

Acta Cryst. (1958). **11**, 54

The compound $\text{Sr}_3\text{Ti}_2\text{O}_7$ and its structure. By S. N. RUDDLESSEN and P. POPPER, *The British Ceramic Research Association, Stoke-on-Trent, England*

(Received 7 July 1957)

The compound $\text{Sr}_3\text{Ti}_2\text{O}_7$ has been formed by firing to 1400°C . mixtures of SrCO_3 and TiO_2 in the molecular proportions 3:2. Its structure may be considered as, in a sense, intermediate between those of Sr_2TiO_4 (K_2NiF_4 type) (see Ruddlesden & Popper, 1957) and SrTiO_3 (perovskite). Whereas in Sr_2TiO_4 perovskite layers are interleaved with SrO layers, forming a tetragonal, body-centred unit cell with axial ratio about 3.2, in $\text{Sr}_3\text{Ti}_2\text{O}_7$ double perovskite layers are interleaved with SrO layers, the axial ratio being increased to about 5.2. The unit cell (Fig. 1) contains two formula units.

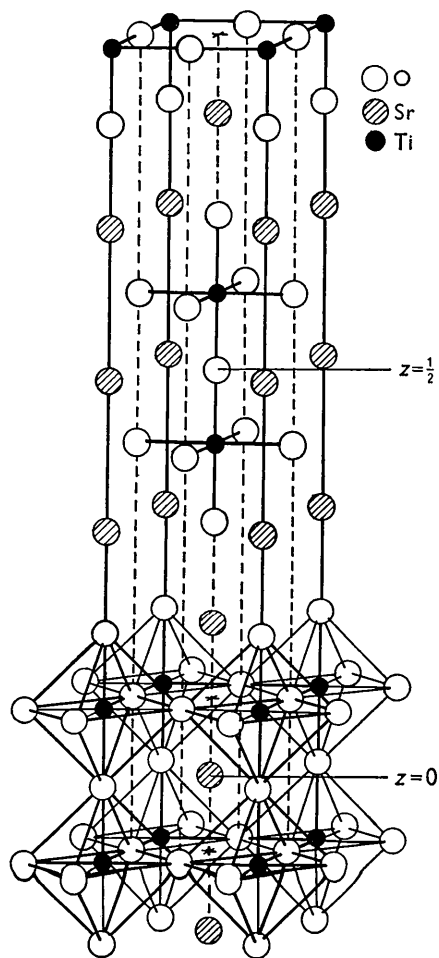


Fig. 1. The $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure.

The samples have been examined by powder diffraction methods, using $\text{Co K}\alpha$ radiation and a 9 cm. camera. This has given the lattice parameters of the tetragonal cell as

$$a = 3.90, c = 20.38 \text{ \AA}$$

and a calculated density of 5.04 g.cm.^{-3} . The atomic

positions proposed have been estimated by analogy with those of SrTiO_3 and Sr_2TiO_4 , i.e. to give similar atomic co-ordinations. In terms of the positions of the space group $I4/mmm$ the proposed positions are:

- (0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) +
 4 Ti in (e) 0, 0, z; 0, 0, \bar{z} ; with $z = z_1$.
 2 O_I in (a) 0, 0, 0.
 8 O_{II} in (g) $0, \frac{1}{2}, z; 0, \frac{1}{2}, \bar{z}; \frac{1}{2}, 0, z; \frac{1}{2}, 0, \bar{z}$; with $z = z_2$.
 4 O_{III} in (e) with $z = z_3$.
 2 Sr_I in (b) 0, 0, $\frac{1}{2}$.
 4 Sr_{II} in (e) with $z = \frac{1}{2} - z_4$.

We have taken $z_4 = z_3 = 2z_1$ and $z_2 = z_1 = 0.094$. This value of z_1 is derived from the relation $(\frac{1}{2} - 4z_1)/z_1 = 1.33$, which gives the same ratio of the Sr-O and Ti-O distances as in the Sr_2TiO_4 case, the z value 0.15 there giving $(\frac{1}{2} - 2z)/z = 1.33$.

Table 1. $\text{Sr}_3\text{Ti}_2\text{O}_7$: X-ray powder diffraction data

Spacings are calculated for a tetragonal unit cell, with
 $a = 3.90, c = 20.38 \text{ \AA}$

<i>hkl</i>	<i>d_c</i> (Å)	<i>d_o</i> (Å)	<i>I_c</i>	<i>I_o</i>
002	10.19	—	3	—
004	5.10	—	0	—
101	3.83	3.84	6	10
006	3.40	3.39	6	10
103	3.38			
—	—	3.08	—	2
105	2.82	2.83	100	100
110	2.76	2.75	63	60
112	2.66	2.66	1	2
008	2.55	2.55	2	2
114	2.42	2.42	6	5
107	2.33	2.33	3	2
—	—	2.26	—	2
116	2.14	2.14	26	30
0,0,10	2.04	2.04	17	10
109	1.96	—	0	—
200	1.95	1.95	40	50
202	1.92	—	0	—
118	1.87	1.87	3	2
204	1.82	—	0	—
—	—	1.77	—	2
211	1.74	1.74	1	2
0,0,12	1.698	—	2	—
206	1.691	1.69 ₃	3	5
213	1.689			
1,0,11	1.673	1.67 ₀	3	5
1,1,10	1.640	1.63 ₃	16	15
215	1.603	1.60 ₂	33	30
208	1.548	1.54 ₆	2	2
217	1.496	1.49 ₅	1	2
0,0,14	1.456	—	0	—
1,0,13	1.455	—	1	—
1,1,12	1.446	1.446	2	2
2,0,10	1.409	1.409	17	15
219	1.381	—	0	—
220	1.379	1.379	11	10
222	1.366	—	0	—
224	1.331	—	0	—
301	1.298	—	1	—
1,1,14	1.287	—	0	—

Table 1 (cont.)

<i>hkl</i>	<i>d_c</i> (Å)	<i>d_o</i> (Å)	<i>I_c</i>	<i>I_o</i>
1,0,15	1.283	1.281	4	5
2,0,12	1.280		3	
226	1.278	—	1	—
303	1.277	—	0	—
0,0,16	1.274	—	1	—
2,1,11	1.270	1.270	2	2
305	1.239	1.239	7	5
310	1.233	1.235	9	5
312	1.224	—	0	—
228	1.212	—	1	—
314	1.199	—	1	—
307	1.187	—	0	—
2,0,14	1.166	—	1	—
2,1,13	1.166	—	1	—
316	1.160	1.160	6	5
1,1,16	1.157	1.156	5	5
1,0,17	1.146	1.143	3	10
2,2,10	1.141		10	
0,0,18	1.132	—	0	—
309	1.128	—	0	—
318	1.111	—	1	—
321	1.080	—	1	—
2,1,15	1.072	1.072	7	5
2,2,12	1.070		2	
323	1.068	—	0	—
2,0,16	1.066	1.066	2	2
3,0,11	1.064		1	
3,1,10	1.054	1.055	12	10
1,1,18	1.048	—	0	—
325	1.046	1.046	14	10
1,0,19	1.035	1.034	1	2
0,0,20	1.019	—	1	—
327	1.013	1.014	1	2
2,2,14	1.000	—	1	—
3,0,13	1.000	—	0	—
3,1,12	0.997	0.998	3	5
2,1,17	0.988	0.987	7	5
2,0,18	0.979	—	1	—
329	0.976	—	0	—
400	0.975	0.976	9	5
402	0.970	—	0	—
404	0.957	—	0	—
1,1,20	0.955	—	2	—
411	0.944	—	1	—
1,0,21	0.942	—	2	—
3,1,14	0.941	—	1	—
3,0,15	0.939	0.939	6	5
406	0.937	—	1	—
413	0.937	—	1	—
2,2,16	0.935	0.934	3	5
3,2,11	0.934		4	
0,0,22	0.926	0.926	4	2
415	0.921	0.921	30	15
330	0.919	0.919	10	5
332	0.915	—	0	—
2,1,19	0.914	0.913	2	2
408	0.910		2	
334	0.905	—	2	—

Acta Cryst. (1958), **11**, 55

Berechnung von Madelung'schen Zahlen für den NiAs-Typ. Von J. ZEMANN, *Mineralogisch-Kristallographisches Institut der Universität Göttingen, Deutschland*

(Eingegangen am 2. August 1957)

Die Madelung'sche Zahl für den NiAs-Typ, welche sich in der bisherigen Literatur nicht findet (vgl. die Zu-

These positions gave satisfactory agreement (Table 1) between calculated and observed relative line intensities and are considered sufficient to identify the structure type. Temperature and absorption factors were not taken into account in the calculations of relative line intensities. No refinement of parameters has been attempted.

The possibility of the existence of related compounds in which treble or quadruple perovskite layers are interleaved with SrO layers was investigated by firing mixtures of the appropriate compositions, i.e. of SrCO₃ and TiO₂ in the molecular proportions 4:3 and 5:4. Examination of the reaction products showed the occurrence of Sr₄Ti₃O₁₀ but not of Sr₅Ti₄O₁₃. In the products from both compositions, Sr₄Ti₃O₁₀ was found associated with SrTiO₃ and Sr₃Ti₂O₇. The proportion of Sr₄Ti₃O₁₀ depended on the firing schedule. The proportions of SrTiO₃ and Sr₃Ti₂O₇ varied, indicating incomplete reaction, with unreacted strontium undetected by the X-ray analysis.

The lattice parameters of the tetragonal unit cell of Sr₄Ti₃O₁₀, which again contains two formula units, are

$$a = 3.90, \quad c = 28.1 \text{ \AA}, \quad c/a = 7.2$$

and the calculated density is 5.10 g.cm.⁻³. This cell has the same space group *I4/mmm* as for Sr₃Ti₂O₇, the proposed atomic positions for Sr₄Ti₃O₁₀ being

- (0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) +
 2 Ti_I in (a) 0, 0, 0.
 4 Ti_{II} in (e) 0, 0, z ; 0, 0, \bar{z} ; with $z = z_3$.
 4 O_I in (c) 0, $\frac{1}{2}$, 0; $\frac{1}{2}$, 0, 0.
 4 O_{II} in (e) with $z = z_1$.
 8 O_{III} in (g) 0, $\frac{1}{2}$, z ; 0, $\frac{1}{2}$, \bar{z} ; $\frac{1}{2}$, 0, z ; $\frac{1}{2}$, 0, \bar{z} ; with $z = z_4$.
 4 O_{IV} in (e) with $z = z_5$.
 4 Sr_I in (e) with $z = \frac{1}{2} - z_2$.
 4 Sr_{II} in (e) with $z = \frac{1}{2} - z_6$.

The z 's are related by $z_6 \simeq z_5 \simeq 3z_1$, $z_4 \simeq z_3 \simeq 2z_1$ and $z_2 \simeq z_1$. We have considered these equalities to hold exactly and taken $z_1 = 0.068_2$, to give $(\frac{1}{2} - 6z_1)/z_1 = 1.33$. The agreement between calculated and observed powder diffraction data is comparable with that for Sr₃Ti₂O₇, all lines with calculated intensities of 5% or more of that of the strongest line being observed.

We should like to express our thanks to Dr T. A. Ingles for preparing the samples and to Mr F. G. Wilde for taking the diffraction photographs. We wish to thank also Dr A. T. Green, Director of the British Ceramic Research Association, for permission to publish this communication.

Reference

- RUDDLESDEN, S. N. & POPPER, P. (1957). *Acta Cryst.* **10**, 538.

sammenstellungen von Molière (1955) und Hoppe (1956)), wurde nach der Ewald'schen Methode (Ewald, 1921) für