JOURNAL OF SOLID STATE CHEMISTRY **50**, 173–179 (1983)

$K_{1.4}P_4W_{14}O_{50}$: An Odd-m Member (m = 7) of the Monophosphate Tungsten Bronze Series $K_xP_4O_8(WO_3)_{2m}$.

B. DOMENGES, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU

Laboratoire de Cristallographie, Chimie, et Physique des Solides, L.A. 251, Institut des Sciences de la Matière et du Rayonnement, Université de Caen, 14032 Caen Cedex, France

Received April 11, 1983; in revised form July 6, 1983

The crystal structure of $K_xP_4W_{14}O_{50}$ (x = 1.4) has been solved by three-dimensional single crystal X-ray analysis. The refinement in the cell of symmetry $A2/m$, with a = 6.660(2) Å, b = 5.3483(3) Å, c = 27.06(5) Å, and β = 97.20(2)°, Z = 1, has led to R = 0.036 and R_w = 0.039 for 2436 reflections with $\sigma(I)/I \leq 0.333$. This structure belongs to the structural family $K_xP_4O_8(WO_3)_{2m}$, called monophosphate tungsten bronzes (MPTB), which is characterized by ReO_3-type slabs of various widths connected through PO_4 single tetrahedra. This bronze corresponds to the member m = 7 of the series and its framework is built up alternately of strands of three and four WO_6 octahedra. The structural relationships with the $P_4O_8(WO_3)_{2m}$ series, called M′PTB, are described and the possibility of intergrowth between these two structures is discussed.

Introduction

Recent investigations of the Rb–P–W–O system have shown the existence of a new structural family $Rb_xP_4O_8(WO_3)_{2m}$ for $x \leq 1$, called the diphosphate tungsten bronzes (DPTB) (*1–4*). An isostructural series has been isolated in the case of potassium for $m > 4$ (*4–6*). However, for m = 4, another structural type corresponding to the formula $K_xP_4W_8O_{32}$ (*7*) has been isolated for x ranging from 0.8 to 3. The host lattice of this phase is closely related to that of the monoclinic form of Mo_4O_{11} described by Kihlborg (*8*). The structural relationships between $K_xP_4W_8O_{32}$ and the DPTB structure have been studied. The octahedral framework of both compounds is built up from ReO_3 type slabs, but these slabs are connected through "diphosphate planes" in DPTB, and through planes of PO_4 single tetrahedra (i.e., PO_4 tetrahedra only linked to WO_6 octahedra) in $K_xP_4W_8O_{32}$. These results let us predict a new structural series, $K_xP_4O_8(WO_3)_{2m}$, called monophosphate tungsten bronzes (MPTB), which would have the same formulation as DPTB in spite of a different amount x of potassium which could be inserted in the tunnels of the structure. Thus compositions corresponding to higher amounts of potassium ($x > 1$) have been investigated. The present work deals with the member m = 7, $K_{1.4}P_4W_{14}O_{50}$, which is the first odd-m member of the series which has been obtained. The structural relationships between the MPTB structure and that of $P_4W_8O_{32}$ (*9*) have been examined and the possibility of intergrowth of these structures has been described.

0022-4596/83 $3.00

Experimental

Sample Preparation

A mixture of $(NH_4)_2HPO_4$, K_2CO_3, and WO_3 in appropriate ratios was first heated in air at 873 K to decompose the phosphate and carbonate; the resultant product was then mixed with an adequate amount of W and heated in an evacuated silica ampoule at 1223 K. Crystals were selected from the preparation of nominal composition $KP_2W_7O_{25}$.

Structure Determination

The crystal selected for the structure determination was a **b** axis needle colored dark-red with dimensions about 25 × 25 × 144 μm. The Laue patterns revealed monoclinic symmetry ($2/m$) and the cell parameters, measured on Weissenberg films, were confirmed later by diffractometric techniques with a least-squares refinement based on 25 reflections: $a = 6.660(2)$ Å, $b = 5.3483(3)$ Å, $c = 27.06(5)$ Å, and $\beta = 97.20(2)°$. The data were collected on a CAD-4 Enraf–Nonius diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å), filtered with a graphite monochromator. The intensities were measured up to $2\theta = 90°$ with a maximum scan width 1.35° and a counter slit aperture 2 mm. These parameters were fixed after an analysis of the shapes of three reflections which also gave the $\omega - \theta$ scan type. The background intensity was measured on both sides of each reflection and a periodic control verified the stability of the crystal. Among the 2472 measured reflections, the 2436 intensities which had $\sigma(I)/I \leq 0.333$ were corrected for Lorentz and polarization effects and then for absorption with a program based on the crystal morphology. The extremum transmission factors were 0.151 and 0.324 with $\mu = 448$ cm^{-1}.

The only conditions limiting possible reflections (hkl, $k + l = 2n$) led to the existence of an A lattice and the structure was solved by the heavy-atom method in the centrosymmetric $A2/m$ space group. All the W atom positions were located from the Patterson function and K, P, and O atoms fixed in the subsequent difference synthesis and least-squares refinement (Table I). The cell content in potassium was refined at 1.4 (1). Scattering factors for W^{6+}, K^+, and P were from the data of *International Tables* (*10*) corrected for anomalous dispersion (*10*) and for O^{2-} from Suzuki (*11*). A linear weighting scheme was adjusted according to $\langle\sqrt{w}||F_0| - |F_c||\rangle$ in terms of sin θ/λ. A secondary extinction correction applied in the final refinement led to conventional values $R = 0.036$ and $R_w = 0.039$. A projection of atomic positions onto (010) is shown in Fig. 1.

Description of the Structure and Discussion

$K_{1.4}P_4W_{14}O_{50}$ belongs to the monophos-

TABLE I

$K_{1.4}P_4W_{14}O_{50}$: POSITIONAL AND THERMAL PARAMETERS AND e.s.d.'s

	Position	x	y	z	B (Å^2)
K	4(i)	0.363(1)	0	0.2498(3)	1.1(2)[a]
P	4(i)	0.1970(4)	½	0.2928(1)	0.42(3)
W(1)	2(a)	0	0	0	B_{eq} = 0.33(1)[b]
W(2)	4(i)	0.70062(7)	½	0.05464(2)	B_{eq} = 0.30(1)[b]
W(3)	4(i)	0.40226(7)	0	0.11184(2)	B_{eq} = 0.27(1)[b]
W(4)	4(i)	0.09390(7)	½	0.16777(2)	B_{eq} = 0.28(1)[b]
O(1)	2(d)	½	½	0	0.71(15)
O(2)	8(j)	0.846(1)	0.249(2)	0.0278(3)	0.76(6)
O(3)	4(i)	0.197(2)	0	0.0602(4)	0.67(10)
O(4)	8(j)	0.546(1)	0.253(1)	0.0885(3)	0.93(9)
O(5)	4(i)	0.906(1)	½	0.1137(4)	0.70(11)
O(6)	8(j)	0.250(1)	0.253(2)	0.1488(3)	0.92(8)
O(7)	4(i)	0.592(2)	0	0.1767(4)	0.77(11)
O(8)	8(j)	0.920(1)	0.238(2)	0.1977(3)	1.27(10)
O(9)	4(i)	0.237(1)	½	0.2383(3)	0.71(10)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	0.0039(2)	0.0030(2)	0.0050(2)	0	−0.0012(2)	0
W(2)	0.0038(1)	0.0029(2)	0.0043(2)	0	−0.00128(9)	0
W(3)	0.0036(2)	0.0027(2)	0.0037(2)	0	−0.00119(9)	0
W(4)	0.0041(1)	0.0027(2)	0.0032(1)	0	−0.00137(9)	0

[a] The occupation of the corresponding site obtained by refinement is 35(2)%.

[b] The values of the anisotropic thermal coefficients were obtained from $U_{ij} = (1/2\pi^2)\beta_{ij}a_ia_j$ (Å^2).

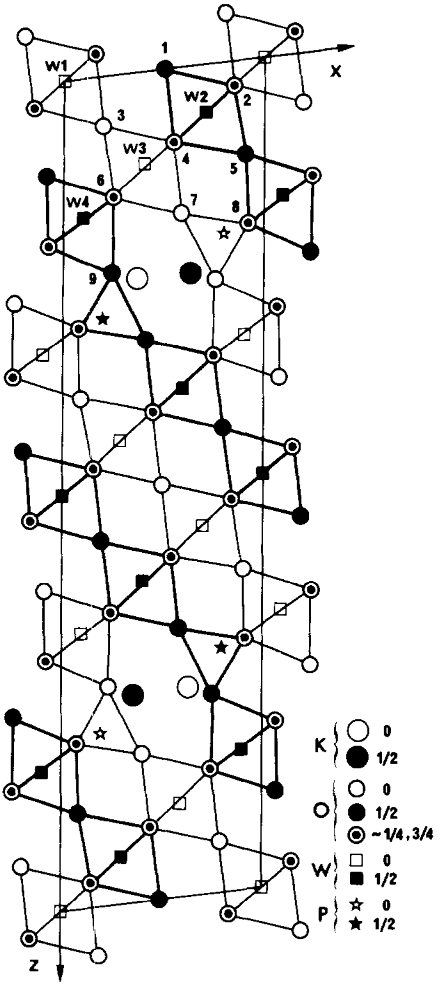

FIG. 1. $K_{1.4}P_4W_{14}O_{50}$: projection of the structure onto (010). The polyhedra with dark and light outlines, respectively, lie at the levels $y = \frac{1}{2}$ and 0.

phate tungsten bronze series $K_xP_4O_8(WO_3)_{2m}$. Its framework is built up from corner-sharing octahedra and tetrahedra which form infinite chains running along the mean direction [301] (Fig. 2), according to the following scheme: ||3 octahedra |1 tetrahedron |4 octahedra |1 tetrahedron ||. In this scheme, both sequences of octahedra are almost parallel to the [11·0·3] direction. Two adjacent chains located, respectively, at $y = 0$ and $y = \frac{1}{2}$ are translated through $\mathbf{a} + (\mathbf{b}/2) + (\mathbf{c}/2)$ with respect one to the other, involving a doubling of the c parameter contrary to the case of $K_xP_2W_4O_{16}$ (*7*). As in the latter the framework can be described as ReO_3-type slabs connected through "planes" of single PO_4 tetrahedra; in these slabs the direction [11·0·3] of the octahedra chains is parallel to the $[001]_{ReO_3}$ direction. The width of the ReO_3-type slabs can be characterized by the number ($m = 7$) of octahedra along direction $[1\underline{1}0]_{ReO_3}$, i.e., approximately the direction $[50\overline{1}]$ of the monoclinic cell (Fig. 3).

In $K_{1.4}P_4W_{14}O_{50}$ each PO_4 tetrahedron shares its corners with four octahedra, as in $K_xP_2W_4O_{16}$. The four W atoms involved in the W–O–P bonds (W (3) + 3W (4)) form a quite distorted tetrahedron, while the P atom is located 0.61 Å from the center of gravity G of this tetrahedron (0.60 Å in $K_xP_2W_4O_{16}$). Each $W(4)O_6$ octahedron shares its corners with three PO_4 tetrahedra

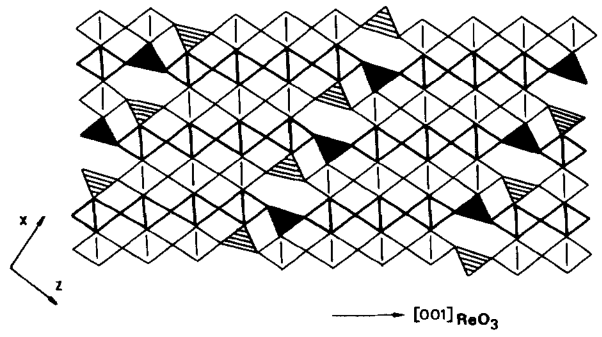

FIG. 2. Projection onto (010) of $K_{1.4}P_4W_{14}O_{50}$ showing the chains of mean direction [301].

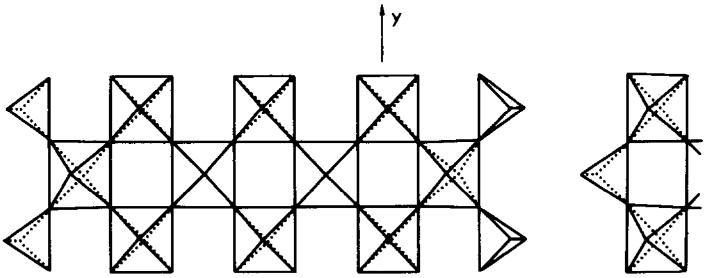

FIG. 3. Projection onto (105) of a ReO_3-type slab of $K_{1.4}P_4W_{14}O_{50}$ showing its width of seven octahedra along the direction $[110]_{ReO_3}$.

and three WO_6 octahedra, whose respective centers (3P, 2W(3), W(2)) form a rather distorted octahedron. Each $W(3)O_6$ shares its corners with one PO_4 and five WO_6. The atoms P, 2W(4), 2W(2), and W(1) form an almost regular octahedron with W(3) at its center. The two other kinds of WO_6 octahedra share their corners with six octahedra, as in ReO_3. According to the bond distances and angles (Table II), they are the most regular octahedra in the structure. The W(1) atom lies on a center of symmetry. It is characterized by a nearly perfect 6 coordination and is at the very center of gravity of its octahedron. The $W(2)O_6$ octahedron is nearly regular and the W(2) atom can be considered as 6-coordinated and close to its center of gravity. The $W(3)O_6$ octahedron is still regular, but the neighboring PO_4 tetrahedron requires a displacement of the W(3) atom which leads to a 3 + 3 coordination with three longest W(3)–O bonds which correspond to the O atoms linked, respectively, to the P and two W(4) atoms. Moreover, the $W(4)O_6$ octahedron is quite distorted owing to its neighboring polyhedra. For both W(3) and W(4) atoms, the W–G distance is much greater than in $K_xP_2W_4O_{16}$ (Table III). The W(4) atom is involved in a 3 + 3 coordination where the three longest W(4)–O bonds are in a P–O elongation. The PO_4 tetrahedron is rather similar in both structures. It is almost regular and the P atom is only shifted 0.05 Å from the center of its tetrahedron.

As shown from Table II, the presence of phosphorous induces along the P–O–W–O–W . . . chains, W–O distances in the octa-

TABLE II

COORDINATION OF W AND P ATOMS IN $K_{1.4}P_4W_{14}O_{50}$ (INTERATOMIC DISTANCES ARE GIVEN IN Å)

Bond neighbor N	W(1)–N	W(2)–N	W(3)–N	W(4)–N	P–N
O(1)		1.864(2)			
O(2)	4 × 1.893(9)	2 × 1.856(9)			
O(3)	2 × 1.96 (1)		1.83(1)		
O(4)		2 × 1.968(8)	2 × 1.818(8)		
O(5)		1.971(9)		1.800(9)	
O(6)			2 × 2.026(8)	2 × 1.797(8)	
O(7)			2.03(1)		1.54(1)
O(8)				2 × 2.050(9)	2 × 1.528(9)
O(9)				2.025(9)	1.53(1)

TABLE III

COMPARISON OF THE W–G DISTANCES (Å) WHERE G IS AT THE CENTER OF GRAVITY OF THE WO_6 OCTAHEDRON

$K_{1.4}P_4W_{14}O_{50}$		$K_xP_2W_4O_{16}$	
W(1)–G	0.000(6)		
W(2)–G	0.086(7)		
W(3)–G	0.190(8)	W(1)–G	0.079(4)
W(4)–G	0.204(9)	W(2)–G	0.157(6)

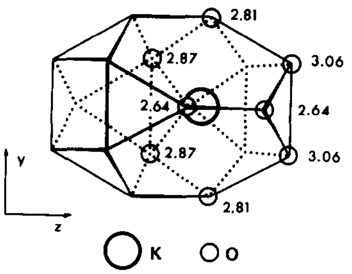

FIG. 4. A cage bounded by 18 oxygen atoms drawn from a projection onto (100). The neighboring O atoms for K are given with the K–O distances in Å.

hedra which are alternately long and short, owing to its covalent character. Moreover the difference between these two distances decreases as the octahedron is further distant from the PO_4 tetrahedron, the difference being of course minimum at half the distance between the two PO_4 tetrahedra which limit the chain. This is in agreement with the results observed for the recently studied phosphate tungsten bronzes $K_xP_2W_4O_{16}$ (*7*), the two members $m = 4$ and $m = 6$ of the series $Na_xP_4O_8(WO_3)_{2m}$ (*12*), $P_4W_8O_{32}$ (*9*), and the diphosphate tungsten bronzes $A_xP_4O_8(WO_3)_{2m}$ (1–6). It must, however, be pointed out that the structural evolution seems to be simpler in the MPTB series than in the DPTB series. In the latter case it has indeed been shown that the distortion and the tilting of the octahedra varies in a complex way from one member to the other, whereas for the two members of the MPTB series it seems that the ReO_3 type slabs are less disturbed by the presence of the PO_4 tetrahedra. This difference is easily explained by the greater contraints imposed by the diphosphate groups involving an anisotropic character of the structure much greater for DPTB than for MPTB: in DPTB, the strands of corner-sharing octahedra of the ReO_3-type slabs are limited by PO_4 tetrahedra along two directions, and exhibit an infinite chain along the third direction; in MPTB, the strands are built of $m/2$ (or $(m-1)/2$ and $(m+1)/2$) octahedra along one direction and of m octahedra along the two other directions. The neighbors of PO_4 are more distorted in $K_{1.4}P_4W_{14}O_{50}$ than in $K_xP_2W_4O_{16}$.

The cavities of the structure are very similar to those observed in $K_xP_2W_4O_{16}$. Three sorts of cages are observed, two of which are almost identical to those of $K_xP_2W_4O_{16}$: cages bounded by seven octahedra and one tetrahedron, and the cavities forming the hexagonal tunnels. These cavities are bounded by 18 oxygen atoms and enclose the potassium ions leading to K–O distances close to these of $K_xP_2W_4O_{16}$ (Fig. 4). The last type of cage is a perovskite cage built up from eight octahedra.

After the structure determination of $K_xP_2W_4O_{16}$ (*7*), i.e., $K_xP_4W_8O_{32}$ ($m = 4$), it was quite easy to predict the structure of the other even-m members of the series $K_xP_4O_8(WO_3)_{2m}$. But for compositions cor-

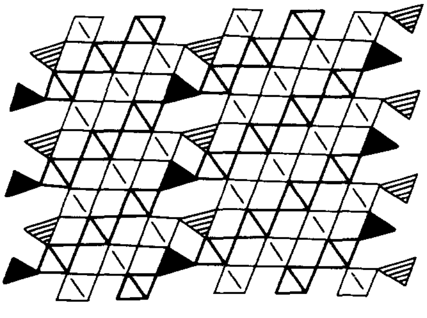

FIG. 5. Projection onto (010) of the idealized intergrowth of the two even $m = 6$ and $m = 8$ members, which corresponds to the composition $K_xP_4W_{14}O_{50}$.

responding to the odd-m members two structural hypotheses had to be considered:

(1) the odd-m members could result from an intergrowth of two even $(m - 1)$ and $(m + 1)$ members (Fig. 5);

(2) the odd-m members would correspond to a new member of the series $K_xP_4O_8(WO_3)_{2m}$, which would differ from the even m member only by a glide parallel to **a** of every second "plane" of tetrahedra.

This structural study shows clearly that the first hypothesis must be rejected. These results can be compared to those observed for the DPTB series and for the

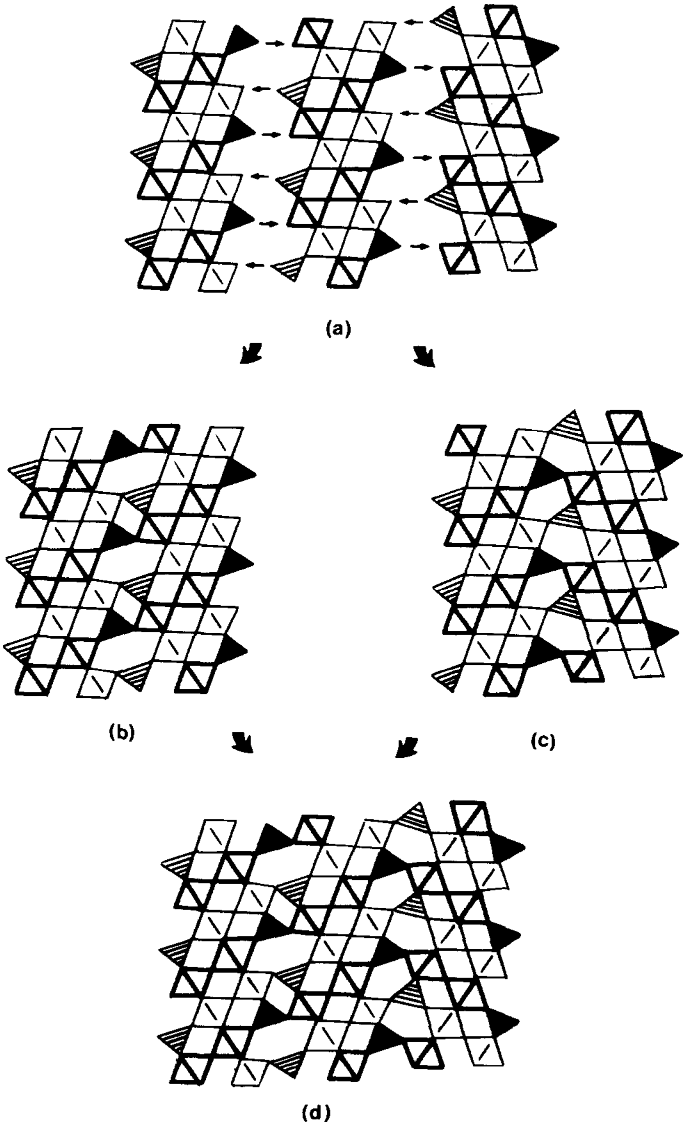

FIG. 6. Projection onto (010) of the "elementary" layers whose different arrangements (a) lead successively to the idealized structure of $K_xP_2W_4O_{16}$ (b), the idealized structure of $P_4W_8O_{32}$ (c), and the hypothetical structure of the intergrowth of the latter (d).

$P_4O_8(WO_3)_{2m}$ series. The DPTB series exhibits indeed a very similar behavior since the odd-*m* members corresponding to a glide of the diphosphate "planes" are always synthesized, whereas intergrowths only appear for nonintegral *m* values (*5, 6*). Curiously, the $P_4O_8(WO_3)_{2m}$ oxides are characterized by the two possibilities: $P_4W_{10}O_{38}$ which corresponds to $m = 5$, is an intergrowth of the even-*m* members $m = 4$ and 6, while our recent electron microscopy investigation (*13*) shows that for other odd-*m* values we do not observe intergrowths but single members of the series characterized by a glide of the phosphate planes with respect to the even-*m* members.

The structure of $K_xP_2W_4O_{16}$ (*7*) has shown that the MPTB structure is closely related to that of DPTB and $P_4O_8(WO_3)_{2m}$. Moreover it has been shown that the two Mo_4O_{11} forms γ and η described by Magneli and Kihlborg (*14, 8*) belong, respectively, to the $P_4O_8(WO_3)_{2m}$ series and to the MPTB series. However, the phase transition γ–η has not been explained up to the present in spite of the close relationships between these structures. A detailed analysis of the $K_xP_4O_8(WO_3)_{2m}$ and $P_4O_8(WO_3)_{2m}$ structures shows that for the same *m* value both structures are formed of identical mixed layers of octahedra and tetrahedra. These layers correspond in fact to the *m* octahedra wide ReO_3-type layers bordered by rows of tetrahedra which share three of their corners with the same octahedral layer. Figure 6a shows, as an example for $m = 4$, how such identical layers can be associated to form either distorted hexagonal tunnels (Fig. 6b) in the MPTB series or the pentagonal tunnels in the $P_4O_8(WO_3)_{2m}$ series (Fig. 6c). It appears that these structures will only differ one from the other by the stacking of those mixed layers: the $P_4O_8(WO_3)_{2m}$ structure is deduced from the MPTB structure only by rotation of 180° of one mixed layer out of two around the **a** axis. The very close relationships between these structural types indicate that the $P_4O_8(WO_3)_{2m}$ series is also a monophosphate tungsten bronze and can be labelled M'PTB.

Thus it appears that a new family of bronzes can be predicted which is characterized by the presence of alternate rows of hexagonal and pentagonal tunnels and which results from the intergrowth of the MPTB and M'PTB structure (Fig. 6d). The possibility of order–disorder phenomena in the distribution of the MPTB and M'PTB slabs should also be considered. From the previous studies on the Mo_4O_{11} oxides and from this study it is now obvious that two factors will be of importance in the stabilization of these structures and of their intergrowths: the temperature and the amount of potassium. The time of annealing will, of course, play a role in the order–disorder transition.

References

1. J. P. Giroult, M. Goreaud, Ph. Labbé, and B. Raveau, *Acta Crystallogr. Sect. B* **36**, 2570 (1980).
2. J. P. Giroult, M. Goreaud, Ph. Labbé, and B. Raveau, *Acta Crystallogr. Sect. B* **37**, 1163 (1981).
3. J. P. Giroult, M. Goreaud, Ph. Labbé, and B. Raveau, *Acta Crystallogr. Sect. B* **38**, 2342 (1982).
4. M. Hervieu and B. Raveau, *J. Solid State Chem.* **43**, 299 (1982).
5. M. Hervieu and B. Raveau, *Chem. Scr.*, **22**, 117 (1983).
6. M. Hervieu and B. Raveau, *Chem. Scr.*, **22**, 123 (1983).
7. J. P. Giroult, M., Goreaud, Ph. Labbé, and B. Raveau, *J. Solid State Chem.* **44**, 407 (1982).
8. L. Kihlborg, *Ark. Kemi* **21** (35), 365 (1963).
9. J. P. Giroult, M. Goreaud, Ph. Labbé, and B. Raveau, *Acta Crystallogr. Sect. B* **37**, 2139 (1981).
10. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England (1974).
11. T. Suzuki, *Acta Crystallogr.* **13**, 279 (1960).
12. A. Benmoussa, D. Groult, Ph. Labbé, and B. Raveau, *Acta Crystallogr. Sect. C*, in press.
13. B. Domengès, F. Studer, and B. Raveau, *Mat. Res. Bull.* **18**, 669 (1983).
14. A. Magneli, *Acta Chem., Scand.* **2**, 861 (1948).