

# Polymorphism in $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$

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The compound  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ , with variable iron valence, was investigated by X-ray powder techniques, both at room and at high temperatures. If the material is examined in massive form, a single phase called  $\alpha\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$  appears as previously reported in the literature. This  $\alpha$ -phase is tetragonal and exhibits the lattice parameters:  $a = 3.874$  and  $c = 40.314$  Å. Two other phases, called  $\beta$  and  $\gamma\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$ , respectively, can be obtained on heating the finely powdered material when laid on a flat platinum support. The  $\gamma$  form is stable up to  $1275^\circ\text{C}$ , while the  $\beta$  form is revealed only above  $1275^\circ\text{C}$  and changes always into  $\gamma\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$  when quenched. Both  $\beta$  and  $\gamma$  phases are tetragonal, with  $a = 4.001$  and  $c = 58.251$  for the  $\beta$  form and  $a = 4.013$ ,  $c = 57.092$  Å for the  $\gamma$  form. The transition  $\beta \leftrightarrow \gamma$  involves a true phase equilibrium, while the transformation  $\alpha \leftrightarrow \gamma$  is possible only by means of a suitable mechanical treatment of the material.

## 1. Introduction

The magnetic properties of strontium hexaferrite,  $\text{SrFe}_{12}\text{O}_{19}$ , are technologically important and have led to the disclosure of the phase relationships in the system  $\text{SrO-Fe}_2\text{O}_3$ . In this phase diagram compositions corresponding to  $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$ ,  $7\text{SrO} \cdot 5\text{Fe}_2\text{O}_3$ ,  $2\text{SrO} \cdot \text{Fe}_2\text{O}_3$  and  $3\text{SrO} \cdot \text{Fe}_2\text{O}_3$  occur as single phases [1]. A systematic study of the structural relationships in the mentioned compounds and in other alkaline earth ferrites was undertaken in this laboratory in order to contribute to the knowledge of their properties. Object of the present investigation is the characterization of  $3\text{SrO} \cdot \text{Fe}_2\text{O}_3$ , the most basic compound in the system  $\text{SrO-Fe}_2\text{O}_3$ .

The compound  $3\text{SrO} \cdot \text{Fe}_2\text{O}_3$  was examined by Brisi *et al* [2, 3] and by Mac Chesney *et al* [4]; these authors suggested the presence of partially tetravalent iron atoms placed in the centre of perovskite layers. The formula  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  was then assigned to this compound, with iron valence depending upon temperature, firing atmosphere and cooling rate.

Brisi [2] suggested an isomorphism between  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  and  $\text{Sr}_3\text{Ti}_2\text{O}_7$ ; the structure of the latter was reported by Ruddlesden and Popper [5].  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  was indexed according to a tetragonal symmetry [2, 3] with  $a$ -axis varying from 3.868 to 3.897 Å and  $c$ -axis from 20.140 to 20.060 Å as a function of decreasing  $\text{Fe}^{+4}$  percentage.

Mac Chesney *et al* [4] prepared  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$

at variable oxygen pressures and obtained a broad range of compounds with oxygen stoichiometry varying from  $\text{Sr}_3\text{Fe}_2\text{O}_6$  to  $\text{Sr}_3\text{Fe}_2\text{O}_{6.90}$ . These authors also suggested the mentioned isomorphism and yielded lattice parameters in good agreement with those proposed by Brisi *et al* [2, 3].

Brisi *et al* [2, 3] obtained their specimens by air quenching, by slow air cooling and by quenching in vacuum or in  $\text{CO} + \text{H}_2$  atmosphere, while Mac Chesney *et al* [4] did not report their cooling techniques; all these authors, according to the mentioned experimental procedures, detected the same type of phase.

Since other similar ferrites, with iron partially tetravalent, as  $2\text{BaO} \cdot \text{Fe}_2\text{O}_3$  and  $2\text{SrO} \cdot \text{Fe}_2\text{O}_3$  exhibit several crystal forms [3, 6-10], we have undertaken a systematic investigation of  $3\text{SrO} \cdot \text{Fe}_2\text{O}_3$  to ascertain the suspected polymorphism of this compound by observation of powder patterns of materials, both at high and room temperature.

## 2. Experimental

Mixtures of  $\text{SrCO}_3$  and  $\text{Fe}_2\text{O}_3$ , of reagent grade purity, were mixed in a 3:1 molecular ratio in agate mortar, pressed into pellets and pre-fired both in air and in oxygen in an electric resistance furnace at  $1200^\circ\text{C}$ . After quenching, the resulting crystalline material was reground, pressed again into discs and fired in a controlled atmosphere at  $1200^\circ\text{C}$  to attain phase equilib-

rium. This was checked by examining polished sections of the samples by reflected light microscopy and powdered specimens by X-ray diffraction techniques; equilibrium was considered to have been attained when no change in phase composition could be detected by the mentioned techniques.

The equilibrated specimens were then reheated at fixed temperatures ranging from 1350 to 500°C in controlled atmosphere, both in massive and in finely powdered form. The air-quenched products obtained were then examined by X-ray equipment. The percentage of  $\text{Fe}^{4+}$  in these samples was determined by iodometric titration [11]. Great care was taken to avoid the hydration of the specimens, since  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  easily absorbs water when in air atmosphere [1, 12].

X-ray powder diffraction data were recorded by a Guinier-de Wolff camera using  $\text{CuK}\alpha$  radiation; the reflections were also collected by means of a horizontal goniometer with a scintillation counter, using  $\text{CoK}\alpha$  radiation. A high-temperature attachment mounted on the goniometer permitted us to obtain powder diffraction data at various temperatures.

### 3. Results

Initially, the massive samples quenched from 1350°C were tested by X-ray powder diffraction methods; a single phase appeared as known from literature [2-4]. However, the possibility of obtaining reliable low angle data by means of the high resolution Guinier-de Wolff camera, permitted us to collect a reflection line of medium intensity at 13.5 Å  $d$ -value. This fact showed that the lattice parameters suggested by Brisi *et al* [2, 3] and Mac Chesney *et al* [4] were not correct. The powder pattern was then indexed on the basis of a new tetragonal unit cell by a computer program [13], with  $a = 3.874 \pm 0.002$  and  $c = 40.314 \pm 0.018$  Å and a formula  $\text{Sr}_3\text{Fe}_2\text{O}_{6.16}$  on iodometric determination of the percentage of  $\text{Fe}^{4+}$ . This phase, hereafter called  $\alpha\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$ , was subsequently obtained by quenching massive samples from various temperatures down to 850°C; the lattice parameters and the stoichiometry [11] of this  $\alpha$ -phase, the structure of which was recently established [14], are summarized as a function of equilibrium conditions in Table I.

The quenched massive specimens were then finely powdered and laid on a flat Pt-Pt/Rh 40% sample holder of the high-temperature attachment and heated to 1350°C in order to investigate the behaviour of the material at high

TABLE I Lattice parameters and composition of  $\alpha\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$

Composition	Temperature (°C)	$a$ (Å)	$c$ (Å)
$\text{Sr}_3\text{Fe}_2\text{O}_{6.18}$	850	3.873	40.335
$\text{Sr}_3\text{Fe}_2\text{O}_{6.17}$	1000	3.873	40.320
$\text{Sr}_3\text{Fe}_2\text{O}_{6.16}$	1250	3.874	40.314

temperatures. After 4 to 5 h at 1350°C, a new phase could be detected owing to the change of powder pattern. This phase, hereafter called  $\beta\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$ , exhibited a further reversible phase transformation on cooling the superimposed sample below  $1275^\circ \pm 20^\circ\text{C}$ . This new phase, called  $\gamma\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$ , is stable over the whole range of the temperatures up to 1275°C, because quenched or slowly cooled specimens of it showed no substantial change in X-ray diffraction pattern. The  $\beta$ -phase, instead, could be observed only in its thermal stability range and yielded by quenching always  $\gamma\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$ .

The existence of a polymorphism in  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  encouraged us to investigate the possibility of obtaining the  $\gamma$ -phase by other procedures. The massive samples were then finely powdered, reheated in a furnace at 1250°C and quenched both in air and in oxygen; the resulting X-ray pattern showed the presence of pure  $\alpha$ -phase. Pure  $\gamma$ -phase was obtained by quenching powdered samples previously laid on a platinum strip and heated at 1250°C in a furnace; the same procedure yielded only  $\gamma\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$  also from temperatures above 1275°C. If  $\gamma\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$ , however, was scratched out of its metallic support and reheated in furnace at 1250°C, the quenched product again exhibited only the  $\alpha$ -phase.

The X-ray Guinier-de Wolff powder pattern of the  $\gamma$ -phase, obtained by quenching specimens superimposed on a metallic support both in the high-temperature attachment and in furnace below 1275°C, exhibited two important reflection lines at low angles;  $\gamma\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$  was then indexed according to a tetragonal symmetry [13] with  $a = 4.013 \pm 0.003$  and  $c = 57.092 \pm 0.050$  Å and a formula  $\text{Sr}_3\text{Fe}_2\text{O}_{6.33}$  on iodometric determination of  $\text{Fe}^{4+}$ . The lattice parameters and the stoichiometry [11] of this  $\gamma$ -phase are reported in Table II as a function of equilibrium conditions.

The presence of low angle reflections could not be detected in  $\beta\text{-Sr}_3\text{Fe}_2\text{O}_{7-x}$ , because our high-temperature recording technique did not

TABLE II Lattice parameters and composition of  $\gamma$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ 

Composition	Temperature (°C)	$a$ (Å)	$c$ (Å)
$\text{Sr}_3\text{Fe}_2\text{O}_{6.47}$	800	4.002	57.135
$\text{Sr}_3\text{Fe}_2\text{O}_{6.40}$	1000	4.010	57.111
$\text{Sr}_3\text{Fe}_2\text{O}_{6.33}$	1250	4.013	57.092

enable us to investigate the Bragg interval below  $< 10^\circ 2\theta$ ; yet the indexing of the  $\beta$ -phase, belonging to a tetragonal symmetry, showed that the  $c$ -axis length was of the same order of magnitude as in the  $\gamma$ -phase and any attempt to reduce the  $c$ -axis failed to yield any significant convergence between experimental and calculated spacing values. The least-squares refined [13] lattice parameters of  $\beta$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  are  $a = 4.001 \pm 0.005$  and  $c = 58.251 \pm 0.080$  Å at 1350°C.

The experimental density for  $\alpha$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  is  $5.1 \text{ g cm}^{-3}$  by pycnometry methods ( $D_{\text{calc}} = 5.19 \text{ g cm}^{-3}$ ,  $Z = 4$ ); the calculated density values of the other phases are  $5.03 \text{ g cm}^{-3}$  for  $\beta$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  ( $Z = 6$ ) and  $5.15 \text{ g cm}^{-3}$  for  $\gamma$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  ( $Z = 6$ ).

The X-ray powder diffraction data of our phases are summarized in Tables III, IV and V, respectively. The spacing values were corrected for absorption using  $\text{Pb}(\text{NO}_3)_2$  as internal standard.

#### 4. Conclusions

Our investigation showed that the transition between  $\beta$  and  $\gamma$  forms is a reversible transformation depending on temperature, while both  $\alpha$  and  $\gamma$  forms are strictly correlated to their material appearance. Neither  $\alpha$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  changes into the  $\gamma$  form nor  $\gamma$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  into the  $\alpha$  form owing to a thermal treatment and, therefore, we cannot describe the transformation  $\alpha \leftrightarrow \gamma$  as a true phase change.

The  $\alpha$ -phase is stable over the whole range of temperatures up to the decomposition point and also the  $\gamma$  form, once obtained, changes into  $\alpha$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  only when heated and quenched after a mechanical treatment which reproduces the primitive conditions of the grain state. In spite of the absence of a true thermodynamic equilibrium between  $\alpha$  and  $\gamma$  phases, both these forms remain unaltered indefinitely until they are submitted to one of the above described procedures.

To justify partially these phenomena, various

TABLE III X-ray powder diffraction data of  $\alpha$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ 

$h k l$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$
0 0 3	13.5	13.438	m
0 0 4	10.0	10.078	vw
0 0 6	6.80	6.719	vvw
0 0 8	5.035	5.039	w
1 0 2	3.794	3.804	w
0 0 12	3.358	3.359	w
1 0 6		3.356	
1 0 10	2.793	2.793	vs
1 1 0	2.738	2.739	s
1 1 1		2.733	
1 1 2	2.708	2.714	w
1 1 4	2.642	2.643	vw
0 0 16	2.521	2.520	vw
1 0 14	2.311	2.311	w
1 1 12	2.123	2.123	ms
0 0 19		2.122	
1 0 17	2.018	2.023	m
0 0 20		2.016	
1 0 18	1.936	1.939	s
2 0 0		1.937	
2 0 1	1.916	1.935	w
0 0 21		1.920	
1 1 15	1.916	1.918	w
2 0 3		1.917	
0 0 24	1.679	1.680	w
2 0 12		1.678	
2 1 6	1.657	1.6776	vvw
1 1 19		1.677	
2 1 7	1.657	1.659	w
1 0 22		1.656	
1 1 20	1.624	1.624	w
2 1 10	1.591	1.592	ms
1 1 21	1.575	1.572	w
2 0 15		1.571	
2 1 11	1.485	1.566	w
0 0 27		1.493	
1 0 25	1.485	1.489	w
2 1 14		1.485	
1 1 24	1.432	1.432	w
2 0 19		1.431	
2 1 16	1.398	1.428	w
2 1 17		1.399	
2 0 20	1.398	1.397	w
1 0 27		1.393	
2 1 18	1.370	1.370	m
2 2 0		1.3697	
2 2 1	1.370	1.369	m
2 2 2		1.367	

Intensities: vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, vvw = very very weak

hypotheses may be advanced. A certain discrepancy in oxygen stoichiometry between  $\alpha$

TABLE IV X-ray powder diffraction data of  $\beta$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ 

$h k l$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$
0 0 10	5.78	5.825	vwv
0 0 12	4.853	4.854	w
1 0 12	3.098	3.087	m
1 1 3	2.803	2.800	vs
1 1 15	2.295	2.287	w
1 0 21	2.275	2.279	w
0 0 26	2.250	2.241	w
0 0 28	2.090	2.080	m
1 0 24	2.067	2.074	m
2 0 3	1.990	1.990	s
1 0 26	1.950	1.955	m
2 0 7		1.945	
2 1 4	1.775	1.776	vw
2 1 12	1.682	1.679	w
2 1 15	1.625	1.625	w
1 0 34	1.576	1.575	ms

Intensities: vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, vwv = very very weak

and  $\gamma$  phases could suggest a role of the percentage of  $\text{Fe}^{4+}$  in phase transformation; this phenomenon, however, is probably due to the great surface area of  $\gamma$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ , as involved in the experimental procedure, which aids the oxygen absorption in the lattice.

The experimental results suggest the grain constraint of the material to be an important factor in the appearance of several phases; the massive samples always yield a single phase, the same detected in previous investigations [2-4]. However, the simple powdering of the specimens is not sufficient to reveal the presence of  $\beta$  and  $\gamma$  phases, which appear only when the powder is laid on a platinum flat layer. All these features in the  $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$  behaviour seem therefore to suggest the existence of a complex mechanism regarding the formation of the  $\gamma$ -phase, which should be the object of further investigations.

Our X-ray powder techniques evidenced a remarkable  $c$ -axis length in all the phases. The ratio  $c/a$  is 10.4 for  $\alpha$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ , 14.6 for  $\beta$  and 14.2 for the  $\gamma$ -phase. The presence of a 003 reflection in the  $\alpha$  form implies a decrease of the symmetry proposed by Brisi [2] and Mac Chesney *et al* [4], thus suggesting a more distorted lattice; this hypothesis was confirmed in the structure determination of the  $\alpha$ -phase [14], belonging to  $P4mmm$  space group. No further structural work is contemplated at present for  $\beta$

TABLE V X-ray powder diffraction data of  $\gamma$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ 

$h k l$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$
0 0 3	18.1	19.03	w
0 0 4	14.1	14.27	w
0 0 10	5.70	5.709	vw
0 0 12	4.800	4.759	vw
1 0 4	3.868	3.864	vw
1 0 12	3.075	3.069	m
1 1 4	2.787	2.784	s
1 0 15	2.757	2.762	vs
1 1 5		2.754	
1 1 10	2.540	2.541	vw
1 0 21	2.250	2.251	m
1 1 16	2.224	2.221	vw
1 1 19	2.064	2.063	m
0 0 28	2.038	2.039	m
2 0 7	1.949	1.949	s
2 0 12	1.844	1.849	vwv
0 0 31		1.842	
2 0 13	1.824	1.825	vwv
1 1 24		1.823	
2 0 16	1.749	1.749	w
2 0 19	1.663	1.669	w
2 1 13		1.662	
2 1 15	1.623	1.623	vwv
2 0 21	1.611	1.614	w
1 0 33	1.591	1.589	s
2 0 22		1.588	
2 1 18	1.561	1.562	w
2 0 23		1.561	
2 2 7	1.396	1.398	w
0 0 41		1.393	
2 0 30	1.379	1.381	m
2 2 10		1.377	

Intensities: vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, vwv = very very weak.

and  $\gamma$  forms, because the great number of atoms in the unit cell greatly increases the evaluation difficulties. The presence of  $\text{Fe}^{4+}$  in  $\gamma$ - $\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ , however, suggests the existence of perovskite layers also in this phase.

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