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The Structure of the Seven Layer Barium Niobium Silicon Oxide, $Ba_3Nb_{21-x}Si_2O_{44}$ ($x \simeq 0.2$)

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One of the products of reaction between Nb_2O_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 $Ba_3Nb_{21-x}Si_2O_{44}$. The compound has an hexagonal unit cell of dimensions $a = 7.774 \pm 0.004$ Å, $c = 16.765 \pm 0.007$ Å, 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 BaO_6, O_6 (oxygen layer with 1/7 of the oxygen missing), O_7, BaO_6, BaO_6, O_7, O_6. Between two BaO_6 layers there is one Nb in an octahedral site (population parameter $\simeq 0.8$); between BaO_6 and O_7 layers there are three Nb in octahedral sites; between BaO_6 and O_6 layers there are three Nb in sites coordinated by five O in a square pyramidal arrangement; and between O_6 and 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 O_6 layer and engage in metal–metal bonding, the Nb–Nb distances ranging from 2.78 to 2.85 Å.

Nb_6O_{18} clusters can be identified in which the 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 Nb_2O_5, Nb, and BaO react in the presence of SiO_2, various complex oxides may be produced. The first such compound to be described was $Ba_3Nb_6Si_4O_{26}$, which Shannon determined to have a structure composed of strings of NbO_6 octahedra joined by corner-sharing, both among each other and with Si_2O_7 groups (two SiO_4 tetrahedra sharing one vertex), with bariums occupying holes between the chains (*1*). The compound $Ba_3Nb_7Si_2O_{25-x}$ ($x \simeq 0.5$) has a similar but somewhat more complex structure (*2*), in which some edge-sharing of NbO_6 octahedra occurs. A third oxide, $Ba_3Nb_{21-x}Si_2O_{44}$, however, has an entirely different structure which will be described herein.

In it Nb_6O_{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 Nb_2O_5 and Nb were obtained commercially. BaO was prepared by heating 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 $Ba_3Nb_7Si_2O_{25-x}$. 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 *P3* or $P\bar{3}$. Unit-cell dimensions of $a = 7.78$ Å, $c = 16.75$ Å 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 Mo$K\sigma$ radiation and operating in the θ–2θ scan mode. The base scan width was 3° in 2θ; 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 2θ, 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 f these intensities were set equal to the observe intensities plus twice their standard deviatio $(I_0 + 2\sigma_{I_0})$. A standard deviation was calculate for each reflection according to the formula

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

for observed reflections and

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

for unobserved reflections, where σ_g is the percen standard deviation in a group of symmetry related reflections (set to 10 for single reflections) *Lp* is the product of Lorentz and polarizatio factors, N_T is the total counts recorded on th scan through the peak, and *BG* is the backgroun counts for the scan. These standard deviation are derived from counting statistics, the equation used being based on those given by Stout an Jensen (*4*).

Lorentz and polarization corrections wer made using the program package "The X-ra System" (*5*), which was also used to calculat accurate cell dimensions of $a = 7.774 \pm 0.004$ Å and $c = 16.765 \pm 0.007$ Å from the 2θ values o twelve individually centered reflections, an in all subsequent calculations of Fourier map least squares refinements, and so forth.

A rough determination of relative compositio was made with a KEVEX–Quanta/Metri energy dispersive spectrometer, using $Ba_3Nb_7Si_2O_{25-x}$ as the standard. This measuremen indicated a Ba/Si ratio of about 3/2 and a Ba/N ratio of about 1/7. The statistical distributio of normalized structure factors indicated th presence of a center of symmetry, making th probable space group $P\bar{3}$.

Structure Determination and Refinement

Examination of the *hk*0 reflections revealed 140 and 630 to be very strong, suggesting tha many of the heavy atoms lie on or near the inter sections 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 fo barium, since use of any of the other three woul place symmetry-related bariums uncomfortably close together. All five sites are possible fo

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

One particularly large peak indicated the posble presence of a heavy atom at 1/3, 2/3, 0.14. difference Fourier map calculated from a model f just one barium at this location was used in onjunction with the Patterson to suggest niobium locations. Structure solution proceeded y trial and error, using ΔF maps as the primary ol for revision of the model. In order to reduce alculation time, only observed reflections of $\sin\theta \leqslant 0.5$ (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 $Ba_3Nb_{21}Si_2O_{44}$. 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 $Ba_3Nb_{21-x}Si_2O_{44}$

tom	Ba(1)	Ba(2)	Nb(1)	Nb(2)	Nb(3)	Nb(4)	Nb(5)[a]
osition	1a	2d	6g (general)	6g	6g	2c	1b
nitial coordinates	0, 0, 0	$\frac{1}{3}, \frac{2}{3}, \frac{21}{50}$	$\frac{2}{21}, \frac{10}{21}, \frac{7}{100}$	$\frac{1}{7}, \frac{5}{7}, \frac{21}{100}$	$\frac{3}{7}, \frac{1}{7}, \frac{35}{100}$	0, 0, $\frac{21}{100}$	0, 0, $\frac{1}{2}$
inal							
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)	$\frac{1}{2}$
$U_{11} \times 100$	1.582	2.623	0.801(52)	0.740(52)	1.757(68)	1.586	2.313
$U_{22} \times 100$	1.582	2.623	0.814(53)	0.851(53)	1.415(62)	1.586	2.313
$U_{33} \times 100$	0.738(52)	0.872(42)	0.248(28)	0.306(28)	0.383(30)	0.542(57)	1.197(145)
$U_{12} \times 100$	0.791(31)	1.311(29)	0.391(46)	0.461(45)	1.094(57)	0.793(35)	1.157(91)
$U_{13} \times 100$	0	0	0.042(35)	−0.100(34)	−0.185(39)	0	0
$U_{23} \times 100$	0	0	−0.045(35)	0.000(36)	−0.132(39)	0	0

tom	Si(1)	O(1)	O(2)	O(3)	O(4)	O(5)
osition	2d	6g	6g	6g	6g	6g
nitial coordinates	$\frac{1}{3}, \frac{2}{3}, \frac{79}{100}$	$\frac{1}{7}, \frac{5}{7}, 0$	$\frac{1}{21}, \frac{5}{21}, \frac{7}{50}$	$\frac{10}{21}, \frac{8}{21}, \frac{7}{50}$	$\frac{5}{21}, \frac{4}{21}, \frac{14}{50}$	$\frac{2}{21}, \frac{10}{21}, \frac{14}{50}$
inal						
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)
$U \times 100$	0.727(107)	0.964(165)	0.918(162)	0.633(140)	0.996(162)	0.983(159)

tom	O(6)	O(7)	O(8)
osition	6g	6g	2d
nitial coordinates	$\frac{10}{21}, \frac{8}{21}, \frac{21}{50}$	$\frac{1}{21}, \frac{5}{21}, \frac{21}{50}$	$\frac{1}{3}, \frac{2}{3}, \frac{36}{50}$
inal			
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)
$U \times 100$	2.159(237)	1.282(171)	0.697(258)

[a] 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 $Ba_3Nb_{21-x}Si_2O_{44}$ ($x \simeq 0.2$). 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 ΔF 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 $Ba_3Nb_{21-x}Si_2O_{44}$ 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: BaO_6, O_6 (an oxygen layer with one-seventh of the oxygens missing), O_7 (a complete oxygen layer), BaO_6, BaO_6, O_7, O_6, respectively.

The BaO_6 layer found here has not, to our knowledge, been reported previously. It is, however, analogous to the KF_6 layer found in $KOsF_6$ and similar compounds. $KOsF_6$ has a structure based on a cubic stacking of approximately close-packed KF_6 layers, with one Os occupying the only available octahedral site between each pair of layers (*7*). Between the two adjacent BaO_6 layers in $Ba_3Nb_{21-x}Si_2O_{44}$ there is, similarly, a single niobium (Nb(5)) in the only available octahedral site, although here its population parameter is somewhat less than one.

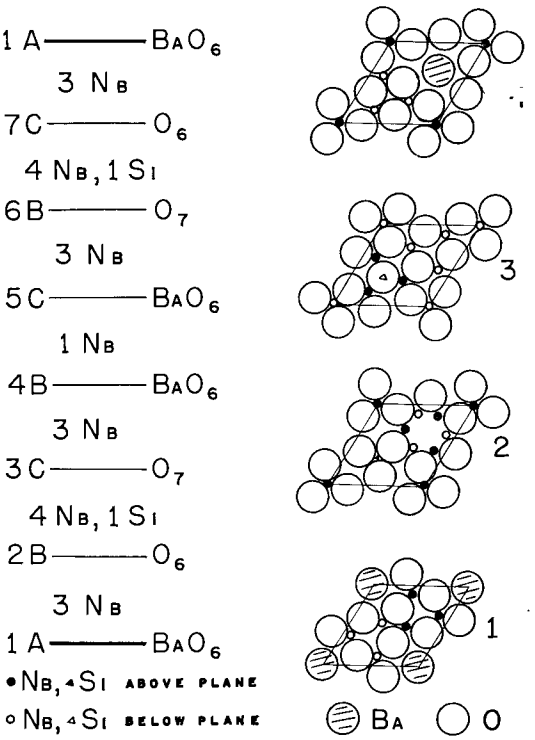


FIG. 2. Layer structure of $Ba_3Nb_{21-x}Si_2O_{44}$.

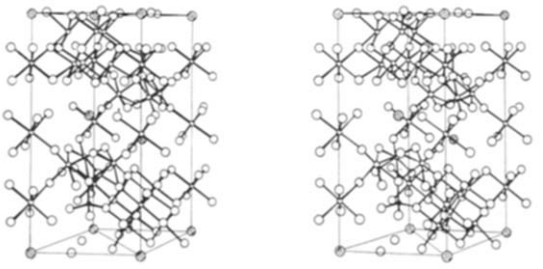


FIG. 1. Stereo view of the unit cell of $Ba_3Nb_{21-x}Si_2O_{44}$. Shaded circles are Ba, large open circles O, small open circles Nb, and small closed circles Si.

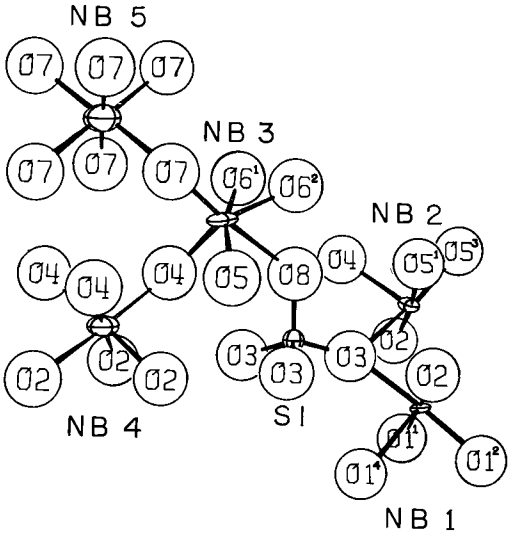


FIG. 3. Niobium and silicon coordination in $Ba_3Nb_{21-x}Si_2O_{44}$. See Table II for explanation of superscripts.

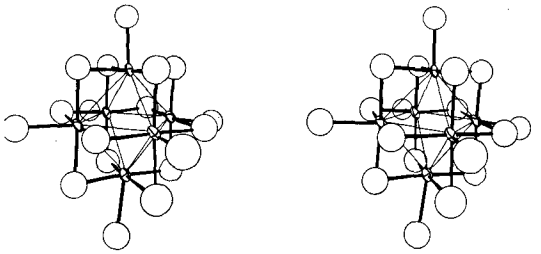


FIG. 4. Stereo view of Nb_6O_{18} cluster.

Between BaO_6 and O_7 layers there are three niobiums in octahedral sites; between BaO_6 and O_6 layers there are three niobiums in sites coordinated by square pyramids of oxygens with the niobiums in the pyramid bases; and between O_6 and 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 O_6 layer. The absence of an oxygen at the site is established by the lack of any peak on the final ΔF map and by the fact that, when an oxygen atom was introduced there, upon refinement it quickly acquired a thermal parameter so large ($U \simeq 55$) 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 $Ba_3Nb_{21-x}Si_2O_{44}$

Distances:	
Ba(1)–O(1)	2.907 ± 0.014 Å
Ba(1)–O(2)	2.933 ± 0.009
Ba(2)–O(5)	3.018 ± 0.008
Ba(2)–O(6) (same layer)	3.039 ± 0.017
Ba(2)–O(6) (different layers)	2.953 ± 0.013
Ba(2)–O(7)	3.008 ± 0.012
Nb(1)–Nb(1)	2.793 ± 0.002
Nb(1)–Nb(2)^1	2.840 ± 0.002
Nb(1)–Nb(2)^2	2.854 ± 0.002
Nb(1)–O(1)^1	2.080 ± 0.012
Nb(1)–O(1)^2	2.028 ± 0.011
Nb(1)–O(1)^4	2.197 ± 0.008
Nb(1)–O(2)	2.076 ± 0.011
Nb(1)–O(3)	2.115 ± 0.007
Nb(2)–Nb(2)	2.783 ± 0.002
Nb(2)–O(2)	2.104 ± 0.010

TABLE II—*continued*

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

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

TABLE III

ELECTROSTATIC BOND STRENGTHS TO OXYGEN IN $Ba_3Nb_{21-x}Si_2O_{44}$

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 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 $Nb_6O_{19}^{8-}$, for instance, the arrangement of niobium and oxygen is the same as in the present Nb_6O_{18} grouping except that an additional oxygen is present in the center of the group. The shortest Nb–Nb distance there, however, is about 3.2Å (*8*). In that case, niobium is present as Nb^V. In $Ba_3Nb_{21-x}Si_2O_{44}$, 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 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 $Nb_6O_{19}^{8-}$ group is found in the $Nb_6Cl_{12}^{2+}$ 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 $Ba_3Nb_{21-x}Si_2O_{44}$ (*9*). An even more similar Nb–Nb distance is found in NbO_2, in which edge-sharing 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.

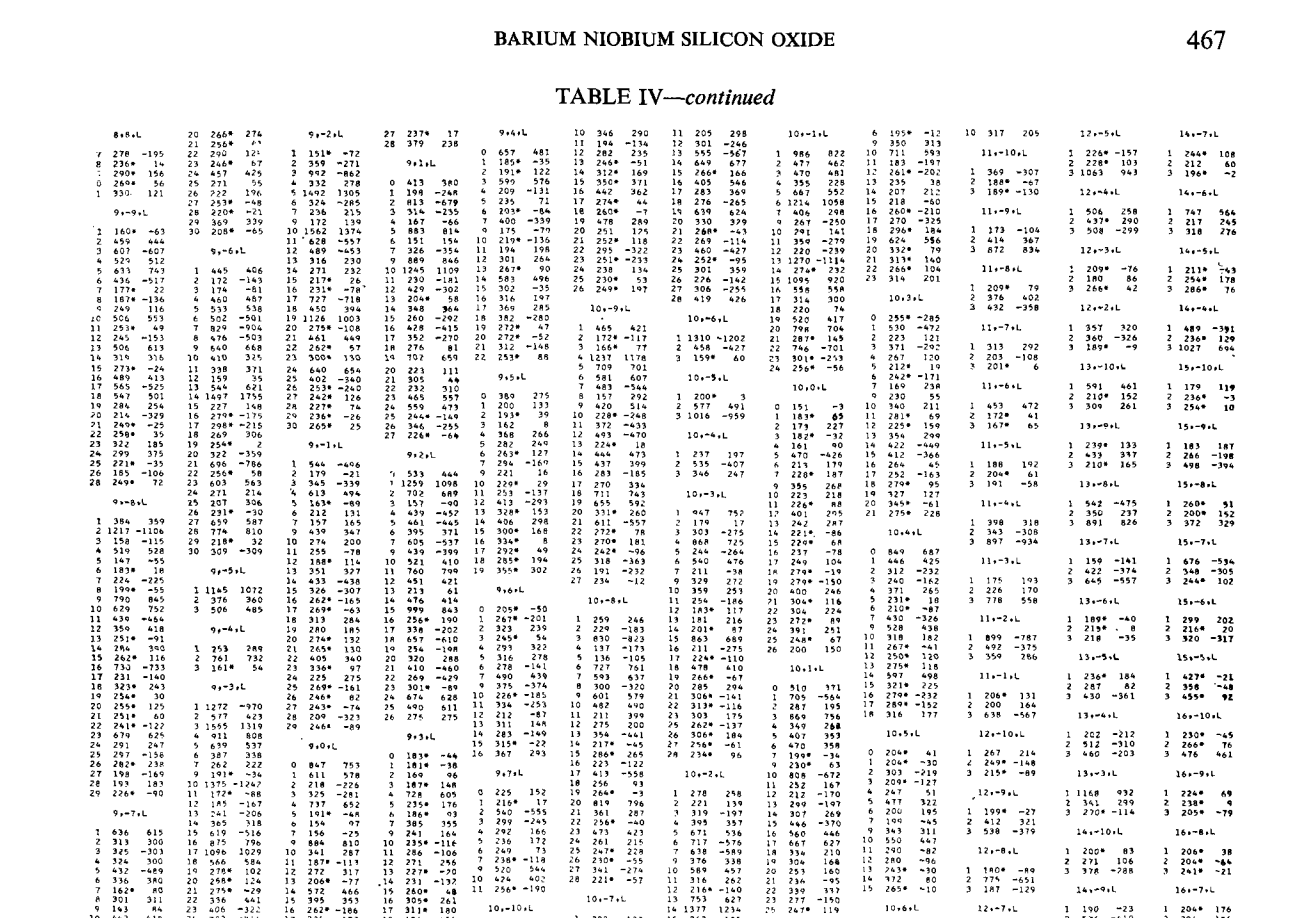
Nb(1) and Nb(2), then, form an octahedral cluster of niobiums held together by metal–metal bonding, each niobium being coordinated to four others. The coordination sphere of each niobium consists of five oxygens in a square pyramidal arrangement, with the niobium in the base of the pyramid. Nb_6O_{18} clusters can be identified in which the 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 l, $10|F_o|$, $10|F_c|$. UNOBSERVED REFLECTIONS ARE MARKED WITH ASTERISKS.

TABLE IV—*continued*

TABLE IV—*continued*



assuming that all Nb have the average oxidation state of 3.56, and then supposing Nb(1) and Nb(2) to be +2.5 and Nb(3), Nb(4), and Nb(5) to be +5. The second supposition gives more reasonable bond strengths in five out of eight cases; it makes the situation worse only for O(8), and the lengthening of Nb–O(8) distances may be sufficient compensation for the abnormal bond strength calculated to that atom even under the second distribution of oxidation states. This distribution is therefore presumed to be more nearly correct than the original assumption of average oxidation states.

The SiO_4 tetrahedron is quite regular, with Si–O distances ranging from 1.60 to 1.62 Å. Ba(1) has a very regular 12-fold coordination, with Ba–O distances 2.91 to 2.93 Å. The coordination about Ba(2) is somewhat distorted with Ba–O distances ranging from 2.95 to 3.04 Å; the barium is displaced out of its layer towards the oxygens of the adjoining BaO_6 layer, thus helping to hold the two layers together by electrostatic attraction.

Observed and calculated structure factors are shown in Table IV. The relatively poor agreement is attributed to the instrumental instability. However, convergence was attained.

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