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$Mo_2P_4O_{15}$ – the most complex oxide structure solved by single crystal methods?

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We report the crystal structure and phase transitions of $Mo_2P_4O_{15}$ which, despite a simple chemical formula, has 441 crystallographically unique atoms in its asymmetric unit and thus has the most complex structure of any extended oxide reported to date.

We have an on-going interest in the chemistry, structural and physical properties of framework oxide materials – that is materials whose structure can be described as a network of corner-sharing metal-centred polyhedra. Such materials display a wealth of fascinating and potentially exploitable properties. Corner sharing of SiO_4 and AlO_4 tetrahedra in zeolites creates materials with a range of important catalytic and sorption applications. Corner sharing of WO_6 octahedra in WO_3 gives a material with a series of complex phase transitions as a function of temperature and which undergoes intercalation chemistry and associated photochromic behaviour. Materials in the ZrW_2O_8, ZrP_2O_7, $Sc_2(WO_4)_3$ and nasicon families contain both octahedra and tetrahedra which share corners and have been shown to display the unusual property of negative thermal expansion;[1,2] structurally related phases are of interest as battery cathode materials. In this communication we report the results of recent studies on $Mo_2P_4O_{15}$, which contains corner-sharing MoO_6 and PO_4 tetrahedra, which show it is the structurally most complex inorganic oxide studied to date. The role of geometric frustration giving rise to such structural complexity in an apparently simple material is an under appreciated facet of the chemistry of framework materials.

The structure of $Mo_2P_4O_{15}$ was described by Costentin and co-workers in 1991.[3] They reported that the material crystallises in space group $P2_1/c$ with $a = 8.3065$, $b = 6.5154$, $c = 10.7102$ Å, $\beta = 106.695°$ giving a cell volume of 555.20 $Å^3$ with 2 formula units in the cell. The basic structure can be described as a network of corner sharing MoO_6 octahedra and PO_4 tetrahedra. Each octahedron shares 5 of its 6 corners with a PO_4 group, the sixth corner being a short unshared Mo=O group. The four PO_4 groups in the formula unit themselves share corners to form P_4O_{13} units, with the resulting 10 free vertices coordinating to the Mo of Mo=O groups to complete the MoO_6 octahedra. However the low R-factor reported (3.6%) was achieved by invoking a disordered site for one of the P–O–P bridging oxygens and with unusual anisotropic displacement parameters (adps) for other atoms. Difficulties in trying to Rietveld fit powder diffraction data of $Mo_2P_4O_{15}$ encouraged us to reinvestigate the published crystal structure.

A pure sample of $Mo_2P_4O_{15}$ was prepared following the method of Lezama[4] by heating a 3 : 1 molar ratio of $(NH_4)_2HPO_4$ and MoO_3 in a Pt crucible to 873 K followed by washing to remove excess P. Examination of a single crystal revealed that whilst the strongest reflections could be indexed using the cell reported by Costentin, a large number of superstructure reflections were also present requiring a cell (at room temperature) of $a = 24.133(2)$, $b = 19.579(2)$, $c = 25.109(2)$ Å, $\beta = 99.962(3)°$ with a cell volume of 11685(1) $Å^3$ – some 21 times larger in volume than that reported by Costentin. We note that earlier work on this material had suggested a possible superstructure along *b*, but that no such effect was observed by Costentin.[5] The existence of the large supercell observed implies that the structure of the material is considerably more complex than had been realised and must contain 42 formula units in the cell.

The true structure of $Mo_2P_4O_{15}$ was solved using data recorded at 120 K.† Careful examination of the data set revealed the supercell could be related to the subcell by the transformation matrix (3 0 1; 0 3 0, −1 0 2). Given the space group symmetry of *Pn* this implies that $Mo_2P_4O_{15}$ contains 441 crystallographically unique atoms in its asymmetric unit. To solve a structure of this complexity we adopted methodologies we have developed for solving complex superstructures from powder diffraction data.[6] Approximate coordinates for the substructure were refined using reflections predicted by the subcell of Costentin from which "ideal" coordinates of the superstructure were calculated. We note that our subcell R-factor (9.5%) was considerably higher than that reported by Costentin. Restraints were then created to describe the 84 PO_4 groups as essentially rigid tetrahedra and the 42 MoO_6 groups as octahedra allowed to distort to have a combination of long, short and medium bonds. The structure was solved by a simulated annealing process using the Topas suite of software.[7] In this process all atomic coordinates and a single overall temperature factor were allowed to refine to convergence from their ideal starting values using a limited data range ($<25°$ 2θ). On convergence atomic coordinates were reset to values randomly displaced from "ideal" positions by up to 0.1 Å and the structure re-refined. The best solution after several rounds of refinement/perturbation gave good agreement to the diffraction data. Subsequent free refinement of this model against the whole data set gave an R-factor of 3.49% using isotropic temperature factors for all atoms.‡ The quality of the structural refinement can be judged from the low R-factor, the narrow spread of temperature factors obtained [minimum, maximum and average values for the 3 atom types were: 42 × Mo 0.0051–0.0062, average $= 0.0056$ $Å^2$; 84 × P 0.0049–0.0068, average $= 0.0058$ $Å^2$; 315 × O 0.0069–0.0170, average $= 0.0097$ $Å^2$] and bond valence sums for the 42 MoO_6 octahedra and 84 PO_4 tetrahedra which deviated by <0.15 units from expected values.

The structure of $Mo_2P_4O_{15}$ is shown in Fig. 1. The relationship between the substructure and superstructure is probably shown most succinctly in Fig. 2. This figure shows the adps that result from the use of the incorrect substructure with our data, and the actual atomic coordinates of individual atomic sites in the superstructure transformed into a single unit cell for comparison. The relationship between the adps (which are unusually large for a material at 120 K and have unusual orientations) and the true static displacement of atoms is clear.

It is instructive to compare the complexity of $Mo_2P_4O_{15}$ to other inorganic materials. If one takes the number of atoms in the asymmetric unit as a measure of complexity for a commensurate structure, inspection of the ICSD[8] shows that $Mo_2P_4O_{15}$ has the fifth largest inorganic (using accepted database definitions) structure reported to date. The four larger structures include complex molecular species (such as $Na_{15}[Mo_{144}O_{409}(OH)_{28}(H_2O)_{56}]$-$(H_2O)_{250}$) from the group of Müller[9–11] and the complex ternary phase $Ba_{45}Cu_{28}Al_{17}F_{197}$.[12] In each case the structural complexity is perhaps unsurprising given the chemical composition of the

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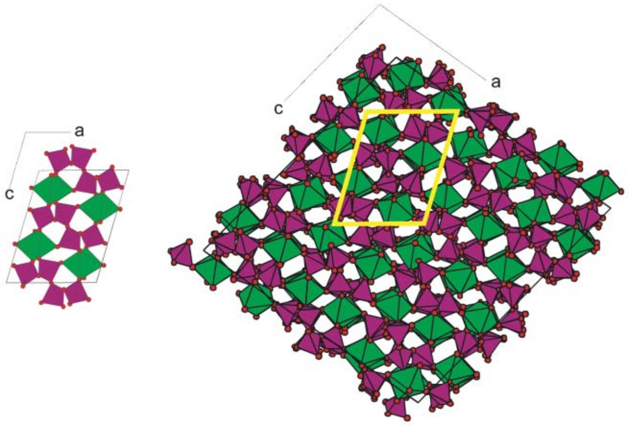

Fig. 1 A polyhedral representation of the true structure of $Mo_2P_4O_{15}$ and its relationship to the subcell proposed by Costentin. MoO_6 octahedra (green) share five of their six corners with P_4O_{13} units made of corner-sharing PO_4 tetrahedra (pink). The *b* axis of the true structure (perpendicular to the page) is three times that of the substructure.

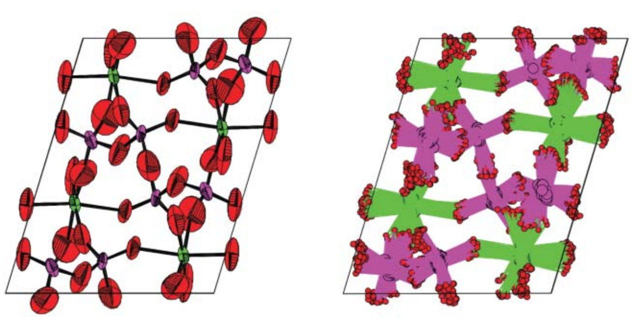

Fig. 2 The relationship between the anisotropic displacement parameters (drawn at 70% level) obtained assuming the simple subcell structure of $Mo_2P_4O_{15}$ and the true statically ordered atomic positions of the supercell. Coordinates of the full superstructure have been transformed into a single subcell to allow comparison.

materials. Aside from the title material the most complex crystallographically ordered extended oxide structure determined reliably from single crystal methods in the ICSD appears to be $Ru(PO_3)_3$ with 105 atoms in the asymmetric unit.[13]

In the case of $Mo_2P_4O_{15}$, the origin of the complex superstructure can be related to the competition between local bonding requirements of the constituent polyhedra and the 3D connectivity requirements of the overall framework. MoO_6 octahedra have a preference for 1 short, 4 medium and 1 long bond whereas phosphate groups of P_2O_7 units would ideally have 3 P–O bonds of ~1.50 Å, a P–O–P bridging bond length of ~1.58 Å and a bridging bond angle of ~145°. In the simple subcell these preferences cannot be achieved and, most notably, one P–O–P bond angle is required to be 180° by symmetry. By adopting this complex superstructure all groups in the material can obtain favourable coordination geometries (fuller details will be given elsewhere). Presumably at the high temperature at which the material forms the relatively soft P–O–P bending potential leads to dynamic disorder of these groups. On cooling strain effects drive the formation of an ordered superstructure and it is the inherent frustration between short range bonding requirements and 3D connectivity that leads to the remarkable structural complexity of the material.

Variable temperature powder diffraction studies on $Mo_2P_4O_{15}$ reveal that it undergoes a reversible first order displacive phase transition at around 523 K with a ΔV of $\sim +1\%$. Such symmetry raising phase transitions on heating are commonly observed for framework materials with complex superstructures and correspond to an unbuckling of constituent polyhedra on heating. More details of the phase transition and high temperature structure of $Mo_2P_4O_{15}$ will be given elsewhere.

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Notes and references

† A green prismatic crystal of approximate dimensions 0.08 × 0.08 × 0.2 mm^3 was mounted on a hair and cooled to 120 K. Diffraction data were collected using a Bruker AXS Smart 6000 diffractometer. A total of 4140 frames were collected and integrated using the SAINT[14] software package to give 451577 reflections and unit cell parameters of $a = 24.1134(6)$, $b = 19.5324(5)$ $c = 25.0854(6)$ Å, $\beta = 100.015(1)°$. Correction for absorption using SADABS[15] and merging ($R_{INT} = 1.8\%$) resulted in 48060 reflections of which 43783 had $I > 3\sigma(I)$). Systematic extinctions were consistent with space group *Pn*. Satisfactory refinement could not be achieved in $P2_1/n$ (R ~ 15%). CCDC 242574. See http://www.rsc.org/suppdata/cc/b4/b408413f/ for crystallographic data in .cif or other electronic format.

‡ For final cycles of refinement fractional coordinates and an isotropic temperature factor were refined for each atom along with an overall extinction parameter (1766 parameters in total) in the Crystals software suite.[16] A 3 term weighting scheme was applied resulting in final R-factors of R = 3.49% and wR = 5.99% for 43783 reflections with $I > 3\sigma(I)$). Use of anisotropic temperature factors gave only a small improvement in R-factor (R = 3.2%) for the introduction of 2205 extra parameters. Full coordinates have been deposited as supplementary data. Refinement of data collected at room temperature revealed no phase transitions between 120 and 300 K.

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