

A Single-Crystal Study of Barium Tungsten Lithium Oxide: a Compound with a Ten-Layer Structure

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A single-crystal study of a sample of barium tungsten lithium oxide, supplied by Dr. T. Negas and identified as $\text{Ba}_5\text{W}_3\text{Li}_2\text{O}_{15}$, confirms the |(5)|(5)| layer stacking scheme (Zhdanov notation) for the ten BaO_3 layers per unit cell. Pairs of face-sharing MO_6 octahedra ($M=\text{W}$ or Li) are linked through corner sharing by strings of three corner-sharing octahedra. In these strings of three, the two outer octahedra are occupied by W ; but no X-ray evidence was found for the existence of Li in the middle one. The compound has a hexagonal cell of dimensions $a = 5.7614 \pm 0.0008 \text{ \AA}$ and $c = 23.719 \pm 0.007 \text{ \AA}$, probable space group $P6_3/mmc$, $Z = 2$. Its structure was determined from 757 independent reflections, of which 426 were considered observed, collected by automated counter methods, and refined by least-squares methods to a conventional R of 0.064. The X-ray refinement based on the assumption that two octahedral sites in the unit cell are empty suggests formulas such as $\text{Ba}_5\text{W}_{3.2}\text{Li}_{0.8}\text{O}_{15}$ or $\text{Ba}_5\text{W}_3\text{LiO}_{14.5}$ rather than the "ideal" formula $\text{Ba}_5\text{W}_3\text{Li}_2\text{O}_{15}$.

Introduction

A discussion of structure relations in mixed metal oxides which can be described in terms of various stacking sequences of close-packed layers of composition AO_3 has been given by Katz and Ward (1). Recently, Negas et al. (2) have studied the crystal chemistry of lithium in octahedrally coordinated structures and have among other compounds prepared a compound with an eight-layer structure of composition $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ and a compound with a ten-layer structure containing tungsten.

Crystals of both of these compounds were kindly sent to us by Dr. Negas. A single crystal study of $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ has been published (3). We now report the results of a single crystal study of the compound with a ten-layer structure.

Experimental

The crystal chosen for study was clear, had well-defined faces, and approximated a sphere 0.1 mm in diameter. Precession photo-

graphs showed hexagonal symmetry and indicated the probable space group to be one of $P\bar{6}2c$, $P6_3mc$, or $P6_3/mmc$. A least-squares method using 12 well-centered reflections on a Picker automated diffractometer gave cell dimensions of $a = 5.7614 \pm 0.0008 \text{ \AA}$ and $c = 23.719 \pm 0.007 \text{ \AA}$, in reasonable agreement with those previously reported (2). Full rotation photographs were used to confirm that these cell dimensions were not fractions of true cell dimensions.

The hemisphere of reflections with positive l values for 2θ out to 15° and the quadrant with positive k and positive l for 2θ out to 75° were recorded with a Picker automated diffractometer with graphite monochromatized Mo radiation, pulse height discrimination, and a scintillation counter. The θ - 2θ scan technique was used at $1^\circ 2\theta/\text{min}$. Background was counted for 10 sec at each end of the 2.67° scan range.

After averaging symmetry related reflections, 757 independent reflections were obtained of which 426 were greater than 2σ for the background and were considered

observed. An absorption correction was applied using a spherical approximation for the shape of the crystal.

Structure Determination

Statistical analysis of the reflection intensities indicated a centric distribution, so the probable space group is $P6_3/mmc$. Taking 2.3–2.4 Å as the thickness of a BaO_3 layer, the c axial length of 23.7 Å suggests a 10-layer structure. Three ten-layer stacking sequences are possible in space group $P6_3/mmc$. In Zhdanov notation these are $|(5)|(5)|$; $|1(3)1|1(3)1|$; and $|2(1)2|2(1)2|$. These correspond to 80% cubic layers (adjacent layers different) and 20% hexagonal layers (adjacent layers alike) for $|(5)|(5)|$, and 40% cubic layers, 60% hexagonal layers for the other two sequences. In terms of face-sharing and corner-sharing octahedra the sequences may be described, respectively, as pairs of face-sharing octahedra connected by triplets of corner-sharing octahedra; quadruplets of face-sharing octahedra connected by single corner-sharing octahedra; and triplets of face-sharing octahedra connected by pairs of face-sharing octahedra (no octahedra sharing only corners). For " $Ba_5W_3Li_2O_{15}$," Negas et al. (2) established the $|(5)|(5)|$ sequence from powder data, the ten-layer sequence with the minimum amount of face sharing; this arrangement is confirmed in our study. The ten octahedral sites correspond to positions $2a$ and $4f$ (twice). Both $4f$ positions were assumed occupied by W, and the population parameters were allowed to vary. The population parameter for the fourfold face-sharing position refined to 52%, thus supporting the idea that the face-sharing octahedra are randomly filled by Li and W.

An initial difficulty in the isotropic refinement was encountered when the population parameter for the W in the fourfold corner-sharing position refined to 108%, suggesting possible Pt substitution from the Pt tubes in which the crystals were grown. However, microprobe analysis revealed no Pt in the crystal. Since the population parameter and temperature factor are highly correlated, it

was concluded that the high value for the population parameter was an accident of the refinement in which a high value for the population parameter was compensated for by a relatively high value for the temperature factor. With the population parameter reset to 100%, there was no difficulty in obtaining convergence for the W in the corner-sharing octahedra.

A different problem arose with the Li which was assumed to be in the twofold corner-sharing position, i.e., in the octahedra in the centers of the strings of three corner-sharing octahedra. Attempts to refine the temperature factor for Li led to an astronomical increase which after a few cycles stopped the refinement. Alternatively, holding the temperature factor fixed and allowing the population parameter to vary, led to an emptying of the site. All the evidence up to this point, therefore, indicated that Li does not occupy the centers of the middle octahedra of the strings of three corner-sharing octahedra.

Refinement of the model with ten BaO_3 layers, four W in corner-sharing octahedra and W and Li randomly arranged in the four face-sharing octahedra (approximated by using W with a population parameter of 0.52) led to a conventional R of 0.085 with isotropic temperature factors. Anisotropic thermal parameters for the metal atoms lowered R to 0.069. Application of a weighting scheme previously described (4) lowered R to 0.064 and the weighted R to 0.060.

Atomic scattering factors for the neutral atoms and the real and imaginary parts of the anomalous dispersion factors were taken from the International Tables (5). Calculations were carried out with X-ray system (6). Final atomic parameters are given in Table I, bond lengths and angles in Table II, and observed and calculated structure factors in Table III.¹ Eleven reflections strongly affected by extinction were omitted from the refinement; these are labeled with an E in Table III.

The stereo illustration of the unit cell contents (Fig. 1) and the drawing of the small cation environment (Fig. 2) were prepared using ORTEP (7).

¹ Copies of Table III are available from Prof. Katz.

TABLE I
 ATOMIC PARAMETERS FOR $\text{Ba}_5\text{W}_3\text{LiO}_{15-x}$ ^a SPACE GROUP $P6_3/mmc$ (No. 194)

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	U_{12}^b	U_{33}^b
Ba(1)	2 <i>d</i>	1/3	2/3	3/4	42 (5)	59 (14)
Ba(2)	4 <i>f</i>	1/3	2/3	0.0489 (1)	40 (3)	67 (11)
Ba(3)	4 <i>e</i>	0	0	0.1529 (1)	44 (3)	143 (11)
W(1) ^c	4 <i>f</i>	1/3	2/3	0.2004 (1)	23 (5)	39 (19)
W(2)	4 <i>f</i>	1/3	2/3	0.9031 (1)	14 (2)	11 (7)
<i>U</i>						
O(1)	12 <i>k</i>	0.5061 (25)	0.0122	0.1479 (7)	106 (29)	
O(2)	6 <i>h</i>	0.1740 (35)	0.3479	1/4	307 (81)	
O(3)	12 <i>k</i>	0.1740 (16)	0.3480	0.5538 (7)	55 (27)	

^a Thermal parameters have been multiplied by 10⁴.

^b $U_{11} = U_{22} = 2U_{12}$ and $U_{13} = U_{23} = 0$.

^c W(1) has a population parameter of 0.52. Its position is assumed to be randomly occupied by W and Li.

TABLE II
 INTERATOMIC DISTANCES AND ANGLES, $\text{Ba}_5\text{W}_3\text{LiO}_{15-x}$

Distances					
W(1)–O(1)	2.125 (18) Å	3×	O(1)–O(1)	2.777 (11) Å	
–O(2)	1.978 (2)	3×		2.778 (18)	
–W(1)	2.337 (2)			2.989 (18)	2×
W(2)–O(1)	2.007 (17)	3×	–O(2)	2.931 (15)	2×
–O(3)	1.890 (14)	3×	–O(3)	2.740 (21)	2×
Ba(1)–O(1)	2.898 (14)	6×	O(2)–Ba(1)	2.884 (2)	2×
–O(2)	2.884 (2)	6×	–Ba(3)	2.880 (3)	2×
Ba(2)–O(1)	2.908 (13)	2×	–O(1)	2.931 (15)	4×
	2.909 (17)		–O(2)	2.757 (2)	2×
–O(3)	2.887 (10)	6×		3.010 (2)	2×
	2.904 (15)	3×	O(3)–Ba(2)	2.887 (10)	2×
Ba(3)–O(1)	2.886 (15)	6×		2.904 (15)	
–O(2)	2.881 (3)	3×	–Ba(3)	2.916 (14)	
–O(3)	2.916 (14)	3×	–O(1)	2.740 (21)	2×
O(1)–Ba(1)	2.898 (14)		–O(3)	2.755 (7)	
–Ba(2)	2.908 (13)			2.756 (12)	
–Ba(3)	2.886 (15)	2×		3.082 (21)	2×
				3.011 (12)	2×
Angles					
	O(1)–W(1)–O(1)	89.4 (6)°			
	O(1)–W(1)–O(2)	91.1 (4)			
	O(1)–W(1)–O(2)	179.3 (14)			
	O(2)–W(1)–O(2)	88.4 (1)			
	O(1)–W(2)–O(1)	87.6 (6)			
	O(1)–W(2)–O(3)	89.3 (5)			
	O(1)–W(2)–O(3)	175.7 (7)			
	O(3)–W(2)–O(3)	93.6 (5)			
	W(1)–O(1)–W(2)	178.7 (8)			

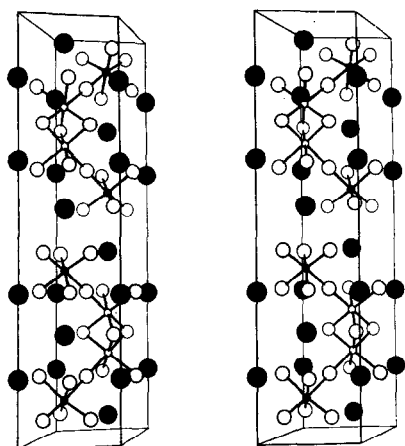


FIG. 1. Stereo view of unit cell and contents. Ba atoms are shown as large black circles, O atoms as large open circles, W atoms as small black circles, and W/Li sites as small open circles.

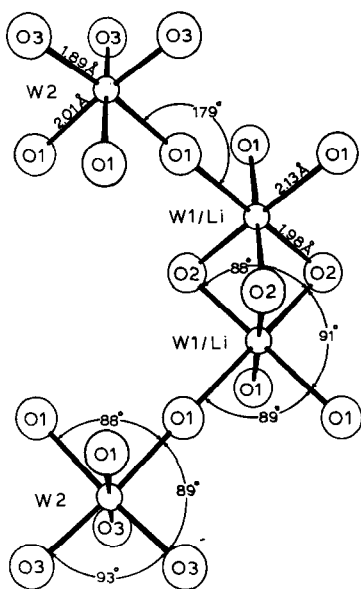


FIG. 2. Portion of structure showing face-sharing and corner-sharing octahedra.

Discussion

Negas et al. (2) have discussed the use of lithium to lower the average oxidation state of octahedrally coordinated cations in a variety of well-known structure types. In $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ (eight-layer) the random arrangement of

Li^+ and Nb^{5+} in the face-sharing pairs of octahedra removes the necessity for close approaches of highly charged cations. A similar situation appears to exist in the ten-layer structure of the tungsten containing compound.

The formula $\text{Ba}_5\text{W}_3\text{Li}_2\text{O}_{15}$ meets the charge balance requirements and fits the available crystallographic sites so well that it is hard to accept the X-ray indication that two octahedral sites (position $2a$ of the space group $P6_3/mcc$) are empty. Dr. Negas has conducted extensive phase studies which indicate a fixed composition for the compound, rather than a solid solution, so that a range of composition of the kind $\text{Ba}_5\text{W}_3\text{Li}_{2-x}\text{O}_{15-1/2x}$ with variable x does not seem likely. In addition, Jacobson, Collins, and Fender (8) have recently carried out a powder neutron diffraction study of the same compound. Concerned about the possibility of loss of lithium, they analyzed for lithium by atomic absorption spectroscopy and found the lithium content to be 0.91 ± 0.01 wt. % (theoretical 0.930 wt. %). Jacobson et al. (8) also refined occupation numbers for the various octahedral positions. Their findings were: for the $2a$ position, Li, 1.96 (4), W, 0.04 (4); for $4f$ corner-sharing octahedra, Li, 0.24 (6), W, 3.76 (6); for $4f$ face-sharing octahedra, Li, 1.78 (7), W, 2.22 (7). In particular, there is no reason to believe from their findings that the $2a$ position is empty. Indeed, Jacobson et al. (8) remark that "the unusual feature of the $\text{Ba}_5\text{W}_3\text{Li}_3\text{O}_{15}$ (sic) structure is the presence of the additional lithium confined to the central of the string of three corner-shared octahedra." In examining the evidence, however, it becomes clear that the case for the stoichiometry $\text{Ba}_5\text{W}_3\text{Li}_2\text{O}_{15}$ is not indisputable. Another composition might correspond to $\text{Ba}_5\text{W}_{3.2}\text{Li}_{0.8}\text{O}_{15}$, for example, with local and overall charge balance dictating the stoichiometry. The fact that the chemical analysis corresponds to the expected stoichiometry only means that the bulk sample has the composition of the original starting materials, not that individual crystals of a particular phase have this composition. A weakness of inorganic chemical analysis is that if no material is lost or gained, the analysis must correspond to the starting

composition. However, if the product is not completely single phase, the analysis need not correspond to that of the phase studied. Although both Negas et al. (2) and Jacobson et al. (8) have shown that the composition $\text{Ba}_5\text{W}_3\text{Li}_2\text{O}_{15}$ is single phase when prepared below the melting point, Negas has stated that this composition begins to melt above 1400°C and the preparation from which the present crystal was taken may have had some liquid present. Finally, insofar as the occupation number refinement is concerned, it is clear that the total occupancy has been constrained to be two for position $2a$ and four for position $4f$. There was thus no possibility of obtaining a value near zero for the total occupancy of position $2a$ in the neutron diffraction refinement, and it is not known what would have happened if the total occupancy were not a constraint in the refinement. It should also be pointed out that the neutron diffraction refinement could not have indicated missing Li atoms via abnormal temperature factor behavior, since a single overall temperature factor was used. This procedure is indeed reasonable if all the atoms are present, since the measurements were made at liquid helium temperature and the differences in individual atom temperature factors would be small. However, unusual behavior for individual atoms would be concealed, and in particular, if some Li atoms were missing, this fact could not be discovered from the least-squares refinement.

The conclusion to be reached from the the above discussion is that structures in which position $2a$ is empty, corresponding to compositions such as $\text{Ba}_5\text{W}_{3.2}\text{Li}_{0.8}\text{O}_{15}$ or $\text{Ba}_5\text{W}_3\text{LiO}_{14.5}$, are still possible. That the first mentioned requires the face-sharing octahedra to be 60% occupied by W, and 40% by Li is not even incompatible with the occupancy refinement for this position by Jacobson et al. (8), where an unbalance of 55% W, 45% Li is obtained.

Verification for the random occupancy of the face-sharing octahedra by W and Li was attempted by testing an ordered model in space group $P6_3mc$. Convergence was obtained (at a conventional R of 0.076) only when, using a combined W and Li scattering

factor, the population parameters for the 2 twofold face-sharing octahedral positions were allowed to vary. These population parameters refined to 48 and 61%, certainly more in keeping with the disordered model than the ordered one. In addition, attempts to place Li in the corner-sharing octahedra were completely unsuccessful. With a fixed temperature factor, these lithium atoms wandered over a wide range of z values. Allowing the temperature factor to vary led to very large values (~ 385). It is of course possible that the difficulties experienced were due to pseudo-symmetry and parameter interactions. The fact remains that the only model which could be refined was centrosymmetric and had no lithium in corner-sharing octahedra.

Empty O_6 octahedra in AO_3 layer structures are not uncommon. Examples in related oxides are $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ (9) and $\text{Ba}_2\text{Cr}_{7-x}\text{O}_{14}$ (10), although in these cases the octahedra involved are face-sharing. Empty corner-sharing octahedra are found in a number of layer halide structures (11). Missing oxygen from what would otherwise be anion octahedra also has been reported, e.g., in $\text{Ba}_3\text{Si}_4\text{Ta}_6\text{O}_{23}$ (12). Thus, the suggested compositions would not involve completely novel structural features. We are left, however, with a case which is not quite closed, since the evidence is indeed contradictory.

A comparison of the results from the single crystal X-ray and the powder neutron diffraction studies is summarized in Table IV. The X-ray results show smaller distortions than do the neutron results in that bond length and bond angle ranges are narrower in the X-ray case.

TABLE IV
A COMPARISON OF SINGLE CRYSTAL X-RAY AND POWDER NEUTRON DIFFRACTION RESULTS

	X-Ray	Neutron
Ba-O range	2.881-2.916 Å	2.858-2.962 Å
O-O range	2.74-3.08	2.69-3.12
W-O(1); W-O(3)	2.01, 1.89	2.03, 1.85
W/Li-O(1) (corner)	2.13	2.17
W/Li-O(2) (face)	1.98	1.90
O-W-O angles	88, 89, 93°	86, 89, 110°
O-W/Li-O angles	88, 89, 91°	79, 90, 92°

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