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The synthesis and structure of a new oxide fluoride, $LaSrMnO_4F$, with staged fluorine insertion

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$LaSrMnO_4F$ has been synthesised and shown to have a staged structure in which the insertion of F atoms into the parent $LaSrMnO_4$ structure has occurred only in alternate (La,Sr)O rocksalt blocks.

In recent years the synthesis of materials which are superconducting or exhibit high magnetoresistance behaviour has been the focus of much attention from solid state chemists. Interestingly, although the detailed mechanistic principles for both classes of materials remain incomplete, the structural and electronic requirements are sufficiently clear to allow the design and synthesis of new materials. The two-dimensional structural features and mixed valence (generally Cu^{2+}/Cu^{3+}) observed in high temperature superconductors are now well known, and similar criteria appear to be important for some oxides which show high magnetoresistance at fairly low magnetic fields. The importance of such materials was illustrated in the $n = 2$ Ruddlesden–Popper phase $La_{1.2}Sr_{1.8}Mn_2O_7$,[1] which contains Mn^{3+}/Mn^{4+} and double layers of MnO_6 octahedra linked through corners. We have previously shown that for both superconductors and layered manganese oxides, low temperature fluorine insertion reactions provide not only the means for achieving controlled increases in cation oxidation states (associated with reduction of F atoms to F^- ions), but also new low dimensional oxide–fluoride structures. This is exemplified by the reactions of F_2 gas with Sr_2CuO_3 or $La_{1.2}Sr_{1.8}Mn_2O_7$ to form, respectively, superconducting $Sr_2CuO_2F_{2.3}$ and ferromagnetic $La_{1.2}Sr_{1.8}Mn_2O_7F_2$.[2,3] In both reactions, fluorine inserts between two adjacent AO rocksalt layers (these rocksalt 'bilayers' exist in both precursor oxides, with A = Sr for the former compound and A = Sr/La for the latter). The insertions cause increases in transition metal oxidation states, from Cu^{2+} to $Cu^{2.3+}$ and $Mn^{3.4+}$ to $Mn^{4.4+}$.

Here, we report the structure and basic magnetic properties of a new phase, $LaSrMnO_4F$, in which fluorine is inserted between *alternate* rocksalt bilayers. This is an example of a staged insertion reaction for which the product contains layers with fully occupied interstitial sites, regularly spaced between completely empty layers, rather than a random distribution of inserted species in all layers. Although staging occurs for the intercalation of alkali metal and halogen atoms into graphite,[4] and has also been reported for other layered materials, *e.g.* Ag_xTiS_2,[5] we believe $LaSrMnO_4F$ provides the first example relating to fluorine insertion in oxides. Synthetically the observation could be significant, especially for magnetic systems such as manganese oxides. For example, the successful synthesis of a series of staged manganese oxide–fluorides with different fluorine contents would produce materials with not only a gradual change in Mn oxidation state, but also a gradation of magnetic exchange interactions perpendicular to the 'MnO_2' layers.

The precursor oxide $LaSrMnO_4$ was prepared as described in previous reports,[6,7] and fluorination was achieved by exposing the sample to a $10\%F_2/90\%N_2$ gas mixture for 2 h at 200 °C. Chemical analysis of the fluorinated phase (mass change on fluorination, Mn oxidation state *via* titrimetry and F content *via* thermogravimetric decomposition in $10\%H_2/90\%N_2$) suggested the approximate composition $LaSrMnO_4F_{1.7}$, which is indicative of incomplete filling of the interstitial sites between the rocksalt layers, since full occupancy would correspond to $LaSrMnO_4F_2$. In order to prepare $LaSrMnO_4F$, the original fluorinated sample was mixed with an appropriate amount of the precursor oxide (mole ratio 1.2 : 0.8) followed by heating the mixture in air at 300 °C for 12 h. Iodometric titration indicated a manganese oxidation state of 3.93(3)+, in satisfactory agreement with the value of 4.0 expected for stoichiometric $LaSrMnO_4F$. Thermogravimetric analysis (to 600 °C, $10\%H_2/90\%N_2$) revealed a 3.5% weight loss during decomposition to give a multi-phase product consisting of SrF_2, $La_{2-x}Sr_xMnO_4$ and MnO according to X-ray powder diffraction (XRPD) analysis. The weight loss is sensitive to the F content and agrees well with that expected (3.3%) for 1 mol of $LaSrMnO_4F$ producing $\frac{1}{2}SrF_2 + \frac{3}{4}La_{1.333}Sr_{0.667}MnO_4 + \frac{1}{4}MnO$. In addition, phase analysis of the product using Rietveld refinement procedures[8] indicated a $SrF_2 : La_{1-x}Sr_xMnO_4$ ratio of 0.72, slightly higher than the 0.67 ratio expected for $LaSrMnO_4F$. The analytical data support a composition close to stoichiometric $LaSrMnO_4F$, although a small amount of F substitution at O sites may have occurred ($LaSrMnO_{3.93}F_{1.07}$ would correspond to $Mn^{3.93+}$ and produce a $SrF_2 : La_{1-x}Sr_xMnO_4$ ratio of 0.73).

In order to obtain an insight into the structural characteristics of $LaSrMnO_4F$, XRPD data were collected (Siemens D5000, primary Ge monochromator, PSD). It was clear that a fairly close structural relationship existed between $LaSrMnO_4F$ and its parent oxide $LaSrMnO_4$, and the pattern was satisfactorily indexed on a tetragonal unit cell ($P4/nmm$, $a = 3.7749(1)$ Å, $c = 14.1049(3)$ Å). Fluorination results in a symmetry reduction and a significant expansion of *ca.* 7.3% along c compared to the precursor oxide $LaSrMnO_4$ ($I4/mmm$, $a = 3.7952(1)$ Å, $c = 13.1410(9)$ Å). Structure refinement, using the program FULLPROF[8] was performed. Several structural models were examined including those with F atoms statistically occupying interstitial sites between all the (La/Sr)O rocksalt layers and those where occupancy is confined to alternate layers only. Only the latter model provided a basis to achieve satisfactory agreement between the calculated and experimental XRPD patterns. The F^- ions are located in the ideal interstitial positions between one of the two (La/Sr)O bilayers in the unit cell, and are tetrahedrally coordinated to 4 La/Sr sites. The fitted profile is shown in Fig. 1 and Table 1 gives the refined atomic coordinates and selected interatomic bond distances. In the refinement, all sites occupied by a given ion were constrained to have equal thermal parameters. The refined structure (Fig. 2) clearly displays the staged arrangement of guest F^- ions within the $LaSrMnO_4$ host structural framework. Although O and F atoms cannot be differentiated by XRPD, the anion assignments in Table 1, which restrict F to only one of the two interstitial positions, are supported by Madelung energy calculations.[9] This analysis, based purely on electrostatic arguments, indicates that the Madelung energy for the proposed anion distribution (24 110 kJ mol^{-1}) is the highest of all possible arrangements; the next highest (22 880 kJ mol^{-1}) corresponds to F occupying the neighbouring O2 apical site. Bond valence sum calculations[10] for the Mn–O bonds using r_o for Mn(IV) yields a value of 4.2 at the Mn site indicating that the Mn coordination is consistent with Mn^{4+}. The structure refinement clearly indicates that fluorine insertion has occurred between alternate rocksalt layers only. As a result, two quite different Mn–O apical bonds

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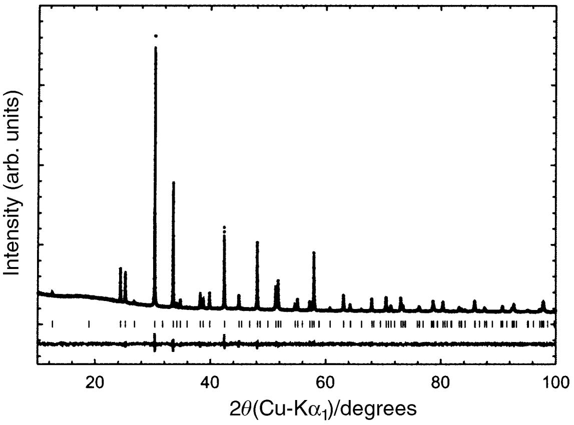

Fig. 1 Rietveld structure refinement based on XRPD data: solid curves calculated and difference profiles; dots, observed profile; vertical bars, reflection positions.

Table 1 Refined atomic coordinates and selected bond lengths for $LaSrMnO_4F$

Atom	*x/a*	*y/b*	*z/c*	*B*/Å^2	Unit cell occupancy
La1/Sr1	0.75	0.75	0.1167(1)	0.431(3)	1.00/1.00
La2/Sr2	0.75	0.75	0.4020(1)	0.431(3)	1.00/1.00
Mn	0.25	0.25	0.2720(2)	0.30(8)	2.00
O1	0.25	0.75	0.2781(6)	0.8(1)	4.00
O2	0.25	0.25	0.1483(8)	0.8(1)	2.00
O3	0.25	0.25	0.4197(8)	0.8(1)	2.00
F	0.25	0.75	0.0	0.3(2)	2.00
	Bond lengths (Å):				
	Mn–O1 (×4)		1.889(1)	O2–F 2.817(8)	
	Mn–O2		1.745(12)		
	Mn–O3		2.083(12)		

*P*4/*mmm*; $a = 3.77486(8)$, $c = 14.1049(3)$; $R_{wp} = 2.53\%$. $R_{exp} = 1.4\%$, $\chi^2 = 2.97$.

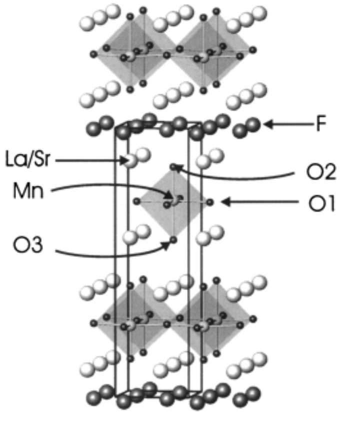

Fig. 2 Structure of $LaSrMnO_4F$ showing the unit cell.

are present (Table 1 and Fig. 2): Mn–O2 bonds, which point towards the F-containing layers, are significantly shorter than the *trans*-Mn–O3 bonds owing to the influence of F–O2 repulsions.

Studies of the magnetic properties of this material (Cryogenics S100 SQUID, Fig. 3) revealed paramagnetic behaviour above 10 K. Above 95 K, application of the Curie–Weiss law [$\chi = C/(T - \theta)$], provides a negative value of the Curie–Weiss constant ($\theta = -80$ K), suggesting antiferromagnetic interactions are taking place. The effective moment, $\mu_{eff} = 4.3\ \mu_B$, estimated from the linear part of the $1/\chi$ *vs.* T plot (Fig. 3), is slightly higher than that expected for Mn^{4+} (spin-only moment 3.9 μ_B), and is consistent with the presence of some Mn^{3+}. At temperatures below 95 K we see the appearance of a ferromagnetic component to the magnetic interactions. Further studies are required to establish whether these are intrinsic or extrinsic to the bulk $LaSrMnO_4F$ phase.

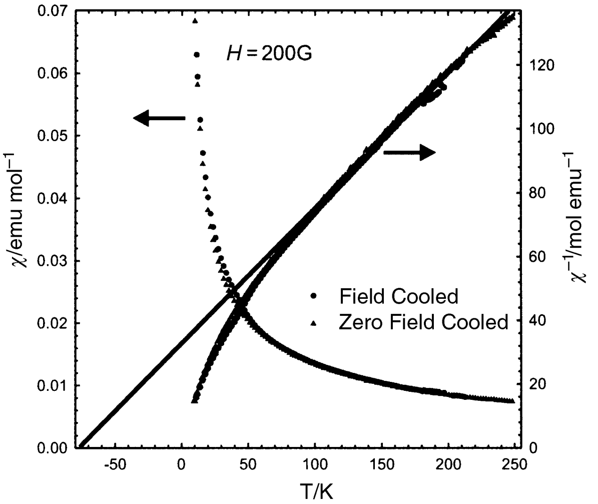

Fig. 3 Variation of magnetic susceptibility (χ) and χ^{-1} with temperature (T).

$LaSrMnO_4F$ has been synthesised and the most important structural characteristics determined by XRPD. For the first time, staged insertion of fluorine has been demonstrated such that only alternate rocksalt regions of the parent structure have been subject to intercalation. This is the first example of this type of fluorinated oxide and suggests that other staged products may be possible, not only for $n = 1$ Ruddlesden–Popper phases such as $LaSrMnO_4$ studied here, but for family members with higher n. Such possibilities are currently under investigation.

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