Experimental Report

Proposal: **5-31-2265** **Council:** 10/2012

Title: Nuclear and magnetic structures ofnew Ruddlesden-Popper oxide fluorides

This proposal is a new proposal

Researh Area: Chemistry

Main proposer: **GREAVES Colin**

Experimental Team: FONES Julia
GREAVES Colin

Local Contact: SUARD Emmanuelle

Samples: La2BaFe2O6F2
La2BaFe2O5F4

Instrument	Req. Days	All. Days	From	To
D2B	3	3	26/02/2013	01/03/2013

Abstract:

La2BaFe2O7 (n=2 Ruddlesden-Popper structure) has been shown by the applicant to have a high degree of La/Ba order. This material undergoes an interesting magnetic reorientation at ~200 K. We have now synthesised two new oxide-fluoride phases from F-insertion reactions - La2BaFe2O5F4 and La2BaFe2O6F2. The structures of these phases have been partially determined by poweder XRD, but NPD is essential to resolve the O/F distribution, to determine whether any La/Ba redistribution occurs during fluorination, and to determine the magnetic order. In particular magnetic reorientation on cooling will be examined. Thes eobjectives can only be achieved using NPD data. These phases are extremely unusual in that the charge balance associated with fluorine insertion involves an equivalent amount of anion substition (F for O) rather than oxidation of Fe3+ to Fe4+.

Background

Fluorine insertion into the n=2 Ruddlesden-Popper phase $La_2BaFe_2O_7$ has been investigated using XRD, NPD, magnetic measurements and Mössbauer spectroscopy. $La_2BaFe_2O_7$ was synthesised using conventional ceramic methods: heating at 1375°C for 20 hours in air for four heat treatments with intermediate grinding. Initial fluorination was performed for 20 min in 10% F_2 (in N_2) at 290°C. Thermal analysis (reduction in H_2) and Mössbauer spectroscopy surprisingly revealed that the oxidation state of Fe remained at +3, and the final composition was $La_2BaFe_2O_5F_4$ – a combination of fluorine insertion and substitution had occurred. A "half-fluorinated" derivative was synthesised by heating an equimolar mixture of $La_2BaFe_2O_7$ and $La_2BaFe_2O_5F_4$ at 425°C in air for 15 minutes. TG and Mössbauer spectroscopy suggested a composition of $La_2BaFe_2O_6F_2$. XRD suggested single phase products for both fluorinated phases, but with different symmetry as shown in Table 1.

Table 1. Structural data (XRD) for $La_2BaFe_2O_5F_4$ and $La_2BaFe_2O_6F_2$.

	Symmetry	*a* / Å	*b* / Å	*c* / Å
$La_2BaFe_2O_5F_4$	I4/mmm	3.9671(1)	3.9671(1)	22.4218(9)
$La_2BaFe_2O_6F_2$	Fmmm	5.6989(1)	5.5980(1)	21.2396(8)

SQUID magnetometry and Mössbauer spectroscopy indicated both materials were antiferromagnetic at ambient temperature.

NPD (D2B)

NPD data were collected at various temperatures up to 550 K, which was found to be above the Néel temperature. The high temperature data were useful in determining the defect structures of the materials, and the low temperature data were used to determine the magnetic order. The 4 K data for both samples are shown in Figures 1 and 2 after structure refinement was achieved with the GSAS package. The refined structural parameters are provided in Table 2 (for $La_2BaFe_2O_5F_4$) and Table 3 (for $La_2BaFe_2O_6F_2$).

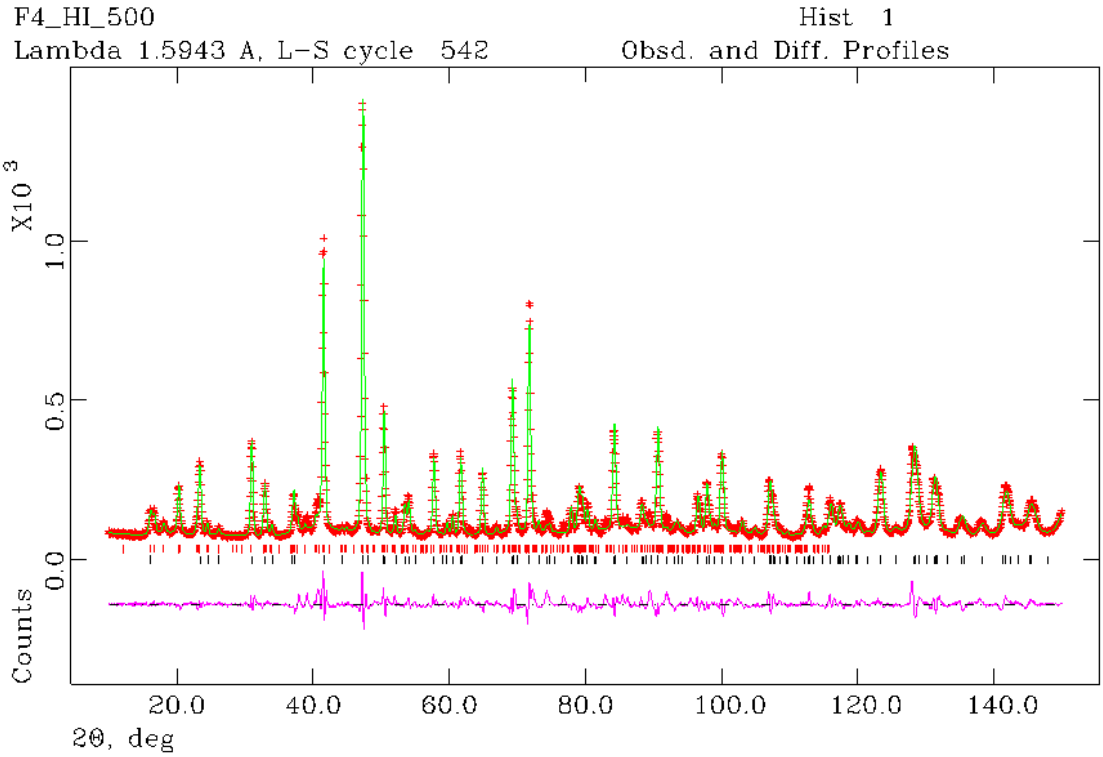

Figure 1. NPD fitted profiles for $La_2BaFe_2O_5F_4$.

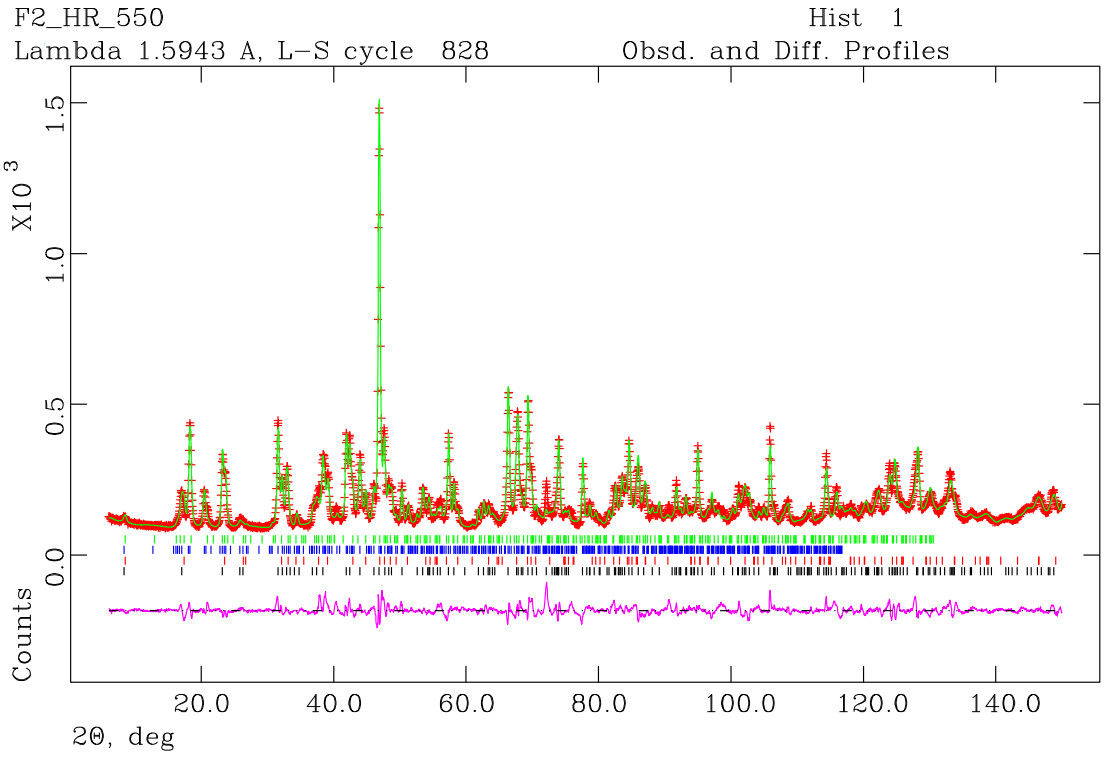

Figure 2. NPD fitted profiles for $La_2BaFe_2O_6F_2$.

Table 2. Structural parameters for $La_2BaFe_2O_5F_4$.						
Atom	**Site**	***x***	***y***	***z***	**$100\times U_{iso}/Å^2$**	**Occupancy**
La/Ba(1)	2b	0	0	0.5	1.4(1)	0.52(4)/0.48(4)
La/Ba(2)	4e	0	0	0.3237(2)	1.4(1)	0.74(2)/0.26(2)
Fe	4e	0	0	0.0865(1)	0.0(8)	1
O/F(1)	2a	0	0	0	1.5(2)	1
O/F(2)	8g	0	0.5	0.0962(2)	2.1(1)	1
O/F(3)	16n	0.093(2)	0	0.8262(3)	0.6(3)	0.25
O/F(4)	4d	0.5	0	0.25	3.2(2)	1
I4/mmm; *a*=3.9598(2) Å; *c*=22.377(1) Å; Fe magnetic moment 3.4(1) μB						

Table 3. Structural parameters for $La_2BaFe_2O_6F_2$.						
Atom	**Site**	***x***	***y***	***z***	**$100\times U_{iso}/Å^2$**	**Occupancy**
La/Ba(1)	4b	0.5	0	0	0.9(1)	0.40(3)/0.60(3)
La/Ba(2)	8i	0.5	0	0.1786(2)	0.9(1)	0.80(2)/0.20(2)
Fe	8i	0	0	0.0917(2)	0.8(1)	1
O/F(1)	4a	0	0	0	4.8(4)	1
O/F(2)	16j	0.25	0.25	0.1007(3)	1.5(1)	1
O/F(3)	16n	0.073(1)	0	0.1950(5)	2.4(3)	0.5
O/F(4)	8f	0.25	0.25	0.25	2.1(3)	0.5
Fmmm; *a*=5.6944(2) Å; *b*=5.5875(2) Å *c*=21.173(1) Å; Fe magnetic moment 4.1(1) μB						

Notes:

- The La and Ba distribution indicate a preference of the larger Ba ion for the 12-coordinate perovskite position as in the oxide;
- The apical site O/F(3) shows a significant displacement in both phases which probably arises because of the mixed occupancy of the La/Ba(2) site.
- The Fe magnetic moments are aligned antiferromagnetically in the *ab* plane and point along the {110} direction of the tetragonal unit cell;
- The $La_2BaFe_2O_6F_2$ sample actually contained a significant amount (25%) of unreacted $La_2BaFe_2O_7$ indicating incomplete conversion of $La_2BaFe_2O_5F_4$ to $La_2BaFe_2O_6F_2$. This phase, and its magnetic contribution were modelled in Figure 2.