(Edwards & Jones, 1968*b*) of WOF_4 found the structural unit to be a tetramer, $[WF_4O_{2/2}]_4$, with the tungsten atoms approximately at the corners of a square and bridging W–O–W bonds. However the infrared and Raman spectra strongly suggest terminal W=O bonds and bridging fluorine atoms (Beattie, Livingston, Reynolds & Ozin, 1970; Beattie & Reynolds, 1968; Winfield, 1972). The X-ray result is clearly a 'correct' structure in the sense that the centres of the electron density distribution were located. On close examination, it appears that it is impossible to propose an ordered structure with fluorine bridging and satisfy the valence requirements of W within the symmetry of the possible space groups, $C_{2/m}$, C_2 and C_m. This, together with the spectral evidence, enforces the conclusion that there must be O, F disorder in the WOF_4 crystal studied by Edwards & Jones (1968*b*). By analogy with ordered $ReOF_4$ (Edwards & Jones, 1968*a*), which X-ray analysis indicates is fluorine-bridged, the O–F disorder is probably mainly in the shorter in-plane terminal bonds. We have refined a disordered model with the published X-ray data for WOF_4, but failed to obtain a significantly lower *R* value for the disordered model. Difference maps were also inconclusive, and more accurate data would appear necessary for a clear demonstration of the possible disorder in WOF_4.

Polymorphism has been found in other oxide tetrafluorides. $TcOF_4$ has a blue monoclinic form (Edwards, Jones & Sills, 1968) with a structure similar to VF_5 and a green hexagonal form comprising the cyclic tetramers $[TcOF_3F_{2/2}]$. $MoOF_4$ also has a similar dimorphism (Edwards, Jones & Sills, 1968) but the hexagonal form changes to the monoclinic form in a few days. The structure of α-UOF_4 is presently being studied in this laboratory.

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A Powder Neutron-Diffraction Determination of the Structure of $Ba_4Sb_3LiO_{12}$: the Preparation and Structure of the Perovskite-Related Compounds $Ba_4M_3LiO_{12}$ (M=Sb, Bi) and $Ba_5M_3Li_2O_{15-x}$ (M=Te, U)

BY A. J. JACOBSON, B. M. COLLINS AND B. E. F. FENDER
*Inorganic Chemistry Laboratory, South Parks Road, Oxford OX*1 3*QR, England*

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The structure of the ordered perovskite-like compound $Ba_4Sb_3LiO_{12}$ has been determined by profile analysis of powder neutron-diffraction data. The preparation of the compounds $Ba_4Sb_3LiO_{12}$ and $Ba_5M_3Li_2O_{15-x}$ (M=Te, U) and X-ray evidence for their structures is described. All are found to contain only cubic stacking of AO_3 layers in contrast to the behaviour of the analogous Nb, Ta and W compounds.

Introduction

In three recent reports the preparation and structure of some lithium-containing perovskites has been described (Negas, Roth, Parker & Brower, 1973; Collins, Jacobson & Fender, 1974; Jacobson, Collins & Fender, 1974). We find that in $Ba_4Ta_3LiO_{12}$, $Ba_4Nb_3LiO_{12}$ and $Ba_5W_3Li_2O_{15}$ both the transition metal ion and the lithium ion can coexist on the *B* site of the perovskite but that the stacking sequence of BaO_3 layers is modified by cation ordering with the result that Nb^{5+} Ta^{5+} or W^{6+} and Li^+ ions are brought into nearest cation positions through a pair of face-shared octahedra. Thus in $Ba_4Ta_3LiO_{12}$ (and in the corresponding Nb compound) an eight-layer sequence (Fig. 1) is observed, while cation ordering in $Ba_5W_3Li_2O_{15}$ gives a ten-layer sequence (Fig. 2).

Can similar compounds be prepared with *B* metal cations? One report (Fesenko *et al.*, 1970) suggests that the corresponding Sb compounds $Ba_4Sb_3LiO_{12}$ and $Sr_4Sb_3LiO_{12}$ exist as simple cubic perovskites with $a=$ 4·110 and 4·003 Å respectively. However, a feature of these perovskites is the slow cation diffusion, so we have re-examined this system and investigated the preparation and X-ray powder diffraction patterns of analogous Bi, Se, Te and U compounds. The details of cation ordering and the local cation environment may be revealed by neutron powder-diffraction studies, and the examination of $Ba_4Sb_3LiO_{12}$ forms the main part of this report.

Experimental

Preparation and characterization of samples

The starting materials employed were $BaCO_3$, Li_2CO_3, TeO_2, Bi_2O_3 as spectrographically standardized chemicals from Johnson Matthey (Chemicals) Ltd., and Sb_2O_3, SeO_2 and $UO_2(NO_3)_2.6H_2O$ as B.D.H. AnalaR reagents. $BaCO_3$ and Li_2CO_3 were fired prior to use at 1000 and 500°C under CO_2 to remove traces of water. The uranyl nitrate was first converted to U_3O_8 by firing at 800°C in oxygen.

Weighed amounts of the appropriate starting materials were hand-mixed in an agate mortar, placed in either impervious Al_2O_3 or Pt crucibles and fired in air. X-ray diffractometer traces were taken with a Philips high-angle goniometer and Cu *Kα* radiation. Lattice parameters were obtained by least-squares refinement of the measured line positions.

$Ba_4Sb_3LiO_{12}$: *preparation and analysis*

The starting mixture of Sb_2O_3, Li_2CO_3 and $BaCO_3$ was fired at 470°C (24 h), 700°C (36 h), 800°C (48 h), 900°C (24 h), 1000°C (24 h), 1100°C (24 h) and 1200°C (72 h). All the products obtained at or below 900°C were light grey in colour. The 1000, 1100 and 1200°C products were cream-coloured. The observed weight changes indicated a final composition of $Ba_4Sb_3LiO_{12\cdot05(2)}$. The compound was dissolved in a 1:1 mixture of HCl and HF and analysed by atomic absorption. The experimental results, with similar determinations for other compounds, are given in Table 1. Loss of lithium by volatilization is very small.

Table 1. *Lithium analysis results*

	Exp. wt.%	Theoret. wt.%
$Ba_4Sb_3LiO_{12}$	0·66	0·623
$Ba_4Bi_3LiO_{12}$	0·49	0·505
$Ba_5Te_3Li_2O_{15}$	0·99	1·049
$Ba_5U_3Li_2O_{14}$	0·80	0·847

$Ba_4Sb_3LiO_{12}$: *structure by powder neutron diffraction*

The X-ray diffractometer trace of the final $Ba_4Sb_3LiO_{12}$ could be indexed as a body-centred cube with $a=8\cdot217$ (1) Å, which is approximately twice as

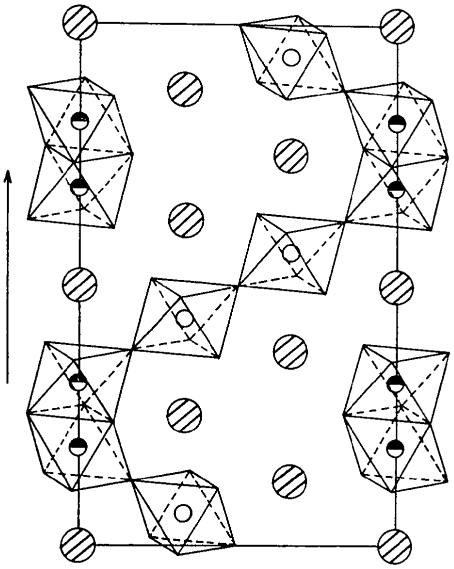

Fig. 1. Hexagonal eight-layer $Ba_4Ta_3LiO_{12}$ structure. Striped circles are Ba; open circles are Ta and half-shaded circles are Ta/Li.

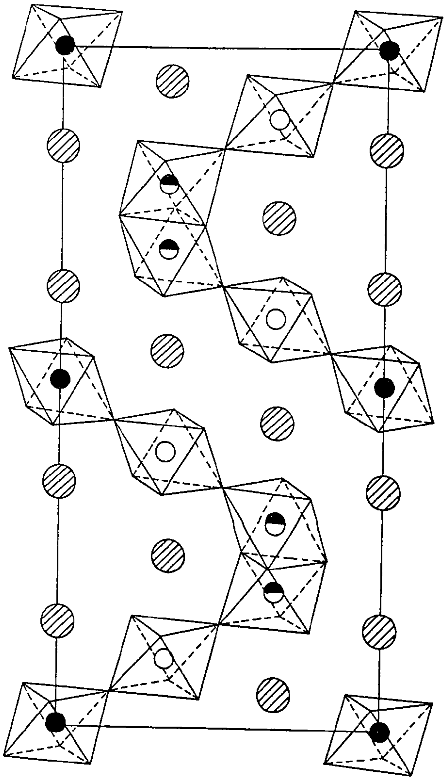

Fig. 2. Hexagonal ten-layer $Ba_5W_3Li_2O_{15}$ structure. Striped circles are Ba, open circles are W, shaded circles are Li and half-shaded circles are W/Li.

large as the value reported by Fesenko *et al.* (1970). The diffraction results are given in Table 2.

Table 2. $Ba_4Sb_3LiO_{12}$ *X-ray diffractometer data*

I(obs)	*I*(cal)	*d*(obs)	*d*(cal)	*h*	*k*	*l*
9·9	10·9	5·80	5·81	1	1	0
1·3	1·3	4·10	4·11	2	0	0
4·7	5·8	3·353	3·355	2	1	1
100·0	94·6	2·905	2·905	2	2	0
2·4	2·5	2·599	2·599	3	1	0
6·1	6·5	2·370	2·372	2	2	2
1·9	3·1	2·195	2·196	3	2	1
28·8	28·7	2·054	2·054	4	0	0
1·8	1·6	1·938	1·937	3	3	0
0·6	0·8	1·839	1·837	4	2	0
0·5	0·7	1·751	1·752	3	3	2
35·8	36·0	1·677	1·677	4	2	2
1·8	1·8	1·611	1·612	5	1	0
1·3	1·0	1·501	1·500	5	2	1
16·8	16·5	1·451	1·453	4	4	0
0·8	0·7	1·410	1·409	5	3	0
0·5	0·5	1·369	1·370	6	0	0
1·4	0·9	1·334	1·333	6	1	1
14·2	14·9	1·300	1·299	6	2	0
0·4	0·6	1·267	1·268	5	4	1
1·4	1·6	1·239	1·239	6	2	2
	0·4		1·212	6	3	1
4·9	5·2	1·1864	1·1861	4	4	4
0·7	0·6	1·1623	1·1621	7	1	0
18·1	17·7	1·0981	1·0981	6	4	2
	0·1		1·0790	7	3	0
0·5	0·5	1·0437	1·0436	7	3	2
2·7	2·6	1·0272	1·0272	8	0	0
0·4	0·5	1·0117	1·0115	8	1	1
0·5	0·2	0·9966	0·9965	8	2	0
0·3	·0·3	0·9822	0·9822	6	5	3
11·4	10·7	0·9682	0·9684	8	2	2
0·5	0·6	0·9551	0·9552	8	3	1
0·5	0·8	0·9428	0·9426	6	6	2
0·2	0·3	0·9304	0·9304	7	5	2
9·6	9·5	0·9189	0·9187	8	4	0
	0·3		0·9074	9	1	0
0·2	0·5	0·8968	0·8966	8	4	2
0·8	0·6	0·8863	0·8861	9	2	1
7·6	7·6	0·8762	0·8760	6	6	4

A neutron diffraction powder pattern was measured at 4·2 K for $Ba_4Sb_3LiO_{12}$ on a powder diffractometer at the reactor PLUTO, AERE Harwell. A wavelength of 1·54 Å from the (511) planes of a germanium monochromator with a take-off angle of 90° was used. The counter was stepped every 0·02° and counts accumulated every 0·1° interval. The complete range of data obtained ($12° < 2\theta < 70°$) was used in the refinement. Absorption and extinction effects were small and no corrections were made. The sample (~10g) was contained in a thin-walled vanadium can. The structural parameters were refined by a full-matrix least-squares analysis of the powder diffraction profile (Rietveld, 1967). The program minimizes the function

$$\chi^2 = \sum_i w_i \left[y_i(\text{obs}) - \frac{1}{c}\, y_i(\text{calc}) \right]^2$$

where *w* is the weighting function, *y* the number of counts at a point in 2θ and *c* is the scale factor.

Space group *Im*3*m* was chosen initially, and the starting parameters were taken as those corresponding to ideal cubic close packing of the BaO_3 layers. Two Li were placed in position 2(*a*) and six Sb in 6(*b*). All the Li atoms are in octahedra which corner-share with six Sb-containing octahedra, while the Sb atoms are surrounded by two Li and four Sb. An overall temperature factor was used. The scattering lengths were $b_{Ba} = 0{\cdot}52$, $b_{Li} = -0{\cdot}214$ and $b_O = 0{\cdot}580$ (10^{-12} cm) (Neutron Diffraction Commission, 1972), and $b_{Sb} = 0{\cdot}564$ from a recent compilation by Shull (see Willis, 1973). The data were refined until all parameter shifts were less than $0{\cdot}3\sigma$, to give the results in Table 3. The Sb and Li total occupation numbers are in excellent agreement with the values expected for ideal stoichiometry. Refinement of the oxygen occupation numbers gave no significant improvement in *R*. With space group *I*23, *R* remains unchanged and the parameters are well within one standard deviation of the *Im*3*m* values.

Table 3. *Atomic positional parameters for* $Ba_4Sb_3LiO_{12}$ *obtained from* 4·2 K *neutron refinement*

x, *y*, *z* are fractions of the unit-cell edge. The errors refer to one standard deviation.

$Ba_4Sb_3LiO_{12}$ (*Im*3*m*)

		x	*y*	*z*
Ba	8(*c*)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
Sb	6(*b*)	0	$\frac{1}{2}$	$\frac{1}{2}$
Li	2(*a*)	0	0	0
O(1)	12(*d*)	$\frac{1}{4}$	0	$\frac{1}{2}$
O(2)	12(*e*)	0·2678 (11)	0	0

Occupation numbers

Site	Sb	Li
Sb	5·94 (6)	0·06 (6)
Li	0·08 (5)	1·92 (5)
Total	6·02 (11)	1·98 (11)

Overall temperature factor = 0·31 (9) Å^2

R(intensities) = 3·7 %
R(profile) = 6·0 %

The experimental and observed profiles, a difference plot and the positions of the Bragg reflexions are shown in Fig. 3 and the structure and *B* cation environment in Figs. 4 and 5.

$Ba_4Bi_3LiO_{12}$

The starting mixture, in a Pt container was fired in flowing oxygen on a Stanton Instruments 'Massflow' thermobalance at the following temperatures: 600°C (24 h), 700°C (48 h), 750°C (48 h), 800°C (48 h) and 900°C (24 h). The product was re-ground between firings and became homogeneous when prepared above 750°C. In each case a weight gain on cooling was observed and the final firing was slowly cooled to constant weight from 900 to 500°C. The thermogravimetric composition of this final product was $Ba_4Bi_3LiO_{11{\cdot}80(10)}$. An X-ray diffractometer trace consisted of fairly broad lines and no high-angle splittings were observed. The positions of the first seven reflexions gave a=4·300 (5) Å. Because of the width of the peaks a full refinement was not attempted but assuming the space group *Pm*3*m* and a disordered cation distribution there is reasonable agreement between the observed and calculated intensities (Table 4).

Table 4. $Ba_4Bi_3LiO_{12}$ *X-ray diffractometer data*

I(obs)	*I*(cal)	*d*(obs)	*d*(cal)	*h k l*
7·3	1·7	4·31	4·30	1 0 0
100·0	106·5	3·047	3·041	1 1 0
34·8	30·4	2·148	2·150	2 0 0
2·0	0·8	1·919	1·923	2 1 0
40·0	42·2	1·756	1·756	2 1 1
15·5	18·2	1·521	1·520	2 2 0
17·7	17·5	1·360	1·360	3 1 0

$Ba_5Te_3Li_2O_{15}$

A sample (~ 1·5 g) was prepared by firing the starting mixture at 450 °C (96 h), 500 °C (24 h), 670 °C (24 h), 820 °C (48 h) and 1000 °C (120 h). The products were re-ground before each firing; those obtained at and below 500 °C were pale yellow, the others were all orange-brown. The final composition was calculated to be $Ba_5Te_3Li_2O_{14\cdot86(10)}$. Attempts to synthesize the analogous Se compound were unsuccessful. In all cases mixtures of $BaCO_3$, Li_2CO_3 and $BaSeO_4$ or $BaSeO_3$ were obtained. The mixtures melted above 700 °C.

An X-ray diffractometer trace of the Te perovskite was obtained over the angular range $5° < 2\theta < 135°$. 32 reflexions were measured, all of which could be indexed on a face-centred unit cell ($h+k$, $k+l$, $h+l=2n$), with a=8·237 (2) Å (Table 5).

Table 5. $Ba_5Te_3Li_2O_{15}$ *X-ray diffractometer data*

I(obs)	*I*(cal)	*d*(obs)	*d*(cal)	*h k l*
16·3	15·9	4·76	4·75	1 1 1
5·1	4·4	4·12	4·12	2 0 0
100·0	94·9	2·913	2·912	2 2 0
7·0	7·0	2·483	2·483	3 1 1
10·7	10·4	2·377	2·378	2 2 2
31·1	29·7	2·058	2·059	4 0 0
2·5	2·5	1·889	1·890	3 3 1
2·1	2·3	1·843	1·842	4 2 0
35·3	35·6	1·681	1·681	4 2 2
2·5	2·6	1·586	1·585	5 1 1
17·9	16·8	1·455	1·456	4 4 0
2·1	2·4	1·392	1·392	5 3 1
1·2	1·2	1·372	1·373	6 0 0
15·4	14·7	1·304	1·302	6 2 0
1·0	0·7	1·256	1·256	5 3 3
2·5	2·5	1·242	1·242	6 2 2
5·6	5·2	1·1888	1·1889	4 4 4
1·2	1·3	1·1539	1·1534	7 1 1
0·4	0·5	1·1419	1·1422	6 4 0
19·1	17·2	1·1004	1·1007	6 4 2
1·7	1·3	1·0728	1·0723	7 3 1
2·3	2·6	1·0296	1·0296	8 0 0
	0·4		1·0063	7 3 3
0·9	0·8	0·9991	0·9988	8 2 0
9·6	10·0	0·9708	0·9707	8 2 2
0·9	0·9	0·9509	0·9511	7 5 1
0·9	1·1	0·9447	0·9448	6 6 2
7·6	9·1	0·9209	0·9209	8 4 0
0·9	1·2	0·9040	0·9041	9 1 1
0·5	0·9	0·8988	0·8987	8 4 2
5·2	7·1	0·8781	0·8780	6 6 4
0·9	1·0	0·8634	0·8634	9 3 1
8·3	10·7	0·8406	0·8407	8 4 4

A refinement was carried out based on the *Fm*3*m* space group with starting parameters which correspond with ideal close packing of the BaO_3 layers. Four Te were placed on 4(*b*) and 0·8 Te and 3·2 Li on 4(*a*).

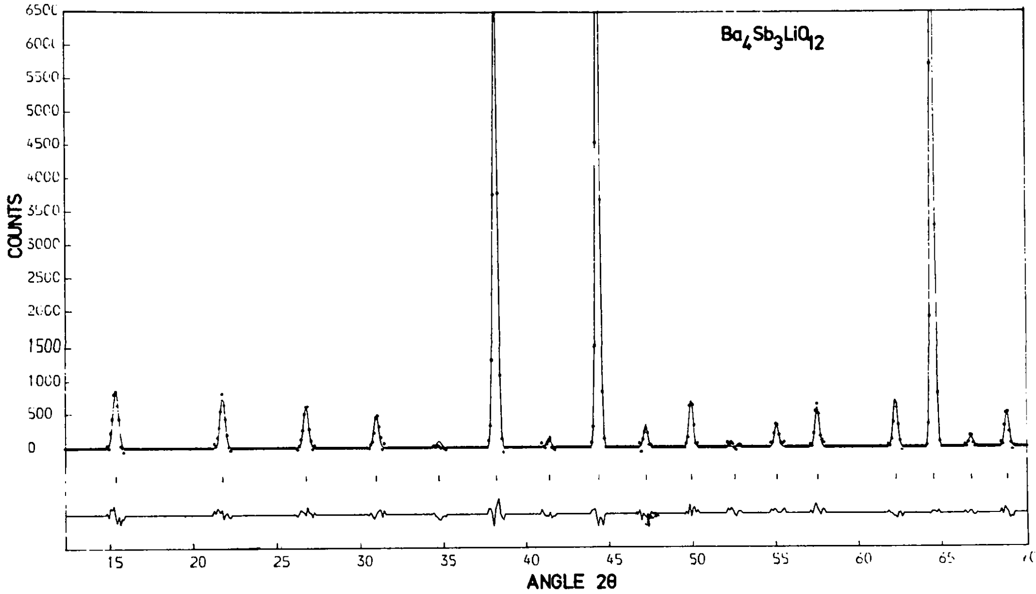

Fig. 3. Powder neutron-diffraction profile for $Ba_4Sb_3LiO_{12}$. Small circles are the experimental points, and the continuous line passes through the calculated points. The small vertical lines are the calculated *hkl* positions and the bottom trace is a difference plot.

This corresponds to 1:1 ordering between four Te and (0·8 Te + 3·2 Li) over the two *B* cation sites (Fig. 5). An overall temperature factor of 1·0 Å^2 was used and an *R* based on intensities of 6·8 % was obtained from a refinement of the scale factor and the O(*x*) parameter. Further refinements including a variable cation distribution gave no improvement and produced no change in the value of O(*x*). The observed and calculated intensities are given in Table 5, the atom positions in Table 6, and the structure and *B* cation environment in Figs. 6 and 7.

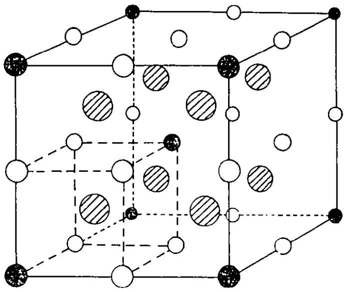

Fig. 4. Body-centred cubic structure of $Ba_4Sb_3LiO_{12}$. Striped circles are Ba, shaded circles are Li and open circles are Sb (oxygens not shown).

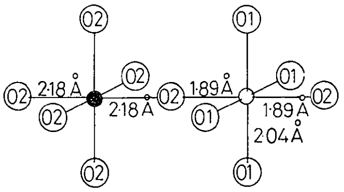

Fig. 5. The *B* cation environments in $Ba_4Sb_3LiO_{12}$.

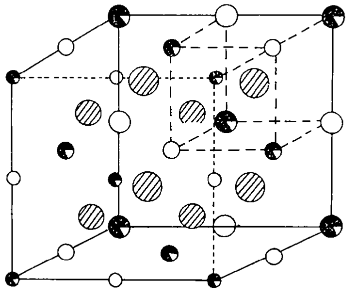

Fig. 6. The face-centred cubic structure of $Ba_5Te_3Li_2O_{15}$. Striped circles are Ba, open circles are Te and five-sixths shaded circles are Li/Te (oxygens not shown).

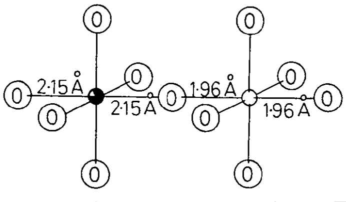

Fig. 7. The *B* cation environments in $Ba_5Te_3Li_2O_{15}$.

Table 6. *Atomic positional parameters for* $Ba_5Te_3Li_2O_{15}$ *obtained from X-ray intensity refinement*

x, *y*, *z* are fractions of the unit-cell edges.
The error refers to one standard deviation.

$Ba_5Te_3Li_2O_{15}$ (*Fm*3*m*)

		x	*y*	*z*
Ba	8(*c*)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
Te	4(*b*)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
0·8Te 3·2Li	4(*a*)	0	0	0
0	24(*e*)	0·262 (4)	0	0

R(intensities) = 6·8 %

$Ba_5U_3Li_2O_{15-x}$

A sample (~1·5g) was prepared by firing the starting mixture at 600 °C (24 h), 800 °C (24 h), 950 °C (48 h), 1000 °C (48 h). The 600 °C product was ochre and the remainder brown. The final composition was $Ba_5U_3Li_2O_{14\cdot05(10)}$. All the low-angle lines of X-ray diffraction patterns could be indexed on a cubic unit cell with *a* = 8·536 (2) Å (Table 7). The high-angle lines, however, were broad and there was evidence of splitting which suggests a small distortion to lower symmetry.

Table 7. $Ba_5U_3Li_2O_{14}$ *X-ray diffractometer data*

I(obs)	*I*(cal)	*d*(obs)	*d*(cal)	*h k l*
1·3		6·04	6·05	1 1 0
29·8	29·2	4·94	4·93	1 1 1
0·9	0·5	4·28	4·27	2 0 0
0·4		3·808	3·818	2 1 0
0·4		3·498	3·485	2 1 1
100·0	99·5	3·017	3·018	2 2 0
0·2		2·843	2·845	2 2 1
14·2	14·3	2·574	2·574	3 1 1
0·9	1·5	2·464	2·464	2 2 2
0·4		2·283	2·281	3 2 1
29·3	28·6	2·133	2·134	4 0 0
5·3	5·5	1·958	1·958	3 3 1
0·9		1·860	1·863	4 2 1
0·9		1·817	1·820	3 3 2
39·1	38·6	1·743	1·742	4 2 2
3·6	5·4	1·642	1·643	5 1 1
0·9		1·586	1·585	5 2 0
20·0	16·8	1·509	1·509	4 4 0
6·2	5·0	1·446	1·443	5 3 1
16·9	16·2	1·350	1·350	6 2 0
0·9	1·6	1·304	1·302	5 3 3
4·9	5·2	1·232	1·232	4 4 4
2·2	2·6	1·195	1·195	7 1 1
17·8	18·4	1·1404	1·1407	6 4 2
2·2	2·7	1·1122	1·1116	7 3 1

A full refinement was not therefore attempted but it is interesting to note that the main reflexions corresponding to the *Fm*3*m* space group (*cf.* $Ba_5Te_3Li_2O_{15}$) could be refined to give an *R*(*I*) of 4·4 % with a model similar to that derived for the Te-containing compound; *i.e.* one *B* site contains U and the other Li/U in a 4:1 ratio.

There are, however, extra features; additional weak reflexions apparently indicate a simple cubic rather than an f.c.c. structure but may be associated with a small lattice distortion and less than ideal stoichiometry. If the low oxygen content arises from U(V) on the U only sites while the remaining U ions are in the (VI) oxidation state then the average formal charge of the mixed U/Li sites would be 2 and the ideal composition $Ba_5U_3Li_2O_{13\cdot 8}$. Heating the compound to 1250°C (24 h) effected further reduction to $Ba_5U_2Li_2O_{12\cdot 96(5)}$ which is fairly close to the limiting composition ($Ba_5U_3Li_2O_{12\cdot 6}$) corresponding to a reduction of U(V) to U(IV). There were no apparent structural changes. Maintaining the original compound under an oxygen pressure of 180 atm at 800°C (24 h), 700°C (48 h) and 500°C (48 h) did not cause any detectable oxidation.

Table 8. *Tolerance factors*

	r_B(Å)	Δr(Å)	t
$Ba_4Ta_3LiO_{12}$	0·64	0·10	1·04
$Ba_4Nb_3LiO_{12}$	0·64	0·10	1·04
$Ba_4Sb_3LiO_{12}$	0·61	0·13	1·05
$Ba_4Bi_3LiO_{12}$	~0·74	~0·0	~1·00
$Ba_5W_3Li_2O_{15}$	0·58	0·16	1·05
$Ba_5Te_3Li_2O_{15}$	~0·56	~0·18	~1·05
$Ba_5U_3Li_2O_{13\cdot 8}$	~0·75	0·01	1·00

Discussion

The tolerance factor [$t=(r_A+r_X)/2(r_B+r_X)$, where r_A, r_B and r_X are the radii of *A* cations, *B* cations and anions respectively] is a useful starting point for discussion of perovskite structures. Estimated tolerance ratios based on the Shannon & Prewitt (1965) compilation of ionic radii and assuming an average *B* cation radius are given in Table 8. With the exception of $Ba_4Bi_3LiO_{12}$ and $Ba_5U_3Li_2O_{13\cdot 8}$ all the ratios are greater than 1·0 so that we might expect mixed stacking sequences containing both cubic and hexagonal stacking of AO_3 layers and some face-shared *B* cation octahedra. The difference in charge between the two *B* cations varies from 5 in $Ba_5W_3Li_2O_{15}$ to 3 in $Ba_5U_3Li_2O_{13\cdot 8}$ so that one would also predict *B* cation ordering though, as this work shows, care must be taken to establish the ordering conditions. These expectations are borne out by the compounds containing Ta, Nb and W where cation ordering and the stacking sequence is clearly linked. In these three compounds the electrostatic repulsive forces between the face-shared octahedra must be reduced by pairing of Li and transition metal ions. A similar argument might also apply to $Ba_4Sb_3LiO_{12}$ and $Ba_5Te_3Li_2O_{15}$; that these two compounds do not show analogous structures suggests specific influences arising from covalency. The major difference between transition metal and *B* group ions is the extent to which π bonding may influence structure in the former. Thus Goodenough & Kafalas (1973) in analysing perovskites of ABO_3 stoichiometry suggest that we should expect 180° cation–anion–cation angles with transition metal ions but bent bonds with the *B* group ions. Such behaviour is borne out by a comparison of $KSbO_3$ and high-temperature $KNbO_3$ but does not apply in the present case.

Examination of the oxygen octahedra in Ba_4(Ta or Nb)$_3LiO_{12}$ and in $Ba_5W_3Li_2O_{15}$ indicates considerable displacement of the transition metal ion from the centre both in the face-shared and corner-shared octahedra. Furthermore, short metal–oxygen distances ensue. For example, in the W compound, the W–O(3) (1·85 Å) and W–O(1) (< 1·90 Å) distances approach those observed in tetrahedral species such as WO_2Cl_2 (W–O = 1·79 Å) and WO_4^{2-} (W–O = 1·80 Å). We take this as an indication that π bonding involving the relatively low-lying 5*d* orbitals is important. By contrast in the Sb and Te compounds where π bonding would involve *d* orbitals which are now much higher in energy, the particular ordering scheme adopted does not affect the centre of symmetry of the octahedron.

In $Ba_4Sb_3LiO_{12}$ the ordered structure is no doubt stabilized by the contraction in the Sb–O–Li link while in $Ba_5Te_3Li_2O_{15}$ the ordered structure allows TeO_6 units be become as isolated as possible, again, strengthening σ bonding. Face sharing of Sb is not always ruled out, however, for compounds of the type $Ba_3Sb_2MO_9$ (M = Mg, Ni, Co, Ca, Sr, Ba) exist with the 6*H* structure. For these compounds two different situations exist. With the transition metal ion incorporated, the tolerance ratio is large ($t\sim 1$) so that we can envisage that the introduction of hexagonal packing is now the dominant effect and presumably leads to the divalent ion and Sb in opposing face-shared octahedra. With the large Group II cations, on the other hand, the discrepancy between the sizes of the Sb^{5+} and M^{2+} cations is now so large that it is unlikely that tolerance-factor arguments are still applicable. Indeed, one can speculate that the larger M^{2+} cation forces Sb ions into face-shared pairs. Some direct evidence on this point would be valuable. The absence of face-shared octahedra in the corresponding compounds Ba_3(Ta or Nb)$_2MO_9$ (M = Ca, Zn, Cd, Ni, Mn) may again appear to run counter to earlier arguments but the 3*C* structure adopted by most of these compounds still allows considerable trigonal displacement of Ta or Nb.

The slightly larger size of Bi(V) would make a cubic structure likely (as observed) but the absence of cation ordering is surprising. Reduction occurs if the product is heated above 900°C and it is possible that the absence of a doubled cell merely reflects failure to achieve the equilibrium cation distribution by heat treatment below this temperature. If $Ba_5U_3Li_2O_{13\cdot 8}$, which we believe to be effectively a V/II perovskite, is truly cubic this would be in line with the V/II perovskites such as Ba_2UZnO_6 and $Ba_3U_2MnO_9$ which also have a doubled cubic cell, but the influence of the oxygen vacancies and the origin of the small lattice distortion requires further investigation.

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The Crystal Structure of 2-*cis*-4-Hydroxyretinoic Acid γ-Lactone*

BY M. M. THACKERAY AND G. GAFNER

National Physical Research Laboratory, C.S.I.R., P.O. Box 395, *Pretoria, South Africa*

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2-*cis*-4-Hydroxyretinoic acid γ-lactone, $C_{20}H_{26}O_2$, is triclinic ($P\bar{1}$) with $a=18{\cdot}67$ (2), $b=7{\cdot}51$ (1), $c=6{\cdot}87$ (1) Å, $\alpha=111{\cdot}04$ (12), $\beta=83{\cdot}77$ (12), $\gamma=98{\cdot}96$ (12)°, $D_c\doteq1{\cdot}12$ g cm^{-3} for $Z=2$. The structure was solved by Patterson and Fourier methods and refined to an R of 0·072. The double-bond system in the molecule is in the all-*trans* configuration except where the chain is attached to the cyclohexene ring. Here the double bonds are in a near *s-cis* configuration, with a dihedral angle of 45·2° between the planes of the chain and the ring. The five-membered butenolide ring is planar, and is almost coplanar with the chain.

Introduction

During studies of the reaction of *trans*-β-ionylideneacetaldehyde with 3-methylbut-2-enolide by Dr B.V. Burger and Mr F. E. Greeff of the Department of Chemistry, University of Stellenbosch, two products were formed which could not be identified by n.m.r. or other methods at their disposal. They were thought to be the isomers depicted in Fig. 1(*a*) and (*b*), but no certainty could be reached on this point. Crystals of these two compounds were therefore submitted to the authors for structure analysis. Here we report the structure of one product which was found to be 2-*cis*-4-hydroxyretinoic acid γ-lactone [Fig. 1(*c*)]. The structure of the other isomer has also been determined and is illustrated in Fig. 1(*d*). It differs in the *cis*-linkage at C(10) and will be reported fully later.

Experimental

Yellow crystals of 2-*cis*-4-hydroxyretinoic acid were provided by Burger & Greeff. Weissenberg photographs indicated that the crystals were triclinic ($P\bar{1}$) with $a=18{\cdot}67(2)$, $b=7{\cdot}51(1)$, $c=6{\cdot}87(1)$ Å, $\alpha=111{\cdot}04$ (12), $\beta=83{\cdot}77(12)$, $\gamma=98{\cdot}96(12)$° and $D_c=1{\cdot}12$ g cm^{-3} for $Z=2$. The density was measured as 1·12 g cm^{-3} by flotation in potassium iodide solution.

A crystal with dimensions $0{\cdot}9\times1{\cdot}0\times1{\cdot}1$ mm was used to collect intensities on a Philips PW 1100 diffractometer at 20°C with graphite-monochromated Mo $K\alpha$ radiation. 2174 reflexions were measured by the ω scan technique between 3 and 22°θ. A scan speed of 0·04° s^{-1} and a scan width of 1·2° were employed. The background was counted for half the scanning time on both sides of each reflexion. 218 were rejected as unobserved by the criterion $I<1{\cdot}65\sigma(I)$, where $\sigma(I)=[(0{\cdot}02N_o)^2+N_o+K^2N_b]^{1/2}$, N_o is the gross count, N_b the background count and K the ratio of scan to background time.

During data collection repetition of three standard reflexions every hour showed that the crystal was stable as the maximum intensity variation was 0·6% from its mean value.

Lorentz and polarization factors were applied to give relative structure factors. No absorption corrections were made as μR was only 0·04. The scattering factors for C and O were those of Cromer & Mann (1968), and for H those of Stewart, Davidson & Simpson (1965).

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* C.S.I.R.- R. Fis. 689.