

## A Single-Crystal Study of Eight-Layer Barium Niobium Lithium Oxide, $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$

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A single-crystal study of a sample of  $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$  provided by Dr. T. Negas has been carried out and confirms the  $|4|(4)|$  layer stacking scheme (Zhdanov notation) for the eight  $\text{BaO}_3$  layers per unit cell. Of the eight  $\text{MO}_6$  octahedra per cell ( $M = \text{Nb}$  or  $\text{Li}$ ), four share faces in pairs, and these pairs are linked by pairs of corner-sharing  $\text{MO}_6$  octahedra. The compound has a hexagonal cell of dimensions  $a = 5.777 \pm 0.006 \text{ \AA}$  and  $c = 18.95 \pm 0.03 \text{ \AA}$ , probable space group  $P6_3/mmc$ ,  $Z = 2$ . The theoretical density is  $6.22 \text{ g/cm}^3$ ; within the limit of error of the pycnometrically measured density,  $6.08 \pm 0.06 \text{ g/cm}^3$ . The study was carried out with 620 independent reflections, of which 437 were considered observed, collected by automated counter methods and refined by least-squares to a conventional  $R$  value of 0.076.

### Introduction

A discussion of structure relations in mixed metal oxides which could be described in terms of close packed layers of composition  $\text{AO}_3$  has been given by Katz and Ward (1). Negas et al. (2), in their studies on the crystal chemistry of lithium in octahedrally coordinated structures, have prepared an 8L ( $L = \text{layer}$ ) compound of composition  $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$  and a 10L compound containing tungsten. Crystals of both of these compounds were sent to us by Dr. Negas. In this paper we report the results of a single-crystal study of the 8L compound.

### Experimental

The crystal chosen for study was a thin, clear, almost colorless plate 0.025 mm thick, and roughly trapezoidal in shape (parallel sides 0.37 mm and 0.25 mm, height 0.25 mm). Precession photographs indicated the probable space group to be one of  $P\bar{6}2c$ ,  $P6_3mc$ , or  $P6_3/mmc$ . The observed unit-cell parameters of  $a = 5.79 \text{ \AA}$  and  $c = 19.04 \text{ \AA}$  were in agreement with those previously reported (2). The cell dimensions obtained by least-squares refinement using 12 well-centered reflections measured with a Picker automated diffractometer gave  $a = 5.777 \pm 0.006$

$\text{\AA}$  and  $c = 18.95 \pm 0.03 \text{ \AA}$ . Full rotation photographs were used to verify that the true cell parameters were not multiples of the values found.

All reflections for which  $k \geq 0$ ,  $h \geq k$ , and  $-32 \leq l \leq 32$ ,  $2\theta \leq 75^\circ$  were measured with a Picker automated diffractometer with graphite monochromatized Mo radiation, pulse height discrimination, and a scintillation counter. The  $\theta$ - $2\theta$  scan technique was used at  $2^\circ 2\theta/\text{min}$ . Background was counted for 20 sec at each end of the  $2.67^\circ$  scan range.

Over 2800 reflections were measured which resulted after averaging in 620 independent reflections of which 437 were greater than  $2\sigma$  for the background and were considered observed. An absorption correction prior to averaging was made using Prewitt's program ACACA (3) by integration over a  $10 \times 10 \times 10$  grid.

Statistical analysis of the reflection intensities indicated a centric distribution. Since the Laue group was  $6/mmm$  and there were no systematic absences other than  $hhl$  when  $l = 2n + 1$ , the probable space group is  $P6_3/mmc$ . (No violations of this absence rule were observed on the photographs, but a couple of counter-measured intensities just exceeded the  $2\sigma$  threshold adopted for observed reflections.)

TABLE I  
 ATOMIC PARAMETERS FOR  $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ <sup>a</sup> SPACE GROUP  $P6_3/mmc$  (No. 194)

Atom	Position	x	y	z	$U_{12}$ <sup>b</sup>	$U_{33}$ <sup>b</sup>
Ba(1)	2a	0	0	0	38(3)	93(8)
Ba(2)	2b	1/3	2/3	3/4	43(3)	79(8)
Ba(3)	4f	1/3	2/3	0.1350(1)	62(3)	132(7)
Nb(2)	4f	1/3	2/3	0.5638(1)	20(3)	37(8)
					U	
Nb(1) <sup>c</sup>	4e	0	0	0.1905(3)	64(8)	
O(1)	6g	1/2	0	0	125(31)	
O(2)	6h	0.1594(35)	0.3187	1/4	253(48)	
O(3)	12k	0.8284(16)	0.6568	0.1188(6)	92(19)	

<sup>a</sup> Thermal parameters have been multiplied by  $10^4$ .

<sup>b</sup>  $U_{11} = U_{22} = 2U_{12}$  and  $U_{13} = U_{23} = 0$ .

<sup>c</sup> Nb(1) has a population parameter of 0.52. Its position is assumed to be randomly occupied by Nb and Li.

The *c* axial length, 18.95 Å, suggests an 8L stacking sequence of  $\text{BaO}_3$  layers. Two 8L stacking sequences are possible in space group  $P6_3/mmc$ . In the Zhdanov notation, these are  $|4)(4)|$ , which corresponds to 75% cubic layers (adjacent layers different) and 25% hexagonal layers (adjacent layers alike), and  $|1(2)1|1(2)1|$ ,

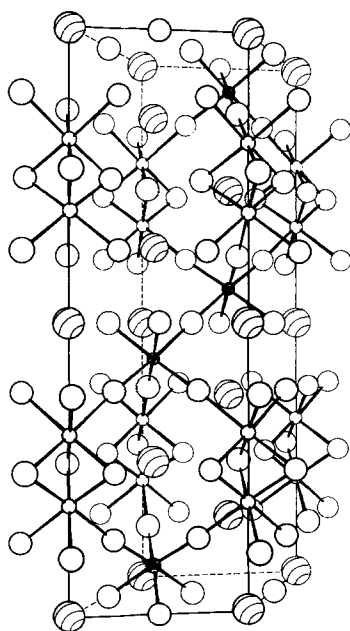


FIG. 1. Structure of  $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ . Ba atoms are shown as striped circles, O atoms as large open circles, Nb atoms as small blackened circles, and Nb/Li sites as small open circles.

which corresponds to 75% hexagonal layers and 25% cubic layers. For 8L  $\text{BaMnO}_3$ , the second arrangement was found (4, 5). For  $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ , however, the first arrangement was established from powder data by Negas et al. (2) and is confirmed in our study.

In order to test for the lithium positions, all the octahedral sites were assumed occupied by niobium, and the positional and occupancy factors were varied in a least-squares refinement with isotropic thermal parameters.

An occupancy factor of 52% was found for the niobium in the 4-fold position corresponding to the face-sharing  $\text{MO}_6$  octahedra, i.e., Nb(1). This value indicates a random filling with Nb and Li and is what one might expect for the face-sharing octahedra. All other occupancy factors remained close to unity. Convergence was obtained with unit weights at a conventional *R* of 7.6% in a refinement in which anisotropic thermal parameters were used for the barium atoms and Nb(2), and isotropic thermal parameters were used for the oxygen atoms and Nb(1). (Three reflections strongly affected by extinction were omitted.) A weighted refinement using a weighting scheme described in other studies (6) lowered the weighted *R* somewhat but did not change the conventional *R* or the atomic parameters significantly, and the results of the unit weight refinement are the ones reported.

Neutral atom form factors as well as the real and imaginary parts of the anomalous dispersion factors were taken from the International Tables (7). Calculations were carried out with

TABLE II

INTERATOMIC DISTANCES AND ANGLES,  $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ 

Distances <sup>a</sup> (Å)			
6Ba(1)–O(1)	2.888(2)	3Nb(2)–O(1)	2.060(2)
6Ba(1)–O(3)	2.831(9)	3Nb(2)–O(3)	1.924(6)
6Ba(2)–O(2)	2.889(20)	O(1)–O(1)	2.888(1)
6Ba(2)–O(3)	2.966(10)	O(1)–O(3)	2.787(10)
3Ba(3)–O(1)	3.053(3)	O(2)–O(2)	2.762(14)
3Ba(3)–O(2)	2.788(3)	O(2)–O(2')	3.014(14)
6Ba(3)–O(3)	2.905(10)	O(2)–O(3)	2.988(15)
3Nb(1)–O(2)	1.952(3)	O(3)–O(3)	2.802(7)
3Nb(1)–O(3)	2.189(8)	Nb(1)–Nb(1)	2.254(8)

Angles (degrees)	
O(2)–Nb(1)–O(2)	90.0(6)
O(2)–Nb(1)–O(3)	92.2(5)
O(2)–Nb(1)–O(3)	176.9(3)
O(3)–Nb(1)–O(3)	85.6(4)
O(1)–Nb(2)–O(1)	89.0(1)
O(1)–Nb(2)–O(3)	88.7(3)
O(1)–Nb(2)–O(3)	176.8(5)
O(3)–Nb(2)–O(3)	93.5(4)
Nb(2)–O(1)–Nb(2)	180 (9)
Nb(1)–O(2)–Nb(1)	70.5(2)
Nb(1)–O(3)–Nb(2)	174.4(5)

<sup>a</sup> Numbers preceding atom symbols indicate bond multiplicities.

X-Ray System (8). Final position and thermal parameters are listed in Table I, bond distances and angles are given in Table II, and observed and calculated structure factors in Table III. An illustration of the unit-cell contents (Fig. 1) and an illustration of the small cation environment (Fig. 2) were prepared with Johnson's program ORTEP (9).

## Discussion

The use of lithium to lower the average oxidation state of octahedrally coordinated cations in a variety of well-known structure types has been discussed in a paper by Negas et al. (2) who have described a number of the possible stoichiometries. A related use of lithium in reducing average oxidation states has been described in compounds  $\text{LiM}^{\text{III}}\text{Mo}_3\text{O}_8$  (10, 11) which adopt structures related to that of  $\text{A}_2^{\text{II}}\text{Mo}_3\text{O}_8$ , where  $\text{A}^{\text{II}}$  may be any of a number of

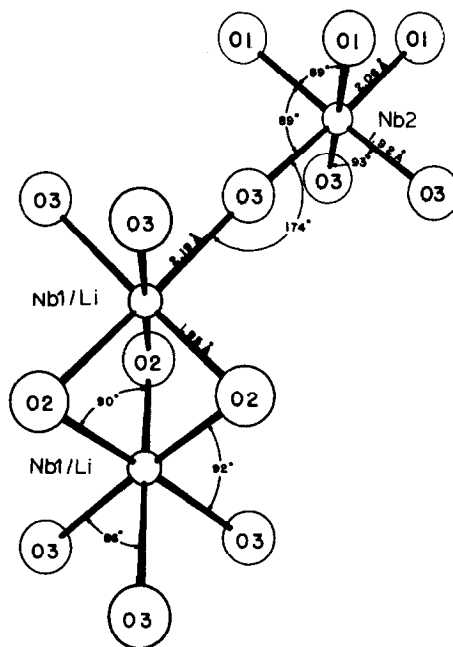


FIG. 2. Portion of structure showing face-sharing octahedra linked to a corner-sharing octahedron.

divalent cations such as those of Mg, Mn, Fe, Co, Ni, Zn, and Cd (12). (In these cases, the Li goes into tetrahedral sites.) The use of  $\text{Li}^+$  also promotes the possibility of face sharing of octahedra by removing the necessity for close approaches of highly charged cations. Thus, in the face-sharing pairs of octahedra in  $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ , half of the octahedra are occupied by  $\text{Li}^+$  and half by  $\text{Nb}^{5+}$ . To be sure, the random arrangement would allow for  $\text{Li}^+\text{--Li}^+$  and  $\text{Nb}^{5+}\text{--Nb}^{5+}$  pairings, but it is more likely that  $\text{Li}^+\text{--Nb}^{5+}$  pairings are the rule and that the randomness is achieved by random up-down orientations of the pairs. Also the  $\text{Nb(1)–Nb(1)}$  distance is only 2.25 Å, which would be extremely short for a Nb–Nb separation.

The possibility of an ordered arrangement of  $\text{Li}^+$  and  $\text{Nb}^{5+}$  in the face-sharing octahedra was tested by placing these ions in 2-fold positions in space group  $P6_3mc$ . When full occupancy of sites was assumed, convergence was not obtained in least-squares refinements since the temperature factor for Li always went strongly negative, and the program reset it to zero. Convergence was obtained when the population parameters for the Li and Nb in the face-sharing octahedra were allowed to vary and the temperature factors held fixed. These population

TABLE III  
OBSERVED AND CALCULATED STRUCTURE FACTORS<sup>a</sup>

Table with multiple columns of Miller indices (hkl) and structure factor values (F\_o, F\_c). Rows are grouped by Miller indices such as h0k0, hk0, hkl, etc. Asterisks indicate unobserved reflections, and E indicates extinction-affected reflections.

<sup>a</sup> The columns are h, 10|F\_o|, 10|F\_c|. Unobserved reflections are marked by asterisks. Extinction-affected reflections not used in refinement are marked by E.

parameters converged to 6.6 and 0.6 for Li and Nb, respectively, which is again indicative of random occupancy. The values obtained for these population parameters are, of course, sensitive to the temperature factor values chosen, and nonconvergence problems could have been aggravated by pseudosymmetry.

However, the evidence favors the conclusion that there is a random arrangement of Li and Nb in the face-sharing octahedra.

With eight-layer BaMnO3 and eight-layer Ba4Nb3LiO12, two of the six possible eight-layer stacking sequences of close packed layers have been observed in complex metal oxides.

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