

# The Structure of the Seven Layer Barium Niobium Silicon Oxide, $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ ( $x \approx 0.2$ )

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Received May 31, 1972

One of the products of reaction between  $\text{Nb}_2\text{O}_5$ , Nb, and BaO in a 1.6:1:2.4 mole ratio at 1250°C in an evacuated silica capsule is the complex oxide  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ . The compound has a hexagonal unit cell of dimensions  $a = 7.774 \pm 0.004 \text{ \AA}$ ,  $c = 16.765 \pm 0.007 \text{ \AA}$ , probable space group  $P\bar{3}$ ,  $Z = 1$ . Its structure has been determined from 4484 independent reflections measured by counter methods. Refinement by Fourier and least-squares methods was carried out to a weighted  $R$  value of 9.8% (conventional  $R = 12.4\%$ ).

The structure consists of a close-stacking of seven close-packed layers in the sequence  $\text{BaO}_6$ ,  $\text{O}_7$  (oxygen layer with 1/7 of the oxygen missing),  $\text{BaO}_6$ ,  $\text{O}_7$ ,  $\text{O}_6$ . Between two  $\text{BaO}_6$  layers there is one Nb in an octahedral site (population parameter  $\approx 0.8$ ); between  $\text{BaO}_6$  and  $\text{O}_7$  layers there are three Nb in octahedral sites; between  $\text{BaO}_6$  and  $\text{O}_6$  layers there are three Nb in sites coordinated by five O in a square pyramidal arrangement; and between  $\text{O}_6$  and  $\text{O}_7$  layers, there are three Nb in similar square pyramidal sites, one Nb in an octahedral site, and one Si in a tetrahedral site. The niobiums in square pyramidal sites form an octahedron about the oxygen vacancy of the  $\text{O}_6$  layer and engage in metal-metal bonding, the Nb-Nb distances ranging from 2.78 to 2.85 Å.

$\text{Nb}_6\text{O}_{18}$  clusters can be identified in which the  $\text{Nb}_6$  octahedron is surrounded by a cuboctahedron of oxygen atoms capped by oxygen atoms on the square faces. Alternatively, the oxygen array may be described as an octahedron of oxygens with oxygens also at the centers of the edges.

## Introduction

When  $\text{Nb}_2\text{O}_5$ , Nb, and BaO react in the presence of  $\text{SiO}_2$ , various complex oxides may be produced. The first such compound to be described was  $\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26}$ , which Shannon determined to have a structure composed of strings of  $\text{NbO}_6$  octahedra joined by corner-sharing, both among each other and with  $\text{Si}_2\text{O}_7$  groups (two  $\text{SiO}_4$  tetrahedra sharing one vertex), with bariums occupying holes between the chains (1). The compound  $\text{Ba}_3\text{Nb}_7\text{Si}_2\text{O}_{25-x}$  ( $x \approx 0.5$ ) has a similar but somewhat more complex structure (2), in which some edge-sharing of  $\text{NbO}_6$  octahedra occurs. A third oxide,  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ , however, has an entirely different structure which will be described herein.

In it  $\text{Nb}_6\text{O}_{18}$  clusters can be identified. Professor Ward has always shown an interest in such clusters, so we are particularly pleased to be able to report on a compound which not only

represents a continuation of his work at the University of Connecticut, but which also has some features of special interest to him.

## Experimental

The reactants  $\text{Nb}_2\text{O}_5$  and Nb were obtained commercially. BaO was prepared by heating  $\text{BaO}_2$  *in vacuo* to 1000°C for one hour. These three reactants were mixed in a 1.6:1:2.4 mole ratio and triturated under petroleum ether. The resulting powder was placed in a silica capsule which was evacuated and sealed, the silica serving as both container and reactant. The sample was held at 1250°C for one week. Upon removal from the furnace, the capsule was in a partially collapsed state, and on cooling it became clouded and crazed on the inside.

When the capsule was opened, black, highly reflective crystals were observed, both loose and

embedded in the walls, many of the former aggregated into clusters that appeared to have been partially melted. The loose non-aggregated crystals occurred in two distinct habits: thick chunks only occasionally exhibiting flat faces, and very thin hexagonal plates, often broken but usually having at least one 120° angle visible. The chunks were eventually determined to be Ba<sub>3</sub>Nb<sub>7</sub>Si<sub>2</sub>O<sub>25-x</sub>. It is, however, the investigation of the thin plates that is of interest here.

A single crystal in the shape of a roughly triangular plate about 0.3 mm across and 0.05 mm thick was selected for study. X-ray precession photographs showed hexagonal (trigonal) symmetry, Laue group  $\bar{3}$ . There were no systematic absences, so the probable space group is either  $P\bar{3}$  or  $P\bar{3}$ . Unit-cell dimensions of  $a = 7.78 \text{ \AA}$ ,  $c = 16.75 \text{ \AA}$  were determined from the photographs. Due to the extremely small quantity of sample, measurement of its density was not feasible.

Data for structure determination were collected on a Picker Nuclear computer-controlled single-crystal diffractometer, using MoK $\alpha$  radiation and operating in the  $\theta$ - $2\theta$  scan mode. The base scan width was 3° in  $2\theta$ ; a dispersion factor of 0.692 was used; background was counted for 20 seconds on each side of the peak; three standard reflections were measured every 40 reflections. Data were collected in the following range:  $h$  and  $k$ , -3 to 10;  $l$ , -3 to 36; and  $2\theta$ , 2° to 100°. In all, 6260 intensities were measured. The standards showed considerable variation with time, which was later shown to be due to instrument instability. Partial correction for this variability was made by dividing the data into groups during whose collection the standards remained reasonably constant and applying scale factors to bring the standards of different groups into agreement. Twenty scale groups were used, containing from 80 to 920 reflections and with scale factors ranging from 0.928 to 1.071. After scaling, the three standards had standard deviations of 1.6%, 6.0%, and 3.6%. The data were corrected for background and absorption, and reflections related by the symmetry of the Laue group were averaged. The absorption correction was made using Prewitt's program ACACA (3), with a few modifications to compensate for errors presumably due to diffractometer alignment problems. Averaging reduced the data set to 4484 independent reflections.

Of these, 1148 had intensities less than twice the standard deviation of the background and

were labelled as unobserved. Upper bounds for these intensities were set equal to the observed intensities plus twice their standard deviation ( $I_0 + 2\sigma_{I_0}$ ). A standard deviation was calculated for each reflection according to the formula

$$\sigma_F = \frac{\sigma_g}{10} \frac{1}{2\sqrt{Lp}} \{ (N_T + BG + [0.02(N_T - BG)]^2 / (N_T - BG))^{1/2} \}$$

for observed reflections and

$$\sigma_F = \frac{\sigma_g}{10} \frac{1}{2\sqrt{Lp}} (BG)^{1/2}$$

for unobserved reflections, where  $\sigma_g$  is the percent standard deviation in a group of symmetry related reflections (set to 10 for single reflections),  $Lp$  is the product of Lorentz and polarization factors,  $N_T$  is the total counts recorded on the scan through the peak, and  $BG$  is the background counts for the scan. These standard deviations are derived from counting statistics, the equation used being based on those given by Stout and Jensen (4).

Lorentz and polarization corrections were made using the program package "The X-ray System" (5), which was also used to calculate accurate cell dimensions of  $a = 7.774 \pm 0.004 \text{ \AA}$  and  $c = 16.765 \pm 0.007 \text{ \AA}$  from the  $2\theta$  values of twelve individually centered reflections, and in all subsequent calculations of Fourier maps, least squares refinements, and so forth.

A rough determination of relative composition was made with a KEVEX-Quanta/Metric energy dispersive spectrometer, using Ba<sub>3</sub>Nb<sub>7</sub>Si<sub>2</sub>O<sub>25-x</sub> as the standard. This measurement indicated a Ba/Si ratio of about 3/2 and a Ba/Nb ratio of about 1/7. The statistical distribution of normalized structure factors indicated the presence of a center of symmetry, making the probable space group  $P\bar{3}$ .

### Structure Determination and Refinement

Examination of the  $hk0$  reflections revealed 140 and 630 to be very strong, suggesting that many of the heavy atoms lie on or near the intersections of the corresponding planes, i.e. a sites  $0, 0, z$ ;  $1/3, 2/3, z$ ;  $1/21, 5/21, z$ ;  $2/7, 3/7, z$ ;  $2/21, 10/21, z$  (and symmetry-related sites). Of these, only the first two are suitable for barium, since use of any of the other three would place symmetry-related bariums uncomfortably close together. All five sites are possible for

niobium (and also for oxygen). A Patterson map as calculated and showed strong concentrations of peaks corresponding to the interatomic vectors along the above hypothesized locations.

One particularly large peak indicated the possible presence of a heavy atom at  $1/3, 2/3, 0.14$ . A difference Fourier map calculated from a model with just one barium at this location was used in conjunction with the Patterson to suggest niobium locations. Structure solution proceeded by trial and error, using  $\Delta F$  maps as the primary tool for revision of the model. In order to reduce calculation time, only observed reflections of

$\sin \theta \leq 0.5$  (1770 reflections) were used in this process. Although the initial barium had actually been wrongly placed, a reasonable model was eventually produced in this way, having parameters close to the final values shown in Table I. The ideal formula of the compound was determined from this model to be  $\text{Ba}_3\text{Nb}_{21}\text{Si}_2\text{O}_{44}$ . After refinement of isotropic thermal parameters, using a weighting function  $w = 1/\sigma_F^2$ , the weighted  $R$ -value was 0.115 and the conventional  $R$  was 0.119 for the restricted data set.

Anisotropic thermal parameters were introduced for barium and niobium and the full data

TABLE I  
ATOMIC PARAMETERS FOR  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$

Atom	Ba(1)	Ba(2)	Nb(1)	Nb(2)	Nb(3)	Nb(4)	Nb(5) <sup>a</sup>
Position	1a	2d	6g (general)	6g	6g	2c	1b
Initial coordinates	0, 0, 0	$\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$	$\frac{2}{21}, \frac{1}{21}, \frac{7}{100}$	$\frac{1}{7}, \frac{5}{7}, \frac{21}{100}$	$\frac{3}{7}, \frac{1}{7}, \frac{35}{100}$	0, 0, $\frac{21}{100}$	0, 0, $\frac{1}{2}$
Final							
x	0	$\frac{1}{3}$	0.1123(2)	0.1423(2)	0.3938(2)	0	0
y	0	$\frac{2}{3}$	0.4762(2)	0.6951(2)	0.1317(2)	0	0
z	0	0.4406(1)	0.0765(1)	0.2165(1)	0.3601(1)	0.2112(1)	$\frac{1}{2}$
$J_{11} \times 100$	1.582	2.623	0.801(52)	0.740(52)	1.757(68)	1.586	2.313
$J_{22} \times 100$	1.582	2.623	0.814(53)	0.851(53)	1.415(62)	1.586	2.313
$J_{33} \times 100$	0.738(52)	0.872(42)	0.248(28)	0.306(28)	0.383(30)	0.542(57)	1.197(145)
$J_{12} \times 100$	0.791(31)	1.311(29)	0.391(46)	0.461(45)	1.094(57)	0.793(35)	1.157(91)
$J_{13} \times 100$	0	0	0.042(35)	-0.100(34)	-0.185(39)	0	0
$J_{23} \times 100$	0	0	-0.045(35)	0.000(36)	-0.132(39)	0	0
Atom	Si(1)	O(1)	O(2)	O(3)	O(4)	O(5)	
Position	2d	6g	6g	6g	6g	6g	
Initial coordinates	$\frac{1}{3}, \frac{2}{3}, \frac{7}{100}$	$\frac{1}{7}, \frac{5}{7}, 0$	$\frac{1}{21}, \frac{5}{21}, \frac{7}{50}$	$\frac{1}{21}, \frac{8}{21}, \frac{7}{50}$	$\frac{5}{21}, \frac{4}{21}, \frac{14}{50}$	$\frac{2}{21}, \frac{1}{21}, \frac{14}{50}$	
Final							
x	$\frac{1}{3}$	0.1265(14)	0.0715(14)	0.5202(14)	0.2358(16)	0.0992(15)	
y	$\frac{2}{3}$	0.7061(15)	0.2367(15)	0.4112(14)	0.1726(15)	0.4708(14)	
z	0.8199(3)	0.0080(5)	0.1453(5)	0.1487(5)	0.2784(5)	0.2915(5)	
$J \times 100$	0.727(107)	0.964(165)	0.918(162)	0.633(140)	0.996(162)	0.983(159)	
Atom	O(6)	O(7)	O(8)				
Position	6g	6g	2d				
Initial coordinates	$\frac{1}{21}, \frac{8}{21}, \frac{21}{50}$	$\frac{1}{21}, \frac{5}{21}, \frac{21}{50}$	$\frac{1}{3}, \frac{2}{3}, \frac{3}{50}$				
Final							
x	0.4975(18)	0.0274(16)	$\frac{1}{3}$				
y	0.3903(18)	0.2327(16)	$\frac{2}{3}$				
z	0.4107(7)	0.4298(5)	0.7247(8)				
$J \times 100$	2.159(237)	1.282(171)	0.697(258)				

<sup>a</sup> Population parameter 0.79(1).

Anisotropic thermal vibration expressed as:

$$\exp[-1/4(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$$

Errors in the last digit are given in parentheses; where no error is shown, the parameter is not independent.

Isotropic thermal motion expressed as:  $[\exp -8\pi^2 U \sin^2 \theta / \lambda^2]$

set was used for the final stages of refinement. Allowing population parameters to vary resulted in a significant change only for Nb(5), whose final refined occupancy factor is 0.79. The compound formula is thus  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$  ( $x \approx 0.2$ ). A correction for secondary extinction was made to the 118 reflections having intensities greater than 10,000 and  $\sin\theta/\lambda$  less than 0.40, using the empirical method described by Stout and Jensen (4). Anomalous dispersion was included in all structure factor calculations. Neutral atom scattering factors taken from the International Tables (6) were used throughout. The final weighted  $R$  was 0.098, the conventional  $R$  0.124. The maximum shift to error ratio in the final cycle of refinement was 0.084. A final  $\Delta F$  map showed no peak higher than one-third the height of the peak produced by deliberate omission of a single oxygen atom. Atomic parameters are listed in Table I.

### Discussion

The unit cell of  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$  is shown in stereo in Fig. 1. It may be conveniently described in terms of the layer structure diagrammed in Fig. 2. Considering each layer simply as a close-packing of equal spheres, the stacking sequence is  $ABCBCBC$ . The compositions of the seven layers are:  $\text{BaO}_6$ ,  $\text{O}_6$  (an oxygen layer with one-seventh of the oxygens missing),  $\text{O}_7$  (a complete oxygen layer),  $\text{BaO}_6$ ,  $\text{BaO}_6$ ,  $\text{O}_7$ ,  $\text{O}_6$ , respectively.

The  $\text{BaO}_6$  layer found here has not, to our knowledge, been reported previously. It is, however, analogous to the  $\text{KF}_6$  layer found in  $\text{KOsF}_6$  and similar compounds.  $\text{KOsF}_6$  has a structure based on a cubic stacking of approximately close-packed  $\text{KF}_6$  layers, with one Os occupying the only available octahedral site between each pair of layers (7). Between the two

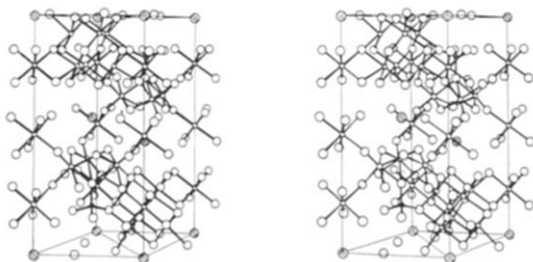


FIG. 1. Stereo view of the unit cell of  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ . Shaded circles are Ba, large open circles O, small open circles Nb, and small closed circles Si.

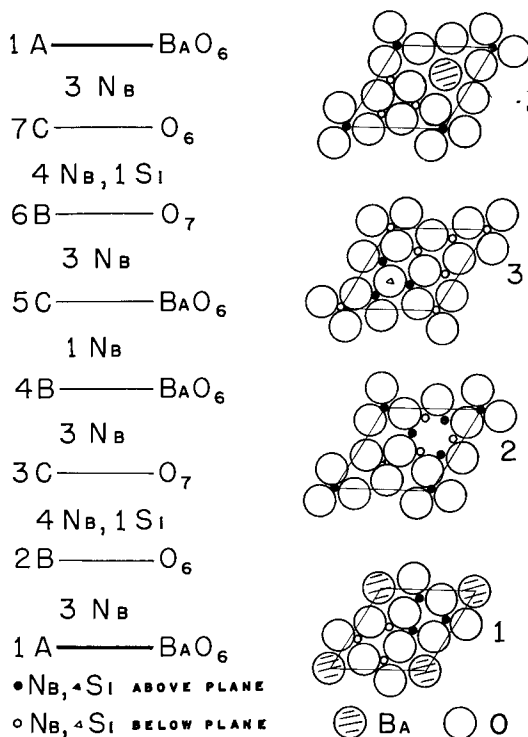


FIG. 2. Layer structure of  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ .

adjacent  $\text{BaO}_6$  layers in  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$  there is, similarly, a single niobium (Nb(5)) in the only available octahedral site, although here its population parameter is somewhat less than one.

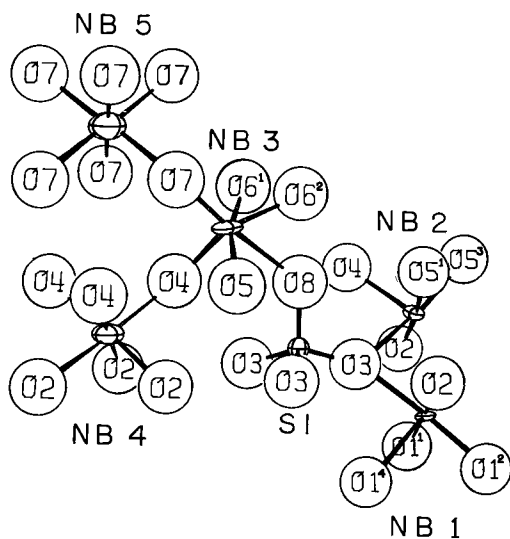
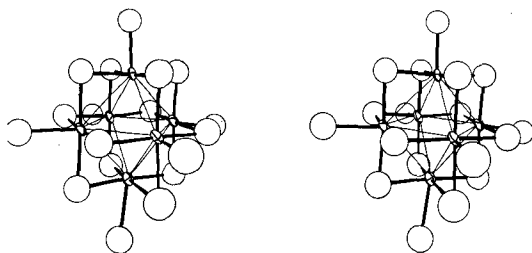


FIG. 3. Niobium and silicon coordination in  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ . See Table II for explanation of superscripts.

FIG. 4. Stereo view of  $\text{Nb}_6\text{O}_{18}$  cluster.

Between  $\text{BaO}_6$  and  $\text{O}_7$  layers there are three niobiums in octahedral sites; between  $\text{BaO}_6$  and  $\text{O}_6$  layers there are three niobiums in sites coordinated by square pyramids of oxygens with the niobiums in the pyramid bases; and between  $\text{O}_6$  and  $\text{O}_7$  layers there are three niobiums in square pyramidal sites, one niobium in a normal octahedral site, and one silicon in a tetrahedral site. The coordination of the various niobiums and of the silicon is shown in Fig. 3.

The square pyramidal sites mentioned above would be octahedral except for the oxygen vacancy in the  $\text{O}_6$  layer. The absence of an oxygen at the site is established by the lack of any peak on the final  $\Delta F$  map and by the fact that, when an oxygen atom was introduced there, upon refinement it quickly acquired a thermal parameter so large ( $U \approx 55$ ) as to indicate that the atom was not there at all. The six niobiums in square pyramidal sites surround the vacancy in an octahedral arrangement, as shown in Fig. 4. The Nb-O distances, as shown in Table II,

TABLE II

INTERATOMIC DISTANCES AND ANGLES IN  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ 

Distances:	
Ba(1)-O(1)	$2.907 \pm 0.014 \text{ \AA}$
Ba(1)-O(2)	$2.933 \pm 0.009$
Ba(2)-O(5)	$3.018 \pm 0.008$
Ba(2)-O(6) (same layer)	$3.039 \pm 0.017$
Ba(2)-O(6) (different layers)	$2.953 \pm 0.013$
Ba(2)-O(7)	$3.008 \pm 0.012$
Nb(1)-Nb(1)	$2.793 \pm 0.002$
Nb(1)-Nb(2) <sup>1</sup>	$2.840 \pm 0.002$
Nb(1)-Nb(2) <sup>2</sup>	$2.854 \pm 0.002$
Nb(1)-O(1) <sup>1</sup>	$2.080 \pm 0.012$
Nb(1)-O(1) <sup>2</sup>	$2.028 \pm 0.011$
Nb(1)-O(1) <sup>4</sup>	$2.197 \pm 0.008$
Nb(1)-O(2)	$2.076 \pm 0.011$
Nb(1)-O(3)	$2.115 \pm 0.007$
Nb(2)-Nb(2)	$2.783 \pm 0.002$
Nb(2)-O(2)	$2.104 \pm 0.010$

TABLE II—continued

Distances:	
Nb(2)-O(3)	$2.154 \pm 0.006$
Nb(2)-O(4)	$2.185 \pm 0.009$
Nb(2)-O(5) <sup>1</sup>	$2.037 \pm 0.011$
Nb(2)-O(5) <sup>3</sup>	$2.114 \pm 0.006$
Nb(3)-O(4)	$1.969 \pm 0.012$
Nb(3)-O(5)	$2.065 \pm 0.011$
Nb(3)-O(6) <sup>1</sup>	$1.947 \pm 0.013$
Nb(3)-O(6) <sup>2</sup>	$1.973 \pm 0.014$
Nb(3)-O(7)	$1.797 \pm 0.007$
Nb(3)-O(8)	$2.378 \pm 0.008$
Nb(4)-O(2)	$1.973 \pm 0.011$
Nb(4)-O(4)	$1.992 \pm 0.011$
Nb(5)-O(7)	$2.078 \pm 0.012$
Si(1)-O(3)	$1.622 \pm 0.013$
Si(1)-O(8)	$1.595 \pm 0.015$
Angles:	
O(1) <sup>1</sup> -Nb(1)-O(1) <sup>4</sup>	$97.3 \pm 0.4$
O(1) <sup>1</sup> -Nb(1)-O(1) <sup>4</sup>	$82.1 \pm 0.4$
O(1) <sup>2</sup> -Nb(1)-O(1) <sup>4</sup>	$87.2 \pm 0.4$
O(1) <sup>2</sup> -Nb(1)-O(2) <sup>1</sup>	$86.2 \pm 0.4$
O(1) <sup>4</sup> -Nb(1)-O(2) <sup>1</sup>	$94.5 \pm 0.4$
O(1) <sup>1</sup> -Nb(1)-O(3) <sup>3</sup>	$90.0 \pm 0.4$
O(1) <sup>4</sup> -Nb(1)-O(3) <sup>3</sup>	$87.0 \pm 0.4$
O(2)-Nb(1)-O(3)	$86.2 \pm 0.4$
O(2)-Nb(2)-O(3)	$91.3 \pm 0.3$
O(2)-Nb(2)-O(4)	$79.3 \pm 0.3$
O(2)-Nb(2)-O(5)	$90.5 \pm 0.3$
O(3)-Nb(2)-O(4)	$87.2 \pm 0.3$
O(3)-Nb(2)-O(5)	$87.9 \pm 0.4$
O(4) <sup>3</sup> -Nb(2)-O(5) <sup>1</sup>	$95.2 \pm 0.4$
O(4) <sup>3</sup> -Nb(2)-O(5) <sup>3</sup>	$88.6 \pm 0.3$
O(4)-Nb(3)-O(5)	$88.0 \pm 0.4$
O(4)-Nb(3)-O(6)	$96.1 \pm 0.6$
O(4)-Nb(3)-O(7)	$101.8 \pm 0.4$
O(4)-Nb(3)-O(8)	$84.3 \pm 0.4$
O(5)-Nb(3)-O(6)	$82.0 \pm 0.3$
O(5)-Nb(3)-O(7)	$94.5 \pm 0.4$
O(5)-Nb(3)-O(8)	$84.2 \pm 0.2$
O(6)-Nb(3)-O(6)	$88.8 \pm 0.5$
O(6) <sup>1</sup> -Nb(3)-O(7) <sup>3</sup>	$101.6 \pm 0.5$
O(6) <sup>2</sup> -Nb(3)-O(7) <sup>3</sup>	$95.4 \pm 0.4$
O(6)-Nb(3)-O(8)	$78.7 \pm 0.4$
O(2)-Nb(4)-O(2)	$91.7 \pm 0.5$
O(2) <sup>1</sup> -Nb(4)-O(4) <sup>1</sup>	$87.3 \pm 0.4$
O(2) <sup>1</sup> -Nb(4)-O(4) <sup>2</sup>	$89.8 \pm 0.4$
O(4)-Nb(4)-O(4)	$91.2 \pm 0.4$
O(7)-Nb(5)-O(7) (O's in same layer)	$91.1 \pm 0.5^\circ$
O(7)-Nb(5)-O(7) (O's in different layers)	$88.9 \pm 0.5$
O(3)-Si(1)-O(3)	$110.0 \pm 0.5$
O(3)-Si(1)-O(8)	$109.0 \pm 0.4$

Where necessary, symmetry-related atoms are distinguished by superscripts referring to the list of general position coordinates for space group  $\text{P}\bar{3}$  (No. 147) in the International Table (11).

TABLE III  
ELECTROSTATIC BOND STRENGTHS TO OXYGEN IN  
 $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$

Assuming all niobium to be in average oxidation state (+3.56):

O(1): 1 Ba at 1/6 + 3 Nb at 0.71	= 2.30
O(2): 1 Ba at 1/6 + 2 Nb at 0.71 + 1 Nb at 0.59	= 2.18
O(3): 1 Si at 1 + 2 Nb at 0.71	= 2.42
O(4): 1 Nb at 0.71 + 2 Nb at 0.59	= 1.89
O(5): 1 Ba at 1/6 + 2 Nb at 0.71 + 1 Nb at 0.59	= 2.18
O(6): 2 Ba at 1/6 + 2 Nb at 0.59	= 1.51
O(7): 1 Ba at 1/6 + 1.8 Nb at 0.59	= 1.23
O(8): 1 Si at 1 + 3 Nb at 0.59	= 2.77

Assuming Nb(1) and Nb(2) to be in +2.5 oxidation state and Nb(3), Nb(4), and Nb(5) to be  $\text{Nb}^V$ :

O(1): 1 Ba at 1/6 + 3 Nb at 1/2	= 1.67
O(2): 1 Ba at 1/6 + 2 Nb at 1/2 + 1 Nb at 5/6	= 2.00
O(3): 1 Si at 1 + 2 Nb at 1/2	= 2.00
O(4): 1 Nb at 1/2 + 2 Nb at 5/6	= 2.17
O(5): 1 Ba at 1/6 + 2 Nb at 1/2 + 1 Nb at 5/6	= 2.00
O(6): 2 Ba at 1/6 + 2 Nb at 5/6	= 2.00
O(7): 1 Ba at 1/6 + 1.8 Nb at 5/6	= 1.67
O(8): 1 Si at 1 + 3 Nb at 5/6	= 3.50

range from 2.03 Å to 2.20 Å, well within the normal range for niobium oxides, but the Nb–Nb distances, averaging 2.81 Å, are extremely short.

In the ion  $\text{Nb}_6\text{O}_{19}^{8-}$ , for instance, the arrangement of niobium and oxygen is the same as in the present  $\text{Nb}_6\text{O}_{18}$  grouping except that an additional oxygen is present in the center of the group. The shortest Nb–Nb distance there, however, is about 3.2 Å (8). In that case, niobium is present as  $\text{Nb}^V$ . In  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ , however, the average niobium oxidation state is +3.56, assuming  $x = 0.21$ . Moreover, Nb(3), Nb(4), and Nb(5) are found in the centers of simple  $\text{NbO}_6$  octahedra joined by corner- and edge-sharing and probably have oxidation numbers not much below +5. Hence Nb(1) and Nb(2), which make up the octahedral cluster, probably have oxidation states in the neighborhood of +2.5.

Thus a more appropriate analogy than the  $\text{Nb}_6\text{O}_{19}^{8-}$  group is found in the  $\text{Nb}_6\text{Cl}_{12}^{2+}$  ion, which consists of an octahedron of niobiums with chlorines placed some distance out from the midpoints of the edges. The niobium oxidation state is  $+2\frac{1}{3}$ , the average Nb–Nb distance 2.9 Å, and the shortest distance 2.85 Å, quite comparable to the values in  $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$  (9). An even more similar Nb–Nb distance is found

in  $\text{NbO}_2$ , in which edge-sharing  $\text{NbO}_6$  octahedra in a rutile-type chain are distorted so as to bring pairs of niobiums into metal–metal bonding range. The Nb–Nb distances along the chain are alternately 2.80 Å and 3.20 Å (10). The bonding distance of 2.80 Å is virtually identical to the 2.81 Å Nb–Nb distance found in the present compound.

Nb(1) and Nb(2), then, form an octahedral cluster of niobiums held together by metal–metal bonding, each niobium being coordinated to four others. The coordination sphere of each niobium consists of five oxygens in a square pyramidal arrangement, with the niobium in the base of the pyramid.  $\text{Nb}_6\text{O}_{18}$  clusters can be identified in which the  $\text{Nb}_6$  octahedron is surrounded by a cuboctahedron of oxygen atoms capped by oxygen atoms on the square faces. Alternatively, the oxygen array may be described as an octahedron with oxygens also at the centers of the edges. The remaining niobiums in the structure are in octahedral sites, having Nb–O distances of 1.95 to 2.08 Å, with the exception of the Nb(3)–O(8) distance of 2.38 Å. The extreme length of this bond relative to the normal Nb–O distance is due to the very poor local charge balance around O(8) shown in Table III. Electrostatic bond strengths are given first

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS. COLUMNS ARE I, 10|F0|, 10|F1|. UNOBSERVED REFLECTIONS ARE MARKED WITH ASTERISKS.

Table with multiple columns of numerical data representing structure factors. Includes sub-headers like 10L, 10|F0|, 10|F1|, and various reflection indices. Asterisks indicate unobserved reflections.





TABLE IV—continued

8+9L	20 266* 274	9+2L	27 237* 17	9+4L	10 346 290	11 205 298	10+1L	6 195* -12	10 317 205	12+5L	14+7L
7 270 -195	21 250* 61	1 151* -72	28 379 238	0 657 481	11 194 -134	12 301 -246	9 350 313	11+10L	1 226* -157	1 264* 108	
8 230* -14	23 246* 87	2 356* -271	9+1L	1 185* -35	13 246* -51	14 649 677	2 477 467	2 278* 103	2 212 60	2 237 265	
9 290* 356	24 457 425	3 932 -352	0 193 -678	2 191* 132	15 311* 169	16 270 481	3 261 -201	3 369 -307	3 163* 943	3 126* -92	
0 260* 56	25 271 35	4 332 278	0 413 380	3 599 576	15 350* 31	16 405 546	4 355 238	3 288* -67	3 189* -130	3 164* -61	
1 303 121	26 222 196	5 1492 1305	1 198 -248	4 209 -121	16 442 362	17 283 369	5 467 552	4 207 212	4 189* -130	4 144* -6L	
2 251* -186	27 251* -186	6 214 -678	2 813 -678	5 235 71	17 278* -265	18 216 -265	6 1214 1098	5 218 -90	5 117* -9L	5 506 258	
3 9+9L	28 220* -67	7 236 215	3 514 -235	6 203* -84	18 260* -87	19 639 624	7 406 298	6 260* -210	6 113* -10L	6 506 258	
4 250* -63	29 209* 239	8 214 -186	4 460 -459	7 176 -186	19 478 286	20 350 399	8 498 -280	7 270 -325	7 330* 390	7 237 265	
5 459 444	30 266* 274	9 1562 1374	5 1052 1374	8 175 -77	20 251* 129	21 248* -43	9 291 141	8 229* 184	8 117* -10L	8 308 -259	
6 407 407	31 6+6L	11 628 -557	6 151 156	10 219* -136	21 252* 118	22 249 -114	11 359 -979	9 634 586	9 414 367	9 113* -8L	
7 425 512	32 316 230	12 489 -653	7 326 -356	11 194 -158	22 250* -122	23 246* -427	12 220 -289	10 332* 79	10 312* 934	10 312* 934	
8 431 743	33 316 230	13 316 230	8 889 846	12 301 264	23 251* -233	24 252* -95	13 1270 -1114	11 317* 104	11 209* -76	11 213* -543	
9 435 457	34 445 406	14 217* 232	10 174* 1109	13 281* 90	24 238 184	25 301 359	14 270* 392	12 246* 104	12 280 86	12 280 86	
0 177* 22	35 172 -143	15 217* 232	12 429 -302	14 581 496	25 230* 53	26 274 -142	15 1095 920	13 314 201	13 209* 79	13 266* 42	
1 187* 136	36 172 -143	16 231* -78	13 250* 408	15 326 257	26 274 -142	27 306 -255	16 558 558	14 317* 104	14 209* 79	14 266* 42	
2 249 116	37 440 459	17 727 -718	14 348 364	16 369 285	27 274 -142	28 419 426	17 314 300	15 218* 19	15 432* -358	15 432* -358	
3 505 593	38 533 538	18 450 394	15 348 364	17 369 285	28 419 426	29 306 -255	18 220 74	16 255* -285	16 357 320	16 357 320	
4 253* 49	39 532 -301	19 1120 1093	16 200* -292	18 382 -280	29 306 -255	30 350 399	19 270 704	17 530 -492	17 357 320	17 357 320	
5 124* 153	40 476 -503	20 275* -158	16 428 -415	19 272* 47	30 350 399	31 366* 87	20 280* -43	18 229* 19	18 229* 19	18 229* 19	
6 187* 619	41 460 468	21 441 449	17 352 -270	20 272* -52	31 366* 87	32 413 1178	21 280* -43	19 229* 19	19 229* 19	19 229* 19	
7 141 316	42 476 -503	22 300* 350	18 107 659	21 253* 88	32 413 1178	33 501* 1022	22 287* 145	20 223 121	20 223 121	20 223 121	
8 273* -225	43 338 371	23 500* 350	19 352 -270	22 272* -52	33 501* 1022	34 1330 -1202	23 287* 145	21 223 121	21 223 121	21 223 121	
9 168* 413	44 338 371	24 640 684	20 223 111	23 500* 350	34 1330 -1202	35 1591 -959	24 287* 145	22 223 121	22 223 121	22 223 121	
10 176* 525	45 344 621	25 253* -240	21 305* 484	24 640 684	35 1591 -959	36 2079 204	25 287* 145	23 223 121	23 223 121	23 223 121	
11 947 501	46 140* 1755	26 242* 124	22 485 599	25 485 599	36 2079 204	37 217* 227	26 287* 145	24 223 121	24 223 121	24 223 121	
12 284 254	47 227* -143	27 242* 124	24 559 473	1 200 133	37 217* 227	38 182* -287	27 287* 145	25 223 121	25 223 121	25 223 121	
13 214 -239	48 220* -175	28 238* -26	25 464* -149	2 193* 30	38 182* -287	39 306* -255	28 287* 145	26 223 121	26 223 121	26 223 121	
14 249* -225	49 209* 239	29 258* 108	26 366 -295	3 182 80	39 306* -255	40 242* 124	29 287* 145	27 223 121	27 223 121	27 223 121	
15 228* 35	50 533 538	30 258* 108	27 272* -64	4 368 266	40 242* 124	41 242* 124	30 287* 145	28 223 121	28 223 121	28 223 121	
16 224 185	51 209* 239	31 9+1L	28 9+2L	5 294 266	41 242* 124	42 242* 124	31 287* 145	29 223 121	29 223 121	29 223 121	
17 249 375	52 222 359	32 9+1L	29 9+2L	6 263* 127	42 242* 124	43 242* 124	32 287* 145	30 223 121	30 223 121	30 223 121	
18 221* -75	53 216 786	33 9+1L	30 9+2L	7 294 266	43 242* 124	44 242* 124	33 287* 145	31 223 121	31 223 121	31 223 121	
19 205 106	54 209* 239	34 9+1L	31 9+2L	8 294 266	44 242* 124	45 242* 124	34 287* 145	32 223 121	32 223 121	32 223 121	
20 249* -32	55 203 363	35 9+1L	32 9+2L	9 294 266	45 242* 124	46 242* 124	35 287* 145	33 223 121	33 223 121	33 223 121	
21 249* -32	56 203 363	36 9+1L	33 9+2L	10 294 266	46 242* 124	47 242* 124	36 287* 145	34 223 121	34 223 121	34 223 121	
22 249* -32	57 203 363	37 9+1L	34 9+2L	11 294 266	47 242* 124	48 242* 124	37 287* 145	35 223 121	35 223 121	35 223 121	
23 249* -32	58 203 363	38 9+1L	35 9+2L	12 294 266	48 242* 124	49 242* 124	38 287* 145	36 223 121	36 223 121	36 223 121	
24 249* -32	59 203 363	39 9+1L	36 9+2L	13 294 266	49 242* 124	50 242* 124	39 287* 145	37 223 121	37 223 121	37 223 121	
25 249* -32	60 203 363	40 9+1L	37 9+2L	14 294 266	50 242* 124	51 242* 124	40 287* 145	38 223 121	38 223 121	38 223 121	
26 249* -32	61 203 363	41 9+1L	38 9+2L	15 294 266	51 242* 124	52 242* 124	41 287* 145	39 223 121	39 223 121	39 223 121	
27 249* -32	62 203 363	42 9+1L	39 9+2L	16 294 266	52 242* 124	53 242* 124	42 287* 145	40 223 121	40 223 121	40 223 121	
28 249* -32	63 203 363	43 9+1L	40 9+2L	17 294 266	53 242* 124	54 242* 124	43 287* 145	41 223 121	41 223 121	41 223 121	
29 249* -32	64 203 363	44 9+1L	41 9+2L	18 294 266	54 242* 124	55 242* 124	44 287* 145	42 223 121	42 223 121	42 223 121	
30 249* -32	65 203 363	45 9+1L	42 9+2L	19 294 266	55 242* 124	56 242* 124	45 287* 145	43 223 121	43 223 121	43 223 121	
31 249* -32	66 203 363	46 9+1L	43 9+2L	20 294 266	56 242* 124	57 242* 124	46 287* 145	44 223 121	44 223 121	44 223 121	
32 249* -32	67 203 363	47 9+1L	44 9+2L	21 294 266	57 242* 124	58 242* 124	47 287* 145	45 223 121	45 223 121	45 223 121	
33 249* -32	68 203 363	48 9+1L	45 9+2L	22 294 266	58 242* 124	59 242* 124	48 287* 145	46 223 121	46 223 121	46 223 121	
34 249* -32	69 203 363	49 9+1L	46 9+2L	23 294 266	59 242* 124	60 242* 124	49 287* 145	47 223 121	47 223 121	47 223 121	
35 249* -32	70 203 363	50 9+1L	47 9+2L	24 294 266	60 242* 124	61 242* 124	50 287* 145	48 223 121	48 223 121	48 223 121	
36 249* -32	71 203 363	51 9+1L	48 9+2L	25 294 266	61 242* 124	62 242* 124	51 287* 145	49 223 121	49 223 121	49 223 121	
37 249* -32	72 203 363	52 9+1L	49 9+2L	26 294 266	62 242* 124	63 242* 124	52 287* 145	50 223 121	50 223 121	50 223 121	
38 249* -32	73 203 363	53 9+1L	50 9+2L	27 294 266	63 242* 124	64 242* 124	53 287* 145	51 223 121	51 223 121	51 223 121	
39 249* -32	74 203 363	54 9+1L	51 9+2L	28 294 266	64 242* 124	65 242* 124	54 287* 145	52 223 121	52 223 121	52 223 121	
40 249* -32	75 203 363	55 9+1L	52 9+2L	29 294 266	65 242* 124	66 242* 124	55 287* 145	53 223 121	53 223 121	53 223 121	
41 249* -32	76 203 363	56 9+1L	53 9+2L	30 294 266	66 242* 124	67 242* 124	56 287* 145	54 223 121	54 223 121	54 223 121	
42 249* -32	77 203 363	57 9+1L	54 9+2L	31 294 266	67 242* 124	68 242* 124	57 287* 145	55 223 121	55 223 121	55 223 121	
43 249* -32	78 203 363	58 9+1L	55 9+2L	32 294 266	68 242* 124	69 242* 124	58 287* 145	56 223 121	56 223 121	56 223 121	
44 249* -32	79 203 363	59 9+1L	56 9+2L	33 294 266	69 242* 124	70 242* 124	59 287* 145	57 223 121	57 223 121	57 223 121	
45 249* -32	80 203 363	60 9+1L	57 9+2L	34 294 266	70 242* 124	71 242* 124	60 287* 145	58 223 121	58 223 121	58 223 121	
46 249* -32	81 203 363	61 9+1L	58 9+2L	35 294 266	71 242* 124	72 242* 124	61 287* 145	59 223 121	59 223 121	59 223 121	
47 249* -32	82 203 363	62 9+1L	59 9+2L	36 294 266	72 242* 124	73 242* 124	62 287* 145	60 223 121	60 223 121	60 223 121	
48 249* -32	83 203 363	63 9+1L	60 9+2L	37 294 266	73 242* 124	74 242* 124	63 287* 145	61 223 121	61 223 121	61 223 121	
49 249* -32	84 203 363	64 9+1L	61 9+2L	38 294 266	74 242* 124	75 242* 124	64 287* 145	62 223 121	62 223 121	62 223 121	
50 249* -32	85 203 363	65 9+1L	62 9+2L	39 294 266	75 242* 124	76 242* 124	65 287* 145	63 223 121	63 223 121	63 223 121	
51 249* -32	86 203 363	66 9+1L	63 9+2L	40 294 266	76 242* 124	77 242* 124	66 287* 145	64 223 121	64 223 121	64 223 121	
52 249* -32	87 203 363	67 9+1L	64 9+2L	41 294 266	77 242* 124	78 242* 124	67 287* 145	65 223 121	65 223 121	65 223 121	
53 249* -32	88 203 363	68 9+1L	65 9+2L	42 294 266	78 242* 124						

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