Table 3. *Coordination number* CN, *values of the local error parameter* E_p, *the local average dihedral angles* $\theta_{m,p}$ *and the minimum and maximum dihedral angle of the tetrahedra in the five distinct coordination polyhedra*

	CN	E_p	$\theta_{m,p}$ (°)	$\theta_{\min}$ (°)	$\theta_{\max}$ (°)
Co1	12	0.0623	70.571	59.288	79.972
*M*1	12	0.0596	70.567	60.319	77.132
Nb1	15	0.0649	70.515	54.748	79.972
Nb2	16	0.0634	70.536	59.288	77.132
Nb3	14	0.0663	70.486	54.748	79.972

Table 4. *Values for the error parameter E and the average dihedral angle* θ_m *of selected Frank–Kasper phases*

Phase	Type	$E \times 10^{-2}$	θ_m (°)
Cr_3Si^a	A15	0.0631	70.435
$Al_3Zr_4{}^b$	Z	0.0612	70.500
$Fe_7W_6{}^c$	μ	0.0658	70.540
$Co_{6.30}Nb_{6.70}$	μ	0.0633	70.540
Cu_2Mg^d	C15	0.0621	70.588

Calculations are based on crystal data as reported by (*a*) Boren (1933); (*b*) Wilson, Thomas & Spooner (1960); (*c*) Arnfelt & Westgren (1935), and (*d*) Laves & Witte (1935).

The quality of the crystal was checked by precession photographs (Mo $K\alpha$). The structure of the observe–reverse twinned crystal was refined with the program *SHELXL*93 (Sheldrick, 1993). The geometrical analyses of the tetrahedral close (german: *dicht*) packed structures were performed with the program *TDP* (Wagner, 1994). The error parameters *E* were calculated using the algorithm of Brandon, Chieh, Pearson & Riley (1975).

Data collection: CAD-4 software. Cell refinement: CAD-4 software. Data reduction: *SDP* (Frenz, 1978). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL* (Keller, 1992).

Financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is acknowledged.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Semiconducting Perovskite-Related Phase: $Sr_5Nb_5O_{17}$

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(*Received* 30 *August* 1994; *accepted* 19 *January* 1995)

Abstract

The structure of strontium niobium oxide, $Sr_5Nb_5O_{17}$, prepared by the floating-zone melting technique, has been determined by single-crystal X-ray analysis. The structure contains distorted perovskite-type slabs parallel to (100) formed from five NbO_6 octahedra and Sr atoms. The Nb—O distances range from 1.89 (2) to 2.10 (2) Å for Nb1, from 1.809 (5) to 2.282 (6) Å for Nb2, and from 1.851 (6) to 2.167 (6) Å for Nb3. The NbO_6 conformations are (4+1+1) distorted. Sr2 and Sr3 are coordinated by 12 O atoms with Sr—O distances in the range 2.64 (1) to 3.04 (1) Å for Sr2 and 2.50 (1) to 3.06 (1) Å for Sr3. Sr1, placed near the boundary of the slab, is irregularly coordinated by five O atoms in the same slab and two O atoms in the neighbouring slab [Sr—O 2.46 (1) to 2.915 (6) Å] and by a further three O atoms at long coordination distances [3.345 (8) to 3.544 (9) Å]. The title compound is isotypic with $La_5Ti_5O_{17}$ and both structures belong to the homologous

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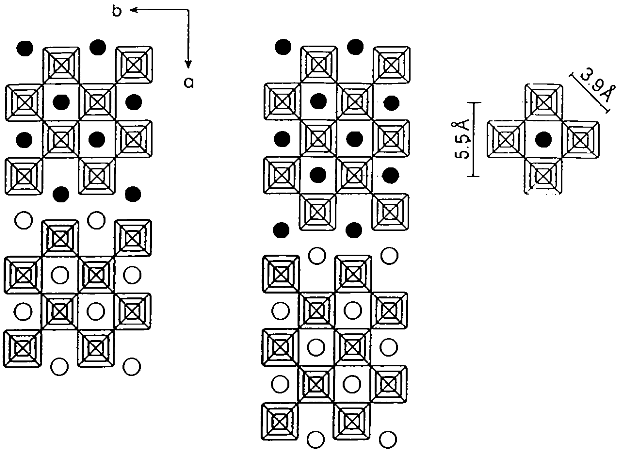
Acta Crystallographica Section C
ISSN 0108-2701 ©1995

series $A_{n+1}B_{n+1}O_{3n+5}$ with $n = 4$, being diamagnetic (B = Nb) or paramagnetic (B = Ti) electrically conducting compounds.

Comment

The systems $SrNbO_x$, $CaNbO_x$ ($3.40 < x < 3.50$) and $LaTiO_x$ ($3.00 < x < 3.50$) have been studied recently because of their interesting physical and structural properties, which are tunable by changing only the oxygen content, x (Lichtenberg, Widmer, Bednorz, Williams & Reller, 1991*a*; Lichtenberg, Williams, Reller, Widmer & Bednorz, 1991*b*; Williams, Schmalle, Reller, Lichtenberg, Widmer & Bednorz, 1991; Schmalle, Williams, Reller, Linden & Bednorz, 1993; Williams, Lichtenberg, Widmer, Bednorz & Reller, 1993). These perovskite-related compounds are members of the homologous series $A_{n+1}B_{n+1}O_{3n+5}$ (A = Sr, Ca, La and B = Nb, Ti), where n is merely determined by the oxygen content x (Fig. 1). The structure type for $x = 3.40$ is known from the electrically non-conducting La–Ca–Ti–O and Na–Ca–Nb–O systems in which Ti and Nb are in their highest oxidation state (Ti^{4+}, $3d^0$ and Nb^{5+}, $4d^0$) (Portier, Fayard, Carpy & Galy, 1974; Nanot, Queyroux & Gilles, 1973).



$n = 3$	$n = 4$	$n = \infty$
$A_4B_4O_{14} = ABO_{3.5}$	$A_5B_5O_{17} = ABO_{3.4}$	$ABO_{3.0}$ Perovskite structure
$La_4Ti_4O_{14}$	$La_5Ti_5O_{17}$	$LaTiO_3$
$Sr_4Nb_4O_{14}$	$Sr_5Nb_5O_{17}$	
$Ca_4Nb_4O_{14}$	$Ca_5Nb_5O_{17}$	
Ti^{4+} ($3d^0$)	$Ti^{3.8+}$ ($3d^{0.2}$)	Ti^{3+} ($3d^1$)
Nb^{5+} ($4d^0$)	$Nb^{4.8+}$ ($4d^{0.2}$)	
Transparent	Black	
Highest-T_C ferroelectrics	Semiconducting	

Fig. 1. Projection along the c axis of the idealized structure of the n = 3, 4 and ∞ members of the homologous series $A_{n+1}B_{n+1}O_{3n+5}$. The cations La, Sr and Ca are represented by circles. Light and heavy ruling of the BO_6 octahedra and filled and open circles indicate a height difference along the projection direction.

This work describes the structure of $Sr_5Nb_5O_{17}$ (x = 3.40, n = 4), which is a diamagnetic electrically conducting compound ($Nb^{4.8+}$, $4d^{0.2}$). It was prepared by the floating-zone melting technique under an Ar atmosphere. The true stoichiometry was determined by thermogravimetric analysis to be $Sr_5Nb_5O_{17.1}$ ($x = 3.42$). It was found that for $3.40 < x < 3.42$ the structure type ($n = 4$) remains unchanged (Lichtenberg *et al.*, 1991*b*).

The conditions for systematic absences, taken from Weissenberg and precession photographs, led to the possible space groups *Pnnm* (No. 58) and *Pnn*2 (No. 34). Statistics based on E values showed hypercentricity of the data (*e.g.* E^6 = 37.228, compared to theoretical values for non-centrosymmetric, centrosymmetric and hypercentric data of 6.00, 15.00 and 37.50, respectively) and the E^2 values of the eight parity groups are far from unity (by definition $\langle E^2\rangle = 1.0$). Reflection groups with $h + k + l = 2n$ have higher values than those with $h + k + l = 2n + 1$, influenced by superposition effects of heavy atoms along the a direction. Average values are *eee* = 2.443, *eoo* = 2.909, *ooe* = 0.675, *oeo* = 0.497; *oee*, *eoe*, *eeo* and *ooo* (e = even, o = odd h, k, l) showed values between 0.303 and 0.364; $\langle E^2\rangle$ for all reflections was calculated to be 0.971.

The structure was solved in both space groups using Patterson interpretation routines of *SHELXS*86 (Sheldrick, 1985) and subsequent difference Fourier calculations and refinement were carried out using *SHELX*76 (Sheldrick, 1976). A comparison of final R (wR) values [0.0461 (0.0601) for *Pnnm* and 0.0387 (0.0449) for *Pnn*2] favoured the non-centrosymmetric space group *Pnn*2. The absolute-structure parameter χ (Flack, 1983; Bernardinelli & Flack, 1987) refined to −0.025 (32) using the γ-test version of *SHELXL*92 (Sheldrick, 1992), providing evidence that no inversion twinning was present in the crystal studied.

The atomic numbering scheme and perovskite-block separation are shown in Fig. 2. The NbO_6 octahedra have average apical distances of 1.851 and 2.184 Å. [The apical O atoms are defined by the shortest and longest Nb—O distances in *trans* positions: for Nb1

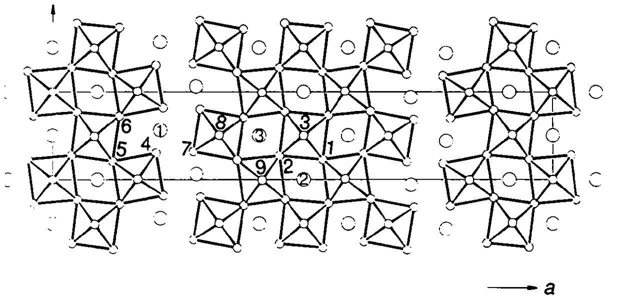


Fig. 2. A [001] projection of the crystal structure of $Sr_5Nb_5O_{17}$. Circled numbers 1, 2, and 3 refer to the refined Sr-atom positions, other numbers correspond to the refined O-atom positions shown in Table 1.

the apical O atoms are O3 and O3^{ii}, for Nb2 they are O4^{v} and O6^{iii}, and for Nb3 they are O1^{iv} and O6^{iii} (see also Table 2).] The mean value of the 12 equatorial Nb—O distances for the three independent octahedra is 2.005 Å. Like the NbO_6 octahedra in $Sr_2Nb_2O_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1975) and the TiO_6 octahedra in the structure of $La_2Ti_2O_7$ (Gasperin, 1975; Schmalle *et al.*, 1993), the NbO_6 conformations of the title compound are also (4+1+1) distorted. The NbO_6 octahedral blocks are shifted by a *c*/2 crystallographic shear, a term first used by Wadsley (1964) and reviewed by Anderson & Hyde (1989) (see the *ac* projection of the structure deposited with the supplementary material).

The Sr—O coordination distances vary considerably; the coordination spheres are shown in Fig. 3. The interplanar Sr1 cation is coordinated by seven O atoms at distances between 2.46 (1) and 2.915 (6) Å, but three further O atoms, O6, O6^{ii}, and O8^{iv}, at distances between 3.35 (1) and 3.54 (1) Å (Table 2), are also indicated in Fig. 3. The intraplanar Sr2 and Sr3 cations have cubo-octahedral coordination spheres in the form of cubes of eight O atoms capped by the four O atoms O3, O3^{ix}, O9 and O9^{v} for Sr2 and the four O atoms O3, O8, O9 and O9^{x} for Sr3, with Sr—O distances up to 3.04 (1) Å for Sr2 and 3.06 (1) Å for Sr3. The coordination number is obviously not given correctly by the sum of the covalent radii of Sr and O (2.81 Å). If this distance were taken as a borderline criterion, Sr1 and Sr2 would be only coordinated by six and Sr3 by seven O atoms, which is obviously not the case for this structure.

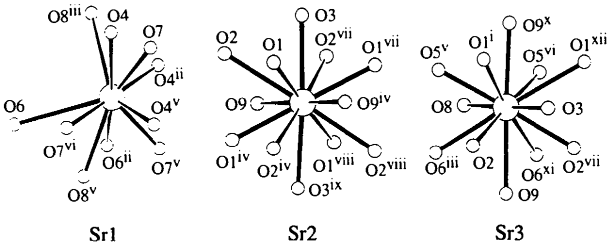


Fig. 3. Ball-and-stick perspective *SCHAKAL* (Keller, 1986) plot of the three Sr—O coordination spheres of $Sr_5Nb_5O_{17}$. The O-atom numbering corresponds to that in Table 2.

Experimental

$Sr_5Nb_5O_{17}$ was prepared by the floating-zone melting technique under an Ar atmosphere.

Crystal data

$Sr_5Nb_5O_{17}$
$M_r = 1174.62$
Orthorhombic
*Pnn*2
$a = 32.456 (5)$ Å
$b = 5.674 (2)$ Å
$c = 3.995 (2)$ Å
$V = 735.7 (6)$ Å^3
$Z = 2$
$D_x = 5.302$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.6–12.0°$
$\mu = 21.11$ mm^{-1}
$T = 296$ K
Ledge-shaped
0.387 × 0.135 × 0.035 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: analytical (based on six crystal faces)
$T_{min} = 0.0717$, $T_{max} = 0.4744$
2674 measured reflections
2118 independent reflections

1796 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.0581$
$\theta_{max} = 30.0°$
$h = -45 \rightarrow 45$
$k = 0 \rightarrow 8$
$l = -5 \rightarrow 0$
3 standard reflections
frequency: 180 min
intensity decay: <1%

Refinement

Refinement on *F*
$R = 0.0387$
$wR = 0.0449$
$S = 3.396$
1785 reflections
80 parameters
$w = 8.826/[\sigma^2(F_o) + 0.000010F_o^2]$

$(\Delta/\sigma)_{max} = 0.116$
$\Delta\rho_{max} = 2.19$ e Å^{-3}
$\Delta\rho_{min} = -3.09$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for O atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Nb and Sr.

	x	*y*	*z*	U_{eq}/U_{iso}
Nb1	1/2	1/2	0.5	0.0035 (2)
Nb2	0.32270 (2)	0.5339 (1)	0.5051 (12)	0.0044 (1)
Nb3	0.40928 (2)	0.0053 (1)	0.5120 (12)	0.0031 (1)
Sr1	0.21443 (2)	0.5628 (1)	0.5130 (12)	0.0136 (2)
Sr2	1/2	0	−0.0010 (14)	0.0068 (2)
Sr3	0.41131 (3)	0.4996 (1)	0.0027 (11)	0.0072 (2)
O1	0.5376 (2)	0.2258 (8)	0.4890 (37)	0.009 (1)
O2	0.4518 (2)	0.2693 (8)	0.5267 (33)	0.006 (1)
O3	1/2	1/2	0.0264 (41)	0.015 (2)
O4	0.2089 (2)	0.2966 (9)	0.0153 (39)	0.009 (1)
O5	0.1207 (2)	0.2070 (8)	0.0171 (37)	0.006 (1)
O6	0.1328 (2)	0.7236 (9)	−0.0300 (28)	0.010 (1)
O7	0.2794 (2)	0.3177 (9)	0.5073 (40)	0.007 (1)
O8	0.3311 (2)	0.5054 (10)	0.0196 (38)	0.017 (2)
O9	0.4169 (2)	−0.0108 (10)	0.0138 (38)	0.015 (1)

Table 2. *Selected geometric parameters* (Å, °)

Nb1—O3	1.892 (16)	Sr2—O1^{viii}	2.699 (13)
Nb1—O1	1.978 (5)	Sr2—O9	2.699 (7)
Nb1—O1^{i}	1.978 (5)	Sr2—O9^{iv}	2.699 (7)
Nb1—O2	2.042 (5)	Sr1—O4^{v}	2.821 (6)
Nb1—O2^{i}	2.042 (5)	Sr1—O8^{v}	2.915 (6)
Nb1—O3^{ii}	2.103 (16)	Sr1—O6^{ii}	3.345 (8)
Nb3—O6^{iii}	1.851 (6)	Sr1—O8^{iii}	3.492 (6)
Nb3—O5^{iii}	1.952 (5)	Sr1—O6	3.544 (9)
Nb3—O9	2.007 (16)	Sr2—O3	2.839 (1)
Nb3—O9^{ii}	2.022 (16)	Sr2—O3^{ix}	2.839 (1)
Nb3—O2	2.039 (5)	Sr2—O2^{vii}	2.888 (10)
Nb3—O1^{iv}	2.167 (6)	Sr2—O2^{viii}	2.888 (10)
Nb2—O4^{v}	1.809 (5)	Sr2—O2	3.037 (11)
Nb2—O7	1.866 (5)	Sr2—O2^{iv}	3.037 (11)
Nb2—O8	1.966 (16)	Sr3—O5^{vi}	2.495 (13)
Nb2—O8^{ii}	2.080 (16)	Sr3—O5^{v}	2.586 (13)
Nb2—O5^{v}	2.084 (5)	Sr3—O8	2.603 (7)
Nb2—O6^{iii}	2.282 (6)	Sr3—O2^{vii}	2.656 (11)
Sr1—O7^{v}	2.456 (14)	Sr3—O9^{x}	2.784 (6)
Sr1—O7^{vi}	2.493 (14)	Sr3—O2	2.797 (11)
Sr1—O4	2.504 (13)	Sr3—O6^{iii}	2.826 (9)
Sr1—O4^{ii}	2.518 (13)	Sr3—O3	2.880 (1)

Sr1—O7	2.525 (6)	Sr3—O9	2.902 (6)
Sr2—O1	2.639 (12)	Sr3—O1^{i}	2.992 (11)
Sr2—O1^{iv}	2.639 (12)	Sr3—O6^{xi}	3.005 (10)
Sr2—O1^{vii}	2.699 (13)	Sr3—O1^{xii}	3.064 (11)
O3—Nb1—O1	88.7 (4)	O7—Nb2—O6^{iii}	88.3 (2)
O3—Nb1—O1^{i}	88.7 (4)	O8—Nb2—O8^{ii}	161.9 (4)
O3—Nb1—O2	93.0 (4)	O8—Nb2—O5^{v}	86.5 (4)
O3—Nb1—O2^{i}	93.0 (4)	O8—Nb2—O6^{iii}	77.7 (4)
O3—Nb1—O3^{ii}	180.0	O8^{ii}—Nb2—O5^{v}	84.1 (5)
O1—Nb1—O1^{i}	177.8 (5)	O8^{ii}—Nb2—O6^{iii}	85.3 (3)
O1—Nb1—O2	88.2 (2)	O5^{v}—Nb2—O6^{iii}	78.8 (2)
O1—Nb1—O2^{i}	91.9 (2)	O6^{iii}—Nb3—O5^{iii}	102.3 (2)
O1—Nb1—O3^{ii}	91.3 (4)	O6^{iii}—Nb3—O9	91.8 (4)
O1^{i}—Nb1—O2	91.9 (2)	O6^{iii}—Nb3—O9^{ii}	102.1 (4)
O1^{i}—Nb1—O2^{i}	88.2 (2)	O6^{iii}—Nb3—O2	90.6 (2)
O1^{i}—Nb1—O3^{ii}	91.3 (4)	O6^{iii}—Nb3—O1^{iv}	170.9 (5)
O2—Nb1—O2^{i}	174.0 (7)	O5^{iii}—Nb3—O9	91.8 (5)
O2—Nb1—O3^{ii}	87.0 (4)	O5^{iii}—Nb3—O9^{ii}	90.6 (5)
O2^{i}—Nb1—O3^{ii}	87.0 (4)	O5^{iii}—Nb3—O2	167.0 (2)
O4^{v}—Nb2—O7	96.6 (2)	O5^{iii}—Nb3—O1^{iv}	82.7 (2)
O4^{v}—Nb2—O8	99.7 (6)	O9—Nb3—O9^{ii}	165.0 (4)
O4^{v}—Nb2—O8^{ii}	96.7 (6)	O9—Nb3—O2	88.8 (4)
O4^{v}—Nb2—O5^{v}	96.4 (2)	O9—Nb3—O1^{iv}	80.4 (4)
O4^{v}—Nb2—O6^{iii}	174.7 (3)	O9^{ii}—Nb3—O2	85.5 (4)
O7—Nb2—O8	93.2 (5)	O9^{ii}—Nb3—O1^{iv}	85.3 (4)
O7—Nb2—O8^{ii}	92.5 (5)	O2—Nb3—O1^{iv}	84.7 (2)
O7—Nb2—O5^{v}	166.9 (2)		

Symmetry codes: (i) $1-x, 1-y, z$; (ii) $x, y, 1+z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (iv) $1-x, -y, z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (vii) $x, y, z-1$; (viii) $1-x, -y, z-1$; (ix) $x, y-1, z$; (x) $x, 1+y, z$; (xi) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (xii) $1-x, 1-y, z-1$.

Data collection, cell refinement and crystal-face indexing: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *MolEN* (Fair, 1990). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement and absorption correction: *SHELX*76 (Sheldrick, 1976). 12 reflections affected by extinction were excluded from the final cycles of least-squares refinement. Anisotropic displacement factors were refined only for Sr and Nb atoms. Molecular graphics: *SCHAKAL* (Keller, 1986). Geometry calculations: *ORFFE*3 (Busing *et al.*, 1971)

Gratitude is expressed to Professor H. R. Oswald, the University of Zürich, for standing support for this work, and the Swiss National Foundation of Science for financial support under project NF 2.772-0.87. The authors also thank the coeditor, Dr I. David Brown, for helpful suggestions and for improving the style of the paper.

Lists of structure factors, anisotropic displacement parameters and complete geometry, and a plot of the projection of the structure on the *ac* plane, have been deposited with the IUCr (Reference: BR1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C51, 1246–1249

A New Type of Mixed Anionic Framework in the Structure of $K_3[Al_4F_9(PO_4)_2]$

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(*Received* 8 *November* 1994; *accepted* 11 *January* 1995)

Abstract

X-ray analysis of a hydrothermally synthesized potassium aluminium fluoride orthophosphate, $K_3[Al_4F_9(PO_4)_2]$, showed that this compound has a new type of