

## The Crystal Structure of $\alpha$ -Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub>

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The structure of the compound  $\alpha$ -Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub>, isotypic with Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>, was solved by trial-and-error powder methods. The unit cell is tetragonal with  $a=3.874$  and  $c=40.314$  Å, space group  $P4mmm$ .

### Introduction

The compound Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub>, with iron valence depending upon temperature, firing atmosphere and cooling rate, has been examined by several authors (Brisi, 1961; Batti, 1962; MacChesney, Williams, Sherwood & Potter, 1966; Brisi & Rolando, 1969).

Brisi (1961) and MacChesney *et al.* (1966) suggested an isomorphism between this compound and Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> (Ruddlesden & Popper, 1958) and established that the lattice parameters of this phase are a function of iron valence, with  $c$ -axis length about 20.12 Å. A further investigation, performed with high-temperature X-ray equipment by Lucchini, Minichelli & Slocari (1973), revealed the presence of several phases in Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub>; furthermore, the Guinier-de Wolff X-ray data showed that the phase investigated by Brisi (1961) and MacChesney *et al.* (1966), hereinafter called  $\alpha$ -Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub>, exhibits double length of the  $c$  axis. The present investigation was then undertaken to ascertain the real structure of this  $\alpha$ -phase.

### Experimental

The  $\alpha$ -Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub> phase was obtained by sintering pressed pellet mixtures of SrCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in a 3:1 molecular ratio in oxygen at 1250°C. The sintered product was air-quenched from 1250°C. The product obtained exhibited a tetragonal symmetry and a formula Sr<sub>3</sub>Fe<sub>2</sub>O<sub>6.16</sub> on iodometric determination of the percentage of Fe<sup>4+</sup>.

The reflexions of the samples were collected by means of a Guinier-de Wolff camera and a Siemens goniometer using Co  $K\alpha$  radiation. Intensities were recorded by means of a scintillation counter in conjunction with a pulse-height analyser.

Comparison between experimental and theoretical intensities was performed with a computer program (Smith, 1967). The measured intensities were corrected only with a Lorentz-polarization factor, and no absorption correction appeared necessary. At the last stage of refinement the coefficient  $T_0=3.0$  was introduced in the expression of the overall temperature factor ( $-T_0 \sin^2 \theta/\lambda$ ); no thermal parameter for each atom was considered.

### Determination of the structure

X-ray powder diagrams of the  $\alpha$ -Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub> form could be indexed on the basis of a tetragonal unit cell;

the presence of a reflexion line at a 13.5 Å  $d$ -value, however, showed that the lattice parameters suggested by Brisi (1961) and MacChesney *et al.* (1966) were not correct. A new tetragonal cell was then introduced, with  $a=b=3.874 \pm 0.002$  and  $c=40.314 \pm 0.018$  Å at room temperature ( $Z=4$ ,  $D_{\text{obs}}=5.1$ ,  $D_{\text{calc}}=5.19$  g cm<sup>-3</sup>). The structure determination was then carried out on the basis of the atomic skeleton of Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> (Ruddlesden & Popper, 1958); however, the space group proposed by these authors,  $I4/mmm$ , could not be assumed because 00 $l$  reflexions with  $l=2n+1$  were observed in our phase. Since the unique condition in  $I4/mmm$ ,  $h+k+l=2n$ , is absent in  $\alpha$ -Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub>, the choice of a space group with no condition was suggested for our compound. Hence the tetragonal space groups  $P4$ ,  $P\bar{4}$ ,  $P4/m$ ,  $P422$ ,  $P4mm$ ,  $P\bar{4}2m$ ,  $P\bar{4}m2$  and  $P4mmm$  were tested as possibilities; on the basis of structure refinement  $P4mmm$ , centrosymmetric, was chosen as definitive.

The atomic positions have been estimated by analogy with those of Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>; the best parameters for the atoms were collected by a trial-and-error procedure, based on comparison of observed and calculated intensities. The final coordinates show a slightly distorted lattice as suggested by the presence of the 003 reflexion which reduces the symmetry proposed by Brisi (1961) and MacChesney *et al.* (1966). The short calculated O-O distances occurring in the perovskite layers of the molecule are probably due to the partial vacancy of oxygen atoms in this sites.

Table 1. X-ray powder diffraction data of  $\alpha$ -Sr<sub>3</sub>Fe<sub>2</sub>O<sub>7-x</sub>  
Unobserved reflexions with  $I_c \ll 1$  are omitted.

$h$	$k$	$l$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$	$I_{\text{calc}}$
0	0	3	13.5	13.438	10.5	10.8
0	0	4	10.0	10.078	2	8.6
0	0	5		8.063	<1	<1
0	0	6	6.80	6.719	<1	<1
0	0	8	5.035	5.039	6.5	9.6
0	0	9		4.479	<1	5.1
1	0	2	3.794	3.804	6	2
0	0	11		3.665	<1	<1
1	0	4		3.616	<1	<1
1	0	5		3.492	<1	<1
0	0	12		3.359		6.7
1	0	6		3.356	7.1	4.4
1	0	7		3.214	<1	3.4
0	0	14		2.880	<1	2.4
1	0	10	2.793	2.793	100	100
1	1	0		2.739		80.1
1	1	1	2.738	2.733	75	0
1	1	2	2.708	2.714		0.1

Table 1 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>
0	0	15		2.688	< 1	1
1	1	3		2.683		0.7
1	0	11		2.662		2.8
1	1	4	2.642	2.643	2	0.1
1	0	12		2.538		0.2
1	1	6		2.536	1.5	0.2
0	0	16	2.521	2.520		1
1	0	13			2.421	< 1
1	1	8		2.407	< 1	4.3
0	0	17		2.371	< 1	< 1
1	1	9		2.337	< 1	2
1	0	14	2.311	2.311	6.1	6.7
1	0	15		2.208		< 1
1	1	11		2.194	< 1	< 1
1	1	12	2.123	2.123	22.5	20.7
0	0	19		2.122		0.1
1	0	16		2.112		1.2
1	1	13		2.053	< 1	< 1
1	0	17	2.018	2.023	10.3	0.5
0	0	20		2.016		9.5
1	1	14		1.986	< 1	< 1
1	0	18	1.936	1.939	45	0.9
2	0	0		1.937		46.8
2	0	1		1.935		0
0	0	21		1.920		1.3
1	1	15	1.916	1.918	3.3	2.1
2	0	3		1.917		0.3
1	0	19		1.861	< 1	2.1
1	1	16		1.854	< 1	6
2	0	9		1.778	< 1	1
0	0	23		1.753	< 1	< 1
2	1	2		1.726	< 1	< 1
0	0	24	1.679	1.680	5.5	1.7
2	0	12		1.678		2.4
2	1	6		1.6776		1
1	1	19		1.677		0.3
2	1	7	1.657	1.659	< 1	< 1
1	0	22		1.656		< 1
1	1	20	1.624	1.624	6.2	6.1
2	0	14		1.607		< 1
2	1	10	1.591	1.592	25	25.3
1	1	21		1.572		4
2	0	15	1.575	1.571	4.8	0.5
2	1	11		1.566		0.7
1	0	24		1.541	< 1	< 1
2	0	16		1.536	< 1	< 1
2	1	13		1.512	< 1	< 1
0	0	27	1.485	1.493	3	0.3
1	0	25		1.489		0.7
2	1	14		1.485		2.2
1	1	23		1.476	< 1	1
0	0	28		1.440	< 1	< 1
1	0	26		1.439	< 1	< 1
1	1	24	1.432	1.432	2.5	3.9
2	0	19		1.431		0.1
2	1	16		1.428	< 1	< 1
2	1	17	1.398	1.399	7.5	0.2
2	0	20		1.397		7
1	0	27		1.393		0
2	1	18		1.370		0.4
2	2	0	1.370	1.3697	9.5	9.3
2	2	1		1.369		0
2	2	2		1.367		0

The final reliability index, of the form  $R = \sum |I_o| - |I_c| / \sum |I_o|$  is about 0.16. Because of the heavy overlapping of many reflexions and because the refinement procedure was limited by our computing facilities, further refinement could not be expected to lead to a

Table 2. Final fractional coordinates

			<i>x</i>	<i>y</i>	<i>z</i>
2	Sr(1)	in (g)	0	0	0.155
2	Sr(2)	in (g)	0	0	0.240
2	Sr(3)	in (g)	0	0	0.342
1	Sr(4)	in (c)	$\frac{1}{2}$	$\frac{1}{2}$	0
1	Sr(5)	in (d)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
2	Sr(6)	in (h)	$\frac{1}{2}$	$\frac{1}{2}$	0.097
2	Sr(7)	in (h)	$\frac{1}{2}$	$\frac{1}{2}$	0.419
2	Fe(1)	in (g)	0	0	0.048
2	Fe(2)	in (g)	0	0	0.457
2	Fe(3)	in (h)	$\frac{1}{2}$	$\frac{1}{2}$	0.203
2	Fe(4)	in (h)	$\frac{1}{2}$	$\frac{1}{2}$	0.293
1	O(1)	in (a)	0	0	0
1	O(2)	in (b)	0	0	$\frac{1}{2}$
2	O(3)	in (g)	0	0	0.093
2	O(4)	in (g)	0	0	0.415
2	O(5)	in (h)	$\frac{1}{2}$	$\frac{1}{2}$	0.160
2	O(6)	in (h)	$\frac{1}{2}$	$\frac{1}{2}$	0.249
2	O(7)	in (h)	$\frac{1}{2}$	$\frac{1}{2}$	0.340
4	O(8)	in (i)	0	$\frac{1}{2}$	0.061
4	O(9)	in (i)	0	$\frac{1}{2}$	0.202
4	O(10)	in (i)	0	$\frac{1}{2}$	0.301
4	O(11)	in (i)	0	$\frac{1}{2}$	0.446

Table 3. Relevant interatomic distances (Å)

Sr(1)–Sr(2)	3.43	Sr(7)–O(11)	2.23
Sr(1)–O(3)	2.50	Fe(1)–O(1)	1.94
Sr(1)–O(9)	2.71	Fe(1)–O(3)	1.81
Si(2)–Fe(3)	3.12	Fe(1)–O(8)	2.01
Sr(2)–O(6)	2.76	Fe(2)–O(2)	1.73
Sr(2)–O(9)	2.47	Fe(2)–O(4)	1.70
Sr(3)–O(4)	2.94	Fe(2)–O(11)	1.99
Sr(3)–O(7)	2.74	Fe(3)–Fe(4)	3.63
Sr(3)–O(10)	2.55	Fe(3)–O(5)	1.73
Sr(4)–Sr(6)	3.91	Fe(3)–O(6)	1.85
Sr(4)–Fe(1)	3.35	Fe(3)–O(9)	1.94
Sr(4)–O(1)	2.74	Fe(4)–O(6)	1.77
Sr(5)–Sr(7)	3.27	Fe(4)–O(7)	1.89
Sr(5)–Fe(2)	3.24	Fe(4)–O(10)	1.94
Sr(5)–O(2)	2.74	O(2)–O(11)	2.91
Sr(5)–O(11)	2.92	O(3)–O(8)	2.34
Sr(6)–Fe(1)	3.38	O(4)–O(11)	2.33
Sr(6)–O(5)	2.54	O(5)–O(9)	2.57
Sr(6)–O(8)	2.42	O(6)–O(9)	2.71
Sr(7)–Fe(2)	3.14	O(6)–O(10)	2.85
Sr(7)–O(4)	2.75	O(7)–O(10)	2.35

more reliable structure. The final list of observed and calculated values of intensity is given in Table 1. In terms of the positions of the space group  $P4mmm$  the final fractional parameters are presented in Table 2 and the interatomic distances in Table 3.

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