A Single-Crystal Study of Eight-Layer Barium Niobium Lithium Oxide, Ba₄Nb₃LiO₁₂

EUGENE F. JENDREK, JR., ALAN D. POTOFF, AND LEWIS KATZ

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268

Received July 3, 1973

A single-crystal study of a sample of $Ba_4Nb_3LiO_{12}$ provided by Dr. T. Negas has been carried out and confirms the |(4)|(4)| layer stacking scheme (Zhdanov notation) for the eight BaO_3 layers per unit cell. Of the eight MO_6 octahedra per cell (M = Nb or Li), four share faces in pairs, and these pairs are linked by pairs of corner-sharing MO_6 octahedra. The compound has an hexagonal cell of dimensions $a = 5.777 \pm 0.006$ Å and $c = 18.95 \pm 0.03$ Å, probable space group $P6_3/mmc$, Z = 2. The theoretical density is 6.22 g/cm³; within the limit of error of the pycnometrically measured density, 6.08 ± 0.06 g/cm³. 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 AO₃ 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 = layer) compound of composition Ba₄Nb₃LiO₁₂ 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 $P\overline{6}2c$, $P\overline{6}_3mc$, or $P\overline{6}_3/mmc$. The observed unit-cell parameters of a = 5.79Å and c = 19.04 Å 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 $a = 5.777 \pm 0.006$

graphs were used to verify that the true cell parameters were not multiples of the values found. All reflections for which $k \ge 0$, $h \ge k$, and $-32 \le l \le 32$. $2\theta \le 75^{\circ}$ were measured with a Picker

Å and $c = 18.95 \pm 0.03$ Å. Full rotation photo-

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

Over 2800 reflections were measured which resulted after averaging in 620 independent reflections of which 437 were greater than 2σ 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 2σ threshold adopted for observed reflections.)

Atom	Position	x	У	Z	U12 ^b	U33	
Ba(1)	2 <i>a</i>	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) ^c	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)		

 TABLE I

 tomic Parameters for Ba4Nb3LiO12" Space Group P63/mmc (No. 19)

" Thermal parameters have been multiplied by 10⁴.

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

^e 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 BaO₃ 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 $Ba_4Nb_3LiO_{12}$. 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 BaMnO₃, the second arrangement was found (4, 5). For Ba₄Nb₃LiO₁₂, 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 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 facesharing octahedra. All other occupancy factors remained close to unity. Convergence was obtained with unit weights at a conventional Rof 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

TADLE II								
Interatomic	DISTANCES A	and Angles,	Ba4Nb3LiO12					
Distances ^a (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)-N	b(1) 2.254(8)					
	Angles	(degrees)						
	O(2)-Nb(1)-	O(2) 90.0(6)					
	O(2)-Nb(1)-	D(3) 92.2(5)					
	O(2)-Nb(1)-	O(3) 176.9(3)					
	O(3)-Nb(1)-	O(3) 85.6(4	4)					
	O(1)-Nb(2)-	O(1) 89.0()	1)					
	O(1)-Nb(2)-0	D(3) 88.7(3)					
	O(1)-Nb(2)-	D(3) 176.8(5)					
	O(3)-Nb(2)-	O(3) 93.5(4	4)					
	Nb(2)-O(1)-N	b(2) 180 (9)					
	Nb(1)-O(2)-N	b(1) 70.5(2	2)					
	Nb(1)-O(3)-N	b(2) 174.4(5)					

TADIE II

^a 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 $\text{LiM}^{11}\text{Mo}_3\text{O}_8$ (10, 11) which adopt structures related to that of $A_2^{11}\text{Mo}_3\text{O}_8$, where A^{11} 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 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 Ba₄-Nb₃LiO₁₂, half of the octahedra are occupied by Li⁺ and half by Nb⁵⁺. To be sure, the random arrangement would allow for Li+-Li+ and Nb⁵⁺-Nb⁵⁺ pairings, but it is more likely that Li⁺-Nb⁵⁺ pairings are the rule and that the randomness is achieved by random up-down orientations of the pairs. Also the 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 Li^+ and 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^a

M.D.D	7 133 98	H	4 990 -44	H.4.9	5 313 307	4 582 -529	7 285 265	H+2+21	3 241 282
1 436 -425	8 159 146	4 106 95	5 920 13 6 1049 22	5 254 -270	6 329 293 7 200+ 236	5 564 555 6 118* -1	H+1+18	3 1054 1080	4 116* 2
2 696 -559 3 3369E 4107	H+2+2	5 458 418	7 111* -20	H.0.10	H+2+12	7 464 -437	1 612 -799	5 117• -9	H+2+25
4 411 -323 5 224 -153	2 192 197 3 257 289	H.0.5	H+2+7	0 1014 -929	2 355 336	H01019	3 545 516	M+3+21	4 197 180
6 2483 2755 7 145 -121	4 438 443 5 107 108	1 2725 3004 2 3123 -3328	3 89° -29 4 130 -120	2 2408 2354	4 492 313	3 792 719	5 389 395	4 776 827	H+0+26
8 124* -91	6 306 285 7 181 163	3 920 D 4 2471 2293	5 103* 35	4 1935 1734	6 341 355	3 529 -518	No2018	H+0+22	0 476 -518
H+1+0	4.3.2	5 1629 -1578 6 106* 0	7 120* -13	6 442 -404	H+3+12	7 139 -18	1 411 -468	0 256 228	2 1095 1153
1 3177E 5087 2 524 -293	3 118 109	7 1129 1043 8 1033 -947	M1347	6 957 813	3 251 344	H+2+15	3 424 445	2 711 777	4 927 971 5 912 868
3 294 -265 4 2710 3084	5 195 195	H+1+5	5 979 10	H+1+10	5 240 250	3 637 -664	5 386 -378	4 701 438 5 445 419	H+1+26
6 117 -131	6 1290 98	1 64* 0	6 2260 -36 Midaa7	1 1228 -1090	H+4+12	5 131+ 49	H.J.18	6 137- 95	1 676 -683
8 105* -40		3 1740 -2047	4 2044 -12	3 1744 1664	4 205 222	H+3+15	3 441 -475 4 333 374	H+1+22	2 1133 1088 3 1064 982
M+2+0	5 126 152	5 1265 1410	Hadaa	5 1242 1219 6 1020 997	5 241 238	4 378 -444	5 291 287	1 321 354 2 446 521	4 501 -509
2 3931E 4774	H.Q.3	7 108* -5	0 2577 2654	7 402 -367	H+0+13	5 353 411	M+4+18	3 539 494 4 1750 233	H+2+26
4 249 -221	1 475 -415	H+2+3	1 299 -279 2 420 -172	H+2+10	1 997 919 2 1192 -1109	H.0.16	4 188* -196	5 442 404	2 387 -413 3 927 891
6 143* -119	3 89* -13	3 1486 1779 4 1466 -1703	3 994 850	2 633 -672 3 1260 1455	3 104* -8	0 3304 3461	H+0+19	H+2+22	H+0+27
H+3+0	5 277 257 6 109* 0	5 92° 8 6 1179 1128	5 150 -46 6 911 855	4 1198 1376 3 430 -491	5 538 -518 6 119* 0	2 106 -36 3 2439 2341	2 192 -185	3 471 468	1 291 -287
3 2846 2748	7 166 -126 8 261 222	7 849 -316	7 1210 -62 8 149 -34	6 962 934 7 751 755	7 354 314	5 108+ 20	4 103 149	5 149 139	3 162* -12
• 111 -110 5 144 -106	H+1+3	H.3.5	Ho I +8	H+3+10	H01010	7 125+ -4	6 109* 0	H+3+22	Hala27
6 1759 1560	1 62• 0	4 1073 1276 5 1026 -1057	1 1049 973	3 545 -612	3 742 -663	H.1.16	H+1+19	3 178 201 4 345 373	2 316 -281
H+4=0	2 408 -381 3 314 336	6 103+ -4	3 160 -177	5 820 923	5 481 462	1 2664 2630	2 494 479	H+0+23	3 284 265 4 117* 11
6 2639 2262 5 111 -95	5 242 -227	H.4.7	5 113 - 63	B 908 -999	7 117• 0	3 109= -9	4 116* 14 5 343 326	I 682 -684	H+2+27
H.0.1	7 108* 9	y you gru	7 309 328	4 295 -121	H+2+13	5 111+ 10	6 270 -292	2 420 510 3 104+ 29	3 291 -246
1 134 115	0 12105 M-7-3	A 1129 -38	M+2+6	5 689 771	3 581 596 4 586 -602	H+2+16	M=2+19	6 369 -408 5 424 438	H.0+28
3 117 -79	2 73+ 0	1 1759 1667	2 1274 1569 3 168 -154	H+0+11	5 113* -2 6 *13 370	2 2494 2671	3 373 407 4 146 -151	6 116 - 0	0 715 774
5 1194 -53	3 270 -281	3 174 121	4 146 -140 5 393 454	1 1501 -1391 2 1996 1894	н.3.13	3 127° -11 4 123° -13	5 121* -14	H=1=23	1 1200
7 125 117	5 89* -19	5 1067 978	6 110+ -5C 7 109+ 16	3 102* -18 * 1550 -1373	* 355 404	5 1465 1466 6 137* 5	N=3+19	2 579 -600 3 547 555	3 637 652 4 1194 15
H+1+1	7 119• 9•	7 676 681 8 723 672	H+3+8	5 945 881 6 115* 0	5 290 -324	H+3+16	4 244 299 5 248 -263	4 1130 -23 5 405 -407	H+1+28
1 94 0	H+3+3	H+1+6	3 424 592	7 726 -602 8 774 690	H.4.13	3 1591 1749	H.0.70	H+2+23	1 707 706
2 63• 47 3 92 -88	4 192 -196 5 162 146	1 208 158	4 103 -50 5 104 -48	H.1.11	5 230 253	5 123+ 8	0 748 718	3 499 -516	3 125+ -72
5 83° 76	6 130* 16	3 1253 1207	6 324 287	1 112 0	0 1140 1255	H.4.16	2 473* 640	8+3+23	H=2-28
7 101- 17	H+4+3	5 824 886	4 419 474	3 1175 1076	1 143+ -183	4 1324 1530	4 596 528 5 328 311	4 323 -345	2 616 653 3 110+ -56
# 118- #U	5 1344 -42 NoCo4	7 98+ 16	5 10340	5 848 -805	3 1284 1184	H.0.17	6 438 416	H.Q.24	M-0-29
7 89 0	0 98* 81	H.2.6	H.D.9	7 105* 11	5 105+ -80 5 706 574	1 132* -69 2 143* -34	M=1=20	585 756 0	1 103 103
5 115 111	1 1429 1334	2 84* 40 3 928 1065	1 1076 -1037 7 1037 - 934	H#2+11	7 106+ -34	3 1150 -17 6 1170 -81	1 733 637 2 440 424	1 140* 192 2 140* 187	2 195* -160 3 176* +10
5 104+ -50	3 135 106	4 1105 1126 5 97• 39	3 979 -46	3 063 -953 4 1046 1087	H+1+14	5 1140 -16 6 1100 0	3 462 412 4 518 509	3 1120 -61 6 1030 168	H+1+29
7 101* -7*	5 631 614 6 130 92	6 780 782 7 601 553	5 630 567 6 207# 0	5 138° -24 4 794 -758	1 1466 1357 2 177 -140	7 125+ 34	5 336 304 6 325 287	3 267 261	2 176 197
H+3+1	7 541 501 8 529 487	H+3+6	7 384 -330 8 332 297	M+9+11	3 1400 -108	H,1,17	H. 2.20	1 1135	J [40 -]0]
5 894 67 5 99 -94	H+1+4	3 78+ 54	H.1.9	* *7* -738	6 1190 -42	3 1129 15	2 608 584	2 192 104	0 724 663
6 117• 32	1 130 87	4 778 812 5 655 688	1 95 0	6 117 20		5 112- 30	4 454 447	4 119* -54	1 1744 -64
H.4.1	3 803 901	8 120- 14	3 675 716	H+4+11	2 449 995	H.2.17	No 3929	N+2+24	3 696 693
9 137 113	5 537 587	4 1089 22	5 527 -419	5 465 -319	3 1174 -88	3 123+ 21	3 438 471	2 245 236	H+1+30
1 454 404	7 124* 139	\$ \$75 590	7 120- 12	H.0.12	5 677 703 5 1394 91	a 1220 -50 5 1290 -16	4 280 247	3 147 155 4 144* 152	1 776 769 2 1309 -63
2 1164 995 3 165 132	H.2.4	H+0+7	H+ 2 + 9	0 482 428	H+3+14	6 119+ 61	H+0+31	H=3+24	H.0.31
4 748 604 5 332 308	2 103 76	1 874 -10 2 296 -255	3 539 -605	2 986 879 3 437 361	3 756 840	H+3+17	2 1296 -1442	3 116= -53	1 648 -650
6 1540 163 7 165 179	3 734 833 4 755 863	3 115 75	5 1090 -34	4 738 646 5 546 309	5 1249 -38	5 1180 -53	4 1241 1176	H+0+25	e -37 367 H10113
8 270 236	5 126 141 6 574 575 7 331 200	5 98* -33 6 104* -1 7 94* -1	1 273 271	7 339 284	H.4.14	H.0.10	6 117- 0	1 2490 -344	0 10+2 991
1 144 150	, 331 29 0	d 117• -74	A 417 -444	Hele12	4 475 \$71	0 611 -616 1 612 649	H.1.21	3 131+ -3	1 1434 141
2 443 411	3 110 120	H+1+7	5 311 344	1 449 390	H+0+15	2 776 722 3 742 -484	2 1343 1301 3 1244 -1183	5 234 238	
4 142 115 5 271 247	6 490 899 5 520 459	1 82* 0 2 85* 3*		2 510 471 3 533 461	1 1003 -928 2 678 667	4 975 963 9 496 495	5 932 902	H+1+29	
6 185 204	6 149 141	3 100+ 7		4 912 918	3 109- 48	6 269 -260	6 785 -770	\$ 205 -274	

^a 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 $BaMnO_3$ and eight-layer $Ba_4Nb_3LiO_{12}$, two of the six possible eightlayer stacking sequences of close packed layers have been observed in complex metal oxides.

Acknowledgments

The authors are grateful to the National Science Foundation for financial assistance. We thank Dr. T. Negas of the National Bureau of Standards for providing samples of the crystals studied. Computations were carried out in the Computer Center of the University of Connecticut, which is supported in part by Grant GJ-9 of the National Science Foundation. Photographs of the figures and Table III were prepared by the University of Connecticut Photographic Laboratory.

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