

THE CRYSTAL STRUCTURE OF SnTa_2O_7 , THOREAULITE,
AN EXAMPLE OF TIN IN
FIVE-FOLD COORDINATION

W. G. MUMME, *Division of Mineral Chemistry, CSIRO,
Melbourne, Australia*

ABSTRACT

SnTa_2O_7 crystallizes in the monoclinic system, space group $C2/c$, with the unit cell dimensions $a = 17.140(5)$, $b = 4.865[2]$, $c = 5.548[2]$ Å and $\beta = 91.0[1]^\circ$. The structure was determined by Fourier methods and refined by several three-dimensional least-squares cycles to give a residual R , of 15.1 percent. It contains double layers formed by Ta-O octahedra sharing edges and corners, which are joined through the five-coordinated tin atoms lying in interlayer positions. Structural relationships with other multiple oxides of Ta, Nb and Ti are discussed on the basis of their octahedral groupings.

INTRODUCTION

In their study of brannerite (ThTi_2O_6), Ruh and Wadsley (1966) pointed out that appreciable gaps of knowledge exist regarding the structural inorganic chemistry of the multiple oxides of niobium, tantalum and titanium, listed in Dana's System of Mineralogy (1944, p. 745 *et seq.*). Like brannerite many of these minerals are metamict, possibly due to the disintegration of radioactive elements originally present in them, and it is difficult to select naturally occurring specimens of adequate crystallinity. One of the chemically less complicated of these minerals, and one which does not suffer from this breakdown of structure, is SnTa_2O_7 , thoreaulite. We had begun an investigation of thoreaulite in this laboratory and were in the last stages of the refinement of its structure when a note describing it was published by Maksimova and Ilyukhin (1967). Although based only on projection data, their result was clearly similar to ours, and as the note promised a more detailed account and refinement was to follow, we forebore to publish our results at that time. However, no further communication has been forthcoming, and in view of the structure determinations of triclinic BiTaO_4 (Keve and Skapski, 1967), SbNbO_4 (stibiotantalite) and the closely related $\alpha\text{-Sb}_2\text{O}_4$ (Skapski and Rogers, 1965) we feel that a more detailed description of the crystal chemistry of thoreaulite will be useful.

EXPERIMENTAL PROCEDURE

A specimen of the thoreaulite which occurs with cassiterite in pegmatite at Monono, Belgium Congo, was kindly donated by Dr. Brian Mason from the collection of the American Museum of Natural History (Spec. No. 21932). A chemical analysis of thoreaulite from this locality is given in Dana (1944).

Using the description of the cleavage habit of these crystals, also given in Dana, it was possible to align two small fragments along b and c axes. The unit cell dimensions ob-

TABLE 1. LATTICE PARAMETERS

	This Study	Berry and Thompson	Maksimova and Ilyukhin
<i>a</i>	17.140 ± .005 Å	17.07	17.11
<i>b</i>	4.865 ± .002 Å	4.87	4.85
<i>c</i>	5.548 ± .002 Å	5.52	5.56
β	91.00 ± .05°	91.20	90.9
Unit cell volume	469.6 cm ³		
ρ_m	7.6-7.9 (Dana, 1944)		
ρ_x	7.5		
<i>Z</i>	4		
Space group alternatives	C2/ <i>c</i> , C <i>c</i>		

tained from zero level single-crystal films using the Weissenberg method were in close agreement with those given by Berry and Thompson (1962). Lattice parameters (Table 1) were obtained by least-squares refinement of powder data obtained using a Guinier-type focussing camera internally calibrated with KCl (Table 2). These are compared with those of Berry and Thompson and Maksimova and Ilyukhin.

Intensity data were collected from these two crystals, both measuring 0.02 × 0.02 × 0.1 mm. The levels *hk*0 and *hkl* with *k* = 0, 1 . . . 5 were recorded by the integrating Weissen-

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR SnTa₂O₇

<i>sin</i> ² θ (obs)	<i>sin</i> ² θ (calc)	<i>hkl</i>	<i>I</i>	<i>sin</i> ² θ (obs)	<i>sin</i> ² θ (calc)	<i>hkl</i>	<i>I</i>
0.0081	0.0081	200	VW	0.0860	0.0861	202	MS
.0461	.0461	$\bar{1}11$	MS	.1003	.1002	020	S
.0465	.0465	111	MS	.1073	.1077	$\bar{4}02$	W
					.1083	220	
.0529	.0525	401	W	.1521	.1524	421	VW
.0619	.0619	$\bar{3}11$	VS		.1525	602	
.0631	.0631	311	VS	.1728	.1732	$\bar{6}20$	MS
					.1727	620	
.0727	.0727	600	S	.1771	.1771	022	MS
.0771	.0771	002	MS	.1997	.1998	113	S
.0844	.0843	$\bar{2}02$	W				

berg method, using molybdenum filtered radiation to reduce absorption. Three films interleaved with tin-foil were used for each level. Intensities were measured by visual comparison with a calibrated film strip, and specimen absorption was neglected because the specimens are small. Scattering curves were taken from the compilation of Cromer and Waber (1965) based upon relativistic Dirac-Slater wave functions, and corrected for both the real and imaginary components of anomalous scattering for $\text{MoK}\alpha$, while Suzuki's (1960) data for O^{2-} were used for oxygen.

A total of 366 nonsymmetry-related reflections were recorded on the five levels of data around b and a further 60 on the zero level around c . The hkl data recorded around b , scaled by comparison with structure factors calculated from the final model, have been placed in the NAPS file. All calculations were made on an Elliott 803 computer with a programming system by J. J. Daly, F. S. Stevens and P. J. Wheatley of Monsanto Research S.A.

SOLUTION OF THE STRUCTURE

With a b repeat distance of only 4.86 Å it was likely that there would be very little overlap of atoms in the (010) projection. Furthermore this length is one characteristic for pairs of edge-shared metal octahedra packed such that their oxygen atoms lie in hexagonal close-packed positions with the packing axis parallel to b . With the space group $C2/c$ and the contents of the unit cell defined by the density (Table 1) as $4\text{SnTa}_2\text{O}_7$, it was necessary that the tin atom and at least one oxygen atom should occupy four-fold positions. Patterson projections $P(u, w)$ and $P(u, v)$ were calculated and because of the very strong Sn-Sn, Sn-Ta and Ta-Ta vector interactions, it was possible to determine quickly the positions of the tantalum atom relative to a tin atom chosen at the origin 4(a). However the possibility that the tin atom occupied the more general position 4(e) was not overlooked, and later refinement of the heavy atom positions using the hkl data showed that this was in fact the correct position for tin.

A Fourier projection $\rho(u, w)$ (Figure 1(a)) then revealed the (x, z) positions of three of the oxygen atoms which were in a hexagonal close-packed array around the tantalum atoms. Another Fourier projection $\rho(u, v)$ (Figure 1(b)), and a number of three-dimensional least-squares cycles finally located all the oxygen atoms. The one occupying the four-fold position was found to overlie the tin atom at a slightly less than normal Sn-O distance in the position 4(e).

The weighting scheme for the least-squares refinement was that of Cruickshank, Pilling, Bujosa, Lovell and Truter (1961) and the matrices were inverted with the block diagonal approximation. The final R -value of 15.1 percent was high, possibly due to anisotropic vibration of the metal atoms, and the replacement of some Sn and Ta by other elements. The atomic parameters, and the individual temperature factors and their e.s.d.'s are given in Table 3. The oxygen temperature factors, while consistent, are large and must be looked upon as mathematical correction factors which are only partially due to the temperature.

DESCRIPTION OF THE STRUCTURE

The structure is illustrated as a ball-and-spoke drawing in Figure 2, and as an assemblage of octahedra in Figure 3. The basis of the structure is provided by two parallel layers of edge-shared Ta octahedra. Each such pair is joined by two corners to a neighbouring pair. The considerable distortion of the coordination around the Ta atom from that of

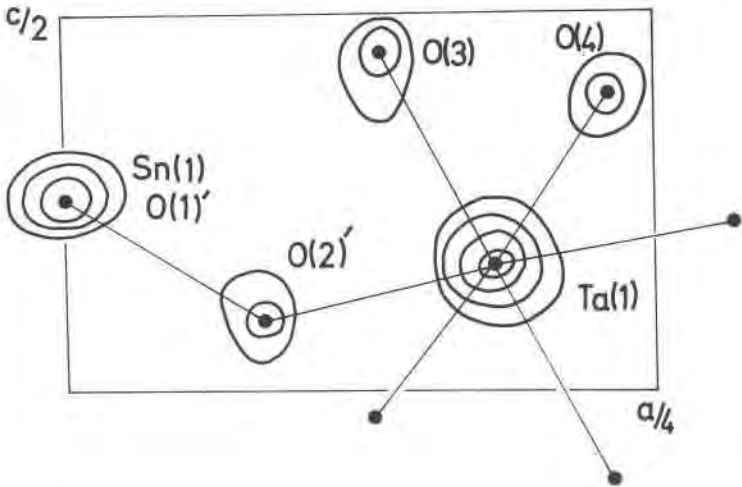


Fig 1a

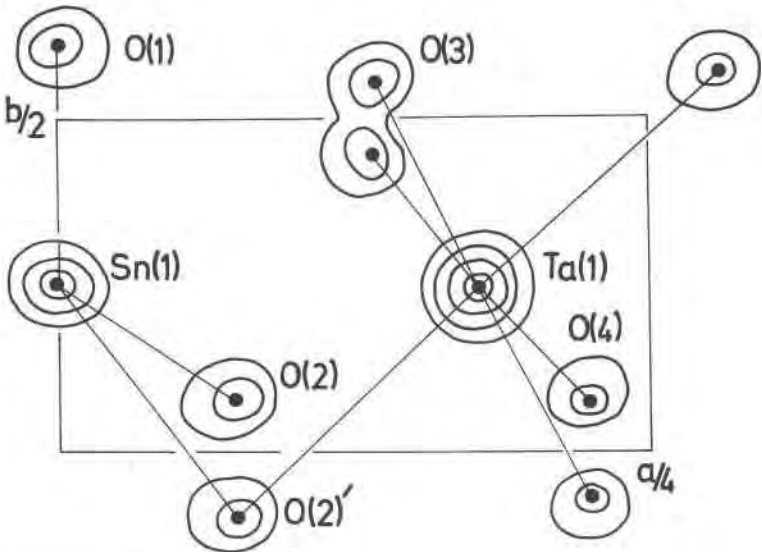


Fig 1b

FIG. 1. F_0 projection, contoured at arbitrary intervals, onto (a) (010); (b) (001).

an ideal octahedron is shown in Figure 4, the Ta-O distances ranging from 1.80 to 2.21 Å (Table 4). The tin atoms which bind the sheets together have the five-fold coordination shown in Figure 5(a). The Sn-O dis-

TABLE 3. FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS FOR SnTa_2O_7 . Standard deviations are given in brackets.

Point position		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Sn(1)	4(<i>e</i>)	0	0.2300 (58)	$\frac{1}{4}$	1.2 (.2)
Ta(1)	8(<i>f</i>)	0.1698 (4)	.2403 (38)	0.6675 (11)	.9 (.1)
O(1)	4(<i>e</i>)	0	.392 (50)	$\frac{3}{4}$	3.6 (2.4)
O(2)	8(<i>f</i>)	.075 (9)	.097 (29)	.599 (25)	2.6 (2.2)
O(3)	8(<i>f</i>)	.124 (10)	.567 (35)	.427 (27)	3.6 (2.4)
O(4)	8(<i>f</i>)	.217 (8)	.077 (30)	.342 (23)	3.5 (1.9)

tances to those oxygen atoms which also take part in the octahedral coordination of the tantalum atoms are substantially longer than normal and results in greatly weakened bonding between the layers as evidenced by the perfect (100) cleavage of the mineral. The fifth bond to the apical oxygen is 1.8 \AA in length which is considerably less than normal.

It should be pointed out that this apical oxygen is differently disposed from that in the structure proposed by Maksimova and Ilyukhin. The tin coordination described by them, and shown in Figure 5(b), seems unlikely as it results in an unacceptably short oxygen-oxygen distance of 1.5 \AA between O(1)' and O(2)'. The tin coordination found in this study, shown in Figure 5(a), results in a value for this distance of 2.1 \AA . This is still shorter than normal, but is possibly tolerated due to the strong metal-oxygen bonding that both of these oxygen atoms experience. This strong metal-oxygen bonding is evidenced by the short bond distances of 1.8 \AA for both the Ta-O(2) and Sn-O(1) bonds.

The overall coordination for tin is similar to that found in K_2SnO_3 (Hoppe, Röhrborn and Walker, 1964) and is best described as a rectangu-

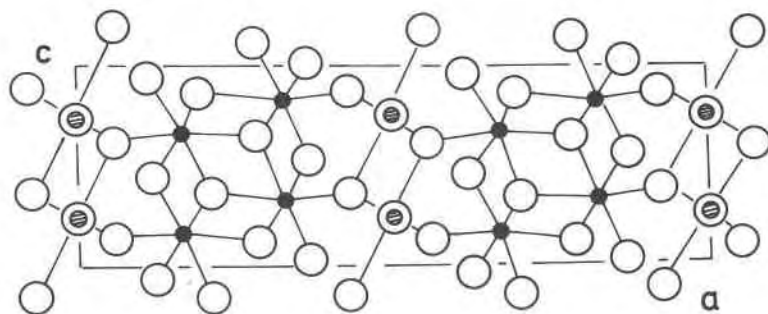


FIG. 2. Crystallographic sites in SnTa_2O_7 projected onto (010). Small full circles Ta sites, small shaded circles Sn, and large open circles oxygen. The numbers in the asymmetric unit cell correspond to those in Table 5.

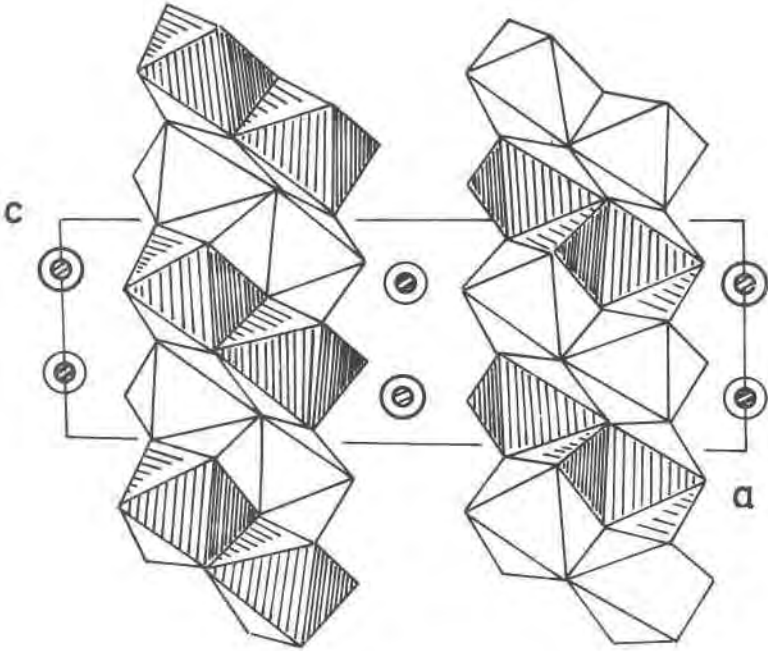


FIG. 3. The structure of thoreaulite as an assemblage of octahedra, projected onto (010). Tin atoms are small shaded circles and the one oxygen atom not octahedrally coordinated to Ta is represented as a large open circle. Similar shading signifies atoms at similar levels.

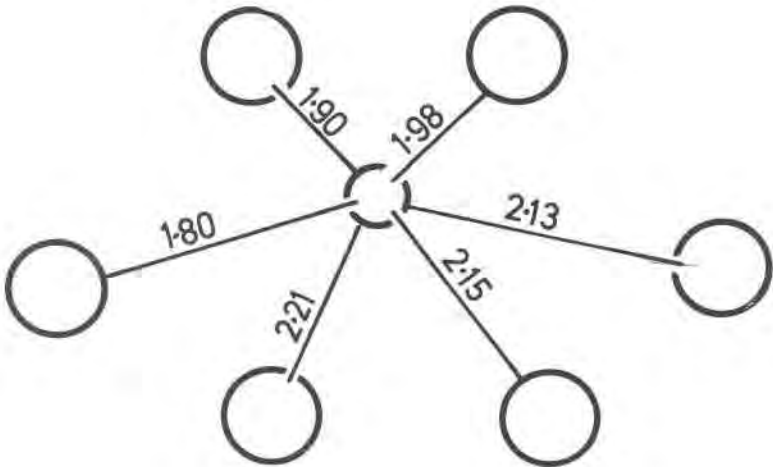


FIG. 4. The Ta coordination.

TABLE 4. INTERATOMIC DISTANCES, AND THEIR E.S.D.'S

A. Within the SnO ₅ polyhedron.	
	Metal-oxygen
Sn-O(2)	2×2.39 (15)
-O(2)'	2×2.21 (15)
-O(1)	1×1.82 (14)
	Oxygen-oxygen
O(1)-O(2)	2×3.4 (2)
O(1)-O(2)'	2×3.7 (2)
O(2)-O(2)'	2×2.9 (2)
O(2)-O(2)''	2×4.7 (2)
B. Within the TaO ₆ octahedron.	
	Metal-oxygen
Ta-O(2)'	1×1.80 (15)
-O(3)	1×1.90 (16)
-O(4)	1×1.98 (13)
-O(4)''	1×2.13 (13)
-O(4)'	1×2.15 (13)
-O(3)'	1×2.21 (16)
	Oxygen-oxygen
O(3)-O(4)	1×3.0 (2)
O(4)-O(4)'	1×2.9 (2)
O(4)'-O(3)	1×2.9 (2)
O(3)'-O(3)	1×2.9 (2)
O(2)'-O(3)	1×2.6 (2)
-O(4)	1×2.9 (2)
-O(4)'	1×2.8 (2)
-O(3)'	1×2.6 (2)
O(4)'-O(3)	1×3.1 (2)
-O(4)	1×2.9 (2)
-O(4)''	1×2.7 (2)
-O(3)'	1×3.1 (2)

lar-based pyramid with the tin displaced slightly up from the center of the base.

DISCUSSION

The AB_2O_6 and ABO_4 compounds with Nb(Ta) in the *B* position, to which thoreaulite is related chemically, fall into a small number of groups. They all have as the basis of their structure BO_6 octahedra, joined in a variety of configurations which allow interstitial sites for *A*.

Columbite (FeNb_2O_6) has groups of BO_6 octahedra joined by edges to form chains, which then corner share with members of adjacent chains. Tapiolite (FeTa_2O_6) is built up for three layers of the rutile structure stacked end-on-end with ordering of the Fe and Ta. The compounds stibiotantalite (SbNbO_4), $\beta\text{-Sb}_2\text{O}_4$ and BiNbO_4 are all built up of slices of the ReO_3 structure. In SbNbO_4 and $\alpha\text{-Sb}_2\text{O}_4$ single layers analogous to ReO_3 slices parallel to (100) have Sb atoms sandwiched in between to form two closely related structures both of which are very similar to

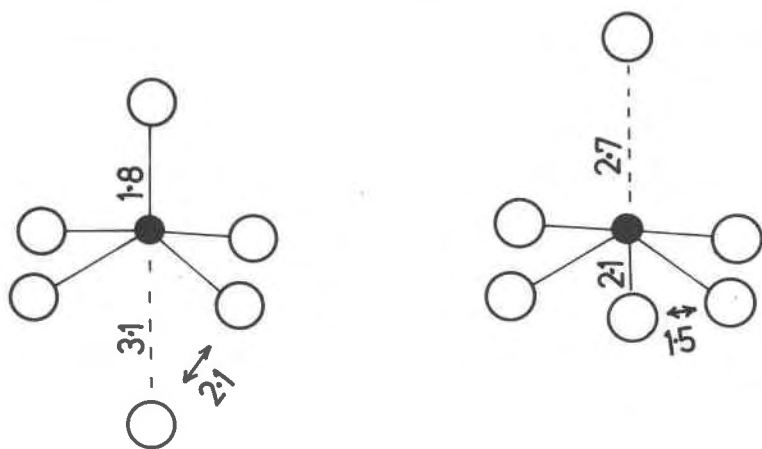


Fig 5 a

b

FIG. 5. The Sn coordination: (a) From this study; (b) From the study of Maksimova and Ilyukhin.

thoreaulite (Figure 6(a), (b)). BiNbO_4 can be derived by slicing the ReO_3 structure diagonally (parallel to (110)), pulling the sheets of octahedra so formed apart, and moving them vertically with respect to one another. The Bi atoms then occupy the holes in the framework (Figure 7 (b)). In thoreaulite the layers of edge-shared BO_6 octahedra represent an infinite slice of the rutile structure parallel to (001) which are two octahedra thick. These double layers of edge-shared octahedra are held together by the tin atoms.

The presence of octahedra joined together by edges into pairs, linear groups of three, or into layers, has been found to be a characteristic feature of titanates (Wadsley, 1967). A pertinent example in the present case is ThTi_2O_6 (brannerite) (Ruh and Wadsley, 1966) which is related

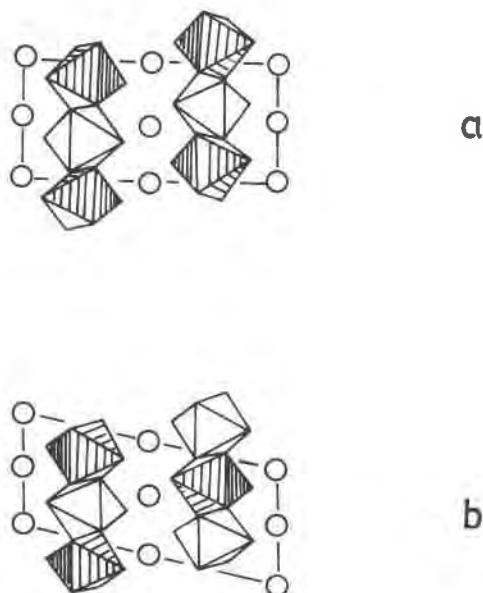


FIG. 6. (a) SbNO_4 ; (b) $\beta\text{-Sb}_2\text{O}_4$. Shown as assemblages of octahedra projected onto (010). Sb atoms not octahedrally coordinated to oxygen atoms are shown as open circles.

to the anatase form of TiO_2 by the slicing of the latter along (101) at unit cell intervals. Corrugated sheets built up of pairs of edge-shared octahedra are thus formed which accommodate the Th ions in large octahedral holes (Figure 7(a)).

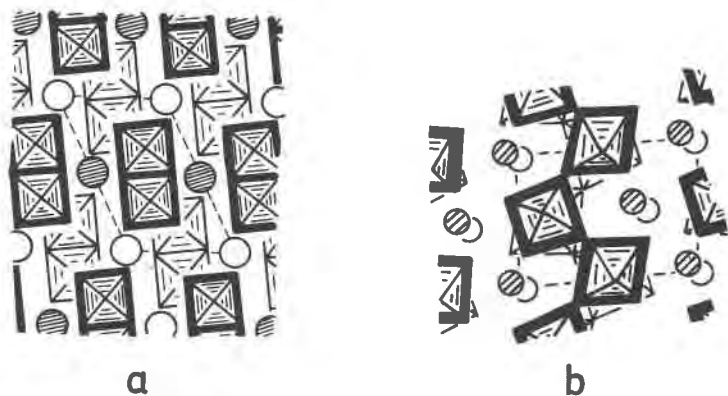


FIG. 7. (a) Idealized octahedral drawing of ThTi_2O_6 projected onto (010). Th atoms are large open circles. (b) Triclinic BiNbO_4 projected onto (010). Bi atoms are large open circles.

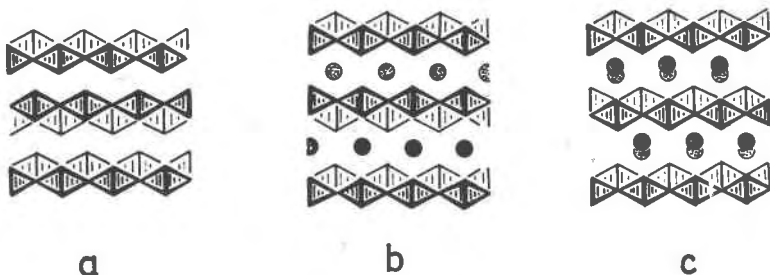


FIG. 8. Structures of (a) Lepidocrocite; (b) $Rb_xMn_xTi_{2-x}O_4$; (c) $K_xMg_{x/2}Ti_{2-x/2}O_4$ in projection as idealized octahedra. Hydrogen atoms are not shown. Rb and K atoms are shown as stippled circles.

In the general disposition of double sheets of metal-oxygen octahedra in relation to the ions which hold them together, thoreaulite is remarkably similar to the mineral lepidocrocite (Ewing, 1935) and the two classes of layer compounds $M_x(A_xTi_{2-x})O_4$, $0.6 < x < 0.8$ typified by $Rb_xMn_xTi_{2-x}O_4$ (Reid, Mumme and Wadsley, 1968) and $M_xMg_{x/2} \cdot Ti_{2-x/2}O_4$ (Mumme, Reid and Watts, 1969). These are all layer structures (Figures 8(a), (b), (c)), and are simply related to one another by shifts of the alternate layers of metal-oxygen octahedra making up the structures. The main difference between them and thoreaulite lies in the manner of edge-sharing of octahedra within the layers themselves.

The existence of further structures composed of layers similar to those found in thoreaulite, but related by a simple relative translation of alternate layers is a possibility which will be explored by the replacement of Sn by other suitable ions.

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