# research papers

Structures of Na$_{0.74}$WO$_3$

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The structures of the four phases exhibited by Na$_{0.74}$WO$_3$, sodium tungstate, with a change in temperature have been refined from powder diffraction patterns obtained on the high-resolution powder diffractometer (HRPD), ISIS, Rutherford Appleton Laboratory, England. At temperatures above 430 K, the stable phase has the ideal perovskite structure, with space group $Pm\bar{3}m$ (No. 221). Below that temperature, the octahedra are tilted about pseudocubic $\langle 100 \rangle$ directions; the tilts are produced by the condensation of the normal modes of vibration of the octahedra in the high-temperature cubic phase. Using Glazer's notation, the tilt system undergoes the following sequence:

$$a^+a^+a^+ \xrightarrow{293\,\text{K}} a^+a^+a^0 \xrightarrow{343\,\text{K}} a^0a^0a^+ \xrightarrow{430\,\text{K}} a^0a^0a^0.$$
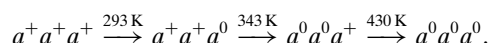
The structural refinements presented here confirm the sequence of the transitions first proposed by Clarke [(1977). *Phys. Rev. Lett.* **39**, 1550–1553]. This is the first time that a structure determination of a perovskite with the tilt system $a^+a^+a^0$ has been reported in the literature. In addition, we evaluate the weights, or importance, of the condensed modes in each low-temperature phase.

1. Introduction

Clarke (1977) reported precise measurements of the temperature dependence of the lattice parameters of single crystals of Na$_{0.81}$WO$_3$, using X-rays and a back-scattering technique. He found four distinct phases with transitions at approximately 293, 343 and 430 K. Above 430 K the structure is that of the ideal perovskite: space group $Pm\bar{3}m$, described as the aristotype (Megaw, 1973). Below this temperature weak superlattice reflections were observed which, if indexed on a unit cell doubled in each pseudocubic direction, were of the type {even, odd, odd}. Clarke interpreted the existence of these superlattice reflections as evidence of the condensation of normal modes associated with octahedral rotations in the cubic phase. The octahedral tilts in the phases with lower symmetry – described as hettotypes (Megaw, 1973) – can be identified with the normal modes of vibrations of the octahedra in the aristotype associated with the M-point of the cubic Brillouin zone.

Clarke found the symmetry of the structures to be

cubic → tetragonal → tetragonal → cubic.

Table 1
Fractional coordinates in the three hettotypes $a^+a^+a^+$, $a^+a^+c^0$ and $a^0a^0c^+$.

Hettotype	Space group	Atom	Wyckoff position; symmetry	Fractional coordinates
$a^+a^+a^+$	$Im\bar{3}$			$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ +
		A1	2(a); m3	$(0, 0, 0)$
		A2	6(b); mmm	$(0, \frac{1}{2}, \frac{1}{2})\ (\frac{1}{2}, 0, \frac{1}{2})\ (\frac{1}{2}, \frac{1}{2}, 0)$
		B	8(c); $\bar{3}$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\ (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})\ (\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$
		OI/II/III	24(g); m	$\pm(0, \frac{1}{4}+y, \frac{1}{4}-z)\ \pm(0, \frac{1}{4}+y, \frac{3}{4}+z)$ $\pm(\frac{1}{4}-z, 0, \frac{1}{4}+y)\ \pm(\frac{1}{4}-z, 0, \frac{3}{4}-y)$ $\pm(\frac{1}{4}+y, \frac{1}{4}-z, 0)\ \pm(\frac{1}{4}+y, \frac{3}{4}+z, 0)$
$a^+a^+c^0$	$I4/mmm$			$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ +
		A1	2(a); 4/mmm	$(0, 0, 0)$
		A2	2(b); 4/mmm	$(0, 0, \frac{1}{2})$
		A3	4(c); mmm	$(0, \frac{1}{2}, 0)\ (\frac{1}{2}, 0, 0)$
		B	8(f); 2/m	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\ (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})\ (\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$
		OI	8(h); mm	$\pm(\frac{1}{4}-x, \frac{1}{4}-x, 0)\ \pm(\frac{1}{4}-x, \frac{3}{4}+x, 0)$
		OII/III	16(n); m	$\pm(0, \frac{1}{4}+y, \frac{1}{4}+z)\ \pm(0, \frac{1}{4}+y, \frac{3}{4}-z)$ $\pm(\frac{1}{4}+y, 0, \frac{1}{4}+z)\ \pm(\frac{1}{4}+y, 0, \frac{3}{4}-z)$
$a^0a^0c^+$	$P4/mbm$	A	2(c); mmm	$(0, \frac{1}{2}, \frac{1}{2})\ (\frac{1}{2}, 0, \frac{1}{2})$
		B	2(a); 4/m	$(0, 0, 0)\ (\frac{1}{2}, \frac{1}{2}, 0)$
		OI	2(b); 4/m	$(0, 0, \frac{1}{2})\ (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
		OII/III	4(g); mm	$\pm(\frac{1}{4}+x, \frac{3}{4}+x, 0)\ \pm(\frac{3}{4}+x, \frac{3}{4}-x, 0)$

Clarke, following Glazer (1972) and using his notation, pointed out that the only hettotype with cubic symmetry and tilted octahedra is $a^+a^+a^+$. He proposed that the transitions in $Na_{0.81}WO_3$ followed the sequence

$$a^+a^+a^+ \rightarrow a^+a^+c^0 \rightarrow a^0a^0c^+ \rightarrow a^0a^0a^0.$$
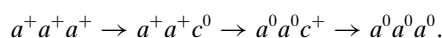
The symmetries of $a^+a^+c^0$ and $a^0a^0c^+$ are tetragonal (Glazer, 1972). Clarke argued that as the temperature is raised the tilt system tends to simplify and that at sufficiently high temperatures the structure is often that of the aristotype. However, no structural determinations were attempted. Clarke also showed that compositions of Na_xWO_3 in the range $0.6 < x < 0.9$ exhibited the same sequence of phase transitions, with a small increase in transition temperatures with increasing x.

We report here the structural determinations of $Na_{0.74}WO_3$ in each hettotype. The structures of the hettotypes were determined by Rietveld (1969) refinements. Our findings are in complete agreement with the structures proposed by Clarke. This is the first time a structural determination of the hettotype $a^+a^+c^0$ has been reported (Lufaso & Woodward, 2001). We also discuss the possible ordering of the Na cation that could occur in the hettotypes $a^+a^+a^+$ and $a^+a^+c^0$. In addition, in each phase we evaluate the magnitude of the octahedral tilt and the weights of the condensed modes (Cochran & Zia, 1968).

The transitions $a^+a^+a^+ \rightarrow a^+a^+c^0$ and $a^+a^+c^0 \rightarrow a^0a^0c^+$ are necessarily discontinuous, while the transition $a^0a^0c^+ \rightarrow a^0a^0a^0$ could be continuous. Clarke's results appear to indicate that the latter transition is continuous. We have measured the lattice parameters at 5 K intervals (and at 2 K intervals where relevant) over the whole temperature range

and find that all three transitions are discontinuous; the results will be reported elsewhere.

2. Experimental

2.1. Sample preparation

The sample was prepared using the method of Wiseman & Dickens (1976). Appropriate quantities of anhydrous Na_2WO_4, WO_3 and W were ground together and placed in a gold-lined vitreous silica tube. After evacuation, the tube was sealed and heated for 6 d at 1123 K and then cooled slowly to room temperature. X-ray powder diffraction with a Siemens D5000 system equipped with a primary-beam germanium mono-chromator and *PSD* detector indicated that the sample was essentially phase pure, with a lattice constant of 3.8451 (3) Å at room temperature. This equates to a sodium content of 0.74, based on the work of Brown & Banks (1954), and matches the value previously reported for $Na_{0.73}WO_3$ (Wiseman & Dickens, 1976).

2.2. Collection of diffraction patterns and their initial analysis

The high-resolution powder diffractometer HRPD on the neutron spallation source at the Rutherford Appleton Laboratory was used to collect the diffraction patterns. Back-scattering and 90° geometries were employed with the sample at the 1 m position. Approximately 2 cm³ of powder was loaded into a rectangular aluminium can with vanadium front and back windows, which was then placed into an 'orange' cryostat. The temperature was controlled to ±0.2 K. Counts were accumulated for 70 μA h at each temperature.

Diffraction patterns were collected in the time-of-flight mode using logarithmic time-channel binning of $\Delta t/t = 1 \times 10^{-4}$ from 30 to 130 ms, which corresponds to a d-spacing of 0.62–2.7 Å for the back-scattering detectors and 0.87–3.77 Å for the 90° detectors. The resolution of the instrument, full-width at half-maximum intensity, was $\Delta d/d = 4 \times 10^{-4}$ over the whole diffraction pattern.

The raw counts from the detector banks were focused to a common scattering angle (163.329° for the back-scattering bank and 89.58° for the 90° detectors), normalized to an upstream monitor and corrected for detector efficiency using a vanadium standard. These were then re-binned with $\Delta t/t = 3 \times 10^{-4}$ from 32 to 120 ms for the back-scattering bank, and $\Delta t/t = 7 \times 10^{-4}$ from 35 to 114 ms for the 90° detectors, which gave a resolution sufficient for the analysis.

Initial analysis of the diffraction patterns was carried out using a fitting procedure that is independent of the crystal

Table 2
Lattice parameters, occupancy, fractional coordinates, thermal parameters and R factors for each phase at a single temperature within each phase.

Hettotype	Atom	Occupancy	$x \times 10^2$	$y \times 10^2$	$z \times 10^2$	$U_{\mathrm{iso}} \times 10^2$	$U^{11} \times 10^2$	$U^{22} \times 10^2$	$U^{33} \times 10^2$	$U^{23} \times 10^2$	$U^{31} \times 10^2$	$U^{12} \times 10^2$
$a^+a^+a^+$	Na1	0.96 (7)				1.1 (9)						
$Im\bar{3}$ (204)	Na2	0.67 (3)				1.8 (5)						
243 K	W	1				0.65 (3)						
$a = b = c =$	OI/II/III	1		1.54 (4)	1.29 (4)		0.73 (5)	1.3 (3)	1.0 (3)	−0.1 (1)		
7.69327 (2) Å												
$wR_p = 0.0588$												
$R_p = 0.0525$												
$\chi^2 = 2.779$												
(38 variables)												
$a^+a^+c^0$	Na1	0.82 (5)				1.7 (7)						
$I4/mmm$ (139)	Na2	0.70 (6)				1.6 (9)						
303 K	Na3	0.72 (5)				2.1 (7)						
$a = b = 7.70190$ (3),	W	1				0.77 (3)						
$c = 7.69267$ (6) Å												
$wR_p = 0.0599$	OI	1	1.52 (3)	1.52 (3)			1.4 (1)	1.4 (1)	0.7 (1)			0.0 (2)
$R_p = 0.0485$	OII/III	1	0.03 (9)	1.45 (3)			0.9 (1)	1.3 (1)	1.5 (1)	0.2 (2)		
$\chi^2 = 2.448$												
(43 variables)												
$a^0a^0c^+$	Na	0.74 (2)				2.27 (6)						
$P4/mbm$ (127)	W	1				0.85 (3)						
363 K	OI	1					1.50 (9)	1.50 (9)	0.65 (9)			
$a = b = 5.44556$ (2),	OII/III	1	1.61 (1)				1.26 (6)	1.26 (6)	1.68 (9)			0.39 (7)
$c = 3.85598$ (3) Å												
$wR_p = 0.0540$												
$R_p = 0.0481$												
$\chi^2 = 2.240$												
(37 variables)												
Aristotype	Na	0.74 (2)				2.77 (6)						
$Pm\bar{3}m$	W	1				0.84 (3)						
493 K	OI/II/III	1					0.89 (5)	1.94 (3)	1.94 (3)			
$a = b = c =$												
3.85772 (1) Å												
$wR_p = 0.0513$												
$R_p = 0.0462$												
$\chi^2 = 2.360$												
(32 variables)												

structure (Pawley, 1981) for each temperature, using the modified time-of-flight Rietveld program *TF*12*LS* (David *et al.*, 1992).

3. Refinements

The high-temperature cubic phase (the arisotype) is taken to have the following fractional coordinates:

A $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$
B $(0\ 0\ 0)$
OI $(0\ 0\ \frac{1}{2})$
OII $(0\ \frac{1}{2}\ 0)$
OIII $(\frac{1}{2}\ 0\ 0)$

The atoms are labelled following the convention adopted by Cowley (1964). We use the same convention so that condensed modes can be readily identified with the irreducible representations and wavevectors of the normal modes of the aristotype which are listed in the Appendix of Cowley's paper (Cowley describes the structure with A at the origin, but this difference is irrelevant).

The relationship between the lattice vectors of each hettotype, **a**, **b** and **c**, and the pseudocubic subcell vectors extrapolated to the relevant temperature, $\mathbf{a}_c$, $\mathbf{b}_c$ and $\mathbf{c}_c$ are as follows follows

$$a^+a^+a^+ \quad \mathbf{a} = 2\mathbf{a}_c \quad \mathbf{b} = 2\mathbf{b}_c \quad \mathbf{c} = 2\mathbf{c}_c$$
$$a^+a^+c^0 \quad \mathbf{a} = 2\mathbf{a}_c \quad \mathbf{b} = 2\mathbf{b}_c \quad \mathbf{c} = 2\mathbf{c}_c$$
$$a^0a^0c^+ \quad \mathbf{a} = \mathbf{a}_c - \mathbf{b}_c \quad \mathbf{b} = \mathbf{a}_c + \mathbf{b}_c \quad \mathbf{c} = \mathbf{c}_c.$$

In the entries for each hettotype listed in Table 1, the fractional coordinates are expressed so that if (x, y, z) are set equal to zero, the O atoms are positioned on the sites they would occupy in the aristotype.

A full Rietveld analysis of each diffraction pattern was implemented using the *GSAS* suite of programs (Larson & von Dreele, 1986).[1]

In the aristotype and in hettotype $a^0a^0c^+$ there is a single A site and hence in these phases the sodium atoms must be disordered with an average site occupancy of 0.74. However, in hettotypes $a^+a^+a^+$ and $a^+a^+c^0$, there are distinguishable A sites with multiplicities of [2, 6] and [2, 2, 4], respectively, thus allowing the possibility of ordering of both sodium ions and vacancies. In the Rietveld refinement of these two hettotypes,

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: WS0005). Services for accessing these data are described at the back of the journal.

Table 3
Condensed modes of the aristotype.

Normal mode	Displacements	Glazer's notation	Symbol	Character
$(0, \frac{1}{2}, \frac{1}{2})$, M_3	OI(y) = −OII(z)	$a^+b^0c^0$	M_1	Octahedral tilt
$(\frac{1}{2}, 0, \frac{1}{2})$, M_3	OI(x) = −OIII(z)	$a^0b^+c^0$	M_2	Octahedral tilt
$(\frac{1}{2}, \frac{1}{2}, 0)$, M_3	OII(x) = −OIII(y)	$a^0b^0c^+$	M_3	Octahedral tilt
$(0, \frac{1}{2}, \frac{1}{2})$, M_1	OI(y) = OII(z)		H_1	Octahedral distortion
$(\frac{1}{2}, 0, \frac{1}{2})$, M_1	OI(x) = OIII(z)		H_2	Octahedral distortion
$(\frac{1}{2}, \frac{1}{2}, 0)$, M_1	OII(x) = OIII(y)		H_3	Octahedral distortion

Table 4
Weights of the condensed modes and tilt angles in the three hettotypes.

Hettotype	Condensed modes	W (u Å^2)	Tilt about $\langle 100 \rangle_{pc}$ (°)	Total tilt (°)
$a^+a^+a^+$	$M_1 = M_2 = M_3$	1.14	3.24	5.61
243 K	$H_1 = H_2 = H_3$	0.009		
$a^+a^+c^0$	$M_1 = M_2$	0.89	3.40	4.81
303 K	$H_1 = H_2$	0.0006		
	H_3	0.0001		
$a^0a^0c^+$	M_3	0.49	3.69	3.69
363 K				

strict constraints were set up between the possible A-site occupancies such that the overall sodium stoichiometry was maintained. The refinements of the sodium occupancies in hettotypes $a^+a^+a^+$ and $a^+a^+c^0$ showed no evidence of significant ordering; the occupancies of atoms Na1 and Na2 differ by less than 3 s.u. These values are shown in Table 2. The magnitudes of the fractional coordinates (x, y, z), as defined in Table 1, temperature factors, lattice parameters and R factors are listed in Table 2.

4. Analysis

The condensed modes in each phase involve *plus* tilts and the small octahedral distortions associated with these tilts. These are listed in Table 3: the first column describes the condensed modes in the notation used by Cowley (1964); the second gives the displacements of the O atoms in these modes from the positions they would have occupied in the aristotype; the third uses Glazer's notation where appropriate; the fourth gives a convenient short-hand symbol to describe the condensed mode, as used in Table 4; and the fifth column depicts the character of the mode.

Following Cochran & Zia (1968), the strength, W, of each condensed mode can be evaluated in terms of the displacements of the atoms from their high-symmetry positions. The expression for W is

$$W = [v/v']\Sigma_{\lambda k} m_k u^2(\lambda k, \mathbf{q}R),$$

where m_k is the mass of the atom k; $u(\lambda k, \mathbf{q}R)$ is the displacement of atom k in subcell λ by the mode $[\mathbf{q}R]$ acting on its

own; v' is the volume of the unit cell of the hettotype and v the volume the aristotype would have at the temperature under consideration. The number of condensed modes is equal to the number of independent fractional coordinates in each hettotype.

The weights of the condensed modes in each phase are listed in Table 4. The angles of tilt of the octahedra about pseudocubic $\langle 100 \rangle$ directions, and the total tilt angles, are also listed. The only modes with weights significantly different from zero involve octahedral tilts. The weights of the modes involving octahedral distortion are insignificant; they may not have condensed out at the transition. Therefore, the overall symmetry of some of the subsets of displacements in a hettotype may be higher than that required by the space group of the hettotype. The same observation concerning atomic displacements in hettotypes of other perovskites has been made earlier (Darlington, 2002).

The lack of distortion of an octahedron does not indicate that it is regular; it may be deformed. For example, in $a^0a^0a^+$ there could be an elongation or flattening of the octahedron in the direction of the fourfold axis of symmetry. Evaluation of the deformation of the octahedron requires accurate determination of the lattice parameters, which would then enable the macrostrain to be calculated. We intend to publish our results concerning such calculations elsewhere.

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