

Synthesis and Structural Characterization of $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$. The First Member of the New Barium Niobium(IV/V) Oxosilicate Series $(\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26})_n(\text{Ba}_3\text{Nb}_8\text{O}_{21})$, $n = 1$

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Received February 25, 1992; accepted April 7, 1992

The crystal structure of the mixed-valence barium niobium(IV/V) oxosilicate, $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$, has been determined by single crystal X-ray diffraction. The title compound crystallizes in the hexagonal crystal system with the space group $P6_3cm$ (No. 185) and $Z = 2$. The lattice parameters are $a = 9.022(2) \text{ \AA}$, $c = 27.890(6) \text{ \AA}$, and $V = 1966(1) \text{ \AA}^3$. The structure can be described as the intergrowth of two structure types, barium niobium oxosilicate and barium niobium oxide, which form the series $(\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26})_n(\text{Ba}_3\text{Nb}_8\text{O}_{21})$. $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ corresponds to the first member of the series, $n = 1$. The unit cell consists of columns of ReO_3 -type quasi-one-dimensional, fused NbO_6 octahedra. The parallel octahedral columns are interconnected through shared corner oxygen atoms with isolated NbO_6 octahedra and Si_2O_7 pyrosilicate units. The framework is closely related to that of the $\text{Ba}_{6+x}\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ ($x = 0.23$) phase, reported by Evans and Katz in 1973 (1), yet the title compound is stoichiometric and has an acentric unit cell. A detailed structure analysis and structure comparison with the nonstoichiometric phase, as well as a brief comparison with the fully oxidized compound $\text{Ba}_6\text{Nb}_{10}\text{Ti}_4\text{Si}_4\text{O}_{47}$, are presented. © 1992 Academic Press, Inc.

Introduction

Our recent exploration of the niobium-rich system $A\text{-Nb-X-O}$ ($A =$ alkali or alkaline-earth metal cation, $X = \text{P}$ or Si) has led us to look further at the synthesis of oxophosphate and oxosilicate compounds with quasi-low-dimensional structures. These compounds possess mixed frameworks built up from chains of corner and/or edge sharing NbO_6 octahedra, and XO_4 tetrahedra or X_2O_7 groups. During our investigation two phosphate compounds with frameworks of this type were found, NbPO_5

(with an orthorhombic structure) (2) and $\text{CaNb}_2\text{P}_2\text{O}_{11}$ (3). Both structures possess corner sharing NbO_6 octahedra and PO_4 tetrahedra. The novel structure of $\text{CaNb}_2\text{P}_2\text{O}_{11}$ is interesting in that it contains double-layered, zig-zag chains of NbO_6 octahedra which are isolated by PO_4 tetrahedra. These chains are separated from each other by channels which contain the Ca atoms. Both NbPO_5 and $\text{CaNb}_2\text{P}_2\text{O}_{11}$, as well as the title compound, are oxo-compounds, meaning that these materials possess pseudo one-dimensional (1D) chain or two-dimensional layer transition metal oxide structures which are preserved and isolated by closed-shell phosphate or silicate groups. In con-

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trast to NbPO_5 and $\text{CaNb}_2\text{P}_2\text{O}_{11}$, the title compound contains mixed valent niobium.

The structure of the nonstoichiometric phase $\text{Ba}_{6+x}\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ ($x = 0.23$) (1) was reported by Evans and Katz in 1973. The title compound has been refined similarly but with a different space group and stoichiometric composition ($x = 0$). This reduced oxosilicate $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ phase has a structure that can be considered the intergrowth of two structure types: $\text{Ba}_3\text{M}_6\text{Si}_4\text{O}_{26}$ ($M = \text{Nb}$ and Ta) (4), and $\text{A}_3(\text{Nb}_{8-x}\text{M}_x)\text{O}_{21}$ ($A = \text{K}$ and Ba ; $M = \text{Mg}$, Ti , Cr , Fe , Ni , Zn , and Nb) (5). $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ is the first member ($n = 1$) of the intergrowth series $(\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26})_n(\text{Ba}_3\text{Nb}_8\text{O}_{21})$. The unit cell is closely related to the compound $\text{Ba}_6\text{Nb}_{10}\text{Ti}_4\text{Si}_4\text{O}_{47}$ (6) characterized by Raveau and co-workers using X-ray diffraction patterns and electron microscopy. In this paper, we will present the refined single crystal structure of $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ and discuss the structural comparisons to $\text{Ba}_{6+x}\text{Nb}_{14}\text{Si}_4\text{O}_{47}$. We will also take a brief look at the similarities between the title compound and the family $(\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26})_n(\text{Ba}_3\text{Nb}_8\text{O}_{21})$ (6).

Experimental

Synthesis. Single crystals of $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ were first grown using the procedures described by Kersting and Jeitschko for the synthesis of $\text{BaNb}_{10}\text{SiO}_{19}$ (7). The reaction was performed in two steps. Initially, BaNb_2O_6 was prepared by calcining in air a stoichiometric mixture of BaCO_3 (AFSAR, 99.98%) and Nb_2O_5 (Aldrich, 99.99%). Next, stoichiometric Nb powder (Aldrich, 99.8%), Nb_2O_5 , and P (Aldrich, red phosphorus, 99%) were added to the barium niobate precursor to prepare the phosphorus analog, $\text{BaNb}_{10}\text{PO}_{19}$. The salt, BaCl_2 (EM Science, dried, 99%), was also added as a flux. The mixture was placed in an evacuated, carbon-coated silica ampule and

heated for several days at ca. 1100°C. Black, round-stump crystals of the title compound were isolated by washing the reaction products with deionized water while using a suction filtration method. Qualitative chemical analysis by energy and wavelength dispersive spectroscopy using a Cameca SX-50 was performed on the data crystal and showed three cationic elements, Ba, Nb, and Si (no P). This analytical result indicated that the reaction product was a contaminated phase due to the silica tube. Subsequent attempts without the addition of elemental phosphorus in the reaction resulted in the isolation of the title compound in a nice crystalline form. It should also be noted that a second phase, $\text{Ba}_3\text{Nb}_{21-x}\text{Si}_2\text{O}_{44}$ reported in Ref. (1), has not yet been seen in our synthesis.

Structure determination. Diffraction data were collected at room temperature on a Rigaku AFC5S four-circle diffractometer. Crystallographic data for the title compound are summarized in Table I. The unit cell parameters and the orientation matrix for data collection were determined by a least-squares fit of 25 peak maxima with $7^\circ < 2\theta < 30^\circ$. There was no detectable decay, during the data collection, according to the intensities of three standard reflections ($\bar{1}2\bar{7}$; $11\bar{7}$; $\bar{2}24$) which were measured every 150 reflections. The TEXSAN (8) software package was used for the crystal structure solution and refinement. Data reduction, intensity analysis, and extinction conditions were determined with the program PROCESS. Lorentz-polarization and empirical absorption corrections based on three computer chosen azimuthal scans ($2\theta = 13.82^\circ, 13.90^\circ, 13.91^\circ$) were applied to the intensity data. On the basis of the extinction conditions, two space groups were selected, $P6_3cm$ (No. 185) and $P6_3/mcm$ (No. 193). Originally the structure was refined using the centric space group (No. 193) and the atom coordinates reported by Evans and Katz (1). The results were far

TABLE I
CRYSTALLOGRAPHIC DATA FOR $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$

Formula mass (amu)	2988.98
Space group	$P6_3cm$ (No. 185)
Cell parameters ^a	
a (Å)	9.022(2)
c (Å)	27.890(6)
V (Å ³)	1966(1)
Z	2
T (K) of data collection	296 K
ρ calculated (g cm ⁻³)	5.068
Radiation (graphite monochromated)	MoK α ($\lambda = 0.71069$ Å)
Crystal shape, color	Round-stump, black
Crystal size (mm)	0.05 \times 0.05 \times 0.05
Linear absorption coefficient (cm ⁻¹)	99.3
Transmission factors	0.85–1.0
Scan type	ω -scan
Scan speed (degrees min ⁻¹)	4.0
Scan range (degrees)	–0.36 to 0.36 in ω
Background counts	$\frac{1}{4}$ of scan range on each side of reflection
2θ (max)	55°
Data collected	$\pm h, +k, \pm l$
p for σ (F^2)	0.03
No. of reflections measured	4917
No. of unique data ($F_0^2 > 0$)	1014
No. of unique data with $F_0^2 > 3\sigma(F_0^2)$	787
F_{000}	2684
$R(F^2)$	0.025
$R_w(F^2)$	0.031
R_{int} (on F for $F_0^2 > 3\sigma(F_0^2)$)	0.042
Goodness of fit	1.14
Extinction coefficient ($\times 10^{-7}$)	1.2(1)
No. of variables	84

^a The refinement of cell constants is constrained in the hexagonal crystal system.

from satisfactory. The refinement for anisotropic cations and isotropic oxygen atoms gave $R = 0.120$, $R_w = 0.179$, and GOF = 6.20 and negative temperature factors for Si(1), O(1), O(2), and O(5) of the originally reported coordinates. We also found that the partially occupied barium atom site, Ba(2), was no longer occupied; i.e., no electron density was found in that site. Subsequently, the acentric space group $P6_3cm$ (No. 185) was chosen. During the course of the second least-squares refinement, we initially used the atom coordinates from the former refinement and added a new set of

independent coordinates that would otherwise be symmetry related by the inversion center. In this case, we had a much improved refinement with $R = 0.027$, $R_w = 0.034$, and GOF = 1.20. However, there were still five nonpositively defined oxygen thermal parameters. Finally, the structure was solved based upon a new set of cation coordinates obtained from the program SHELXS-86 (9) resolved from the space group $P6_3cm$ (No. 185) and a different origin than (0, 0, 0). A Patterson map was constructed and after refinement, a difference map was calculated to obtain the positions

TABLE II
POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR Ba₆Nb₁₄Si₄O₄₇

Atom	Wyckoff notation	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²) ^{a,b}
Ba(1)	6 <i>c</i>	0.6001(1)	0	0.2971 ^c	0.78(5)
Ba(2)	6 <i>c</i>	0.5847(1)	0	0.01437(4)	0.75(5)
Nb(1)	6 <i>c</i>	0.2159(2)	= <i>x</i>	0.44947(8)	0.32(3)
Nb(2)	6 <i>c</i>	0.2363(2)	0	0.08959(8)	0.38(6)
Nb(3)	6 <i>c</i>	0.2380(2)	0	0.22195(8)	0.38(6)
Nb(4)	6 <i>c</i>	0.2550(2)	0	0.36154(8)	0.34(6)
Nb(5)	4 <i>b</i>	$\frac{2}{3}$	$\frac{1}{3}$	0.41211(8)	0.36(4)
Si(1)	4 <i>b</i>	$\frac{2}{3}$	$\frac{1}{3}$	0.0984(2)	0.6(1)
Si(2)	4 <i>b</i>	$\frac{2}{3}$	$\frac{1}{3}$	0.2145(2)	0.3(1)
O(1)	6 <i>c</i>	0.217(1)	0	0.0158(6)	0.3(2)
O(2)	12 <i>d</i>	0.488(1)	0.184(1)	0.0764(3)	0.6(1)
O(3)	6 <i>c</i>	0.177(2)	= <i>x</i>	0.0914(5)	0.9(2)
O(4)	4 <i>b</i>	$\frac{2}{3}$	$\frac{1}{3}$	0.1566(7)	0.9(2)
O(5)	6 <i>c</i>	0.281(1)	0	0.1574(6)	0.5(2)
O(6)	6 <i>c</i>	0.180(1)	= <i>x</i>	0.2206(5)	0.8(2)
O(7)	12 <i>d</i>	0.487(1)	0.181(1)	0.2378(3)	0.4(1)
O(8)	6 <i>c</i>	0.217(1)	0	0.2967(6)	1.0(2)
O(9)	12 <i>d</i>	0.486(1)	0.173(1)	0.3609(4)	1.0(2)
O(10)	6 <i>c</i>	0.186(1)	= <i>x</i>	0.3755(4)	0.5(2)
O(11)	6 <i>c</i>	0.235(1)	0	0.4395(4)	0.3(2)
O(12)	12 <i>d</i>	0.479(1)	0.310(1)	0.4482(3)	0.4(1)

^a Isotropic equivalent thermal parameters defined as $B_{\text{eq}} = (8\pi^2/3) \text{trace } U$, for those atoms refined using anisotropic displacement parameters.

^b Oxygen atoms were refined isotropically.

^c In the least-square refinements, the *z* parameter was fixed for a preferred origin.

of the oxygen atoms. The structural and thermal parameters were refined by full-matrix least-squares methods and based on F^2 to $R = 0.025$, $R_w = 0.031$, and GOF = 1.14. Both potential space groups were carefully examined for the structure solution and the space group $P6_3cm$ (No. 185) was decided based upon the successful refinement. An anisotropic refinement was applied for the heavy atoms, Ba, Nb, and Si, while the oxygen atoms were refined isotropically. Table II lists the final positional and thermal parameters.

Structure Description and Discussion

The currently studied structure may be a revision of Evans and Katz's reported structure for the nonstoichiometric phase, Ba_{6+x}

Nb₁₄Si₄O₄₇ (1). In fact, the unit cell constants of these two phases are quite comparable, i.e., $a = 9.034(4)$ and $c = 27.81(2)$ for the nonstoichiometric phase and $a = 9.022(2)$ and $c = 27.890(6)$ for the title compound. In their publication, the authors stated that the nonstoichiometry resulting from the partially occupied barium site, Ba(2), was uncertain. In our refinement, we do not find any electron density at the equivalent position. Thus the uncertainty mentioned by Evans and Katz could have been attributed to a crystallographic problem. The structure of the title compound can be refined nicely in an acentric space group accompanied by moving the origin of the unit cell ca. -0.09 in the *z* direction. The labeling of the atoms from Evans and Katz's

report (excluding the Ba(2) atom) compared with that for the current structure is summarized below.

Evans and Katz	This work
Ba(1)	Ba(1), Ba(2)
Nb(1)	Nb(1), Nb(4)
Nb(2)	Nb(2), Nb(3)
Nb(3)	Nb(5)
Si(1)	Si(1), Si(2)
O(1)	O(1), O(8)
O(2)	O(5)
O(3)	O(10), O(11)
O(4)	O(3), O(6)
O(5)	O(4)
O(6)	O(2), O(7)
O(7)	O(9), O(12)

The unit cell of the title compound shows a mixed-framework oxosilicate structure. In Fig. 1, the unit cell, as shown in the partial structure, is built up from fused NbO_6 octahedral columns interconnected by isolated NbO_6 and pyrosilicate Si_2O_7 units through corner sharing oxygen atoms. The niobium oxide octahedral columns are composed of a 3×4 NbO_6 unit in which the 12 NbO_6 octahedra share apex and waist oxygen atoms to form a ReO_3 -type array. This structural unit is four NbO_6 octahedra thick, consisting of four asymmetric niobium atoms, i.e., Nb(1), Nb(2), Nb(3), and Nb(4). The 12-octahedral unit is centered around the 6_3 axis and extended along the c -dimension. As the unit propagates along the c -axis, the symmetry related consecutive units are fused together by the edge sharing octahedra Nb(4) O_6 and Nb(1) O_6 to form an extended NbO_6 octahedral column. The neighboring parallel columns are interrelated by a threefold axis where the two connecting units, isolated Nb(5) O_6 octahedra and Si_2O_7 pyrosilicate groups, symmetrically rest along the c -axis.

Alternatively, the structure of the title compound can be viewed as the intergrowth of two structure types, $\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26}$ (nio-

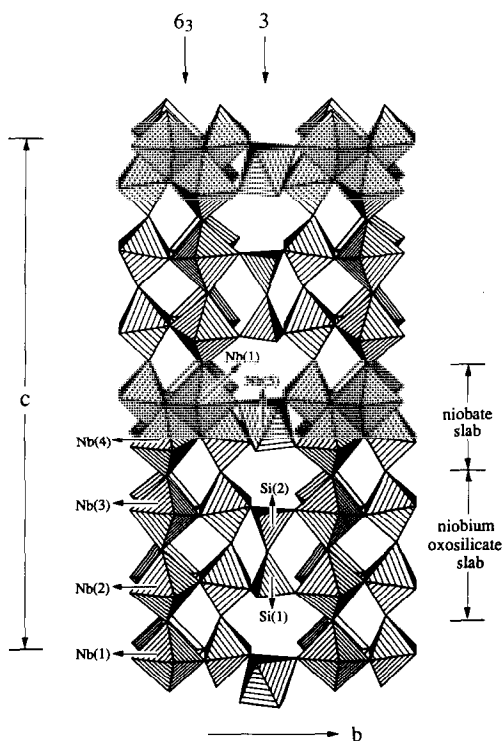


FIG. 1. A STRUPLO polyhedral plot shows a pair of fused, parallel NbO_6 columns interconnected by isolated Nb(5)O_6 and Si_2O_7 groups. The structure can be viewed as the intergrowth of two types of slabs; niobium oxosilicate and niobate. The barium atoms and the third symmetry related column (by the threefold axis) are omitted for clarity.

bium oxosilicate) and $\text{Ba}_3\text{Nb}_8\text{O}_{21}$ (niobium oxide) as indicated by the two slabs in Fig. 1. This is derived from the fact that this newly synthesized oxosilicate compound has a great structural resemblance with the $\text{Ba}_6\text{Nb}_{10}\text{Ti}_4\text{Si}_4\text{O}_{47}$ phase (6). In the latter compound, the structure of this fully oxidized, mixed-metal oxosilicate phase has been described as the first member of the family $(\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26})_n(\text{Ba}_3\text{Nb}_4\text{Ti}_4\text{O}_{21})$. The single crystal structure of the title compound shows that the structural formula can be written as the $n = 1$ member of the family $(\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26})_n(\text{Ba}_3\text{Nb}_8\text{O}_{21})$, in which the niobium cation is substituted for titanium.

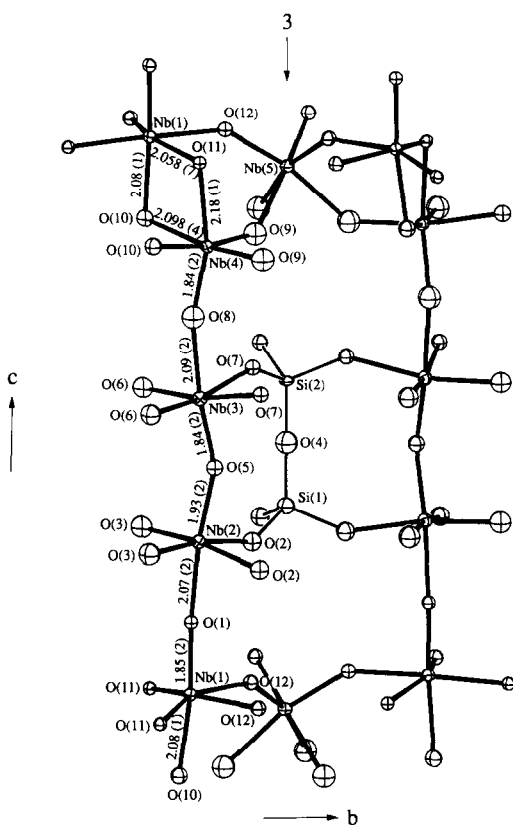


FIG. 2. An ORTEP drawing of the partial structure of Ba₆Nb₁₄Si₄O₄₇. All the atoms are drawn at 90% probability. Only the Nb–O distances along the columns are included.

Members of this family with n values equal to 2 and 4 have also been synthesized and their structures will be reported in the future (10).

An interesting feature of the Ba₆Nb₁₄Si₄O₄₇ structure is its quasi-one-dimensionality. In Fig. 2, two columns of corner sharing octahedra are shown to be interconnected by NbO₆ and Si₂O₇ groups. The bond distances and angles in the NbO₆ octahedra, listed in Table III, are typical compared to known niobium oxo-compounds (1–4). However, the Nb–O–Nb bond distance distribution along the column and the resulting bond valence sum calculations (11) for the

TABLE III
BOND DISTANCES (Å) AND ANGLES (DEGREES) FOR
THE NbO₆ OCTAHEDRA IN Ba₆Nb₁₄Si₄O₄₇

Nb(1)O ₆		
Nb(1) ^a –O(1) ^b	1.85(2)	
Nb(1) ^a –O(10) ^a	2.08(1)	
Nb(1) ^a –O(11) ^{a,c}	2.058(7)	(2 ×)
Nb(1) ^a –O(12) ^{a,d}	2.087(9)	(2 ×)
O(1) ^b –Nb(1) ^a –O(10) ^a	172.8(5)	
O(1) ^b –Nb(1) ^a –O(11) ^{a,c}	97.8(4)	(2 ×)
O(1) ^b –Nb(1) ^a –O(12) ^{a,d}	90.8(4)	(2 ×)
O(10) ^a –Nb(1) ^a –O(11) ^{a,c}	79.1(4)	(2 ×)
O(10) ^a –Nb(1) ^a –O(12) ^{a,d}	94.8(4)	(2 ×)
O(11) ^a –Nb(1) ^a –O(11) ^c	126.3(6)	
O(11) ^{a,c} –Nb(1) ^a –O(12) ^{a,d}	76.4(4)	(2 ×)
O(11) ^{a,c} –Nb(1) ^a –O(12) ^{d,a}	153.8(4)	(2 ×)
O(12) ^a –Nb(1) ^a –O(12) ^d	78.7(5)	
Nb(2)O ₆		
Nb(2) ^a –O(1) ^a	2.07(2)	
Nb(2) ^a –O(2) ^{a,c}	2.070(9)	(2 ×)
Nb(2) ^a –O(3) ^{a,f}	1.920(4)	(2 ×)
Nb(2) ^a –O(5) ^a	1.93(2)	
O(1) ^a –Nb(2) ^a –O(2) ^{a,c}	83.3(3)	(2 ×)
O(1) ^a –Nb(2) ^a –O(3) ^{a,f}	88.1(5)	(2 ×)
O(1) ^a –Nb(2) ^a –O(5) ^a	172.8(4)	
O(2) ^a –Nb(2) ^a –O(2) ^e	87.9(5)	
O(2) ^{a,e} –Nb(2) ^a –O(3) ^{a,f}	89.5(5)	(2 ×)
O(2) ^{a,e} –Nb(2) ^a –O(3) ^{f,a}	171.3(5)	(2 ×)
O(2) ^{a,e} –Nb(2) ^a –O(5) ^a	91.5(3)	(2 ×)
O(3) ^a –Nb(2) ^a –O(3) ^f	91.8(8)	
O(3) ^{a,f} –Nb(2) ^a –O(5) ^a	96.9(5)	
Nb(3)O ₆		
Nb(3) ^a –O(5) ^a	1.84(2)	
Nb(3) ^a –O(6) ^{a,f}	1.941(4)	(2 ×)
Nb(3) ^a –O(7) ^{a,c}	2.062(9)	(2 ×)
Nb(3) ^a –O(8) ^a	2.09(2)	
O(5) ^a –Nb(3) ^a –O(6) ^{a,f}	97.2(5)	(2 ×)
O(5) ^a –Nb(3) ^a –O(7) ^{a,c}	93.6(3)	(2 ×)
O(5) ^a –Nb(3) ^a –O(8) ^a	172.9(5)	
O(6) ^a –Nb(3) ^a –O(6) ^f	93.2(7)	
O(6) ^{a,f} –Nb(3) ^a –O(7) ^{a,c}	88.9(4)	(2 ×)
O(6) ^{a,f} –Nb(3) ^a –O(7) ^{e,a}	168.6(5)	(2 ×)
O(6) ^{a,f} –Nb(3) ^a –O(8) ^a	87.6(5)	(2 ×)
O(7) ^a –Nb(3) ^a –O(7) ^e	86.8(5)	
O(7) ^{a,e} –Nb(3) ^a –O(8) ^a	81.2(4)	(2 ×)
Nb(4)O ₆		
Nb(4) ^a –O(8) ^a	1.84(2)	
Nb(4) ^a –O(9) ^{a,e}	1.879(10)	(2 ×)
Nb(4) ^a –O(10) ^{a,f}	2.098(4)	(2 ×)
Nb(4) ^a –O(11) ^a	2.18(1)	

TABLE III—Continued

O(8) ^a —Nb(4) ^a —O(9) ^{a,c}	96.8(4)	(2 ×)
O(8) ^a —Nb(4) ^a —O(10) ^{a,f}	93.1(4)	(2 ×)
O(8) ^a —Nb(4) ^a —O(11) ^a	164.6(5)	
O(9) ^a —Nb(4) ^a —O(9) ^c	92.1(6)	
O(9) ^{a,e} —Nb(4) ^a —O(10) ^{a,f}	89.2(5)	(2 ×)
O(9) ^{a,e} —Nb(4) ^a —O(10) ^{f,a}	169.8(4)	(2 ×)
O(9) ^{a,e} —Nb(4) ^a —O(11) ^a	93.9(4)	(2 ×)
O(10) ^a —Nb(4) ^a —O(10) ^f	87.8(7)	
O(10) ^{a,f} —Nb(4) ^a —O(11) ^a	76.0(4)	(2 ×)
Nb(5)O ₆		
Nb(5) ^a —O(9) ^{a,g,h}	2.104(10)	(3 ×)
Nb(5) ^a —O(12) ^{a,g,h}	1.886(9)	(3 ×)
O(9) ^{a,g} —Nb(5) ^a —O(9) ^{g,h}	79.0(4)	(3 ×)
O(9) ^{a,g,h} —Nb(5) ^a —O(12) ^{a,g,h}	86.8(3)	(3 ×)
O(9) ^{a,g,h} —Nb(5) ^a —O(12) ^{g,h,a}	100.1(3)	(3 ×)
O(9) ^{a,g,h} —Nb(5) ^a —O(12) ^{h,a,g}	165.6(4)	(3 ×)
O(12) ^{a,g} —Nb(5) ^a —O(12) ^{g,h}	94.1(4)	(3 ×)

Note. Symmetry codes: ^a +x, +y, +z; ^b +x - y, +x, $\frac{1}{2}$ +z; ^c -y, +x - y, +z; ^d +y, +x, +z; ^e +x - y, -y, +z; ^f -x + y, -x, +z; ^g 1 - y, +x - y, +z; ^h 1 - x + y, 1 - x, +z.

niobium cations show some unusual variations. The Nb—O distances along the column are rather diverse, ranging from 1.84 to 2.18 Å, compared to the Nb—O distances of the waist oxygen, ranging from 1.88 to 2.06 Å. This trend of irregularity indicates that the Nb is off-centered in each octahedron which may be due to the uneven charge distribution on the niobium centers. The corresponding bond valence sum calculations based on the observed Nb—O distances are striking. The valence sum varies from Nb(1) to Nb(4) along the column, i.e., 4.40 for Nb(1), 4.85 for Nb(2), 5.00 for Nb(3), and 5.08 for Nb(4). (The fifth niobium cation Nb(5) surrounded by the parallel columns is calculated to be fully oxidized, i.e., 4.99.) The formula Ba₆Nb₁₄Si₄O₄₇ gives an average niobium oxidation state of +4.71, presumably attributed to a mixed valence between IV and V. The inhomogeneous bond distances and charge distribution stated above may further indicate that the electrons are by-in-large localized in the fused NbO₆ octa-

hedral column. Thus, the compound may be non-metallic even though the color of the material is black.

For the Si₂O₇ pyrosilicate group, the bond distances and angles in the SiO₄ tetrahedra are listed in Table IV. The bond distances of Si—O^t (t, terminal) vs Si—O^b (b, bridging) are in a reverse order in Si(2)O₄ compared to the Si(1)O₄ tetrahedron. It is normal to see longer bond distances for Si—O^b than for Si—O^t, as observed in the case of the Si(1)O₄ tetrahedron. However, in the Si(2)O₄ tetrahedron the Si—O(7)^t distance, 1.644(9) Å, is longer than Si—O(4)^b, 1.61(2) Å. This is because the electrostatic interaction in Nb⁵⁺—O—Si⁴⁺ is different than that in Si⁴⁺—O—Si⁴⁺ with respect to the central oxygen atoms, i.e., O(7) and O(4), respectively. That is to say, the niobium cation in the first case is formally pentavalent and draws more electrostatic interaction from the common oxygen atom in forming a covalent bond than the formally tetravalent silicon cation in the latter. As a result, the terminal oxygen to silicon, Si(2), interaction is weaker and in turn the bond length is longer compared to the bridging oxygen in the Si(2)O₄ tetrahedra. A similar trend is also observed in the Ba₃Nb₆Si₄O₂₆ phase, where the Si—O^t distance, 1.63 Å, is longer than

TABLE IV
BOND DISTANCES (Å) AND ANGLES (DEGREES) FOR
SiO₄ TETRAHEDRA IN Ba₆Nb₁₄Si₄O₄₇

Si(1)O ₄ tetrahedron		
Si(1) ^a —O(2) ^{a,g,h}	1.617(9)	(3 ×)
Si(1) ^a —O(4) ^a	1.62(2)	
O(2) ^{a,g} —Si(1) ^a —O(2) ^{g,h}	106.5(4)	(3 ×)
O(2) ^{a,g,h} —Si(1) ^a —O(4) ^a	112.3(4)	(3 ×)
Si(2)O ₄ tetrahedron		
Si(2) ^a —O(4) ^a	1.61(2)	
Si(2) ^a —O(7) ^{a,g,h}	1.644(9)	(3 ×)
O(4) ^a —Si(2) ^a —O(7) ^{a,g,h}	113.3(4)	(3 ×)
O(7) ^{a,g} —Si(2) ^a —O(7) ^{g,h}	105.4(4)	(3 ×)
Si(1) ^a —O(4) ^a —Si(2) ^a	180.00	

Note. See Table III for symmetry codes.

Si-O^b, 1.60 Å (4a). Nevertheless, these Si-O distances are still comparable with the sum of the Shannon crystal radii, 1.64 Å (12).

Finally, the coordination number of the barium atoms in the current structure is also slightly modified compared to the $Ba_{6+x}Nb_{14}Si_4O_{47}$ phase. Two asymmetric barium atoms are located in channels having pentagonal windows, as shown in the projected structure of the $Ba_3Nb_6Si_4O_{26}$ slab (Fig. 3). They are obviously off-centered from each other. Each barium is coordinated by 12 oxygen atoms. In the nonstoichiometric phase the coordination differs, 13 for Ba(1) and 15 for Ba(2). The Ba-O distances in both structures are comparable although we report a narrower range, e.g., 2.65–3.25 Å (Table V), than in the previously reported structure, e.g., 2.63–3.37 Å. It should also be noted that for the title compound the calculated valence sums of 1.96 for Ba(1) and 2.02 for Ba(2) are in excellent agreement

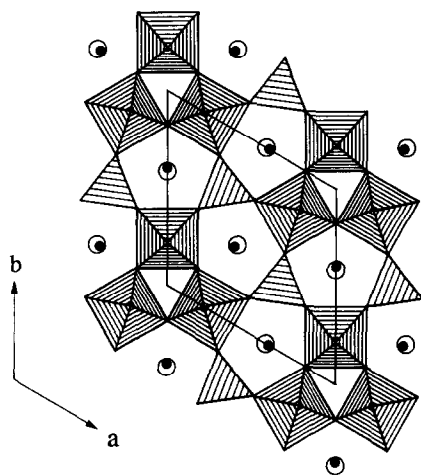


FIG. 3. A STRUPLO structure shows the projected view of the $Ba_3Nb_6Si_4O_{26}$ slab. The barium atoms (closed circles for Ba(1) and open circles for Ba(2)) are located in channels with pentagonal windows which are formed by the edges of three NbO_6 octahedra and two SiO_4 tetrahedra.

TABLE V
Ba-O DISTANCES (Å) IN BaO_{12} POLYHEDRA

Ba(1)O ₁₂	
Ba(1) ^a -O(6) ^g	2.91(1)
Ba(1) ^a -O(7) ^{a,c}	2.849(8) (2×)
Ba(1) ^a -O(7) ^{g,i}	2.966(9) (2×)
Ba(1) ^a -O(8) ^{g,j}	3.129(1) (2×)
Ba(1) ^a -O(9) ^{a,c}	2.88(1) (2×)
Ba(1) ^a -O(9) ^{g,i}	3.09(1) (2×)
Ba(1) ^a -O(10) ^g	2.91(1)
Ba(2)O ₁₂	
Ba(2) ^a -O(1) ^{g,j}	3.246(1) (2×)
Ba(2) ^a -O(2) ^{a,c}	2.820(9) (2×)
Ba(2) ^a -O(2) ^{g,i}	3.028(9) (2×)
Ba(2) ^a -O(3) ^g	3.04(1)
Ba(2) ^a -O(11) ^k	2.65(1)
Ba(2) ^a -O(12) ^{l,m}	2.845(9) (2×)
Ba(2) ^a -O(12) ^{k,n}	3.153(9) (2×)

Note. Additional symmetry codes: ⁱ 1 - x, -x + y, +z; ^j 1 - x + y, -x, +z; ^k 1 - x, -y, -½ + z; ^l +y, -x + y, -½ + z; ^m +x, +x - y, -½ + z; ⁿ 1 - x + y, +y, -½ + z. The bond angles for the BaO_{12} configurations are given in Appendix II.

with the 2+ formal oxidation state of the barium cation.

Acknowledgments

Acknowledgment is given to the National Science Foundation, Solid State Chemistry (SGER), Grant DMR-9012983, and, in part, to the Petroleum Research Fund, administered by the ACS, for support of this research (Grant ACS-PRF 21154-G3). D.L.S. is indebted to the Dow Chemical Co. (1990–1991) and the Wray Trust (1991–1992) for fellowships. Financial support for the single crystal X-ray diffractometer by the National Science Foundation is gratefully acknowledged.

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