HP-XRD measurements determined that the HP phase of AlIn₂S₄ ($A = \text{Cd, Mg, Mn}$) thiospinels was a defect LiTiO₂-type structure.⁷² In this context, it must be stressed that both LiTiO₂ and α -NaFeO₂ structures are typical phases of ABX₂ compounds and that both structures derive from the NaCl-type structure (with all cations in octahedral coordination). The main difference between both structures is that in cubic LiTiO₂ cations are alternated in the sequence A–X–B–X along the different spatial directions, much like the NaCl structure, while in rhombohedral α -NaFeO₂ different types of cations and anions are grouped in different layers in a sequence A–X–B–X, thus resulting in the formation of a layered structure with atomic planes perpendicular to the c axis of the hexagonal unit cell. It may be speculated that the different arrangement of cations in these two structures can be related to the different size of the cations (Li and Ti have similar ionic radii, while Na and Fe have rather different ionic radii). Following this line of reasoning, the different ionic radii of In, on one hand, and the average of the mixture of an In atom and two vacancies, on the other hand, could be responsible for the different behaviour at HP of In₂S₃ with respect to AlIn₂S₄ ($A = \text{Cd, Mg, Mn}$) thiospinels.

C. Structural stability of β -In₂S₃ at HP and pressure-induced PTs

Let us now discuss the stability of β -In₂S₃ under compression based on the information provided in this and previous HP

Table 6 Experimental (exp.) zero-pressure frequencies (ω_0 , in cm^{-1}), pressure coefficients (a_1 , in $\text{cm}^{-1} \text{GPa}^{-1}$; a_2 , in $10^{-2} \text{cm}^{-1} \text{GPa}^{-2}$) and Grüneisen parameters, $\gamma = B_0 a_1 / \omega_0$ (ω_0 at 0 GPa), of the observed modes in ϕ -In₂S₃ as obtained from fits of Raman data to $\omega_0 + a_1(P - P_0) + a_2(P - P_0)^2$. Also summarized are theoretical (th.) zero-pressure frequencies, pressure coefficients, and Grüneisen parameters of the Raman-active modes in NaInS₂ with α -NaFeO₂ structure. The theoretical data of NaInS₂ have been fitted to $\omega_0 + a_1P + a_2P^2$. To calculate γ we have used $B_0 = 78$ GPa for ϕ -In₂S₃ and 51 GPa for NaInS₂

Mode	ϕ -In ₂ S ₃ (exp.)					NaInS ₂				
	ω_0^a	a_1	a_2	γ	ω_0^b	ω_0^c	a_1^c	a_2^c	γ^c	ω_0^d
E_g	242(2)	5(1)	1(7)	1.6(2)	195(5)	165.1(2)	5.1(1)	−5.0(2)	1.5(1)	158
A_{1g}	331(1)	4(1)	−14(4)	0.9(2)	279(5)	284.6(2)	4.6(1)	−5.1(2)	0.8(1)	289

^a Frequencies of ϕ -In₂S₃ at 9.7 GPa (from data fitting). ^b Frequencies of ϕ -In₂S₃ at 0 GPa (extrapolated from fits to HP data). ^c Values for the NaInS₂ obtained from our theoretical calculations. ^d Experimental frequencies of NaInS₂ at ambient conditions from ref. 78.

works, as summarized in Table 1, and the implications of the pressure-induced PTs found in β - In_2S_3 .

Clearly, our measurements show two PTs up to 20 GPa for the β phase. Our first transition pressure (~ 4.8 GPa according to our HP-XRD and HP-RS measurements) is in agreement with that observed in $\text{In}_2\text{S}_3\text{:Ce}$ nanoparticles³² and smaller than those reported in In_2S_3 nanoparticles³² and in In_2S_3 powders.^{37,40,41} We assume that the difference in transition pressures between different works comes from the different PTM and techniques employed since in many previous HP works, rather non-hydrostatic PTMs have been used, especially considering the softness of an OVC such as β - In_2S_3 .

On the other hand, results from ref. 39 are more controversial since no PTs were detected with different PTM, despite the fact that we consider that the two PTs were observed in ref. 39. According to Fig. 2 in ref. 39, the (1 1 2) reflection disappears and the (1 1 6) decreases sharply at about 5.1 GPa with M-E (run-1), meanwhile both reflections disappear at 5.9 GPa with Ne (run-2). The same feature occurs in our HP-XRD measurements at 4.9 GPa (Fig. 2), thus supporting the observation of the first PT in ref. 39. On the other hand, it must be stressed that in Fig. 3 of ref. 39, peaks corresponding to d spacing values greater than 5.0 Å are not reported. Above this value, the weak (0 0 4) peak, observed at 3.03 degree at 0.9 GPa, as well as the (1 0 1) and (1 0 3) reflections can be observed in Fig. 2(a). In fact, the (1 0 3) peak is observed at 0.4 GPa in Fig. 1 of ref. 39, but not the (0 0 4) and (1 0 1) peaks. In this context, it is important to notice that both (0 0 4) and (1 0 1) reflections disappear at 4.9 GPa, and only the (1 0 3) reflection remains in our HP-XRD measurements at that pressure (Fig. 2). Besides, the disappearance of some reflections was observed in ref. 39 below 5.0 Å (Fig. 3(a) and (b) of ref. 39) for run-1 and run-2 at 5.1 and 5.9 GPa, respectively, as occurs in our HP-XRD measurements at 4.9 GPa (Fig. 2(a)). Noteworthy, the same authors from ref. 39 performed electrical measurements under HP in ref. 38, where they reported a semiconductor–metal transition at 6.8 GPa by electrical measurements, which is likely related to the cation-vacancy disorder occurring in β - In_2S_3 upon the first PT. In this respect, it is also noticeable that the HP-RS measurements from ref. 39 evidenced an abrupt change in the Raman modes at 7.2 and 6.8 GPa, with He and without PTM, respectively. Therefore, the β phase is not stable under compression between 4.8 and 6.8 GPa. In conclusion, we can confirm, on the basis of the similarities between our HP-XRD measurements and those from ref. 39, that the first PT is well observed in our HP-XRD measurements and also in earlier HP works.^{37,38,40,41}

The existence of phase transitions in β - In_2S_3 below 20 GPa is further confirmed by our theoretical simulations of the energy vs. volume and relative enthalpy vs. pressure between β - In_2S_3 and ϕ - In_2S_3 (see Fig. S6(a) and (b), respectively, in the ESI†). Clearly, the simulated ϕ - In_2S_3 shows an enthalpy smaller than β - In_2S_3 above 5 GPa. This result is consistent with the α - ϕ PT observed above 8.2 GPa. The disordered ϕ - In_2S_3 could be simulated because it can be described with a few possible supercells (only 7 combinations), as suggested by Supercell program.⁶⁶ However, the number of possible supercells to

simulate α - In_2S_3 is computationally prohibitive (2.3×10^{13}), so no simulation of this phase has been performed.

We also want to comment on the reversibility of the pressure effects on β - In_2S_3 . In agreement with our HP-XRD measurements at 0.6 GPa on downstroke from 16 GPa (Fig. 2(a)), our HP-RS measurements below 1.2 GPa on downstroke from 21 GPa also show the appearance of β - In_2S_3 (Fig. 5(a)). The reversibility of β - In_2S_3 was already commented in a previous HP-RS work.³⁵ In that work, the β phase was recovered when the pressure was relaxed from 8.6 and 7.8 GPa, with He and without PTM, respectively; however, the β phase was not recovered from 43.0 GPa in both runs. This lack of reversibility of β - In_2S_3 from pressures beyond 40 GPa does not match with the reversibility observed by HP electrical measurements up to 41.6 GPa.⁴⁰ Therefore, we can conclude that the different PTMs used and the compression/decompression rates seem to provide different conditions that influence in the reversibility of the pressure-induced PTs in β - In_2S_3 .

It must be stressed that the two observed PTs we have observed up to 20 GPa seem to be reversible under suitable conditions. The reversibility of pressure-induced PTs was also found in AlIn_2S_4 thiospinels,⁷² but not in pseudocubic CdIn_2Se_4 .⁹⁴ The reversibility of the pressure-induced PTs of β - In_2S_3 is very interesting since α - In_2S_3 is a metastable phase at ambient conditions, which is even sold by Sigma Aldrich company, and it could be potentially retained upon decompression from pressures above 12 GPa (once the PT to the 2nd HP phase of β - In_2S_3 is completed). As already commented, the β phase was not recovered on decreasing pressure from 43.0 GPa in ref. 41; however, the Raman spectrum at ambient pressure of our commercial α - In_2S_3 sample (Fig. S4(b), ESI†) and that obtained at ambient pressure on downstroke in ref. 41 are rather similar. Both show a broad band between 150 and 380 cm^{-1} that has a maximum near 300 cm^{-1} and two shoulders near 200 and 350 cm^{-1} . Therefore, we think that the sample recovered from 43.0 GPa in ref. 41 corresponds to a very disordered or amorphous α - In_2S_3 structure. We consider that this recovered sample has disorder also at anion sites because the bands near 300 and 350 cm^{-1} , corresponding to S vibrations, are much broader in the Raman spectrum of the recovered sample in ref. 41 than in the Raman spectrum of commercial α - In_2S_3 . Therefore, we can conclude that the pressure-induced PTs of β - In_2S_3 are reversible from 20 GPa, but are not reversible from 40 GPa. In the last case, a disordered or amorphous α phase can be recovered, which is in good agreement with the nature of the 1st HP phase of β - In_2S_3 we have reported.

Finally, we want to comment that this work has complemented previous HP works on $\text{B}_2^{\text{III}}\text{X}_3^{\text{V}}$ and $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ compounds and has found a new nexus between thiospinels and tetrahedrally-coordinated OVCs of these two families of compounds. In particular, it has been found that thiospinels undergo pressure-induced order–disorder PTs either to the defect NaCl structure (typical of AX compounds and tetrahedrally-coordinated OVCs), like CdAl_2S_4 ,⁹³ or to defect LiTiO_2 and defect α - NaFeO_2 structures (two distorted NaCl-type structures typical of ABX_2 compounds), like thiospinel AlIn_2S_4 compounds ($\text{A} = \text{Cd}, \text{Mg}, \text{and Mn}$)⁷² and In_2S_3 , respectively.

In any case, the previous statement is far from being completely proved and more studies need to be conducted. For instance, on the basis of HP-RS measurements, ZnAl_2S_4 thiospinel has been proposed to undergo a PT towards the CaFe_2O_4 structure, as many oxospinel.¹⁰⁴ On the other hand, an alternative sequence of pressure-induced PTs related to corundum has been recently predicted for Al_2S_3 up to 200 GPa.¹⁰⁵ In particular, a PT from the tetragonal defect spinel ($I4_1/amd$) to corundum ($R\bar{3}c$) and then to the $Pbcn$ structure of In_2O_3 at HP¹⁰⁶ have been proposed for Al_2S_3 . Therefore, this work prompts to carry out HP-XRD measurements on Al_2S_3 and spinel ZnAl_2S_4 to prove whether the post-spinel phase of these thiospinels is a defect NaCl-related phase, a CaFe_2O_4 phase, or a corundum-type phase.

Conclusions

We have revisited the pressure behavior of $\beta\text{-In}_2\text{S}_3$ with tetragonal defect spinel structure using HP-XRD and HP-RS measurements. Our measurements have been supported by *ab initio* calculations to evaluate the effect of pressure on the stability of this interesting OVC. As a result, we have observed two pressure-induced PTs above 5.0 and 10.5 GPa, respectively. The 1st PT is a first-order PT characterized by a 3.3% decrease of the relative volume per formula unit and corresponds to the order-disorder $\beta\text{-}\alpha$ PT. The 2nd PT is a first-order PT characterized by a 2.0% decrease of the relative volume per formula unit and corresponds to the $\alpha\text{-}\phi$ PT. Curiously, the α phase (cubic spinel) exhibits a lower bulk modulus than the β phase due to the larger fraction of vacancies in the volume per formula unit in the α than in the β phase. Furthermore, this disorder also explains the smaller bulk modulus of $\alpha\text{-In}_2\text{S}_3$ than those of isostructural AlIn_2S_4 thiospinels ($A = \text{Cd}, \text{Mg}, \text{Mn}$).

After an extensive search through phases of materials with AX, ABX_2 , B_2X_3 and AB_2X_4 composition, we have proposed that the 2nd HP phase of $\beta\text{-In}_2\text{S}_3$ ($\phi\text{-In}_2\text{S}_3$) has the defect $\alpha\text{-NaFeO}_2$ -type structure. This structure is a derivative of the NaCl-type structure typical of ABX_2 compounds. This is the first time that this structure has been found as a post-spinel phase, to our knowledge. $\phi\text{-In}_2\text{S}_3$ is less compressible than $\beta\text{-}$ and $\alpha\text{-In}_2\text{S}_3$ because it has vacancies in octahedrally coordinated positions that are less compressible than vacancies in tetrahedrally coordinated sites, as it occurs in $\beta\text{-}$ and $\alpha\text{-In}_2\text{S}_3$.

From the vibrational perspective, the $\beta\text{-}\alpha$ PT is characterized by an abrupt change in the Raman spectra. A decrease in the number of peaks, a considerable broadening of the peaks, and a much smaller Raman intensity were observed. On the other hand, the $\alpha\text{-}\phi$ PT is characterized by a reduction in the number of broad bands from 8 to 2 and further decrease of the Raman intensity. Thanks to our lattice-dynamic calculations and their good agreement with our experimental results, we have tentatively assigned the symmetry of the experimentally observed Raman modes of the β phase. Moreover, we have assigned the symmetry of the experimentally observed Raman modes of the α phase by comparison with the calculated Raman-, IR-, and silent-active modes of isostructural CdIn_2S_4 as an approach to

$\alpha\text{-In}_2\text{S}_3$. Similarly, we have assigned the symmetry of the experimentally observed Raman modes of the ϕ phase by comparing them with the calculated Raman-active modes of isostructural NaInS_2 as an approach to $\phi\text{-In}_2\text{S}_3$. Moreover, our identification of the α phase as the 1st HP phase of $\beta\text{-In}_2\text{S}_3$ is supported by the comparison of the XRD and RS measurements of commercial $\alpha\text{-In}_2\text{S}_3$ powder samples at ambient pressure.

As regards the reversibility of the pressure-induced PTs, both our HP-XRD and HP-RS measurements show the reversibility of the changes induced by applying pressure on $\beta\text{-In}_2\text{S}_3$ up to 21 GPa. Moreover, we have shown that previous HP measurements on $\beta\text{-In}_2\text{S}_3$ up to 40 GPa are consistent with the recovery of strongly disordered or amorphous $\alpha\text{-In}_2\text{S}_3$ at ambient pressure. In summary, the present work proposes for the first time: (i) that $\alpha\text{-In}_2\text{S}_3$ is accessible from the stable β phase not only by HT or by varying composition, but also at HP, and that it can be recovered from HP experiments under suitable conditions, and (ii) that a defect $\alpha\text{-NaFeO}_2$ -type structure can be another post-spinel phase in thiospinels.

Finally, we have shown that our present work represents an important complement to previous HP works in thiospinels. In particular, we have evidenced that many cubic group-13 thiospinels undergo pressure-induced phase transitions to defect NaCl related structures (defect LiTiO_2 and defect $\alpha\text{-NaFeO}_2$), which are typical of AX and ABX_2 compounds (with the same number of cations and anions). Since pressure-induced PTs to the defect NaCl structure are common in tetrahedrally-coordinated OVCs, our work suggests that group-13 thiospinels with $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ and $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ (with a group-2 or group-12 A cation) compositions show a pressure behavior closer to tetrahedrally OVCs than to oxospinel or thiospinels with transition metals. In summary, this work paves the way to better understand the behaviour under pressure of compounds with $\text{B}_2^{\text{III}}\text{X}_3^{\text{VI}}$ and $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4^{\text{VI}}$ composition. We hope this work will stimulate HP-XRD measurements on Al_2S_3 and spinel ZnAl_2S_4 that will be important to validate the hypothesis here stated and get a more complete picture of pressure-induced PTs in thiospinels.

Author contributions

F. J. M. and O. G. conceived the project. S. G.-P., O. G. and F. J. M. planned and organized experiments. S. G.-P. analysed the data. Concerning the experimental part, HP-XRD measurements were carried out by R. V., V. P. C.-G., C. P. and F. J. M.; HP-RS measurements by S. G.-P. Concerning the theoretical part, the total-energy and lattice dynamics DFT calculations were performed by P. R.-H. and A. M., meanwhile the minima hopping and evolutionary genetic methods for the structural search were performed by A. R., A. M. and R. A. The first manuscript draft was prepared by S. G.-P. The authors reviewed the manuscript and participated actively in the discussion of the results.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This publication is part of the project MALTA Consolider Team network (RED2018-102612-T), financed by MINECO/AEI/10.13039/501100003329; by I+D+i projects PID2019-106383GB-I/10.13039/501100003329; by MCIN/AEI/10.13039/5011000011033; by project PROMETEO/2018/123 (EFIMAT), financed by Generalitat Valenciana; and by projects DMREF-NSF 1434897 and DOE DE-SC0016176, financed from US agencies. A. M., and P. R.-H. acknowledge computing time provided by Red Española de Supercomputación (RES) and MALTA-Cluster, and we also thank ALBA synchrotron light source for funded experiment 2017022088 at the MSPD-BL04 beamline. A. H. R. acknowledges the computational resources awarded by XSEDE, a project supported by National Science Foundation grant number ACI-1053575, as well as the time from the Super Computing System (Thorny Flat) at WVU, which is funded in part by the National Science Foundation (NSF) Major Research Instrumentation Program (MRI) Award #1726534, and West Virginia University. The authors also acknowledge the support from the Texas Advances Computer Center (with the Stampede2 and Bridges supercomputers). A. M. and R. A. acknowledge the support from Olle Engkvists stiftelse, Sweden, Carl Tryggers Stiftelse for Vetenskaplig Forskning (CTS) and the Swedish Research Council (Grant no. VR-2016-06014 and VR-2020-04410). SNIC and HPC2N are also acknowledged for providing computing resources.

References

- N. Naghavi, S. Spiering, M. Powalla, B. Cavana and D. Lincot, *Prog. Photovoltaics Res. Appl.*, 2003, **11**, 437–443.
- D. Hariskos, S. Spiering and M. Powalla, *Thin Solid Films*, 2005, **480**, 99–109.
- N. Allsop, A. Schönmann, H. J. Muffler, M. Bär, M. C. Lux-Steiner and C. H. Fischer, *Prog. Photovoltaics Res. Appl.*, 2005, **13**, 607–616.
- S. Rasool, K. Saritha, K. R. Reddy, M. Tivanov, A. Trofimova, S. Tikoto, L. Bychto, A. Patryn, M. Maliński and V. Gremenok, *Curr. Appl. Phys.*, 2019, **19**, 108–113.
- N. Barreau, *Sol. Energy*, 2009, **83**, 363–371.
- S.-H. Choe, T.-H. Bang, N.-O. Kim, H.-G. Kim, C.-I. Lee, M.-S. Jin, S.-K. Oh and W.-T. Kim, *Semicond. Sci. Technol.*, 2001, **16**, 98.
- P. Rao and S. Kumar, *Thin Solid Films*, 2012, **524**, 93–99.
- Y. X. Chen, A. Yamamoto and T. Takeuchi, *J. Alloys Compd.*, 2017, **695**, 1631–1636.
- Y. X. Chen, K. Kitahara and T. Takeuchi, *J. Appl. Phys.*, 2015, **118**, 245103.
- J. Zhang, H. Wang, X. Yuan, G. Zeng, W. Tu and S. Wang, *J. Photochem. Photobiol., C*, 2019, **38**, 1–26.
- L. Wang, S. K. Karuturi and L. Zan, *Appl. Surf. Sci.*, 2020, 148063.
- K. Hara, K. Sayama and H. Arakawa, *Sol. Energy Mater. Sol. Cells*, 2000, **62**, 441–447.
- N. Barreau, C. Deudon, A. Lafond, S. Gall and J. Kessler, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 1840–1848.
- X. Fu, X. Wang, Z. Chen, Z. Zhang, Z. Li, D. Y. Leung, L. Wu and X. Fu, *Appl. Catal., B*, 2010, **95**, 393–399.
- C.-H. Ho, M.-H. Lin, Y.-P. Wang and Y.-S. Huang, *Sens. Actuators, A*, 2016, **245**, 119–126.
- W. Huang, L. Gan, H. Yang, N. Zhou, R. Wang, W. Wu, H. Li, Y. Ma, H. Zeng and T. Zhai, *Adv. Funct. Mater.*, 2017, **27**, 1702448.
- H. Hahn and W. Klingler, *Z. Anorg. Chem.*, 1949, **260**, 97–109.
- C. Adenis, J. Olivier-Fourcade, J.-C. Jumas and E. Philippot, *Rev. Chim. Miner.*, 1987, **24**, 10–21.
- G. King, *Acta Crystallogr.*, 1962, **15**, 512.
- G. Steigmann, H. Sutherland and J. Goodyear, *Acta Crystallogr.*, 1965, **19**, 967–971.
- N. S. Rampersadh, A. M. Venter and D. G. Billing, *Phys. B*, 2004, **350**, E383–E385.
- P. Donohue, *J. Solid State Chem.*, 1970, **2**, 6–8.
- K.-J. Range and H.-J. Hübner, *Z. Naturforsch. B*, 1973, **28**, 353–355.
- J. Van Landuyt, H. Hatwell and S. Amelinckx, *Mater. Res. Bull.*, 1968, **3**, 519–528.
- R. Diehl and R. Nitsche, *J. Cryst. Grow.*, 1975, **28**, 306–310.
- P. Pistor, J. M. Merino Álvarez, M. León, M. Di Michiel, S. Schorr, R. Klenk and S. Lehmann, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, **72**, 410–415.
- H. Schäfer, G. Schäfer and A. Weiss, *Z. Anorg. Allg. Chem.*, 1963, **325**, 77–88.
- P. Wyżga, W. Carrillo-Cabrera, L. Akselrud, I. Veremchuk, J. Wagler, C. Hennig, A. A. Tsirlin, A. Leithe-Jasper, E. Kroke and R. Gumeniuk, *Dalton Trans.*, 2020, **49**, 15903–15913.
- A. Lafond, X. Rocquefelte, M. Paris, C. Guillot-Deudon and V. Jouenne, *Chem. Mater.*, 2011, **23**, 5168–5176.
- P. Wyżga, I. Veremchuk, C. Himcinschi, U. Burkhardt, W. Carrillo-Cabrera, M. Bobnar, C. Hennig, A. Leithe-Jasper, J. Kortus and R. Gumeniuk, *Dalton Trans.*, 2019, **48**, 8350–8360.
- P. Wyżga, S. Grimm, V. Garbe, E. Zuñiga-Puelles, C. Himcinschi, I. Veremchuk, A. Leithe-Jasper and R. Gumeniuk, *J. Mater. Chem. C*, 2021, **9**, 4008–4019.
- R. Diehl and R. Nitsche, *J. Cryst. Growth*, 1973, **20**, 38–46.
- R. Diehl, C. D. Carpentier and R. Nitsche, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1976, **32**, 1257–1260.
- A. Likforman and M. Guittard, *C. R. Seances Acad. Sci., Ser. C*, 1974, **279**, 33.
- K. J. Range and M. Zabel, *Z. Naturforsch. B*, 1978, **33**, 463–464.
- J. Flahaut, *Ann. Chim.*, 1952, **12**, 632–696.
- X. Lai, F. Zhu, Y. Wu, R. Huang, X. Wu, Q. Zhang, K. Yang and S. Qin, *J. Solid State Chem.*, 2014, **210**, 155–159.
- B. Yao, H. Zhu, S. Wang, P. Wang and M. Zhang, *J. Solid State Chem.*, 2014, **210**, 150–154.
- Y. Li, Q. Wang, Y. Gao, B. Liu, C. Gao and Y. Ma, *Mater. Res. Express*, 2017, **4**, 085902.

- 40 Y. Li, Y. Gao, N. Xiao, P. Ning, L. Yu, J. Zhang, P. Niu, Y. Ma and C. Gao, *AIP Adv.*, 2018, **8**, 115202.
- 41 K. Liu, L. Dai, H. Li, H. Hu, L. Yang, C. Pu and M. Hong, *Chem. Phys.*, 2019, **524**, 63–69.
- 42 F. Manjón, R. Vilaplana, O. Gomis, E. Pérez-González, D. Santamaría-Pérez, V. Marín-Borrás, A. Segura, J. González, P. Rodríguez-Hernández and A. Muñoz, *Phys. Status Solidi B*, 2013, **250**, 669–676.
- 43 S. Klotz, J. C. Chervin, P. Munsch and G. Le Marchand, *J. Phys. D: Appl. Phys.*, 2009, **42**, 075413.
- 44 D. Errandonea, A. Muñoz and J. Gonzalez-Platas, *J. Appl. Phys.*, 2014, **115**, 216101.
- 45 F. Fauth, I. Peral, C. Popescu and M. Knapp, *Powder Diffr.*, 2013, **28**, S360–S370.
- 46 A. Dewaele, P. Loubeyre and M. Mezouar, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 094112.
- 47 C. Prescher and V. B. Prakapenka, *High Press. Res.*, 2015, **35**, 223–230.
- 48 B. H. Toby and R. B. Von, Dreele, *J. Appl. Crystallogr.*, 2013, **46**, 544–549.
- 49 H. K. Mao, J. A. Xu and P. M. Bell, *J. Geophys. Res.: Solid Earth*, 1986, **91**, 4673–4676.
- 50 A. Debernardi, C. Ulrich, M. Cardona and K. Syassen, *Phys. Status Solidi B*, 2001, **223**, 213–223.
- 51 B. Garcia-Domene, H. Ortiz, O. Gomis, J. Sans, F. Manjón, A. Muñoz, P. Rodríguez-Hernández, S. Achary, D. Errandonea and D. Martínez-García, *J. Appl. Phys.*, 2012, **112**, 123511.
- 52 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
- 53 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 558.
- 54 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.
- 55 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- 56 J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406.
- 57 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188.
- 58 K. Parlinski, *Computer Code Phonon*, see: <http://www.computingformaterials.com/index.html>.
- 59 M. Amsler and S. Goedecker, *J. Chem. Phys.*, 2010, **133**, 224104.
- 60 S. Goedecker, *J. Chem. Phys.*, 2004, **120**, 9911–9917.
- 61 A. R. Oganov and C. W. Glass, *J. Chem. Phys.*, 2006, **124**, 244704.
- 62 A. R. Oganov, A. O. Lyakhov and M. Valle, *Acc. Chem. Res.*, 2011, **44**, 227–237.
- 63 A. R. Oganov, Y. Ma, A. O. Lyakhov, M. Valle and C. Gatti, *Rev. Mineral. Geochem.*, 2010, **71**, 271–298.
- 64 A. O. Lyakhov, A. R. Oganov, H. T. Stokes and Q. Zhu, *Comput. Phys. Commun.*, 2013, **184**, 1172–1182.
- 65 P. V. Bushlanov, V. A. Blatov and A. R. Oganov, *Comput. Phys. Commun.*, 2019, **236**, 1–7.
- 66 K. Okhotnikov, T. Charpentier and S. Cadars, *J. Cheminf.*, 2016, **8**, 1–15.
- 67 S. Gallego-Parra, R. Vilaplana, O. Gomis, E. L. da Silva, A. Otero-de-la-Roza, P. Rodríguez-Hernández, A. Muñoz, J. González, J. Sans and V. Cuenca-Gotor, *Phys. Chem. Chem. Phys.*, 2021, **23**, 6841–6862.
- 68 M. Takumi, Y. Koshio and K. Nagata, *Phys. Status Solidi B*, 1999, **211**, 123–129.
- 69 R. Vilaplana, S. G. Parra, A. Jorge-Montero, P. Rodríguez-Hernández, A. Munoz, D. Errandonea, A. Segura and F. J. Manjón, *Inorg. Chem.*, 2018, **57**, 8241–8252.
- 70 J. L. Da Silva, A. Walsh and H. Lee, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 224111.
- 71 K.-J. Range, W. Becker and A. Weiss, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, 1968, **23**, 1009.
- 72 D. Santamaría-Pérez, M. Amboage, F. Manjón, D. Errandonea, A. Muñoz, P. Rodríguez-Hernández, A. Mújica, S. Radescu, V. Ursaki and I. Tiginyanu, *J. Phys. Chem. C*, 2012, **116**, 14078–14087.
- 73 L. Gerward, J. S. Olsen and U. Benedict, *Phys. B + C*, 1986, **144**, 72–78.
- 74 R. Hoppe, W. Lidecke and F. C. Frorath, *Z. Anorg. Allg. Chem.*, 1961, **309**, 49–54.
- 75 K.-J. Range, M. Keubler and A. Weiss, *Z. Naturforsch. B*, 1969, **24**, 1060–1061.
- 76 W. Schanow and K.-J. Range, *Mater. Res. Bull.*, 1983, **18**, 39–44.
- 77 H. Beister, S. Ves, W. Hönle, K. Syassen and G. Kühn, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1991, **43**, 9635.
- 78 P. Brüesch and C. Schüller, *J. Phys. Chem. Solids*, 1971, **32**, 1025–1038.
- 79 G. C. Mather, C. Dussarrat, J. Etourneau and A. R. West, *J. Mater. Chem.*, 2000, **10**, 2219–2230.
- 80 H. Porthault, R. Baddour-Hadjean, F. Le Cras, C. Bourbon and S. Franger, *Vib. Spectrosc.*, 2012, **62**, 152–158.
- 81 M. M. Rahman, W.-Y. Chen, L. Mu, Z. Xu, Z. Xiao, M. Li, X.-M. Bai and F. Lin, *Nat. Commun.*, 2020, **11**, 1–13.
- 82 J. Dismukes and J. White, *Inorg. Chem.*, 1964, **3**, 1220–1228.
- 83 M. Onoda and M. Saeki, *Chem. Lett.*, 1980, 665–666.
- 84 F. K. McTaggart and A. Wadsley, *Aust. J. Chem.*, 1958, **11**, 445–457.
- 85 K. Kambas, J. Spyridelis and M. Balkanski, *Phys. Status Solidi B*, 1981, **105**, 291–296.
- 86 P. Pistor, R. Caballero, D. Hariskos, V. Izquierdo-Roca, R. Wächter, S. Schorr and R. Klenk, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 148–152.
- 87 E. Kärber, K. Otto, A. Katerski, A. Mere and M. Krunks, *Mater. Sci. Semicond. Process.*, 2014, **25**, 137–142.
- 88 S. Gallego-Parra, O. Gomis, R. Vilaplana, H. M. Ortiz, E. Perez-Gonzalez, R. Luna, P. Rodríguez-Hernández, A. Muñoz, V. Ursaki and I. Tiginyanu, *J. Appl. Phys.*, 2019, **125**, 115901.
- 89 R. Vilaplana, M. Robledillo, O. Gomis, J. A. Sans, F. J. Manjón, E. Pérez-González, P. Rodríguez-Hernández, A. Muñoz, I. M. Tiginyanu and V. V. Ursaki, *J. Appl. Phys.*, 2013, **113**, 093512.
- 90 R. Vilaplana, O. Gomis, E. Pérez-González, H. M. Ortiz, F. J. Manjón, P. Rodríguez-Hernández, A. Munoz,

- P. Alonso-Gutiérrez, M. L. Sanjuán, V. V. Ursaki and I. M. Tiginyanu, *J. Appl. Phys.*, 2013, **113**, 233501.
- 91 O. Gomis, R. Vilaplana, F. J. Manjón, E. Pérez-González, J. López-Solano, P. Rodríguez-Hernández, A. Muñoz, D. Errandonea, J. Ruiz-Fuertes, A. Segura, D. Santamaria-Pérez, I. M. Tiginyanu and V. Ursaki, *J. Appl. Phys.*, 2012, **111**, 013518.
- 92 R. Vilaplana, O. Gomis, F. J. Manjón, H. M. Ortiz, E. Pérez-González, J. López-Solano, P. Rodríguez-Hernández, A. Muñoz, D. Errandonea, V. V. Ursaki and I. M. Tiginyanu, *J. Phys. Chem. C*, 2013, **117**, 15773–15781.
- 93 J. A. Sans, D. Santamaria-Pérez, C. Popescu, O. Gomis, F. J. Manjón, R. Vilaplana, A. Muñoz, P. Rodríguez-Hernández, V. V. Ursaki and I. M. Tiginyanu, *J. Phys. Chem. C*, 2014, **118**, 15363–15374.
- 94 D. Santamaria-Perez, O. Gomis, A. L. Pereira, R. Vilaplana, C. Popescu, J. A. Sans, F. J. Manjón, P. Rodríguez-Hernandez, A. Muñoz and V. V. Ursaki, *J. Phys. Chem. C*, 2014, **118**, 26987–26999.
- 95 P. Canepa, R. M. Hanson, P. Ugliengo and M. Alfredsson, *J. Appl. Crystallogr.*, 2011, **44**, 225–229.
- 96 E. Kroumova, M. Aroyo, J. Perez-Mato, A. Kirov, C. Capillas, S. Ivantchev and H. Wondratschek, *Phase Transitions: A Multinational Journal*, 2003, **76**, 155–170.
- 97 H. Lutz, W. Becker, B. Müller and M. Jung, *J. Raman Spectrosc.*, 1989, **20**, 99–103.
- 98 V. Ursaki, F. Manjón, I. Tiginyanu and V. Tezlevan, *J. Phys.: Condens. Matter*, 2002, **14**, 6801.
- 99 B. Weinstein, *Phys. Rev. B*, 2021, **104**, 054105.
- 100 Y. Sim, J. Kim and M.-J. Seong, *J. Alloys Compd.*, 2016, **685**, 518–522.
- 101 H. Izadneshana and V. Gremenok, *J. Appl. Spectrosc.*, 2014, **81**, 765–770.
- 102 V. F. Gremenok, K. T. R. Reddy, M. S. Tivanov and A. Patryn, *Przegl. Elektrotech.*, 2017, **93**, 89–91.
- 103 R. Souissi, N. Bouguila, M. Bendahan, T. Fiorido, K. Aguir, M. Kraini, C. Vázquez-Vázquez and A. Labidi, *Sens. Actuators, B*, 2020, **319**, 128280.
- 104 V. V. Ursaki and I. M. Tiginyanu, in *Pressure-induced phase transitions in AB₂X₄ chalcogenide compounds*, ed. F. J. Manjón, I. Tiginyanu and V. Ursaki, Springer, 2014, pp. 213–235.
- 105 S. Shao, W. Zhu, J. Lv, Y. Wang, Y. Chen and Y. Ma, *npj Comput. Mater.*, 2020, **6**, 1–6.
- 106 B. García-Domene, J. Sans, O. Gomis, F. Manjón, H. Ortiz, D. Errandonea, D. Santamaria-Pérez, D. Martínez-García, R. Vilaplana and A. Pereira, *J. Phys. Chem. C*, 2014, **118**, 20545–20552.