

Synthesis, Crystal Structure, and Physical Properties of $\text{Sr}_{0.93}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x = 0.87$)

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We present here the synthesis, crystal structure, and physical properties of a reduced niobium oxide $\text{Sr}_{0.93}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x = 0.87$). Its structure was determined on single crystal by X-ray diffraction in the space group $R\bar{3}$ ($a_h = 7.843(1)$, $c_h = 42.26(2)$ Å, $V_h = 2251.3(9)$ Å³, and $Z = 6$). The compound is isostructural to $\text{Na}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x \approx 0.75$) and exhibits discrete $[\text{Nb}_6\text{O}_{12}]$ clusters, Nb_2O_{10} dimers, NbO_6 octahedra, SrO_{12} cubo-octahedra, and SiO_4 tetrahedra. The compound is insulating with a room-temperature resistivity ~ 50 Ω cm. The magnetic susceptibility data yields $\mu_{\text{eff}} = 3.16$ μ_B/Nb, which is consistent with a 15-electron $[\text{Nb}_6\text{O}_{12}]$ cluster, with Nb(IV) in the dimers and Nb(V) in the isolated NbO_6 octahedra. © 2000

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INTRODUCTION

In the last decade, many reduced oxoniobate compounds presenting cluster units have been synthesized. Discrete Nb_6O_{12} cluster is the most frequently observed in the niobates. Several of these compounds crystallize in a trigonal or hexagonal space group with a unit-cell parameter of about $a = 7.8$ Å. Six different structure types exhibit these different features: $M_3\text{Al}_2\text{Nb}_{34}\text{O}_{64}$ ($M = \text{Na}, \text{K}$) (1, 2), $M_4\text{Al}_2\text{Nb}_{35}\text{O}_{70}$ ($M = \text{K}, \text{Rb}$) (2, 3), $\text{Rb}_4(\text{Si}/\text{Nb})_2\text{Nb}_{35}\text{O}_{70}$ (4), $M\text{SiNb}_{10}\text{O}_{19}$ ($M = \text{K}, \text{Ba}$) (2, 5), $\text{Ba}_3\text{Si}_2\text{Nb}_{20.8}\text{O}_{44}$ (6), $\text{Ba}_2\text{Nb}_{15}\text{O}_{32}$ (7), and $\text{Na}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x = 0.75$) (1). The latter compound with sodium is said to exhibit 14.33 electrons per Nb_6O_{12} cluster. We present here an isostructural compound where the monovalent Na^+ is replaced by divalent Sr^{2+} in order to change the number of valence electrons per Nb_6O_{12} cluster.

EXPERIMENTAL PROCEDURES

Synthesis

Single crystals of $\text{Sr}_{0.93}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x = 0.87$) were prepared by heating stoichiometric mixtures of

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SrNb_2O_6 (Johnson-Matthey, 99.5%), SiO_2 (Alfa, 99.9%), NbO_2 (Alfa, 99 + %), Nb (Alfa, 99.8%), and (3% of weight) NH_4F as mineralizer (Aldrich, 99.99%) or KF (Alfa, 98 + %). The mixtures were pressed into pellets, sealed in evacuated quartz ampoules, and then heated at 50°/h to 1000°C for 96 h and cooled down to room temperature with a rate of 20°/h. Fluxes were removed by alternate repeated washings with deionized water and ethanol in an ultrasonic bath leaving a mixture of powder and black crystals that were easily separated due to their hexagonal shapes.

Electrical Resistivity and Magnetic Susceptibility Measurements

Resistivity experiments were carried out on two samples: a single crystal and a cold-pressed pellet of well-ground selected single crystals. Measurements were made using conventional 4-point probe techniques. Ohmic contacts were made on the samples with gold wires and silver paint. Resistivity as a function of temperature was measured from 20–300 K with a Displex Cryostat (ADP Cryogenics, DE202). There was no appreciable variation of the resistivity curve between heating and cooling cycles.

Temperature-dependent susceptibility measurements were made with a Quantum Design SQUID magnetometer (MPMS) over the temperature range 5–300 K in an applied field of 1 kG on a cold pressed pellet (ca. 87.3 mg) of crushed selected crystals.

Structure Determination

Black, platelet single crystals of $\text{Sr}_{0.93}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x = 0.87$) were grown with NH_4F as mineralizer. A crystal with approximate dimensions of $0.18 \times 0.18 \times 0.05$ mm³ was selected for X-ray intensity data collection. The intensities of 2398 reflections (1450 unique reflections, $R_{\text{int}} = 0.0238$) were collected by the ω scan method in the 2–60° 2θ range (h, k, l range: $-9 < h < 5$; $0 < k < 11$; $-59 < l < 59$) on a Nonius CAD4 diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å)



TABLE 1
Crystal Data and Structure Refinement for
Sr_{0.93}(Si_xNb_{1-x})Nb₁₀O₁₉ (x = 0.87)

Formula	Sr _{0.93} Si _{0.87} Nb _{10.13} O ₁₉
Molecular weight	1351.03
Space group	R $\bar{3}$ (No. 148)
a (Å)	7.843(1)
c (Å)	42.26(2)
V (Å ³)	2251.3(1)
Z	6
Density (calcd, g cm ⁻³)	5.979
Temperature (K)	293
Diffractometer	Nonius CAD4
Radiation	MoK α (λ = 0.71073 Å)
Crystal color	Black
Morphology	Hexagonal plate
Crystal size	0.18 × 0.18 × 0.05 mm ³
Linear absorption coeff (mm ⁻¹)	10.869
Monochromator	Graphite
Scan mode	ω
Recording range 2 θ (deg)	2–60
hkl range	–9 < h < 5, 0 < k < 11, –59 < l < 59
No. of measured reflections	2398
No. of independent reflections	1450
No. of observed reflections with F ² > 2 σ (F ²)	1309
R _{int}	0.0238
Absorption correction method	ψ scan/ Φ plot (MoLEN)
Transmission factors (min.–max.)	0.455–0.999
Refinement	F ²
Calculated weights	w = 1/[$\sigma^2(F_o^2) + (0.0116P)^2$ + 13.4442P] where P = (F _o ² + 2F _c ²)/3
Extinction coefficient (SHELXL 97)	0.000187(14)
R[F _o > 2 σ (F _o)]	0.0224
R(F _o) on all data ^a	0.0278
wR(F _o ²) on all data ^b	0.0474
Goodness-of-fit, S (all data) ^c	1.217
No. of refined parameters	101
Residual peaks (e/Å ³)	–0.88, +1.43

$$^a R(F_o) = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^b wR(F_o^2) = (\sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4])^{1/2}$$

$$^c S = \{ \sum [w(F_o^2 - F_c^2)^2] / (N_{obs} - N_{parm}) \}^{1/2}$$

at room temperature. Three intensity control reflections were checked every hour and showed no systematic variations throughout data collection. The raw data were corrected for Lorentz and polarization effects and for absorption, the latter by employing the ψ scan method (8) on 2 reflections using MoLEN (9). Examination of the data set did not show any systematic extinctions other than that corresponding to the R-type lattice. The lattice constants were determined by least-squares refinement of the setting angles of 25 reflections in the 2 θ range 15–25°. The structure was refined by use of the atomic positions of the isostructural sodium compound and SHELXL97 (10). The refinement of the occupancy of the heavy atom sites showed that Nb5

and Si1 were partially occupied as in the sodium compound but with a different value of x = 0.868(3) (or 0.132(3) for Nb5). The refinement of the occupancy of the Sr2 site showed an occupancy of 0.854(6), the Sr1 site was totally occupied. The final refinement converged to wR(F_o²) = 0.0474 on all data and for those 1309 having F_o² > 2 σ (F_o²) to the conventional reliability factor R(F_o) = 0.0224. The largest shift/e.s.d. was <0.01. Maximum and minimum electron densities in the final difference Fourier map were +1.43 and –0.88 e Å⁻³, respectively. The maximum is located near the Nb3 atom of the Nb₂ dimer and the minimum is near the Nb1 atom of the Nb₆ octahedron. Data collection and refinement parameters are given in Table 1. The final values of the positional parameters, isotropic-equivalent atomic displacement parameters, and their standard uncertainties are reported in Table 2. Selected interatomic distances are given in Table 3. Intensities of a crystal grown with KF as mineralizer were also collected, and the structure was refined. The results show the same structural features as before, with values of the occupancies for Si1 and Sr2 of 0.864(6) and 0.862(9), respectively, giving a corresponding formula Sr_{0.93}(Si_xNb_{1-x})Nb₁₀O₁₉ (x = 0.87).

Microprobe Analysis

Quantitative analysis was performed on single crystals with a JEOL JXA-8600 microprobe. The analysis did not show any other element than Sr, Si, Nb, and O. The results obtained in atomic percentage for Sr, Si, Nb, and O are 2.84, 2.75, 33.17, and 61.24% (rest), respectively. The corresponding formula is Sr_{0.89(5)}Si_{0.85(4)}Nb_{10.3(2)}O₁₉ and thus

TABLE 2
Positional Parameters and Equivalent Isotropic Displacement Parameters for Sr_{0.93}(Si_xNb_{1-x})Nb₁₀O₁₉ (x = 0.87)

Atom	Position	x	y	z	U _{eq} (Å ²) ^a	SOF ^b
Sr1	3b	0.0000	0.0000	0.5000	0.0115(2)	$\frac{1}{6}$
Sr2	3a	0.0000	0.0000	0.0000	0.0260(5)	0.142(1)
Nb1	18f	0.2182(1)	0.1910(1)	0.4183(1)	0.00429(8)	1.0
Nb2	18f	0.0270(1)	0.2188(1)	0.3631(1)	0.00483(9)	1.0
Nb3	18f	0.5360(1)	0.6062(1)	0.4740(1)	0.00491(8)	1.0
Nb4	6c	0.0000	0.0000	0.0833(1)	0.00562(12)	$\frac{1}{3}$
Nb5	6c	0.0000	0.0000	0.2961(1)	0.0033(9)	0.044(1)
Si1	6c	0.0000	0.0000	0.2626(1)	0.0048(4)	0.289(1)
O1	18f	0.1940(4)	0.9730(4)	0.4479(1)	0.0078(5)	1.0
O2	18f	0.4341(4)	0.1738(4)	0.3897(1)	0.0069(5)	1.0
O3	18f	0.0810(4)	0.2281(4)	0.2739(1)	0.0083(5)	1.0
O4	18f	0.5796(4)	0.8478(4)	0.4978(1)	0.0070(5)	1.0
O5	18f	0.4936(4)	0.3988(4)	0.4432(1)	0.0074(5)	1.0
O6	18f	0.2380(4)	0.2041(4)	0.3355(1)	0.0112(6)	1.0
O7	6c	0.0000	0.0000	0.2223(1)	0.0079(9)	$\frac{1}{3}$

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^b SOF is the quotient of the atom site occupancy and the atom site multiplicity.

TABLE 3
Selected Interatomic Distances (Å) for $\text{Sr}_{0.93}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$
($x = 0.87$)

Nb1–Nb1	2.7976(6) ($\times 2$)	Nb2–O6	2.031(3)
Nb1–Nb2	2.8348(10)	Nb2–O6	2.076(3)
Nb1–Nb2	2.8367(10)	Nb2–O2	2.087(3)
		Nb2–O3	2.149(3)
Nb2–Nb2	2.8069(6) ($\times 2$)	Nb2–O6	2.178(3)
Nb2–Nb1	2.8348(10)		
Nb2–Nb1	2.8367(10)	Nb3–O5	1.978(3)
		Nb3–O4	2.018(3)
Nb3–Nb3	2.6389(11)	Nb3–O4	2.033(3)
		Nb3–O1	2.078(3)
Sr1–O1	2.742(3) ($\times 6$)	Nb3–O4	2.118(3)
Sr1–O4	2.893(3) ($\times 6$)	Nb3–O7	2.254(3)
Sr2–O2	2.877(3) ($\times 6$)	Nb4–O2	1.979(3) ($\times 3$)
Sr2–O6	2.988(3) ($\times 6$)	Nb4–O5	2.015(3) ($\times 3$)
Nb1–O1	2.052(3)	Nb5–O3	1.830(3) ($\times 3$)
Nb1–O1	2.057(3)	Nb5–O6	2.415(4) ($\times 3$)
Nb1–O3	2.116(3)		
Nb1–O2	2.138(3)	Si1–O3	1.641(3) ($\times 3$)
Nb1–O5	2.217(3)	Si1–O7	1.703(5)
		Nb5–Si1	1.415(5)

confirms the stoichiometry determined by the crystal structure analyses. The experiment was conducted on three single crystals, analyzing different regions of each crystal. The fact that all the results were the same, within experimental error, not only in the same crystal but also within different crystals, indicates that the samples are homogeneous with no microdomains of variable stoichiometry.

STRUCTURAL DESCRIPTION AND DISCUSSION

Figure 1 shows a projection of the structure along the [100] axis. It presents two different slabs (and their symmetrical equivalents) that lie perpendicular to the [001] axis. The first slab is composed of discrete Nb_6 clusters (Nb1, Nb2), NbO_6 octahedra (Nb4, Nb5), and SiO_4 tetrahedra (Si1) while the second slab is based on Nb_2 (Nb3) dimers and Sr atoms (Sr1, Sr2) in cubo-octahedral oxygen environments. The Nb_6 cluster is surrounded by 18 oxygen atoms [$\text{Nb}_6\text{O}_{12}\text{O}_6^a$] where each Nb atom is linked by four inner and one apical O atoms (Fig. 2) with Nb–O distances ranging from 2.031(3) to 2.217(3) Å. Within the Nb_6 cluster (C_3 symmetry), Nb–Nb bond distances range from 2.7976(6) to 2.837(1) Å with average value of 2.819 Å. The Nb_2 dimer is surrounded by 10 oxygen atoms and each Nb3 atom is in pseudo-octahedral oxygen environment where Nb–O bond distances are between 1.978(3) and 2.254(3) Å. The Nb3–Nb3 bond distance is 2.639(1) Å. The Nb4 atom is in a pseudo-octahedral oxygen environment (Nb–O distances ranging from 1.979(3) to 2.015(3) Å), forming a NbO_6 unit that occupies a position in between the [Nb_6O_{12}] clusters.

For the whole structure, the smallest distance between different units is 3.113(1) Å, between the isolated Nb4 atom and Nb1 from the Nb_6 cluster, and thus excludes any direct

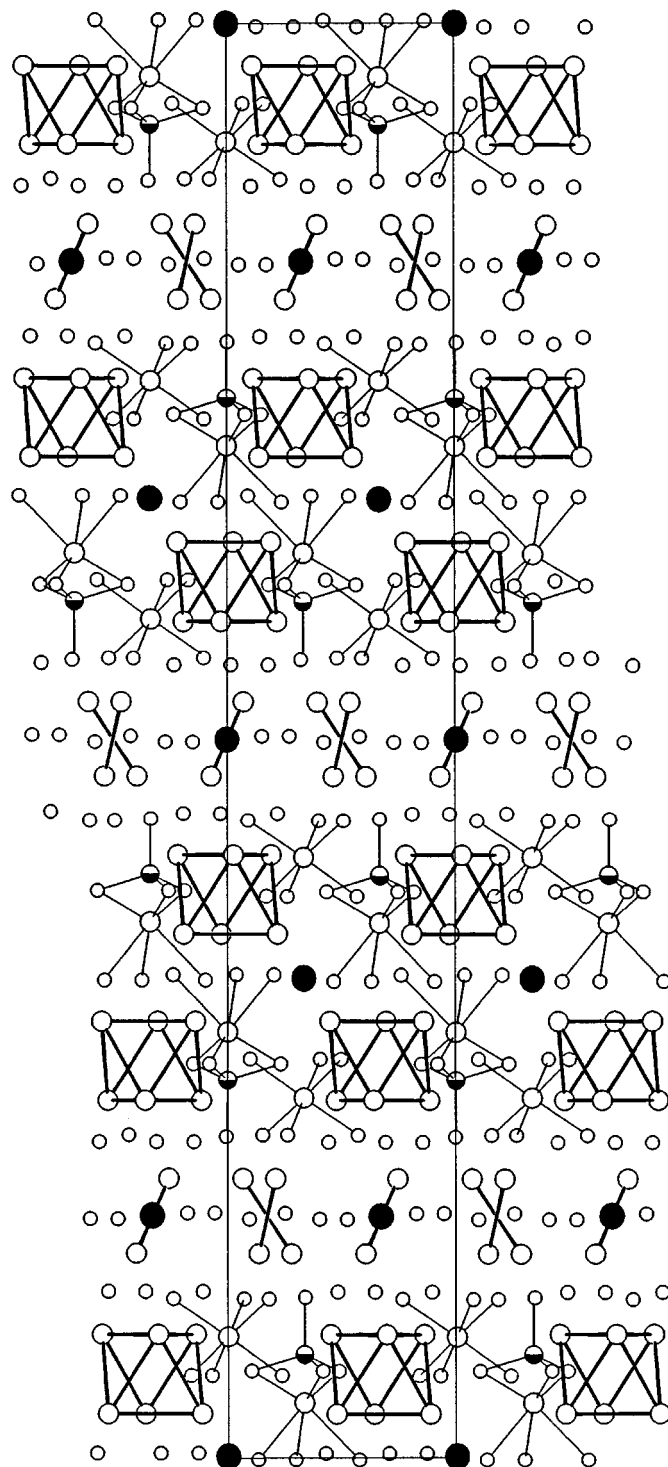


FIG. 1. View of the unit cell contents of $\text{Sr}_{0.93}(\text{Si}_{0.87}\text{Nb}_{0.13})\text{Nb}_{10}\text{O}_{19}$ perpendicular to the a axis, where the long axis is the c axis. The Sr and Si atoms are represented by filled and half-filled circles, respectively, and the Nb and O atoms are the large and small open circles, respectively. The bonds of the Nb_2 dimers and the Nb_6 clusters are solid for emphasis.

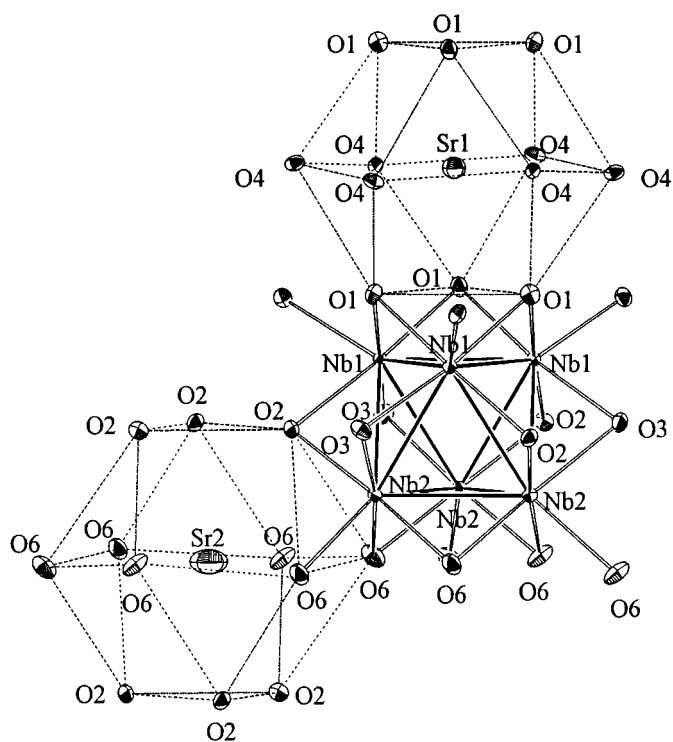


FIG. 2. The $[\text{Nb}_6\text{O}_{12}\text{O}_6]^{6+}$ unit and the cubo-octahedral environment of the Sr atoms (70% ellipsoids). The Nb–Nb and Nb–O bonds are drawn with solid and open lines, respectively. Cubo-octahedra edges are represented by dashed lines. The vector from the centroid of the Nb_6 clusters to the Sr(1) atom is along the c axis.

metal–metal interaction. Within the same slab lies the Nb5 atom in a strongly distorted octahedral site (Nb–O distances are 1.830(3) ($\times 3$) and 2.415(4) Å ($\times 3$)) and the Si1 atom that is surrounded by four oxygen atoms forming a distorted tetrahedron where Si–O bond distances range from 1.641(3) to 1.703(5) Å (Fig. 3). The distance between these two sites is 1.415(5) Å and thus clearly shows that the Nb5 and Si1 sites cannot be occupied at the same time. The final least-squares refinement showed a partial occupancy of 0.868(3) for Si1 and 0.132(3) for Nb5. These sites are occupied alternatively, and as no ordering or superstructure was found, the occupancy of the sites is statistical. The Nb5 atom is strongly displaced along the c axis from the center of the octahedron formed by six oxygen atoms (O3 ($\times 3$) and O6 ($\times 3$)) due to cationic repulsion with the Nb2 atom of the Nb_6 cluster. The Nb5–Nb2 distance is 3.1256(7) Å long and is thus nonbonding. If the Nb5 atom was placed in the center of the octahedron with all Nb–O distances being equal (≈ 2.11 Å), the Nb5–Nb2 distance would be about 2.85 Å and would thus be bonding. Strontium atoms occupy large cavities, where 12 oxygen atoms form a cubo-octahedron as represented in Fig. 2. Due to partial vacancy of the Sr2 atom, the oxygen atoms connected to Sr2 (O2 ($\times 6$), O6 ($\times 6$)) have average positions and the Sr2 site exhibits larger

Sr–O bond distances (2.877(3)–2.988(3) Å) than the Sr1 site (2.742(3)–2.893(3) Å).

This strontium compound presents similar features to that of the isostructural sodium compound. The latter has been found to have a variable Si/Nb ratio ($0.6 \leq x \leq 0.8$), but the strontium compound seems to have a precise stoichiometry of $\text{Sr}_{0.93}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x = 0.87$) that is confirmed by structure refinement of two single-crystal samples and microprobe analysis. Another difference between the two compounds is a partial occupancy of the Sr2 site that does not seem to occur for the sodium compound; however, the authors have reservations concerning the occupancy of the Na2 site (1, 12).

Bond-Order Considerations

An assignment of oxidation numbers can be made qualitatively on the basis of bond-order sums according to the equation for the bond valence, $s = \exp[(d_0 - d)/B]$ ($B = 0.37$, $d_0(\text{Nb}-\text{O}) = 1.911$ Å, $d_0(\text{Si}-\text{O}) = 1.624$ Å, $d_0(\text{Sr}-\text{O}) = 2.118$ Å) (11). The results for $\sum s_i$ in Table 4 suggest that the valence state for Nb1 and Nb2 (Nb_6 cluster) is $\sim +3$, for Nb3 (Nb_2 dimer) is $+4$, and for the isolated Nb4 atom,

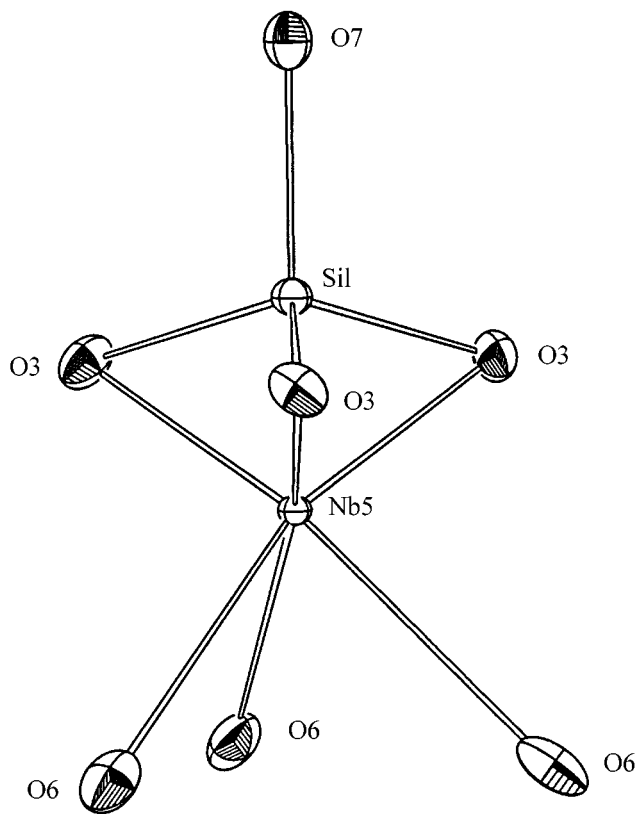


FIG. 3. View of the Si(1) and Nb(5) atoms in their mutually exclusive near-tetrahedral and near-octahedral environments, respectively (70% ellipsoids). The vector from Nb(5) to Si(1) is along the c axis.

TABLE 4
Bond-Order Sums in $\text{Sr}_{0.93}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ ($x = 0.87$)

	O1 ⁱ	O2 ⁱ	O3 ⁱ	O4	O5 ^a	O6 ^{i-a}	O7	CN	$\sum s_i$
Sr1	6/1			6/1				12	1.85
Sr2		6/1				6/1		12	1.34
Nb1	2/2	1/1	1/1		1/1			5	2.91
Nb2		1/1	1/1			3/3		5	3.00
Nb3	1/1			3/3	1/1		1/3	6	3.91
Nb4		3/1			3/1			6	4.76
Nb5			3/1			3/1		6	4.50
Si1			3/1				1/1	4	3.68
CN	4	4	4	4	3	5	4		
$\sum s_i^a$	2.18	2.10	2.09	2.16	2.03	1.98	1.89		

$$^a s = \exp[(d_0 - d)/B].$$

it is +5. Due to partial occupancies of the Sr2, Nb5, and Si1 sites, the oxygen atoms connected to these atoms have mean positions. In particular, O3 is linked 87% of the time to Si1 and 13% to Nb5. The O6 atom may be linked sometimes to Sr2 or/and Nb5 or can even face vacancies. These features directly affect bond-order sums for the three different cationic sites. As in the sodium compound, isolated Nb5 atom can be assigned the +5 oxidation state while the Si1 atom is assumed to be +4 and strontium is +2.

Calculations with O^{2-} , Sr^{2+} , and Si^{4+} show that there are $19 \times 2 - 0.93 \times 2 - 0.87 \times 4 = 32.66$ negative charges to be compensated by niobium atoms. Thus, considering $\text{Nb}3^{4+}$, $\text{Nb}4^{5+}$, and $\text{Nb}5^{5+}$, there are 15 electrons [$32.66 - 3 \times 4 - 1 \times 5 - 0.13 \times 5 = 15.01$] per Nb_6 cluster. The average Nb–Nb bond distance of 2.819 Å within the Nb_6 cluster is similar to what has usually been found in reduced oxoniobates with 15 electrons per Nb_6 cluster: it is 2.817 Å in $\text{Ba}_2\text{Nb}_{15}\text{O}_{32}$, 2.818 Å in $\text{LaNb}_8\text{O}_{14}$, and 2.821 Å in $\text{Rb}_4\text{Al}_2\text{Nb}_{35}\text{O}_{70}$. The occurrence of Nb_6 clusters in a compound with a low Nb oxidation state indicates that these clusters can act as valence electron reservoirs. It has been shown that there is a requirement of 14 electrons to be present in metal–metal bonding states in discrete Nb_6O_{12} clusters (12) and the theoretical maximum corresponding to the filling of antibonding states would be 16 electrons. Even though the number of valence electrons available for Nb–Nb bonding has been observed to vary between 13 and 15.5. $\text{KNb}_8\text{O}_{14}$ (13) is the only compound presenting 13 electrons per cluster. This number is 14 in the $M_3\text{Nb}_6\text{O}_{11}$ ($M = \text{Mg}, \text{Mn}$) compounds (14, 15), $M\text{Nb}_8\text{O}_{14}$ ($M = \text{Sr}, \text{Ba}, \text{Eu}$) (16–18), $\text{LaNb}_7\text{O}_{12}$ (19), and $\text{BaSiNb}_{10}\text{O}_{19}$ (5), 15 in $\text{Ba}_3\text{Si}_2\text{Nb}_{20.8}\text{O}_{44}$ (6), $\text{Ba}_2\text{Nb}_{15}\text{O}_{32}$ (7), $\text{Na}_3\text{Al}_2\text{Nb}_{34}\text{O}_{64}$ (1), $\text{Rb}_4\text{Al}_2\text{Nb}_{35}\text{O}_{70}$ (3), $\text{NaNb}_{10}\text{O}_{18}$ (20), and $\text{LaNb}_8\text{O}_{14}$ (13), and 15.5 in $\text{Rb}_4(\text{Si}, \text{Nb})_2\text{Nb}_{35}\text{O}_{70}$ (4). The compound $\text{Na}(\text{Si}_x\text{Nb}_{1-x})\text{Nb}_{10}\text{O}_{19}$ (1) is reported to exhibit 14.33 electrons per Nb_6O_{12} cluster. In the case of the strontium compound, the partial occupancy of the Sr2 site coupled with the proper

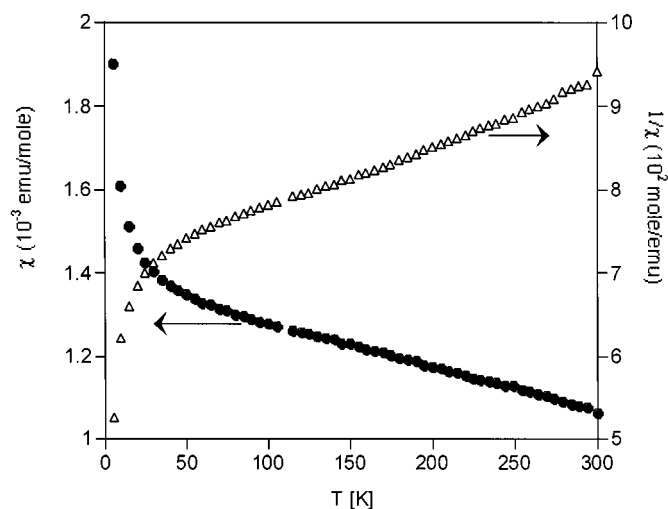


FIG. 4. Temperature dependence of the magnetic susceptibility (5–300 K).

Si/Nb ratio leads to a slightly more reduced compound that exhibits 15 electrons per Nb_6 cluster. The stoichiometry seems to be electronically driven concerning the partial occupancies of the Sr2, Si1, and Nb5 sites in order to accommodate 15 electrons per Nb_6 cluster.

There are three types of metallic atoms in the structure: isolated Nb atoms (Nb4, Nb5), Nb_2 dimers (Nb3), and Nb_6 clusters (Nb1, Nb2). On the basis of the stoichiometry, the overall oxidation state for Nb in this compound is +3.3, while in the literature, similar compounds range from +2.7 for $M_3\text{Nb}_6\text{O}_{11}$ ($M = \text{Mg}, \text{Mn}$) (14, 15) to +4 in $\text{Ba}_2\text{Nb}_{15}\text{O}_{32}$ (7).

RESISTIVITY

The resistivity of a single crystal in the (*ab*) plane was larger than we could determine with our instruments. The pressed pellet had a room temperature resistivity of ~ 50 Ω cm. The resistivity of the pellet increased with decreasing temperature down to 20 K, indicating that the sample was an insulator. From the plot of the $\ln \rho$ versus $1/T$ the E_a was determined to be ~ 5.39 eV, confirming that the sample is a highly resistive insulator.

MAGNETIC SUSCEPTIBILITY

Molar susceptibility as a function of temperature is shown in Fig. 4, $\chi_{290} = 1.07 \times 10^{-3}$ emu/mol. The calculated diamagnetic correction was an order of magnitude smaller than the susceptibility, therefore it was not included in the calculations. Analysis of the high-temperature susceptibility data (150–295 K) using the Curie–Weiss law resulted in a Curie constant, C , of 1.25 emu K/mol, which yielded a μ_{eff} of $3.16 \mu_B/\text{Nb}$ and a Curie–Weiss temperature, θ , of

–865 K. The observed μ_{eff} is somewhat higher than the spin-only theoretical value of $2.77 \mu_{\text{B}}$ /Nb assuming that the Nb3 ion is d^1 ($\mu_{\text{theo}} = 1.73 \mu_{\text{B}}$), the Nb1 and Nb2 in the cluster each have an average oxidation state of 2.5 and equal distributions of d^2/d^3 ($\mu_{\text{theo}} = 2.83, 3.87 \mu_{\text{B}}$) Nb ions, and the Nb4 and Nb5 both have d^0 electronic configuration. The deviation of the observed μ_{eff} from that of the spin-only calculated value is attributed to orbital contributions. The very large negative Curie–Weiss temperature is indicative of magnetic moment reductions due to covalency effects rather than antiferromagnetic interactions. The localization of electrons within the clusters and dimers is consistent with the high resistivity of the compound.

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