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$Na_7Nb_{15}W_{13}O_{80}$ – A New Type of Tunnel Structure Studied by X-ray Diffraction and HREM Techniques

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Abstract. $M_r = 5224{\cdot}5$, orthorhombic, *Pmab*, $a = 21{\cdot}962\ (2)$, $b = 17{\cdot}763\ (2)$, $c = 3{\cdot}9165\ (3)$ Å, $V = 1527{\cdot}9\ (3)$ Å^3, $Z = 1$, $D_m = 5{\cdot}61\ (1)$, $D_x = 5{\cdot}664\ (1)$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo } K\alpha) = 241$ cm^{-1}, $F(000) = 2292{\cdot}7$, $T = 293$ K, $R = 0{\cdot}058$ for 936 independent reflexions. The structure is built up of pentagonal columns connected to each other directly and *via* a string of MO_6 octahedra, running parallel to the *c* axis. Large tunnels with an S-shaped cross section are formed, in which the Na atoms are statistically distributed. Four of the five heavy-atom sites are randomly occupied by Nb and W; the fifth entirely by Nb. X-ray and electron diffraction experiments indicate that the K and Ag analogues are isostructural. HREM images of the K compound confirm the structure.

Introduction. In the course of our studies of compounds with solid-electrolyte properties we have investigated among others the system $NaNbO_3$–Nb_2O_5–WO_3 in some detail (Hörlin, Marinder & Nygren, 1982). Besides an extended region where a phase of tetragonal tungsten-bronze type (or tripled TTB) is stable we found a new phase with the approximate composition $Na_{0.27}Nb_{0.53}W_{0.47}O_{2.87}$.

Experimental. Samples of the title compound were prepared by heating finely ground mixtures of $NaNbO_3$, Nb_2O_5 and WO_3 (all of high purity) in proportions close to 4:2:7. The reactions were carried out in sealed platinum tubes, at 970 K for 1 d and 1170 K for 3 or 4 d. A small amount of the microcrystalline product was mixed with a large excess of sodium chloride, sealed in an evacuated silica tube and heated to 1170 K. Slow cooling of the melt (~ 1 K h^{-1}) for 4 d, quenching and dissolving the sodium chloride in water produced a residue containing several crystalline phases, *inter alia* a single crystal of the title compound.

D_m determined from the apparent loss of weight in *n*-hexane. X-ray powder pattern registered in a Guinier–Hägg focusing camera with monochromatized Cu $K\alpha_1$ radiation, and evaluated as described elsewhere (Hörlin, Marinder & Nygren, 1982) to give the lattice parameters.* Electron optical investigations on the microcrystalline sample made with a Siemens ELMISKOP 102 and, later, with a JEOL JEM 200 CX, in a way described recently (Marinder & Sundberg, 1984). Dimensions of the single crystal ($0{\cdot}004 \times 0{\cdot}031 \times 0{\cdot}237$ mm) determined in a device constructed from a single-crystal orienter with a quarter χ-circle and a Nikon measuring microscope equipped with an Epi-Illuminator (Marinder, 1984).

Weissenberg photographs taken to check the quality of the crystal and to verify its symmetry. Diffraction intensities measured on a PW 1100 four-circle diffractometer (Mo $K\alpha$, graphite monochromator), $4° <$

*JCPDS Diffraction File No. 34–1486. See also deposition footnote.

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$2\theta < 70°$, ω-scan technique, layers $hk0$–$hk6$, 3989 measured reflexions. Reflexions with intensities $I < 3\sigma(I)$ considered unobserved and removed, giving a final set of 938 independent reflexions. Three test reflexions checked every 2 h: no significant change of intensity. Net intensities corrected for Lorentz and polarization effects; absorption correction, transmission factor 0·42 to 0·90.

Electron diffraction patterns exhibited weak spots indicating a doubling of the *c* axis. Inspection of amply exposed Weissenberg rotation photographs obtained with the crystal rotating along its *c* axis did not, however, reveal any extra layer lines that might be due to a doubled *c* axis. The structure determination had thus to be based on the unit-cell dimensions given in the *Abstract*.

Systematically absent reflexions in both the X-ray and electron diffraction material indicated the presence of an *a* glide perpendicular to the *b* axis. The X-ray reflexions were also consistent with a *b* glide perpendicular to the *c* axis while very weak reflexions in the electron diffraction data violated this symmetry. We have chosen as possible space groups *Pmab* (No. 57) and $P2_1ab$ (No. 29) from the X-ray diffraction data. As the structure refined satisfactorily in *Pmab*, the lower space group was not further considered.

From high-resolution electron-microscopy (HREM) images recorded with the Siemens microscope it was inferred that the title compound contains structural elements of the type found in $LiNb_6O_{15}F$ (Lundberg, 1965), Nb_2WO_8 (Lundberg, 1972) and $NaNb_6O_{15}F$ (Andersson, 1965). This assumption was supported by the fact that the *b* axis is, within less than 1%, equal to twice the distance between two pentagonal columns (PC's) joined *via* a triangular link in these three compounds (for nomenclature see Lundberg, Sundberg & Magnéli, 1982). A number of trial structures were designed, each with straight slabs of triangularly linked PC's, which in turn were linked *via* *M*–O octahedra. It was assumed that the Nb and W atoms were distributed statistically over the heavy metal atom sites. Least-squares refinement of one of these structures (with heavy metal atoms only) gave an *R* value of 0·41 indicating that part of the proposed structure might be correct. Electron density maps and full-matrix least-squares refinements were used to establish the coordinates, site occupation factors and isotropic temperature factors of all the heavy atoms. By then, the *R* value was 0·11. Difference Fourier maps revealed the positions of all the O atoms and most of the Na atoms. Subsequent refinements with anisotropic thermal parameters for all heavy metal atoms and isotropic parameters for the remaining atoms terminated at $R = 0{\cdot}058$ and $R_w = 0{\cdot}040$ for 936 reflexions. $(\Delta/\sigma)_{max}$ in the final refinement cycle was less than 0·21 [*U* for Na(21)].

In the final stage of the refinement a weighting scheme was used: $w = 1/\sigma^2(F)$, $\sigma(F)$ from counting statistics; $\sum w(|F_o| - |F_c|)^2$ minimized. Two strong reflexions, 001 and 002, were excluded in the final least-squares refinements rather than being corrected for extinction. A final difference synthesis showed electron density values ranging from +4·0 to −4·7 e Å^{-3}. A peak with a density of 5·2 e Å^{-3} that appeared at (0·25, 0·10, 0·65) 1·3 Å from O(31) is unexplained. Analytical scattering factors and their real and imaginary corrections for neutral atoms from *International Tables for X-ray Crystallography* (1974). Program for structural analysis was *SHELX*76 (Sheldrick, 1976). Calculations performed on the Amdahl and VAX computing systems at the University of Stockholm.

Discussion. Final atomic parameters are given in Table 1.* The crystal structure of $Na_7Nb_{15}W_{13}O_{80}$ is shown in Fig. 1. Two types of building units can be recognized; one is a pentagonal MO_7 bipyramid and the other an MO_6 octahedron (M = Nb or W). Each bipyramid is linked by equatorial edge-sharing to five octahedra forming a star-shaped cluster of polyhedra. Along the *b* axis the units are coupled together *via* triangular links in the manner found in the structures of $LiNb_6O_{15}F$, Nb_2WO_8 and $NaNb_6O_{15}F$ (see above). Along the *a* axis the units are linked *via* an additional octahedron, through corner-sharing. In this way tunnels are formed which are S-shaped in cross section and in which the Na atoms reside.

The star-shaped clusters of polyhedra are stacked on top of each other forming pentagonal columns (Lundberg, 1971) running parallel to the *c* axis. Likewise, the bridging octahedra share corners to form strings running in the same direction.

All *M* atoms are displaced from $z = 0$, just as in Nb_2WO_8 (Lundberg, 1972). On the other hand, the O atoms are less than 3σ from $z = 0$ or $z = \frac{1}{2}$ (see Table 1). The *M*-atom sites are all fully occupied. The W and Nb atoms are more or less disordered; *M*(41) and *M*(01) are almost entirely Nb, however.

Some interatomic distances with their e.s.d.'s are given in Table 2. The equatorial O—O distances vary between 2·39 and 2·42 Å in the pentagonal MO_7 bipyramid and between 2·39 and 2·89 Å in the MO_6 octahedra. The remaining O—O distances in the polyhedra range from 2·64 to 2·93 Å. The distances are quite similar to the corresponding ones in Nb_2WO_8.

The Na atoms are statistically distributed among two possible sites in the tunnels. The occupancy at each site has been used as a parameter in the least-squares refinement. The number of Na atoms sums to 5·9 (8)

* Lists of structure factors, anisotropic thermal parameters and the powder diffraction data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39385 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional and thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j .$$

	Occupancy	x	y	z	B_{eq} or B(Å^2)
Na(11)	4·4 (4)	0·047 (2)	0·090 (2)	0·512 (9)	3·2 (6)
Na(21)	1·6 (4)	0·091 (3)	0·077 (4)	0·510 (30)	2·4 (1·6)
M(11)	4·46 (7)W+ 3·54 (7)Nb	0·1616 (1)	0·2059 (1)	−0·0607 (7)	0·41 (3)
M(21)	6·96 (6)W+ 1·04 (6)Nb	0·1060 (1)	0·4137 (1)	−0·0574 (5)	0·48 (3)
M(31)	1·17 (5)W+ 2·83 (5)Nb	¼	0·0338 (1)	0·0671 (12)	0·36 (6)
M(41)	0·06 (5)W+ 3·94 (5)Nb	¼	0·3508 (2)	0·0701 (15)	0·19 (7)
M(01)	0·28 (5)W+ 3·72 (5)Nb	0	¼	0·0582 (15)	0·54 (7)
O(11)		0·161 (1)	0·205 (2)	0·489 (8)	2·1 (6)
O(21)		0·111 (2)	0·408 (2)	0·505 (9)	2·9 (6)
O(31)		¼	0·032 (2)	0·519 (12)	1·6 (7)
O(41)		¼	0·353 (2)	0·512 (9)	0·3 (5)
O(01)		0	¼	0·508 (14)	2·8 (9)
O(51)		0·079 (1)	0·196 (2)	−0·001 (8)	2·4 (6)
O(61)		0·162 (1)	0·316 (1)	0·013 (6)	0·9 (4)
O(71)		0·184 (1)	0·104 (1)	0·013 (7)	1·2 (5)
O(81)		0·192 (1)	0·445 (1)	−0·002 (8)	1·0 (4)
O(91)		¼	0·235 (2)	−0·004 (10)	1·5 (7)
O(101)		0·073 (2)	0·503 (2)	−0·006 (10)	3·0 (6)
O(111)		0·038 (1)	0·349 (2)	−0·003 (8)	1·3 (5)

Table 2. *Selected interatomic distances* (Å)

Standard deviations are in parentheses.

Na(11)–O(101^{i})	2·54 (5)	Na(21)–O(101^{i})	2·38 (10)
–O(101^{ii})	2·58 (5)	–O(101^{ii})	2·41 (10)
–O(51^{iii})	2·76 (4)	–O(11)	2·74 (7)
–O(51)	2·84 (5)	–O(71)	2·86 (9)
–O(111^{iv})	2·88 (4)	–O(51^{iii})	2·86 (9)
–O(111^{v})	2·96 (4)	–O(71^{iii})	2·88 (9)
–O(01)	3·02 (3)	–O(51)	2·92 (7)
		–O(21^{vi})	3·04 (7)
M(11)–O(11^{vii})	1·76 (4)	*M*(21)–O(21^{vii})	1·72 (4)
–O(51)	1·84 (3)	–O(101)	1·76 (3)
–O(71)	1·89 (2)	–O(111)	1·89 (2)
–O(61)	1·97 (2)	–O(81)	1·99 (2)
–O(91)	2·02 (1)	–O(61)	2·14 (2)
–O(11)	2·16 (4)	–O(21)	2·21 (4)
M(31)–O(31)	1·77 (5)	*M*(41)–O(41)	1·73 (4)
–O(71^{viii})(×2)	1·92 (2)	–O(61^{viii})(×2)	2·05 (2)
–O(81^{ix})(×2)	2·03 (2)	–O(91)	2·07 (3)
–O(31^{vii})	2·15 (5)	–O(81^{viii})(×2)	2·12 (2)
		–O(41^{vii})	2·18 (4)
M(01)–O(01^{vii})	1·76 (6)		
–O(111^{x})(×2)	1·96 (2)		
–O(51^{x})(×2)	2·00 (3)		
–O(01^{vii})	2·16 (6)		

Symmetry code: (i) $x,(\frac{1}{2}+y)-1,1-z$; (ii) $x,(\frac{1}{2}+y)-1,-z$; (iii) $x,y,1+z$; (iv) $-x,\frac{1}{2}-y,1+z$; (v) $-x,\frac{1}{2}-y,z$; (vi) $x,\frac{1}{2}+y,1-z$; (vii) $x,y,z-1$; (viii) x,y,z and $\frac{1}{2}-x,y,z$; (ix) $\frac{1}{2}-x,(\frac{1}{2}+y)-1,-z$ and $x,(\frac{1}{2}+y)-1,-z$; (x) x,y,z and $-x,\frac{1}{2}-y,z$.

per unit cell. It seems likely, however, that additional Na atoms are present in the tunnels, at sites that offer suitable coordination. This assumption is supported by the amounts of heavy atoms found in the structure. The structure analysis shows that there are 12·9 (3) W and 15·1 (3) Nb atoms present. If 80 O atoms per unit cell are assumed, this requires 7 (3) Na atoms, *e.g.* a somewhat higher figure than that given above. The formula of the compound as found here will accordingly be given as $Na_7Nb_{15}W_{13}O_{80}$.

The Na atoms of the two sets found are situated in a trigonal prism of O, whilst a seventh O is coordinated through the center of one of the rectangular faces of the prism. Na(21) might even coordinate an eighth O, likewise through a rectangular face. The Na–O distances are quite long (see Table 2) compared with the sum of the radii (2·40 Å). Apparently the Na atoms are too small to fit properly into the tunnels, which manifests itself as disorder in the average structure obtained by the X-ray diffraction technique. It may be that there is short-range order among the Na atoms in the direction parallel to the *c* axis, which accounts for the doubling of that axis as found from the very weak, extra reflexions in the electron diffraction patterns (see above). The Na atoms may also be the cause of the observed violation of the *b*-glide symmetry. We think, however, that the small e.s.d.'s in the positional parameters and the reasonable size of the temperature factors suggest that our model describes the true structure fairly well.

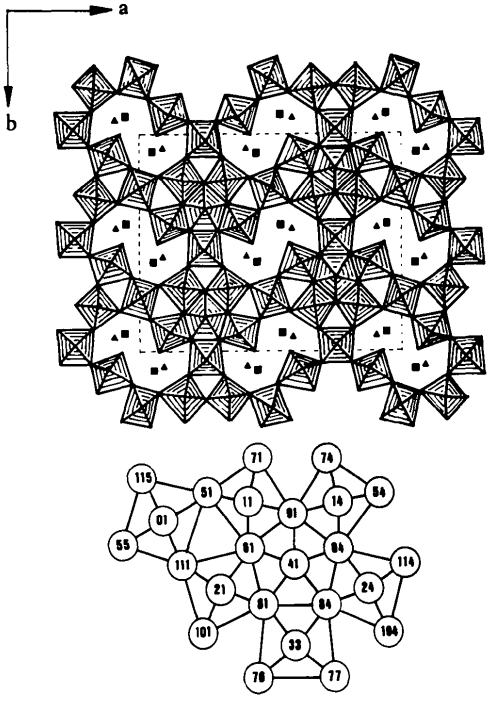

Fig. 1. Orthogonal projection of a single (001) layer of the $Na_7Nb_{15}W_{13}O_{80}$ structure. The two partly occupied point positions of Na are marked ■ and ▲ (*cf.* Table 1).

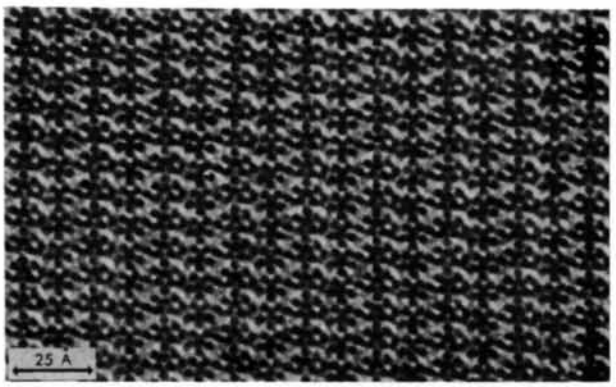

Fig. 2. HREM image of a thin crystallite from the $K_2Nb_4W_4O_{23}$ sample. Accelerating voltage 200 kV, defocus ~−630 Å, objective-aperture radius 0·42 Å^{-1}.

The size of the S-shaped tunnels makes it likely that cations larger than Na can be accommodated in this structure type. Thus the Ag and the K analogues have been prepared. Fig. 2 shows a crystal structure image (recorded with the JEOL microscope) of a crystal obtained from a sample of the overall composition $K_2Nb_4W_4O_{23}$. There is obviously good agreement between the recorded micrograph and the structure model (Fig. 1), although it seems difficult to locate the K atoms in the tunnels. The homogeneity ranges of the Na, K and Ag compounds are now being investigated as well as their behavior as solid electrolytes.

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Structure de la Phase Cubique de l'Hexacyanoferrate(III) de Zinc: $Zn_3[Fe(CN)_6]_2.nH_2O$

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(*Reçu le 21 juillet 1983, accepté le 19 avril 1984*)

Abstract. $M_r = 872{\cdot}2$ (for $n = 14$), cubic, $Fm3m$, $a = 10{\cdot}342$ (2) Å, $V = 1106{\cdot}1$ (2) Å^3, $Z = 1\frac{1}{3}$, $D_m = 1{\cdot}74$ (1), $D_x = 1{\cdot}749$ Mg m^{-3} (for $n = 14$), Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}15$ mm^{-1}, $F(000) = 584$ (for $n = 14$), room temperature, $R = 0{\cdot}016$ for 176 independent reflections. FeC_6 octahedra and $ZnN_4(H_2O)_2$ octahedra are linked by cyanide bridging. In the disordered model, the 4(a) site is occupied by iron (2/3), or by water (9%), or is vacant (24%). When iron is not there the octahedral environment of zinc is completed by water. Another portion of the water is zeolitic.

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Introduction. Cette étude de l'hexacyanoferrate de zinc s'intègre dans notre investigation des hexacyanométallates qui présentent des propriétés zéolithiques et(ou) d'échangeurs d'ions. Les études sur poudres ont permis de caractériser l'existence de deux phases pour $Zn_3[Fe(CN)_6]_2.nH_2O$ (Garnier, Gravereau, Ahmadi & Hardy, 1984):

–une phase cubique, instable, hydratée, et dont une partie de l'eau est zéolithique (n variable de 12 à 14 dans les conditions ambiantes);

–une phase rhomboédrique, stable, anhydre ($n \simeq 0$), et qui semble devoir être considérée comme un terme