

$\cdots\text{H}(\text{C}20)$ of 2.05 Å would be even less if the angle $\text{C}(14)\text{--}\text{C}(18)\text{--}\text{C}(20)$ had the expected value of 115° rather than the observed 118° .

The most dominant feature in the packing is the hydrogen-bond formation $\text{O--H}\cdots\text{N}$ which is essentially the same as in the *dl*-compound, although the six-membered ring, which is planar within 0.15 Å, has lost its centre of symmetry (Fig. 4). The distances $\text{O}(1)\cdots\text{N}(2)$ and $\text{O}(2)\cdots\text{N}(1)$ are 2.793 (5) and 2.806 (6) Å respectively.

References

BAERT, F. & FOURET, R. (1975). *Cryst. Struct. Commun.* **4**, 307–310.

- BHUIYA, A. K. & STANLEY, E. (1964). *Acta Cryst.* **17**, 746–748.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 MAIN, P., WOLFFSON, M. M. & GERMAIN, G. (1971). *MULTAN, A Computer Program for the Automatic Solution of Crystal Structures*. Univ. of York.
 OONK, H. A. J. & KROON, J. (1976). *Acta Cryst.* **B32**, 500–504.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1976). **B32**, 2564

Compounds with Perovskite-Type Slabs. II. The Crystal Structure of $\text{Sr}_2\text{Ta}_2\text{O}_7$

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The crystal structure of $\text{Sr}_2\text{Ta}_2\text{O}_7$ has been determined from three-dimensional X-ray diffraction data and refined to a conventional *R* value of 0.036 for 697 observed reflexions. $\text{Sr}_2\text{Ta}_2\text{O}_7$ crystallizes in the orthorhombic space group *Cmcm*, with $a=3.937$ (6), $b=27.198$ (6), $c=5.692$ (7) Å and $Z=4$. The crystal is essentially isostructural with $\text{Sr}_2\text{Nb}_2\text{O}_7$, having a structure composed of perovskite-type slabs parallel to (010). There are two independent Ta atoms surrounded octahedrally by O atoms. The $\text{Ta}(1)\text{--}\text{O}$ and $\text{Ta}(2)\text{--}\text{O}$ distances range from 1.87 (1) to 2.16 (1) Å and 1.89 (1) to 2.07 (1) Å respectively. The $\text{Sr}(2)$ atom is surrounded by 12 O atoms with distances ranging from 2.70 (3) to 2.85 (1) Å. The $\text{Sr}(1)$ atom near the boundary of a slab is surrounded by six O atoms in the same slab and two O atoms in the neighbouring slab with distances ranging from 2.47 (1) to 3.27 (1) Å.

Introduction

Recently, some $\text{A}_2\text{B}_2\text{O}_7$ compounds were revealed to form a structural family characterized by the perovskite-type slabs in their structures. Examples are $\text{Ca}_2\text{Nb}_2\text{O}_7$ (Scheunemann & Müller-Buschbaum, 1974), $\text{Sr}_2\text{Nb}_2\text{O}_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1975) and $\text{La}_2\text{Ti}_2\text{O}_7$ (Gasperin, 1975). Though crystals of $\text{Sr}_2\text{Ta}_2\text{O}_7$ had been supposed to have a tetragonal pyrochlore-type structure with $a=10.63$, $c=10.91$ Å (Ismailzade, 1958), it was found by Nanamatsu, Kimura & Kawamura (1975) that the symmetry and the cell dimensions rather suggest a close similarity in the structure to $\text{Sr}_2\text{Nb}_2\text{O}_7$. $\text{Sr}_2\text{Ta}_2\text{O}_7$ is paraelectric at room temperature, having a markedly lower ferroelectric phase transition temperature (-107°C) than $\text{Sr}_2\text{Nb}_2\text{O}_7$ (1342°C), $\text{La}_2\text{Ti}_2\text{O}_7$ ($\sim 1500^\circ\text{C}$) and $\text{Ca}_2\text{Nb}_2\text{O}_7$ ($> 1500^\circ\text{C}$) (Nanamatsu *et al.*, 1975). Therefore, the crystal structure of $\text{Sr}_2\text{Ta}_2\text{O}_7$ at room temperature is expected to afford important information on the structures of the paraelectric phases of these compounds.

Experimental

Transparent, colourless crystals were synthesized from a 2:1 mixture of SrCO_3 and Ta_2O_5 with a floating-zone technique. From Weissenberg photographs, the crystal was found to have orthorhombic symmetry, and systematic absences, $h+k$ odd in hkl and l odd in $h0l$, restricted the possible space groups to *C2cm* (No. 40), *Cmc2₁* and *Cmcm*. Since the crystal is paraelectric at room temperature, the space group *Cmcm* seemed to be most plausible, and has been justified in the course of the structure determination. The cell dimensions were determined from 15 2θ values in the range between 20 and 70° measured with $\text{Cu K}\alpha$ radiation on a powder diffractometer, by the least-squares procedure. The crystal data are given in Table 1.

Intensities were collected on a four-circle diffractometer (Philips PW 1100) with $\text{Mo K}\alpha$ radiation from a graphite monochromator. A crystal with dimensions of about $0.166 \times 0.024 \times 0.166$ mm was used. The ω - 2θ scan technique was employed with a scanning speed of 4°min^{-1} in ω . In all, 697 independent reflexion

Table 1. *Crystal data of Sr₂Ta₂O₇*

Crystal system: orthorhombic	
Space group: <i>Cmcm</i>	
Cell dimensions	
$a = 3.937$ (6) Å	$Z = 4$
$b = 27.198$ (6)	M.W. 649.16
$c = 5.692$ (7)	$D_x = 7.07$ g cm ⁻³
$U = 609.5$ Å ³	μ (for Mo $K\alpha$) = 555.4 cm ⁻¹

data, whose $|F|$'s were larger than $3\sigma(|F|)$, were obtained within the range of $2\theta < 100^\circ$. $\sigma(|F|)$ is the estimated standard deviation of $|F|$ due to counting statistics. Intensities were corrected for the Lorentz and polarization factors. Absorption corrections were also carried out with the program *ACACA-4* (Wuensch & Prewitt, 1965), by taking the crystal shape into account. The maximum and minimum transmission factors for the observed reflexions were 0.2545 and 0.0373 respectively.

Structure determination

The metal atom positions were derived from Patterson maps. They were concordant with the centrosymmetric space group *Cmcm*. All the O atoms were found on the electron-density maps synthesized with phases calculated with the heavy atoms. The structure was refined with a full-matrix least-squares program, *LINUS* (Coppens & Hamilton, 1970), to a conventional R value of 0.061, with isotropic temperature factors for all the atoms. At this stage, the possibility of slight deviations from the centrosymmetric atomic arrangements was examined. Refinements based on the space group *Cmc*₂ or *C2cm* gave negative or unreasonably large temperature factors for some O atoms. In addition, the R values were even larger for these models than for the centrosymmetric one. Therefore the non-centrosymmetric models were discarded. Further refinements were undertaken introducing anisotropic temperature factors for metal atoms as well as the isotropic secondary extinction parameter, and were terminated when all the calculated shifts became less than one tenth of the estimated standard deviations. The extinction parameter obtained was 0.3×10^{-4} and the largest correction factor was about 35% of F .

Scattering factors for Sr²⁺ and Ta⁵⁺ ions were taken from *International Tables for X-ray Crystallography* (1974) and the values given by Tokonami (1965) were used for O²⁻. Unit weight was assigned for all the terms. The final positional and thermal parameters are listed in Table 2.* Selected bond lengths and angles are given in Table 3 with their estimated standard deviations in parentheses.

Table 2. *Final atomic parameters*

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

	x	y	z	B
Sr(1)	0.0	0.2884 (1)	0.25	0.87*
Sr(2)	0.0	0.4468 (1)	0.75	0.99*
Ta(1)	0.5	0.3399 (1)	0.75	0.53*
Ta(2)	0.5	0.4447 (1)	0.25	0.42*
O(1)	0.5	0.2930 (6)	0.510 (2)	0.9 (1)
O(2)	0.0	0.3475 (10)	0.75	1.5 (3)
O(3)	0.5	0.4009 (6)	0.508 (2)	1.2 (2)
O(4)	0.0	0.4524 (10)	0.25	1.3 (2)
O(5)	0.5	0.5	0.5	1.1 (2)
	B_{11}	B_{22}	B_{33}	$B_{12} = B_{13} = B_{23}$
Sr(1)	0.0077 (6)	0.00058 (6)	0.0033 (3)	0.0
Sr(2)	0.0062 (6)	0.00053 (6)	0.0079 (4)	0.0
Ta(1)	0.0037 (2)	0.00036 (3)	0.0022 (1)	0.0
Ta(2)	0.0027 (2)	0.00031 (2)	0.0013 (1)	0.0

* Calculated from anisotropic temperature factors according to the formula: $B = 4(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)/3$.

Discussion

The projections of the structure along the a and c axes are shown in Fig. 1 (a) and (b) respectively. The projection of the structure of Sr₂Nb₂O₇ along the a axis is also given in Fig. 1(c) for comparison. The structure is composed of perovskite-type slabs with a thickness corresponding to twice the face diagonal of a perovskite cube. The slabs consist of TaO₆ octahedra connected by sharing corners, with Sr(2) atoms in the spaces of the twelfold coordination. The Sr(1) atoms are near the boundaries of the slabs.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31741 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Ta(1)–O(1)	1.87 (1)	($\times 2$)	Sr(2)–O(2)	2.70 (3)	
Ta(1)–O(2)	1.979 (4)	($\times 2$)	Sr(2)–O(4 ⁱⁱⁱ)	2.74 (3)	
Ta(1)–O(3)	2.16 (1)	($\times 2$)	O(2)–Ta(1)–O(1)	94.1 (5)	($\times 4$)
Sr(1)–O(1)	2.47 (1)	($\times 4$)	O(2)–Ta(1)–O(3)	85.4 (6)	($\times 4$)
Sr(1)–O(1 ^{iv})	2.60 (1)	($\times 2$)	O(1)–Ta(1)–O(3)	93.4 (5)	($\times 2$)
Sr(1)–O(2)	3.27 (1)	($\times 2$)	O(1)–Ta(1)–O(1 ⁱ)	94.0 (6)	
Ta(2)–O(3)	1.89 (1)	($\times 2$)	O(3)–Ta(1)–O(3 ⁱ)	79.3 (5)	
Ta(2)–O(4)	1.980 (4)	($\times 2$)	O(4)–Ta(2)–O(3)	93.8 (5)	($\times 4$)
Ta(2)–O(5)	2.070 (1)	($\times 2$)	O(4)–Ta(2)–O(5)	85.6 (5)	($\times 4$)
Sr(2)–O(3)	2.71 (1)	($\times 4$)	O(3)–Ta(2)–O(5)	85.6 (4)	($\times 2$)
Sr(2)–O(5)	2.827 (3)	($\times 4$)	O(3)–Ta(2)–O(3 ⁱⁱ)	102.0 (6)	
Sr(2)–O(4)	2.850 (4)	($\times 2$)	O(5)–Ta(2)–O(5 ⁱⁱ)	86.8 (1)	

Symmetry code: None x, y, z ; (i) $0.5, y, 1.5 - z$; (ii) $0.5, y, -0.5 + z$; (iii) $0, 1 - y, 1 - z$; (iv) $0, 0.5 - y, 1 - z$.

Adjacent slabs are mutually shifted by $a/2$. All the atoms of $\text{Sr}_2\text{Ta}_2\text{O}_7$ are on the mirror planes at $x=0$ and 0.5 . All these features are the same as in the structure of $\text{Sr}_2\text{Nb}_2\text{O}_7$ (Ishizawa *et al.*, 1975). In $\text{Sr}_2\text{Ta}_2\text{O}_7$ the metal atoms and O(2) and O(4) are also on the mirror planes at $z=0.25$ and 0.75 . O(5) is at the centre of symmetry. Only O(1) and O(3) have z parameters, although their actual shifts from the plane $z=0.5$ are very small, *i.e.* $0.06(1)$ and $0.05(1)$ Å respectively. The Sr(2)–O distances are in the range $2.70(3)$ – $2.850(4)$ Å. The Sr(1) atom is surrounded by six O atoms in the same slab and two in the neighbouring slab with distances between $2.47(1)$ and $3.27(1)$ Å.

Ta(1) and Ta(2) atoms are displaced from the centre of respective TaO_6 octahedra toward the boundary of the slab by about 0.20 and 0.17 Å respectively (Fig. 2a). These displacements of Ta atoms result in the formation of two short and two long bonds on the mirror planes in each octahedron. In the case of Ta(1)O_6 they are $1.87(1)$ [Ta(1)–O(1), $\times 2$], and $2.16(1)$ Å [Ta(1)–O(3), $\times 2$], and in Ta(2)O_6 , $1.89(1)$ [Ta(2)–O(3), $\times 2$] and $2.070(1)$ Å [Ta(2)–O(5), $\times 2$] respectively. The two remaining Ta–O distances are nearly equal to the mean bond length in each octahedron. Sr(2) is also displaced from the centre of the coordination polyhedron toward the boundary of the slab by 0.09 Å. These cation displacements are supposed to be chiefly due to the repulsive forces between the Ta^{5+} and Sr^{2+} cations.

The most conspicuous structural difference between $\text{Sr}_2\text{Ta}_2\text{O}_7$ and $\text{Sr}_2\text{Nb}_2\text{O}_7$ is in the degree of deformation of the perovskite-type layers. In $\text{Sr}_2\text{Nb}_2\text{O}_7$, the arrangement of O atoms is largely deformed from that in the ideal perovskite structure, in contrast to the nearly regular arrangement in $\text{Sr}_2\text{Ta}_2\text{O}_7$, as seen in Fig. 1. The displacements of Nb atoms from the centres of NbO_6 octahedra have z components as well as y components (Fig. 2b), and consequently the mirror planes at $z=0.25$ and 0.75 observed in $\text{Sr}_2\text{Ta}_2\text{O}_7$ are lost in $\text{Sr}_2\text{Nb}_2\text{O}_7$. The centrosymmetric structure obtained explains well the paraelectric character of the $\text{Sr}_2\text{Ta}_2\text{O}_7$ crystals at room temperature.

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References

- COPPENS, S. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
 GASPERIN, P. M. (1975). *Acta Cryst.* B31, 2129–2130.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–97, 149–150. Birmingham: Kynoch Press.

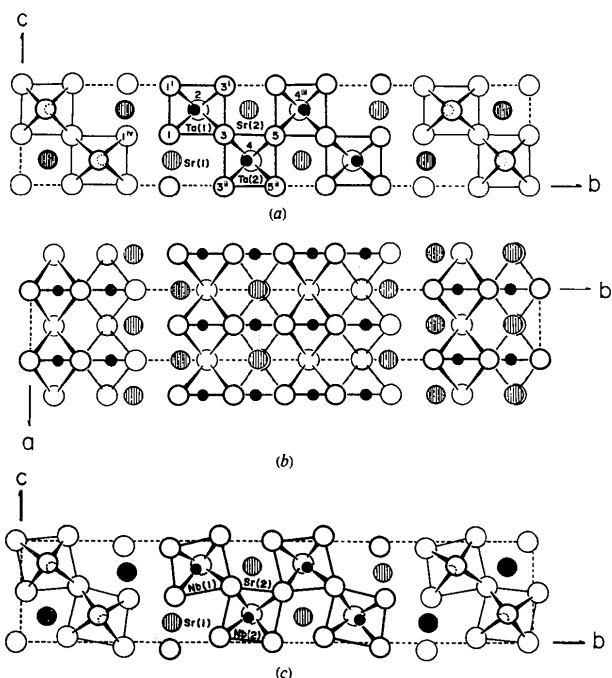


Fig. 1. The crystal structure of $\text{Sr}_2\text{Ta}_2\text{O}_7$ viewed (a) along a , (b) along c , and (c) the structure of $\text{Sr}_2\text{Nb}_2\text{O}_7$ viewed along a . The unit cell of $\text{Sr}_2\text{Nb}_2\text{O}_7$ is moved along the c axis for comparison, since the origin can be taken at any point on the twofold screw axis. The thick circles in (a) and (c) are at the level $x=0$, and the others at $x=0.5$. Atoms are labelled in accordance with the nomenclature of Table 2.

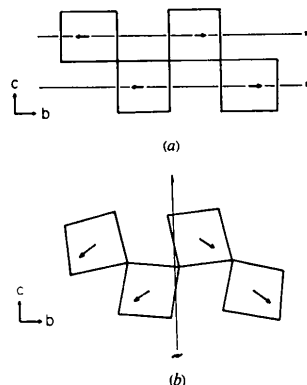


Fig. 2. (a) The displacements of the Ta atoms and (b) those of the Nb atoms from the centres of respective octahedra in a slab.

- ISHIZAWA, N., MARUMO, F., KAWAMURA, T. & KIMURA, M. (1975). *Acta Cryst.* B31, 1912–1915.
 ISMAILZADE, I. G. (1958). *Izv. Akad. Nauk SSSR, Ser. Fiz.* 22, 1485.
 NANAMATSU, S., KIMURA, M. & KAWAMURA, T. (1975). *J. Phys. Soc. Japan*, 38, 817–824.
 SCHEUNEMANN, K. & MÜLLER-BUSCHBAUM, H. (1974). *J. Inorg. Nucl. Chem.* 36, 1965–1970.
 TOKONAMI, M. (1965). *Acta Cryst.* 19, 486.
 WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* 122, 24–59.