# Study of the orpiment and anorpiment phases of As$_2$S$_3$ under pressure

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## Related content

# Study of the orpiment and anorpiment phases of $As_2S_3$ under pressure

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**Abstract.** In this work we study the pressure behaviour of the orpiment (monoclinic) and anorpiment (triclinic) layered structures of $As_2S_3$ by means of *ab initio* calculations performed within the density functional theory, as part of an ongoing theoretical and experimental joint effort to provide a comprehensive picture of the bonding of this interesting material and the evolution of its structural, electronic, and vibrational properties under pressure.

## 1. Introduction

Arsenic sulfide binary compounds with different stoichiometries have been researched in the past following interest in their optical, electronic, and structural properties, and in particular $As_2S_3$ has been found to be an excellent glass former at high temperatures, with some significant properties [1-5]. Under normal conditions, the stable phase of $As_2S_3$ is a semiconductor named orpiment with a crystalline layered structure in which each atom of As is surrounded by three atoms of S whereas each atom of S is surrounded by two atoms of As. Despite efforts to synthesize new polymorphs of this material no other crystalline metastable phases at normal conditions could be artificially produced in laboratories for a long time. Quite recently however, a low symmetry (triclinic) new phase of $As_2S_3$ named anorpiment has been naturally discovered analyzing the mineral specimens of an old peruvian mine [3]. The structure of this anorpiment phase is similar to that of the long known orpiment phase in that it is made of covalently bonded layers of As and Se atoms with a similar coordination (though the interlayer pattern is not exactly the same) arranged in a different stacking sequence, with interlayer van der Waals forces playing a significant role in the structural properties. In this work we study the orpiment and anorpiment phases of $As_2S_3$ theoretically (within the first-principles framework of the density functional theory) as part of an ongoing theoretical and experimental joint effort to provide a comprehensive picture of the bonding of this interesting material and the evolution of its structural, electronic, and vibrational properties under pressure.

## 2. Details of the calculations

All the calculations were done within the first-principles theoretical framework of the density functional theory (DFT) implemented in the computational scheme of pseudopotentials and plane waves. The Vienna Ab Initio Simulation Package (VASP) code was used [6-8]. Both the Perdew-Burke-Ernzerhof (PBE) [9] and its PBEsol modified version [10] of the generalized gradient approximations to the exchange and correlation (XC) energy were used as well as the projector-augmented wave scheme [11,12]. The $4s$ and $4p$ outermost electrons of As and the $3s$ and $3p$ electrons of S were dealt with explicitly in the valence, the rest of the electrons being considered frozen at the core. The cutoff in the kinetic energy of the plane-waves basis set was 360 eV which together with the use of dense Monkhorst-Pack grids of k-points for integrations in reciprocal space [13] ($6\times4\times2$ for orpiment and $4\times2\times2$ for anorpiment), ensured a convergence in the energy differences between phases of around 1 meV. The van der Waals (vdW) corrections to the total energy were taken into account within the DFT using Grimme's so-called D2 method [14].

All the results that we present in this short communication correspond to zero temperature, with zero-point energy neglected, and hydrostatic pressure conditions (that is, diagonal and isotropical stress tensor). For each phase, a full structural optimization at fixed volumes (of both internal parameters and cell shape) was performed through the calculation of the forces on atoms and the components of the stress tensor. The structural relaxation was deemed complete when the forces on atoms were less than 0.005 eV $\text{Å}^{-1}$ and the anisotropy in the diagonal components of the stress tensor was less than 0.1 GPa. The calculated total energy $E$ as a function of volume $V$ for the fully relaxed configurations were fitted using a Birch-Murnaghan equation of state (EoS) [15] from which the pressure $p$, enthalpy $H = E + pV$, and properties at zero pressure (equilibrium volume $V_0$, bulk modulus $B_0$ etc) were obtained [16].

For the calculation of phonons at the zone center we used the small-displacements method as implemented in the PHON code [17] followed by the symmetry analysis of the eigenvectors for each mode in order to identify its possible Raman or infrared activity. These calculations were done at a range of volumes (and respective pressures) allowing the study of the pressure evolution of the frequencies of the different modes.

## 3. Results and discussion

Both structural evolution and the change in energetics, lattice vibrations, and electronic structure have been studied under compression, of which we will give here a very brief account.

The orpiment structure is monoclinic with space group (SG) P2$_1$/c, No. 14, with $Z$=4 and As and S atoms at 2e positions whereas, the recently discovered anorpiment structure is triclinic, SG P-1, No. 2, $Z$=4 and As and S atoms at 2i positions. The orpiment and anorpiment structures are plotted in projection in Figures 1 and 2, respectively, and Figures 3 and 4 show the calculated evolution of the first few neighbours distances under compression.

Figure 5 shows the calculated energy-volume ($E$-$V$) curves of the orpiment and anorpiment phases of $As_2S_3$ obtained using different XC functionals with and without van der Waals corrections, which shows the effects of the different approximations. Thus, for example, for the orpiment phase the zero-pressure equilibrium volumes $V_0$ (per cell) obtained using the PBE functional are 477.8 $\text{Å}^3$ and 584.8 $\text{Å}^3$, with and without van der Waals corrections, respectively, whereas using the PBEsol functional the values obtained are 418.6 $\text{Å}^3$ (with vdW) and 445.1 $\text{Å}^3$ (without vdW), cf. the experimental value of 467.7(4) $\text{Å}^3$ [3]. For the anorpiment phase the results for the equilibrium volume are 502.0 $\text{Å}^3$ (PBE with vdW), 582.3 $\text{Å}^3$ (PBE without vdW), 454.5 $\text{Å}^3$ (PBEsol with vdW), and 485.2 $\text{Å}^3$ (PBEsol without vdW) - cf. the experimental value of 488.4 $\text{Å}^3$. [3]. In general, including vdW corrections decreases the equilibrium volume and results in $E$-$V$ curves with a better defined minimum, in comparison to those $E$-$V$ curves obtained without vdW, that is, the vdW corrections enhance the stability of the zero-pressure
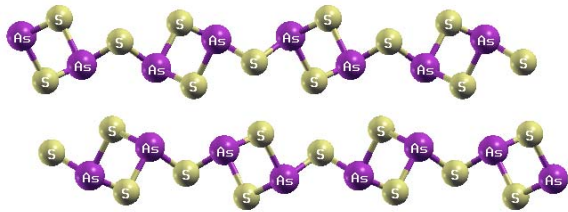
**Figure 1.** Plot of the orpiment structure, showing the positions of As and S atoms in projection, perpendicularly to the layers.
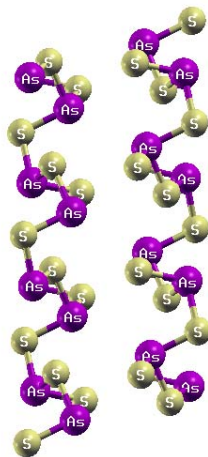


**Figure 2.** Plot of the anorpiment structure, showing the positions of As and S atoms in projection, perpendicularly to the layers.

state. On the other hand, the PBEsol XC functional and the PBE XC functional with vdW corrections provide the results that are closer to the experimental values of $V_0$, and for this last functional the calculated bulk moduli at zero pressure are 14 GPa and 19 GPa for the orpiment and anorpiment phases, respectively.

Finally, in this brief account of our theoretical results we show in Figures 6-8 the evolution of the calculated frequencies of the phonon modes at $\Gamma$ under pressure for the two phases. The mechanical representation of the orpiment structure yields the following multiplicities for the symmetry of the modes at the zone center: $15A_g + 15B_g + 15A_u + 15B_u$, of which the $A_g$ and $B_g$ modes are active in Raman and the $A_u$ and $B_u$ modes are infrared-active (two $B_u$ and one $A_u$ acoustic modes excepted). For the triclinic anorpiment phase, the symmetry analysis results in $30A_g + 30A_u$ modes, of which the $A_g$ modes are Raman active and the 27 non-acoustic $A_u$ modes are infrared active. The results of our assignment will be useful for the experimental
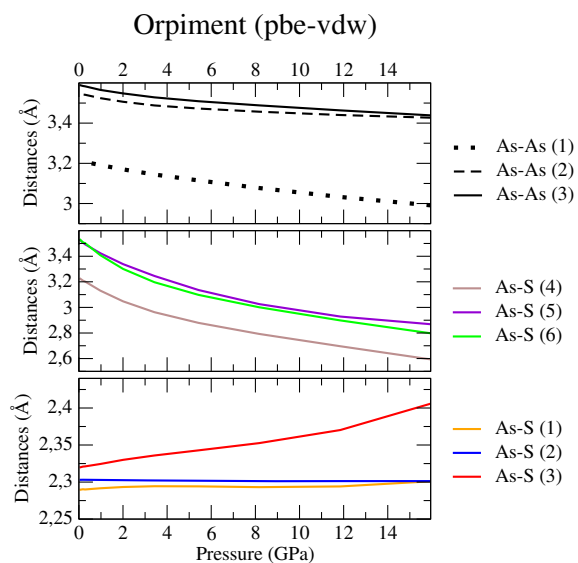
**Figure 3.** Calculated evolution of the inter-atomic distances between near neighbours of the orpiment phase obtained using the PBE funtional and van der Waals corrections. The species for each neighbour is specified in the labels to each curve.
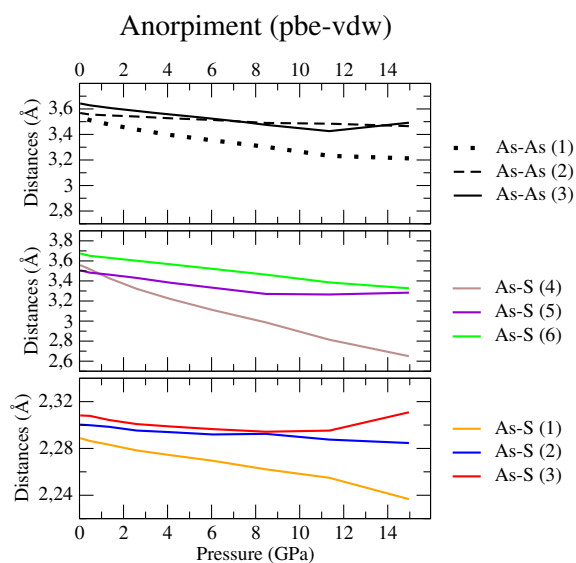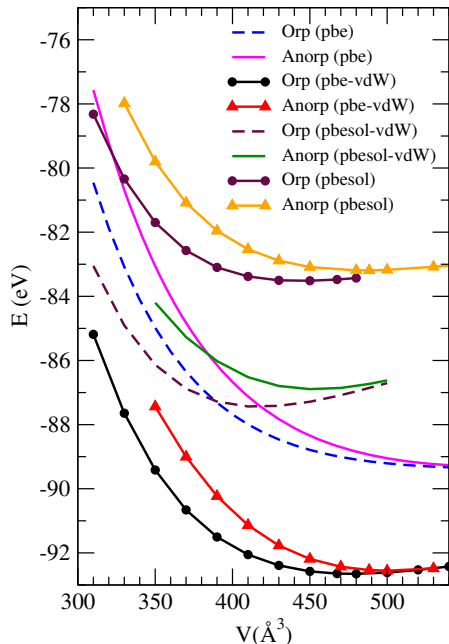


**Figure 4.** Calculated evolution of the inter-atomic distances between near neighbours of the anorpiment phase obtained using the PBE funtional and van der Waals corrections. The species for each neighbour is specified in the labels to each curve.



**Figure 5.** Calculated energy-volume ($E$-$V$) curves for the orpiment (Orp) and anorpiment (Anorp) phases of $As_2S_3$ obtained using the PBE and PBEsol XC functionals, with and without van der Waals (vdW) corrections. Both $E$ and $V$ are given per cell.

study of the modes, as this information is not easy to obtain experimentally.

## 4. Summary

The pressure behaviour of the orpiment and anorpiment layered structures of $As_2S_3$ has been investigated by means of *ab initio* calculations performed within the density functional theory.
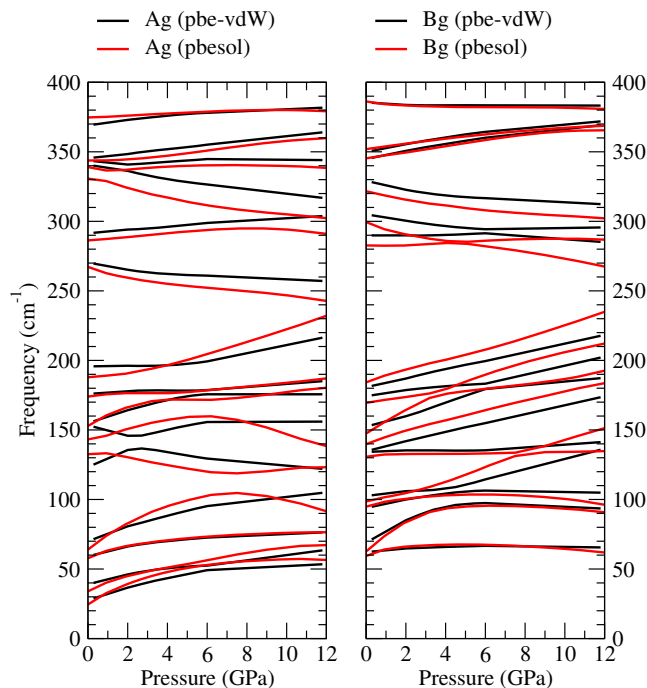
**Figure 6.** Calculated pressure evolution of the phonon frequencies of the Raman-active modes of the orpiment phase (Ag and Bg modes), obtained using the PBE XC functional with vdW corrections (pbe-vdW) and the PBEsol XC functional (pbesol).
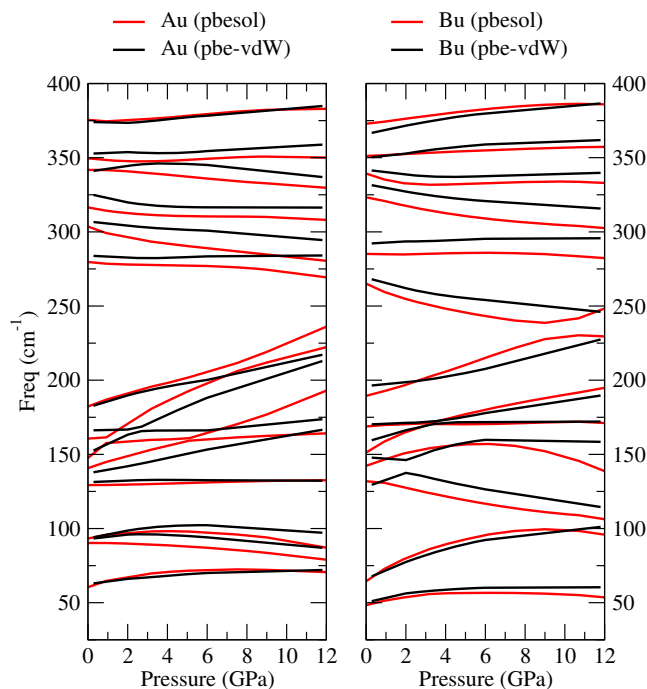


**Figure 7.** Calculated pressure evolution of the phonon frequencies of the infrared-active modes of the orpiment phase (Au and Bu modes), obtained using the PBE XC functional with vdW corrections (pbe-vdW) and the PBEsol XC functional (pbesol).

The phonon frequencies at the zone center were calculated using the finite displacements method, and the symmetry of the modes were assigned, which will help in future Raman and infrared experimental studies of these phases under compression. The effect of van der Waals interactions was especifically investigated and found to be important for the structural response of these layered structures, enhancing their stability. These results are part of an ongoing comprehensive effort to shed further light on the properties of $As_2S_3$, with a particular emphasis on their pressure evolution.
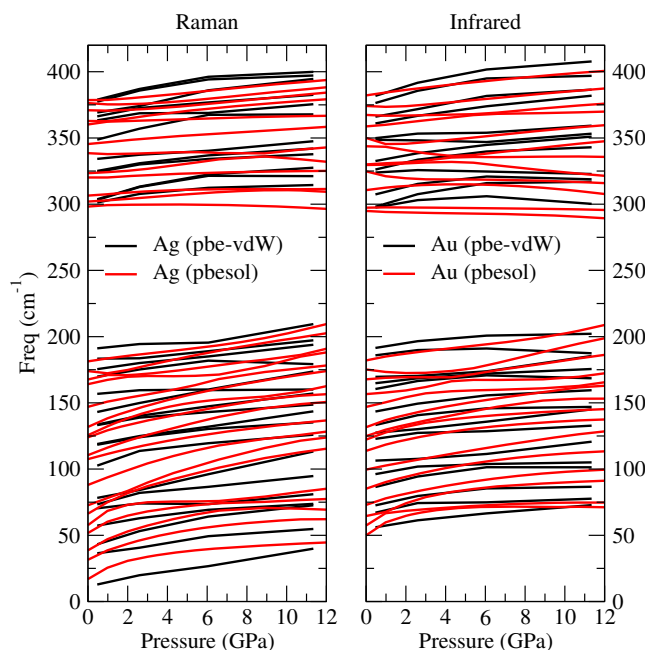
**Figure 8.** Calculated pressure evolution of the phonon frequencies of the Raman-active (Ag) and infrared-active (Au) modes of the anorpiment phase, obtained using the PBE XC functional with vdW corrections (pbe-vdW) and the PBEsol XC functional (pbesol).

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