High-pressure and low-temperature structural study of claudetite I, a monoclinic layered $\text{As}_2\text{O}_3$ polymorph†

Piotr A. Günka, a b Michael Hanfland, b Yu-Sheng Chen c and Janusz Zachara a

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High-pressure structural studies of arsenic(III) oxide polymorphs are completed by presenting crystal structures of claudetite I determined using synchrotron powder X-ray diffraction up to $\sim$30 GPa. The crystal structure of claudetite I is also redetermined based on synchrotron single-crystal X-ray diffraction measurements at room and low temperatures. Claudetite I undergoes no phase transitions under high pressure nor at low temperature. It is the densest and least compressible ambient-pressure $\text{As}_2\text{O}_3$ polymorph with the following third-order Vinet equation of state parameters: $V_0 = 312.1(13)$ Å$^3$, $B_0 = 21.0(11)$ GPa, and $B'_0 = 6.72(17)$. Fitting of a simple Berman thermal equation of state to the low-temperature single-crystal data yields $V_0 = 307.4(4)$ Å$^3$ and $a_0 = 9.1(7) \times 10^{-5}$ K$^{-1}$ with a reference temperature of 298 K. The coordination sphere of arsenic atoms is thoroughly characterized by the valence entropy coordination number and the description of their lone electron pair stereoactivity using bond-valence vectors. Surprisingly, it is found that although claudetite I is the densest ambient-pressure arsenic(III) oxide polymorph, it does not exhibit the highest arsenic coordination numbers. The pressure dependence of secondary $\text{As} \cdots \text{O}$ bond lengths follows the same trends for all crystalline $\text{As}_2\text{O}_3$ polymorphs confirming the same nature of the interactions in all forms. It is also found that pressure does not affect the stereoactivity of arsenic lone electron pairs.

Introduction

Arsenic(III) oxide has been known to humanity since antiquity. Initially used as a poison, it has found numerous applications in medicine, where it is used in the treatment of acute promyelocytic leukemia, and in industry, where it is used as an additive to various glasses and for the production of elemental arsenic, wood preservatives and pesticides. The basic building block of all arsenic(III) compounds is the $\text{AsO}_3$ $\psi$-tetrahedron containing three $\text{O}^-$ ligands and a stereoactive lone electron pair (LEP) acting as a pseudoligand. The $\psi$-tetrahedra have to share all oxide ligands to yield $\text{As}_2\text{O}_3$ stoichiometry which gives rise to rich polymorphism of arsenic(III) oxide. It occurs in nature in the form of two minerals – cubic arsenolite built of $\text{As}_8\text{O}_{26}$ molecules and layered monoclinic claudetite I. In the 1940s, the third polymorph was discovered and called $\alpha$-claudetite II due to its resemblance to claudetite I (see Fig. S1 and Table S1† for comparison of the crystal structures of ambient-pressure $\text{As}_2\text{O}_3$ polymorphs). A few years ago, three more layered polymorphs of arsenic(III) oxide were discovered when claudetite II was subjected to high pressure (HP). It transformed at 2 GPa and 6 GPa into $\alpha'$- and $\alpha''$-claudetite II, respectively, gradually losing the symmetry of inversion centers until it formed polar $\beta$-claudetite II at 11 GPa.2 It was also found that arsenolite does not undergo phase transitions under (quasi)hydrostatic conditions up to 40 GPa,5,4 but undergoes amorphization at around 15 GPa when the non-hydrostaticity of pressure transmitting media is significant.5,6 Claudetite I is formed from highly corrugated $\text{As}_2\text{O}_3$ layers and crystallizes in the $\text{P2}_1/\text{n}$ space group with the following unit cell parameters at ambient pressure and temperature: $a = 5.25(1)$ Å; $b = 12.99(3)$ Å; $c = 4.53(1)$ Å; $\alpha = 93.9(3)$ Å; $\beta = 308.2(12)$ Å$^3$ (see Fig. 1).7 There are two independent arsenic atoms in the structure whose coordination modes may be described as 3 + 1 and 3 + 2. Soignard et al. carried out HP Raman measurements of claudetite I crystals up to 40 GPa and observed no signs of amorphization up to this pressure.8 The appearance of new peaks and changes in relative intensities for peaks below 400 cm$^{-1}$ were noted between 7 and 13 GPa and, according to a recent review, these could indicate a phase transition.8,9 Herein, we finalize the HP structural characterization of arsenic(III) oxide crystalline...
Experimental and methodology

HP synchrotron powder X-ray diffraction

HP powder diffraction experiments were carried out at the ID09A beamline of the European Synchrotron Radiation Facility. Claudetite I powder was obtained by slow decomposition of ammonium arsenite (NH₄AsO₃) crystals dissolved in water carried out at around 10 °C. Claudetite I pellets were loaded together with ruby chips and helium as the pressure transmitting medium into a membrane diamond anvil cell. Diamonds with culets of 500 μm and a stainless-steel gasket with a hole of 250 μm in diameter were used. Diffraction data were collected with X-ray radiation of 0.41328 Å. Details of scans are provided in the ESI.

The pressure was determined from the shift in the ruby wavelength and were recorded on a Mar555 flat panel detector. The background was fitted with Chebyshev polynomials typically with 15 coefficients. First Pawley refinements were carried out to obtain the unit cell parameters and instrument parameters. Then profile refinements (usually referred to as Rietveld refinements) were performed to obtain the positions of arsenic and oxygen atoms in the asymmetric unit. Only one isotropic displacement parameter was refined for all atoms. Due to the weak scattering power of oxygen, the As–O bond lengths were restrained to 1.77 Å with an estimated standard deviation of 0.01 Å. The pressure and thermal equation of states were fitted using the EosFit7 program. CCDC 2031863–2031890 records contain the supplementary crystallographic data for the HP crystal structures. These data can be obtained free of charge from the joint CCDC’s and FIZ Karlsruhe’s service to view and retrieve structures via https://www.ccdc.cam.ac.uk/structures/.

LT synchrotron single-crystal X-ray diffraction

Single-crystal X-ray diffraction experiments were carried out at the ID-15B ChemMatCARS beamline of the Advanced Photon Source synchrotron in Argonne National Laboratory. Diffraction data were collected using an Apex detector and X-ray radiation with a wavelength of 0.41328 Å. Details of scans are provided in the ESI.

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Bond valence vectors (BVVs) and VECN calculations

The bond valences of As–O bonds were calculated according to the exponential correlation

\[ s_i = \exp((R_0 - r_i)) \]

where \( R_0 \) is the bond length of a bond with unit valence, \( r_i \) is the bond length and \( B \) is the bond softness, using parameters derived by Gagné and Hawthorne. The dependence of \( s_i \) on pressure was taken into account using the approach proposed by Brown and co-workers. The BVV is defined according to the following relationship:

\[ |\mathbf{v}_i| = s_i(1 - s_i/Q_{cc}) \]

where \( Q_{cc} \) is the electric charge of the coordination center’s atomic core. If a coordination center is electronically strained e.g. due to the presence of a stereoactive LEP, the sum of BVVs around a coordination center can be brought back to zero by treating the LEP as a pseudoligand bonded to the coordination centre with \( s_{\text{LEP}} \leq 2 \) and the equality holds when the LEP is fully stereoactive. When calculating BVVs, arsenic was treated as being in the +5 oxidation state since the LEP was treated as a pseudoligand.

The valence entropy coordination number of order \( n \) (VECN), defined by Guika and Zachara, was calculated according to the following formula:

\[ \ln^{n}\text{VECN} = -\sum_{i=1}^{N} \left( \frac{s_{i}^n}{N_i} \right) \ln \left( \frac{s_{i}^n}{N_i} \right) \]
where $S_n = \sum_{i=1}^{N} s_i^n$, $n$ is the VECN order and $N$ is the number of ligands taken into calculations. LibreOffice functions provided by Guńka and Zachara were used for the computations of the $^1$VECN.\textsuperscript{10}

**DFT computations**

Density functional theory (DFT) computations were carried out with VASP ver. 5.4.4.\textsuperscript{38} Projector augmented plane waves were used with an energy cut-off of 1200 eV.\textsuperscript{27,28} The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional based on general gradient approximation was applied together with Grimme’s D3 correction for dispersion interactions and the Becke–Johnson damping function which, according to our experience, works best for arsenic(III) oxide.\textsuperscript{29–31} SCF computations and geometry optimizations were considered converged when the energy difference between consecutive steps was smaller than 0.1 μeV and when forces acting on atoms were smaller than 1 meV Å\textsuperscript{-1}. The calculations were performed in three steps with external pressure applied by using the PSTRESS keyword. The first and second steps involved optimizations of both unit cell parameters and atomic positions with Fermi smearing of partial orbital occupancies, whereas the third step involved only optimization of atomic positions, and the tetrahedron method with Blöchl corrections was applied for smearing of partial occupancies.\textsuperscript{32} The length parameter controlling the automatic generation of the $\Gamma$-centered Monkhorst–Pack $k$-point grid was set to 40 in the KPOINTS file.\textsuperscript{33} No convergence study was carried out and we used the strictest parameters from previous convergence tests that we found to work well for arsenolite and its inclusion compound with helium.\textsuperscript{4}

**Results**

Pawley and profile fittings of claudetite I HP powder X-ray diffraction patterns reveal that it undergoes monotonic compression up to 30 GPa (see Fig. 2 for the $V(p)$ curve and Fig. S2† for exemplary diffraction patterns and profile fits) with no signs of phase transitions. The volume decrease of 32.9% at 29.91(5) GPa with respect to $V_0$ determined by the equation of state fit (EoS, see below) results mainly from a 13.7% compression along the crystallographic $a$ direction and to a smaller extent from compressions of 11.0% and 11.1% along the $b$ and $c$ crystallographic directions, respectively (see Fig. 3 and S3† for variation of the $\beta$ angle with pressure). These relative shrinkages correspond well to the values of linear moduli of claudetite I along the crystallographic $a$, $b$ and $c$ directions obtained with linearized third-order Vinet EoS. These linear moduli amount to 35(3), 69(2) and 108(4) GPa, respectively. LT single-crystal X-ray diffraction measurements indicate that claudetite I does not undergo any phase transitions down to 10 K either (see Fig. 2). Fitting of a simple Berman thermal EoS of the form $V_0T = V_{00}(1 + \alpha_0(T - T_{ref}))$ to the LT single crystal data yields $V_{00} = 307.4(4) \text{ Å}^3$ and $\alpha_0 = 9.1(7) \times 10^{-5} \text{ K}^{-1}$ with a reference temperature of 298 K.\textsuperscript{34}

The herein described room-temperature (294 K) structural model of claudetite I determined from single-crystal diffraction is significantly better than the model refined by Pertlik in 1978 although the general picture of the structure...
analogous parameters of other As₂O₃ polymorphs. The data yields parameters which are listed in Table 1 together with experiments as well as from DFT computations.

The third-order Vinet EoS fitted to the herein presented HP data yields parameters which are listed in Table 1 together with analogous parameters of other As₂O₃ polymorphs. The comparison of all arsenic(III) oxide polymorphs’ densities reveals that claudetite I is the densest of all of them with the exception of β-claudetite II which is a high-pressure polymorph formed above 11 GPa (see Fig. S4†). As expected based on our results of DFT computations for arsenolite, the PBE-D3(BJ) model reproduces the experimental V(p) curve of claudetite I even better than the previously applied PBE-D2 model (see Fig. S5†). Interestingly, the value of unit cell parameter a predicted by DFT is overestimated while b and c parameters are underestimated by computations. This indicates that in the DFT modelled crystal structure, As₂O₃ layers are less corrugated than in reality (see Fig. 1). It is noteworthy that herein DFT calculations were carried out with initially set external pressure does not change. In particular, the precision and accuracy of As–O bond lengths are much better and they lie in the range of 1.754(3)–1.790(3) Å compared to 1.72(1)–1.81(1) Å reported by Pertlik. The same is true for bond angles spanning a range of 91.20(14)° to 102.26(14)° in our model compared to 89.7(6)°–103.3(6)° in Pertlik’s model. Tables S1–S3† contain numerical values of unit cell parameters from the HP and LT experiments as well as from DFT computations.

Table 1 Third-order Vinet EoS parameters for As₂O₃ polymorphs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>V₀/Z’/Å³</th>
<th>B₀/GPa</th>
<th>K’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Claudetite I</td>
<td>78.0(3)</td>
<td>21.0(11)</td>
<td>6.72(17)</td>
</tr>
<tr>
<td>α-Claudetite II</td>
<td>82.21(2)</td>
<td>15.4(3)</td>
<td>6.7(2)</td>
</tr>
<tr>
<td>β-Claudetite II</td>
<td>76.3</td>
<td>30(10)</td>
<td>5(1)</td>
</tr>
<tr>
<td>Arsenolite</td>
<td>84.90(4)</td>
<td>10.78(14)</td>
<td>8.14(6)</td>
</tr>
</tbody>
</table>

† One set of parameters fitted to α, α’ and α” polymorphs. V(p) data for fitting taken from ref. 2. †† EoS parameters taken from ref. 4. 

Fig. 3 Experimental (large symbols) and DFT (small symbols) unit cell parameters of claudetite I plotted as a function of pressure. Open and filled symbols for experimental data correspond to the pressure increase and decrease, respectively.

Fig. 4 presents the comparison of experimentally determined primary As–O bond lengths as well as valence angles were utilized to calculate the bond valences (BVs) of all these bonds and then the bond valence sums (BVSs), resultative bond valence vectors (BVVs) and first-order valence entropic coordination numbers (1VECNs) for both symmetry independent As atoms from the claudetite I asymmetric unit (see the Experimental and methodology section for the definitions of the quantities and details of these calculations). The results are plotted together with the same quantities for other As₂O₃ polymorphs in Fig. 5. The BVs for claudetite I are practically constant in the whole studied pressure range although they are scattered. The magnitude of As resultative BVs which represents the stereoactivity of the As LEP is fairly constant around 1.03 v. u. and is slightly smaller than the values observed for arsenolite. The BVV lengths are noisier for claudetite I than (using the PSTRESS tag in the INCAR file) before constant volume optimizations had been run. Nonetheless, tests carried out for arsenolite and for claudetite I (using the DFT-D2 model) both revealed that the results are independent of the way external pressure is administered in the input files.

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phase transitions as Manjón and co-workers suggested.\textsuperscript{8,9} The third-order Vinet EoS parameters of As\textsubscript{2}O\textsubscript{3} polymorphs show that claudetite I is the densest and least compressible ambient-pressure arsenic(III) oxide polymorph. The analysis of EoS parameters reveals that the compressibility of claudetite I is comparable to that of the high-pressure β-claudetite II form and that the less dense a polymorph is, the more compressible it is. The same trend can be observed for silica polymorphs.\textsuperscript{37} It is noteworthy that, unlike for α-\textsuperscript{″}, α-′, α-′′- and β-claudetite II, all unit cell parameters of claudetite I decrease with increasing pressure. This indicates that not only interlayer distances shrink with increasing pressure but also As\textsubscript{2}O\textsubscript{3} layers become more corrugated and denser as the pressure increases. The secondary As⋯O interactions fall on the same line for all As\textsubscript{2}O\textsubscript{3} polymorphs (see Fig. 4) which demonstrates that the nature of As⋯O interactions is the same in all compounds. The stereoactivity of the LEP for arsenolite and claudetite I, which are stable As\textsubscript{2}O\textsubscript{3} polymorphs, does not change with pressure. Similarly, it is constant for α-′, α-′′ and α-′′′-claudetite II and decreases abruptly upon the first-order phase transition to β-claudetite II. This shows that pressure exerts additional strain on the arsenic coordination sphere, which is independent of the electronic strain coming from LEP stereoactivity. The fairly constant value of the LEP BVV of 1.03 v. u. for claudetite I and 1.05 v. u. for arsenolite corresponds to the LEP valence of 1.45 and 1.50 v. u., respectively, indicating that the LEPs are not fully stereoactive. If the LEPs were fully stereoactive, their valence would be 2 and the corresponding BVV magnitude would be 1.2 v. u. The stereoactivity of arsenic LEPs is lower than that of nitrogen and phosphorus LEPs observed in nitrogen(III) and phosphorus(III) organic compounds, respectively, where a resultant BVV average length of 1.15 v. u. corresponding to an average LEP valence of 1.78 was found.\textsuperscript{26} This is in agreement with the prevalent trend observed in the periodic table of elements that LEPs of elements lying in higher periods are less stereoactive than those of lighter congeners.

Surprisingly, the \textsuperscript{1}VECNs of As atoms in claudetite I are the lowest among all arsenic(III) oxide polymorphs even though it is the densest ambient-pressure polymorph. This is the case because of the different numbers of primary and secondary As–O bonds that one may observe in the polymorphs. In arsenolite, there is one symmetry independent As atom which forms 3 primary and 3 secondary bonds and its coordination number may be described as 3 + 3. For claudetite I and α-′, α-′′ and α-′′′-claudetite II, there are more symmetry independent As atoms whose coordination numbers may be denoted as 3 + 1 and 3 + 2 while for β-claudetite II there is even one As atom that does not form any secondary bonds (see Table 2 for details). These results indicate that higher density of a polymorph does not necessarily imply higher coordination numbers of the constituting atoms and, vice versa, higher coordination numbers of atoms do not have to imply higher density of a material.

\textbf{Discussion}

Smooth compression of claudetite I unit cell parameters and volume agrees with the results of Soignard \textit{et al.} and confirms their conclusion that the observed changes in Raman spectra between 7 and 13 GPa are changes in Raman activity of vibrations rather than indications of possible

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig5}
\caption{(a) Bond valence sum, (b) magnitude of the resultant bond valence vector of As atoms and (c) first-order valence entropic coordination number of As atoms for various As\textsubscript{2}O\textsubscript{3} polymorphs plotted as a function of pressure. Data for α-, α-′, α-′′- and β-claudetite II as well as arsenolite come from ref. 10. The grey dotted line indicates the pressure of the first-order phase transition from α-′′- to β-claudetite II.\textsuperscript{2}}
\end{figure}
Table 2  Coordination numbers of As atoms in various As₂O₃ polymorphs

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Number of independent As atoms</th>
<th>Coordination number ratios of As</th>
<th>3 + 0</th>
<th>3 + 1</th>
<th>3 + 2</th>
<th>3 + 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenolite</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Claudetite I</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>α'-Claudetite II</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
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<tr>
<td>α''-Claudetite II</td>
<td>4</td>
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<td>3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>β-Claudetite II</td>
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<td>1</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

The herein presented HP powder X-ray diffraction study performed on claudetite I confirms earlier supposition from HP Raman measurements that claudetite I does not undergo any phase transitions up to at least 30 GPa. The comparison of the structural data of claudetite I with those of other As₂O₃ polymorphs revealed that no direct and simple relationship between the coordination number of arsenic atoms, herein expressed as 1VECN, in a polymorph and the density of that crystalline form exists. In particular, the coordination numbers of arsenic atoms in claudetite I are not the highest among all As₂O₃ polymorphs at a particular pressure even though it is the densest polymorph at that pressure. The pressure dependence of the arsenic resultant bond-valence vector indicates that the stereoactivity of arsenic lone electron pairs is not affected by pressure.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references