Fluorination of the $n = 2$ Ruddlesden–Popper phase La$_2$BaFe$_2$O$_7$ occurs at ~300 °C in flowing 10% F$_2$ in N$_2$ to form La$_2$BaFe$_2$O$_5$F$_4$. This oxide fluoride contains 2F$^-$ ions in interstitial sites within the rocksalt regions and 2F$^-$ ions that have substituted for O$^{2-}$ ions in apical sites within the rocksalt layers. The fluorination results in an expansion along $c$ of 7.6% to yield a tetragonal unit cell of dimensions $a = 3.96237(7)$ Å, $c = 22.3972(5)$ Å. The structure and magnetic properties have been examined by Mössbauer spectroscopy, neutron powder diffraction and magnetic susceptibility measurements. La$_2$BaFe$_2$O$_5$F$_4$ becomes antiferromagnetically ordered at temperatures below ~500 K, and the magnetic order shows a striking resemblance to that observed in La$_2$BaFe$_2$O$_7$. The magnetic moments on Fe$^{3+}$ are perpendicular to [001] and aligned along ±[100] directions above 300 K, but at temperatures below 200 K, they rotate by 45° to lie along ±[110]. Mössbauer spectroscopy suggests the presence of Fe$^{3+}$ within the primary phase, but also indicates that fluorination results in some particle fragmentation to form a paramagnetic component of the fluorinated material.

Introduction

The synthesis of metastable oxide fluorides via the low temperature fluorination of layered inorganic oxides has received significant attention since the discovery of superconductivity in the perovskite-related oxide Sr$_2$CuO$_2$F$_2$. Subsequent fluorination of perovskite-related oxides has demonstrated the amenability of these structures to either substitution of oxide ions by fluoride ions, or to fluoride ion insertion into interstitial sites, especially in layered materials. These studies have led to modifications in both structural and physical properties. For example, fluorination of the $n = 1$ Ruddlesden–Popper phase LaSrMnO$_4$ can result in the staged oxide fluoride LaSrMnO$_4$F in which fluoride ions fully occupy the interstitial sites in alternate rock-salt layers. In this reaction, simple fluoride insertion occurs in an alternating fashion, with concerted oxidation of Mn$^{3+}$ to Mn$^{4+}$ in the perovskite regions. Where cations are more reluctant to oxidation, substitution reactions (the replacement of one O$^{2-}$ ion by two F$^-$ ions) can occur with one of the fluoride ions occupying an interstitial position. In this way, the fluorination of Sr$_2$TiO$_4$ can form Sr$_2$TiO$_3$F$_2$ which contains one interstitial fluoride ion located within alternate rocksalt layers.

The $n = 2$ Ruddlesden–Popper phases have also attracted interest. For example, the paramagnetic Ru$^{4+}$ oxide Sr$_3$Ru$_2$O$_7$ has been converted by oxidative insertion of fluoride ions to form the Ru$^{5+}$ oxide fluoride Sr$_3$Ru$_2$O$_7$F$_2$, which exhibits canted antiferromagnetic behaviour below 185 K. We have recently reported results of a study of the cationic order and magnetic properties of the $n = 2$ Ruddlesden–Popper phase La$_2$BaFe$_2$O$_7$, and we now report the product of its fluorination and its structural and magnetic characterisation.

Experimental

Samples of La$_2$BaFe$_2$O$_7$ (100–200 mg), prepared as previously described, were placed in a nickel boat and heated between 290 °C and 315 °C for 15 min in a flowing mixture of gaseous 10% fluorine/90% nitrogen. X-ray powder diffraction (XRPD) data were collected on a Bruker D8 diffractometer operating in transmission geometry and utilising Cu-Kα radiation. Thermogravimetric analysis (TG) was performed with a Netzsch STA 449 instrument. The sample was heated at a rate of 10 °C per minute in a gaseous mixture of 10% hydrogen/90% nitrogen to 1100 °C. The products from fluorination were mixed together to provide a suitably sized sample (ca. 2.5 g) for the
collection of neutron powder diffraction (NPD) data. The NPD experiment was performed on diffractometer D2B at ILL, Grenoble, France; the wavelength was 1.5943 Å and the sample was contained in a vanadium can (8 mm diameter). Refinements in this report were based on high resolution data obtained using only the central portion of the detector bank. Structure refinements based on NPD and XRPD data were performed using the GSAS programme and the EXPGUI interface. The site distribution of $O^{2-}$ and $F^{-}$ ions was investigated using Madelung energy calculations.

The $^{57}$Fe Mössbauer spectra were recorded in constant acceleration mode with a ca. 25 mCi Co/Rh source using a helium closed-cycle cryorefrigerator. All the spectra were computer fitted and the chemical isomer shift data are quoted relative to metallic iron at room temperature.

Magnetic susceptibility information was collected on a Quantum Design MPMS SQUID magnetometer; data were obtained on warming in a field of 500 Oe following cooling in the same field (FC) or zero field (ZFC).

Results and discussion

TG analysis of the fluorinated La$_2$BaFe$_2$O$_7$ resulted in a product at 1100 °C which was shown by XRPD to be a mixture of LaOF, BaF$_2$, Fe metal and a small amount of a perovskite phase. We assume that the latter is barium-doped LaFeO$_3$ which was present (1.9% by weight) in the starting oxide (vide infra). The decomposition corresponds to:

$$3H_2 + La_2BaFe_2O_5F_4 \rightarrow 2LaOF + BaF_2 + 2Fe + 3H_2O$$

After correction for perovskite impurity, the observed mass loss (7.01%) compares well with a calculated loss of 7.03% for the decomposition reaction above giving strong support for the fluorinated product to have a composition La$_2$BaFe$_2$O$_5F_4$. Surprisingly, this indicates no oxidation of the Fe$^{3+}$, and suggests a fluorination mechanism resulting in the replacement of $2O_2^{-}$ by $4F^{-}$ ions and hence the full occupancy of all interstitial sites within the rocksalt regions of the structure. XRPD structure refinements were performed in space group $I4_1/mmm$ for both phases; the results supported the occupancy of interstitial sites in the rocksalt regions and indicated a substantial (7.6%) unit cell expansion along $c$, with a small expansion in the $ab$ plane: $La_2BaFe_2O_5F_4$ ($a = 3.92308(4)$ Å, $c = 20.8122(3)$ Å), $La_2BaFe_2O_5F_4$ ($a = 3.96237(7)$ Å, $c = 22.3972(5)$ Å).

The $^{57}$Fe Mössbauer spectrum recorded from La$_2$BaFe$_2$O$_7$ at 298 K is shown in Fig. 1 and was best fitted to two sextets with chemical isomer shifts $\delta = 0.36$ mm s$^{-1}$ (characteristic of Fe$^{3+}$ and accounting for ca. 97% of the spectral area) together with a singlet with chemical isomer shift $\delta = 0.10$ mm s$^{-1}$ (characteristic of Fe$^{4+}$ and accounting for ca. 3% of the spectral area). The two sextet patterns represent a distribution of magnetic hyperfine fields reflecting the statistical probability of the distribution of lanthanum and barium around the FeO$_6$ octahedra which influences the positions of the oxygen atoms as shown by NPD data. The paramagnetic Fe$^{4+}$ component observed in the spectrum recorded at 298 K from La$_2$BaFe$_2$O$_7$ was associated with a barium-doped LaFeO$_3$ impurity phase.

The $^{57}$Fe Mössbauer spectra recorded from La$_2$BaFe$_2$O$_5F_4$ at 298 K and 16 K are shown in Fig. 1 and the fit parameters are contained in Table 1.

![Fig. 1](image-url) $^{57}$Fe Mössbauer spectra recorded from La$_2$BaFe$_2$O$_7$ at 298 K and from La$_2$BaFe$_2$O$_5F_4$ at 298 K and 16 K. Data for La$_2$BaFe$_2$O$_7$ reprinted from ref. 9 with permission from Elsevier.
Further the nature of its magnetic properties. It should be noted that the almost identical neutron scattering lengths for O (5.80 × 10⁻¹⁵ m) and F (5.65 × 10⁻¹⁵ m) make it impossible to determine directly the distribution of oxygen and fluorine on the anion sites. At 300 K, the NPD pattern revealed strong peaks that were inconsistent with the nuclear structure and were attributed to magnetic scattering from a unit cell for which a₀ = b₀ = \sqrt{2}a₀ (the subscript m refers to the magnetic cell). These peaks disappeared only at 500 K (Fig. 3), and the data at this temperature were used for the initial structure refinement. This confirmed the overall composition to be \( \text{La}_2\text{BaFe}_2(O/F)_9 \), in accordance with the Mössbauer and TG data, which suggested the specific composition \( \text{La}_2\text{BaFe}_2\text{O}_5\text{F}_4 \).

Fig. 3 shows that the magnetic reflections at 2θ ∼ 18° and 2θ ∼ 20° undergo a significant change in relative intensity between 200 K and 300 K, but no further change occurred at lower temperatures. The change in relative intensities of the magnetic peaks is very similar to that observed in \( \text{La}_2\text{BaFe}_2\text{O}_7 \), for which a rotation of the magnetic moments occurs: above ∼200 K the moments are aligned along ±{100} directions but at lower temperatures they rotate 45° to point along ±{110} directions. Full Rietveld structural analyses were therefore performed on 5 K and 300 K NPD data to provide complete structural and magnetic details.

The final structural parameters resulting from the refinements are given in Table 2, and some experimental details are provided in Table 3. The Rietveld diffraction profiles for the 300 K and 5 K data are shown in Fig. 4. Because of the low temperature fluorination, some minor contamination of the product occurs (e.g. a (La, Ba)FeO₃ perovskite, LaF₃, starting oxide) and these inevitably are reflected in minor deviations in the difference plots (Fig. 4). However, the inclusion of additional phases into the refinements did not result in significant improvements, given the additional variables introduced. On the basis of Madelung calculations (vide infra), the F atoms have a strong preference for the interstitial sites (F₁) and the apical sites on the edges of the perovskite blocks (F₂),

Table 1 ⁵⁷Fe Mössbauer parameters recorded from \( \text{La}_2\text{BaFe}_2\text{O}_5\text{F}_4 \)

| Temperature/K | δ ± 0.02/ mm s⁻¹ | ε|^2q/Q ± 0.02/ mm s⁻¹ | H ± 0.5 T | Area ± 3% |
|---------------|------------------|------------------------|-----------|-----------|
| 298           | 0.10             | 0.74                   | 3         |
|               | 0.26             | −0.10                  | 25        |
|               | 0.39             | −0.09                  | 42        |
|               | 0.38             | −0.09                  | 38        |
| 16            | 0.46             | 0.88                   | 6         |
|               | 0.51             | −0.08                  | 55        |
|               | 0.48             | −0.09                  | 53        |

Fig. 2 Variation of magnetic susceptibility of \( \text{La}_2\text{BaFe}_2\text{O}_5\text{F}_4 \) with temperature.
which are closest to F1. This distribution is consistent with the F− ions substituting for O2− ions at the closest positions, and thereby facilitating egress of the replaced O2− ions. The barium ions are located preferentially in the larger 12-coordinate sites within the perovskite block (La/Ba1) rather than the smaller, 9-coordinate sites in the rocksalt layers (La/Ba2). This is exactly as was found in the precursor oxide and is expected, since cation rearrangement is unlikely to be significant at the fluorination temperature.

The refinement of magnetic moment and magnetic order were achieved using a second, purely magnetic phase with low (P1) symmetry to allow flexibility of the direction of the moment. The unit cell dimensions of this magnetic phase were constrained to comply with the dimensions of the nuclear phase. This procedure is fairly standard, although refinements were also performed using single unit cells with lower symmetries that were compatible with the magnetic structures at 5 K and 300 K. However, the results indicated no significant structural distortion or improvement to the fitting statistics. We therefore preferred to maintain the high

Table 2  Refined structural data from NPD data at room temperature and 5 K (italics)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Site occupancy</th>
<th>Uiso × 100 Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>La/Ba1</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.39(3)/0.61(3)</td>
<td>1.35(7)</td>
</tr>
<tr>
<td>La/Ba2</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.3241(2)</td>
<td>0.453(5)/0.553(5)</td>
<td>1.36(7)</td>
</tr>
<tr>
<td>Fe</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.0863(2)</td>
<td>1</td>
<td>0.51(6)</td>
</tr>
<tr>
<td>O1</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.02(6)</td>
</tr>
<tr>
<td>O2</td>
<td>8g</td>
<td>0</td>
<td>0.5</td>
<td>0.0969(2)</td>
<td>0.0960(2)</td>
<td>1.68(7)</td>
</tr>
<tr>
<td>F1</td>
<td>4d</td>
<td>0.5</td>
<td>0</td>
<td>0.25</td>
<td>1</td>
<td>3.2(2)</td>
</tr>
<tr>
<td>F2</td>
<td>16n</td>
<td>0.083(3) / 0.091(2)</td>
<td>0.8240(4) / 0.8257(2)</td>
<td>0.25</td>
<td>2.7(4)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3  Details relating to the Rietveld refinements

<table>
<thead>
<tr>
<th>Site occupancies</th>
<th>Isotropic displacements</th>
<th>Background</th>
<th>Magnetic refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>The F2 (apical) position is shifted from the ideal position (0, 0, z) so that each site is split to provide 4 closely spaced positions. The La and Ba occupancies are constrained to provide the correct composition but allow the ions to distribute unevenly between La/Ba1 (12-coordinate) and La/Ba2 (9-coordinate). Isotropic values were constrained to be equal for all La and Ba ions. This was modelled using a Shifted Chebyshev function. The NPD data were analysed using a separate magnetic phase with P1 symmetry to allow full flexibility to model the structure. The unit cell dimensions were constrained to correspond with the crystallographic unit cell.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

symmetry nuclear structure with a separate magnetic phase that allowed flexible orientation of the moment.

As has been observed for La2BaFe2O7, the magnetic moments at 300 K are directed along ±{100} directions but have rotated to ±{110} directions at 5 K. Fig. 3 shows that the re-orientation occurs between 200 K and 300 K (the relative intensities of the magnetic peaks are very similar at 200 K and 5 K). Although we would expect the magnetic moment from NPD data to be significantly lower than the ideal 5μB, because of covalence and low dimensionality effects, the magnetic moment at 5 K is much smaller than that in the oxide: 3.03(5)μB (at 2 K). The moments at 200 K and 300 K were found to be 2.57(5)μB and 2.1(1)μB, respectively. The low moment is a little surprising but may relate to a weakening of magnetic exchange along [001] resulting from the significant expansion across the rocksalt regions. The overall crystal and magnetic structures at 300 K and 5 K are shown in Fig. 5.

As is usual in oxide fluoride systems of the type studied here, bond valence sum calculations15 were not useful for discrimination between possible distributions of the O2− and F− ions. For example, assuming the interstitial sites to be occupied by F−, there are three possible sites bonded to Fe3+. Therefore, bond valence sum calculations were not useful for discrimination between possible distributions of the O2− and F− ions.
could be occupied by F\(^-\). All of these models gave a bond valence sum in the range 3.07–3.10. The location of the fluoride ions within the structure was therefore investigated using Madelung energy calculations to probe the electrostatic preferences for various ion distributions. For a model involving a random distribution of O/F over all anions sites, the sites labelled F1 and F2 in Table 2 have electrostatic potentials substantially lower than the other two anion sites (labelled O1 and O2). In fact, the interstitial site in the rocksalt region (F1) has a slightly negative potential. This confirms a very strong preference of fluorine for the interstitial sites in accordance with expectation and previous results from similar reactions. Further calculations were performed with fluorine located on F1, and other possible distributions on the other anion positions. This revealed a very strong preference for all the remaining fluorine to be located only on the apical anion site (F2) that forms part of the rocksalt layers. This distribution has a Madelung energy of 3.24 \times 10^4 \text{ kJ mol}^{-1}, 5\% higher than that of the next most stable anion distribution. These results provide unequivocal evidence that the fluoride ions in \( \text{La}_2\text{BaFe}_2\text{O}_7\) \(_\text{F}_4\) are located in the two adjacent rocksalt layers and the interstitial sites between them, as indicated in Table 2 and Fig. 5.

The main changes in cation coordination that occur upon fluorination of \( \text{La}_2\text{BaFe}_2\text{O}_7\) are shown in Fig. 6. The site primarily occupied by La in the oxide increases its coordination to 12 in an arrangement very similar to that found for \( \text{La}^{3+}\) ions in the perovskite structure. Because of the negative charge on the interstitial sites in \( \text{La}_2\text{BaFe}_2\text{O}_7\) \(_\text{F}_4\), the apical F\(^-\) anions are repelled to provide a 12\% decrease in its bond distance to Fe. The equatorial Fe–O bonds are slightly expanded in the oxide fluoride phase, which is consistent with the small expansion of the unit cell edge length from 3.92308(4) Å to 3.96237(7) Å (based on XRPD data).

The Mössbauer and NPD data clearly show that \( \text{La}_2\text{BaFe}_2\text{O}_7\) \(_\text{F}_4\) is antiferromagnetically ordered between 5 K and 300 K. The magnetic susceptibility data (Fig. 2) therefore show some unexpected features that are worthy of comment. The paramagnetic behaviour is probably due to a component that has very small particle size, as was implied by Mössbauer spectroscopy (vide supra). The magnetic feature at ~40 K, appears to be caused by the main phase \( \text{La}_2\text{BaFe}_2\text{O}_7\) \(_\text{F}_4\), although we cannot dismiss the possibility of a very small amount of a ferromagnetic impurity. The oxide \( \text{La}_2\text{BaFe}_2\text{O}_7\) does not give such a transition, and we are unaware of such a transition being reported for the perovskite \( \text{La}_{1-x}\text{Ba}_x\text{FeO}_{3-y}\), which we often see as an impurity during the synthesis of \( \text{La}_2\text{BaFe}_2\text{O}_7\). We have shown that the same susceptibility data were obtained from two samples of \( \text{La}_2\text{BaFe}_2\text{O}_7\) \(_\text{F}_4\), obtained totally independently, and the transition could possible imply the occurrence of a canted ground state for the principal phase at this temperature. Analysis of NPD data either side of this temperature (at 30 K and 80 K) revealed no change in the...
magnetic order, but this is normal for canted structures where the canting angle is small.

Given the significant structural change that occurs on fluorination of \( \text{La}_2\text{BaFe}_2\text{O}_7 \), it is somewhat surprising that the same reorientation of the magnetic moments occurs in \( \text{La}_2\text{BaFe}_2\text{O}_5\text{F}_4 \) as has been previously reported in \( \text{La}_2\text{BaFe}_2\text{O}_7 \).\(^9,13,14\) It suggests that the dominant 180° exchange interactions within the perovskite layers are entirely accountable for this transition; otherwise the large expansion of the rocksalt region by accommodation of the interstitial fluoride ions would be expected to have a significant effect.

**Conclusions**

We report the results of fluorine insertion into the \( n = 2 \) Ruddlesden–Popper phase \( \text{La}_2\text{BaFe}_2\text{O}_7 \). Unlike similar phases containing manganese, the fluorination occurs with no oxidation of the \( \text{Fe}^{3+} \) species, which is indicative of the higher reluctance of the \( \text{d}^5 \) ion (\( \text{Fe}^{3+} \)) to oxidation compared to \( \text{Mn}^{3+} \). The fluorination results in the formation of \( \text{La}_2\text{BaFe}_2\text{O}_5\text{F}_4 \) with two \( \text{F}^- \) ions in interstitial sites and two which have substituted at the apical positions in the rocksalt layers. The 9-coordinate cation site, predominantly occupied by \( \text{La} \) in \( \text{La}_2\text{BaFe}_2\text{O}_7 \), becomes 12-coordinate in \( \text{La}_2\text{BaFe}_2\text{O}_5\text{F}_4 \). \( \text{La}_2\text{BaFe}_2\text{O}_5\text{F}_4 \) is antiferromagnetic with a Néel temperature \( \sim500 \) K. The ordered structure has moments directed along \( \pm\{100\} \) directions above 300 K, but at temperatures below 200 K, reorientation results in an alignment along \( \pm\{110\} \). This rotation through 45° is similar to that observed in \( \text{La}_2\text{BaFe}_2\text{O}_7 \).

**Acknowledgements**

We are grateful to Emma Suard for assistance with the collection of NPD data and acknowledge the provision of financial support for NPD facilities by the UK Engineering and Physical Sciences Research Council. NNMG is grateful for the provision of a research scholarship from the University of Birmingham. The Bruker D8 diffractometer and the Netzsch STA 449 F1 Jupiter TG instrument used in this research were obtained through Birmingham Science City: Creating and Characterising Next Generation Advanced Materials (West Midlands Centre for Advanced Materials Project 1), with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF). Financial support from the Spanish Ministry of Science and Technology through project MAT2012-38045-C04-01 is also acknowledged.

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