

(ii) The calculated structure factors are in better agreement with experiments than other theoretical calculations as shown by the very small R factors obtained (using no, or only one, fitting parameter) varying between 0.07 and 0.14%, compared with a smallest value of 0.35% in other calculations. The experimental results of Saka & Kato (1986) are seen to be better than the older ones of Aldred & Hart (1973).

(iii) The temperature factor B fitting our calculations to the measurements of Saka & Kato (1986) and with Cummings & Hart (1988) is 0.464 \AA^2 , in excellent agreement with earlier reported values.

The agreement with experiment deteriorates with smaller cluster size, a phenomenon which possibly can only be overcome by using much larger clusters to reduce observed charge density waves inside the cluster.

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References

- ALDRED, P. J. E. & HART, M. (1973). *Proc. R. Soc. London Ser. A*, **332**, 223–238, 239–254.
- ALKIRE, R. W., YELON, W. B. & SCHNEIDER, J. R. (1982). *Phys. Rev. B*, **26**, 3097–3104.
- BAERENDS, E. J., ELLIS, D. E. & ROS, P. (1973). *Chem. Phys.* **2**, 41.
- BAERENDS, E. J. & ROS, P. (1973). *Chem. Phys.* **2**, 52.
- CLEMENTI, E. (1965). *IBM J. Res. Dev.* **9**, Suppl. Tables of Atomic Functions, 2–19.
- CUMMINGS, S. & HART, M. (1988). *Aust. J. Phys.* **41**, 423–431.
- DAWSON, B. & WILLIS, B. T. M. (1967). *Proc. R. Soc. London Ser. A*, **298**, 307–315.
- ELLIS, D. E. & PAINTER, G. S. (1970). *Phys. Rev. B*, **2**, 2887–2898.
- FEHLMANN, M. & FUJIMOTO, I. (1975). *J. Phys. Soc. Jpn*, **38**, 208–215.
- HIRSHFELD, F. L. (1977). *Theor. Chim. Acta*, **44**, 129–138.
- HOHENBERG, P. & KOHN, W. (1964). *Phys. Rev.* **136**, B864.
- KOHN, W. & SHAM, L. J. (1965). *Phys. Rev.* **140**, A1133–A1138.
- PAINTER, G. S. & ELLIS, D. E. (1970). *Phys. Rev. B*, **1**, 4747–4752.
- PRICE, P. F., MASLEN, E. N. & MAIR, S. L. (1978). *Acta Cryst.* **A34**, 183–193.
- SAKA, T. & KATO, N. (1986). *Acta Cryst.* **A42**, 469–478.
- SCHERINGER, C. (1980). *Acta Cryst.* **A36**, 205–210.
- SPACKMAN, M. A. (1986). *Acta Cryst.* **A42**, 271–281.
- STUKEL, D. J. & EUWEMA, R. N. (1970). *Phys. Rev. B*, **1**, 1635–1643.
- TEWORTE, R. & BONSE, U. (1984). *Phys. Rev. B*, **29**, 2102–2108.
- TISCHLER, J. Z. & BATTERMAN, B. W. (1984). *Phys. Rev. B*, **30**, 7060–7066.
- WANG, C. S. & KLEIN, B. M. (1981). *Phys. Rev. B*, **24**, 3393–3416.
- YANG, Y. W. & COPPENS, P. (1974). *Solid State Commun.* **15**, 1555–1559.
- YIN, M. T. & COHEN, M. L. (1982). *Phys. Rev. B*, **26**, 5668–5687.

Acta Cryst. (1989). **B45**, 364–370

Coupling of Ferroelasticity to Ferroelectricity in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ and the Structure at 295 K

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Abstract

$\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, $M_r = 905.485$, monoclinic $P2$ but refined in $I2$, $a = 7.3597$ (7), $b = 10.6342$ (15), $c = 7.3618$ (10) \AA , $\beta = 90.77$ (2)°, $V = 576.1$ (2) \AA^3 , $Z = 2$, $D_m = 5.1$ (1) (by flotation), $D_x = 5.219$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ \AA , $\mu = 308.3$ cm^{-1} , $F(000) = 788$, $T = 295$ K, $R = 0.042$ for 1939 symmetry-independent reflections with $F_m^2 > 3\sigma(F_m^2)$. Refinement in $P2$ was not feasible owing to the small number of weak reflections that violated the body-centered condition. Relationships among the atomic coordinates show that

the a and c axes are ferroelastically interchangeable, with the c -axis direction inverted, as the sense of the polar b axis is reversed ferroelectrically. The spontaneous polarization (P_s) is hence structurally coupled directly to the spontaneous strain (e_s). The largest total atomic displacement as P_s is reversed and e_s is reoriented is about 0.73 \AA , by an O,F anion. The largest polar displacement by a W atom within its octahedron of anions that results in zero polarization is about 0.19 \AA , corresponding to a predicted transition temperature of 710 K as compared with a measured temperature of 800 (10) K. Each of the three independent W atoms occupies a distorted octahedron, with average W–O,F distance of 1.90 (5) \AA . The O^{2-} and F^- anions are randomly distributed among the eight

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independent O,F sites. All three sets of octahedra form corner-sharing chains along the *a* and *c* axes. The thermal displacements by the W atoms are fitted by anharmonic tensor coefficients to fourth order. The atomic arrangement of monoclinic $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ at 295 K is only slightly distorted from that of tetragonal $\text{Na}_5\text{Al}_3\text{F}_{14}$ at room temperature. The latter has a transition to monoclinic symmetry at 150 K. It is possible that these two structures represent the low- and high-temperature forms, respectively, for a wide group of isostructural materials.

Introduction

Ferroelasticity in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ was first reported by Doumerc, Elaammani, Ravez, Pouchard & Hagenmuller (1979) who showed by X-ray powder diffraction that the spontaneous strain decreases with increasing temperature, becoming zero at 800 (10) K; above this temperature, the crystal symmetry becomes tetragonal with unit-cell volume comparable to that of $\text{Na}_5\text{Al}_3\text{F}_{14}$ (Brosset, 1938), which may be the prototypic structure. A heat-capacity maximum at 800 (5) K confirms the phase transition. Crystals grown from the melt (1075 K) are invariably twinned, with a characteristic domain pattern that is readily seen optically in thin polished plates of the material (Ravez, Elaammani & Chaminade, 1979). The domains disappear on heating to 800 K and reappear on cooling. $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ crystals are most readily detwinned by the application of a small compressive stress (about 0.1 MN m^{-2}), in a universal detwinning cell (Abrahams, Bernstein, Chaminade & Ravez, 1983; Ravez, Abrahams, Zyontz & Chaminade, 1983), on cooling from above the phase-transition temperature. $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ efficiently generates second harmonics at $1.06 \mu\text{m}$, demonstrating the lack of inversion centers in the structure, and undergoes a major anomaly in the dielectric permittivity at 800 (5) K over a frequency range of at least 10^2 – 10^6 Hz (Ravez, Elaammani & Chaminade, 1979). The pyroelectric coefficient at 300 K increases sharply on detwinning, strongly suggestive of ferroelectric–ferroelastic coupling (Ravez, Elaammani, Hagenmuller & Abrahams, 1981). The structural investigation reported below was based on the use of detwinned $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ crystals.

Experimental

A colorless detwinned crystal of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ (Ravez, Elaammani & Chaminade, 1979; Abrahams *et al.*, 1983) was ground to a sphere with radius 0.0687 (14) mm and mounted with arbitrary orientation on a glass fiber in a CAD-4 diffractometer controlled by a PDP 11/24-8e minicomputer under Enraf–Nonius (1980) software, with graphite monochromator. All reflections with $-11 < h < 11$, $-16 < k < 16$, $-11 < l < 11$ and

$(\sin\theta)/\lambda \leq 0.77 \text{ \AA}^{-1}$ were measured at 295 K. Intensity measurements were made by the $\theta, 2\theta$ step-scan technique with $\Delta 2\theta = 0.80^\circ + 0.35^\circ \tan\theta$. A total of 8659 reflections resulted in $4279 I > 3\sigma(I)$. Nine standard reflections were measured at 6 h intervals: no systematic trends with exposure were detectable. Total exposure time was 396 h. The average internal agreement factor for each standard is 0.023. The absorption coefficient of 30.83 mm^{-1} resulted in maximum, minimum transmission factors of 9.55, 6.32%. Lorentz, polarization and absorption corrections were applied.

The variance in F_m^2 [*i.e.* $\sigma^2(F_m^2)$] was taken as the larger of V_1 or V_2 , where V_1 is the variance due to counting statistics, absorption, attenuation factor and variation in the standard intensity measurements, and V_2 is derived from the difference between magnitudes of the form $F^2(hkl)$ and $F^2(\bar{h}\bar{k}\bar{l})$. The least-squares weights were taken as the reciprocal of the variance in each observation. The value of R_{int} from merging 2139 pairs of equivalent reflections was 0.0229, that for wR_{int} was 0.0151 for $I_m > 3\sigma(I_m)$, giving rise to 1939 usable structure factors that fulfilled the condition $h + k + l = 2n$.* An additional 358 reflections, only some of which were slightly greater than a nominal $3\sigma(I_m)$, violated the body-centered condition and corresponded to space group $P2$. These, together with $F(202)$, were not used in the following analysis. The weak reflections required a doubling in the number of variables and resulted in numerous parameter correlations that gave rise to pervasive instability in all models investigated. It may be noted that the amplitudes of structure factors with odd-valued $h + k + l$ are generally less than about 1% of those with even value. As a consequence of the strong (X-ray) scattering by W, any displacement of the independent and massive W atoms from the twofold axes in $P2$ must be small compared to their r.m.s. amplitudes of thermal displacement in order to make such a minor contribution to the structure factors. The principal displacements from a completely body-centered arrangement are hence associated with the Na and O,F atoms; these however are unlikely to be larger than on the order of 0.1 \AA . It is thus apparent that strong correlations must occur in least-squares refinement between atom positions in the body-centered and in the displaced locations.

Neglecting the information content in the odd-valued $h + k + l$ reflections is equivalent to averaging each body-centered and displaced location for every independent atom. The information thereby lost would certainly make an important contribution to a full

* Lists of structure factors, anisotropic thermal parameters for all atoms and anharmonic displacement coefficients to fourth order for the W atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51785 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

understanding of the physical properties of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$. However, the differences between averaged and independent atomic positions in similar cases reported, such as ferroelectric–ferroelastic barium sodium niobate in which weak reflections result in the doubling of two orthorhombic axes (Labbé, Leligny, Raveau, Schneck & Tolédano, 1989), are often small with mean displacements on the order of 0.01 Å. It was thus considered that the averaged structure would lead to an adequate interpretation of the ferroelectric and ferroelastic properties of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$. Extinction effects in $F(202)$ that appeared stronger than in all remaining reflections led to its exclusion.

The lattice constants at 295 K were measured on the Bond (1960) diffractometer, with $\lambda(\text{Cu } K\alpha_1) = 1.540598 \text{ \AA}$ (Deslattes & Henins, 1973); values determined previously by Ravez, Elaati, Hagenmuller & Abrahams (1981) are in agreement with the present more-accurate measurements. The three independent W atoms were located directly from solution of the Patterson function. Both $I2$ and Im are consistent with observation, excluding the weak reflections noted above, hence each was investigated; only the former, however, gave a satisfactory solution. With the polar y coordinate of W(1) placed at zero to define the origin, the light atoms were readily located in a series of difference Fourier series following least-squares refinement of the remaining two y coordinates [for W(2) and W(3)]; the anisotropic thermal parameters for all three W atoms were also taken as variables. Atomic scattering factors and the f' and f'' anomalous-dispersion corrections for Mo $K\alpha$ radiation were taken from *International Tables for X-ray Crystallography* (1974). No attempt was made initially to distinguish O from F; a distinction could not be made later on the basis of W–O bond lengths, hence the same composite scattering factor was used throughout for both anions.

A model in which the six metal atoms have anisotropic and each anion has isotropic thermal parameters, for a total of 66 variables, refined to give $R = 0.0851$, $wR = 0.0860$ and $S = 5.422$ but with substantial oscillations in parameter shifts between refinement cycles. In the final model all tensor coefficients to fourth order were included for the W atoms, based upon a Gram–Charlier expansion for the probability density function, and anisotropic thermal parameters were assigned to the Na and anion atoms. The thermal parameters for O,F(2) were set equal to those for O,F(1) in order to minimize correlations. An isotropic correction for extinction (Becker & Coppens, 1974) was made, for which the spherulite radius refined to 1.7 (2) μm . The final agreement indicators are $R = 0.0424$, $wR = 0.0415$ and $S = 2.660$, for 139 variables. The introduction as variables of higher than fourth order tensor coefficients for the W atoms did not result in further improvement. All refinements were made with a heavily modified local version of the

ORXFLS4 (Busing, Martin & Levy, 1973) least-squares program. Instabilities persisted on inverting the full matrix corresponding to the final model, with some values of Δ/σ exceeding unity accompanied by sign changes after successive iterations. The final difference Fourier synthesis contained maximum positive and negative electron densities of 3.5 and -2.4 e \AA^{-3} .

The principal sources of instability in the refinement model are the necessary neglect of all weak reflections with $h + k + l = 2n + 1$, thereby resulting in averaged atomic positions, and the likely minor presence of domains within the ground crystal sphere that may have reversed spontaneous polarization and reoriented spontaneous strain. An entirely satisfactory model that takes full account of all reflections observed and domain orientations present would be expected to result in values of R and wR that are close to R_{int} and wR_{int} , with S approaching unity. However, the present model is expected to allow satisfactory analysis of the principal dielectric and elastic properties of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, as presented below.

Coupling of ferroelasticity to ferroelectricity

Examination of Table 1 shows that a fully coupled ferroelastic–ferroelectric relationship holds for the atomic coordinates of W(1) and for those of Na(1) as individual atoms, and also between the coordinates of the following pairs of atoms: W(2), W(3); Na(2), Na(3); O,F(1), O,F(2); O,F(3), O,F(4); O,F(5), O,F(6) and O,F(7), O,F(8). The specific relationship is given by

$$xyz = \bar{z}'\bar{y}'x' + \Delta, \quad (1)$$

where Δ is a displacement vector between the xyz coordinates of the given atom and the $x'y'z'$ coordinates for the same or a related atom as rearranged in the form $\bar{z}'\bar{y}'x'$. Table 2 gives the transformed coordinates, the component displacements along the unit-cell axes and the total atomic displacement Δ required by (1) both to reorient the spontaneous strain and reverse the sense of the spontaneous polarization.

All displacements in Table 2 fall well within the limits presented by Abrahams (1988) for predicting ferroelectricity on the basis of structure, hence $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ meets the structural criteria for this property. Equation (1) is equivalent to the unit-cell transformation $\mathbf{abc} \rightarrow \bar{\mathbf{c}}\bar{\mathbf{b}}\mathbf{a}$, *i.e.* the \mathbf{a} and \mathbf{c} basis vectors exchange as both the \mathbf{c} and the polar \mathbf{b} basis vectors reverse sign under the application of a stress or electric field. The two ferroic properties are hence fully coupled structurally in this material, *i.e.* ferroelastic detwinning necessarily results in ferroelectric poling, and *vice versa*.

$\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ is reported by Doumerc *et al.* (1979) to undergo a transformation to tetragonal symmetry at 800 (10) K, on the basis of powder diffraction measurements, resulting in $a = 7.435$ and $c = 10.825 \text{ \AA}$.

Table 1. Atomic coordinates ($\times 10^4$) and r.m.s. radial amplitudes of thermal vibration (\AA) in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ at 295 K

	x	y	z	u_{eq}
W(1)	0	0	0	0.15 (10)
W(2)	$\frac{1}{2}$	-38 (8)	0	0.14 (12)
W(3)	0	-7 (10)	$\frac{1}{2}$	0.16 (8)
Na(1)	$\frac{1}{2}$	-52 (57)	$\frac{1}{2}$	0.27 (4)
Na(2)	2529 (27)	2380 (22)	2546 (31)	0.22 (2)
Na(3)	2507 (31)	-2526 (35)	7505 (42)	0.23 (5)
O,F(1)	0	1753 (35)	0	0.36 (25)
O,F(2)	0	-1754 (35)	0	0.36 (25)
O,F(3)	2449 (11)	358 (12)	137 (28)	0.24 (17)
O,F(4)	4 (19)	326 (11)	-2500 (17)	0.18 (17)
O,F(5)	1996 (26)	1138 (17)	5316 (22)	0.21 (6)
O,F(6)	5123 (53)	-1276 (24)	-2062 (64)	0.31 (15)
O,F(7)	1791 (25)	-1289 (17)	4679 (23)	0.21 (8)
O,F(8)	-5042 (35)	1274 (19)	-1785 (38)	0.22 (14)

Table 2. Transformed coordinates ($\times 10^4$) in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ at 295 K and displacements (\AA) involved in spontaneous strain reorientation and polarization reversal

$\Delta x = x - z'$, $\Delta y = y - y'$, $\Delta z = z - x'$ and $\Delta = (\Delta^2 x + \Delta^2 y + \Delta^2 z)^{1/2}$, with xyz as given in Table 1 and as $\bar{z}'\bar{y}'x'$ in Table 2.

	\bar{z}'	\bar{y}'	x'	Δx	Δy	Δz	Δ
W(1)	0	0	0	0	0	0	0
W(2)	$\frac{1}{2}$	7	0	0	-0.048	0	0.048
W(3)	0	38	$\frac{1}{2}$	0	-0.048	0	0.048
Na(1)	$\frac{1}{2}$	52	$\frac{1}{2}$	0	-0.111	0	0.111
Na(2)	2495	2526	2507	0.025	-0.155	0.029	0.160
Na(3)*	2546	-2380	7471	-0.029	-0.155	0.025	0.160
O,F(1)	0	1754	0	0	-0.001	0	0.001
O,F(2)	0	-1753	0	0	-0.001	0	0.001
O,F(3)	2500	-326	4	-0.038	0.724	0.098	0.732
O,F(4)	137	-358	-2449	0.098	0.724	-0.038	0.732
O,F(5)	2062	1276	5123	0.049	-0.147	0.142	0.210
O,F(6)*	5316	-1138	-1996	-0.142	-0.147	0.049	0.210
O,F(7)	1785	-1274	5042	-0.004	-0.016	-0.267	0.268
O,F(8)	-4679	1289	-1791	-0.267	-0.016	-0.004	0.268

*The atomic coordinates xyz and $\bar{x}\bar{y}\bar{z}$ are equivalent in space group $I2$.

Although a definitive determination of the space group above 800 K has not been made, the cell dimensions and average structure obtained from Tables 1 and 2 are close to those of the mineral chiolite (see below). It is hence likely that the space group of chiolite, namely $P4/mnc$, represents the prototype for $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$. In this case, following Aizu (1970), the spontaneous strain at 295 K is given by

$$e_s = [(x_{33} - x_{11})^2 + x_{13}^2]^{1/2} \\ = \{[(c-a)/(c+a)] + [(\cos\beta)/2]\}^{1/2} = 67.2 \times 10^{-4},$$

where a , c and β are lattice constants.

The coupling of ferroelasticity to ferroelectricity is not uncommon. Two examples are Mg-Cl-boracite (Torre, Abrahams & Barns, 1972) and $\text{Tb}_2(\text{MoO}_4)_3$ (Svensson, Abrahams & Bernstein, 1979; Abrahams, Svensson & Bernstein, 1980). In the former, each atom

at $x_1y_1z_1$ in space group $Pca2_1$ is related to another atom of the same species at $x_2y_2z_2$ such that $(x_1y_1z_1) = (y_2, \bar{x}_2, \frac{1}{2} - z_2) + \Delta$, with no value of $\Delta > 0.60 \text{\AA}$. Ferroelastic interchange of the \mathbf{a} and \mathbf{b} basis vectors in which the sense of one is reversed must hence occur simultaneously with reversal of the sense of the polar \mathbf{c} axis, *i.e.* the spontaneous-polarization direction is reversed as the spontaneous strain is reoriented, and *vice versa*.

In the case of $\text{Tb}_2(\text{MoO}_4)_3$, the controlling relationship among the atomic coordinates in space group $Pba2$ is $(x_1y_1z_1) = (\frac{1}{2} - y_2, x_2, 1 - z_2) + \Delta$, with no value of $\Delta > 0.68 \text{\AA}$. Here also, ferroelastic interchange of the \mathbf{a} and \mathbf{b} basis vectors resulting in spontaneous strain reorientation as one axis reverses sense is simultaneously accompanied by reversal of the polar \mathbf{c} -axis sense.

Structural prediction of phase-transition temperature and spontaneous-polarization estimation

The maximum displacement by a W atom from its location at room temperature to a position in the paraelectric phase that results in zero net polarization corresponds to the quantity Δy in

$$T_c = (\mathcal{N}/2k)(\Delta y)^2 \text{ K}, \quad (2)$$

where \mathcal{N} is a force constant, k is Boltzmann's constant and $\mathcal{N}/2k \simeq 2.0 \times 10^4 \text{ K \AA}^{-2}$ (Abrahams, Kurtz & Jamieson, 1968). The largest such displacement is only 0.048\AA , for W(2) and W(3), see Table 2. However, this displacement does not result in zero polarization since the average y coordinate of the O,F(3), O,F(6) and O,F(8) octahedron is 0.0119 and the corresponding average transformed y' coordinate for these atoms is -0.0058 , *cf.* Table 2. The full displacement is hence between W(2) in the center of its octahedron at $\langle y \rangle \simeq 0.0119$ and W(3) in the center of its octahedron at $\langle y' \rangle \simeq -0.0058$, *i.e.* $\Delta y \simeq 0.188 \text{\AA}$. The corresponding T_c from (2) is hence about 710 K. Experimentally, $T_c = 800 (10) \text{ K}$ (Doumerc *et al.*, 1979), a temperature that is in excellent agreement with prediction in view of its e.s.d. of about 300 K, a consequence of the positional uncertainty in the O,F atoms.

The identical displacement Δy can also be used to estimate the spontaneous polarization P_s in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ by means of (3), see Abrahams *et al.* (1968),

$$P_s = (258 \pm 9)\Delta y \times 10^{-2} \text{ C m}^{-2}. \quad (3)$$

Taking Δ at about 0.19\AA as above, then $P_s \simeq 49 \times 10^{-2} \text{ C m}^{-2}$, with an e.s.d. of about $13 \times 10^{-2} \text{ C m}^{-2}$. This value of P_s is comparable to that in many complex oxides, such as LiTaO_3 with $P_s = 50 \times 10^{-2} \text{ C m}^{-2}$ and PbTiO_3 with $P_s = 60 \times 10^{-2} \text{ C m}^{-2}$, but is much larger than is generally found in non-oxides. For example, BaCoF_4 has $P_s = 8 \times 10^{-2} \text{ C m}^{-2}$. A compilation of spontaneous polarization values is provided by Landolt-Börnstein (1981, 1982). Experimental

measurement of P_s in a detwinned crystal of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ would be most appropriate, as a test of the prediction.

The suggestion was made by a referee that an alternative mechanism might account for the ferroelectric phase transition. In this approach, disordered W atoms distributed over several neighboring sites would undergo a correlated displacement at T_c to form a single equivalent position. However, as noted above, any disorder among the W atoms must be quite minor, with effective Δy component too small to result in the experimental phase-transition temperature.

Structural discussion

The average W—O,F distance in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, as taken from Table 3, is 1.90 (5) Å. Comparison with the average W—O = 1.944 (18) and W—F = 1.798 (8) Å distances reported in $\text{Pb}_3\text{W}_3\text{O}_9\text{F}_{10}$ (Abrahams, Marsh & Ravez, 1987) and with the survey of W—O,F distances presented therein (overall average W—O = 1.967 and W—F = 1.769 Å) indicates that the O^{2-} and F^- ions are most likely randomly distributed among the eight unique anion sites since the expected average W—O,F distance in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ is 1.892 Å. Consideration of the O,F(1) and O,F(2) twofold atomic sites in particular (all other anions occupy sites of fourfold multiplicity) offers strong support for the random distribution inference. Satisfaction of the chemical formula requires that one of these two sites be occupied only by O atoms, the other only by F atoms, if these atoms are ordered. The same requirement holds in space group $P2$. However, the W(1)—O,F(1) and W(1)—O,F(2) distances are not significantly different (see Table 3), hence the composition of the two sites cannot be differentiated. A stereoview of the content of one unit cell of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ illustrating the atomic arrangement with respect to the polar axis is presented in Fig. 1.

The resemblance between this structure and that found in the mineral chiolite, $\text{Na}_5\text{Al}_3\text{F}_{14}$, is notable. The structure of $\text{Na}_5\text{Al}_3\text{F}_{14}$ was initially determined by Brosset (1938) and later confirmed and refined by Jacoboni, Leble & Rousseau (1981). Chiolite crystallizes in space group $P4/mnc$ with unit-cell dimensions $a = 7.0138$ (8) and $c = 10.402$ (2) Å at room temperature. A representation of the structure close to the plane at $z = 0$ is given in Fig. 2(a). Chains of Al(1) and Al(2) octahedra, sharing corner F atoms, run along the a_1 and a_2 axes. The Al(1)F₆ octahedron has a major axis coincident with the tetragonal c axis, but not the Al(2)F₆ octahedron. The two independent Na⁺ ions are located at $00\frac{1}{2}$ and, approximately, at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; layers of octahedra are hence separated by cations. Failure to generate second harmonics confirms the centrosymmetric choice of space group at room temperature (Jacoboni *et al.*, 1981).

Table 3. *Interatomic distances (Å) in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ at 295 K*

W(1)—O,F(1)	1.86 (4)	W(3)—O,F(4)	1.87 (1) × 2
—O,F(2)	1.87 (4)	—O,F(5)	1.92 (2) × 2
—O,F(3)	1.84 (1) × 2	—O,F(7)	1.91 (2) × 2
—O,F(4)	1.87 (1) × 2		
W(2)—O,F(3)	1.93 (1) × 2	Na(1)—O,F(5)	2.56 (4) × 2
—O,F(6)	2.01 (4) × 2	—O,F(6)	2.52 (5) × 2
—O,F(8)	1.92 (3) × 2	—O,F(7)	2.71 (3) × 2
		—O,F(8)	2.76 (4) × 2
Na(2)—O,F(1)	2.71 (2)	Na(3)—O,F(1)	2.73 (3)
—O,F(2)	2.71 (2)	—O,F(2)	2.75 (3)
—O,F(3)	2.79 (3)	—O,F(3)	2.98 (4)
—O,F(4)	2.87 (2)	—O,F(4)	2.93 (3)
—O,F(5)	2.47 (3)	—O,F(5)	2.17 (4)
—O,F(6)	2.30 (4)	—O,F(6)	2.36 (5)
—O,F(7)	2.23 (3)	—O,F(7)	2.51 (4)
—O,F(8)	2.27 (3)	—O,F(8)	2.28 (4)

Chiolite is reported to undergo a phase transition at 150 K (Rocquet, Couzi, Tressaud, Chaminade & Hauw, 1985). Both single-crystal and powder diffraction data at 120 and 80 K, respectively, are consistent with a lower symmetry, probably monoclinic. Raman scattering and group theory suggest that the space group may be $P2_1/n$, consistent with the formation of ferroelastic domains below T_c , although $P2$ may be equally compatible. Rocquet & Couzi (1985) have proposed a microscopic model in which the phase transition is caused by the coupling between a soft optic mode and a strain tensor, both of which conform to E_g symmetry.

The phase transition at 800 K in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ may be taken as resulting in a high-temperature atomic arrangement similar to that found in chiolite at room temperature, with the atomic coordinates in Table 1 leading, on appropriate averaging, to those given in Table 4. These derived coordinates, as those at 295 K, remain close to the values reported by Jacoboni *et al.* (1981) for chiolite, noting that the position $\frac{1}{2}\frac{1}{2}0$ is equivalent to $00\frac{1}{2}$ in space group $P4/mnc$. The

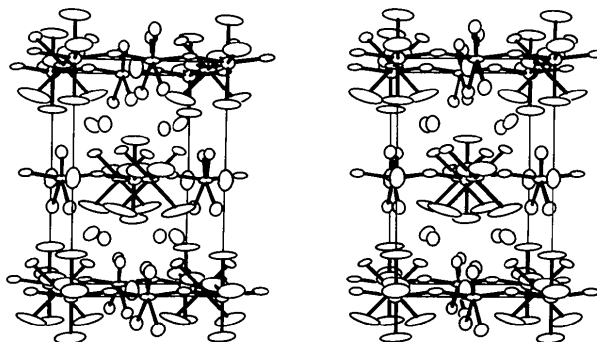


Fig. 1. Stereoview of content of one unit cell of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ at 295 K. The origin is at lower left, with b axis vertical and c axis horizontal, viewed down a axis. Atom identification is readily made from Table 1. Thermal ellipsoids are represented at the 50% probability level.

possibility that a polar space group forms above T_c appears low, in view of the sharp dielectric permittivity maximum observed by Ravez, Elaammani & Chaminade (1979) in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ that is characteristic of a ferroelectric–paraelectric phase transition. It is noted that the spontaneous polarization in isomorphous $(\text{Na}_4\text{Nd})(\text{WNb}_2)\text{O}_9\text{F}_5$ decreases rapidly on approaching T_c , becoming zero at higher temperatures (Ravez, Elaammani, von der Mühl & Hagenmuller, 1979), as expected for the transition to a centrosymmetric phase.

The possibility that chiolite at room temperature may be isostructural with tetragonal $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ at $T > T_c$ is probably best examined by careful Rietveld analysis of the high-temperature powder patterns. Alternatively, however, if second-harmonic generation by chiolite were to be detected below 150 K, then this would eliminate the choice of $P2_1/n$ as proposed by Rocquet, Couzi *et al.* (1985). In such a case, the two phase transitions would be fully comparable.

Comparison of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ with K_2TeBr_6 is also of interest. Both crystals are monoclinic at room temperature, the latter in space group $P2_1/n$, and both transform to space group $P4/mnc$ at higher temperatures. The lattice constants of K_2TeBr_6 at 295 K are $a = 7.4908$ (10), $b = 7.5492$ (7), $c = 10.6984$ (11) Å with $\beta = 90.307$ (6)° and at 410 K are $a =$

Table 4. *Derived prototype atomic coordinates* ($\times 10^4$) for $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ in space group $P4/mnc$

	<i>x</i>	<i>y</i>	<i>z</i> *
W(1)	0	0	0
W(2)	$\frac{1}{2}$	0	0
Na(1)	$\frac{1}{2}$	$\frac{1}{2}$	0
Na(2)	2495	-2505	$\frac{1}{2}$
O,F(1)	0	0	1753
O,F(2)	2475	71	0
O,F(3)	1909	5040	1244

* With fourfold axis along [001].

7.5755 (10), $c = 10.7702$ (22) Å (Abrahams, Ihringer, Marsh & Nassau, 1984); these values agree with the corresponding $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ values within 2.5% for both phases. Group-theoretical normal-mode analysis of the antifluorite A_2BX_6 structure in space group $P4/mnc$ has identified two effective modes with E_g symmetry (Ihringer & Abrahams, 1984), one of which produces a displacement of the A^+ ions and the other a rotation of the BX_6^{2-} octahedron. Condensation of either mode leads to the phase transition and consequent formation of monoclinic symmetry. A structural thermal-dependence study (Abrahams, Ihringer & Marsh, 1989) reveals the detailed coupling between the two sets of atomic displacements and the strain tensors e_{13} and $e_{22} - e_{11}$.

In the case of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, a similar normal-mode analysis must include coupling with the polarization order parameter. Furthermore, the larger number of atoms in the $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ unit cell as compared with that of K_2TeBr_6 [owing to the smaller radius of ${}^{\text{VI}}\text{Na}^+ = 1.16$ Å (${}^{\text{VI}}\text{K}^+ = 1.52$ Å)] and decreased W–O,F = 1.90 Å distance (Te–Br = 2.700 Å)] results in 30 positional parameters for $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, whereas K_2TeBr_6 has only 12 in the monoclinic phase. Nevertheless, an analysis of the normal-mode condensations in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ comparable to that for the case of K_2TeBr_6 would provide detailed information on the thermal dependence of P_s in relation to the ionic displacements and rotations.

The coordination about Na^+ is similar in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ and $\text{Na}_5\text{Al}_3\text{F}_{14}$. In the former, Na(1) is eight-coordinated with average Na–O,F distance of 2.67 Å; Na(2) and Na(3) are both six-coordinated with Na–O,F distances averaging 2.45 and 2.47 Å, respectively, see Table 3. Both polyhedra are also associated with two additional O,F atoms, at Na–O,F distances greater than 2.8 Å. In the case of $\text{Na}_5\text{Al}_3\text{F}_{14}$, one Na is eight-coordinated with a unique Na–F distance of 2.583 Å; the second independent Na atom is six-coordinated with two Na–F distances of 2.268 Å, two of 2.290 Å and two of 2.583 Å (Jacoboni *et al.*, 1981).

A large family of structures related to $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ has been prepared by Ravez, Elaammani & Hagenmuller (1981), with (a) substitution of W by Mo, (b) substitution of Na by K or Li, (c) substitution of Na by

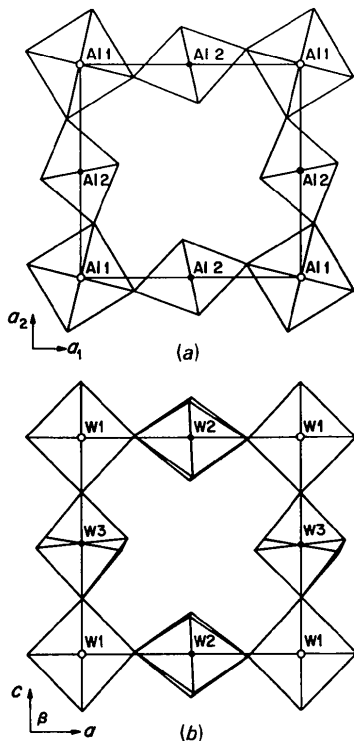


Fig. 2. (a) Corner-sharing AlF_6 octahedra in $\text{Na}_5\text{Al}_3\text{F}_{14}$ at the plane with $z = 0$. The Na^+ ions are located at $00\frac{1}{2}$ and, approximately, at $\frac{1}{4}\frac{1}{4}$, see text. (b) Corner-sharing $\text{W}(\text{O},\text{F})_6$ octahedra in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ at the plane with $y = 0$. The Na^+ ions are located at $0\frac{1}{2}0$ and, approximately, at $\frac{1}{4}\frac{1}{4}$ and $\frac{3}{4}\frac{1}{4}$, see text.

a rare-earth ion and of W by Nb, (*d*) substitution of W by Ti, and (*e*) substitution of W by Ta. A total of about 40 such compounds related to $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ has been prepared and each has been shown to undergo a phase transition at which P_s vanishes and the ferroelastic-ferroelectric domain structure disappears.

References

- ABRAHAMS, S. C. (1988). *Acta Cryst.* **B44**, 585–595.
 ABRAHAMS, S. C., BERNSTEIN, J. L., CHAMINADE, J. P. & RAVEZ, J. (1983). *J. Appl. Cryst.* **16**, 96–98.
 ABRAHAMS, S. C., IHRINGER, J. & MARSH, P. (1989). *Acta Cryst.* **B45**, 26–34.
 ABRAHAMS, S. C., IHRINGER, J., MARSH, P. & NASSAU, K. (1984). *J. Chem. Phys.* **81**, 2082–2087.
 ABRAHAMS, S. C., KURTZ, S. K. & JAMIESON, P. B. (1968). *Phys. Rev.* **172**, 551–553.
 ABRAHAMS, S. C., MARSH, P. & RAVEZ, J. (1987). *J. Chem. Phys.* **87**, 6012–6020.
 ABRAHAMS, S. C., SVENSSON, C. & BERNSTEIN, J. L. (1980). *J. Chem. Phys.* **72**, 4278–4285.
 AIZU, K. (1970). *J. Phys. Soc. Jpn.* **28**, 706–716.
 BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–147, 148–153.
 BOND, W. L. (1960). *Acta Cryst.* **13**, 814–818.
 BROSSET, C. (1938). *Z. Anorg. Allg. Chem.* **238**, 201–208.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1973). *J. Appl. Cryst.* **6**, 309–346.
 DESLATTES, R. D. & HENINS, A. (1973). *Phys. Rev. Lett.* **31**, 972–975.
 DOUMERC, J. P., ELAATMANI, M., RAVEZ, J., POUCHARD, M. & HAGENMULLER, P. (1979). *Solid State Commun.* **32**, 111–113.
 Enraf–Nonius (1984). *CAD-4 Operators Manual*. Enraf–Nonius, Delft, The Netherlands.
 IHRINGER, J. & ABRAHAMS, S. C. (1984). *Phys. Rev. B*, **30**, 6540–6548.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JACOBONI, C., LEBLE, A. & ROUSSEAU, J. J. (1981). *J. Solid State Chem.* **36**, 297–304.
 LABBÉ, PH., LELIGNY, H., RAVEAU, B., SCHNECK, J. & TOLÉDANO, J. C. (1989). Private communication.
 LANDOLT-BÖRNSTEIN (1981). *Ferroelectrics and Related Substances: Oxides*. New Series III/16a. Berlin: Springer-Verlag.
 LANDOLT-BÖRNSTEIN (1982). *Ferroelectrics and Related Substances: Nonoxides*. New Series III/16b. Berlin: Springer-Verlag.
 RAVEZ, J., ABRAHAMS, S. C., ZYONTZ, L. E. & CHAMINADE, J. P. (1983). *Studies in Inorganic Chemistry*, edited by R. METSELAAR, H. J. M. HEIJLIGERS & J. SCHOONMAN. Amsterdam: Elsevier.
 RAVEZ, J., ELAATMANI, M. & CHAMINADE, J. P. (1979). *Solid State Commun.* **32**, 749–754.
 RAVEZ, J., ELAATMANI, M. & HAGENMULLER, P. (1981). *Mater. Res. Bull.* **16**, 1253–1259.
 RAVEZ, J., ELAATMANI, M., HAGENMULLER, P. & ABRAHAMS, S. C. (1981). *Ferroelectrics*, **38**, 777–780.
 RAVEZ, J., ELAATMANI, M., VON DER MÜHLL, R. & HAGENMULLER, P. (1979). *Mater. Res. Bull.* **14**, 1083–1087.
 ROCQUET, P. & COUZI, M. (1985). *J. Phys. C*, **18**, 6571–6579.
 ROCQUET, P., COUZI, M., TRESSAUD, A., CHAMINADE, J. P. & HAUW, C. (1985). *J. Phys. C*, **18**, 6555–6569.
 SVENSSON, C., ABRAHAMS, S. C. & BERNSTEIN, J. L. (1979). *J. Chem. Phys.* **71**, 5191–5195.
 TORRE, L. P., ABRAHAMS, S. C. & BARNS, R. L. (1972). *Ferroelectrics*, **4**, 291–298.

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Structural Study of the Incommensurate and Lock-In Phases of Rb_2ZnCl_4

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Abstract

The crystal structures of Rb_2ZnCl_4 at 210 K [incommensurate structure, $a = 7.253$ (5), $b = 12.646$ (9), $c = 9.221$ (7) Å] and 115 K [threefold commensurate superstructure, $a = 7.230$ (5), $b = 12.608$ (9), $c = 9.199$ (7) Å] have been investigated from X-ray single-crystal diffraction data. The refine-

ment program *REMOS* was used. The final wR factors at 210 and 115 K are respectively 0.045 and 0.041 for 1073 and 1215 main reflections, and 0.187 and 0.136 for 587 and 1065 first-order satellite reflections. The superspace groups are designated as $P(Pmcn):(s,s,\bar{1})$ and $P(P2_1cn):(\bar{1},s,\bar{1})$ in the incommensurate and lock-in phases, respectively. The modulation is interpreted as rotations of rigid ZnCl_4 tetrahedra around two crystal-