Staged fluorine insertion into manganese oxides with Ruddlesden–Popper structures: $LaSrMnO_4F$ and $La_{1.2}Sr_{1.8}Mn_2O_7F$

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The synthesis, structures and magnetic properties of two fluorine-intercalated layered manganates, $LaSrMnO_4F$ and $La_{1.2}Sr_{1.8}Mn_2O_7F$, are reported. Rietveld structure refinement based on time of flight neutron powder diffraction data indicates that both compounds are tetragonal (space group $P4/nmm$) with cell parameters $a = 3.77696(7)$ Å, $c = 14.1026(8)$ Å ($LaSrMnO_4F$) and $a = 3.8103(1)$ Å, $c = 21.7220(2)$ Å ($La_{1.2}Sr_{1.8}Mn_2O_7F$). Fluorine occupies interstitial sites in only one of the two rock salt layers available in the unit cell, leading to novel staged intercalation structures. The interstitial fluorine increases the spacing between the two adjacent rock salt layers and thereby causes a significant reduction in the Mn–O apical bonds directed towards the intercalated regions. The Mn valences of both compounds are close to 4+, and no long range magnetic order was observed in the title compounds down to 5 K.

Introduction

Mixed metal manganese oxides with perovskite related structures have attracted significantly increased attention after the report that $LaMnO_3$ doped with alkaline earth cations undergoes major reductions in resistance in applied magnetic fields, the effect being known as Colossal Magnetoresistance (CMR).[1] The relatively high field needed to induce such an effect hinders its potential applications in recording devices, but the subsequent discovery that small fields (below 1 T) can induce substantial resistance change in $La_{1.2}Sr_{1.8}Mn_2O_7$ triggered new hopes for the industrial application of materials of this type.[2] $La_{1.2}Sr_{1.8}Mn_2O_7$ is an $n = 2$ member of the Ruddlesden–Popper (RP) structural family with general formula $(AO)(ABO_3)_n$, where typically A is a lanthanide or alkaline earth cation (here La,Sr) and B is a transition metal cation (here Mn). The sensitivity of the conductivity of $La_{1.2}Sr_{1.8}Mn_2O_7$ to low magnetic fields was attributed to the 2-dimensional nature of the RP structure. In order to study the effect of dimensionality on the magnetic properties of related low dimensional manganates, we are investigating the effects of increasing the space between the MnO_2 layers caused by fluorine insertion into the interstitial sites in the AO rock salt layers which separate the ABO_3 perovskite blocks in RP phases. Previous knowledge of such F insertion tells us that F treatment not only increases the layer spacing but also provides valence control and sometimes induces structural rearrangement as well. Fluorination of Sr_2CuO_3 leads to the formation of $Sr_2CuO_2F_{2+x}$, which contains complete CuO_2 planes and is superconducting at 40 K.[3] After fluorination, paramagnetic (PM) $Sr_3Ru_2O_7$ (Ru(IV)) forms $Sr_3Ru_2O_7F_2$ (Ru(V)), which is antiferromagnetic (AFM) with a weak ferromagnetic (FM) moment below 185 K.[4] Recently, we found that F intercalation into layered manganates is also possible: $La_{1.2}Sr_{1.8}Mn_2O_7F_2$ can be prepared from $La_{1.2}Sr_{1.8}Mn_2O_7$ via F_2 gas treatment or reaction with CuF_2.[5] Surprisingly, in fluorinating the single layer $LaSrMnO_4$ sample, a staged compound with composition of $LaSrMnO_4F$ was discovered. A preliminary X-ray powder diffraction study[6] showed that it crystallizes in a staged structure in which F occupies only alternate rock salt layers in the structure. Further studies have indicated that the staged

compound of the $n = 2$RP layered manganate can also be prepared. Here we report the synthesis of this new phase, $La_{1.2}Sr_{1.8}Mn_2O_7F$, and its magnetic properties. We describe a neutron powder diffraction study of its structure and provide a full and detailed comparison of the structural properties of $LaSrMnO_4F$ and $La_{1.2}Sr_{1.8}Mn_2O_7F$.

Experimental

The precursor oxide $LaSrMnO_4$ was prepared under reducing conditions (10% H_2 in N_2) as reported elsewhere,[7] and $La_{1.2}Sr_{1.8}Mn_2O_7$ was prepared from La_2O_3, $SrCO_3$ and Mn_2O_3 using a standard solid state reaction in air at 1400 °C. Maximum fluorination of the oxides (to give $LaSrMnO_4F_{1.5}$ and $La_{1.2}Sr_{1.8}Mn_2O_7F_2$) was achieved through treatment in F_2 gas (10% in N_2) for two periods of 30 minutes at 200 °C. The staged compounds were prepared from simply mixing appropriate amounts of the starting oxides and the fully fluorinated products. The purity of the starting, fully fluorinated, and partially fluorinated samples were monitored by X-ray powder diffraction (XRD) using a Siemens D-5000 diffractometer. In order to produce homogeneous samples of the title compounds extended heat treatments at 500 °C for a total of 72 hours were necessary. Thermogravimetric analysis (TG) was performed with a Rheometric Scientific STA 1500 in 10% H_2 in N_2 at 700 °C. Magnetic susceptibilities of the samples were measured with a Cryogenics S100 SQUID magnetometer. Time of flight neutron powder diffraction (NPD) data were collected at POLARIS (ISIS, RAL, UK) and the structure refinements were carried out with the GSAS package.[8]

Results and discussion

The oxide fluoride $LaSrMnO_4F$ shows no evidence of magnetic ordering down to 10 K, as reported previously,[6] and NPD data collected at 4 K confirmed this, showing no scattering associated with long range magnetic order. For $La_{1.2}Sr_{1.8}$-Mn_2O_7F, a small FM moment was observed in magnetic susceptibility measurements, with an onset just above room temperature. However, low temperature NPD data again

showed no evidence of magnetic order in the predominant phase, $La_{1.2}Sr_{1.8}Mn_2O_7F$. Subsequent refinements revealed the presence of a second phase, $(La,Sr)MnO_3$, after fluorination. We therefore attribute the FM moment to this impurity phase, although it is not apparent in the XRD profile of the precursor oxide. This assignment is further supported by the fact that the oxide precursor itself also showed identical FM behaviour at room temperature. Attempts to perform full structural analyses based on the NPD data sets revealed significant peak displacements from their ideal positions such that the refinements were of unacceptable statistical quality. This effect was thought to be caused by small deviations of the F contents from the target 1.0, and new samples of both $LaSrMnO_4F$ and $La_{1.2}Sr_{1.8}Mn_2O_7F$ were therefore synthesised, and particular attention was given to minimising this problem by careful monitoring of the XRD patterns. Higher quality NPD data were collected for these two samples at 300 K, and the structural study described below is based on the data from the high resolution back scattering ($2\theta = 145°$, C-bank) detectors.

As observed previously in the XRD pattern, new diffraction peaks that violate the extinction rules of $I4/mmm$, adopted by $LaSrMnO_4$, were apparent in the NPD pattern of $LaSrMnO_4F$. All the peaks could, however, be indexed using the $P4/nmm$ space group previously proposed.[6] Taking the XRD refined structure of $LaSrMnO_4F$ as the starting model and a pseudo-Voigt peak shape function, refinement proceeded smoothly to give agreement indices $\chi^2 = 2.89$ and $R_{wp} = 2.53\%$ (Fig. 1). Although the difference profile in Fig. 1 reveals some regions of quite poor agreement, these relate to the peak shape/positions rather than intensities, and the refined structural parameters (Table 1) are therefore considered to be reliable; they are generally consistent with the XRD results. The discrepancies in peak positions, which are seen to be most apparent for the peaks at $d \sim 2.1$ Å (114 reflection) and
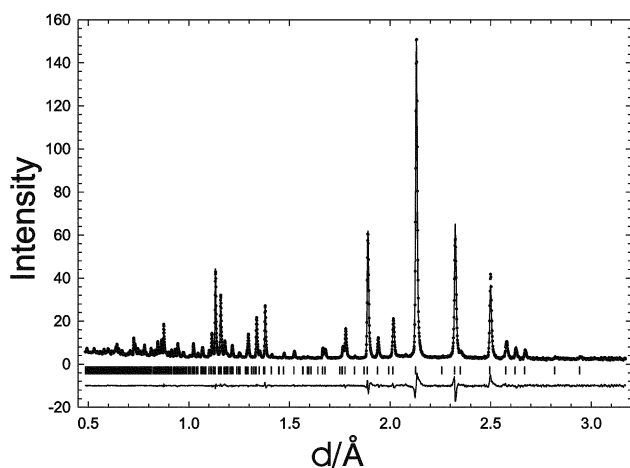
$d \sim 2.3$ Å (113 reflection), have been shown from a detailed X-ray powder diffraction study to occur when the fluorine content deviates slightly from the ideal value. It should be noted, however, that models involving partial occupation of the other rock salt layers were rejected since they consistently implied insignificant occupation of these sites and confirmed the staged model previously proposed. The major difference between the present NPD results and those from the XRD refinement concerns the Mn–O bond lengths: the NPD one gives significantly longer apical Mn–O bonds than those derived from the XRD data. Since X-ray scattering is relatively insensitive to the precise positions of F and O, the NPD results are considered to be substantially more reliable than those from the X-ray data and provide the basis for further discussion.

In the fluorination of the double layered, $n = 2$, manganate $La_{1.2}Sr_{1.8}Mn_2O_7$ by the CuF_2 route,[5] full fluorination yields a phase with $a = 3.7694(1)$ Å, $c = 23.389(1)$ Å, which compare with the precursor oxide unit cell size $a = 3.8833(1)$ Å, $c = 20.142(1)$ Å. An intermediate phase with $a \sim 3.81$ Å, $c \sim 21.7$ Å was observed when the ratio of CuF_2 to precursor oxide was less than 1, especially in the region of 0.5. The fluorination behaviour of the $n = 1$ analogue, $LaSrMnO_4$, pointed to a probable staged structure model for the intermediate phase of the $n = 2$ compound. $La_{1.2}Sr_{1.8}Mn_2O_7F$ was subsequently synthesized in fairly pure form by reacting together equimolar fractions of the fully fluorinated $La_{1.2}Sr_{1.8}Mn_2O_7F_2$, obtained *via* direct fluorination using F_2 gas, and unfluorinated $La_{1.2}Sr_{1.8}Mn_2O_7$. The XRD and NPD patterns were successfully indexed with the same space group, $P4/nmm$, previously assigned to $LaSrMnO_4F$. Structure refinement was performed using the staged model (occupancy of only alternate rock salt regions) and the atomic positions deduced from the RP precursor oxide as starting parameters. During the refinement, several weak diffraction peaks were observed and were attributable to the impurity phase $(La,Sr)MnO_3$. A multiphase refinement, with fixed structural parameters for the impurity phase,[9] quickly converged to $\chi^2 = 4.24$ and $R_{wp} = 2.95\%$. The refined structural parameters are listed in Table 2 and the fitted profile in Fig. 2. As observed in the structure of $LaSrMnO_4F$, no evidence was found for any F occupancy of the interstitial sites in the rock salt regions that are empty in the ideal staged structure. As previously discussed for $LaSrMnO_4F$, the main discrepancies between observed and calculated profiles can be traced to very small shifts in peak positions which are dependent on fluorine content and suggest a very small deviation from the ideal $La_{1.2}Sr_{1.8}Mn_2O_7F$ composition.

The structural data indicate that fluorination of both the $n = 1$ and $n = 2$ RP manganates results in a contraction in the lattice constant a, whereas expansion occurs along c. Three major factors control the change in unit cell dimensions. First of all, insertion of F into the interstitial sites expands the thickness of the rock salt layer thus increasing c. In

Fig. 1 Observed (dots), calculated and difference neutron diffraction plots for $LaSrMnO_4F$. The tick marks are the diffraction peak positions of $LaSrMnO_4F$.

Table 1 Refined structural parameters of $LaSrMnO_4F^a$

Atom	x	y	z	$100U_{iso}/Å^2$	Occupancy
La/Sr1	0.25	0.25	0.09857(7)	0.33(2)	0.5/0.5
La/Sr2	0.25	0.25	0.38277(9)	0.90(2)	0.5/0.5
Mn	0.75	0.75	0.2287(1)	0.22(2)	1
O1	0.75	0.25	0.22103(9)	0.83(2)	1
O2	0.75	0.75	0.0764(1)	0.88(3)	1
O3	0.75	0.75	0.3546(1)	1.24(3)	1
F	0.75	0.25	0.5	1.34(3)	1

^{a}Space group $P4/nmm$, $a = 3.77696(7)$ Å, $c = 14.1026(8)$ Å, $\chi^2 = 2.89$, $R_{wp} = 2.53\%$.

Table 2 Refined structural parameters of $La_{1.2}Sr_{1.8}Mn_2O_7F^a$

Atom	x	y	z	$100U_{iso}/Å^2$	Occupancy
La/Sr1	0.25	0.25	0.2366(1)	0.66(4)	0.4/0.6
La/Sr2	0.25	0.25	0.4245(2)	1.80(6)	0.4/0.6
La/Sr3	0.25	0.25	0.0610(1)	0.74(4)	0.4/0.6
Mn1	0.75	0.75	0.1423(1)	0.30(6)	1
Mn2	0.75	0.75	0.3257(2)	0.33(5)	1
O1	0.75	0.75	0.0519(2)	1.26(7)	1
O2	0.75	0.25	0.1430(1)	0.83(4)	1
O3	0.75	0.75	0.2298(2)	1.15(7)	1
O4	0.75	0.25	0.3193(1)	1.64(5)	1
O5	0.75	0.75	0.4070(2)	0.69(6)	1
F	0.75	0.25	0.5	2.9(1)	1

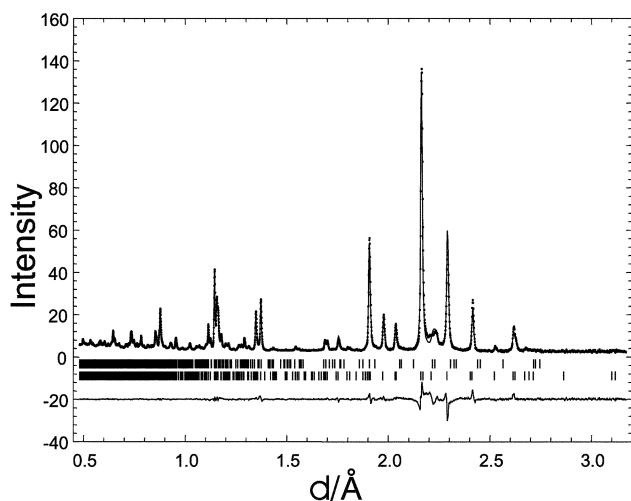^{a}Space group $P4/nmm$, $a = 3.8103(1)$ Å, $c = 21.722(2)$ Å, $\chi^2 = 4.24$, $R_{wp} = 2.95\%$.

Fig. 2 Observed (dots), calculated and difference neutron diffraction plots for $La_{1.2}Sr_{1.8}Mn_2O_7F$. The bottom tick marks are the diffraction peak positions of $La_{1.2}Sr_{1.8}Mn_2O_7F$ and the top ones are those of the impurity phase $(La,Sr)MnO_3$.

$LaSrMnO_4F$ the spacing between MnO_2 layers separated by rock salt units containing F is 7.65 Å, whereas that separated by unfluorinated rock salt regions is only 6.45 Å. The latter distance is very similar to the value 6.57 Å observed in $LaSrMnO_4$. The corresponding spacings for the $n = 2$ phases are: $La_{1.2}Sr_{1.8}Mn_2O_7$ (6.18 Å);[10] $La_{1.2}Sr_{1.8}Mn_2O_7F$ (7.57 Å and 6.18 Å); $La_{1.2}Sr_{1.8}Mn_2O_7F_2$ (7.68 Å).[6] It is clearly shown that F insertion introduces significant changes only to the rock salt region it occupies. Secondly, F insertion raises the oxidation states of the Mn ions and correspondingly reduces the Mn–O bond lengths in all directions; this explains the decrease in a observed for all fluorinated compounds. Thirdly, since Mn^{3+} is a d^4 Jahn–Teller stabilized ion, its oxidation to Mn^{4+} is expected to reduce the Mn–O apical bond length (and therefore reduce c), and may also increase the equatorial bond lengths to some extent (increase a). The last effect is not obvious but may explain the similarity of apical and equatorial Mn–O distances observed in the Mn1–O layer in $La_{1.2}Sr_{1.8}Mn_2O_7F$. Another important structural feature, which is apparent in both $LaSrMnO_4F$ and $La_{1.2}Sr_{1.8}Mn_2O_7F$, is that the Mn–O apical bonds directed towards the fluorine layers are significantly shortened. This is shown in Fig. 3 and is thought to relate
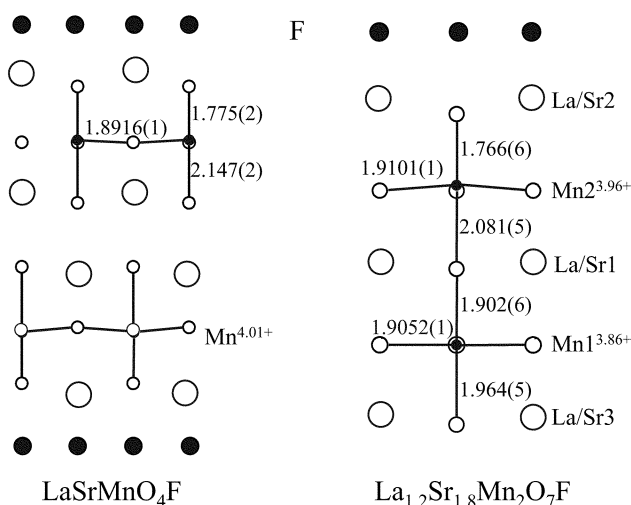
primarily to electrostatic repulsions between the F^- and O^{2-} ions. It is also interesting to note that electrostatic effects extend also to other ions in the vicinity of the F layer: Mn ions move towards the F layer whereas the O^{2-} ions equatorially coordinated to the Mn ions relax in the opposite direction (see Fig. 3). As a result, the Mn–O apical bonds in the MnO_6 octahedra adjacent to the F layers are markedly asymmetric: 1.775 Å and 2.147 Å in $LaSrMnO_4F$; 1.766 Å and 2.081 Å in $La_{1.2}Sr_{1.8}Mn_2O_7F$.

Since F and O cannot be differentiated using either XRD or NPD techniques, the actual composition (F : O ratio) cannot be directly determined by the structural refinements. However, oxidation states of both compounds can be determined by either titrimetry or thermogravimetric analysis using reduction in 10% H_2–90% N_2 at 600–700 °C to give SrF_2, $(La,Sr)_2MnO_4$ and MnO. Results for both fluorinated phases suggested that the Mn oxidation state is very close to its expected value: 4+ in $LaSrMnO_4F$ (determined 3.93+) and 3.9+ for $La_{1.2}Sr_{1.8}Mn_2O_7F$ (determined 3.99+). Our structural models are supported by bond valence sum calculations,[11] which gave $Mn^{4.01+}$ for $LaSrMnO_4F$ and $Mn1^{3.96+}$, $Mn2^{3.86+}$ for $La_{1.2}Sr_{1.8}Mn_2O_7F$, in good agreement with their ideal compositions and the analytical values. Madelung energy calculations[12] also support that F bonds only to La/Sr ions and does not substitute significantly within the MnO_6 octahedra. From the bond valence sums, it is possible that a slightly asymmetric charge distribution may exist between the two Mn species in the unit cell of $La_{1.2}Sr_{1.8}Mn_2O_7F$, the higher oxidation state, as expected, being that in proximity to the inserted fluorine.

Whereas the parent oxides $LaSrMnO_4$ and $La_{1.2}Sr_{1.8}Mn_2O_7$ both exhibit long range magnetic order at low temperature,[13,14] no evidence of such order is found for the staged fluorinated compounds studied here. This is consistent with the d^3 electronic configuration of these Mn^{4+} compounds, for which strong superexchange e_g^1–$O2p$–e_g^1 and double exchange e_g^1–$O2p$–e_g^0 cannot exist. The only interaction will be of a weak π-type, t_{2g}^1–$O2p$–t_{2g}^1. CMR behaviour related to double exchange is consequently not expected in such systems. However, variations in the La/Sr ratio and the F content might be expected to provide considerable electronic control to enable materials synthesis with more useful magnetic and electronic properties.

Conclusions

The structures of two fluorinated layered manganates, $LaSrMnO_4F$ and $La_{1.2}Sr_{1.8}Mn_2O_7F$, have been determined using neutron powder diffraction. It has been confirmed that both phases can be described as staged fluorine insertion compounds: fluorine occupies the interstitial sites in only one of the two rock salt regions of the respective unit cell. Electrostatic Mn···F attractions and O···F repulsions result in extremely short Mn–O apical bonds directed towards the layers of F ions. The successful preparation of such staged F intercalation compounds in layered manganates suggests the possible synthesis of not only other staged layered compounds, but also compounds exhibiting different types of staging and having different F contents.

Fig. 3 Selected parts of the structures of $LaSrMnO_4F$ and $La_{1.2}Sr_{1.8}Mn_2O_7F$ showing Mn–O bond lengths and Mn bond valence sums. The large open circles represent La/Sr atoms, the small open circles are oxygen atoms, the small filled circles are Mn atoms and the large filled circles are F atoms.

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