

LETTERS TO THE EDITOR

The Synthesis and Structure of Sr_2FeO_4

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Strontium ferrate(IV), Sr_2FeO_4 , crystallizes with a tetragonal unit cell, $I4/mmm$, $a = 3.8642(1)$, $c = 12.3968(2)$ Å, and $V = 185.1$ Å³. The structure of this compound is of the K_2NiF_4 type as refined by Rietveld analysis of powder X-ray diffraction data. This material contains iron(IV) in a very slightly distorted octahedral environment (4×1.93) + (2×1.95). © 1991 Academic Press, Inc.

Introduction

Iron in the 4+ state is rarely found in mixed oxides though SrFeO_3 has been prepared by a number of workers, including ourselves, using high-pressure techniques (1–3). Fe^{4+} has the electronic configuration d^4 , and as such it would be expected to exhibit Jahn–Teller distortions in a high-spin configuration. However, SrFeO_3 exhibits cubic symmetry, with no sign of structural distortion down to 4.2 K. Early attempts at the preparation of Sr_2FeO_4 (4, 5) were not entirely successful, generally with only partial oxidation of the iron forming $\text{Sr}_2\text{FeO}_{4-8}$ and little structural characterization. Scholder *et al.* (1956) attempted the preparation of Sr_2FeO_4 using the thermal oxidation of some strontium/iron hydroxy salts under atmospheric oxygen pressure whereas MacChesney *et al.* (1966) using a method similar to ours, but at higher temperatures, produced a sample of composition $\text{Sr}_2\text{FeO}_{3.7}$.

In this letter we report the preparation of

Sr_2FeO_4 under high oxygen gas pressures and its structural characterization using powder X-ray diffraction methods.

Experimental

SrCO_3 and Fe_2O_3 , in a 4:1 molar ratio, were intimately ground and fired at 1100°C for 24 hr; the product was reground and heated for a further 24 hr at 1300°C. Examination of the sample by powder X-ray diffraction revealed the presence of $\text{Sr}_3\text{Fe}_2\text{O}_{7-8}$ and SrO. Further heat treatments, including annealing in 1 atm of flowing O_2 gas, produced no change in sample composition beyond a small increase in oxygen content. The final conversion to Sr_2FeO_4 was achieved through annealing at 750°C under 200 atm of flowing O_2 gas for 24 hr. Initial powder X-ray data collected on a Siemens D5000 diffractometer showed complete conversion to a K_2NiF_4 type phase.

Structural Determination

Following initial identification of the phase, powder X-ray diffraction data were

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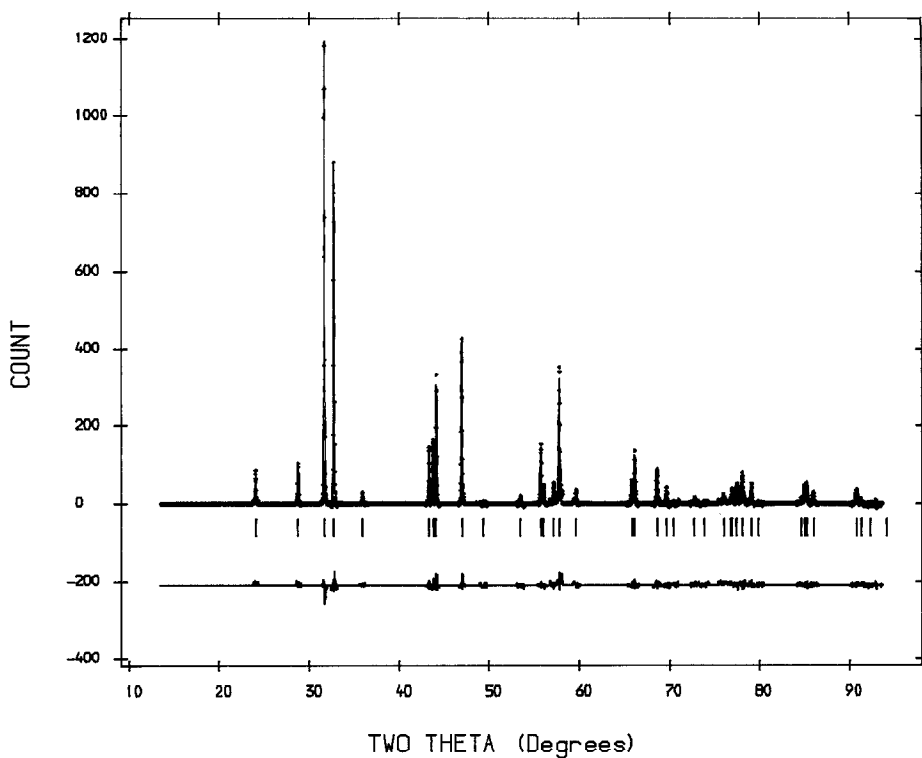


FIG. 1. Profile fit to powder X-ray data. Dots are the observed points, upper continuous line is the calculated profile, and lower continuous line is the difference. Tick marks show reflection positions.

collected in the range 13.5 to 93.5°C over a period of 9 hr. Monochromatic $\text{CuK}\alpha_1$ was employed together with a step size of 0.02°C. The data obtained could be fully indexed on a tetragonal unit cell of dimensions $a = 3.864$ and $c = 12.397$ Å in $I4/mmm$ and all further data analysis was undertaken in this space group. A version of the least-squares Rietveld (1966) (6) profile refinement program running on the Convex computer at the Daresbury Laboratory was used for the refinement. Background points were estimated where possible between peaks and data included in the 2θ range 20.0–93.5°C.

Initial stages of the refinement used the typical coordinates of the K_2NiF_4 structure, for example, those given by Soubeyroux *et*

al. (1981) for LaSrFeO_4 (7). Final stages of the refinement included all atomic coordinates and isotropic temperature factors for all atoms. Attempted refinement of the occupancies of the two oxygen sites resulted in only small deviations from unity that were within the e.s.d.'s; the occupancies were consequently fixed at that value. This was confirmed by thermogravimetric analysis during reduction under 5% H_2 in N_2 , which gave an oxygen content of 4.00 ± 0.05 ; powder X-ray diffraction and analysis of the reduced product revealed unequivocally a mixture of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ and SrO .

Final reliability factors achieved were $R_f = 3.70$, $R_{wp} = 8.01$, and $R_{exp} = 5.86$ and the profile fit is shown in Fig. 1. Refined atomic coordinates are summarized in Table

TABLE I
OBSERVED AND CALCULATED REFLECTION INTENSITIES FOR Sr_2FeO_4

<i>h</i>	<i>k</i>	<i>l</i>	2θ	I_{calc}	I_{obs}	<i>h</i>	<i>k</i>	<i>l</i>	2θ	I_{calc}	I_{obs}
1	0	1	24.07	432	471	2	2	0	68.61	796	764
0	0	4	28.75	548	597	1	1	8	69.67	361	322
1	0	3	31.64	6840	6721	2	2	2	70.50	12	13
1	1	0	32.71	5145	5211	1	0	9	72.81	88	115
1	1	2	35.85	143	143	3	0	1	73.88	39	22
1	0	5	43.29	867	866	2	2	4	76.04	169	238
0	0	6	43.75	1063	1103	0	0	10	76.80	46	112
1	1	4	44.12	1981	1985	2	1	7	77.01	364	375
2	0	0	46.96	2854	2868	3	0	3	77.54	511	467
2	0	2	49.33	60	28	3	1	0	78.12	744	734
2	1	1	53.46	156	128	2	0	8	79.14	445	452
1	1	6	55.70	1062	1053	3	1	2	79.92	17	5
2	0	4	56.01	378	354	3	0	5	84.71	98	129
1	0	7	57.14	384	395	2	2	6	85.02	474	482
2	1	3	57.75	2448	2587	3	1	4	85.28	520	489
0	0	8	59.58	279	282	1	1	10	86.02	276	260
2	1	5	65.79	431	418	1	0	11	90.76	427	411
2	0	6	66.13	1035	1029	2	1	9	91.28	101	106

II and derived interatomic distances in Table III. The observed and final calculated intensities are also given in Table I.

Discussion and Results

Sr_2FeO_4 crystallizes with the K_2NiF_4 structure (Fig. 2) but is unusual in that the coordination of the iron is almost perfectly octahedral. This is similar behavior to that seen for the cubic perovskite SrFeO_3 , where no Jahn–Teller distortion has been ob-

served, but in contrast to $\text{Sr}_3\text{Fe}_2\text{O}_{6.25}$ (9), where much greater distortions of the octahedra around Fe^{4+} are apparent. Bond valence calculations using the method devised by Brown (8), calculated using the parameters for an Fe^{3+} ion, gave a derived iron valency of 3.7; no parameters exist in the literature for Fe^{4+} .

The similar ionic radii of Cu^{2+} and Fe^{4+} coupled with the predisposition of these ions to Jahn–Teller like distortions leads to a comparable structural chemistry. This is re-

TABLE II
ATOMIC PARAMETERS AT 298 K; e.s.d.'s ARE GIVEN IN PARENTHESES

Atom	Site symmetry	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Sr	4 <i>e</i>	0	0	0.3570(1)	0.05(5)
Fe	2 <i>a</i>	0	0	0	0.39(9)
O1	4 <i>c</i>	0	0.5	0	0.58(24)
O2	4 <i>e</i>	0	0	0.1573(8)	0.33(20)

TABLE III
CALCULATED INTERATOMIC DISTANCES (Å); e.s.d.'s IN PARENTHESES

Atom	Distances
Sr–O2	1 × 2.475(9)
Sr–O1	4 × 2.623(1)
Sr–O2	4 × 2.738(1)
Fe–O1	4 × 1.932(1)
Fe–O2	2 × 1.950(9)

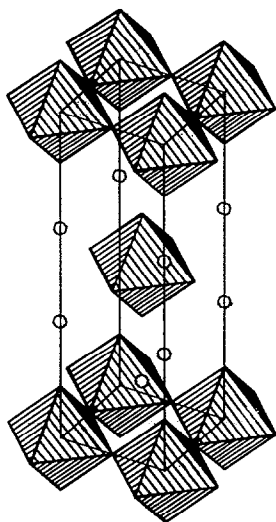


FIG. 2. STRUPLO (10) plot of Sr_2FeO_4 showing FeO_6 octahedra and strontium as open circles.

flected in the corresponding materials $\text{La}_2\text{CuO}_4/\text{Sr}_2\text{FeO}_4$, $\text{La}_2\text{SrCu}_2\text{O}_6/\text{Sr}_3\text{Fe}_2\text{O}_{7-x}$ and the belief that iron substitution into $\text{YBa}_2\text{Cu}_3\text{O}_7$ produces Fe^{4+} on the copper sites. It is therefore possible that the electronic properties found in Ln_2CuO_4 materials following doping may be paralleled in the Sr_2FeO_4 system. We are therefore investigating the possibilities of hole and electron

conduction in this material following substitutions of sodium and lanthanum.

Preliminary electrical measurements on Sr_2FeO_4 , using a four-probe rig, down to 77 K showed typical small band-gap semiconductor behavior with near metallic resistivity at 298 K.

Acknowledgments

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