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$BaNb_{10}SiO_{19}$: A Complex Oxide with a Variety of Different Niobium–Niobium Interactions

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The title compound was obtained by annealing powders of BaO, Nb_2O_5, Nb, and Si with a $BaCl_2$ flux in sealed silica tubes. It crystallizes in the hexagonal space group $P6_3$: $a = 777.7(4)$ pm, $c = 1451.0(6)$ pm, with $Z = 2$ formula units per cell. The structure was determined from single-crystal X-ray data and refined to a residual of $R = 0.060$ for 835 structure factors and 62 variable parameters. The Ba atoms have 12 oxygen neighbors in cube-octahedral arrangement. The Si atoms are tetrahedrally coordinated to oxygen atoms. The Nb atoms occupy four different positions. Two of these are linked to octahedral Nb_6 clusters with Nb–Nb bond lengths varying between 277.5 and 286.5 pm; one kind of Nb atom forms Nb_3 triangles with Nb–Nb distances of 282.9 pm, and finally there are "isolated" Nb atoms with an oxidation number close to +5. The relatively long Nb–Nb distances of 308.8 pm between these Nb atoms and the Nb_6 groups indicate at best only marginal bonding interactions. The compound shows temperature-independent weak paramagnetism and is semiconducting with a band gap of $E_a = 0.30\ (\pm 0.01)$eV. © 1991 Academic Press, Inc.

1. Introduction

The system $BaO–Nb_2O_5$ was already studied some 30 years ago (*1*). Reduced barium niobates also have been known for some time. In the compounds $Ba_5Nb_4O_{13}$ (*2*), $BaNbO_3$ (*3, 4*), $Ba_3Nb_8O_{21}$ (*5, 6*) and $Ba_3Nb_5O_{15}$ (*7–9*) with at least some Nb(IV) the metal atoms are well separated from each other and thus these niobates have no bonding niobium–niobium interactions. In contrast, the recently reported compounds $Ba_2Nb_5O_9$ (*10*) and $BaNb_8O_{14}$ (*11*) contain more strongly reduced niobium which forms Nb_6 clusters. We have studied reduced barium niobates and reported recently on a structure refinement of the tetragonal bronze $Ba_3Nb_5O_{15}$ (*9*). In some of these samples we observed a quaternary phase containing silicon from the silica tubes. Later we prepared this compound also in pure form. We report here on the preparation and crystal structure of this compound. A preliminary account of our work was given before (*12*).

2. Sample Preparation

Starting materials were BaO_2 (Baker, pure), $BaCl_2 \cdot 2H_2O$ (Merck, p.a.), Nb_2O_5 (Ventron, 99.9%), and powders of Nb (Strem Chemical, 99.8%) and Si (Fluka, *puriss.*). BaO was prepared by annealing the peroxide for 1 hr at 1000°C in vacuum. $BaCl_2$ was obtained from the hydrate by heating at 250°C under reduced pressure.

The powders of BaO, Nb_2O_5, Nb, Si, and $BaCl_2$ were mixed in the molar ratio

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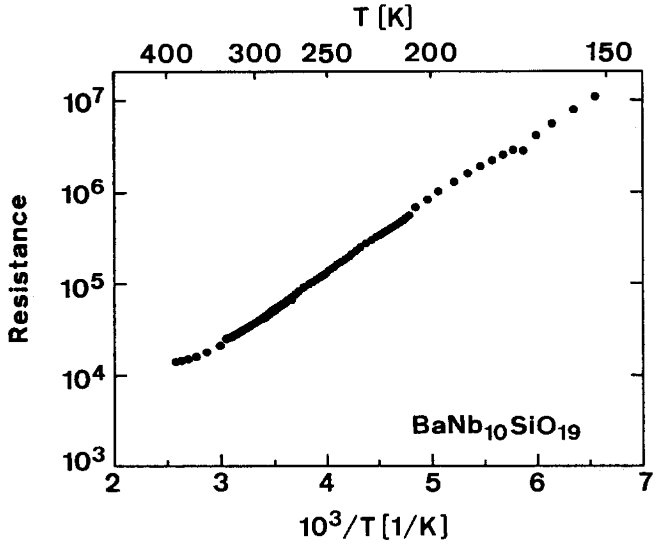

FIG. 1. Electrical resistivity (arbitrary units) of $BaNb_{10}SiO_{19}$ along the *c* direction.

1 : 3.7 : 3.8 : 1.2 : 45, sealed under vacuum in a silica tube, and annealed for 5 days at 1150°C. After quenching in air the $BaCl_2$ matrix was dissolved in water. The resulting product was nearly single-phase $BaNb_{10}SiO_{19}$ with a trace amount of NbO as the only impurity. Samples with a slightly higher content of BaO resulted in the previously characterized compound $Ba_3Nb_{20.8}Si_2O_{44}$ (*13*) as an additional impurity.

3. Properties

The crystals of $BaNb_{10}SiO_{19}$ are black. They have the shape of very thin hexagonal platelets with diameters of up to 0.2 mm. Energy dispersive analyses in a scanning electron microscope showed no impurity elements heavier than sodium.

Electrical resistivity measurements in the direction of the hexagonal axis showed semiconducting behavior (Fig. 1). The resistivity vs $1/T$ plot was linear over the range of 150 to 350 K. The band gap calculated from the relation $\rho = \rho_0 \exp(E_a/2kT)$ is $E_a = 0.30(\pm 0.01)$ eV. The electrical conductivity of these crystals may behave differently in the plane perpendicular to the hexagonal axis with extended metal–metal interactions. We were not successful in applying contacts to the small crystals for electrical conductivity measurements in the directions of the plane, because of the poor mechanical stability of the crystals.

Magnetic susceptibility measurements with a SQUID magnetometer showed very weak temperature-independent paramagnetic behavior. The absolute values of the susceptibility were much smaller than the diamagnetic correction.

4. Structure Determination

A single crystal of $BaNb_{10}SiO_{19}$ with the dimensions 75 × 50 × 13 μm^3 was investigated in a precession camera. It showed the Laue symmetry to be $6/m$, as the only systematic extinctions reflections $00l$ were found to occur only with $l = 2n$. Of the two possible space groups $P6_3$ and $P6_3/m$ only the one with the lower symmetry—$P6_3$ (No. 173)—was found to be correct during the structure determination. The lattice constants were first determined on the single-crystal diffractometer (*12*) and later refined from Guinier powder data with α-quartz (a = 491.30 pm, c = 540.46 pm) as standard: a = 777.7(4) pm, c = 1451.0(6) pm, V = 0.7594 nm^3, with Z = 2 formula units per cell.

Intensity data were collected with graphite monochromated Mo$K\alpha$ radiation, a scintillation counter with pulse-height discriminator, $\theta/2\theta$ scans, and background counts at both ends of each peak. An absorption correction was made on the basis of ψ scan data. A total of 5624 reflections was measured up to 2θ = 65°C in one-half of the reciprocal sphere. After averaging (R_i = 0.080) and omission of reflections with $F < 3\sigma(F)$, 835 reflections remained for the structure determination.

The structure was solved by interpretation of the Patterson map. The lighter atoms were located through difference Fourier syntheses. The structure was refined by full-matrix least-squares cycles using atomic scattering factors (*14*), corrected for anomalous dispersion (*15*). In the resulting structure all atoms had unusally larger thermal parameters in the direction of the hexagonal axis. This was judged to be due to the absorption by the plate-like crystals, which was not corrected by the ψ-scan data. To account for this effect we allowed the scale factors for the reciprocal lattice planes hkl with constant l values to vary during one series of least-squares cycles with isotropic thermal parameter. The thus-obtained 21 different scale factors were then approximated by a smooth function and applied to the data. In the following least-squares cycles with anisotropic thermal parameters only one scale factor was allowed to vary. A refinement of occupancy parameters together with the thermal parameters did not suggest any deviations from the ideal values. A final residual (weighted residual) of R = 0.060 (R_w = 0.058) was achieved for 835 structure factors and 62 variable parameters. Atomic parameters and interatomic distances are given in Tables I and II. Listings of the structure factors and the ellipsoidal thermal parameters of the metal atoms may be obtained from the authors.

TABLE I

ATOMIC PARAMETERS OF $BaNb_{10}SiO_{19}$

Atom	$P6_3$	x	y	z	B^a
Ba	2*b*	1/3	2/3	0.0920(3)	0.73(4)
Nb1	6*c*	0.8641(3)	0.3135(2)	0	0.43(5)
Nb2	6*c*	0.4756(3)	0.3605(3)	0.8388(2)	0.36(4)
Nb3	6*c*	0.2296(3)	0.1826(3)	0.1737(2)	0.62(5)
Nb4	2*b*	1/3	2/3	0.8328(3)	0.56(6)
Si	2*a*	0	0	0.3894(8)	0.2(1)
O1	6*c*	0.592(2)	0.102(2)	0.420(1)	0.4(2)
O2	6*c*	0.731(2)	0.571(2)	0.263(1)	0.3(2)
O3	6*c*	0.648(3)	0.090(3)	0.078(2)	1.0(3)
O4	6*c*	0.151(2)	0.925(2)	0.420(1)	0.3(2)
O5	6*c*	0.303(2)	0.433(2)	0.254(1)	0.3(2)
O6	6*c*	0.949(2)	0.741(2)	0.600(1)	0.5(2)
O7	2*a*	0	0	0.275(4)	2.5(8)

[a] Standard deviations in the positions of the least significant digits are given in parentheses. This column contains the isotropic thermal parameters of the silicon and oxygen atoms and the equivalent isotropic thermal parameters B (x100 in units of nm^2) of the metal atoms.

5. Discussion

Katz and co-workers were the first to report on quaternary compounds containing alkaline earth, niobium or tantalum, silicon, and oxygen. In $Ba_3Nb_6Si_4O_{26}$ (*16*) and$Ba_3Ta_6Si_4O_{26}$ (*17*) the niobium and tantalum atoms are fully oxidized. This is also the case for the related compositions $RbNbGe_3O_9$ (*18*), $ATa(Ge_{3-x}Si_x)O_9$ (A = K, Rb, Tl) (*18*), $Sr_3Ta_6Si_4O_{26}$ (*19*), and $K_6T_6Si_4O_{26}$ (T = Nb, Ta) (*19*). In $Ba_{5.77}Nb_{14}Si_4O_{47}$ (*20*) the niobium atoms have oxidation number 4.7 and in $Ba_3Si_4Ta_6O_{23}$ (*17*) the tantalum atoms are +4.0. In all of these compounds the transition metal atoms have no direct interactions. In contrast, in

TABLE II

INTERATOMIC DISTANCES (pm) IN $BaNb_{10}SiO_{19}$

Ba		Si	
3 O6	281(1)	3 O4	161(2)
3 O5	291(2)	1 O7	166(5)
3 O1	296(2)		
3 O3	297(1)	O1	
		1 Ba	296(2)
		1 Nb4	203(2)
Nb1		1 Nb1	207(1)
2 Nb1	280.2(4)	1 Nb2	211(1)
1 Nb2	281.5(3)		
1 Nb2	286.5(3)	O2	
1 Nb3	316.7(3)	1 Nb4	194(2)
1 O3	206(2)	1 Nb3	209(1)
1 O1	207(1)	1 Nb2	222(2)
1 O3	209(2)		
1 O4	214(2)	O3	
1 O6	224(2)	1 Ba	297(1)
		1 Nb3	205(2)
		1 Nb1	206(2)
Nb2		1 Nb1	209(2)
2 Nb2	277.5(4)		
1 Nb1	281.5(3)	O4	
1 Nb1	286.5(3)	1 Nb1	214(2)
1 Nb4	308.8(3)	1 Nb2	216(2)
1 O5	206(2)	1 Si	161(2)
1 O5	207(2)		
1 O1	211(1)	O5	
1 O4	216(2)	1 Ba	291(2)
1 O2	222(2)	1 Nb2	206(2)
		1 Nb2	207(2)
		1 Nb3	209(2)
Nb3			
2 Nb3	282.9(3)		
1 Nb1	316.7(3)	O6	
1 O6	204(1)	1 Ba	281(1)
1 O3	205(2)	1 Nb3	204(1)
1 O6	206(1)	1 Nb3	206(1)
1 O5	209(2)	1 Nb1	224(2)
1 O2	209(1)		
1 O7	220(3)	O7	
		3 Nb3	220(3)
		1 Si	166(5)
Nb4			
3 Nb2	308.8(3)		
3 O1	203(2)		
3 O2	194(2)		

$NaSi_{0.676}Nb_{10.324}O_{19}$ (*21*) and in $Ba_3Nb_{20.8}Si_2O_{44}$ (*13*), where the niobium atoms on average obtain the relatively low oxidation numbers +3.32 and +3.56, a variety of Nb–Nb interactions was found. This is also the case for the presently determined structure of $BaNb_{10}SiO_{19}$ (Fig. 2), where the niobium atoms have the average oxidation number +3.2, the lowest of all in these compounds.

There are four kinds of niobium atoms in $BaNb_{10}SiO_{19}$ (Fig. 3) The Nb1 and Nb2 atoms form octahedral Nb_6O_{18} clusters, which previously were also found in other reduced niobates, e.g., in $BaNb_8O_{14}$ (*11*), $Ba_3Nb_{20.8}Si_2O_{44}$ (*13*), $NaSi_{0.676}Nb_{10.324}O_{19}$ (*21*), $Mg_3Nb_6O_{11}$ (*22, 23*), $Mn_3Nb_6O_{11}$ (*23*), and $SrNb_8O_{14}$ (*24*). The Nb3 atoms are linked to form triangular Nb_3O_{13} groups. Such groups were found before in $Ba_3Nb_{20.8}Si_2O_{44}$ (*13*); however, there the niobium atoms are far apart from each other (330 pm), while in $BaNb_{10}SiO_{19}$ the corresponding Nb–Nb distances of 283 pm indicate bonding interactions. Similar groups were found in reduced molybdates, e.g., in $M_2Mo_3O_8$ (M = Mg, Mn, Fe, Co, Ni, Zn, Cd) (*25, 26*), $La_3Mo_4SiO_{14}$ (*27*), and halides e.g., β-Nb_3Br_8 (*28*). Finally, the Nb4 atoms have octahedral oxygen coordination with three niobium neighbors at the rather large distance of 309 pm.

An assignment of oxidation numbers to the niobium atoms can be made on the basis of bond-order sums (Table III) following the discussions of the structures of $SrNb_8O_{14}$ (*24*) and $BaNb_8O_{14}$ (*11*). For the calculation of these bond-order sums according to the equation for the bond valence s of $s = \exp[(r_o - r)/B]$ we have used for the Ba and Si atoms the r_o values of 2.285 and 1.624 and the B value of 0.37 given in (*31*); for the Nb atoms $r_o = 1.921$ and $B = 0.319$ were taken from (*30*). For the total valence sum $\Sigma\Sigma s_i$ we thus obtain a value of 38.28 per formula unit, which is in good agreement with the expected value of 38.00 considering the 19 oxygen atoms. The Nb1, Nb2, Nb3, and Nb4 atoms then obtain the oxidation numbers 2.73, 2.69, 3.60, and 4.96, respectively.

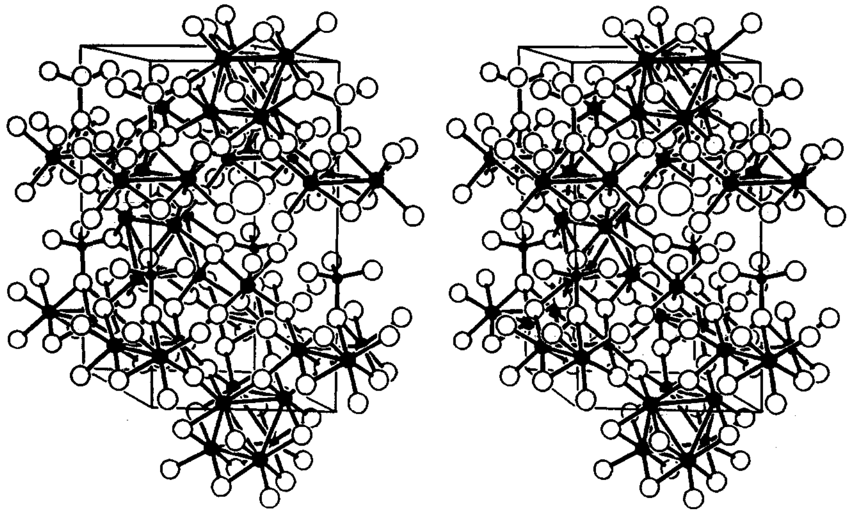

FIG. 2. Stereoplot of the structure of $BaNb_{10}SiO_{19}$. Large and small open circles: Ba and O; large and small filled circles: Nb and Si. The origin of the cell is in the front face at the lower left-hand corner. The x direction goes to the right, y to the back, and z upwards.

In other words, according to this calculation these atoms could have 2.27, 2.31, 1.40, and 0.04 electrons available for metal–metal interactions, if the Nb–Nb distances were short enough for metal–metal bonding.

This is certainly the case for the Nb1 and Nb2 atoms forming the octahedral Nb_6 clusters. These clusters then have a total of $3 \times (2.27 + 2.31) = 13.74$ electrons for metal–metal bonding interactions, which is close to the electron count of 14 frequently observed before for such Nb_6O_{18} clusters (*24*). The average Nb–Nb distance of 281.4 pm for these clusters in $BaNb_{10}SiO_{19}$ is in good agreement with the corresponding values of 280.4 pm in $Mg_3Nb_6O_{11}$ (*23*),

TABLE III

MOTIVES OF MUTUAL ADJUNCTIONS (*29*) AND BOND-ORDER SUMS (*30, 31*) IN $BaNb_{10}SiO_{19}$[a]

	$O1^{i}$	$O2^{a-a}$	$O3^{i-a}$	$O4^{i}$	$O5^{i-a}$	$O6^{a-i}$	$O7^{i}$	C.N.	Σs_i
Ba	3/1	—	3/1	—	3/1	3/1	—	12	2.24
Nb1	1/1	—	2/2	1/1	—	1/1	—	5	2.73
Nb2	1/1	1/1	—	1/1	2/2	—	—	5	2.69
Nb3	—	1/1	1/1	—	1/1	2/2	1/3	6	3.60
Nb4	3/1	3/1	—	—	—	—	—	6	4.96
Si	—	—	—	3/1	—	—	1/1	4	4.02
C.N.	4	3	4	3	4	4	4		
Σs_i	2.05	1.92	2.06	2.01	2.05	1.95	2.16		$\Sigma\Sigma s_i = 38.28$

[a] The superscripts of the oxygen atoms indicate whether these oxygen atoms are inner (i) or outer (a) ligands of the niobium clusters (*32*). If two superscripts are given, the first one corresponds to the Nb_6 cluster formed by the Nb1 and Nb2 atoms and the second one concerns the Nb_3 cluster of the Nb3 atoms.

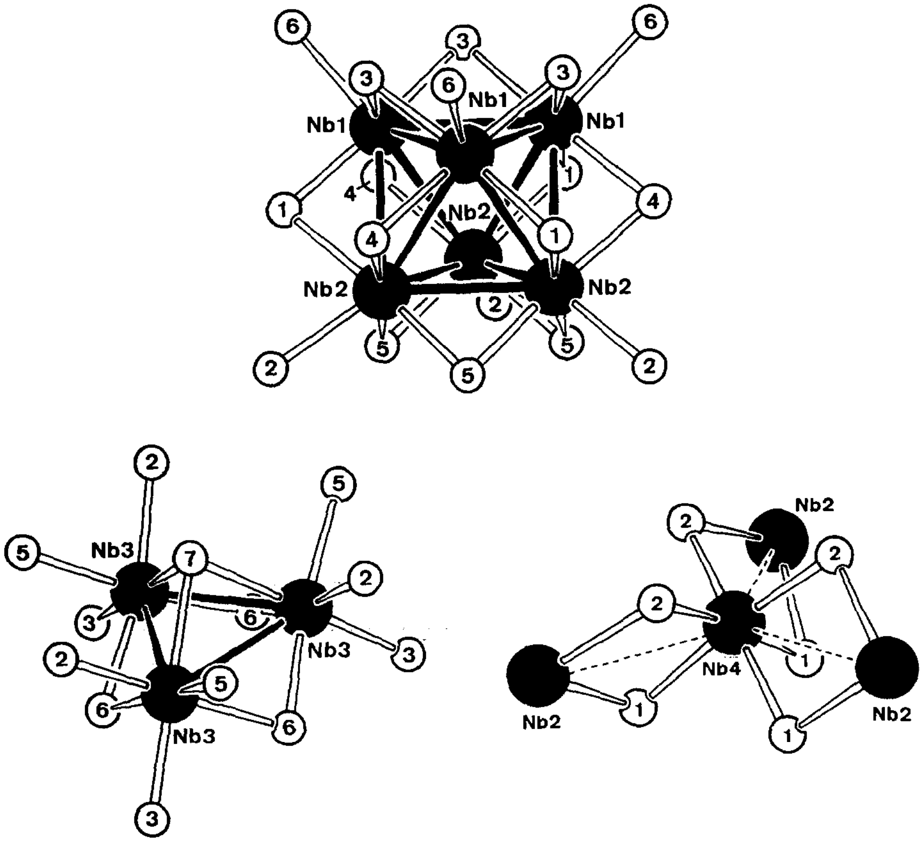

FIG. 3. Oxygen coordination of the niobium atoms in $BaNb_{10}SiO_{19}$. The designations of the oxygen atoms (open circles) are indicated by numbers.

280.9 pm in $Mn_3Nb_6O_{11}$ (*23*), 282.3 pm in $SrNb_8O_{14}$ (*24*), and 280.7 pm in $BaNb_8O_{14}$ (*11*).

For the Nb3 atoms a $d^{1.4}$ system is obtained, i.e., there are 4.2 valence electrons available for metal–metal bonding in each Nb_3O_{13} cluster. The short Nb3–Nb3 distances of 282.9 pm suggest that these electrons are indeed Nb–Nb bonding.

The Nb4 atoms are according to the valence bond sum of $\Sigma s_i = 4.96$ almost in the oxidation state +5 and therefore are hardly expected to form Nb–Nb bonds. Thus the Nb4–Nb2 interactions of 308.8 pm are probably of negligible bond strength. This is even more likely for the case of the Nb1–Nb3 interactions of 316.7 pm. Nevertheless, for Nb–Nb distances of less than 320 pm one cannot entirely and with certainty rule out any direct bonding interactions. Any such weak interactions would probably not result in completely filled bands and thus, metallic conductivity might be considered possible since these very weak interactions are connecting the Nb_6 and Nb_3 clusters via the "isolated" Nb4 atoms to form two-dimensionally infinite sheets (Fig. 4). Our electrical conductivity measurements, however, indicated semiconductivity at least parallel to the *c* axis. Unfortunately we were not successful in obtaining such measurements parallel to the sheets.

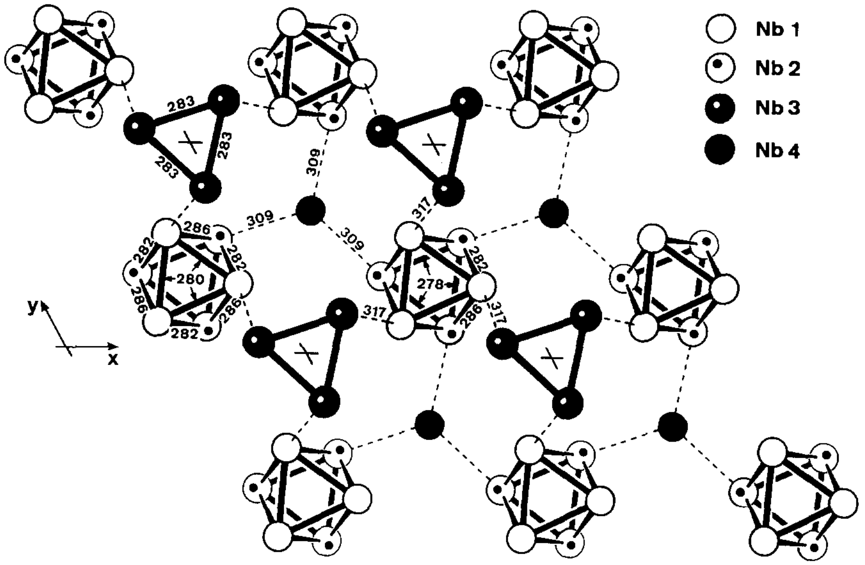

FIG. 4. Projection of the niobium clusters and the marginal Nb–Nb interactions within the *ab* plane of the $BaNb_{10}SiO_{19}$ structure. Only the niobium atoms are shown.

The Ba atoms in $BaNb_{10}SiO_{19}$ have 12 oxygen neighbors in slightly distorted cubeoctahedral arrangement at an average distance of 291.3 pm. This distance is considerably shorter than the distance of 299 calculated from the ionic radii given by Shannon (*33*). However, one has to consider that the Ba atoms are a minority in this structure and because of their low valence they are also relatively soft compared with the niobium atoms. Relatively short Ba–O distances have been observed previously. For example, $Ba_5Ta_4O_{15}$ has three different Ba positions, all with 12 oxygen neighbors and with average distances of 285.8, 287.5, and 296.6 pm (*34*). In $BaNb_8O_{14}$ (*11*), which is similar in composition to $BaNb_{10}SiO_{19}$, the average Ba–O distance for the 12-coordinated Ba atom is 293.7 pm.

The silicon atoms have the usual tetrahedral oxygen coordination with an average Si–O distance of 162.3 pm. This distance is in excellent agreement with the corresponding distance of 162.5 pm, calculated from Shannon's radii for the proper coordination numbers.

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