

## Fluorination- and Reduction- of Strontium Ferrite-Related Phases

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The fluorination of perovskite-related  $\text{SrFeO}_{3-\delta}$  by a low temperature reaction with poly(vinylidene fluoride) to give the compound  $\text{SrFeO}_2\text{F}$  involves the partial replacement of oxygen by fluorine and consequent reduction in the oxidation state of iron. The magnetic properties of the fluorinated material result from interactions between  $\text{Fe}^{3+}$  ions which are not possible in oxides containing only  $\text{Fe}^{4+}$ . The treatment in flowing 90% hydrogen/10%nitrogen of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  (which contains 50%  $\text{Fe}^{4+}$  and 50%  $\text{Fe}^{3+}$ ) at 650°C results in the formation of an oxygen-deficient perovskite-related phase containing only  $\text{Fe}^{3+}$ . Further heating in the gaseous reducing environment at 1150°C results in the formation of  $\text{K}_2\text{NiF}_4$ -related  $\text{SrLaFeO}_4$  and metallic iron.

### 1 Introduction

Perovskite-related oxygen-deficient materials have been the subject of interest for some time partly because of unusual physical properties and partly because of potential applications in high temperature fuel cells, catalysts and sensors [1-4]. Some of these applications involve operation under reducing conditions yet the nature of reduced phases in these systems is poorly understood. Similarly, the possibility of changing the properties of perovskite-related oxides by fluorination has recently attracted significant interest with much of the work focusing on the superconducting properties of cuprate systems [5,6]. An important development has been the identification of a new method of low temperature fluorination which entails heating the precursor oxide with the polymer poly(vinylidene) fluoride which produces high quality samples without impurities [7].

In this paper we review some of our recent work involving the low temperature fluorination of  $\text{SrFeO}_{3-\delta}$  [8] and the examination of the reduction properties of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ [9] formed by temperature programmed reduction.

### 2 Experimental

The oxygen deficient compounds of composition  $\text{SrFeO}_{3-\delta}$  and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  were prepared by the calcination of appropriate quantities of well ground mixtures of strontium(II) carbonate, lanthanum(III) oxide and  $\alpha$ -iron(III) oxide at 1250°C for 24h

in air. Fluorination was achieved by mixing the  $\text{SrFeO}_{3-\delta}$  phase with poly(vinylidene fluoride) in a 1:0.75 molar ratio (precursor oxide:  $\text{CH}_2\text{CF}_2$  monomer unit) and heating the mixture at  $400^\circ\text{C}$  for 24 h in flowing nitrogen.

Temperature programmed reduction (TPR) profiles were recorded from *ca.* 150 mg samples in flowing 10% hydrogen/90% nitrogen (15-20 ml/min) with the temperature being increased by  $5^\circ\text{C}/\text{min}$ . Thermal analysis was performed using a Rheometric Scientific STA 1500 system in a 10% hydrogen/90% nitrogen gas mixture flowing at 20 ml/min. X-ray powder diffraction (XRD) patterns were recorded with a Siemens D5000 diffractometer using  $\text{Cu K}\alpha$  radiation at 298K. The  $^{57}\text{Fe}$  Mössbauer spectra were recorded at 300 and 77K with a constant acceleration spectrometer using a *ca.* 25mCi  $^{57}\text{Co}/\text{Rh}$  source. The  $^{57}\text{Fe}$  Mössbauer chemical isomer shift data are quoted relative to metallic iron at room temperature.

### 3 Results and Discussion

#### a) Fluorination of $\text{SrFeO}_{3-\delta}$

The XRD patterns recorded from  $\text{SrFeO}_{3-\delta}$  and its fluorinated derivative showed that fluorination induces a shift in peak position to lower angles corresponding to an increase in unit cell size. Heating the sample subsequently to  $400^\circ\text{C}$  in air resulted in no further changes consistent with the partial replacement of oxygen by fluorine rather than a simple reduction in oxygen content. The refinement of the XRD data showed that fluorination leads to a significant increase in cell parameters. This is consistent with the partial replacement of  $\text{O}^{2-}$  by  $\text{F}^-$  leading to a reduction in the transition metal oxidation state (see below) and consequently longer bond distances and a larger unit cell.

The  $^{57}\text{Fe}$  Mössbauer spectra recorded from  $\text{SrFeO}_{3-\delta}$  and its fluorinated derivative are shown in Figure 1.

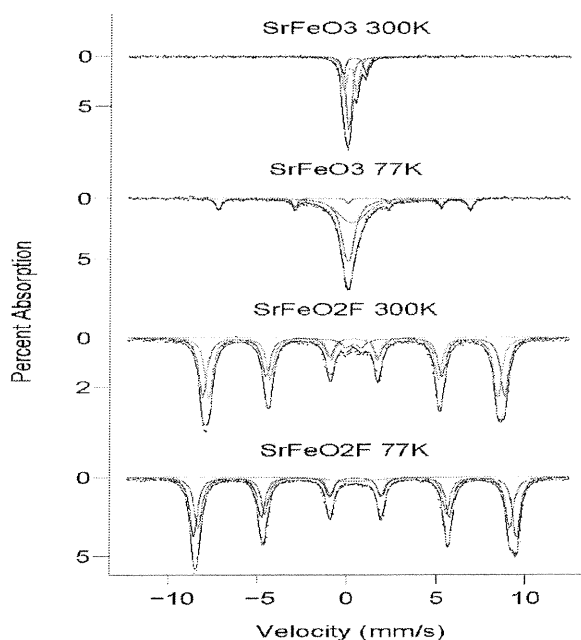


Figure 1.  $^{57}\text{Fe}$  Mössbauer spectra recorded from  $\text{SrFeO}_{3-\delta}$  and its fluorinated derivative and recorded at 300 and 77K.

The spectrum recorded at 300K was best fitted to a doublet ( $\delta = ca. 0.04 \text{ mms}^{-1}$ ,  $\Delta = ca. 0.12 \text{ mms}^{-1}$ ) characteristic of  $\text{Fe}^{4+}$  together with another doublet ( $\delta = ca. 0.14 \text{ mms}^{-1}$ ,  $\Delta = ca. 0.69 \text{ mms}^{-1}$ ) in which the chemical isomer shift  $\delta$  is intermediate between that characteristic of an  $\text{Fe}^{3+}$  species ( $\delta = ca. 0.35 \text{ mms}^{-1}$ ) and an  $\text{Fe}^{4+}$  species ( $\delta = ca. 0.04 \text{ mms}^{-1}$ ) and is indicative of an ion of mean charge. Such a description may imply charge sharing between neighbouring  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$  ions with a time scale smaller than  $10^{-8}$ s in  $\text{Fe}^{4+}$ -containing  $\text{SrFeO}_{3-\delta}$ . The spectrum also contained a quadrupole split absorption ( $\delta = ca. 0.35 \text{ mms}^{-1}$ ,  $\Delta = ca. 1.26 \text{ mms}^{-1}$ ) characteristic of an  $\text{Fe}^{3+}$ -containing impurity phase. By deducting the component corresponding to the  $\text{Fe}^{3+}$ -containing impurity phase it is possible to associate *ca.* 76.82% of the Mössbauer spectral area with  $\text{Fe}^{4+}$  and hence calculate a formula of  $\text{SrFeO}_{2.88}$  for the  $\text{SrFeO}_{3-\delta}$  phase examined here. The spectrum recorded at 77K showed a doublet ( $\delta = ca. 0.04 \text{ mms}^{-1}$ ,  $\Delta = ca. 0.26 \text{ mms}^{-1}$ ) characteristic of  $\text{Fe}^{4+}$  with two sextet patterns, one ( $\delta = ca. 0.27 \text{ mms}^{-1}$ ,  $2\varepsilon = ca. -0.68 \text{ mms}^{-1}$ ,  $H = 3.4\text{T}$ ) characteristic of the mixture of  $\text{Fe}^{4+}$  and  $\text{Fe}^{3+}$  and the other ( $\delta = ca. 0.47 \text{ mms}^{-1}$ ,  $2\varepsilon = ca. -1.33 \text{ mms}^{-1}$ ,  $H = 43.6\text{T}$ ) characteristic of the  $\text{Fe}^{3+}$ -containing impurity phase which was not visible in the XRD pattern and which is therefore presumed to be due to an amorphous impurity.

The spectrum recorded at 300K from the fluorinated derivative was best fitted to the superposition of two sextet patterns together with a profile which can be fitted to a hyperfine field of *ca.* 4.5T but all with chemical isomer shifts characteristic of  $\text{Fe}^{3+}$ . The spectrum recorded at 77K was similar with the component of smallest hyperfine field appearing as a broadened singlet. The results are consistent with fluorination inducing the reduction of  $\text{Fe}^{4+}$  in  $\text{SrFeO}_{3-\delta}$  to  $\text{Fe}^{3+}$ . The predominance of complex magnetically split hyperfine patterns recorded from the fluorinated material reflects the interaction between  $\text{Fe}^{3+}$  ions which are not possible in oxides containing  $\text{Fe}^{4+}$ . Given the presence of only  $\text{Fe}^{3+}$ , the results suggest a formula of  $\text{SrFeO}_2\text{F}$  for the fluorinated phase.

(b) *Reduction of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$*

The XRD pattern recorded from the compound  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  is shown in Figure 2a. The pattern is characteristic of that of a  $\text{SrFeO}_3$ -type structure.

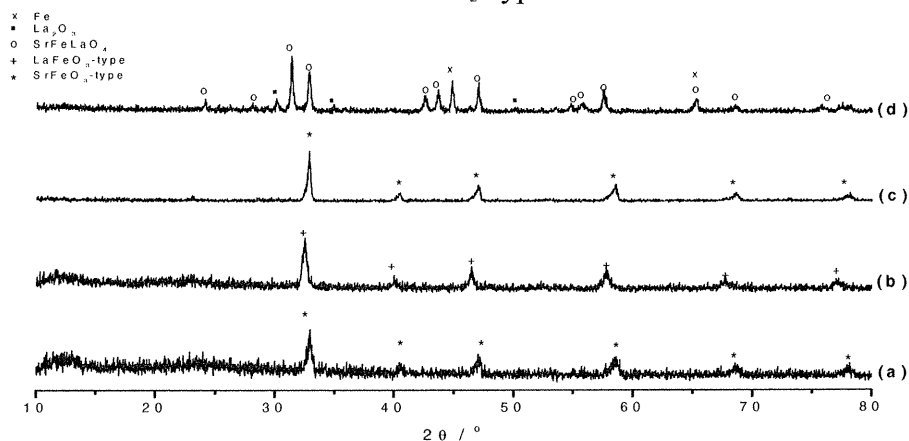


Figure 2. XRD patterns recorded from (a)  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  and following sequential treatment in (b) 90% hydrogen/10% nitrogen at  $650^\circ\text{C}$ , (c) air at  $450^\circ\text{C}$  and (d) 90% hydrogen/10% nitrogen at  $1150^\circ\text{C}$ .

The TPR profile recorded from  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  is shown in Figure 3 and shows an initial narrow peak at *ca.* 570°C followed by a broad peak spanning the temperature range *ca.* 800-1200°C.

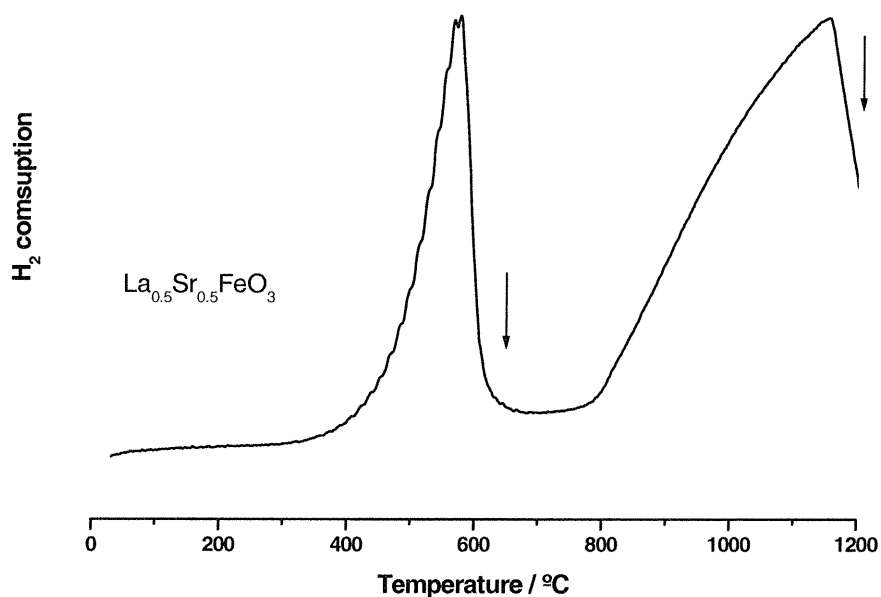


Figure 3 TPR profile recorded from  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$

The XRD pattern (Figure 2b) recorded from  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  following treatment in the reducing atmosphere at 650°C, i.e. after the first reduction peak in the TPR profile (Figure 3), showed all the peaks to shift to lower angle and was more similar to that of an orthorhombic  $\text{LaFeO}_{3-\delta}$ -type phase. No evidence could be found for the presence of strontium oxide. The XRD pattern recorded from the material after reheating in air at 450°C for 12h (Figure 2c) showed the product to return to the cubic  $\text{SrFeO}_3$ -type structure. The XRD pattern recorded from the material following treatment by TPR at 1150°C (Figure 2d) showed the formation of  $\text{SrFeLaO}_4$  which adopts the  $\text{K}_2\text{NiF}_4$ -type structure [10],  $\text{La}_2\text{O}_3$ , and metallic iron.

The  $^{57}\text{Fe}$  Mössbauer spectra recorded at 300K are shown in Figure 4. The spectrum recorded from the pure material (Figure 4a) showed a broad absorption line which was best fitted to two singlet components of equal intensity. The isomer shift of one singlet ( $\delta = \text{ca. } 0.03 \text{ mms}^{-1}$ ) is characteristic of  $\text{Fe}^{4+}$  in octahedral coordination whilst the parameters of the other singlet ( $\delta = \text{ca. } 0.25 \text{ mms}^{-1}$ ) correspond to  $\text{Fe}^{3+}$ .

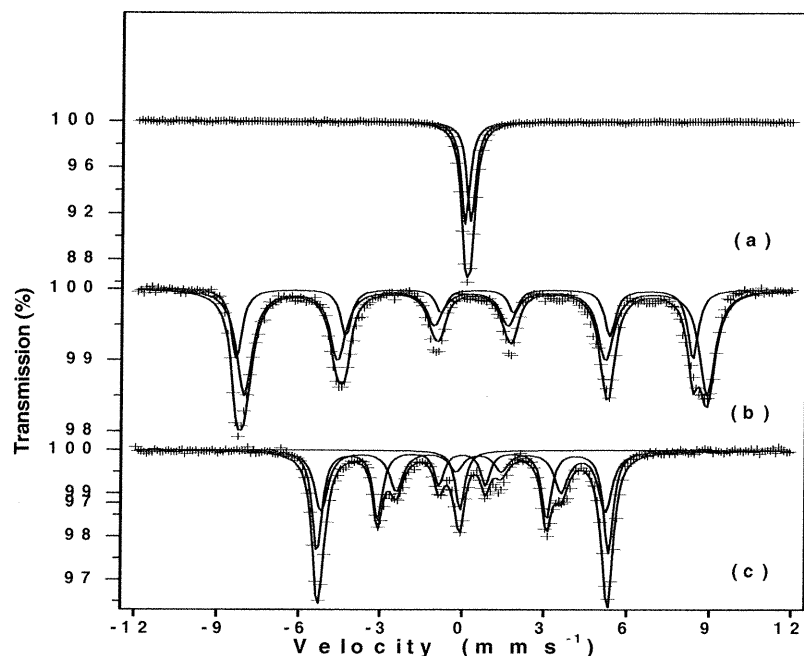


Figure 4  $^{57}\text{Fe}$  Mössbauer spectra recorded at 300K from (a)  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  and following treatment in 90% hydrogen/10% nitrogen at (b) 650°C and (c) 1150°C.

The spectrum recorded following treatment in flowing hydrogen and nitrogen (Figure 4b) at *ca.* 650°C (i.e. after the first peak in the TPR profile, Figure 3) showed the superposition of two magnetically split sextet components both characteristic of  $\text{Fe}^{3+}$  and demonstrating that low temperature treatment induces reduction of  $\text{Fe}^{4+}$  to  $\text{Fe}^{3+}$ . The shift in the XRD peak positions to lower angle (Figure 2b) indicated an increase in unit cell parameters for the partially reduced sample consistent with the presence of an increasing amount of  $\text{Fe}^{3+}$  with larger ionic radius. The thermal analysis of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  in 10% hydrogen/90% nitrogen showed a weight decrease at *ca.* 600°C of *ca.* 2% corresponding to a loss of lattice oxygen and the formation of a material of composition  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{2.72}$ . This agrees well with the formation of a compound of formula  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{2.75}$  which can be calculated on the assumption that all the  $\text{Fe}^{4+}$  in  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3.5}$  is reduced to  $\text{Fe}^{3+}$ . The identification of two sextet patterns is indicative of two  $\text{Fe}^{3+}$  sites. The sextet with smaller chemical isomer shift ( $\delta = \text{ca. } 0.27 \text{ mm s}^{-1}$ ,  $H = \text{ca. } 52.1\text{T}$ ) is characteristic of  $\text{Fe}^{3+}$  in coordination lower than octahedral as has been observed previously in other oxygen-deficient perovskite-related materials [11] whilst the other sextet ( $\delta = \text{ca. } 0.37 \text{ mm s}^{-1}$ ,  $H = \text{ca. } 52.9\text{T}$ ) is characteristic of  $\text{Fe}^{3+}$  in octahedral sites. It is interesting that while the pure material is paramagnetic at room temperature, the material obtained after treatment in the flowing hydrogen and nitrogen at 650°C is magnetically ordered at 300K. This can be associated with the stronger  $\text{Fe}^{3+}\text{-Fe}^{3+}$  interactions in the partially reduced phase as compared to  $\text{Fe}^{4+}\text{-Fe}^{4+}$  or  $\text{Fe}^{4+}\text{-Fe}^{3+}$  interactions which characterise the pure  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  phase.

The spectrum recorded from the material heated at *ca.* 1250°C, that is after the second peak in the TPR profile, showed the superposition of two sextets and a singlet (Figure

4c). One of the sextets, characteristic of  $\text{Fe}^{3+}$  ( $\delta = ca. 0.31 \text{ mms}^{-1}$ ) demonstrated a small hyperfine magnetic field ( $H = ca. 32.4\text{T}$ ). The parameters are similar to those reported for  $\text{LaSrFeO}_4$  [10] which adopts the  $\text{K}_2\text{NiF}_4$  – type structure. The other sextet ( $H = ca. 33.2\text{T}$ ) and the singlet ( $\delta = ca. 0.08 \text{ mms}^{-1}$ ) are characteristic of large- and small-particle metallic  $\alpha$ -iron respectively. Hence, treatment of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  at elevated temperatures in a mixture of flowing hydrogen and nitrogen induces both structural rearrangement of the perovskite-related lattice to the  $\text{K}_2\text{NiF}_4$ -type structure and reduction to metallic iron. It is notable that, even after treatment at the high temperature in the reducing atmosphere, a noticeable amount of iron remains in the trivalent state.

#### 4 Conclusions

The oxygen deficient  $\text{Fe}^{4+}$ -containing perovskite related phase  $\text{SrFeO}_{3-\delta}$  can be successfully fluorinated by a low temperature treatment with poly(vinylidene fluoride). The method leads to the partial replacement of oxygen by fluorine and a consequent reduction in the oxidation state of the transition metal.

The treatment of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  which contains  $\text{Fe}^{4+}$  and  $\text{Fe}^{3+}$  at  $600^\circ\text{C}$  in flowing 90% hydrogen/10% nitrogen results in the formation of an oxygen-deficient perovskite-related phase containing only trivalent iron. Further heating at  $1150^\circ\text{C}$  results in the formation of the  $\text{Fe}^{3+}$ -containing phase  $\text{SrLaFeO}_4$  which has the  $\text{K}_2\text{NiF}_4$ -type structure and metallic iron.

#### References

- [1] Y Nishihata, J Mizuki, T Akao, H Tanaka, M Uenishi, M Kimura, T Okamoto and H Hamada, *Nature* **418**, 164, (2002)
- [2] T Nakamoro, M Misona and Y Yoneda, *J Catal* **83**, 151, (1983)
- [3] J Ohno, S Nogata and H Sato, *Solid State Ionics* **3-4**, 439, (1981)
- [4] G Briceno, X-D Xiang, H Chang, X Sun and PE Schulz, *Science* **270**, 273, (1995)
- [5] MG Francesconi and C Greaves, *Supercond. Sci. Technol.* **10**, A29, (1997)
- [6] C Greaves and MG Francesconi, *Current Opin. Solid State Mater. Sci.* **3**, 132 (1998)
- [7] PR Slater, *J. Fluorine Chem.* **117**, 43, (2002)
- [8] FJ Berry, X Ren, R Heap, PR Slater and MF Thomas, *Solid State Commun.* **134**, 621, (2005)
- [9] FJ Berry, JF Marco and X Ren, *J. Solid State Chem.* **178**, 961, (2005)
- [10] JL Soubeyroux, P Courbin, L Fournès D Fruchart and G Le Fleur, *J. Solid State Chem.* **31**, 313, (1980)
- [11] TC Gibb, *J. Chem. Soc. Dalton Trans*, 1455, (1985)