CAUBÈRE, P., MOURAD, M. S. & GUILLAUMET, G. (1973). *Tetrahedron*, **29**, 1843–1849.

COURTOIS, A., PROTAS, J., GUILLAUMET, G. & CAUBÈRE, P. (1973). *C. R. Acad. Sci. Paris, Sér. C*, **276**, 407–409.

COURTOIS, A., PROTAS, J., MOURAD, M. S. & CAUBÈRE, P. (1972). *C. R. Acad. Sci. Paris, Sér. C*. **275**, 1017–1020.

COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. Roy. Soc.* A **247**, 1–21.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A **27**, 368–376.

GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B **24**, 778–791.

JAMES, V. J. & MCCONNELL, J. F. (1971). *Tetrahedron*, **27**, 5475–5480.

LANGSETH, A. & STOICHEFF, B. P. (1956). *Canad. J. Phys.* **34**, 350.

The Crystal Structure of Sr₂Nb₂O₇, a Compound with Perovskite-Type Slabs

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Crystals of Sr₂Nb₂O₇ are orthorhombic, $Cmc2_1$, with $a = 3.933$ (1), $b = 26.726$ (7), $c = 5.683$ (4) Å, $Z = 4$. The structure has been determined from three-dimentional X-ray diffraction data, and refined to the final R value of 0.081 for 676 observed reflexions. The structure consists of slabs parallel to (010) which have a distorted perovskite-type structure composed of NbO₆ octahedra and Sr atoms. The Nb(1)–O and Nb(2)–O distances range from 1.84 to 2.31 Å and 1.84 to 2.25 Å respectively. The Sr(2) atom is surrounded by 12 oxygen atoms with distances ranging from 2.51 to 3.08 Å, while the Sr(1) atom near the boundary of the slab is surrounded by five oxygen atoms in the same slab and two oxygen atoms in the neighbouring slab with distances ranging from 2.43 to 2.85 Å.

Introduction

Several compounds are known whose structures are composed of slabs with distorted perovskite-type atomic configurations. They are classified into two groups according to the geometrical relations of the slabs to the perovskite structure. The slabs in the first group are obtained by cutting the perovskite structure parallel to (110), those in the second group by cutting parallel to (100). Ca₂Nb₂O₇ (Brandon & Megaw, 1970; Scheunemann & Müller-Buschbaum, 1974), BaZnF₄ (von Schnering & Bleckmann, 1968) and NaNbO₂F₂ (Andersson & Galy, 1969) belong to the first, and Sr₃Ti₂O₇ and Sr₄Ti₃O₁₀ (Ruddlesden & Popper, 1958) to the second group. Brandon & Megaw (1970) also suspected that Sr₂Nb₂O₇ and La₂Ti₂O₇ were essentially isostructural with Ca₂Nb₂O₇.

Only a few structures of these compounds have been determined with reasonable accuracy by single-crystal X-ray diffraction, since it is difficult to prepare a suitable crystal for X-ray work because of their micaceous cleavages. Recently, good single crystals of Sr₂Nb₂O₇ (Nanamatsu, Kimura, Doi & Takahashi, 1971) and Sr₂Ta₂O₇ (Nanamatsu, Kimura & Kawamura, 1975) were synthesized, and it was found that the former crystal is piezoelectric and ferroelectric, while the latter shows no piezoelectricity at room temperature. The structure determination of Sr₂Nb₂O₇ was,

therefore, undertaken to obtain a better knowledge of the crystal chemistry of this family of compounds and to elucidate the structural differences between Sr₂Nb₂O₇ and Sr₂Ta₂O₇.

Experimental

Pale yellow transparent crystals of Sr₂Nb₂O₇ were synthesized from a 2:1 mixture of SrCO₃ and Nb₂O₅ with a floating-zone technique (Nanamatsu, Kimura, Doi & Takahashi, 1971). From Weissenberg photographs, the crystal was found to have orthorhombic symmetry, and systematic absences of hkl for $h + k$ odd and $h0l$ for l odd restricted the space group to $C2cm$ (No. 40), $Cmc2_1$ (non-centrosymmetric) and $Cmcm$ (centrosymmetric). Since the crystal was piezoelectric, the centrosymmetric space group $Cmcm$ was rejected. The space group $C2cm$ is also incompatible with the facts that the crystal is ferroelectric and the spontaneous polarization axis is parallel to c. The cell dimensions were determined from eight 2θ values in the range between 12 and 44°, measured on a four-circle diffractometer, by the least-squares procedure. The crystallographic data are given in Table 1. Intensities were collected on a four-circle diffractometer (Philips PW 1100) with Mo $K\alpha$ radiation reflected from a graphite monochromator, using a crystal with dimensions of about $0.12 \times 0.15 \times 0.07$ mm. The ω–2θ scan

technique was employed with a scanning speed of 4° min^{-1} in ω. In all, 676 independent reflexion data, whose $|F|$'s were larger than $3\sigma(|F|)$, were obtained within the range $2\theta < 100°$. Intensities were corrected for the Lorentz and polarization factors. Absorption corrections were also made by a local version of the program *ACACA* (Wuensch & Prewitt, 1965), the maximum and minimum transmission factors being 0·1212 and 0·0124, respectively.

Table 1. *Crystal data for* Sr$_2$Nb$_2$O$_7$

Crystal system: orthorhombic	Space group: $Cmc2_1$
Cell dimensions:	$U = 597\cdot4$ Å^3
$a = 3\cdot933$ (1) Å	$Z = 4$
$b = 26\cdot726$ (7)	M.W. 473·08
$c = 5\cdot683$ (4)	$D_x = 5\cdot26$ g cm^{-3}
	μ (for Mo $K\alpha$) = 434·1 cm^{-1}

Structure determination

The metal atom positions were derived from the Patterson function, and all the oxygen atom positions were found on the electron-density maps phased with the heavy atoms. The structure was refined with the full-matrix least-squares program *LINUS* (Coppens &

Hamilton, 1970), employing anisotropic temperature factors for metal atoms and isotropic for oxygen atoms, to the conventional R value of 0·081. In the least-squares refinements, the z parameter of Nb(1) was fixed at 0·5062, since the origin can be taken at any point on the twofold screw axis in the space group $Cmc2_1$. The atomic scattering factors used were for neutral atoms taken from *International Tables for X-ray Crystallography* (1968). Unit weight was assigned for all the terms. The refinements were terminated when all the calculated shifts became less than 0·01σ. The final positional and thermal parameters are listed in Table 2.* Selected bond length and angles are given in Table 3 with their estimated standard deviations in parentheses.

Discussion

The projections of the structure along the a and c axes are shown in Fig. 1. All atoms are on the mirror

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30946 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final atomic parameters*

Anisotropic temperature factors are expressed in the form $\exp[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hk B_{12} + 2hl B_{13} + 2kl B_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sr(1)	0	0·7059 (2)	0·4747 (8)	0·0108 (10)	0·0010 (1)	0·0104 (8)	0	0	0·0015 (3)
Sr(2)	0	0·4484 (2)	0·5377 (7)	0·0089 (9)	0·0003 (1)	0·0056 (6)	0	0	−0·0002 (2)
Nb(1)	0·5	0·3381 (2)	0·5062	0·0063 (9)	0·0003 (1)	0·0041 (5)	0	0	0·0003 (2)
Nb(2)	0·5	0·5577 (2)	0·5348 (6)	0·0052 (8)	0·0003 (1)	0·0042 (5)	0	0	−0·0002 (2)

	x	y	z	B		x	y	z	B
O(1)	0	0·007 (2)	0·287 (6)	1·5 (4)	O(5)	0·5	0·299 (2)	0·241 (5)	1·4 (4)
O(2)	0	0·113 (2)	0·340 (7)	2·5 (7)	O(6)	0·5	0·408 (1)	0·336 (5)	1·2 (4)
O(3)	0·5	0·150 (1)	0·048 (5)	1·2 (3)	O(7)	0	0·450 (1)	0·066 (4)	1·1 (3)
O(4)	0	0·213 (2)	0·225 (5)	1·4 (4)					

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *with their estimated standard deviations in parentheses*

Nb(1)–O(3^{iii})	2·01 (1)	(2×)		Nb(2)–O(7^{i})	1·99 (1)	(2×)
Nb(1)–O(5)	1·84 (4)			Nb(2)–O(2^{ii})	1·84 (5)	
Nb(1)–O(6)	2·12 (4)			Nb(2)–O(1^{ii})	1·95 (4)	
Nb(1)–O(4^{iii})	1·85 (4)			Nb(2)–O(1^{iii})	2·25 (4)	
Nb(1)–O(2^{iii})	2·31 (4)			Nb(2)–O(6^{i})	1·93 (3)	
Sr(1)—O(5^{i})	2·49 (2)	(2×)		Sr(2)—O(6)	2·51 (2)	(2×)
Sr(1)—O(4^{ii})	2·43 (2)	(2×)		Sr(2)—O(1^{iii})	2·70 (3)	(2×)
Sr(1)—O(5^{ii})	2·82 (4)			Sr(2)—O(1^{ii})	2·89 (3)	(2×)
Sr(1)—O(3^{ii})	2·85 (3)			Sr(2)—O(2^{iii})	3·08 (3)	(2×)
Sr(1)—O(4^{i})	2·59 (4)			Sr(2)—O(7^{iv})	3·00 (3)	
Sr(1)—O(2^{ii})	3·27 (4)	(2×)		Sr(2)—O(7^{vi})	2·68 (3)	
				Sr(2)—O(3^{iii})	2·64 (4)	
				Sr(2)—O(7^{i})	2·72 (4)	

O(6)—Nb(1)–O(5)	97·7 (15)		O(2^{ii})–Nb(2)–O(1^{ii})	96·7 (19)
O(6)—Nb(1)–O(2^{iii})	82·4 (14)		O(2^{ii})–Nb(2)–O(6^{i})	99·2 (18)
O(4^{iii})–Nb(1)–O(5)	97·3 (18)		O(1^{iii})–Nb(2)–O(1^{ii})	85·8 (16)
O(4^{iii})–Nb(1)–O(2^{iii})	82·6 (16)		O(1^{iii})–Nb(2)–O(6^{i})	78·3 (15)
O(6)—Nb(1)–O(3^{iii})	85·2 (10)		O(2^{ii})–Nb(2)–O(7^{i})	97·9 (9)
O(5)—Nb(1)–O(3^{iii})	100·7 (9)		O(1^{iii})–Nb(2)–O(7^{i})	82·1 (9)
O(4^{iii})–Nb(1)–O(3^{iii})	92·0 (10)		O(1^{ii})–Nb(2)–O(7^{i})	89·5 (9)
O(2^{iii})–Nb(1)–O(3^{iii})	79·3 (9)		O(6^{i})—Nb(2)–O(7^{i})	88·3 (8)

Table 3 *(cont.)*

Symmetry code

None	x	y	z
i	x	$1-y$	$\frac{1}{2}+z$
ii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
iii	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iv	x	y	$1+z$
v	$\frac{1}{2}+x$	$\frac{1}{2}+y$	$1+z$
vi	$1+x$	y	z

planes at $x=0$ and 0.5. Each slab is bounded by oxygen atoms, and has a thickness corresponding to twice the face diagonal of a perovskite cube. The a and c axes correspond to the edge length of the perovskite cube and to the face diagonal, respectively. Successive slabs are shifted relative to one another by $\mathbf{a}/2$.

All the Nb atoms are octahedrally surrounded by oxygen atoms, the Nb–O distances ranging from 1.84 to 2.31 Å. Sr(2) is coordinated to twelve oxygen atoms, like the Ca^{2+} cations in the perovskite structure. However, Sr(1), lying near the boundary of the slab, is greatly displaced towards the boundary from the centre of the cube formed by atoms O(2), O(4), O(5) and O(6). As a result, the atom is surrounded by five oxygen atoms in the same slab and two oxygen atoms

in the neighbouring slab at distances ranging from 2.43 to 2.85 Å. Thus, the Sr(1) atoms link adjacent slabs. Two more oxygen atoms in the same slab are at a distance of 3.27 Å from Sr(1). The mean Sr(1)–O distance is 2.74 Å including these two longer bonds and that of Sr(2)–O is 2.78 Å.

As stated already, $Ca_2Nb_2O_7$ is practically isostructural with $Sr_2Nb_2O_7$, though the unit cell is doubled along the a axis in comparison with $Sr_2Nb_2O_7$. Examples consisting of thinner perovskite slabs are $BaZnF_4$ and $NaNbO_2F_2$. The former substance has the identical symmetry $Cmc2_1$ to that of $Sr_2Nb_2O_7$, and all the atoms are on the mirror planes as in $Sr_2Nb_2O_7$. The thickness of the constituent slabs, however, corresponds to the face-diagonal of a perovskite cube. The structures of $Sr_2Nb_2O_7$ and $BaZnF_4$ are schematically compared in Fig. 2. The structure of $NaNbO_2F_2$ is essentially identical to $BaZnF_4$, though the symmetry is lowered to monoclinic. Recently, Portier, Fayard, Carpy & Galy (1974) reported a family of phases $A_nB_nO_{3n+2}$ in the systems $Ca_2Nb_2O_7$–$NaNbO_3$ and $La_2Ti_2O_7$–$CaTiO_3$ with $n=4$, 5 and 6, the structures of which are composed of perovskite-type slabs. For example, $Ca_4Nb_4O_{14}$ is the member with $n=4$, $(Ca_4Na)Nb_5O_{17}$ with $n=5$ and $(Ca_4Na_2)Nb_6O_{20}$ with
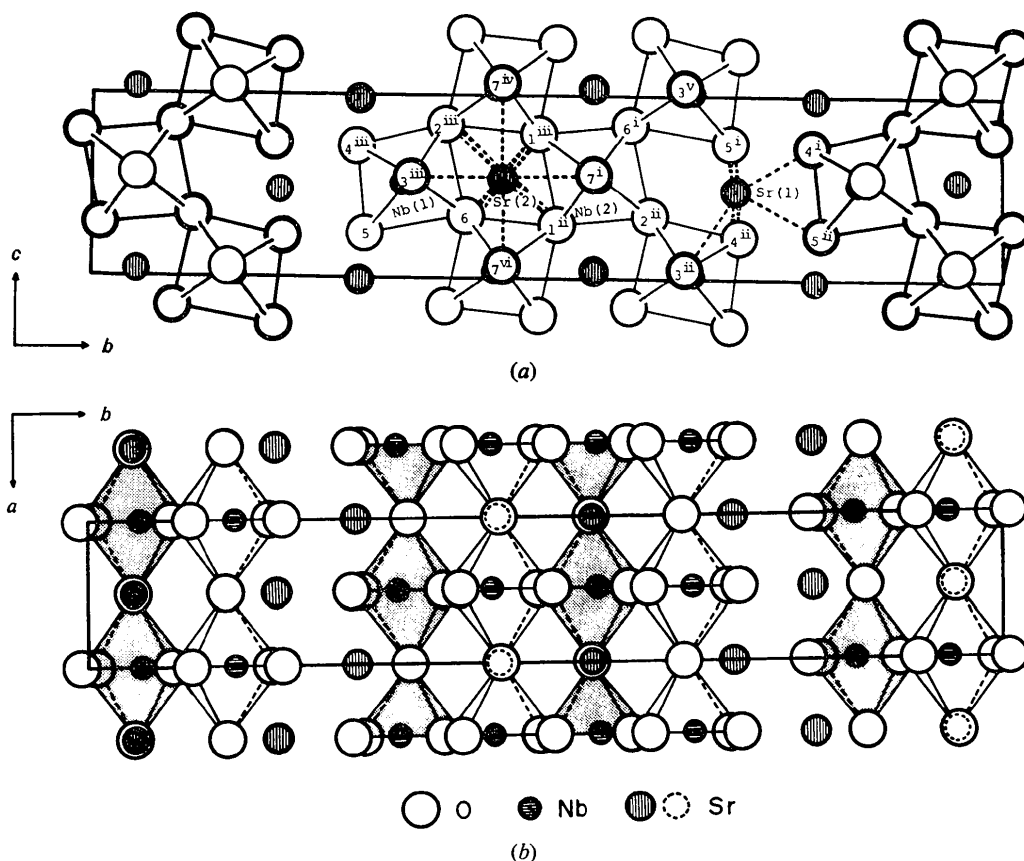

Fig. 1. The crystal structure of $Sr_2Nb_2O_7$ viewed (a) along a and (b) along c. Atoms are labelled in accordance with the nomenclature of Table 2. The thick circles in (a) are at the level $x=0$ and the others at $x=0.5$. The coordinations around Sr are shown by broken lines.
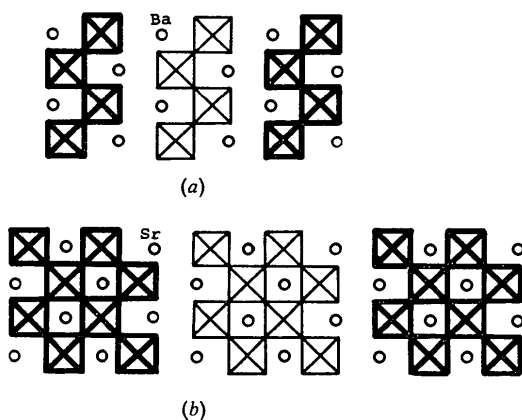
(a)

(b)

Fig. 2. Comparison of the structures of (a) BaZnF$_4$ and (b) Sr$_2$Nb$_2$O$_7$. Perovskite-type slabs are idealized. The slabs drawn in thick lines are shifted with respect to the others by a/2.

$n=6$. The thicknesses of the slabs are $n/2$ times the face-diagonal of the simple perovskite cube in these crystals. Sr$_2$Nb$_2$O$_7$ belongs to the family with $n=4$.

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References

ANDERSSON, S. & GALY, J. (1969). Acta Cryst. B25, 847–850.
BRANDON, J. K. & MEGAW, H. D. (1970). Phil. Mag. 21, 189–194.
COPPENS, S. & HAMILTON, W. C. (1970). Acta Cryst. A26, 71–83.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 201–216. Birmingham: Kynoch Press.
NANAMATSU, S., KIMURA, M., DOI, K. & TAKAHASHI, M. (1971). J. Phys. Soc. Japan, 30, 300–301.
NANAMATSU, S., KIMURA, M. & KAWAMURA, T. (1975). J. Phys. Soc. Japan, 38, 817–824.
PORTIER, R., FAYARD, M., CARPY, A. & GALY, J. (1974). Mat. Res. Bull. 9, 371–378.
RUDDLESDEN, S. N. & POPPER, P. (1958). Acta Cryst. 11, 54–55.
SCHEUNEMANN, K. & MÜLLER-BUSCHBAUM, H. (1974). J. Inorg. Nucl. Chem. 36, 1965–1970.
SCHNERING, H. G. VON & BLECKMANN, P. (1968). Naturwissenschaften, 55, 342–343.
WUENSCH, B. J. & PREWITT, C. T. (1965). Z. Kristallogr. 122, 24–59.

The Structure of an Adduct of N-Methylthiourea and Dimethyl Acetylenedicarboxylate: 2-Imino-3-methyl-5-methoxycarbonylmethylene-1,3-thiazolidin-4-one

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The structure of an adduct of N-methylthiourea and the dimethyl ester of acetylenedicarboxylic acid is shown to be 2-imino-3-methyl-5-methoxycarbonylmethylene-1,3-thiazolidin-4-one (C$_7$H$_8$N$_2$O$_3$S) by X-ray crystallographic analysis. The molecule crystallizes in space group P$\overline{1}$, cell dimensions $a=$ 9·275, $b=12·287$, $c=8·517$ Å, $\alpha=103·62°$, $\beta=96·86°$, $\gamma=100·16°$, with two molecules in the asymmetric unit. The structural model refined to an R of 0·055 with data measured on a four-circle diffractometer. The planar molecules are paired with hydrogen bonds between imine nitrogens and carbonyl oxygens of the carboxyl group; there appears to be sufficient space between packed pairs in the lattice for solvent of crystallization (methanol) to be occasionally included.

The structure of the product(s) derived from the reaction of substituted thioureas and acetylenedicarboxylic acid (or esters) has been the subject of some debate (Lown & Ma, 1967). Three ring systems have received support since the original publication by Mushkalo & Yangol (1956). These are the six-membered 1,3-thia-zines (I) (Lown & Ma, 1967; Winterfeldt & Nelke, 1967; Kishida & Terada, 1968), the five-membered 1,3-thiazolidinone (II) (Mushkalo & Yangol, 1956; Hendrickson, Rees & Templeton, 1964), and the 2-thio-hydantoin structure (III) (Sasaki, Sakata & Iwanami, 1964, 1965). Spectral evidence in support of the six-