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Two New Members of a Series of Monoclinic Sodium Phosphate Tungsten Bronzes $Na_xP_4O_8(WO_3)_{2m}$: $Na_xP_4W_8O_{32}$ ($m = 4$) and $Na_xP_4W_{12}O_{44}$ ($m = 6$)

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Abstract. Monoclinic, $P2_1/a$. $Na_xP_4W_8O_{32}$: $a = 17{\cdot}788\,(11)$, $b = 5{\cdot}277\,(4)$, $c = 6{\cdot}607\,(5)$ Å, $\beta = 99{\cdot}64\,(5)°$, $V = 611{\cdot}42$ Å^3, $Z = 1$, Mo $K\alpha$, $\lambda = 0{\cdot}7093$ Å, $\mu = 400{\cdot}7$ cm^{-1}, 294 K, $R = 0{\cdot}055$ for 2236 unique reflections. $Na_xP_4W_{12}O_{44}$: $a = 23{\cdot}775\,(17)$, $b = 5{\cdot}291\,(1)$, $c = 6{\cdot}588\,(2)$ Å, $\beta = 93{\cdot}47\,(4)°$, $V = 827{\cdot}21$ Å^3, $Z = 1$, Mo $K\alpha$, $\lambda = 0{\cdot}7093$ Å, $\mu = 442{\cdot}9$ cm^{-1}, 294 K, $R = 0{\cdot}043$ for 2305 unique reflections. The frameworks may be described, like that of $K_xP_2W_4O_{16}$, as consisting of ReO_3-type slabs connected by PO_4 tetrahedra with distorted hexagonal tunnels where the sodium ions are located. Furthermore, the results confirm that a new monoclinic family $A_xP_4O_8(WO_3)_{2m}$ ($A = Na^+, K^+$), closely related to the orthorhombic series $P_4O_8(WO_3)_{2m}$ previously described, can form.

Introduction. The investigation of the P–W–O and *A*–P–W–O systems allowed us to synthesize three series of tunnel structures which are all built up from ReO_3-type slabs connected by PO_4 tetrahedra. The first family, the $P_4O_8(WO_3)_{2m}$ orthorhombic phosphate tungsten bronzes (Giroult, Goreaud, Labbé & Raveau, 1981*b*), is characterized by empty pentagonal tunnels, the connection between two successive 'WO_3' slabs being made by 'planes' of single PO_4 tetrahedra. In the second family, $A_xP_4O_8(WO_3)_{2m}$ (Giroult, Goreaud, Labbé & Raveau, 1980, 1981*a*), called monoclinic pyrophosphate tungsten bronzes, the 'WO_3' slabs are connected through planes of P_2O_7 groups; the members of this series, which exhibit wide distorted hexagonal tunnels, are stabilized by big ions such as K^+, Rb^+ or Tl^+. Recently, the structural study of the bronze $K_xP_2W_4O_{16}$ (Giroult, Goreaud, Labbé & Raveau, 1982) led us to predict the existence of a new series of monoclinic phosphate tungsten bronzes with the same formulation $A_xP_4O_8(WO_3)_{2m}$. The framework of the latter bronzes also contains distorted hexagonal tunnels, but with a smaller size than those of the second family, because the 'WO_3' slabs are not connected through pyrophosphate groups but through single PO_4 tetrahedra. Only one member, $m = 4$, could be obtained in this series, and only in the case of potassium; however, the structure of Mo_4O_{11} described by Kihlborg (1963) corresponds to the member $m = 6$ of this series in which MoO_4 tetrahedra replace the PO_4 tetrahedra, the tunnels being empty. Thus, it appeared that this structure could be stabilized by ions smaller than potassium. The present work deals with the structure of two sodium phosphate bronzes belonging to this series, $Na_xP_4W_8O_{32}$ and $Na_xP_4W_{12}O_{44}$.

Experimental. $Na_xP_4W_8O_{32}$ and $Na_xP_4W_{12}O_{44}$ isolated as pure compounds for *x* from 1·1 to 1·5 and from 1·6 to 4, respectively, were prepared by heating a mixture of the appropriate amounts of $H(NH_4)_2PO_4$, WO_3 and Na_2CO_3 in air at 773 K to decompose the phosphate and carbonate; the necessary amount of metallic tungsten was added and the corresponding mixture heated in an evacuated silica tube at 1173 K for 3 d. $Na_xP_4W_8O_{32}$ was obtained in the form of copper-coloured needles, while purple needles were isolated for $Na_xP_4W_{12}O_{44}$. Chemical analysis by atomic absorption spectrometry was made by picking out several crystals from the preparations corresponding to the nominal compositions $Na_{1\cdot5}P_4W_8O_{32}$ and $Na_{2\cdot4}P_4W_{12}O_{44}$; the mean Na compositions were close to that of the initial matrix: $[Na_{1\cdot4(0\cdot2)}]P_4W_8O_{32}$ and $[Na_{2\cdot2(0\cdot2)}]P_4W_{12}O_{44}$.

Crystals were *b*-axis needles with hexagonal section limited by forms {100}, {001}, {70$\bar{4}$} and {010} for $Na_xP_4W_8O_{32}$, {100}, {201}, {$\bar{2}$01} and {010} for $Na_xP_4W_{12}O_{44}$. Crystals 30 × 48 × 456 and 48 × 60 × 380 µm, respectively; monoclinic symmetry deduced from Weissenberg and precession photographs. For the two compounds, *h*0*l*, *h*1*l* and *h*2*l* photographs are similar to those of $K_xP_2W_4O_{16}$ and the cell parameters also seem very similar. Observation of the *hkl* level with $k > 3$ shows additional reflections which lead to doubling of the *a* parameter; systematic absences *h*0*l* ($h = 2n + 1$), 0*k*0 ($k = 2n + 1$) lead to $P2_1/a$ with lattice parameters deduced from least-squares refinement of 25 powder-pattern general reflections registered with a Philips goniometer and Cu $K\alpha$ radiation. CAD-4 Enraf–Nonius diffractometer, graphite monochromator, $2\theta_{max} = 78°$ for $Na_xP_4W_8O_{32}$ ($-31 \le h \le 31$, $0 \le k \le 9$, $0 \le l \le 11$) and $2\theta_{max} = 90°$ for Na_xP_4-

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$W_{12}O_{44}$ ($-47 \le h \le 47$, $0 \le k \le 10$, $0 \le l \le 13$), the ω–2θ technique, scan width 1·40°, background intensity recorded on both sides of each reflection, stability of crystal verified with a periodic control; 4290 reflections for $Na_xP_4W_8O_{32}$ and 2536 for $Na_xP_4W_{12}O_{44}$ within a quarter of the reciprocal space measured; Lorentz and polarization effects corrected for 2236 and 2305 independent reflections which satisfied the criterion $\sigma(I)/I \le 0{\cdot}333$; min. and max. transmission factors 0·168 and 0·345, 0·063 and 0·183, respectively. Structures solved by heavy-atom method; W atom positions fixed by Patterson function, P, O, Na atoms located by a subsequent difference synthesis. Determination of Na composition of crystals by refinement was carried out, in spite of its low accuracy owing to strong correlation between the occupancy factors and the thermal coefficients; observed occupancy factors of the Na sites of 37 (8) and 42 (7)% lead to $Na_{1\cdot5}P_4W_8O_{32}$ and $Na_{1\cdot7}P_4W_{12}O_{44}$; these are in agreement with the formulas deduced from the chemical analysis – $Na_{1\cdot4}P_4W_8O_{32}$ and $Na_{2\cdot2}P_4W_{12}O_{44}$ – if one takes into account the fact that the amount of sodium may vary significantly from one crystal to another. Linear weighting scheme adjusted according to $\langle w^{1/2}||F_o| - |F_c||\rangle$ in terms of $\sin\theta/\lambda$; refinement on F of atom positions, anisotropic, by full-matrix least squares (*ORFLS*; Busing, Martin & Levy, 1962), $(\Delta/\sigma)_{max} = 0{\cdot}1$, $R = 0{\cdot}055$, $R_w = 0{\cdot}048$ for $Na_xP_4W_8O_{32}$, $R = 0{\cdot}043$, $R_w = 0{\cdot}039$ for $Na_xP_4W_{12}O_{44}$; no correction for secondary extinction, final $\Delta\rho$ excursions <1 e Å^{-3}; atomic scattering factors and f', f'' values from *International Tables for X-ray Crystallography*.*

Discussion. The atomic parameters are given in Table 1, and the main interatomic distances in Tables 2 and 3. The projections of the structures for both oxides onto (010) are shown in Figs. 1 and 2.

The host lattices of these bronzes are similar to that of $K_xP_2W_4O_{16}$ (Giroult *et al.*, 1982) in that they are built up from corner-sharing WO_6 octahedra and PO_4 tetrahedra forming ReO_3-type slabs connected through planes of 'single' tetrahedra with distorted hexagonal tunnels in which the sodium ions are located. $Na_xP_4W_8O_{32}$ corresponds, like $K_xP_2W_4O_{16}$, to the fourth member of the series $Na_xP_4O_8(WO_3)_{2m}$, *i.e.* its ReO_3-type slabs are formed of strings of $m = 4$ octahedra running approximately along the [$\bar{1}$14] direction or of two octahedra along [102], while $Na_xP_4W_{12}O_{44}$ corresponds to the sixth member of the series, formed by strings of six octahedra along [118].

* Lists of observed and calculated structure factors and of anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39096 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and thermal parameters with e.s.d.'s in parentheses for* $Na_xP_4W_8O_{32}$ *and* $Na_xP_4W_{12}O_{44}$

	x	y	z	B_{eq}(Å^2)
$Na_xP_4W_8O_{32}$				
W(1) 4(*e*)	0·20591 (1)	0·26064 (11)	0·14025 (5)	0·35 (2)
W(2) 4(*e*)	0·37481 (1)	0·25849 (13)	0·56011 (5)	0·33 (2)
P 4(*e*)	0·0634 (1)	0·2740 (5)	0·7142 (3)	0·25 (2)
O(1) 4(*e*)	0·1105 (5)	0·245 (3)	0·9308 (14)	0·91 (8)
O(2) 4(*e*)	0·0846 (6)	0·067 (2)	0·5751 (18)	0·99 (11)
O(3) 4(*e*)	0·4266 (5)	0·0416 (18)	0·3689 (16)	0·79 (9)
O(4) 4(*e*)	0·4794 (4)	0·2684 (17)	0·7410 (11)	0·51 (7)
O(5) 4(*e*)	0·1505 (5)	0·4829 (17)	0·3021 (16)	0·66 (8)
O(6) 4(*e*)	0·1619 (5)	−0·0241 (16)	0·2642 (14)	0·55 (8)
O(7) 4(*e*)	0·2893 (5)	0·2618 (19)	0·3620 (14)	0·89 (8)
O(8) 4(*e*)	0·2572 (5)	0·0384 (17)	0·9850 (15)	0·68 (9)
Na 4(*e*)	0·008 (2)	0·225 (9)	0·139 (7)	2·7 (5)
$Na_xP_4W_{12}O_{44}$				
W(1) 4(*e*)	0·27960 (1)	0·24069 (13)	0·67190 (13)	0·31 (1)
W(2) 4(*e*)	0·40705 (1)	0·24121 (11)	0·35909 (10)	0·26 (1)
W(3) 4(*e*)	0·15480 (1)	0·23644 (11)	0·99311 (12)	0·27 (1)
P 4(*e*)	0·04687 (8)	0·2256 (4)	0·3261 (8)	0·21 (2)
O(1) 4(*e*)	0·2541 (3)	0·5255 (15)	0·530 (3)	0·66 (9)
O(2) 4(*e*)	0·3468 (3)	0·2308 (19)	0·510 (3)	0·75 (10)
O(3) 4(*e*)	0·3221 (3)	0·4535 (15)	0·866 (3)	0·57 (8)
O(4) 4(*e*)	0·3116 (4)	0·9548 (17)	0·823 (3)	0·69 (9)
O(5) 4(*e*)	0·0819 (4)	0·259 (3)	0·140 (3)	1·01 (10)
O(6) 4(*e*)	0·4464 (3)	0·4588 (15)	0·589 (3)	0·63 (9)
O(7) 4(*e*)	0·4393 (4)	−0·0667 (19)	0·514 (3)	0·95 (11)
O(8) 4(*e*)	0·2151 (3)	0·2395 (18)	0·828 (2)	0·67 (8)
O(9) 4(*e*)	0·1103 (4)	0·0219 (16)	0·789 (3)	0·67 (9)
O(10) 4(*e*)	0·1190 (3)	0·5226 (15)	0·836 (3)	0·61 (9)
O(11) 4(*e*)	0·4852 (2)	0·2318 (14)	0·248 (2)	0·42 (7)
Na 4(*e*)	0·5086 (12)	0·215 (6)	0·862 (7)	2·3 (6)

Table 2. *Interatomic distances and angles with e.s.d.'s in parentheses for* $Na_xP_4W_8O_{32}$

Distances (Å)		Angles (°)	
WO_6 octahedra			
W(1)–O(1)	2·003 (8)	O(1)–W(1)–O(7)	173·2 (4)
W(1)–O(5)	1·960 (10)	O(5)–W(1)–O(6)	87·6 (4)
W(1)–O(6)	1·937 (9)	O(5)–W(1)–O(8^{i})	91·1 (4)
W(1)–O(7)	1·901 (8)	O(6)–W(1)–O(8)	90·8 (4)
W(1)–O(8^{i})	1·890 (9)	O(8)–W(1)–O(8^{i})	90·5 (4)
W(1)–O(8)	1·856 (9)		
⟨W(1)–O⟩	1·924 (9)		
W(2)–O(2^{i})	2·046 (11)	O(2)–W(2)–O(3)	87·0 (4)
W(2)–O(3)	2·035 (10)	O(2)–W(2)–O(6^{i})	88·1 (4)
W(2)–O(4)	2·036 (6)	O(3)–W(2)–O(5^{i})	92·1 (4)
W(2)–O(5^{i})	1·811 (9)	O(5)–W(2)–O(6^{i})	92·3 (4)
W(2)–O(6^{i})	1·828 (9)	O(4)–W(2)–O(7)	170·4 (4)
W(2)–O(7)	1·832 (8)		
⟨W(2)–O⟩	1·931 (9)		
PO_4 tetrahedra			
P–O(1)	1·539 (9)	O(1)–P–O(2)	109·9 (7)
P–O(2)	1·514 (12)	O(1)–P–O(3^{i})	110·3 (7)
P–O(3^{i})	1·536 (10)	O(1)–P–O(4^{ii})	105·3 (5)
P–O(4^{ii})	1·550 (11)	O(2)–P–O(3^{i})	112·9 (7)
		O(2)–P–O(4^{ii})	107·9 (6)
⟨P–O⟩	1·535 (11)	O(3^{i})–P–O(4^{ii})	110·2 (6)
NaO_{18} polyhedra			
Na–O(1)	2·46 (5)		
Na–O(4^{i})	2·53 (5)		
Na–O(3^{ii})	2·58 (5)		
Na–O(4^{ii})	2·59 (4)		
Na–O(5)	2·91 (4)		
Na–O(4^{i})	2·97 (5)		
Na–O(6)	3·02 (4)		
Na–O(2)	3·08 (4)		
Na–O(2^{iii})	3·12 (5)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (iii) $\bar{x}, \bar{y}, \bar{z}$.

Table 3. *Interatomic distances and angles with e.s.d.'s in parentheses for* $Na_xP_4W_{12}O_{44}$

Distances (Å)		Angles (°)	
WO_6 octahedra			
W(1)–O(1)	1·854 (11)	O(1ⁱ)–W(1)–O(4)	175·8 (4)
W(1)–O(1ⁱ)	1·887 (14)	O(1)–W(1)–O(2)	90·0 (5)
W(1)–O(2)	1·973 (12)	O(1)–W(1)–O(8)	93·1 (5)
W(1)–O(3)	1·939 (12)	O(2)–W(1)–O(3)	88·0 (5)
W(1)–O(4)	1·937 (12)	O(3)–W(1)–O(8)	93·0 (5)
W(1)–O(8)	1·894 (11)		
⟨W(1)–O⟩	1·914 (12)		
W(2)–O(2)	1·790 (12)	O(7)–W(2)–O(9)	171·0 (5)
W(2)–O(6)	2·075 (14)	O(2)–W(2)–O(6)	87·5 (5)
W(2)–O(7)	2·043 (11)	O(2)–W(2)–O(10)	97·0 (5)
W(2)–O(9)	1·806 (12)	O(6)–W(2)–O(11)	83·8 (4)
W(2)–O(10)	1·809 (13)	O(10)–W(2)–O(11)	90·7 (5)
W(2)–O(11)	2·036 (7)		
⟨W(2)–O⟩	1·927 (12)		
W(3)–O(3)	1·825 (11)	O(3)–W(3)–O(10)	172·0 (3)
W(3)–O(4)	1·821 (14)	O(4)–W(3)–O(5)	90·1 (6)
W(3)–O(5)	2·035 (13)	O(5)–W(3)–O(9)	85·4 (6)
W(3)–O(8)	1·850 (12)	O(8)–W(3)–O(9)	90·4 (6)
W(3)–O(9)	2·010 (14)	O(4)–W(3)–O(8)	93·5 (6)
W(3)–O(10)	1·991 (11)		
⟨W(3)–O⟩	1·922 (13)		
PO_4 tetrahedra			
P–O(5)	1·533 (17)	O(5)–P–O(6)	110·5 (7)
P–O(6)	1·521 (10)	O(5)–P–O(7)	111·1 (7)
P–O(7)	1·542 (13)	O(6)–P–O(7)	113·2 (8)
P–O(11)	1·540 (7)	O(6)–P–O(11)	109·6 (4)
⟨P–O⟩	1·534 (12)	O(7)–P–O(11)	106·4 (6)
		O(5)–P–O(11)	105·6 (7)
NaO_{18} polyhedra			
Na–O(5)	2·45 (4)		
Na–O(11)	2·47 (3)		
Na–O(6)	2·60 (4)		
Na–O(11)	2·64 (5)		
Na–O(9)	2·85 (3)		
Na–O(10)	2·92 (3)		
Na–O(7)	2·93 (5)		
Na–O(11ⁱ)	3·02 (3)		
Na–O(7ⁱ)	3·11 (4)		

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$.

The geometry of the polyhedra observed for $Na_xP_4W_{12}O_{44}$ is very close to that observed for $Na_xP_4W_8O_{32}$, although it corresponds to a new member of the series. According to their environment with respect to the metallic atoms, three kinds of tungsten atoms can be distinguished: two of them, W(2) and W(3), are identical to those observed in $Na_xP_4W_8O_{32}$ and $K_xP_2W_4O_{16}$ and correspond to the octahedral metallic environment formed by 3P + 3W for W(2) and 1P + 5W for W(3), the distortion of the metallic octahedra P_3W_3 and PW_5 increasing with the number of phosphorus atoms as previously described in $K_xP_2W_4O_{16}$ (Giroult *et al.*, 1982), $P_4W_8O_{32}$ (Giroult *et al.*, 1981) and $P_4W_{10}O_{38}$ (Benmoussa, Labbé, Groult & Raveau, 1982). The third group of tungsten atoms W(1) is octahedrally surrounded by six tungsten atoms 2W(1) + 3W(3) + 1W(2) and appears to be less off-centered [0·06 (1) Å] than for W_5P octahedra [0·10 (1) Å] or for W_3P_3 octahedra [0·24 (1) Å]. These results are to be compared to those observed for $K_xP_2W_4O_{16}$ and $Na_xP_4W_8O_{32}$ for which the W atoms are shifted by 0·13–0·12 (1) Å in the PW_5 octahedra and by 0·24–0·25 (1) Å in the W_3P_3 octahedra. As shown from the interatomic distances and angles (Tables 2 and 3), the PO_4 tetrahedra and WO_6 octahedra of these compounds are almost regular, but the P and W atoms are somewhat off-centered inside their polyhedra. The evolution of the W–O distances and O–W–O angles is indeed correlated to the number of PO_4 tetrahedra linked to each WO_6 octahedron. For the WO_6 octahedra which are linked to three PO_4 tetrahedra, the W(2) atoms of both oxides exhibit a 3 + 3 coordination and are off-centered by 0·16 (1) Å as in $K_xP_2W_4O_{16}$ [0·16 (1) Å]. In the WO_6 octahedra, which are linked to only one PO_4 tetrahedron, the W(1) atoms of $Na_xP_4W_8O_{32}$ and W(3) of $Na_xP_4W_{12}O_{44}$ are less off-centered: 0·08 (1) and 0·15 (1) Å respectively, which can be compared to 0·08 (1) Å in $K_xP_2W_4O_{16}$. Finally, the $W(1)O_6$ octahedra of $Na_xP_4W_{12}O_{44}$, which are only linked to octahedra, are the most regular, W(1) being off-centered by only 0·07 (1) Å. The main difference between the sodium bronzes and $K_xP_2W_4O_{16}$ concerns the nature of the monoclinic cell which exhibits an *a* parameter twice the size of the *c* parameter of $K_xP_2W_4O_{16}$ involving a different space group. In this respect the structure of the sodium phosphate bronzes and especially that of $Na_xP_4W_{12}O_{44}$ is more closely related to η-Mo_4O_{11} which corresponds to the sixth member of the series with empty tunnels; the latter is indeed characterized by the same space

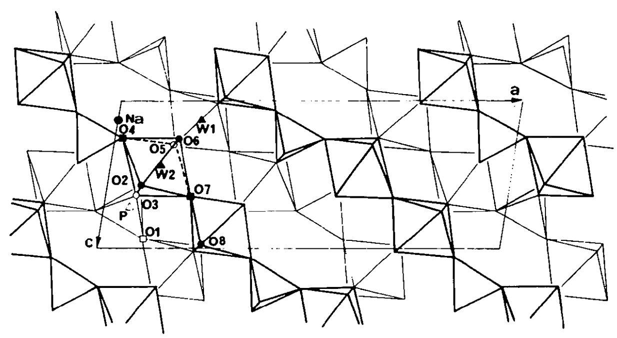

Fig. 1. Projection of the structure of $Na_xP_4W_8O_{32}$ onto (010).

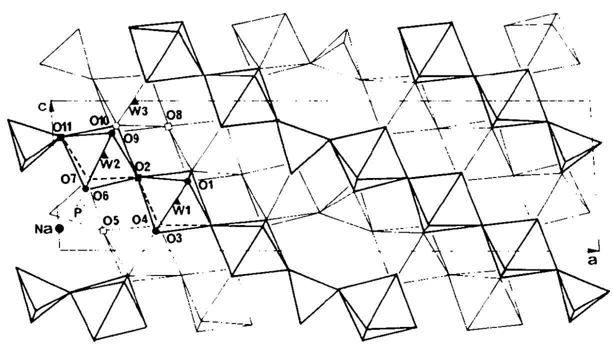

Fig. 2. Projection of the structure of $Na_xP_4W_{12}O_{44}$ onto (010).

group ($P2_1/a$) and very similar distortions. In contrast to $K_xP_2W_4O_{16}$, the P and W or Mo atoms in these compounds are not located at the levels $y = \frac{1}{4}$ and $y = \frac{3}{4}$, but are slightly displaced from these planes. These displacements take place in opposite directions along [010] for two successive ReO_3-type slabs, with the result that the adjacent strings of octahedra belonging to a same slab are tilted with respect to one another. Thus, the structures of these sodium bronzes, as well as that of η-Mo_4O_{11}, are characterized by puckered ReO_3-type slabs.

The distribution of the sodium ions in the structure is worthy of note. In spite of their small size they are located in the distorted hexagonal tunnels while the 'perovskite' cages formed by eight octahedra or by seven octahedra and one tetrahedron are unoccupied. Moreover, the sodium ions which have four closest oxygen neighbors, with Na–O distances ranging from 2·45 (4) to 2·64 (5) Å, are more off-centered inside the tunnels than the K^+ ions in $K_xP_2W_4O_{16}$. The sodium ions are indeed shifted by 1·06 (4) and 1·04 (5) Å for $m = 4$ and $m = 6$ respectively from the center of gravity of the 'O_{18}' cage compared to 0·95 (4) Å for the K^+ ion in $K_xP_2W_4O_{16}$. In the same way, the 'O_{18}' cages of these bronzes are more distorted than those of $K_xP_2W_4O_{16}$ owing to the tilting of the strings of octahedra around their own direction, the angle of the tilt being close to 5° in both oxides.

This structural study shows that several members of the phosphate tungsten bronze family $A_xP_4O_8(WO_3)_{2m}$ of monoclinic symmetry can be stabilized by the presence of sodium in the distorted hexagonal tunnels. It is now established that this family can be synthesized for ions of the same size or smaller than potassium, the monoclinic pyrophosphate tungsten bronzes being obtained for ions of the same size or bigger than potassium. This is to be compared with the results previously obtained by Magnéli (1949, 1953) for the alkali tungsten bronzes A_xWO_3, the hexagonal tungsten bronzes being obtained in normal conditions only for K^+ and ions bigger than K^+, whereas the tetragonal tungsten bronzes were synthesized for K^+ and smaller ions. Studies are being carried out in order to isolate other members of this series, and especially odd-m members, which should differ from even members by a translation of the successive 'phosphate planes' with respect to each other. The influence of the distortion on the electron transport of these oxides will also be studied.

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The Structure of the κ Phase, Mn_5Ge_2

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Abstract. $M_r = 419·87$, orthorhombic, *Ibam*, $a = 11·781$ (8), $b = 6·136$ (6), $c = 5·368$ (2) Å, $V = 388·0$ Å^3, $D_m = 7·19$ (4), $D_x = 7·19$ Mg m^{-3}, $Z = 4$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 31·6 mm^{-1}, $F(000) = 756$, room temperature. The structure was found to be a modification of Mg_5Ga_2 or Cu_5As_2 and was refined by full-matrix least squares to a final $R_w(F)$ value of 0·0402, based on 198 independent reflections. The unit cell is made up of four-by-two-by-two body-centered subcells with four atoms removed and the rest shifted somewhat in position. There are three kinds of coordination polyhedra in the structure, CN12, CN11 and two CN10. Ge atoms are surrounded solely by Mn atoms. The structure is described as a packing of CN10 polyhedra around Ge atoms.

Introduction. In the Mn–Ge system, four intermetallic compounds, $Mn_{3.25}Ge$, Mn_5Ge_2, Mn_5Ge_3 and Mn_3Ge_2, were reported by Elliot (1965). Wachtel & Henig (1969) examined magnetic properties for this system

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