

**Experiment title:****Pressure evolution of arsenic(III) oxide polymorphs crystal structures****Experiment****number:**

CH 4272

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Report:

Our study of claudetite II single crystal, monoclinic polymorph of As_2O_3 , carried out from ambient pressure to 21 GPa has led to the discovery of three new arsenic(III) oxide polymorphs. The ambient α -claudetite II undergoes a second order phase transition to an α' form which has a doubled unit cell volume and two times less inversion centres than the initial structure. The α' form crystallizes in the isomorphic $P2_1/a$ subgroup of the initial $P2_1/n$ space group. Subsequently, another second order phase transition occurs and a new α'' form appears with even less inversion centres and three times larger unit cell than the α' form. Finally, a new non-centrosymmetric β -claudetite II polymorph is formed around 12 GPa. The final $P2_1$ space group is a *translationengleiche* subgroup of the initial $P2_1/n$ space group. The loss of all inversion centres allows for a better packing of $(\text{As}_2\text{O}_3)_n$ layers in the crystal structure. Substantial hysteresis has been observed upon decompression, consisting in β form being changed directly into α' (see Fig. 1). Last but not least, the transition pressure of 12 GPa corresponds very well to the value of 15 GPa which we have predicted computationally before. The unit cell volume of the β form has been predicted very well (Fig. 1), even though the computed crystal structure was incorrect. Manuscript for publication in *Angewandte Chemie* is in preparation.

The high pressure structural study of arsenolite single crystal, cubic molecular arsenic(III) oxide polymorph, effected from ambient pressure to 30 GPa showed arsenolite does not undergo any detectable phase transitions in this pressure range when (pseudo)hydrostatic conditions are kept. The deformation of adamantoid As_4O_6 molecules was unexpected. The intramolecular $\text{As}\cdots\text{As}$ separations rose upon pressure increase, while oxygen ligands were

pushed toward inside of the molecule. This results in the As_4O_6 cage becoming more tetrahedral in shape. Interestingly, starting from 3.28(9) GPa we have observed the appearance of additional weak “ghost” reflections in the diffraction pattern on the lower 2θ -angle side of the main reflections of the As_4O_6 sample. The “ghost” reflections can be indexed according to the face-centered cubic lattice with the lattice parameter about 2% longer than that of the main As_4O_6 crystal. This ratio is somewhat smaller for the series of measurements with the compressed sample than for the decompression run (Fig. 2). After eliminating possibilities of instrumental artefacts, of spurious radiation or multiple diffraction, the origin of the “ghost” reflections has been associated with the formation of an inclusion compound of arsenolite with helium. Despite being very weak and located close to arsenolite main reflections, the “ghost” reflections provided unexpectedly rich structural information about the arsenolite–helium clathrate and we were able to refine its crystal structure and determine its composition to be $\text{As}_4\text{O}_6 \cdot 2\text{He}$ (Fig. 3). The observation the helium clathrate formation for the arsenolite, which is conventionally considered to be non-porous, is very important as it indicates that helium may penetrate even closely packed molecular compounds in high pressure. This should be taken into account when interpreting similar characteristic features in the diffraction pattern when helium is utilized as pressure transmitting medium. The results have been submitted for publication to Journal of the American Chemical Society and are currently under review.

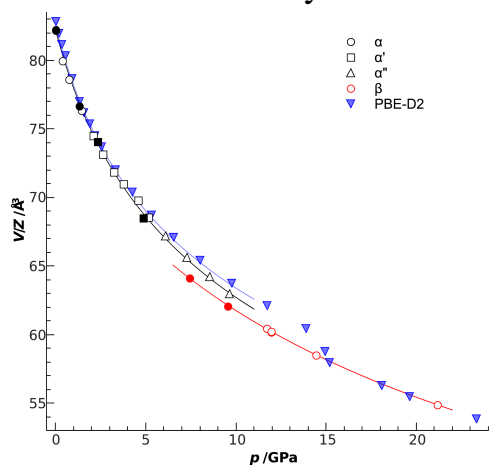


Fig. 1 Experimental and theoretical predictions of claudetite II molecular volume changes as a function of pressure. Empty and filled symbols correspond to compression and decompression, respectively. Solid lines are curves of fitted 3rd order Birch-Murnaghan equation of state.

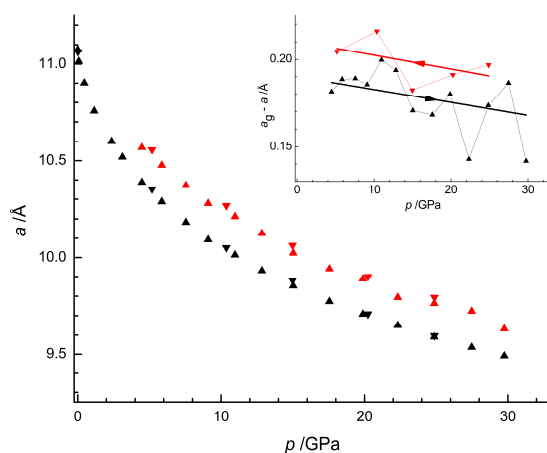


Fig. 2 Lattice parameter a of arsenolite (black symbols) and a_g of the lattice formed by the “ghost” reflections (red symbols). Triangles up stand for compression, triangles down – decompression. In the inset difference between the a and a_g lattice parameters is plotted against pressure. Black and red triangles correspond to the compressed and decompressed sample, respectively.

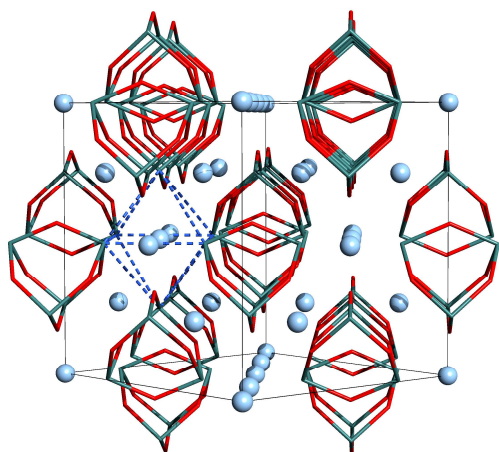


Fig. 3 Crystal structure of $\text{As}_4\text{O}_6 \cdot 2\text{He}$ clathrate viewed along $\sim[110]$. As_4O_6 molecules are represented in wireframe model, whereas He atoms as light-blue balls. Dashed blue lines indicate deformed octahedral surrounding of He by arsenic atoms.