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Synthesis and structure of Sr_2MnGaO_5, a new layered manganese oxide

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A new layered manganese oxide, Sr_2MnGaO_5, has been synthesised and Rietveld analysis of X-ray powder diffraction data has shown it to be an oxygen deficient perovskite with the brownmillerite structure: $a = 5.5033(6)$ Å, $b = 16.234(2)$ Å, $c = 5.3717(6)$ Å. Incomplete order of the oxygen vacancies is best described using the space group *Icmm*. The oxygen content can readily be varied to form $Sr_2MnGaO_{5+\delta}$ ($0 \leqslant \delta \leqslant 0.5$) to provide Mn oxidation states between Mn(III) and Mn(IV).

Manganese oxides have been the subject of much recent attention, principally due to the unique colossal magnetoresistance (CMR) properties displayed by some manganese perovskites and related phases. The technological potential of the perovskites such as $La_{1-x}Ca_xMnO_3$ is, however, difficult to realise due to the high magnetic fields required to observe the highest CMR effects. Reports of similar behaviour, but at lower magnetic fields, in manganese oxides with the Ruddlesden–Popper structure, *e.g.* $La_{1.2}Sr_{1.8}Mn_2O_7$,[1,2] suggest that other manganese oxides with two-dimensional magnetic characteristics may provide interesting, and more useful, alternatives to the simple perovskites. Here we report the synthesis and preliminary characterisation of a new phase, Sr_2MnGaO_5, which demonstrates a new approach to producing two-dimensional manganese oxides. The synthetic strategy was directed towards a cation-ordered perovskite structure in which magnetic Mn ions are ordered in layers and are interleaved with non-magnetic cations. In order to maximise the extent of order, Ga^{3+} ions were selected for the separating cations, based on their strong preference for tetrahedral coordination. In this way, it was hoped to synthesise members of the structural family shown in Fig. 1, with general formula $A_{n+1}Mn_nGaO_{3n+2}$, and originally formulated for perovskites containing Fe/Ti on the octahedral sites.[3,4] The simplest ($n = 1$) member would have the brownmillerite structure, adopted by $Ca_2Fe_2O_5$,[5,6] $Sr_2Fe_2O_5$,[7,8] $Ca_2(Fe,Al)_2O_5$[5,9] *etc.*, and here we describe the phase Sr_2MnGaO_5, and demonstrate, using Rietveld analysis of X-ray powder diffraction data, that it has such a structure. The oxygen vacancies in the GaO layer are ordered to provide chains of corner linked GaO_4 tetrahedra. In brownmillerite phases, subtleties in the relative displacements of atoms within these chains can lead to structures that crystallise in space groups *Icmm*, *Ibm*2 or *Pcmn*.[6,7] We also report a preliminary investigation of the magnetic properties of Sr_2MnGaO_5, and oxygen insertion to form the oxidised variants $Sr_2MnGaO_{5+\delta}$.

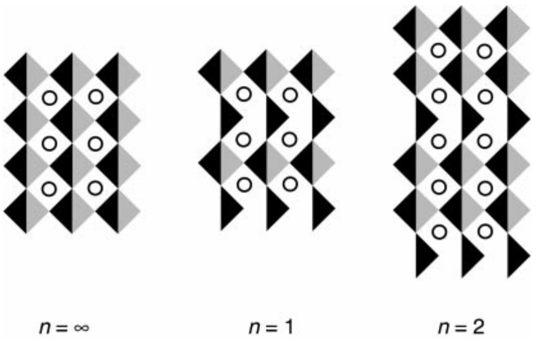

Fig. 1 Schematic representation showing the linking of layers of octahedra and tetrahedra in the $n = \infty$ (perovskite end-member), $n = 1$, and $n = 2$ members of the $A_{n+1}Mn_nGaO_{3n+2}$ family.

Sr_2MnGaO_5 is the first member of the series comprising a GaO layer separated by ever increasing numbers of MnO_2 layers. The synthesis of higher homologues would be extremely important since, for example, a material $A_3Mn_2GaO_8$ with A cations chosen to provide a mixed Mn^{3+}/Mn^{4+} oxidation state, would be expected to be electronically and magnetically similar to $La_{1.2}Sr_{1.8}Mn_2O_7$.

The synthesis of Sr_2MnGaO_5 was achieved by heating (1350 °C for 48 hours in flowing N_2) an intimate mixture of stoichiometric quantities of high purity $SrCO_3$, Mn_2O_3 and Ga_2O_3. Oxygen content determination, *via* thermogravimetric analysis (reduction in H_2/N_2 using a Rheometric Scientific STA 150 thermal analyser) indicated $\delta \sim 0.1$. Further heating (up to 72 hours) at 1350 °C in flowing N_2 enabled the oxygen content to be lowered to $\delta \sim 0$. Structural characterisation was achieved from a Rietveld analysis (using the GSAS suite of programs[10]) of X-ray powder diffraction data collected on a Siemens D5000 diffractometer (Ge monochromator providing CuKα_1, position sensitive detector). Magnetic measurements were obtained using an Oxford Instruments VSM using a field of 1 T.

Rietveld analysis of the powder X-ray diffraction data confirmed a brownmillerite structure with alternate layers of MnO_6 octahedra and GaO_4 tetrahedra (Fig. 2). Oxygen vacancies in the GaO layer provide a distorted tetrahedral coordination for the Ga cation. These GaO_4 tetrahedra corner link to form chains running along [001]. It is well known that the arrangement of such chains in the brownmillerite structure lead to one of three possible space groups: *Icmm*, *Ibm*2 and *Pcmn*.[6,7] Whereas *Ibm*2 and *Pcmn* provide full order between atomic displacements in adjacent GaO layers, *Icmm* describes a disordered arrangement. Although the differences between the space groups are subtle, the refinement results (Table 1, Fig. 3) slightly favoured *Icmm* for Sr_2MnGaO_5 as opposed to *Ibm*2 ($R_{wp} = 2.51\%$, $\chi^2 = 7.16$) and *Pcmn* ($R_{wp} = 2.54\%$, $\chi^2 = 7.35$). No additional peaks indicating primitive symmetry were present, and the preference of *Icmm* over *Ibm2* was supported by higher (and anisotropic) Ga thermal parameters for the Ga atoms in *Ibm*2. It should be noted that locally we would expect the order to correspond to *Pcmn* or, more probably, *Ibm*2 but small domains of such order (on an X-ray diffraction length scale)

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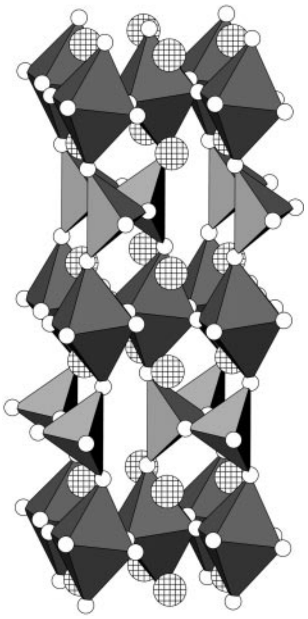

Fig. 2 Structure of Sr_2MnGaO_5 showing MnO_6 octahedra, GaO_4 tetrahedra and Sr (hatched spheres). (This representation is based on the fully ordered *Ibm*2 structure to aid clarity.)

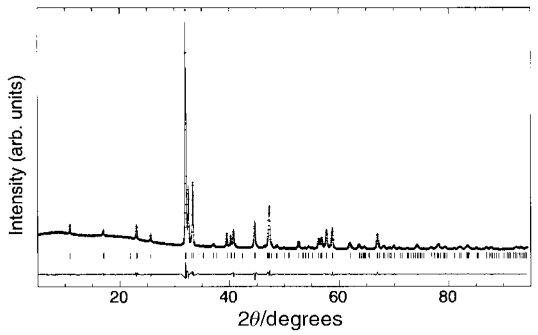

Fig. 3 XRD profiles (continuous lines calculated and difference; crosses observed data) for Sr_2MnGaO_5.

would provide an average structure better described in the higher symmetry *Icmm*. The disorder between GaO layers, indicated by space group *Icmm*, is reflected in the half occupancy of two distinct sites by the atoms in these layers (Ga and O3 in 8i sites). It is expected that within a given layer, only four of the 8i sites will be occupied, certainly over quite large distances, by these atoms in accordance with the lower symmetry space group *Ibm*2. This provides the Ga with approximately tetrahedral coordination, as indicated by the bond distances and angles shown in Table 2. The Mn^{3+} ions are located in tetragonally elongated octahedral coordination, consistent with Jahn–Teller stabilisation.

Table 1 Refined structural parameters for Sr_2MnGaO_5 obtained from Rietveld analysis of X-ray powder diffraction data

Atom	Site	*x*	*y*	*z*	U_{iso}/Å$^{2\,a}$	Occupancy
Sr	8h	0.5143(4)	0.1122(1)	0	0.001(1)	1.0
Mn	4a	0	0	0	0.008(1)	1.0
Ga	8i	0.0608(6)	¼	0.985(4)	0.034(2)	0.5
O1	8g	¼	0.0104(7)	¼	0.005(2)	1.0
O2	8h	0.951(1)	0.1445(4)	0	0.005	1.0
O3	8i	0.364(2)	¼	0.874(2)	0.005	0.5

[a] Values without esd's were constrained to be equal to those of the atom above. $R_{wp}=2.45\%$, $R_p=1.60\%$, $R_F{}^2=2.91\%$, $\chi^2=6.80$, *Icmm*: $a=5.5033(6)$ Å, $b=16.234(2)$ Å, $c=5.3717(6)$ Å.

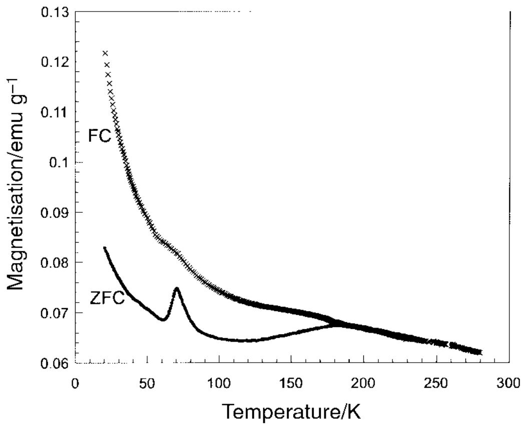

Fig. 4 Magnetisation *versus* temperature for Sr_2MnGaO_5.

Table 2 Selected bond lengths (Å) and angles (°) for Sr_2MnGaO_5

Mn–O1 1.930(1) {×4}	Sr–O1 2.579(7) {×2}
Mn–O2 2.361(6) {×2}	Sr–O1 2.730(8) {×2}
Ga–O2 1.818(7) {×2}	Sr–O2 2.743(1) {×2}
Ga–O3 1.83(1), 1.77(2)	Sr–O2 2.460(8), 3.172(9)
	Sr–O3 2.478(6) {×2}
O1–Mn–O1 88.18(5), 91.82(8), 180	
O1–Mn–O2 88.2(2), 91.8(4), 180.0(5)	
O2–Ga–O2 140.8(6)	
O3–Ga–O3 98.5(8) to 102.3(6)	

The magnetic susceptibility data (Fig. 4) suggest the presence of complex magnetic order. The divergence of the field cooled and zero-field cooled susceptibilities below ~180 K marks the Néel temperature of a basic antiferromagnetically ordered structure which we would expect from simple superexchange coupling between Mn^{3+} moments. This has been confirmed by preliminary examination of neutron diffraction data, which are consistent with a simple antiferromagnetic structure with Mn^{3+} moments of 3.26(3) μ_B at 4 K directed along [010] and [0 −10]. The moment is typical of Mn^{3+} in oxides. The magnetic anomaly at ~80 K and increase in χ at low temperatures are consistently observed and believed to relate to magnetic inhomogeneities, possibly through the formation of ferromagnetic clusters in the antiferromagnetic matrix. We can rationalise this through the presence of localised regions of *Ibm*2 order which possess a small canting of their moments, a phenomenon commonly observed in brownmillerite phases. This preliminary examination of the neutron diffraction data also suggests a small amount (~4%) of Mn–Ga mixing which is currently being modelled and could explain the high Ga thermal parameter (Table 1). A full analysis of these structural and magnetic features will be reported subsequently and will incorporate the neutron diffraction and electron microscopy results.

It is interesting to note that treatment of Sr_2MnGaO_5 at low temperatures (*e.g.* 400 °C) for 12 hours in air yields the single phase product $Sr_2MnGaO_{5.5}$ in which the Mn has been oxidised to Mn^{4+}. A more complete report of the chemistry of the system $Sr_2MnGaO_{5+\delta}$ will follow this communication, but it is important to note the flexible oxygen content of this $n=1$ member of the $A_{n+1}Mn_nGaO_{3n+2}$ family. If higher members can be synthesised, such oxygen non-stoichiometry may be of importance for providing chemical control of the Mn oxidation state and hence magnetic and electronic properties.

Acknowledgements

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