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Fluorination of perovskite-related phases of composition $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$

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Abstract

Perovskite-related compounds of composition $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($x = 0.31, 0.54$) have been prepared. X-ray powder diffraction shows that the materials adopt orthorhombic unit cells. The lattice parameters increase with the incorporation of increasing amounts of tin, which is shown by x-ray absorption near edge structure investigation to be present as Sn^{4+} . ^{57}Fe Mössbauer spectroscopy indicates that iron in these phases is present as Fe^{5+} and Fe^{3+} and that the materials adopt the compositions $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.94}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.88}$. We propose that the disproportionation of Fe^{4+} in $\text{SrFeO}_{3-\delta}$ to Fe^{5+} and Fe^{3+} in $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ is driven by the reduction of local lattice strain.

The materials have been fluorinated by reaction with poly(vinylidene fluoride) to give products of composition $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.31}\text{F}_{0.69}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.54}\text{F}_{0.46}$. The increased iron to oxygen or fluorine distances as revealed by the extended x-ray absorption fine structure are associated with the reduction of Fe^{5+} to Fe^{3+} as evidenced by ^{57}Fe Mössbauer spectroscopy. The ^{57}Fe Mössbauer spectra recorded from the fluorinated materials at low temperature show the coexistence of magnetic sextet and non-magnetic doublet components corresponding to networks of Fe^{3+} coupled through oxide ions. The Sn^{4+} ions disrupt the coupling and the size of the networks. The magnetic susceptibility measurements and Mössbauer spectra recorded between 4.2 and 300 K are used to model the magnetic properties of these materials, with the larger networks appearing to possess random spin orientations consistent with spin glass-type materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recent years have seen renewed interest in the development of new materials with a perovskite-related structure, ABO_3 , in which the B-site cations occupy octahedral oxygen coordination and the A-site cations adopt twelve-fold oxygen coordination. The nature and stoichiometry of the A- and B-site cations determine the physical properties of the compounds and, for many years, substitution on the cation sublattice has been used to manipulate the properties of perovskite-related materials. For example, strontium ferrite, $\text{SrFeO}_{3-\delta}$, is an oxygen deficient metallic conductor which has attracted interest for some time [1], but the substitution of iron by

tin to give materials of the type $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ leads to the generation of magnetic [2]-, electronic- and oxide-ion conduction [3, 4] properties.

There has also been considerable interest in recent years in substitution on the anion sub lattice of perovskite-related structures. Much of the attention has focussed on superconducting cuprate-related systems prepared using fluorinating agents such as gaseous fluorine, NH_4F , MF_2 ($\text{M} = \text{Cu}, \text{Ni}, \text{Zn}$) and XeF_2 . The novel method of fluorination which entails heating a precursor oxide with the polymer poly(vinylidene fluoride) [5] to form high quality products without significant impurities has opened up new opportunities for the fluorination of oxides and we have recently used this method to fluorinate the $\text{SrFeO}_{3-\delta}$ phase [6, 7].

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Table 1. Lattice parameters for materials of composition $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ and their fluorinated derivatives.

Samples	Lattice parameters (Å)	Primitive pseudo-cubic cell volumes (Å ³) ^a
$\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}$	Orth, $a = 5.580(1)$, $b = 5.576(1)$, $c = 7.825(1)$	60.8
$\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}/\text{F}$	Orth, $a = 5.644(1)$, $b = 5.643(1)$, $c = 7.973(1)$	63.4
$\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}/\text{F}$ (following heating at 400 °C in air)	Orth, $a = 5.648(2)$, $b = 5.646(7)$, $c = 7.935(4)$	63.2
$\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$	Orth, $a = 5.578(1)$, $b = 5.653(1)$, $c = 7.989(1)$	62.9
$\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}/\text{F}$	Orth, $a = 5.674(1)$, $b = 5.653(1)$, $c = 8.026(1)$	64.3
$\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}/\text{F}$ (following heating in air at 400 °C)	Orth, $a = 5.681(4)$, $b = 5.640(2)$, $c = 8.027(9)$	64.3

^a The primitive pseudo-cubic cell volumes are quoted to permit direct comparison between samples.

We report here on the synthesis and fluorination of compounds in the $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ system and on the effects of fluorination on the cationic oxidation states and magnetic properties of the pure oxides.

2. Experimental techniques

Compounds of composition $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($x = \text{about } 0.3, 0.5$) were prepared by the calcination of appropriate quantities of well ground strontium(II) carbonate, α -iron(III) oxide and tin(IV) oxide at 1250 °C for 24 h in air. Fluorination was achieved by mixing the $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ phase with poly(vinylidene fluoride) in a 1:0.75 molar ratio (precursor oxide: CH_2CF_2 monomer unit) and heating the mixture at 400 °C for 24 h in flowing nitrogen.

X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ radiation at 298 K. Fe K- and Sn K-edge x-ray absorption spectra were recorded at the Synchrotron Radiation Source at Daresbury Laboratory UK with an average current of 200 mA at 2 GeV. The data were collected at 298 K in transmission geometry on Station 7.1 (Fe K-edge) and Station 9.2 (Sn K-edge). The samples were examined as pressed discs. The position of the Sn x-ray absorption edge was defined as the energy at which the normalized absorption was 0.5, i.e. the absorption at half-height of the edge step. The EXAFS oscillations were isolated after background subtraction of the raw data using the Daresbury program EXBACK and converted into k space. The data were weighted by k^3 , where k is the photoelectron wavevector, to compensate for the diminishing amplitude of EXAFS at high k . The data were fitted [8] using the Daresbury program EXCURV98.

The ^{57}Fe Mössbauer spectra were recorded with a constant acceleration spectrometer using a about 25 mCi $^{57}\text{Co}/\text{Rh}$ source. The ^{57}Fe Mössbauer chemical isomer shift data are quoted relative to metallic iron at 298 K.

DC susceptibility measurements were performed over the temperature range 5–300 K using a Quantum Design SQUID

magnetometer. An applied measuring field of 0.01 T and a cooling field of 0.1 T were used.

3. Results

3.1. X-ray diffraction and x-ray absorption spectroscopy

The x-ray powder diffraction patterns recorded from the pure oxides, which were shown by ICP analysis to have compositions of $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$ similar to those expected from the reactant compositions and consistent with the formation of single phase materials, are shown together with those recorded from the fluorinated derivatives in figure 1. The lattice parameters are collected in table 1.

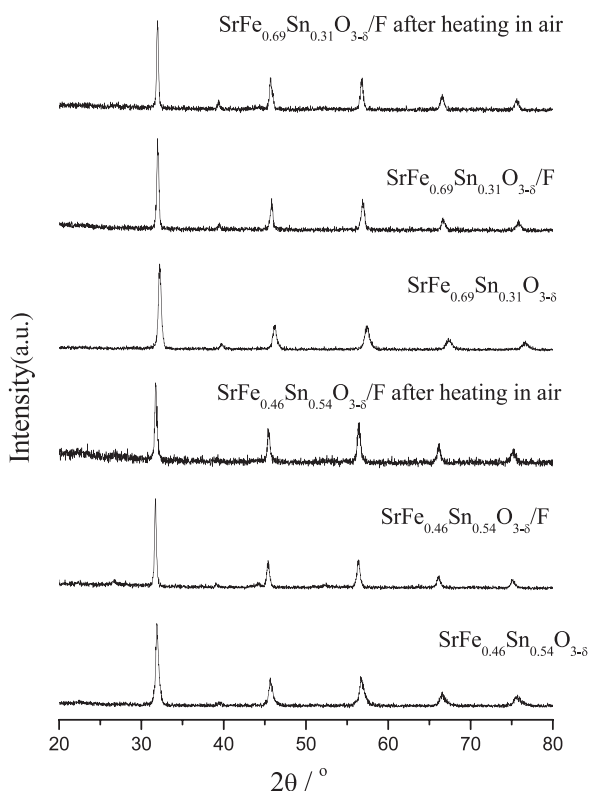
The x-ray powder diffraction data showed $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$ to be orthorhombic. It would seem from previous work [2, 4] that materials with similar composition can be formed with either cubic or orthorhombic unit cells and that such structural differences reflect the method of preparation. The lattice parameter data show a general increase in unit cell size with increasing tin content. Given that the ionic size [9] of Sn^{4+} in six-fold coordination (0.69 Å) is larger than that of octahedrally coordinated Fe^{4+} (0.58 Å) then the expansion of the unit cell size can be associated with incorporation of increasing amounts of the larger Sn^{4+} ion.

The expansion of the unit cell when the compounds $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$ were fluorinated (table 1, figure 1) reflects the reduction of high oxidation state iron to Fe^{3+} upon fluorination (*vide infra*). The observation that the lattice parameters of the fluorinated phases did not change upon heating at 400 °C in air (table 1, figure 1) indicates that fluorination involves substitution of the oxygen sublattice as opposed to simple oxygen loss.

The Fe K-edge EXAFS of the materials of composition $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ showed iron to be surrounded by six oxygen atoms at a distance of about 1.92 Å in the first coordination shell. The first shell coordination of the fluorinated materials

Table 2. ^{57}Fe Mössbauer parameters recorded from compounds of composition $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$.

Compound	Temperature of measurement (K)	Assignment	$\delta \pm 0.01$ (mm s^{-1})	$\Delta \pm 0.05$ (mm s^{-1})	Area $\pm 5\%$
$\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}$	300	Fe^{5+}	-0.05	0.43	42
		Fe^{3+}	0.32	0.82	58
	77	Fe^{5+}	0.03	0.44	42
		Fe^{3+}	0.44	0.86	58
$\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$	300	Fe^{5+}	-0.07	0.43	26
		Fe^{3+}	0.32	0.87	74
	77	Fe^{5+}	0.03	0.39	25
		Fe^{3+}	0.42	0.89	75

**Figure 1.** X-ray powder diffraction patterns recorded from materials of composition $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$ and their fluorinated derivatives at 298 K and after heating the fluorinated derivatives in air at 400 °C for 2 h.

could not be resolved into six distinguishable oxygen and fluorine atoms but, assuming a mixture of both, the distance of about 1.94 Å indicates an increase in distance.

The x-ray powder diffraction data and the EXAFS results are consistent with the partial replacement of O^{2-} by F^- leading to a reduction in the transition metal oxidation state to Fe^{3+} (*vide infra*) and consequently longer bond distances and a larger unit cell. No evidence was observed in the tin K-edge EXAFS for a change in the tin-anion distances (about 2.04 Å) in the octahedral coordination of tin upon fluorination.

The x-ray absorption edge positions of tin in compounds of the type $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($29\,202.6 \pm 0.1$ eV) were deduced from the Sn K-edge x-ray absorption near edge structure (XANES) and were identical to those of tin dioxide recorded as a standard and showed that tin substitutes on the iron site as

Sn^{4+} . The x-ray absorption edge of the fluorinated derivatives ($29\,202.5 \pm 0.1$ eV) showed that tin undergoes no change in oxidation state upon fluorination.

3.2. Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectra recorded at 300 and 77 K from $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{3-\delta}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$ are shown in figure 2. The ^{57}Fe Mössbauer parameters are collected in table 2.

The initial fitting of these spectra was primarily directed at establishing the charge state of the iron ions and hence an evaluation of the oxygen stoichiometry. The classical method of deducing the iron charge state from a Mössbauer spectrum is via the chemical isomer shift where the screening of the 3s electron density at the nucleus by the 3d electrons yields a dependence of the chemical isomer shift upon 3d electron population which results in decreasing values of chemical isomer shift with increasing charge state of the iron. The analysis of Mössbauer spectra reported in the literature from related materials enables a correlation between iron charge state and chemical isomer shift. There is a large body of data recorded from iron-containing oxides at room temperature [10] which demonstrates a chemical isomer shift, δ , of about 0.33 mm s^{-1} for the charge state of Fe^{3+} . In previous studies [6, 7, 11] of strontium ferrites of the type $\text{SrFeO}_{3-\delta}$ the ^{57}Fe Mössbauer spectra have shown components with chemical isomer shifts of about 0.15 mm s^{-1} and 0.05 mm s^{-1} which have been attributed to iron charge states of $\text{Fe}^{3.5+}$ and Fe^{4+} respectively where $\text{Fe}^{3.5+}$ corresponds to fast electron sharing between Fe^{3+} and Fe^{4+} ions with a timescale smaller than 10^{-8} s at 298 K. In other work [12] systems of composition $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2$) were found to give Mössbauer spectra with components with chemical isomer shifts of about 0.33 mm s^{-1} and about -0.06 mm s^{-1} which were assigned to Fe^{3+} and Fe^{5+} . In previous studies [2, 4] of materials of composition $\text{SrSn}_{1-x}\text{Fe}_x\text{O}_{3-y}$ ($x = 0-1$) similar ^{57}Fe Mössbauer spectra were recorded at 298 K to those recorded here and shown in figure 2 and were fitted with similar parameters but the component with chemical isomer shift $-0.05 \pm 0.03 \text{ mm s}^{-1}$ was assigned as Fe^{4+} . From the discussion above we prefer to assign the components in table 2 with chemical isomer shift $-0.06 \pm 0.01 \text{ mm s}^{-1}$ to Fe^{5+} .

By using the assignments of charge states of Fe^{3+} and Fe^{5+} in $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ together with the fitted proportions

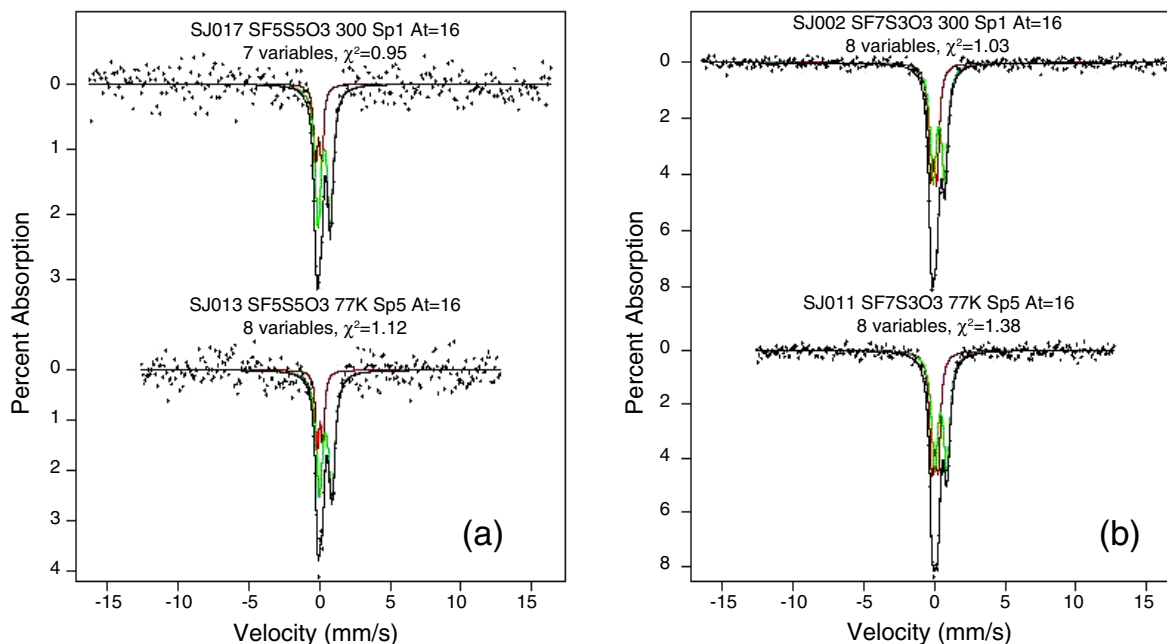


Figure 2. ⁵⁷Fe Mössbauer spectra recorded from (a) SrFe_{0.46}Sn_{0.54}O_{2.88} and (b) SrFe_{0.69}Sn_{0.31}O_{2.94} and at 300 and 77 K.

Table 3. ⁵⁷Fe Mössbauer parameters for the fluorinated compounds of SrFe_{1-x}Sn_xO_{3-δ}.

Compound	Temperature of measurement (K)	Assignment	$\delta \pm 0.02$ (mm s ⁻¹)	Δ or $e^2Qq/2 \pm$ 0.05 (mm s ⁻¹)	$H \pm 5$ (kG)	Area $\pm 5\%$
SrFe _{0.69} Sn _{0.31} O _{2.94} /F	300	Fe ³⁺	0.38	1.01		53
		Fe ³⁺	0.45	0.00	408	47
	200	Fe ³⁺	0.45	1.15		34
		Fe ³⁺	0.49	-0.12	488	43
	100	Fe ³⁺	0.49	-0.40	298	23
		Fe ³⁺	0.46	1.09		10
		Fe ³⁺	0.51	-0.09	510	41
		Fe ³⁺	0.48	-0.01	431	49
	10	Fe ³⁺	0.49	-0.08	546	40
		Fe ³⁺	0.49	-0.07	501	60
SrFe _{0.46} Sn _{0.54} O _{2.88} /F	300	Fe ³⁺	0.39	0.99		100
		Fe ³⁺	0.50	1.09		69
	100	Fe ³⁺	0.50	0.10	489	31
		Fe ³⁺	0.51	1.11		57
	50	Fe ³⁺	0.57	-0.22	519	43
		Fe ³⁺	0.48	1.11		9
10	Fe ³⁺	0.48	-0.28	487	63	

for each of these ions and assuming the presence of other charge states as Sr²⁺, Sn⁴⁺ (XANES results *vide supra*) and O²⁻, the compositions of the samples were determined as SrFe_{0.69}Sn_{0.31}O_{2.94±0.03} and SrFe_{0.46}Sn_{0.54}O_{2.88±0.03} where the uncertainty for the oxygen stoichiometry derives from an estimated 5% error on the proportions of the fitted Fe³⁺ and Fe⁵⁺ components.

The possible causes for the disproportion of Fe⁴⁺ in SrFeO_{3-δ} into Fe³⁺ and Fe⁵⁺ in SrFe_{1-x}Sn_xO_{3-δ} are considered later (*vide infra*) but we do note here that increasing the tin content appears to give a smaller proportion of Fe⁵⁺ (table 2). The decrease in the percentage of iron giving a peak at about -0.05 mm s⁻¹ with increasing amounts of substituted tin is consistent with earlier reports [4].

The ⁵⁷Fe Mössbauer spectra recorded from the fluorinated compounds of SrFe_{0.69}Sn_{0.31}O_{2.94} and SrFe_{0.46}Sn_{0.54}O_{2.88} over the temperature range 10–300 K are shown in figures 3 and 4 respectively. The fitted ⁵⁷Fe Mössbauer parameters are listed in table 3.

Several features concerning the nature of the fluorinated compounds are immediately evident from the spectra.

- (i) All the iron is present as Fe³⁺.
- (ii) All the spectra, except that recorded from fluorinated SrFe_{0.46}Sn_{0.54}O_{2.88} at 300 K, show the coexistence of magnetic (sextet) and non-magnetic (doublet) components.
- (iii) The proportion of the sextet component decreases with increasing tin content and with increasing temperature.

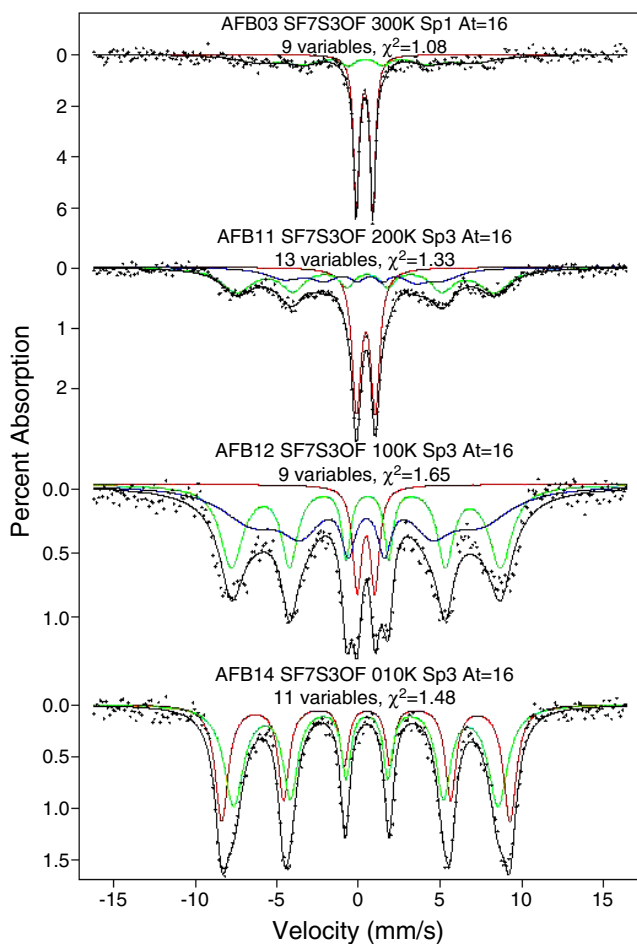


Figure 3. ^{57}Fe Mössbauer spectra recorded from $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.31}\text{F}_{0.69}$ in the temperature range 10–300 K.

Quantitatively the results show that with all the iron present as Fe^{3+} and with fluorine present as F^- the composition of the samples may be evaluated as $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.31}\text{F}_{0.69}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.54}\text{F}_{0.46}$. The result demonstrates that fluorination involves the replacement of some oxide ions by fluoride ions as well as the filling of vacant anion sites by fluoride ions.

The coexistence of the sextet and doublet components in the ^{57}Fe Mössbauer spectra suggests the presence of clusters or networks of coupled Fe^{3+} ions with the coupling being broken by Sn^{4+} ions which consequently limits the size of the networks. Hence networks larger than a critical size, at a given temperature, give rise to the magnetic sextet components whilst those less than the critical size give rise to the non-magnetic doublet component. It is apparent that the increasing tin content results in increased disruption of the magnetically coupled networks and an increase in the non-magnetic component in the ^{57}Fe Mössbauer spectrum. Similarly, for a given tin content, increasing temperature induces more facile disruption of the magnetically ordered networks such that the temperature at which the doublet and sextet components have equal areas—the blocking temperature in superparamagnetism terminology—may be evaluated as $T_B = 275 \pm 10$ K for $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.31}\text{F}_{0.69}$ and $T_B = 40 \pm 5$ K for $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.54}\text{F}_{0.46}$.

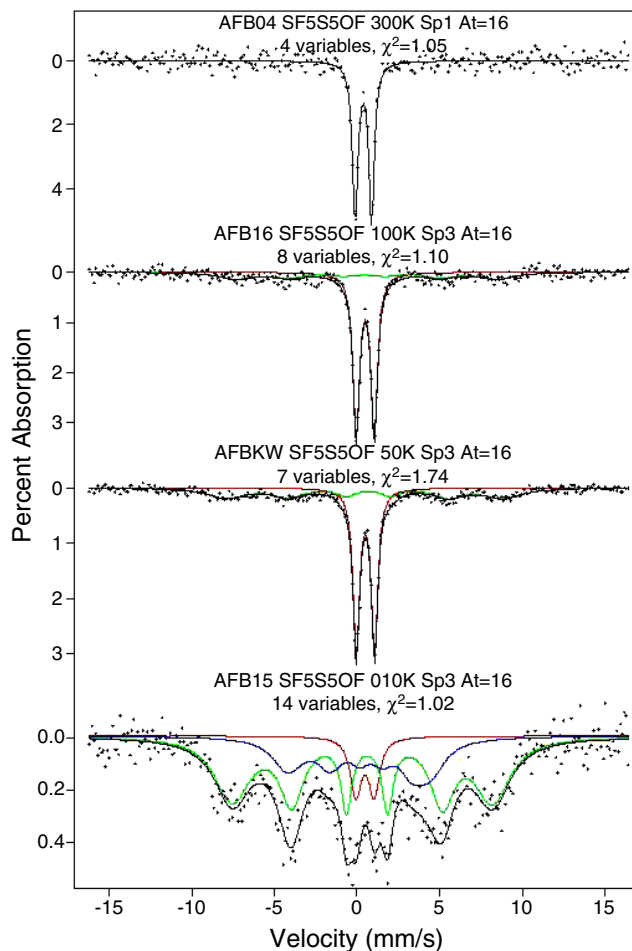


Figure 4. ^{57}Fe Mössbauer spectra recorded from $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.54}\text{F}_{0.46}$ in the temperature range 10–300 K.

3.3. Magnetic susceptibility

The magnetic susceptibility of the materials of composition $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.94}$, $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.88}$, $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.31}\text{F}_{0.69}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.54}\text{F}_{0.46}$ were measured over the temperature range 5–300 K. The samples were cooled to 5 K in zero field (ZFC) and also in an applied field of 0.1 T (FC) and values of χ measured whilst warming in a field of 0.01 T. The results are shown in figure 5.

The results show several features:

- (i) In all cases there is a separation between the zero field cooled and the field cooled data showing that the magnetic response is not purely paramagnetic and that magnetic interactions exist between the iron ions.
- (ii) The magnetic interactions between the iron ions extend over the whole of the measured temperature range and above 300 K.
- (iii) The values of $\chi \text{ mol}^{-1}$ are small. Indeed, the values of $\chi \text{ mol}^{-1}$ estimated from an assumed paramagnetic response from iron ions with moments of $5\mu_B$ are close to the field cooled values. Thus the interactions of the iron ions have a predominantly antiferromagnetic character.

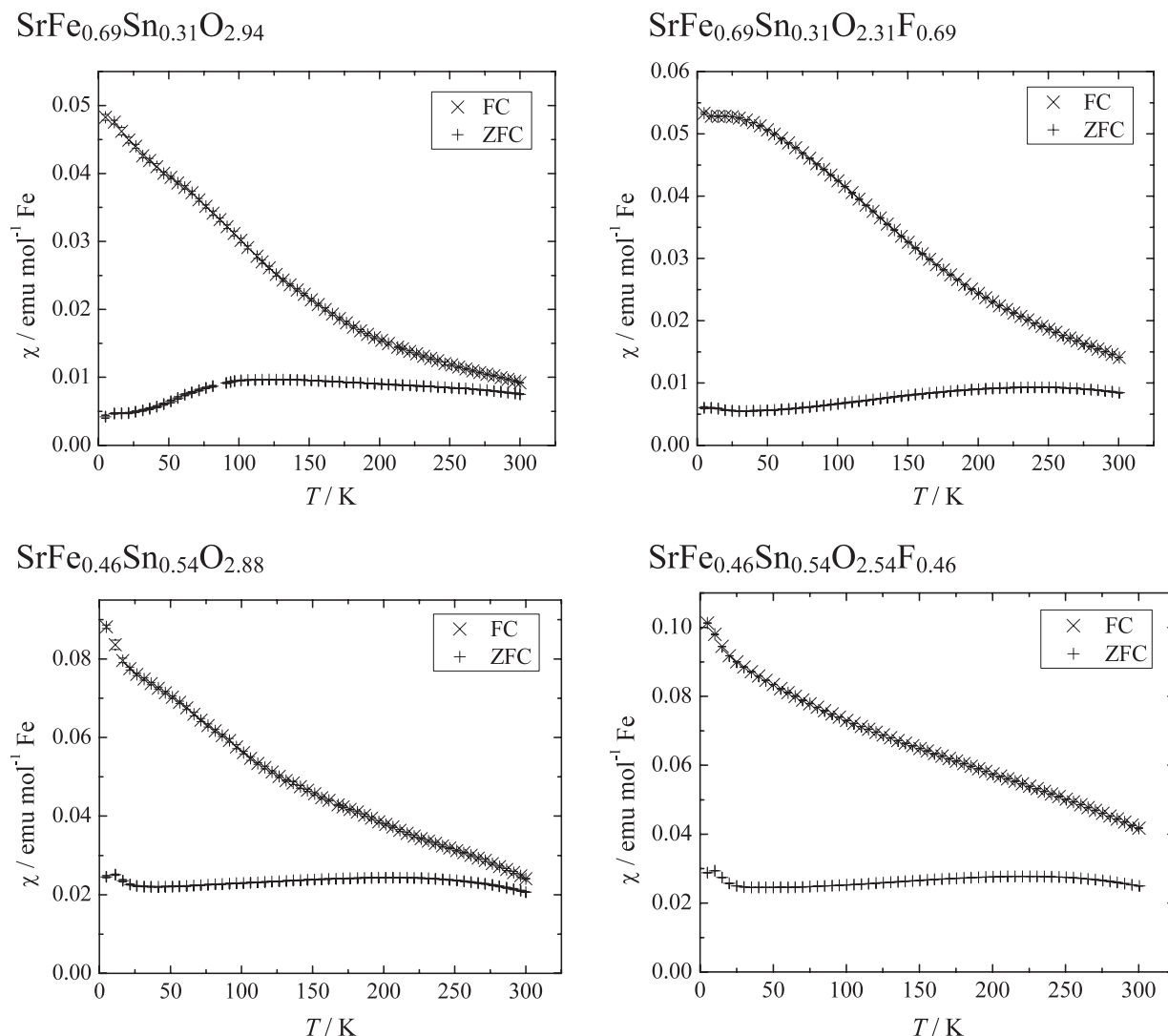


Figure 5. Variation of magnetic susceptibility with temperature for the oxides $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.94}$, $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.88}$ and the oxide fluorides $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.31}\text{F}_{0.69}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.54}\text{F}_{0.46}$.

4. Discussion

The results reported here establish

- (i) An expansion of the lattice when Sn^{4+} ions are incorporated into the parent $\text{SrFeO}_{3-\delta}$ phase and a further lattice expansion upon fluorination of the $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ phases.
- (ii) The disproportionation of Fe^{4+} in $\text{SrFe}^{4+}\text{O}_{3-\delta}$ into Fe^{3+} and Fe^{5+} upon incorporation of Sn^{4+} ions in the compounds of composition $\text{SrFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ with the proportion of Fe^{5+} being smaller in the compound with higher tin content.
- (iii) The reduction of iron to produce only Fe^{3+} ions in the fluorinated compounds.
- (iv) The coexistence of magnetic sextet and non-magnetic doublet components in the ^{57}Fe Mössbauer spectra recorded from the fluorinated materials with the proportion of the doublet component increasing with increased tin content and increased temperature.

- (v) The separate variation of χ with temperature for field cooled and zero field cooled conditions between 5 and 300 K. The value of χ for the zero field cooled variation lies significantly below the estimate for a paramagnetic response.

The main features to rationalize appear to be the disproportionation of Fe^{4+} into Fe^{3+} and Fe^{5+} upon doping $\text{SrFeO}_{3-\delta}$ with Sn^{4+} and the nature of the magnetic state in both the pure oxides and in the fluorinated materials.

Disproportionation by the iron charge state has been reported [13] previously when $\text{SrFeO}_{3-\delta}$ was doped with 1% Sn^{4+} and charge states of Fe^{3+} , Fe^{4+} and Fe^{5+} were observed. The reason suggested for the disproportionation was that in a material in which the lattice parameters are determined by the parent $\text{SrFeO}_{3-\delta}$ phase, strains caused by substituting Fe^{4+} by a larger Sn^{4+} ion are mitigated by adjacent unit cells incorporating a smaller Fe^{5+} ion with the concomitant formation of Fe^{3+} ions (some of which are already present because of oxygen deficiency) to retain electrical neutrality. This demonstration of disproportionation

on incorporation of such a low level of tin would suggest inherent instability in the parent compound.

In the work reported here the tin content greatly exceeds the 1% level of doping in the previous work [13] but the same process may still operate with unit cells incorporating the smaller Fe^{5+} ions being adjacent to cells with the larger Sn^{4+} ion. However the results recorded here from materials with larger amounts of tin failed to show evidence for the presence of Fe^{4+} and thereby indicate complete disproportionation of Fe^{4+} to Fe^{3+} and Fe^{5+} . Furthermore, as the tin content increases the lattice dimensions also increase as demonstrated in table 1. For the compounds with tin content $x = 0.31$ and 0.54 the primitive unit cell volumes are 5.4% and 9.1% greater than the parent $\text{SrFeO}_{3-\delta}$ phase respectively. The increased lattice dimension, particularly for $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{3-\delta}$ may help stabilize the large Fe^{3+} ion such that, although disproportionation of Fe^{4+} to Fe^{5+} and Fe^{3+} continues to occur, the Fe^{3+} content is larger and gives rise to a lower oxygen content. Hence the increased tin content results in an easing of the strain around the Sn^{4+} ions with the result that a smaller proportion of Fe^{5+} ions is required. This is in line with the results contained in table 2 where for the compound in which the tin content $x = 0.31$ the proportion of Fe^{5+} is 42% whilst for the compound with the higher tin content, $x = 0.54$, the proportion of iron present as Fe^{5+} is lower at 26%. Hence we propose here that the disproportionation of Fe^{4+} into Fe^{5+} and Fe^{3+} is driven by energy reduction associated with reducing local lattice strain.

In the fluorinated compounds, in which all iron is in the Fe^{3+} charge state interacting via $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ and $\text{Fe}^{3+}\text{-F}^-\text{-Fe}^{3+}$ superexchange pathways a parent material may be considered to be SrFeO_2F in which a spin-glass like state is reported to exist [7]. The present materials differ from this parent in the substitution of relatively large proportions of Sn^{4+} ions for Fe^{3+} ions. This substitution of non-magnetic for magnetic ions will block superexchange pathways dividing the magnetic material into clusters or networks with a range of sizes. It is proposed that—in a model that resembles superparamagnetism—the larger networks have a temporal stability that allows the establishment of a hyperfine field and give rise to a sextet component in the Mössbauer spectrum while in the smaller networks the fluctuations give rise to a net zero hyperfine field and the doublet component in the Mössbauer spectrum. This picture is qualitatively in agreement with the relative increase in the doublet component in the Mössbauer spectra when the tin content is increased and when the temperature is increased.

An insight into the nature of the magnetic clusters or networks arises from a consideration of the quadrupole interaction in the sextet- and doublet-components of the Mössbauer spectra. The Mössbauer spectra of the non-magnetic doublet components show quadrupole splittings of about 1.0 mm s^{-1} with a linewidth of about 0.4 mm s^{-1} but in the magnetic sextet components the apparent quadrupole interaction is about 0.0 mm s^{-1} and the linewidth is significantly increased. The decrease in apparent quadrupole interaction between the doublet and sextet components can occur if the angle θ between the direction of the hyperfine field

and the principal axis of the electric field gradient gives rise to the relation $(3 \cos^2 \theta - 1) \sim 0$; but if the angle θ is unique then no extra line broadening should occur in the sextet component. The observation of a large increase in linewidth between the doublet and sextet components indicates that there is a range of values of θ in these materials. The fact that the materials show good crystalline structure, as shown by powder x-ray diffraction and also by the small linewidths in the quadrupole split Mössbauer spectra, suggests that the range of θ values arises from a spin glass-type of spin array that has the temporal stability to give rise to the observed hyperfine field.

We are thus led to a model where the random substitution of a large proportion of tin ions onto iron sites causes disruption of the $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ and $\text{Fe}^{3+}\text{-F}^-\text{-Fe}^{3+}$ coupling breaking the magnetic order into clusters or networks of different sizes which contribute to sextet or doublet components of the Mössbauer spectra according to size and temperature.

The oxide materials $\text{SrFe}_{0.69}\text{Sn}_{0.31}\text{O}_{2.94}$ and $\text{SrFe}_{0.46}\text{Sn}_{0.54}\text{O}_{2.88}$ exhibit separated field cooled and zero field cooled variations of χ with temperature which indicate the effect of magnetic interactions up to and above 300 K. In these materials the magnetic interactions between iron ions are expected to be weaker than those in the oxide fluorides because of the presence of Fe^{5+} ions with smaller moments and because of anion vacancies that disrupt superexchange interactions. It is thus proposed that the absence of sextet components in the Mössbauer spectra of the oxides at 77 K is due to the weaker magnetic interactions not being able to sustain the stability to establish a hyperfine field. It is also possible that a weak sextet with some line broadening would be difficult to distinguish from the background in the spectra recorded from the pure oxides. It is thus concluded that the magnetic structure of the oxides is similar to that of the oxide fluorides but that the magnetic interactions in the pure oxides are substantially weaker.

5. Conclusion

The substitution of Sn^{4+} onto Fe^{4+} sites in $\text{SrFeO}_{3-\delta}$ induces disproportionation of Fe^{4+} into Fe^{5+} and Fe^{3+} to reduce lattice strain. Fluorination of tin-doped strontium ferrite gives materials containing iron only as Fe^{3+} . Magnetic interactions between iron ions are evident in both the oxides and the oxide fluorides up to room temperature but the presence of Sn^{4+} ions, which break the superexchange pathways between the iron ions, causes segmentation of the magnetic state into clusters with a range of sizes.

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