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New layered manganese oxide halides

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The first layered manganese(III) oxide chlorides, Sr_2MnO_3Cl and $Sr_4Mn_3O_{8-y}Cl_2$, have been synthesised; Sr_2MnO_3Cl adopts a K_2NiF_4 type structure with sheets of MnO_5 square based pyramids linked through oxygen and separated by SrCl layers; it is the end member of a new family of Ruddlesden–Popper type manganese oxide halides which includes the three-layer member $Sr_4Mn_3O_{8-y}Cl_2$ also reported herein.

The recent discovery of materials that exhibit the phenomena of high temperature superconductivity or giant magnetoresistance (GMR) has resulted in considerable activity in the synthesis of new complex oxides of first row transition metals. In terms of GMR, manganates with mixed Mn(III)/(IV) adopting the perovskite and perovskite intergrowth structures (Ruddlesden–Popper phases) have been the main areas of interest,[1,2] though magnetoresistive behaviour is also exhibited by other systems such as Fe(IV) based materials.[3] Many complex cuprate based systems have now been shown to exhibit superconductivity;[4] initially this behaviour was found only in complex oxides but more recently other anion containing systems such as oxide carbonates, oxide borates and oxide halides have all been shown to contain superconducting phases.[5] The phases $(Sr,Ca)_3Cu_2(O,Cl)_{6-\delta}$ with $T_c = 83$ K and $(Ca,Na)_2CuO_2Br_2$ with $T_c = 24$ K are examples from a wide range of complex copper oxide halide superconductors.[6]

It is clear that for superconducting cuprates mixed anion systems offer additional compositional variation facilitating, for example, the control of the metal oxidation state. Extension of this mixed anion chemistry of copper to other first row transition metals has been achieved with phases such as the iron oxide halides Sr_2FeO_3X (X = F, Cl, Br)[7] and the cobalt oxide chlorides $Sr_3Co_2O_5Cl_2$, Sr_2CoO_3Cl.[8] With respect to manganese chemistry no simple Mn(III) layered oxide halide has previously been described despite the interest in this element and oxidation state with respect to GMR. Greaves *et al.* have investigated the oxidative insertion of fluoride into various manganese oxides and described the formation of LaSrMn(IV)O_4F[9] and $La_{1.2}Sr_{1.8}Mn_2O_7F_2$[10] ($Mn^{4.4+}$) by addition of a fluoride layer between the rocksalt layers of $LaSrMnO_4$, K_2NiF_4 structure, and $La_{1.2}Sr_{1.8}Mn_2O_7$, Ruddlesden–Popper $n = 2$ phase respectively. In both cases the manganese remains octahedrally coordinated to oxygen.

In this paper we report for the first time the synthesis and structural characterisation of complex manganese(III) oxide halides. Such materials should be ideal parent phases for generating new compounds exhibiting magnetoresistance effects.

Sr_2MnO_3Cl was prepared by firing a 1:3:1 mixture of Mn_2O_3 (Aldrich 99.999%), SrO (from $SrCO_3$ at 1000 °C) and $SrCl_2$ (Aldrich 99.99+%) in a silica ampoule sealed under vacuum. The reagents were dried at 400 °C before being ground in a dry box and transferred to a silica reaction vessel and reacted at 850 °C for 20 h to yield a dark green sample. Phase purity was assessed using powder X-ray diffraction data collected on a Siemens D5000 diffractometer (Cu-Kα_1 radiation). By comparison with the powder X-ray diffraction data of Sr_2FeO_3Cl it was clear that the desired phase had been obtained with a small level (~5%) of an impurity. These impurity peaks could be indexed on the basis of an $n = 3$ Ruddlesden–Popper oxychloride phase $Sr_4Mn_3O_{8-y}Cl_2$, $a = 3.85$, $c = 32.3$ Å analogous to $Sr_4Co_3O_{7.5}Cl_2$ reported by Cava and coworkers.[8] This phase was synthesised directly by varying the Sr::Mn ratio in the reaction mixture and a near monophasic sample obtained by employing two 14 h firings at 850 °C with an intermediate regrind. The only detectable impurity was a trace level of MnO. Further high quality powder X-ray data were collected in the 2θ range 10–100° (step size 0.017°) using a Bruker D8 diffractometer (Cu-Kα_1) over a period of 10 h on both materials and the structural models derived from that of Sr_2FeO_3Cl[7] and $Sr_4Co_3O_{7.5}Cl_2$[8] refined using Rietveld profile analysis.[11] Refinements were completed to convergence using the normal data analysis methods. The coordinate descriptions obtained together with derived bond lengths and angles of interest and the profile fit factors are summarised in Tables 1–3. $Sr_4Mn_3O_{8-y}Cl_2$ was introduced as a secondary phase in the Sr_2MnO_3Cl analysis (weight fraction = 7.5%) and the final fit achieved for this phase is shown in Fig. 1. In the refinement of $Sr_4Mn_3O_{8-y}Cl_2$ no direct evidence was found of non-stoichiometry or reduced site occupancy (through variation of this parameter), as for example, occurs with $Sr_4Co_3O_{7.5}Cl_2$. The refinement was therefore maintained with the overall stoichiometry $Sr_4Mn_3O_8Cl_2$ to give an excellent fit to the diffraction data. However on the basis of powder X-ray data alone small variations in site occupancies cannot be discounted. Finally MnO was included and refined to give a weight fraction of 1.5%.

Table 1 Refined atomic coordinates for Sr_2MnO_3Cl; esds are given in parentheses[a]

	x	y	z	B/Å^2	n
Sr(1)	0.25	0.25	0.09083(6)	1.48(3)	1.0
Sr(2)	0.25	0.25	0.34372(7)	1.56(3)	1.0
Mn(1)	0.75	0.75	0.2103(1)	1.22(4)	1.0
O(1)	0.75	0.25	0.2311(3)	1.76(9)	1.0
O(2)	0.75	0.75	0.0734(4)	2.2(1)	1.0
Cl	0.75	0.75	0.4264(2)	2.31(6)	1.0

[a] $P4/nmm$; $a = 3.84170(3)$, $c = 14.7372(2)$ Å; $R_{wp} = 1.76\%$, $R_p = 1.24\%$, $\chi^2 = 4.23$.

Table 2 Refined atomic coordinates for $Sr_4Mn_3O_8Cl_2$; esds are given in parentheses[a]

	x	y	z	B/Å^2	n
Sr(1)	0.0	0.0	0.43977(8)	1.26(6)	1.0
Sr(2)	0.0	0.0	0.32059(6)	1.38(6)	1.0
Mn(1)	0.0	0.0	0.1191(1)	1.4(1)	1.0
Mn(2)	0.0	0.0	0.0	1.6(2)	1.0
O(1)	0.0	0.5	0.127(4)	1.8(3)	1.0
O(2)	0.0	0.0	0.059(5)	3.3(2)	1.0
O(3)	0.0	0.5	0.0	4.5(6)	1.0
Cl	0.0	0.0	0.2167(2)	2.5(2)	1.0

[a] $I4/mmm$; $a = 3.86247(3)$, $c = 32.2796(4)$ Å; $R_{wp} = 1.75\%$, $R_p = 1.20\%$, $\chi^2 = 4.43$.

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Table 3 Selected bond distances (Å) and angles (°) for Sr_2MnO_3Cl and $Sr_4Mn_3O_8Cl_2$

	Sr_2MnO_3Cl	$Sr_4Mn_3O_8Cl_2$
Mn(1)–O(1)	1.9452(8) × 4	1.948(2) × 4
Mn(1)–O(2)	2.019(6) × 1	1.92(2) × 1
Mn(1)–Cl	3.184(4) × 1	3.151(6) × 1
O(1)–Mn(1)-O(1)	161.9(3)	165(1)
Mn(2)–O(3)	—	1.93124(2) × 4
Mn(2)–O(2)	—	1.92(2) × 2
O(3)–Mn(2)–O(3)	—	180

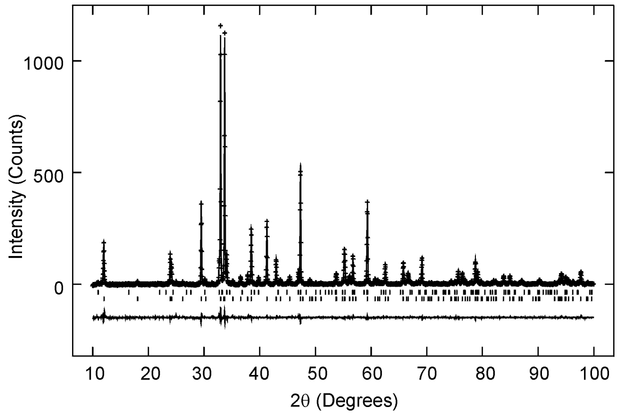

Fig. 1 Fit obtained to the powder X-ray diffraction data from Sr_2MnO_3Cl. Crosses are observed data, upper continuous line the fitted profile and lower continuous line the difference. Tick marks show the reflection positions: lower, Sr_2MnO_3Cl; upper, $Sr_4Mn_3O_8Cl_2$ (7.5% wt. fraction).

The structures of the manganese oxide chlorides are shown in Fig. 2. In Sr_2MnO_3Cl the manganese is formally coordinated to oxygen in a square pyramidal arrangement with a much longer interaction to chloride while in $Sr_4Mn_3O_{8-y}Cl_2$ a central MnO_6 octahedron is bonded through its apices to two MnO_5Cl units akin to those present in Sr_2MnO_3Cl. The manganese environments in all cases are distorted from a regular environment, *e.g.* 4 × 1.9452(8) Å Mn–O(1) basal bonds and apical interactions at 2.019(6) Å (Mn–O(2)) and 3.184(4) Å (Mn–Cl) for Sr_2MnO_3Cl, as might be expected for structures based on a Jahn–Teller ion such as Mn(III). Similar non-uniform Mn–O environments are common for Mn oxides, for example the related single layer Mn^{3+} oxide $BiPbSr_2MnO_6$[12] with four co-planar bonds of 1.90 Å and 2 apical distances at 2.33 Å.

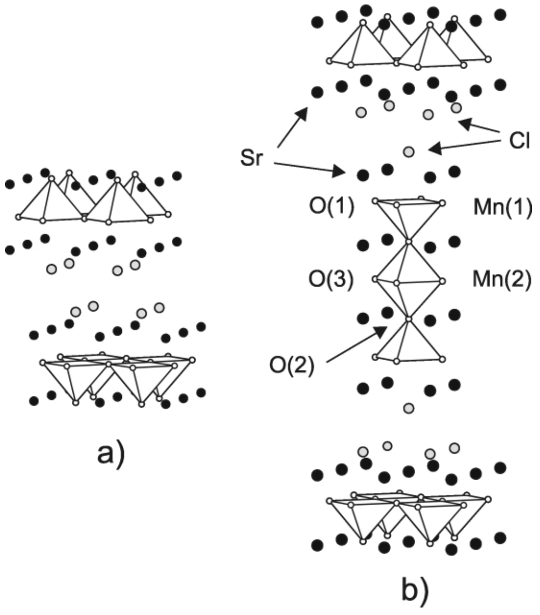

Fig. 2 The structures of Sr_2MnO_3Cl (a) and $Sr_4Mn_3O_8Cl_2$ (b); MnO_5 square based pyramids and MnO_6 octahedra are shown.

Bond valence sum (BVS) calculations[13] for the Mn–O bonds using the r_o for Mn(III) yields a value of 2.9 for Sr_2MnO_3Cl, in good agreement with the expected value. Similar calculations for $Sr_4Mn_3O_{8-y}Cl_2$ give valence sums of 3.0 for the square pyramidal Mn(1) site and, assuming full site occupancies, 3.7 for the octahedral central Mn(2) position. Inclusion of the Mn–Cl interactions, *i.e.* Mn(1)–Cl 3.184 Å (Sr_2MnO_3Cl) and Mn(1)–Cl 3.151 Å ($Sr_4Mn_3O_{8-y}Cl_2$) in the coordination sphere has a negligible effect on the final valence sums indicating very weak metal halide interactions.

The BVS for the formally octahedral $Mn(2)O_6$ site in $Sr_4Mn_3O_{8-y}Cl_2$ is consistent with a level of localised Mn^{4+}. The presence of a small amount of MnO in the sample would allow a degree of oxidation of manganese within the main phase. However, at this stage the possibility that there is oxygen deficiency associated with this position, analogous to that determined for $Sr_4Co_3O_{7.5}Cl_2$, cannot be ruled out. A planned neutron diffraction study will be required to accurately determine the oxygen content and distribution within both materials.

Sr_2MnO_3Cl is formally the end member of a Ruddlesden–Popper type family $Sr_{n+1}Mn_n(O,Cl)_{3n+1}$ where either one or two halides replace oxygen in the terminal positions of the perovskite block, giving $Sr_{n+1}Mn_nO_{3n}Cl$ (L1, $n = 1$ single manganese layer as in Sr_2MnO_3Cl) or $Sr_{n+1}Mn_nO_{3n-1}Cl_2$ (L3, $n = 3$ as in $Sr_4Mn_3O_{8-y}Cl_2$). In both cases the infinite perovskite block ($n = \infty$) end member is formally $SrMnO_3$ (Mn(IV)) and increasing the number of $SrMnO_3$ perovskite blocks is concomitant with increasing the manganese oxidation state above Mn(III). For stoichiometric materials the manganese oxidation state is +3 for Sr_2MnO_3Cl and +3.33 for $Sr_4Mn_3O_8Cl_2$, suggesting the latter compound, in particular, is a strong candidate for magnetoresistance effects.[1,2] Control of oxygen stoichiometry and thus manganese oxidation state in these materials will be crucial in their further development.

The layered manganese oxide halides, Sr_2MnO_3Cl and $Sr_4Mn_3O_{8-y}Cl_2$, have been synthesised and their key structural characteristics identified using powder X-ray diffraction. An analogous series of compounds with bromide replacing chloride can also be synthesised. We will report in a full paper the range of new Mn(III)/(IV) oxide halides that can be produced, detailed structural and compositional analysis, including an understanding of the control oxidation state in $Sr_4Mn_3O_{8-y}Cl_2$ and the results of investigations into magnetoresistive effects in these compounds.

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