Acta Cryst. (1974). **B30**, 816

A Powder Neutron-Diffraction Determination of the Structure of $Ba_5W_3Li_2O_{15}$

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(*Received* 15 *November* 1973; *accepted* 17 *November* 1973)

The structure of the hexagonal ordered perovskite-like compound $Ba_5W_3Li_2O_{15}$ has been determined by profile analysis of powder neutron-diffraction data. The structure is based on a ten-layer stacking sequence (*cccch*) of the BaO_3 layers (space group $P6_3/mmc$) with occupation of the face-shared octahedra by equal amounts of tungsten and lithium. The remaining two tungsten atoms and one lithium atom are ordered over the corner-sharing octahedra in the sequence W–Li–W. The local oxygen environment of the cations is compared with that in $Ba_4Ta_3LiO_{12}$.

Introduction

The perovskite ABO_3 and related structures may be envisaged as consisting of close-packed AO_3 layers with B cations in the interstitial positions. Many polytypes are known [see for example Goodenough & Longo (1970)] which differ in the ratio of the number of cubic to hexagonal stacked AO_3 layers. The main observed polytypes and some theoretical predictions have been summarized by Katz & Ward (1964).

Two recent independent reports (Negas, Roth, Parker & Brower, 1973; Collins, Jacobson & Fender, 1974) have demonstrated that it is possible for Li to coexist on the B sites with cations of high oxidation state (*e.g.* Ta, W) and that unusual stacking sequences occur. Thus eight-layer phases are observed for $Ba_4M_3LiO_{12}$ (M = Nb, Ta) while in $Ba_5W_3Li_2O_{15}$ a ten-layer sequence is found.

In our earlier account we were able to show that even though a quite large cell is involved, profile analysis of the neutron-diffraction powder pattern enables us to determine both the cation distribution and the local oxygen environment of the B cations. In the present investigation, details of the structure of $Ba_5W_3Li_2O_{15}$ are presented.

Experimental

Sample preparation

The starting materials, $BaCO_3$, Li_2CO_3 and WO_3, were obtained from Johnson Matthey Specpure Chemicals Ltd. The $BaCO_3$ and Li_2CO_3 were pre-fired in CO_2 at 1000 and 500 °C respectively. A stoichiometric mixture of the starting material was ground in an agate mortar and heated in a sintered alumina crucible. There was no reaction with the crucible. A 15g sample of $Ba_5W_3Li_2O_{15}$ for the neutron-diffraction experiment was prepared by heating the original mixture in air at 450 °C (24h), 650 °C (48 h), 800 °C (48 h), 900 °C (24 h), 950 °C (72h) and 1000 °C (96 h) and the composition of the final white product, calculated from the weight loss on reaction, was $Ba_5W_3Li_2O_{15\cdot00(3)}$. An attempt to prepare the analogous molybdenum compound by a similar method gave only a mixture of $BaMoO_4$, $BaCO_3$ and Li_2CO_3. From an X-ray diffractometer trace taken with a Philips goniometer and Cu $K\alpha$ radiation the positions of 132 reflexions were measured in the range $5° < 2\theta < 140°$. All the lines were indexed on a hexagonal unit cell with $a = 5\cdot7559$ (6) and $c = 23\cdot719$ (3) Å obtained by least-squares refinement of 98 non-overlapping reflexions. The X-ray cell constants are in good agreement with those determined by Negas *et al.* (1973).

Because of the possibility of lithium volatilization the tungsten compound was dissolved in a mixture of HNO_3, $HClO_4$ and HF and analysed for lithium by atomic absorption spectroscopy. The lithium content was found to be $0\cdot91 \pm 0\cdot01$ wt.% compared with a theoretical value of 0·930 wt.%.

Neutron diffraction

The neutron-diffraction measurements were made at liquid helium temperature on a powder diffractometer at the reactor PLUTO, AERE Harwell. The sample was contained in a thin-walled vanadium can and a wavelength of 1·540 Å, obtained from the (511) planes of a germanium monochromator, was employed. The take-off angle was 90°. The counter was stepped every 0·02° with total counts accumulated every 0·1° interval. Absorption and extinction effects were small and no corrections were made.

The structural parameters were refined from data in the range $13° < 2\theta < 74°$ by full-matrix least-squares analysis of the powder diffraction profile (Rietveld, 1967) which has been described previously (Collins *et al.*, 1974). The refinement was based on the space group $P6_3/mmc$ with the starting parameters corresponding to ideal close packing of BaO_3 layers with stacking sequence *cccch*. Two lithium atoms were placed in position 2(*a*), four tungsten atoms in 4(*f*) and two lithium and two tungsten atoms in 4(*f*). Half of the lithium atoms are consequently in octahedra which corner-share with octahedra containing tungsten atoms (Fig. 1). Because the differences between individual atom temperature factors are small at

4·2°K, a single overall value was used. The scattering lengths were: $b_{Ba}=0{\cdot}52$, $b_W=0{\cdot}48$, $b_{Li}=0{\cdot}214$ and $b_O=0{\cdot}580\times10^{-12}$ cm (Neutron Diffraction Commission, 1972).

The program minimizes the function $\chi^2=\sum_i w_i[y_i(\text{obs})-y_i(\text{calc})/c]^2$ where w is the weighting function, y the number of counts at a point in 2θ and c is a scale factor. 16 parameters (Table 1) were refined. The reliability index defined as R_{profile} (weighted)

$$=\frac{100\sum w\left(y_{\text{obs}}-\frac{1}{c}\,y_{\text{calc}}\right)^2}{\sum w(y_{\text{obs}})^2}$$

converged to a value of 8·7% compared with an idealized minimum of 6·5%. The data were refined until all parameter shifts were less than $0{\cdot}3\sigma$ and in the final refinement all composition constraints were removed.

The atom positions are given in Table 1 and important bond angles and interatomic distances in Table 2. Table 1 shows that the total occupation numbers for lithium and tungsten are in good agreement with the expected stoichiometry. The experimental and calculated profiles, a difference plot and the positions of the Bragg reflexions are shown in Fig. 2. The site occupancies indicate close to ideal ordering. There may be some residual disorder but as the deviations would involve tungsten atoms in both face-sharing octahedra it is quite likely that the ordering is complete, and that the discrepancies represent experimental error.

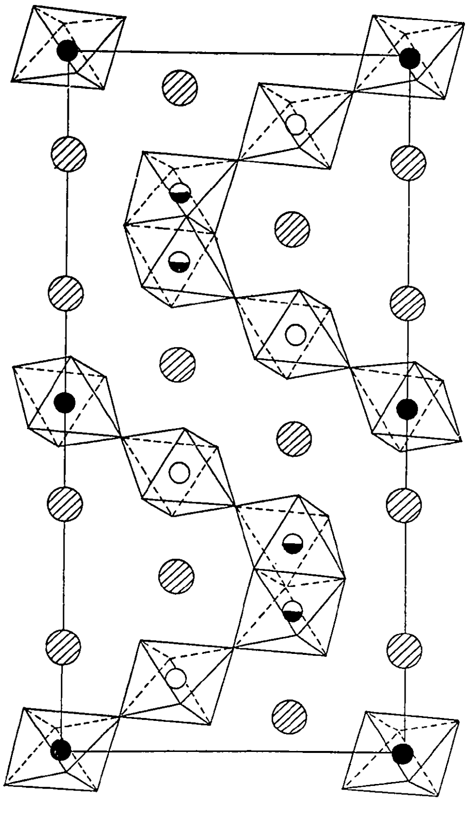

Fig. 1. Ten-layer $Ba_5W_3Li_2O_{15}$ structure. Striped circles are Ba; open circles are W; shaded circles are Li; and half-shaded W/Li.

Table 1. *Atomic positional parameters for* $Ba_5W_3Li_2O_{15}$ *at* 4·2°K *obtained from neutron refinement*

$Ba_5W_3Li_2O_{15}$ ($P6_3/mmc$). Overall temperature factor $B=0{\cdot}38\ (8)$ Å^2

	Positions	x	y	z
Ba(1)	2(*d*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$
Ba(2)	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0·0498 (6)
Ba(3)	4(*e*)	0	0	0·1552 (6)
Li	2(*a*)	0	0	0
W	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0·5957 (6)
W/Li	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0·2037 (12)
O(1)	6(*h*)	0·1774 (12)	0·3548 (12)	$\frac{1}{4}$
O(2)	12(*k*)	0·5056 (9)	0·0112 (9)	0·1482 (3)
O(3)	12(*k*)	0·8246 (8)	0·6492 (8)	0·0545 (2)

Occupation numbers

	Position	Lithium	Tungsten
Li	2(*a*)	1·96 (4)	0·04 (4)
W	4(*f*)	0·24 (6)	3·76 (6)
W/Li	4(*f*)	1·78 (7)	2·22 (7)
Total occupation		3·98 (17)	6·02 (17)

Discussion

The refined structure determined here confirms the B cation ordering suggested by Negas *et al.* (1973) and is closely similar to that found by Collins *et al.* (1974) for $Ba_4Ta_3LiO_{12}$. In both compounds the introduction of the monovalent ion stabilizes the hexagonal structure by reducing the B cation repulsions across the face-shared octahedra. The unusual feature of the $Ba_5W_3Li_3O_{15}$ structure is the presence of the additional lithium confined to the central of the string of three corner-shared octahedra. In an attempt to understand this cation distribution the electrostatic potentials at each of the B cation sites have been calculated by the method of Tosi (1964). These potentials depend on assumptions about cation ordering but, as Table 3 shows, the order of sites of increasing negative potential is unchanged whether a random or the observed distribution is introduced. The most negative site is occupied by W and the least negative by Li with the intermediate sites containing both W and Li so that the cation ordering appears to be determined by electrostatic terms. We also note that cation ordering gives a large contribution (~400 kcals mol^{-1} of ABO_3) to the Madelung part of the lattice energy.

In addition to the cation ordering, neutron analysis reveals details of the atomic positions, and the local cation environments in $Ba_5W_3Li_2O_{15}$ and $Ba_4Ta_3LiO_{12}$ may be compared in Figs. 3 and 4. In both cases the face-shared octahedra are considerably distorted. The distance between the W/Li site and a face-shared oxygen ion is 1·90 Å, whereas the distance between W/Li and the nearest-neighbour corner-shared oxygen ion is relatively long at 2·17 Å. The values represent, however, average interionic distances for occupation of the site by both lithium and the transition metal. In fact the pairs of face-shared octahedra must almost certainly each contain one lithium and one tungsten atom, though this is not a point that can be proved from Bragg data. The oxygen octahedra in the immediate vicinity of an individual W atom will therefore be contracted relative to the average values and there will be a corresponding expansion of the Li-containing octahedra. It is not possible to judge to what extent the

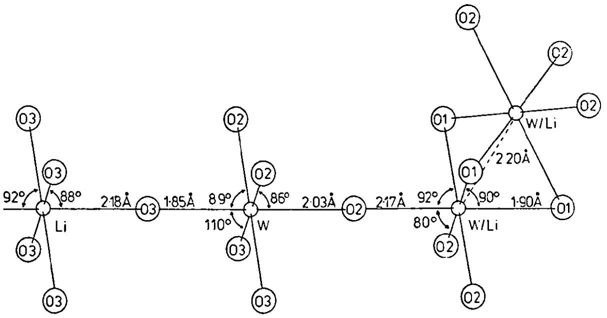

Fig. 3. The B cation environment in $Ba_5W_3Li_2O_{15}$.

Table 2. *Bond distances and angles in* $Ba_5W_3Li_2O_{15}$

Ba(1)–O(1)	2·880 (7) Å	W——O(3)	1·847 (12) Å
Ba(1)–O(2)	2·902 (5)	W/Li–O(1)	1·903 (18)
Ba(2)–O(2)	2·893 (12)	W/Li–O(2)	2·166 (21)
Ba(2)–O(3)*	2·881 (5)	W/Li–W/Li	2·196 (30)
Ba(2)–O(3)†	2·932 (12)	O(1) –O(1)	2·693 (14)
Ba(3)–O(1)	2·962 (11)	O(1) –O(2)	2·922 (13)
Ba(3)–O(2)	2·884 (5)	O(2) –O(2)	2·781 (10)
Ba(3)–O(3)	2·858 (12)	O(2) –O(3)	2·729 (12)
Li——O(3)	2·175 (5)	O(3) –O(3)*	3·031 (9)
W——O(2)	2·031 (13)	O(3) –O(3)†	3·121 (11)
O(2)—W–O(2)	86·4 (0·9)°	O(3) –Li ——O(3)†	91·7 (0·6)°
O(2)—W–O(3)	89·3 (0·6)	O(1) –W/Li–O(1)	90·0 (1·0)
O(3)—W–O(3)	110·3 (1·0)	O(1) –W/Li–O(2)	91·6 (0·5)
O(3)—Li–O(3)*	88·3 (0·6)	O(2) –W/Li–O(2)	79·0 (0·6)
W/Li–L(1)–W/Li	70·4 (0·8)		

* Atoms in same layer.
† Atoms in adjacent layers.

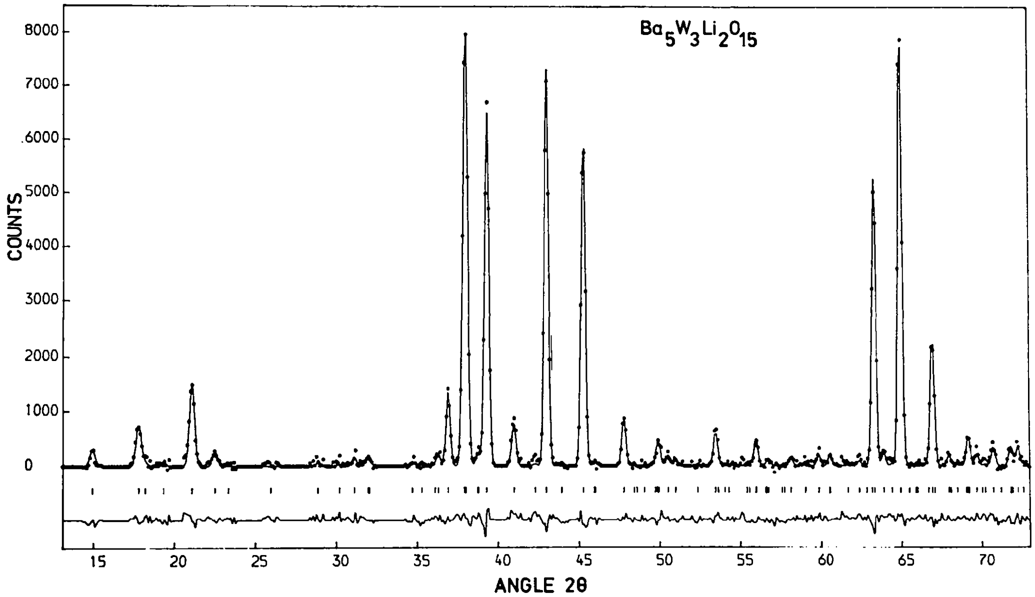

Fig. 2. Powder neutron-diffraction profile for $Ba_5W_3Li_2O_{15}$. Small circles are the experimental points, and the continuous line passes through the calculated points. The small vertical lines are the calculated *hkl* positions and the bottom trace is a difference plot.

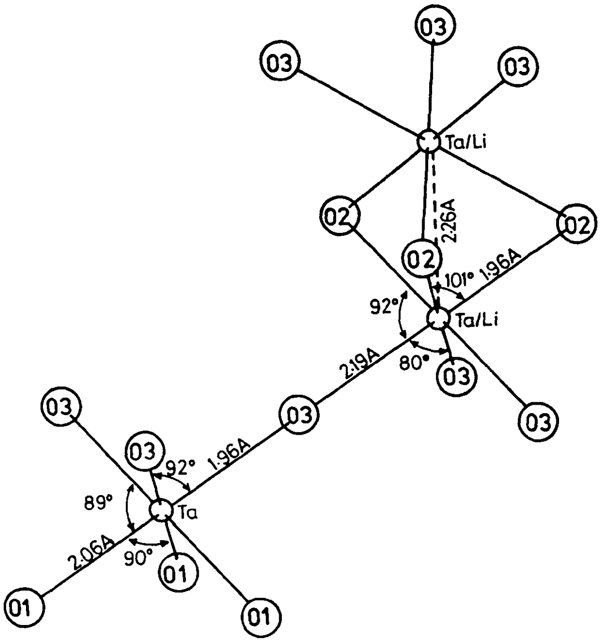

Fig. 4. The B cation environment in $Ba_4Ta_3LiO_{12}$.

Table 3. *Site potentials in* $Ba_5W_3Li_2O_{15}$

	Site potential (observed distribution)	Site potential (random distribution)
Li	−1·627	−2·713
W	−4·205	−3·325
W/Li	−2·477	−2·746

cations in the face-shared octahedra are pushed together by the electrostatic repulsion of neighbouring W ions or how far the observed displacement is favoured by increased π-bonding between tungsten and oxygen. In either case the effects are more pronounced in $Ba_5W_3Li_2O_{15}$ than in $Ba_4Ta_3LiO_{12}$, as expected. The very short W–O(3) distance of 1·85 Å illustrates the large displacements which can occur when an oxygen ion is shared between cations of very different formal charge.

We are grateful to the Science Research Council and AERE Harwell for the provision of neutron facilities, and Mr D. H. C. Harris and members of the University Support Staff for experimental assistance. One of us (B.M.C.) thanks AERE for the provision of a studentship.

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