

# The Crystal Structure of $\text{SrNb}_4\text{O}_6$

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Single crystals of  $\text{SrNb}_4\text{O}_6$  were obtained by heat treatment of a pelleted mixture of  $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ ,  $\text{Nb}_2\text{O}_5$ , and Nb at 1670°C in sealed Nb tubes. High-resolution electron microscopy (HREM) studies showed the structure to be an intergrowth of alternating slabs of  $\text{SrNbO}_3$  (perovskite-type structure) and NbO (ordered deficient NaCl-type structure), both two unit cells wide.  $\text{SrNb}_4\text{O}_6$  has a tetragonal unit cell with  $a = 4.1655(3)$  Å and  $c = 16.223(1)$  Å and space group  $P4/mmm$ ,  $Z = 2$ . The structure model obtained from the HREM images was refined, using single-crystal diffraction data, to  $R_f = 3.0\%$ . © 1995 Academic Press, Inc.

## INTRODUCTION

In recent years, many reduced oxoniobates containing isolated or condensed  $\text{Nb}_6\text{O}_{12}$  clusters have been synthesized. The condensation of  $\text{Nb}_6\text{O}_{12}$  clusters normally occurs via corner sharing of the  $\text{Nb}_6$  octahedra. An extensive discussion is given in Ref. (1). All the compounds with condensed  $\text{Nb}_6\text{O}_{12}$  clusters can be described as intergrowths between the NbO and the perovskite-type structure. NbO has an ordered deficient NaCl-type structure (2) that can alternatively be described as a three-dimensional condensation of  $\text{Nb}_6\text{O}_{12}$  clusters via corner sharing of the central  $\text{Nb}_6$  octahedra (3). A number of such compounds have been synthesized in the BaO–NbO– $\text{NbO}_2$  system. Compounds with one-dimensional (4–8) and two-dimensional infinitely condensed  $\text{Nb}_6\text{O}_{12}$  clusters have been found (9–12). Their structures and formation via a quasicrystalline intergrowth or *phasoid* (13) have been extensively studied by means of high-resolution electron microscopy (HREM) (1, 6, 8, 14). The ordered structures found as pure phases or as microregions in the quasicrystalline crystallites can be considered homologous series. One of these series with infinite two-dimensionally condensed  $\text{Nb}_6\text{O}_{12}$  clusters,  $A_n\text{Nb}_{n+3m}\text{O}_{3n+3m}$  ( $n$  = the width of the perovskite slabs and  $m$  = the width of the NbO slabs), is formed by compounds exhibiting alternating slabs of perovskite and NbO. For barium,  $\text{Ba}_2\text{Nb}_5\text{O}_9$  ( $n = 2, m = 1$ ) (9–11),  $\text{BaNb}_4\text{O}_6$  ( $n = 1, m = 1$ ) (10, 11), and  $\text{BaNb}_7\text{O}_9$  ( $n = 1, m = 2$ ) (12)

have been reported. In the SrO–NbO– $\text{NbO}_2$  system only  $\text{Sr}_2\text{Nb}_5\text{O}_9$  ( $n = 2, m = 1$ ) (15, 16) has been reported thus far. We report here the structure of a new compound belonging to this homologous series,  $\text{SrNb}_4\text{O}_6$ , which differs from that of the isostructural Ba compound.

## EXPERIMENTAL

The starting materials used were Nb (Merck),  $\text{Nb}_2\text{O}_5$  (99.9%, Roth), and  $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ . In some syntheses 10%  $\text{SrCl}_2$  obtained from dried  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  (99.0%, Baker Analyzed) was added as flux.  $\text{Sr}_5\text{Nb}_4\text{O}_{15}$  (17) was synthesized by heating a stoichiometric mixture of  $\text{SrCO}_3$  (99.9%, Baker Analyzed) and  $\text{Nb}_2\text{O}_5$  at 1000°C for 10 hr. The sample was reground and reheated at 1100°C for another 10 hr. A mixture of  $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ ,  $\text{Nb}_2\text{O}_5$ , and Nb, of the nominal composition  $\text{SrNb}_{12}\text{O}_{14.5}$ , was ground, pressed into a pellet, and put in a Nb ampoule which was then sealed in an argon atmosphere. It was heated at 1670°C for 4 hr in a furnace with graphite windings and then cooled (4°C/min) to 1000°C, whereupon the furnace was turned off. After heating, the pellets (both with and without added  $\text{SrCl}_2$ ) had a gray metallic luster, and small black crystals appeared on the surface and in the bulk. X-ray powder diffraction patterns were recorded in Guinier–Hägg cameras ( $\text{CuK}\alpha_1$ , Si as internal standard) and evaluated with a film scanner. The X-ray powder patterns showed that the samples contained mainly the new phase  $\text{SrNb}_4\text{O}_6$  and NbO (and  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  when  $\text{SrCl}_2$  was present in the starting composition). The X-ray pattern of  $\text{SrNb}_4\text{O}_6$  (see Table 1) could be indexed with a tetragonal unit cell having  $a = 4.1655(3)$  and  $c = 16.223(1)$  Å. Samples with the nominal starting composition  $\text{SrNb}_4\text{O}_6$  resulted in multiphase samples containing  $\text{SrNb}_4\text{O}_6$ ,  $\text{Sr}_2\text{Nb}_5\text{O}_9$  and traces of NbO.

### Electron Microscopy

For the electron microscopy studies, a part of the sample with the nominal starting composition  $\text{SrNb}_{12}\text{O}_{14.5}$  was crushed in an agate mortar and dispersed in *n*-butanol. A drop of the suspension was put on a holey carbon film

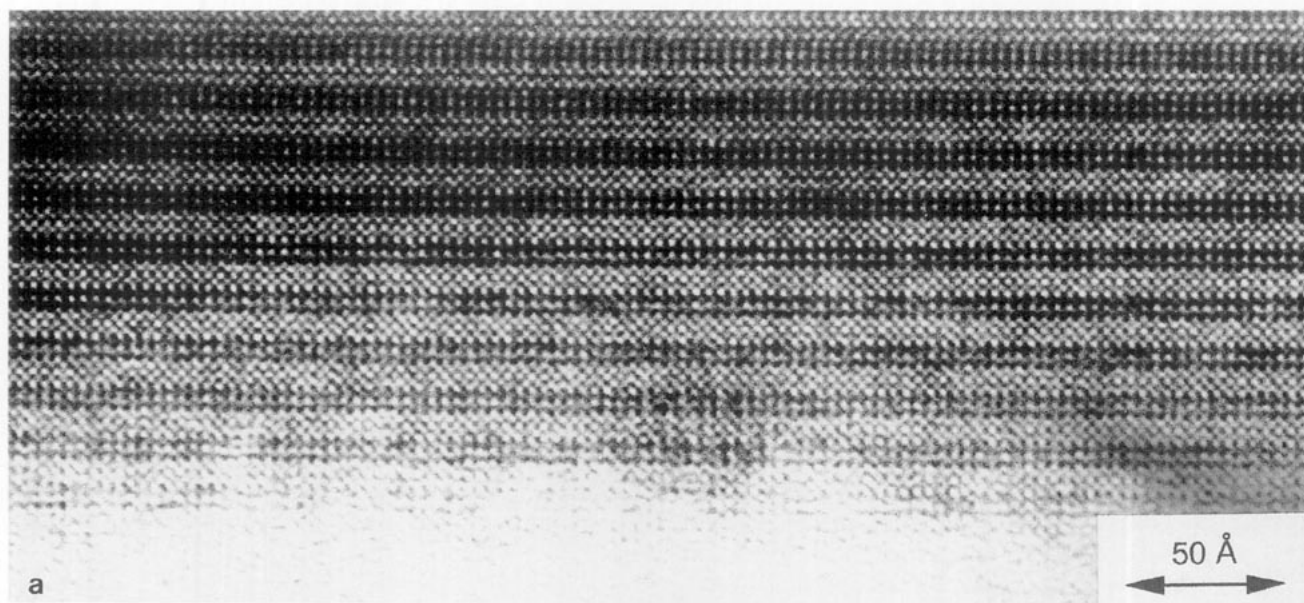


FIG. 1. (a) HREM image of  $\text{SrNb}_4\text{O}_6$  viewed along the  $a$ -axis. The large dark crosses correspond to  $\text{Nb}_6$  octahedra in the  $\text{NbO}$  slabs, and the square lattice of smaller spots in between depict the Sr and Nb in the perovskite-type slabs. (b) Structure model of  $\text{SrNb}_4\text{O}_6$  derived from the HREM image (Sr, large shaded circles; O, empty circles; Nb, small filled circles).

supported by a copper grid. Electron diffraction studies (EDS) and microanalysis were made in an JEOL JEM-2000FX with a LINK QX200 system. For the analysis of the Sr:Nb ratio, the thin film approximation, ( $c_{\text{Sr}}/c_{\text{Nb}} = k_{\text{SrNb}} (I_{\text{Sr}}/I_{\text{Nb}})$ ), was used (e.g., 18) ( $k_{\text{SrNb}}$  was determined with  $\text{Sr}_5\text{Nb}_4\text{O}_{15}$  as standard). The X-ray microanalysis of 50 crystallites showed the presence of two types of phases: one with a Sr:Nb ratio of 0.25(1) and one giving only an Nb signal. Electron diffraction patterns of  $\text{SrNb}_4\text{O}_6$  taken along several zone axes confirmed the unit cell obtained from the X-ray powder patterns, and no indications of superstructure reflections were found. HREM studies were made in a JEOL JEM-200CX microscope having a top-entry double-tilt ( $\pm 10^\circ$ ) goniometer. An HREM image of  $\text{SrNb}_4\text{O}_6$  is shown in Fig. 1 with an interpretation. The interpretation of this type of HREM image is rather straightforward (14). The image consists of double rows of large dark spots, or rather crosses, 4.1 Å apart, corresponding to  $\text{Nb}_6$  octahedra in double  $\text{NbO}$  slabs. The dark double rows are separated by a 2.8 Å square lattice of smaller spots, corresponding to Sr and Nb atoms in perovskite-type slabs. The structure model gives the composition  $\text{SrNb}_4\text{O}_6$ , in agreement with the Sr:Nb ratio obtained from X-ray microanalysis, given above. The HREM study indicated the number of defects in the crystallites to be low; occasionally, though, the double  $\text{NbO}$  slabs were replaced by single or triple slabs. No variation in the perovskite slab width was found in the crystals studied. This differs from what has been reported for  $\text{Sr}_2\text{Nb}_5\text{O}_9$  (15). The reason is probably the

higher synthesis temperature used here. Higher synthesis temperatures resulting in crystallites containing less defects has also been observed in the  $\text{BaO-NbO-NbO}_2$  system.

#### X-Ray Structure Refinement

X-ray diffraction data from a small single crystal of  $\text{SrNb}_4\text{O}_6$  were collected on a Stoe-AED2 diffractometer. Experimental conditions and details of the structural refinement are listed in Table 2. The unit cell parameters were determined from  $2\theta$  positions for 34 reflections in the range  $15^\circ < 2\theta < 25^\circ$ , yielding  $a = 4.1705(7)$  and  $c = 16.234(9)$  Å, in agreement with those from powder data. The program SHELXL-92 (19) was used for the least-square refinements, with X-ray scattering factors and anomalous dispersion terms for Sr, Nb, and O given therein. The crystal dimensions and the morphology were determined with a JEOL JSM-820 scanning electron microscope (SEM). The crystal was found to have an irregular shape with some satellite crystallites. Correction for absorption was carried out by Gaussian integration.

No systematic absences were found among the X-ray reflections or in the ED pattern. After considering the structure model obtained from the HREM images, the space group  $P4/mmm$  was chosen in the refinements. Starting coordinates for the refinement were taken from the structure model shown in Fig. 1b. The strong reflections 0 0 8 and 0 2 0 were obviously affected by severe secondary extinction and were therefore omitted from the

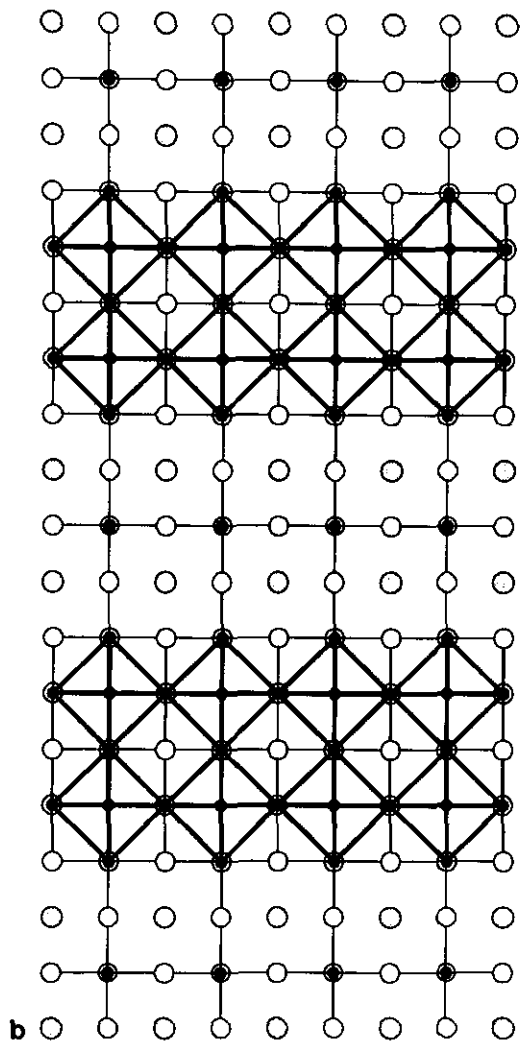


FIG. 1.—Continued

refinement. Atomic coordinates and isotropic displacement parameters are given in Table 3. Refinement of the anisotropic displacement parameters did not result in any improvement. The values of the isotropic displacement parameters for some of the oxygen and niobium atoms are clearly nonphysical. One possible reason for this could be residual absorption effects due to the satellite crystallites which were observed using the SEM. They may also explain the somewhat high inner  $R$  value,  $R_{\text{int}} = 4\%$ . However, the low  $R_f = 3.0$  corroborates the correctness of the structure.

### STRUCTURE

The structure of SrNb<sub>4</sub>O<sub>6</sub> is shown in Fig. 2, and selected bond lengths are given in Table 4. The structure can be described as an intergrowth of SrNbO<sub>3</sub> (perovskite type) and NbO slabs, each two units wide, having bound-

TABLE 1  
Indexed X-Ray Powder Diffraction Pattern of SrNb<sub>4</sub>O<sub>6</sub>

| $h k l$      | $\sin^2\theta_{\text{obs}}$ | $\sin^2\theta_{\text{calc}}$ | $d_{\text{obs}}$ (Å) | $I/I_0$ |
|--------------|-----------------------------|------------------------------|----------------------|---------|
| 0 0 1        | 0.00224                     | 0.00225                      | 16.30                | 14      |
| 0 0 3        | 0.02031                     | 0.02029                      | 5.40                 | 4       |
| 1 0 0        | 0.03422                     | 0.03420                      | 4.164                | 9       |
| 1 0 1        | 0.03644                     | 0.03645                      | 4.035                | 2       |
| 1 0 3        | 0.05448                     | 0.05449                      | 3.3001               | <1      |
| 0 0 5        | 0.05661                     | 0.05636                      | 3.2377               | <1      |
| 1 1 0        | 0.06844                     | 0.06839                      | 2.9443               | 1       |
| 1 0 4        | 0.07028                     | 0.07027                      | 2.9057               | 100     |
| 1 1 1        | 0.07052                     | 0.07065                      | 2.9006               | 40      |
| 1 1 3        | 0.08868                     | 0.08868                      | 2.5867               | 24      |
| 1 0 5        | 0.09055                     | 0.09056                      | 2.5598               | <1      |
| 1 1 4        | 0.10446                     | 0.10447                      | 2.3833               | 14      |
| 0 0 7        | 0.11049                     | 0.11047                      | 2.3174               | 1       |
| 1 1 5        | 0.12477                     | 0.12476                      | 2.1808               | 10      |
| 2 0 0        | 0.13675                     | 0.13679                      | 2.0830               | 61      |
| 2 0 1        | 0.13903                     | 0.13904                      | 2.0659               | 1       |
| 0 0 8/1 0 7  | 0.14427                     | 0.14429                      | 2.0280               | 15      |
| 2 0 3        | 0.15709                     | 0.15708                      | 1.9436               | 2       |
| 2 1 0        | 0.17101                     | 0.17098                      | 1.8627               | 4       |
| 2 0 4/2 1 1  | 0.17293                     | 0.17286                      | 1.8524               | 1       |
| 1 1 7/1 0 8  | 0.17883                     | 0.17887                      | 1.8215               | 17      |
| 2 1 2        | 0.17970                     | 0.18004                      | 1.8171               | <1      |
| 2 1 4        | 0.20705                     | 0.20706                      | 1.6928               | 31      |
| 1 0 9        | 0.21662                     | 0.21682                      | 1.6550               | 5       |
| 2 0 7        | 0.24732                     | 0.24726                      | 1.5489               | 2       |
| 1 1 9        | 0.25089                     | 0.25101                      | 1.5379               | 3       |
| 2 2 0        | 0.27361                     | 0.27358                      | 1.4726               | 22      |
| 2 2 1        | 0.27599                     | 0.27583                      | 1.4663               | 1       |
| 2 0 8        | 0.28102                     | 0.28108                      | 1.4531               | 35      |
| 2 2 3        | 0.29387                     | 0.29387                      | 1.4230               | 2       |
| 2 1 8        | 0.31528                     | 0.31528                      | 1.3719               | 2       |
| 0 0 12       | 0.32494                     | 0.32466                      | 1.3513               | 13      |
| 2 2 5        | 0.33005                     | 0.32994                      | 1.3408               | <1      |
| 1 1 11       | 0.34109                     | 0.34120                      | 1.3189               | 4       |
| 3 1 1/3 0 4  | 0.34405                     | 0.34422                      | 1.3133               | 19      |
| 1 0 12       | 0.35878                     | 0.35885                      | 1.2860               | 5       |
| 2 0 10/3 1 3 | 0.36224                     | 0.36224                      | 1.2798               | 9       |
| 3 1 4        | 0.37803                     | 0.37804                      | 1.2528               | 11      |

Note. The unit cell parameters are  $a = 4.1655(3)$  and  $c = 16.223(1)$  Å; figure of merit,  $M(20) = 81$ .

ary atoms in common. The NbO slab can also be seen as a double layer of corner-sharing Nb<sub>6</sub> octahedra, of composition Nb<sub>7</sub>O<sub>8</sub>.

In the perovskite-type slab the Sr atom is 12-coordinated by oxygen atoms forming a cubo-octahedron. The Nb(4) is coordinated by six oxygen atoms forming an octahedron. These octahedra share corners in the  $a$ - $b$  plane and share apexes with the top of a square pyramid of oxygen atoms around the Nb(3) atom. The base of this square pyramid forms the boundary between the SrNbO<sub>3</sub> and the NbO slabs. On the NbO side of this boundary, Nb(3) is bonded to four Nb(2) atoms. Nb(1) and Nb(2) have a planar four-coordination of oxygen atoms and eight

TABLE 2  
Crystal Data of SrNb<sub>4</sub>O<sub>6</sub> and Experimental Conditions for the  
Crystal Structure Determination

|  |   |
|--|---|
| Chemical formula   | SrNb <sub>4</sub> O <sub>6</sub>  |
| Formula weight   | 1110.5 amu  |
| Crystal system   | Tetragonal  |
| Space group, Z   | <i>P4/mmm</i> , 2   |
| Lattice parameters <sup>a</sup>                              | <i>a</i> = 4.1655(3) Å, <i>b</i> = 16.223(1) Å  |
| <i>V</i> (Å <sup>3</sup> )                                   | 281.49(3)   |
| <i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )                | 6.546(1)  |
| Crystal shape  | Irregular polyhedron  |
| Crystal size (μm <sup>3</sup> ) from center                  | {001}, 8; {100}, 20.8; {140}, 10.5;<br>(010), 24.0; (310), 24.0; (310),<br>16.80; (110), 20.8   |
| Intensity data collection                                    |   |
| Temperature  | 25°C  |
| Diffractometer   | STOE/AED2   |
| λ(MoKα) (Å)  | 0.71069   |
| Maximum sin (θ)/λ (Å <sup>-1</sup> )                         | 0.59065   |
| Range of <i>h</i> , <i>k</i> , <i>l</i> method               | -4 ≤ <i>h</i> ≤ 4, -4 ≤ <i>k</i> ≤ 4,<br>0 ≤ <i>l</i> ≤ 19, ω - 2θ  |
| Standard reflections   | 3   |
| Intensity stability  | Less than ±2%   |
| Internal <i>R</i> value                                      | 0.039   |
| No. of measured reflections                                  | 959   |
| No. of unique reflections                                    | 196 (103 with <i>F</i> <sup>2</sup> > 3σ( <i>F</i> <sup>2</sup> ))  |
| Criterion for significance                                   | <i>F</i> <sup>2</sup> > 3σ( <i>F</i> <sup>2</sup> )   |
| Absorption correction  | Gaussian integration  |
| Linear absorption coefficient                                | 166.5 cm <sup>-1</sup>  |
| Transmission factor range                                    | 0.5686-0.7718   |
| Structure refinement   |   |
| Minimization of  | Σ <i>w</i> (Δ <i>F</i> <sup>2</sup> )   |
| Number of refined parameters                                 | 17  |
| Weighting scheme   | <i>w</i> = 1/(σ <sup>2</sup> ( <i>F</i> <sub>0</sub> <sup>2</sup> ) + (0.0291 * <i>P</i> ) <sup>2</sup> +<br>0.17 * <i>P</i> ), where <i>P</i> = (max( <i>F</i> <sub>0</sub> , 0)<br>+ 2 * <i>F</i> <sub>0</sub> <sup>2</sup> )/3 |
| Final <i>R</i> <sub>f</sub>                                  | 0.030   |
| <i>wR</i> <sup>2</sup>                                       | 0.060   |
| Goodness of fit  | 1.27  |
| (Δ/σ) <sub>max</sub>   | 0.000   |
| Δρ <sub>min</sub> and Δρ <sub>max</sub> (e Å <sup>-3</sup> ) | -1.33 and 2.09  |

<sup>a</sup> Guinier-Hägg technique.

neighboring niobium atoms, each forming a centered tetragonal prism as in NbO.

The cubo-octahedron of oxygen atoms around Sr is distorted as in Sr<sub>2</sub>Nb<sub>5</sub>O<sub>9</sub> (16). The Sr-O bond lengths are close to those in Sr<sub>2</sub>Nb<sub>5</sub>O<sub>9</sub> (2.770, 2.903, and 2.930 Å), and the average (*d*<sub>Sr-O</sub> = 2.866 Å) bond length is close to the value 2.833 found in the Sr<sub>0.87</sub>NbO<sub>3</sub> perovskite (20).

As in all intergrowth compounds between ANbO<sub>3</sub> and NbO, the NbO<sub>6</sub> octahedron in the perovskite-type slab is dilated parallel to the plane of the NbO slab, here the *a*-*b* plane, due to the more rigid Nb<sub>6</sub> octahedra in the NbO

TABLE 3  
Fractional Atomic Coordinates and Thermal Parameters  
of SrNb<sub>4</sub>O<sub>6</sub>

| Atom  | Position   | <i>x</i> | <i>y</i> | <i>z</i>   | <i>B</i> <sub>iso</sub> |
|-------|------------|----------|----------|------------|-------------------------|
| Sr    | 2 <i>g</i> | 0        | 0        | 0.1242(6)  | 1.1(1)                  |
| Nb(1) | 1 <i>d</i> | 1/2      | 1/2      | 1/2        | 0.2(1)                  |
| Nb(2) | 4 <i>j</i> | 0        | 1/2      | 0.3682(1)  | 0.3(1)                  |
| Nb(3) | 2 <i>h</i> | 1/2      | 1/2      | 0.2482(2)  | 0.1(1)                  |
| Nb(4) | 1 <i>c</i> | 1/2      | 1/2      | 0          | 0.6(1)                  |
| O(1)  | 2 <i>e</i> | 0        | 1/2      | 1/2        | 1.6(8)                  |
| O(2)  | 2 <i>g</i> | 0        | 0        | 0.3691(20) | 0.3(6)                  |
| O(3)  | 4 <i>i</i> | 1/2      | 0        | 0.2382(9)  | 1.2(5)                  |
| O(4)  | 2 <i>h</i> | 1/2      | 1/2      | 0.1206(34) | 0.6(7)                  |
| O(5)  | 2 <i>f</i> | 0        | 1/2      | 0          | 2.8(8)                  |

Note. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, W-7514 Eggenstein-Leopoldshafen, FRG, upon giving the depository number CSD-57787, the name of the authors, and the journal citation.

slab. To compensate for this, the remaining Nb-O bond lengths are shortened, here Nb(4)-O(4). Nevertheless, the average Nb(4)-O distance is longer than expected for pentavalent niobium.

The Nb-Nb bond lengths increase ((*d*<sub>Nb(3)-Nb(2)</sub> = 2.853 Å < *d*<sub>Nb(2)-Nb(2)</sub> = 2.945 Å < *d*<sub>Nb(2)-Nb(1)</sub> = 2.984 Å) when going toward the center of the NbO slab. This effect mirrors an increasing similarity in the bonding situation to NbO, *d*<sub>Nb-Nb</sub> = 2.977 Å. A similar trend has often been observed for compounds with condensed Nb<sub>6</sub>O<sub>12</sub> clusters,

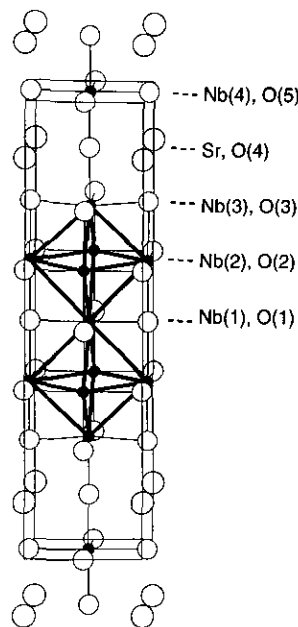


FIG. 2. Structure model of SrNb<sub>4</sub>O<sub>6</sub>.

TABLE 4  
Selected Interatomic Distances (Å)  
with esd's in Parentheses in SrNb<sub>4</sub>O<sub>6</sub>

|                |      |           |
|----------------|------|-----------|
| Sr-4*          | O(3) | 2.786(12) |
| Sr-4*          | O(5) | 2.897(6)  |
| Sr-4*          | O(4) | 2.946(1)  |
| Nb(1)-4* O(1)  |      | 2.083(1)  |
| Nb(1)-8* Nb(2) |      | 2.984(2)  |
| Nb(2)-2* O(2)  |      | 2.083(1)  |
| Nb(2)-O(3)     |      | 2.110(15) |
| Nb(2)-O(1)     |      | 2.137(2)  |
| Nb(2)-2* Nb(3) |      | 2.853(3)  |
| Nb(2)-4* Nb(2) |      | 2.945(1)  |
| Nb(2)-2* Nb(1) |      | 2.984(2)  |
| Nb(3)-O(4)     |      | 2.068(56) |
| Nb(3)-4* O(3)  |      | 2.089(1)  |
| Nb(3)-4* Nb(2) |      | 2.853(3)  |
| Nb(4)-2* O(4)  |      | 1.957(55) |
| Nb(4)-4* O(5)  |      | 2.083(1)  |

e.g., BaNb<sub>7</sub>O<sub>9</sub> (12), Ba<sub>3</sub>Nb<sub>16</sub>O<sub>23</sub> (8), and Sr<sub>2</sub>Nb<sub>5</sub>O<sub>9</sub> (16). The only exception known so far is KNb<sub>4</sub>O<sub>6</sub> (21). This is also reflected in the corresponding volume of the central NbO unit in SrNb<sub>4</sub>O<sub>6</sub> (74.2 Å<sup>3</sup>), defined by the eight Nb(2) atoms around the Nb(1) atom. It is very close to the volume of NbO (74.6 Å<sup>3</sup>) (2) and similar units in other compounds with Nb<sub>6</sub> octahedra sharing at least five corners, e.g., BaNb<sub>7</sub>O<sub>9</sub> (75.7 Å<sup>3</sup>) (12), Ba<sub>3</sub>Nb<sub>16</sub>O<sub>23</sub> (75.6 Å<sup>3</sup>) (8), and Ba<sub>4</sub>Nb<sub>17</sub>O<sub>26</sub> (74.2 Å<sup>3</sup>) (5).

## DISCUSSION

As mentioned above, a number of reduced oxoniobates exist with structures that can be described as intergrowths between perovskite- and NbO-type units. To understand mixed-valence compounds as these—for example, why BaNb<sub>4</sub>O<sub>6</sub> contains a single slab (Fig. 3) whereas SrNb<sub>4</sub>O<sub>6</sub> has double slabs—it is necessary to discuss the electron balance in them. The electron balance is intimately connected with the number of electrons involved in metal-metal bonding. From an ionic model assuming Sr<sup>2+</sup>, O<sup>2-</sup>, and a Nb(4)<sup>4+</sup> in SrNb<sub>4</sub>O<sub>6</sub>, 19 valence electrons are available for Nb-Nb bonding in the NbO block. This is the same number as in BaNb<sub>7</sub>O<sub>9</sub>. However, in SrNb<sub>4</sub>O<sub>6</sub> as well as in several other reduced oxoniobates with Nb<sub>6</sub>O<sub>12</sub> clusters there is a full NbO<sub>6</sub> octahedron, where the valence of the Nb atom is not obvious. In a fully occupied SrNbO<sub>3</sub> it would be +4, while in KNbO<sub>3</sub> it is +5. Consequently, there is the possibility of a charge transfer,  $\delta$  ( $0 \leq \delta \leq 1 e^-$ ), from Nb in the NbO<sub>6</sub> octahedron to the NbO slab in SrNb<sub>4</sub>O<sub>6</sub>, giving  $19 + \delta$  electrons available for metal-metal bonding.

The bonding in discrete Me<sub>6</sub>X<sub>12</sub> clusters has been exam-

ined in some detail. It has been shown that the closed valence-bond description corresponds to eight three-center two-electron ( $3c/2e$ ) bonds at the faces of the Me<sub>6</sub> octahedron, giving a maximum of  $16 e^-$  participating in Nb-Nb bonding (22, 23). For oxoniobates a value of  $14 e^-$  seems to be optimum, due to a strong Nb-O antibonding contribution to the highest Nb-Nb bonding levels (1). A comparison of the maximum number of electrons available for  $3c/2e$  bonds with the average Nb-Nb bond length for condensed Nb<sub>6</sub>O<sub>12</sub> cluster gives a good correlation: from NbO (2.98 Å,  $1.12 e^-$ ) via KNb<sub>4</sub>O<sub>6</sub> (2.96 Å,  $1.12 e^-$ ), BaNb<sub>7</sub>O<sub>9</sub> (2.95 Å,  $1.18 e^-$ ), BaNb<sub>4</sub>O<sub>6</sub> (2.93 Å,  $1.25 e^-$ ), Ba<sub>3</sub>Nb<sub>16</sub>O<sub>23</sub> (2.93 Å,  $1.25 e^-$ ), BaNb<sub>5</sub>O<sub>8</sub> (2.87 Å,  $1.38 e^-$ ) to the discrete Nb<sub>6</sub>O<sub>12</sub> clusters in SrNb<sub>8</sub>O<sub>14</sub> (2.82 Å,  $1.75 e^-$ ) (24).

The shorter average Nb-Nb bond length in SrNb<sub>4</sub>O<sub>6</sub> (2.93 Å,  $1.18 + \delta/16$ , 16 being the number of Nb-Nb  $3c/2e$  bonds) than in BaNb<sub>7</sub>O<sub>9</sub>, would then indicate charge transfer,  $\delta$ , giving more electrons involved in Nb-Nb bonding in the former compound. Similar effects have been observed for the pairs Ba<sub>2</sub>Nb<sub>5</sub>O<sub>9</sub> (2.91 Å,  $1.25 + \delta/8$ )-BaNb<sub>4</sub>O<sub>6</sub> (2.93 Å,  $1.25 e^-$ ) and Ba<sub>3</sub>Nb<sub>16</sub>O<sub>23</sub> (2.93 Å,  $1.25 e^-$ )-Ba<sub>4</sub>Nb<sub>17</sub>O<sub>26</sub> (2.92 Å,  $1.25 + \delta/32$ ). Ba<sub>2</sub>Nb<sub>5</sub>O<sub>9</sub> and Ba<sub>4</sub>Nb<sub>17</sub>O<sub>26</sub> have NbO<sub>6</sub> octahedra in the perovskite-type slabs, while BaNb<sub>4</sub>O<sub>6</sub> and Ba<sub>3</sub>Nb<sub>16</sub>O<sub>23</sub> do not. The significantly longer average Nb-Nb bond in KNb<sub>4</sub>O<sub>6</sub> than in BaNb<sub>4</sub>O<sub>6</sub>, despite the small difference in ionic radius for K<sup>+</sup> = 1.64 Å (25) and Ba<sup>2+</sup> = 1.61 Å (25), indicates that the difference between the average Nb-Nb distances in

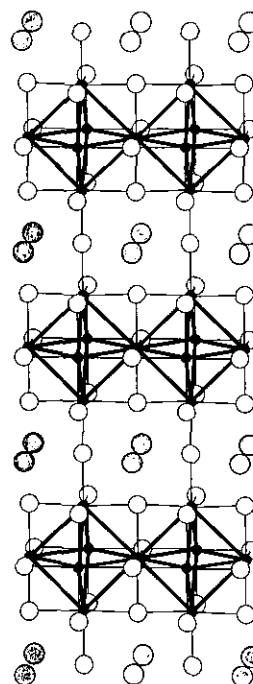


FIG. 3. Structure model of BaNb<sub>4</sub>O<sub>6</sub>.

between  $\text{SrNb}_4\text{O}_6$  and  $\text{BaNb}_7\text{O}_9$  is not only an effect of the size difference between  $\text{Sr}^{2+}$  (1.18 Å (25)) and  $\text{Ba}^{2+}$ .

Motifs of the mutual adjunction (26) and bond order sums (27) are listed in Table 5. An approximate assignment of oxidation state can often be made from bond order sums, but the values can deviate from those expected for an ionic model, as is the case for reduced oxoniobates (1). The deviations for  $\text{SrNb}_4\text{O}_6$  are very similar to those found for other intergrowth compounds containing  $\text{Nb}_6\text{O}_{12}$  clusters, e.g.,  $\text{Sr}_2\text{Nb}_5\text{O}_9$  and  $\text{BaNb}_7\text{O}_9$ . The only exception is Nb(4), with  $\sum s_i = 4.28$ . As discussed above, the valence of this niobium atom is related to the amount of charge transfer ( $\delta$ ) to the NbO slab. The bond order sum for Nb(4) is significantly lower than that found in  $\text{Sr}_{0.95}\text{NbO}_3$  ( $\sum s_i = 4.57$ ),  $\text{Sr}_2\text{Nb}_5\text{O}_9$  ( $\sum s_i = 4.57$ ), and  $\text{SrNb}_8\text{O}_{14}$  ( $\sum s_i = 4.55$ ). This indicates a valence closer to +4 in  $\text{SrNb}_4\text{O}_6$  than in  $\text{Sr}_2\text{Nb}_5\text{O}_9$  and  $\text{SrNb}_8\text{O}_{14}$ , suggesting less charge transfer to the NbO slab than in those compounds.

The structure of the isoelectronic  $\text{BaNb}_4\text{O}_6$  contains single perovskite and NbO slabs. It is obvious that the origin of the structural difference between  $\text{BaNb}_4\text{O}_6$  and  $\text{SrNb}_4\text{O}_6$  is the size difference between  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . In  $\text{Sr}_2\text{Nb}_5\text{O}_9$  and  $\text{SrNb}_4\text{O}_6$  there is a larger mismatch to be compensated for between the perovskite unit and the NbO unit than in the Ba analogues. For  $\text{Sr}_2\text{Nb}_5\text{O}_9$  it has been argued that the large charge transfer (compared to  $\text{Ba}_2\text{Nb}_5\text{O}_9$ ), giving shorter Nb–Nb bonds, stabilized the structure (16). It is interesting that the existence of a Sr

TABLE 5  
Motifs of Mutual Adjunction (26) and Bond Order Sums  $\sum s_i$  (27) in  $\text{SrNb}_4\text{O}_6$

|                   | $2^*\text{O}(1)^{i-i}$ | $2^*\text{O}(2)^{i-i}$ | $4^*\text{O}(3)^{i-i}$ | $2^*\text{O}(4)^a$ | $2^*\text{O}(5)$ | CN | $\sum s_i$ |
|-------------------|------------------------|------------------------|------------------------|--------------------|------------------|----|------------|
| $2^*\text{Sr}$    | —                      | —                      | 4/2                    | 4/4                | 4/4              | 12 | 1.57       |
| Nb(1)             | 4/2                    | —                      | —                      | —                  | —                | 4  | 2.52       |
| $4^*\text{Nb}(2)$ | 1/2                    | 2/4                    | 1/1                    | —                  | —                | 4  | 2.38       |
| $2^*\text{Nb}(3)$ | —                      | —                      | 4/2                    | 1/1                | —                | 5  | 3.13       |
| Nb(4)             | —                      | —                      | —                      | 2/1                | 4/2              | 6  | 4.28       |
| CN                | 4                      | 4                      | 5                      | 6                  | 6                |    |            |
| $\sum s_i$        | 2.34                   | 2.50                   | 2.15                   | 1.96               | 1.74             |    |            |

Note. CN is the coordination number.

compound isotypic with  $\text{BaNb}_4\text{O}_6$  was excluded in that paper due to the absence of stabilizing charge transfer in such a structure.  $\text{SrNb}_4\text{O}_6$  fits well into this picture, since the charge transfer, although smaller than that in  $\text{Sr}_2\text{Nb}_5\text{O}_9$ , between the perovskite slab and the NbO slab decreases the mismatch between them.

Band structure calculations by the extended Hückel method (28) have been used successfully for the interpretation of bonding in metal oxides (29). In  $\text{Ba}_2\text{Nb}_5\text{O}_9$ ,  $\text{Sr}_2\text{Nb}_5\text{O}_9$ , and  $\text{Ba}_4\text{Nb}_{14}\text{O}_{23}$  such calculations indicate full charge transfer,  $\delta$ , from Nb in the  $\text{NbO}_6$  octahedra to the NbO units. The  $t_{2g}$  band of the Nb in the perovskite slab is above the Fermi level, thus giving an  $\text{Nb}^{5+}$  ion. For  $\text{SrNb}_4\text{O}_6$ , a tail of the  $t_{2g}$  band is below the Fermi level, indicating a valence lower than +5, as shown in Fig. 4.

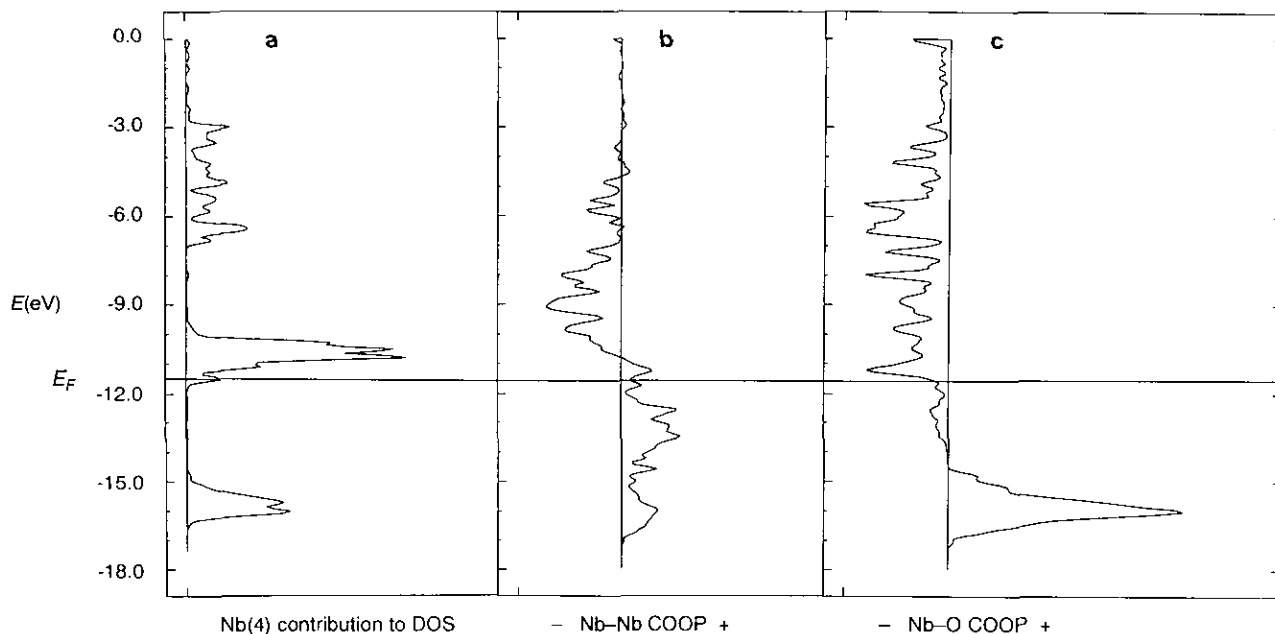


FIG. 4. (a) Projection of the atomic orbitals of Nb(4) in the perovskite slab. The  $t_{2g}$  orbitals extend slightly below the Fermi level, indicating a valence somewhat lower than +5 for Nb(4). COOP curves for Nb–Nb (b) and Nb–O (c) interactions in the NbO slabs, showing a close to optimal filling of the bands.

The COOP (crystal orbital overlap population) (30) for Nb–Nb and Nb–O overlap in the NbO slabs shows a close to optimal filling of the bands, very similar that found for BaNb<sub>7</sub>O<sub>9</sub> (12). The Nb–Nb bonding states are not completely filled. A further filling would also populate the Nb–O antibonding states, which would lead to a net destabilization of the structure.

### CONCLUSIONS

A new compound, SrNb<sub>4</sub>O<sub>6</sub>, has been synthesized, and its structure was determined from HREM images. The structure model was refined using single-crystal X-ray data. The structure consists of alternating slabs of perovskite (SrNbO<sub>3</sub>) and NbO structure, both two units wide. The compound belongs to the homologous series A<sub>n</sub>Nb<sub>n+3m</sub>O<sub>3n+3m</sub> (*n* = the width of the perovskite slabs and *m* = the width of the NbO slabs, A = K, Sr, Ba), with *m* = *n* = 2. This is in contrast to the Ba analogue, BaNb<sub>4</sub>O<sub>6</sub> (*m* = *n* = 1), which contains alternating single unit slabs. The reason for the difference is the size difference between Sr<sup>2+</sup> and Ba<sup>2+</sup>. The interatomic distances found in SrNb<sub>4</sub>O<sub>6</sub> fit well with those found in other intergrowth compounds between perovskite and NbO.

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