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The Structure of a Barium Niobium Silicon Oxide with the Probable Composition $Ba_{6+x}Nb_{14}Si_4O_{47}$ ($x \simeq 0.23$)

DOLETHA M. EVANS AND LEWIS KATZ

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

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Reaction of BaO, Nb_2O_5, and Nb in mole ratios of 2.4:1.6:1 in an evacuated silica capsule at 1250°C produces a mixture of at least two products, one of which has the probable composition $Ba_{6+x}Nb_{14}Si_4O_{47}$ ($x \simeq 0.23$). This compound has an hexagonal unit cell of dimensions $a = 9.034 \pm 0.004$ Å, $c = 27.81 \pm 0.02$ Å, probable space group $P6_3/mcm$, $Z = 2$. Its structure has been determined from 942 independent reflections collected by a counter technique and refined by least squares methods to a conventional R value of 0.062. The basic structure consists of strings of four NbO_6 octahedra sharing opposite corners, each string joined to the next by edge sharing of the end octahedra, so that the c axis corresponds to the length of a strand of seven corner-linked octahedra. Chains of three such strands are formed by corner sharing between the strands. The chains in turn are joined by NbO_6 octahedra and Si_2O_7 groups in which the Si–O–Si linkage is linear. Barium atoms are in sites between the chains coordinated by 13 oxygen atoms. A second site, 15 coordinated, probably has a small amount of barium as well; the fractional occupancy for barium in this site is 0.076.

Introduction

The reaction of BaO, Nb_2O_5, and Nb in the presence of SiO_2 can result in at least three different hexagonal complex oxides containing silicon. The first to be studied was $Ba_3Nb_6Si_4O_{26}$ (*1*). This structure has infinite strings of NbO_6 octahedra sharing opposite corners. These strings extend in the c direction. Each string is joined laterally to two others by corner sharing to form chains; the chains in turn are linked by corner sharing with Si_2O_7 groups and by the electrostatic attraction of Ba^{2+} ions between the chains. A second compound, $Ba_3Nb_{21-x}Si_2O_{44}$ ($x \simeq 0.2$) has a different structure based on a 7 layer stacking of close-packed O_7 and BaO_6 layers with niobium and silicon occupying sites between the layers (*2*).

The compound described here, $Ba_{6+x}Nb_{14}Si_4O_{47}$, has a structure related to that of $Ba_3Nb_6Si_4O_{26}$. However, it is more complex and has some points of individual interest.

Experimental Methods

BaO was prepared from BaO_2 by heating to 1000°C *in vacuo* for 1 hr. It was mixed with Nb_2O_5 and Nb (both obtained commercially) in a 2.4:1.6:1 mole ratio; the resulting gray powder was triturated under petroleum ether and placed in a silica capsule, which served as both container and reactant. The capsule was evacuated, sealed, and placed in a furnace at 1250°C for 1 wk. Upon removal from the furnace, the capsule was in a partially collapsed state, and on cooling it clouded and became crazed on the inside.

The reaction product consisted of black, highly reflective crystals, some embedded in the container walls, some aggregated into chunks that appeared to have been partially melted, and some loose and apparently single. The last-named occurred in two distinct habits: thick chunks only occasionally exhibiting flat faces, and very thin hexagonal plates, rarely complete but usually having at least one 120° angle visible.

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Examination of several of the single crystals indicated that these two types of crystal represented two different compounds. The thin plates proved to be $Ba_3Nb_{21-x}Si_2O_{44}$ and the chunks $Ba_{6+x}Nb_{14}Si_4O_{47}$. A rough density of 4.9 g/cm^3 was measured for the aggregated crystals (by the method of Archimedes, using water as the displacement liquid), which presumably consist mainly of the latter compound. This value is probably low because of trapped air in the aggregates.

A single chunky crystal was selected for structure determination and ground to a sphere of 0.14 mm diameter. Laue and precession X-ray photographs revealed a hexagonal lattice, Laue group $6/mmm$, with hhl reflections present only for $l = 2n$. The probable space group is thus one of $P6_3cm$, $P\bar{6}c2$, and $P6_3/mcm$. Photographic measurements gave $a = 9.00$ Å and $c = 27.67$ Å.

Data for the structure solution were collected on a Picker Nuclear computer-controlled single-crystal diffractometer, using graphite-monochromatized Mo radiation and a scintillation counter detector, and operated in the θ–2θ scan mode. The base scan width was 2.5–2.8° in 2θ, with dispersion factor of 0.692. Background was counted for 20 sec on each side of the peak, and three standard reflections were measured every 40 reflections. In all, three sets of data were collected. Due to errors in interpreting the photographic data, the first collection was based on an assumed c value half the true one and hence missed half the reflections. The data produced were not used in the structure determination, although the final cell parameters, $a = 9.034 \pm 0.004$ Å and $c = 27.81 \pm 0.02$ Å $(= 2x(13.906 \pm 0.009$ Å$)$, were determined at this time by least squares refinement on the diffractometer angles of 12 reflections.

The second collection produced usable data, but instrument instabilities resulted in sizable variations in the standards with time. Dividing the data into a number of groups and scaling each group to bring standards into agreement gave standard deviations of the standards of 1.6, 2.6, and 5.1%. However, the data were still not of very good quality, and when the conventional R value would go no lower than 0.124 for the final refined structure, a third set of data was collected. It was later discovered that part of the refinement problem arose because we were attempting to refine a nearly centrosymmetric structure.

The third data set included all possible reflections with $2\theta \leqslant 25°$, and those within the range $0 \leqslant h \leqslant 9$, $-3 \leqslant k \leqslant 9$, and $-3 \leqslant l \leqslant 33$ for $25° < 2\theta \leqslant 50°$. The three standards had standard deviations of 1.4, 2.2, and 5.4%, with no scaling necessary. The 3329 reflections collected were corrected for background and those related by symmetry were averaged, reducing the data set to 670 reflections, of which 421 had intensities greater than three times the standard deviation of the background and were labeled observed. In the table of structure factors, the number listed in the column of observed F's for unobserved reflections is determined from $I_{obs} + 2\sigma(I_{obs})$.

The data set used for the final structure determination included all the reflections from the third data collection plus 242 reflections of raw intensity greater than 100 and $2\theta > 50°$ from the second data collection. (The intensity restriction was imposed because of the pronounced inverse correlation between magnitude and R factor for the second-set reflections.) Lorentz and polarization corrections and a spherical absorption correction, with $\mu r = 0.76$, were applied by the X-ray system program package (*3*), which was also used in subsequent calculations of Fourier maps, least squares refinements, and so forth.

Structure Determination and Refinement

The $hk0$ reflections of the compound under study are very similar to those of $Ba_3Nb_6Si_4O_{26}$, indicating a resemblance between the projections along c for the two compounds. Ba atoms were therefore placed at 0.59, 0, z positions; Nb at 0.24, 0, z positions and Si at 1/3, 2/3, z positions in the present compound to correspond to $Ba_3Nb_6Si_4O_{26}$. Assuming a barium at 0.59, 0, 0, a Patterson map indicated possible niobium z values of 0.072, 0.211, and 0.350. The four-atom model thus arrived at was used as the starting point for a structure solution by difference Fourier methods. $P6_3cm$ was chosen as the trial space group.

The niobium position and population parameters and the barium x-parameter were refined and a ΔF map was calculated. This was then used to place further atoms and the cycle repeated, with isotropic thermal parameters also being refined on later iterations. After a few such cycles, R was down to the 10% range and the model was making chemical sense. At this point the indicated chemical formula was $Ba_6Nb_{14}Si_4O_{50}$, with $Z = 2$.

Anisotropic thermal parameters were introduced for barium and niobium and all possible parameters refined. This process reduced the R factor by a few percent, but the parameters would not converge. Moreover, the thermal parameters for one niobium and several oxygens became nonpositive definite. A weighting function $w = 1/\sigma_F{}^2$ was introduced, with

$$\sigma_F = \frac{1}{(n)^{1/2}} \frac{1}{2(\mathrm{Lp})^{1/2}} \times [\{N_T + \mathrm{BG} + [0.02(N_T - \mathrm{BG})]^2\}/ [N_T - \mathrm{BG})]^{1/2}$$

for observed reflections and

$$\sigma_F{}' = \frac{1}{(n)^{1/2}} \frac{1}{2(\mathrm{Lp})^{1/2}} (\mathrm{BG})^{1/2}$$

for unobserved reflections, where:

n	number of reflections averaged
Lp	Lorentz and polarization corrections
N_T	total counts measured on the scan through the peak
BG	(background counts accumulated in 40 sec) × (scan time/40).

This produced a weighted R somewhat lower than the conventional R from the unweighted refinement, but did not help the convergence problem.

A careful examination of the model revealed that it had become nearly centrosymmetric. A statistical analysis of the magnitudes of the normalized observed structure factors indicated that a true center of symmetry was present. Accordingly, the atomic z-coordinates were altered so as to place the center at the origin and the probable space group became $P6_3/mcm$ (No. 193). There was no further difficulty in obtaining convergence.

Weighted refinement, however, still resulted in nonpositive definite thermal parameters for one niobium. Hence, the final refinement was done with unit weights. Neutral atom scattering factors with dispersion corrections included, from (*4*), were used throughout.

The formula $Ba_6Nb_{14}Si_4O_{50}$ corresponds to a cell in which one oxygen occupies a position logically more suited to a barium; it is surrounded by 15 oxygens, with no niobium or silicon within bonding range. A corresponding site in $Ba_3Nb_6Si_4O_{26}$ is unoccupied by any species.

TABLE I

ATOMIC PARAMETERS FOR $Ba_{6+x}Nb_{14}Si_4O_{47}$ SPACE GROUP $P6_3/mcm$ (NO. 193)[a]

Atom:	Ba(1)	Ba(2)[b]	Nb(1)	Nb(2)	Nb(3)	Si(1)	
Position:	12*k*	6*g*	12*k*	12*k*	4*d*	8*h*	
x	0.5932(2)	0.6117(39)	0.2383(5)	0.2371(3)	1/3	1/3	
y	0	0	0	0	2/3	2/3	
z	0.1076(1)	1/4	0.0434(1)	0.1833(1)	0	0.1918(3)	
U^c		0.592(711)				0.695(176)	
U_{11}	1.103(64)		2.401(162)	0.253(83)	0.427		
U_{22}	1.132		0.378	0.273	0.427		
U_{33}	1.012(59)		0.472(91)	0.452(76)	1.429(184)		
U_{12}	0.566(43)		0.189(72)	0.137(57)	0.213(62)		
U_{13}	0.159(57)		0.327(98)	−0.098(76)	0		
U_{23}	0		0	0	0		
Atom:	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)
Position:	12*k*	6*g*	12*k*	12*k*	4*c*	24*l*	24*l*
x	0.2203(26)	0.2860(44)	0.2060(38)	0.1773(24)	1/3	0.1801(20)	0.1729(22)
y	0	0	0	0	2/3	0.4898(22)	0.4841(23)
z	0.1094(7)	1/4	0.5326(9)	0.6850(7)	1/4	0.1694(4)	0.4562(5)
U	1.017(358)	1.384(633)	2.213(572)	0.631(369)	1.501(791)	0.752(254)	0.977(295)

[a] Errors in the last digit are given in parentheses. Where no error is shown, the parameter is not independent. Anisotropic thermal vibration expressed as: $\exp[-1/4(a^{*2} U_{11} h^2 + b^{*2} U_{22} k^2 + c^{*2} U_{33} l^2 + 2a^* b^* U_{12} hk + 2a^* c^* U_{13} hl + 2b^* c^* U_{23} kl)]$. Isotropic thermal vibration expressed as: $\exp[-8\pi^2 U \sin^2 \theta/\lambda^2]$.

[b] Population parameter, 0.076(11).

[c] All U's have been multiplied by 100.

In this case, however, leaving the site empty results in a peak on a ΔF map, of approximately the magnitude of a peak produced by omission of one of the normal oxygens. Fully occupying the site with oxygen results in a very large isotropic thermal parameter for the oxygen; allowing both population and thermal parameters to vary results in a low occupancy factor and a negative temperature factor. Placing a barium with a low occupancy factor in the site and refining, however, leads to simultaneous convergence of population and thermal parameters. Accordingly, the probable occupant of the site is a barium of low population parameter, and the compound formula becomes $Ba_{6+x}Nb_{14}Si_4O_{47}$, with $x \simeq 0.23$. The average niobium oxidation state is thus +4.68, presumably corresponding to a mixture of Nb^{IV} and Nb^{V}. Mixed oxidation states are known for other niobium compounds (*5*), and in this case account neatly for the dark color of the compound. The theoretical density is 5.09 g/cm^3, compared to the measured (presumably low) value of 4.9 g/cm^3. A final difference map showed no peak of more than 1/10 the height of that produced by omission of an oxygen.

The final R factor is 0.062 overall, and 0.045 for reflections from the third data collection (presumably the more accurate reflections). The maximum shift/error ratio in the final cycle of refinement was 0.011. The final parameters are given in Table I, and the unit cell contents are shown in stereo in Fig. 1. This and subsequent drawings were produced by the program ORTEP (*6*), using a computer-controlled plotter.

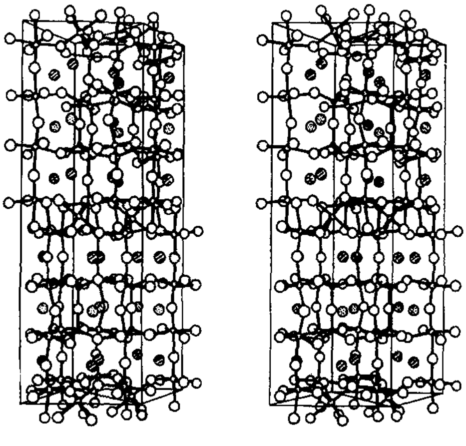

FIG. 1. Stereo view of the unit cell of $Ba_{6+x}Nb_{14}Si_4O_{47}$. Ba(1) is shown as striped circles, Ba(2) as stippled circles, Nb as small open circles, Si as small black circles, and O as large open circles.

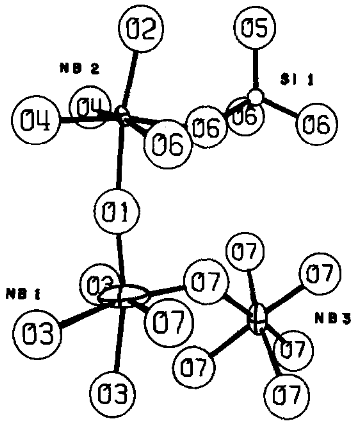

FIG. 2. Niobium and silicon coordination in Ba_{6+x}-$Nb_{14}Si_4O_{47}$.

Discussion

The basic structural unit in $Ba_{6+x}Nb_{14}Si_4O_{47}$ is a string of four NbO_6 octahedra joined end to end. These strings are joined laterally in groups of three by further corner sharing. Figure 5 shows four such groups and the connections among them. It may be seen that each group of three strings is joined to the next group along the c axis by edge sharing of the end octahedra. Thus there are essentially continuous triple chains of NbO_6 octahedra extending along the c axis. Connections perpendicular to c between different triple chains are provided by Si_2O_7 groups and single NbO_6 octahedra. Four of the former and two of the latter appear in Fig. 5. Each Si_2O_7 group joins three separate triple chains by sharing corners with the second and third octahedra of one string in each group. The single NbO_6 octahedra occur at the ends of the triple chains, so that each actually shares corners with octahedra in six different four-octahedron strings. This is clearly shown in Fig. 3, which shows a view along the c-axis of a slice of the unit cell centered around $z = \frac{1}{2}$, a region in which edge sharing occurs. The end octahedra of triple chains appear around the origins; single NbO_6 octahedra are located at 1/3, 2/3 and 2/3, 1/3.

In the $Ba_3Nb_6Si_4O_{26}$ structure (*1*), similar triple chains of niobium–oxygen octahedra appear, but in that case there is no edge sharing; individual chains are infinite in length instead of

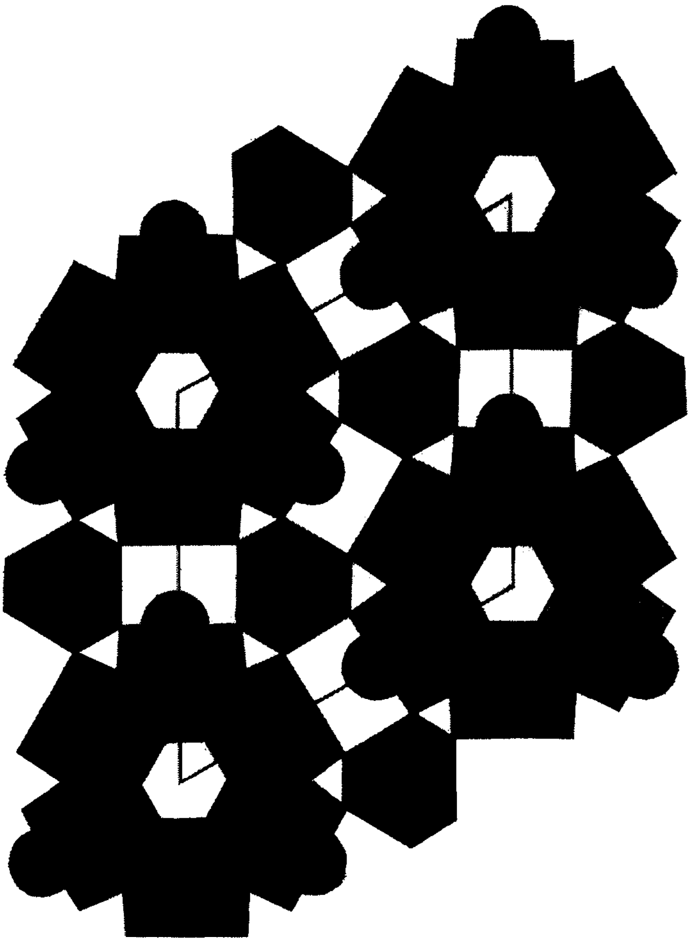

FIG. 3. View along c axis of a section from $z = 0.45$ to $z = 0.60$ of the $Ba_{6+x}Nb_{14}Si_4O_{47}$ cell, showing NbO_6 groups as solid octahedra and Ba as striped circles.

four octahedra long. The triple chains are joined by linear Si_2O_7 groups, as in the present compound, but there is no niobium between chains.

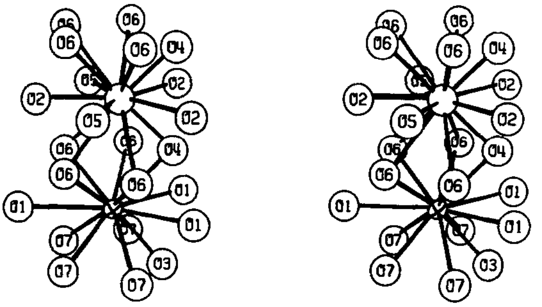

FIG. 4. Stereo view of the barium coordination in $Ba_{6+x}Nb_{14}Si_4O_{47}$. Ba(1) is shown as an ellipsoid and Ba(2) as a circle.

The unit cell of $Ba_3Nb_6Si_4O_{26}$ is two octahedra high; the $Ba_{6+x}Nb_{14}Si_4O_{47}$ cell may be constructed by stacking up four $Ba_3Nb_6Si_4O_{26}$ cells, with the top two rotated 60° relative to the bottom two. The second and third cells are then overlapped so that edge sharing of NbO_6 octahedra is produced, the pairs of silicons brought together by this process are replaced by single niobiums, and Ba(2), which occupies a site vacant in $Ba_3Nb_6Si_4O_{26}$, is introduced to complete the structure.

So $Ba_3Nb_6Si_4O_{26}$ is a fairly close relative to $Ba_{6+x}Nb_{14}Si_4O_{47}$. It may also be instructive to consider some more distantly related compounds. Except for the Si_2O_7 groups, the framework of the $Ba_{6+x}Nb_{14}Si_4O_{47}$ structure is composed of NbO_6 octahedra sharing corners, and in some places edges. The occurrence of a framework of

TABLE II

INTERATOMIC DISTANCES AND ANGLES IN $Ba_{6+x}Nb_{14}Si_4O_{47}$[a]

Distances (Å)		
Ba(1)-O(1)^{1}	3.37(2)	
Ba(1)-O(1)^{2}	3.19(1)	
Ba(1)-O(3)	2.76(3)	
Ba(1)-O(4)	2.99(2)	
Ba(1)-O(6)^{2}	3.04(1)	
Ba(1)-O(6)^{3}	2.83(2)	
Ba(1)-O(7)^{2}	3.09(1)	
Ba(1)-O(7)^{3}	2.84(2)	
Ba(2)-O(2)^{1}	2.94(5)	
Ba(2)-O(2)^{2}	3.15(3)	
Ba(2)-O(4)	2.63(3)	
Ba(2)-O(5)	2.80(1)	
Ba(2)-O(6)^{2}	3.34(1)	
Ba(2)-O(6)^{3}	3.27(3)	
Nb(1)-O(1)	1.84(2)	
Nb(1)-O(3) (atoms at different z values)	2.13(2)	
Nb(1)-O(3) (atoms at about same z)	2.04(4)	
Nb(1)-O(7)	1.98(2)	
Nb(2)-O(1)	2.06(2)	
Nb(2)-O(2)	1.91(1)	
Nb(2)-O(4)	1.93(3)	
Nb(2)-O(6)	2.07(2)	
Nb(3)-O(7)	1.98(2)	
Si(1)-O(5)	1.62(1)	
Si(1)-O(6)	1.63(2)	
Angles (°)		
O(1)-Nb(1)-O(3) [O(3) and Nb at about same z]	95.4(8)	
O(1)-Nb(1)-O(3) [O(3) and Nb at different z's]	167.1(12)	
O(1)-Nb(1)-O(7)	93.3(7)	
O(3)-Nb(1)-O(3) (O's at same z)	104.0(12)	
O(3)-Nb(1)-O(3) (O's at different z's)	76.9(9)	
O(3)-Nb(1)-O(7) [O(3) and Nb at about same z]	84.1(10),	167.5(10)
O(3)-Nb(1)-O(7) [O(3) and Nb at different z's]	96.1(8)	
O(7)-Nb(1)-O(7)	86.5(7)	
O(1)-Nb(2)-O(2)	170.8(13)	
O(1)-Nb(2)-O(4)	88.4(7)	
O(1)-Nb(2)-O(6)	82.3(6)	
O(2)-Nb(2)-O(4)	97.9(10)	
O(2)-Nb(2)-O(6)	91.0(9)	
O(4)-Nb(2)-O(4)	91.9(8)	
O(4)-Nb(2)-O(6)	90.5(8),	170.4(7)
O(6)-Nb(2)-O(6)	85.7(6)	
O(7)-Nb(3)-O(7) (O's at same z)	86.0(7)	
O(7)-Nb(3)-O(7) [O's belonging to two Nb(1) octahedra which share edges]	87.6(7)	
O(7)-Nb(3)-O(7) (O's at different z's not belonging to edge-sharing octahedra)	101.3(7),	170.0(10)
O(5)-Si(1)-O(6)	112.5(5)	
O(6)-Si(1)-O(6)	106.2(9)	
Si-O-Si	180	

[a] Errors in last digit are shown in parentheses. Superscripts on oxygens around Ba(1) and Ba(2) refer to the order in which the symmetry-related coordinates of the general position for $P6_3/mcm$ are listed in (*11*).

corner-sharing MO_6 octahedra is widespread in oxide structures. Examples include the ReO_3 structure (*7*), the hexagonal tungsten bronze structure (*8*), and the tetragonal tungsten bronze structure (*9*). The last-named is of particular interest here. Infinite strings of WO_6 octahedra are joined by a complex pattern of inter-string corner-sharing, so that a projection along the strings shows three-, four- and five-sided rings of octahedra, each ring actually corresponding to an infinite channel bounded by strings of octahedra. Large cations, e.g., K^+, occupy the four- and five-sided channels, being coordinated by 12 and (10 + 5) oxygens, respectively.

In $Ba_3Nb_6Si_4O_{26}$ and in the regions of $Ba_{6+x}Nb_{14}Si_4O_{47}$ where edge sharing does not occur, we have nearly identical three-sided channels, as well as five-sided channels that are similar, but have two "sides" composed of Si_2O_7 groups instead of octahedra. Because of this substitution, Ba(1) of $Ba_{6+x}Nb_{14}Si_4O_{47}$ and the barium in $Ba_3Nb_6Si_4O_{26}$ are coordinated by only (10 + 3) oxygens, rather than having the (10 + 5) coordination of Ba(2) and the bronze K^+.

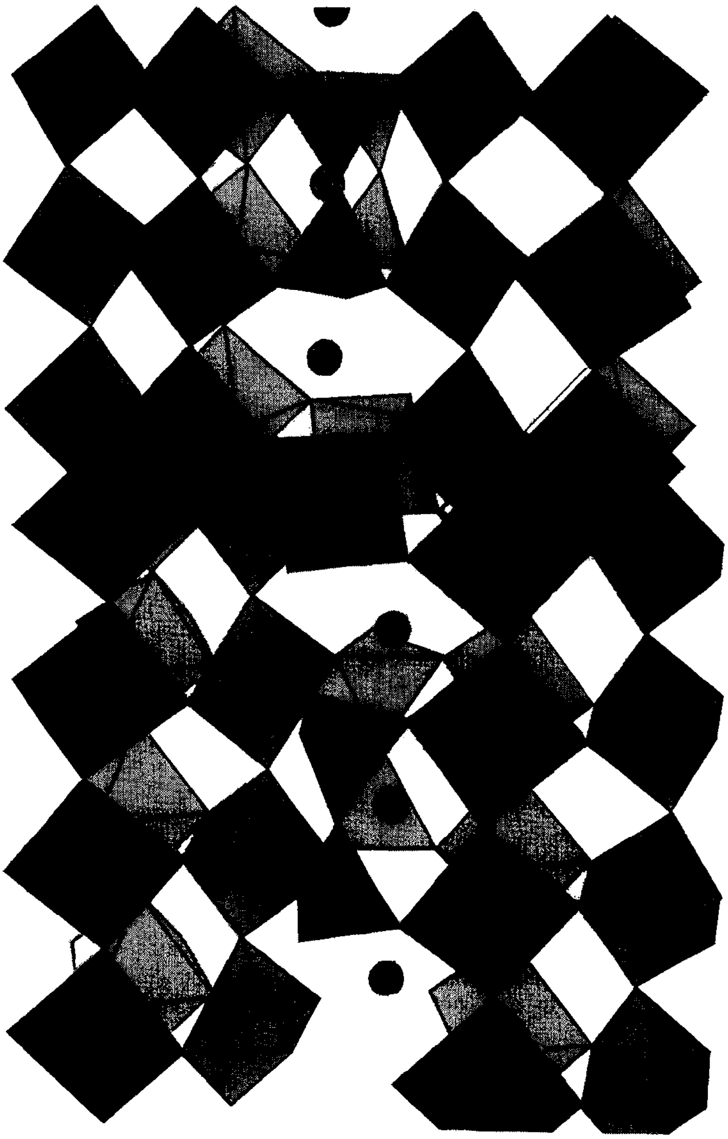

FIG. 5. Arrangement of NbO_6 octahedra and SiO_4 tetrahedra in $Ba_{6+x}Nb_{14}Si_4O_{47}$. Bariums are represented as in Fig. 1.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Ba_{6+x}Nb_{14}Si_4O_{47}$[a]

0,0,L		
2	3550	2990
4	1825	-1876
6	2727	2475
8	3395	-3313
10	3485	3289
12	2538	-2661
14	12452	13250
16	2841	2566
18	4176	4221
20	4169	4044
22	3566	3372
24	1297	-1295
26	3676	3684
28	6011	5823
30	1889	-1800
32	1929	-2116
34	3463	-3210
38	2191	2178
40	1290	-1267
42	1177	-987
44	2089	2230
46	1659	1844
48	2320	2679
52	1169	-1559
0,1,L		
0	888	975
2	366*	-300
4	792	870
6	1104	1018
8	3305	-3118
10	1635	-1583
12	1495	-1402
14	1814	-1668
16	464*	240
18	1530	-1502
20	1061	-1028
22	1983	1886
24	512*	58
26	513*	210
28	532*	141
30	1401	-1413
32	554*	393
36	1840	-1708
0,2,L		
0	1320	-1235
2	473*	161
4	4173	-4230
6	4015	-3835
8	3745	3588
10	2377	2350
12	560*	-411
14	930	-880
16	1800	-1704
18	2057	2029
20	697	648
22	3363	-3226
24	1983	-1977
26	628*	-584
28	906	874
30	753	755
32	1562	-1578
36	1508	1347
42	1105	-1287
0,3,L		
0	4577	5092
2	591	641
4	390*	-130
6	605*	-523
8	2288	2069
10	3260	3089
12	495*	283
14	1932	-1913
16	2061	1841
18	1396	1352
20	2508	2420
22	496*	79
24	902	-859
26	1550	1464
28	1840	1889
30	547*	-94
36	1103	986
0,4,L		
0	5752	6038
2	439*	278
4	778	824
6	2153	2071
8	5186	-5100
10	2375	-2317
12	2052	-2059
14	5066	-4925
16	794	698
18	680	-578
20	511	-446
22	3956	3847
24	563*	456
26	891	887
28	1393	1350
30	2463	-2382
34	1203	-1185
36	2693	-2736
44	1606	1851
0,5,L		
0	6790	7129
2	667	825
4	3703	-3700
6	1996	-1881
8	478*	199
10	2669	2784
12	2330	-2390
14	6783	-6628
16	492*	-179
18	2244	2173
20	1369	1338
22	639*	-247
24	2752	-2888
26	1392	1396
28	3633	3565
30	1331	-1319
32	1729	-1847
34	1508	-1718
38	1693	1875
40	1125	-1314
42	1663	-1903
52	1173	-1461
0,6,L		
0	1007	1027
2	572*	262
4	1882	1940
6	1966	1908
8	698*	-299
10	518*	-242
12	1023	1043
14	1177	1170
16	903	878
16	628*	-277
20	525*	346
22	700	728
24	1410	1473
0,7,L		
0	1535	1815
2	655*	313
4	2130	-2215
6	2099	-2074
8	1250	1197
10	1006	1098
12	830	-839
14	2351	-2337
16	971	-723
18	1420	1526
20	911	969
22	1253	-1216
24	1328	-1380
28	1202	1319
32	1272	-1472
0,8,L		
0	3376	3382
2	671*	-69
4	584*	-700
6	583*	63
8	1678	-1701
10	577*	-45
12	1313	-1235
14	3531	-3405
16	781*	636
22	1384	1486
28	1401	1581
30	1655	-1831
36	1323	-1351
44	1312	1433
0,9,L		
0	3331	3374
2	614*	361
4	870*	950
6	1728	1688
8	1538	-1454
10	973	919
14	1469	-1548
16	1432	1555
22	2027	2272
26	1411	1420
28	1376	1197
44	1155	1040
0,10,L		
0	2125	2206
4	1788	-1945
6	1365	-1583
8	1055	1182
14	2063	-2450
18	1672	1595
20	1103	793
22	1580	-1427
28	1570	1412
32	1749	-1553
1,1,L		
0	2110	-2225
1	1064	-1121
2	428*	-186
3	2180	2090
4	3466	3355
5	1991	-2042
6	3018	2823
7	7624	-7901
8	402*	140
9	428*	-469
10	397*	74
11	2936	2830
12	2267	2100
13	1298	1207
14	4252	4032
15	1912	1803
16	1315	1303
17	1274	-1288
18	1101	-1110
19	1865	1825
20	475*	-78
21	4406	4285
22	673	703
23	1124	-974
24	1467	1519
25	2323	-2289
26	550*	206
27	2020	-1937
28	1508	-1501
29	1165	-1115
30	1114	1123
31	1205	1248
32	1602	1659
33	1198	-1095
34	895	988
35	1624	-1682
37	1613	1319
39	1417	1462
41	1549	1591
1,2,L		
0	4430	-4619
1	4194	-4339
2	489*	-470
3	2924	-3065
4	841	-798
5	423*	-386
6	1219	-1203
7	408*	-319
8	1034	1023
9	1054	959
10	1390	-1231
11	2452	-2497
12	539*	530
13	1878	-1734
14	2309	2176
15	4955	4798
16	1601	-1487
17	1987	1981
18	511*	88
19	864	789
20	1004	-861
21	566*	-73
22	1749	-1686
23	1853	-1726
24	557*	309
25	1190	1351
26	1344	-1312
27	528*	76
28	1252	-1259
29	3585	-3453
30	723	745
31	665*	-768
37	1824	1664
43	1930	1878
1,3,L		
0	1711	-1643
1	2750	2760
2	486*	-486
3	3026	3137
4	1508	1517
5	670	-699
6	1106	1083
7	3071	-3047
8	2723	-2625
9	472*	-354
10	2806	-2741
11	2637	2553
12	518*	-452
13	2237	2173
14	552*	434
15	1998	-1933
16	521*	-72
17	2448	-2485
18	1731	-1554
19	622*	737
20	1317	-1297
21	2605	2533
22	1702	1643
23	559*	52
24	1080	1058
25	1817	-1721
26	648*	-460
27	1444	-1326
28	973	-934
29	1074	1077
30	967	-953
31	1647	1566
35	1814	-1702
36	1552	-1562
39	1159	1106
1,4,L		
0	4611	4606
1	465*	-322
2	690	674
3	612*	-600
4	2273	2226
5	477*	-69
6	3038	2951
7	596	520
8	2258	-2239
9	545*	-222
10	607*	323
11	585*	-170
12	505*	-67
13	533*	-286
14	1487	-1338
15	607*	127
16	2106	1973
17	720	715
18	533*	-461
19	484*	-103
20	768	671
21	503*	-498
22	3037	2904
23	566*	178
24	748	730
25	563*	-29
26	1650	1586
27	602*	195
28	826	762
1,5,L		
0	2612	-2636
1	1827	-1766
2	598*	-457
3	532*	-147
4	492*	208
5	872	-866
6	570*	-106
7	3150	-3115
8	551*	-292
9	541*	-106
10	909	-808
11	606*	382
12	579*	-110
13	632*	-282
14	1254	1159
15	2225	2187
16	643*	-550
17	570*	172
18	1024	-1088
19	888	880
20	1130	-1096
21	1607	1631
22	610*	-312
23	743	-683
24	612*	-50
25	719	-602
26	672*	-501
27	883	-668
28	941	-819
29	1591	-1540
1,6,L		
0	4134	-4238
1	791*	-711
2	618*	-562
3	1064	1056
4	626*	519
5	754*	-782
6	549*	-414
7	4612	-4662
8	538*	325
9	659*	431
10	1271	-1319
11	989	997
12	577*	474
13	637*	579
14	2623	2598
15	1549	1497
16	830	-831
17	1049	-1117
18	1005	-1079
19	1231	1258
20	1157	-1065
21	3075	3107
22	854	-855
23	1411	-1350
25	906	-876
26	1095	-1096
27	1141	-1247
28	1652	-1644
29	1096	-1255
31	1011	1152
35	1467	-1396
37	1344	1486
41	1102	1184
1,7,L		
0	1288	1274
1	1471	-1489
2	599*	113
3	1335	-1439
4	1242	1106
5	591*	71
6	1254	1248
7	654*	515
8	512*	-210
9	638*	281
10	754	627
11	1216	-1194
12	729*	677
13	841	-823
14	641*	424
15	1699	1675
16	1364	1254
17	1237	1215
18	535*	3
19	599*	28
22	972	983
29	1511	-1330
1,8,L		
0	591*	307
1	1683	1651
2	557*	-298
3	1707	1764
4	618	779
5	708	-726
6	1231	1280
7	1468	-1630
8	2426	-2414
9	641*	-721
10	1695	-1705
11	1774	1863
12	600*	-399
13	1430	1400
15	1409	-1475
17	1216	-1332
21	1260	1373
22	1539	1755
25	1744	-1583
27	1166	-917
29	1084	1065
36	1336	-1475
39	1204	1141
1,9,L		
0	1016	-846
1	1033	-870
15	1124	1138
29	1280	-960
1,10,L		
1	1138	-1135
4	1103	1119
7	2162	-2442
14	1531	1597
15	1630	1581
21	1773	1599
23	1158	-835
29	1331	-1323
37	1272	939
41	1166	717
2,2,L		
0	2310	-2277
1	2793	-2718
2	407*	106
3	2770	-2806
4	872	750
5	429*	262
6	418*	-129
7	471*	-168
8	3056	2934
9	461*	82
10	2623	2495
11	1215	-1160
12	1746	1644
13	1437	-1277
14	3397	3200
15	2654	2440
16	1040	940
17	2588	2565
18	488*	109
19	581*	-282
20	1108	1009
21	619*	-620
22	1009	-1027
23	496*	-196
24	504*	-240
25	591*	401
26	492*	315
27	556*	193
28	677	-452
29	1641	-1497
30	1297	1315
31	1505	-1430
32	1089	893
35	1090	896
36	1541	1479
2,3,L		
0	514*	-375
1	2500	2561
2	432*	146
3	503*	417
4	2955	-2984
5	668	656
6	2574	-2509
7	3352	3434
8	2422	2335
9	552*	-401
10	1263	1286
11	507*	105
12	557*	-295
13	766	661
14	972	-918
15	2957	-2901
16	1452	-1475
17	566*	-190
18	1800	1797
19	976	-932
20	577*	350
21	1655	-1726
22	2536	-2547
23	1227	1165
24	1196	-1278
25	572*	151
26	633*	-556
27	649*	563
28	614*	649
29	1888	1983
32	1486	-1445
36	1090	1121
37	1349	-1233
2,4,L		
0	4275	-4288
1	943	-962
2	576*	-544
3	1816	-1869
4	589	649
5	610*	399
6	618*	-81
7	3751	3724
8	535*	-186
9	565*	106
10	1685	-1696
11	2071	-2015
12	576*	399
13	1362	-1225
14	2650	2509
15	837	674
16	949	-906
17	1327	1371
18	1082	-1140
19	710*	-561
20	1372	-1297
21	2547	-2517
22	779*	-525
23	574*	160
24	775	763
25	1511	1561
26	982*	-1087
27	1186	1162
28	1720	-1659
31	1040	-963
35	1481	1348
39	1082	-993
2,5,L		
0	2070	2023
1	1752	-1701
2	671*	654
3	620*	-236
4	1246	-1336
5	597*	-358
6	872	-903
7	2448	-2420
8	2936	2920
9	650	622
10	3088	3126
11	616*	-408
12	788	768
13	561*	-445
14	544*	-240
15	2375	2254
16	548*	306
17	567*	-175
18	1919	1988
19	852	762
20	1870	1801
21	1509	1454
22	1768	-1719
23	1337	-1271
24	1078	-988
28	1053	1076
29	1936	-1782
30	1183	1349
36	1816	2060
37	1117	1272
2,6,L		
0	3469	-3487
1	2252	-2230
2	629*	-521
3	1747	-1853
4	530*	-185
5	585*	498
6	685	-809
7	570*	153
8	852	825
9	781	765
10	701	-562
11	1454	-1582
12	728*	384
13	1375	-1322
14	1972	1970
15	2366	2309
16	706*	-721
17	1507	1538
18	591*	-546
19	557*	-153
20	809*	-794
22	1312	-1234
25	1037	1113
28	1209	-1126
29	1674	-1706
31	1420	-924
43	1154	983
2,7,L		
0	1528	-1486
1	769	773
2	600*	-108
3	691*	-428
4	976	-1010
5	628*	270
6	1031	-991
7	2811	2829
8	911	849
9	626*	-354
10	642*	41
11	748*	-461
12	599*	99
13	605*	48
14	591*	499
15	1064	-1033
16	930	-1002
21	1788	-1792
22	1273	-1244
2,8,L		
0	717	689
1	678*	539
2	642*	401
3	686*	-316
4	714*	-335
5	584*	-151
7	1048	972
8	1877	1946
10	1786	1835
20	1022	1115
22	977	-1068
2,9,L		
0	2553	-2487
1	1758	-1756
3	1263	-1335
11	1111	-1291
14	1542	1548
15	1849	1976
25	1252	992
28	1192	-1106
29	1629	-1595
37	1174	767
2,10,L		
4	1503	-1530
6	1213	-1392
7	992	-1051
8	1329	1384
15	1335	1003
18	1289	957
21	914	757
22	1645	-1624
3,3,L		
0	2156	-2210
1	3988	4149
2	476*	-102
3	2789	2879
4	1648	1598
5	499*	263
6	634*	345
7	1333	1243
8	2075	2041
9	967	-980
10	875	815
11	2256	2315
12	1759	1692
13	1920	1797
14	3427	3318
15	4780	-4716
16	1042	896
17	2176	-2099
18	612*	-378
19	723	-738
20	765	643
21	557*	-241
22	891	-802
23	1772	1803
24	663	793
25	1257	-1339
26	567*	-9
27	496*	-73
28	1198	-989
29	3912	3483
30	1158	1163
32	1050	1052
36	1265	1378
37	1640	-1782
43	1654	-1892
3,4,L		
0	480	-550
1	813	859
2	513*	-142
3	1136	1203
4	643*	-386
5	523*	-118
6	760	-686
7	1672	-1583
8	639*	-282
9	587*	-256
10	899	-813
11	1226	1283
12	609*	-362
13	560*	576
14	539	-362
15	1158	-1104
16	615*	-493
17	623	-840
18	587*	41
19	537*	36
20	535*	-174
21	1068	1007
22	523*	-62
23	587*	308
24	521*	16
25	961	-950
29	1246	1025
3,5,L		
0	2263	2269
1	622*	-439
2	546*	92
3	581*	116
4	1279	-1355
5	514*	120
6	649*	-592
7	816	-896
8	579*	-463
9	554*	322
10	564*	63
11	534*	-35
12	874	-807
13	543*	-118
14	2558	-2516
15	668	529
16	532*	-314
17	577*	-240
18	961	992
19	553*	92
20	536*	176
21	717*	569
28	1079	1076
3,6,L		
0	1141	-1107
1	2464	2485
2	564*	-17
3	1836	1985
4	1608	1692
5	562*	-147
6	1240	1232
7	718*	-538
8	581*	239
9	670*	-562
10	568*	275
11	1735	1825
12	1114	1020
13	1501	1558
14	2332	2235
15	2621	-2632
16	1070	920
17	1459	-1517
18	911	-833
21	929	785
25	1268	-1316
29	2151	1990
32	1170	1299
3,7,L		
0	972	-939
1	2079	2109
2	583*	151
3	600*	353
4	1601	-1628
5	564*	340
6	2233	-2143
7	3205	3159
8	2253	2156
9	705*	-517
13	912	658
15	2580	-2623
16	1016	-1084
21	1593	-1824
22	2134	-2260
23	1162	1205
29	2139	2003
3,8,L		
0	1247	-1180
1	1623	1558
3	1278	1397
10	1358	-1189
11	1308	1340
15	1646	-1743
17	992	-1113
25	1274	-1022
29	1197	1421
35	1139	-673
3,9,L		
0	1755	1712
10	1089	933
16	1160	886
4,4,L		
0	2936	3286
1	1096	-1468
2	508*	131
3	1562	-1896
4	2757	2727
5	818	704
6	3188	3084
7	3174	3102
8	3240	-3124
9	749	758
10	770	-505
11	2429	-2393
12	563	-105
13	1489	-1458
14	1078	-944
15	1414	1298
16	2621	2431
17	981	1171
18	1201	-1249
19	718*	-479
20	640*	213
21	2222	-2167
22	4005	3906
24	1199	954
25	2076	2088
26	1313	1445
27	1302	1199
30	1410	-1495
31	988	-741
35	1235	1227
36	1482	-1721
39	1351	-1424
4,5,L		
0	1566	1816
1	597*	44
2	521*	-18
3	634*	332
4	649*	-18
5	613*	-176
6	953	768
7	662*	-359
8	2193	-2155
9	647*	-199
10	719*	-685
11	634*	406
12	1041	-991
13	530*	112
14	2160	-2057
15	652*	-42
16	623*	148
17	646*	-214
22	1826	1689
30	1210	-1166
36	1125	-1519
4,6,L		
0	1229	-1246
1	592*	-24
2	540*	-92
3	684*	-644
4	679*	162
5	671*	81
6	555*	-137
7	925	962
8	609*	-227
9	602*	-76
10	867	-1112
11	615	-409
4,7,L		
3	1067	-950
4	1509	1511
6	1234	1098
7	1521	1606
11	982	-810
14	963	1141
21	1536	-1279
31	1163	-715
4,8,L		
0	1629	1503
3	1081	763
8	1665	-1730
12	1024	-682
14	1600	-1683
22	1487	1505
30	1254	-1274
4,9,L		
1	1176	-1125
3	1191	-1286
6	1071	1058
7	1295	1202
8	1937	-2039
13	1041	-922
22	1599	1702
36	1338	-1489
5,5,L		
0	3697	4232
1	803	-966
2	863*	962
3	572*	-328
4	1347	-1343
5	743*	-458
6	798*	-648
7	1624	-1408
8	1730	1711
9	556*	50
10	2949	2856
11	539*	-104
12	722*	-362
14	2589	-2405
15	1594	1335
18	1782	1858
20	1691	1868
24	1195	-1307
26	1335	1431
28	2206	2176
29	1040	-1072
35	1138	-103
36	1102	1305
5,6,L		
0	2520	-2452
1	1153	-1002
7	1949	-1964
10	964	-789
14	1351	1436
15	1419	1455
21	1335	1309
5,7,L		
0	1423	1319
4	1693	-1666
6	1216	-1023
7	967	-957
10	1183	1086
14	1752	-1722
15	1011	807
24	1114	-1336
38	1154	824
5,8,L		
0	2759	2875
6	1014	1077
14	1272	-1467
16	1051	1310
5,10,L		
1	1154	-898
4	1158	-1210
6	1340	-1398
22	1269	-1414
6,6,L		
4	1210	1012
7	2351	-2266
12	1103	1004
14	1855	1825
21	1358	1640
6,7,L		
0	1409	-1381
7	1635	1663
21	1132	-1199
25	1139	623
6,8,L		
0	1511	-1589
3	1196	962
14	1073	915
25	1528	-1139
6,9,L		
14	1464	1221
6,10,L		
0	1272	-1274
7,7,L		
7	2217	2337
8	1497	1403
14	1139	899
15	1299	-1472
7,8,L		
15	1123	-745
8,9,L		
8	1148	-1025

[a] The columns are *l*, $10|F_o|$, $10F_c$.

* Unobserved reflections.

The barium coordination in the present compound is shown in stereo in Fig. 4. Each barium has 10 oxygen neighbors located at the vertices of a pentagonal prism, plus 3 [for Ba(1)] or 5 [for Ba(2)] more oxygens located outside three or all five, respectively, of the side faces of the prism. The coordination is not regular; the Ba–O distances range from 2.6 to 3.4 Å (cf. K–O distances of 2.8 to 3.4 Å in the tetragonal bronze K_xWO_3).

$Ba_{6+x}Nb_{14}Si_4O_{47}$ differs from the bronzes, of course, in that edge sharing occurs. We may consider this compound, however, as being constructed from blocks of a bronze-like structure (essentially that of $Ba_3Nb_6Si_4O_{26}$), which are joined by edge sharing, much as blocks of ReO_3-type structure are joined by edge sharing in such compounds as $TiNb_2O_7$ and $TiNb_{24}O_{62}$ (*10*).

The arrangement of oxygen around niobium and silicon is shown in Fig. 2, and Table II lists interatomic distances and angles. As shown, the NbO_6 octahedra are somewhat distorted. In the case of Nb(1) and Nb(3), this is presumably due to the necessity of fitting so many octahedra together in the edge-sharing region. The distortion, and in particular the tilt away from the vertical, of the Nb(2) octahedra are due primarily to the fact that the oxygens of the Si_2O_7 unit are tightly bound by the silicons, so that the length of the unit is more or less fixed at 4.5 Å. If the octahedra were undistorted and aligned, this would be the Nb(2)–O(2)–Nb(2) distance, corresponding to an Nb–O distance of 2.25 Å. This is rather long compared to the usual Nb–O distance of 1.9–2.1 Å. The tilt of the octahedra brings the niobiums closer together and reduces the Nb(2)–O(2) distance to a reasonable 1.91 Å. In the Si_2O_7 unit, the Si–O distances of 1.62 and 1.63 Å are normal for silicon-containing oxides, and the O–Si–O angles show only slight deviations from the tetrahedral angle of 109.5°. The central Si–O–Si bond is constrained to be linear, as all three atoms involved are located on a threefold symmetry axis. The linear Si_2O_7 group is rather uncommon, but it has also been found in, for instance, $Ba_3Nb_6Si_4O_{26}$ (and the corresponding tantalum compound), $Sc_2Si_2O_7$ (*12*), and $NaBa_3Si_2O_7(OH)$ (*13*), and the evidence is convincing that it does exist in $Ba_{6+x}Nb_{14}Si_4O_{47}$.

Table III lists observed and calculated structure factors for the compound.

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