

Crystal chemistry and electronic properties of the $n = 2$ Ruddlesden-Popper manganates: unconventional CMR materials.

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ABSTRACT

The crystallography and electronic properties of the $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Mn}_2\text{O}_7$ manganese oxides adopting the $n = 2$ Ruddlesden-Popper (RP) structure are discussed, focusing on the structural phase diagrams and electronic properties in the vicinity of the Mn +3.5 oxidation state and in particular the ease of synthesis of single phases of these materials.

INTRODUCTION

MASTER

The observation that the metal-insulator transition at the Curie temperature (T_c) of the perovskites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ could be shifted by the application of magnetic fields at temperatures just above T_c to produce a massive decrease in the electrical resistance^{1,2} has become known as colossal magnetoresistance (CMR). Problems of temperature range, saturation field and device noise remain in the way of applications, but recent advances have been made in all of these directions.³⁻⁵ It has become accepted that CMR and field-induced ferromagnetism are closely interrelated, leading to the use of the double exchange mechanism⁶ to interpret the experimental observations. Recently, the $n = 2$ member of the RP homologous series, of which the perovskite is the $n = \infty$ end member, has become the focus of attention.⁷⁻¹⁰ We have demonstrated CMR without bulk ferromagnetism in ceramic samples of $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$.⁹ In the course of this study, we have been forced, through our use of high resolution powder diffraction characterisation, to address detailed and sometimes difficult issues of phase separation and phase purity, which turn out to be sensitive functions of the lanthanide cation in question and the manganese oxidation state. In this paper, we report on the evolution of the phase diagram at the $\text{Sr}_2\text{LnMn}_2\text{O}_7$ composition with lanthanide and Sr/Ln ratio for La, Tb and Nd. We emphasise the need for the application of very high resolution powder diffraction techniques and profile refinement to confirm the synthesis of single phases. We also discuss cation ordering in the single and biphasic samples, and briefly address the evolution of magnetic and magnetotransport behaviour across the series.

The $n = 2$ member of $(\text{La,Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ series had been investigated by several groups before the current interest in manganese oxides for CMR applications¹¹⁻¹³. Ferromagnetic behaviour had been identified in the La,Sr $n = 2$ phases with a saturation moment per Mn which appeared to vary strongly as a function of La/Sr ratio. CMR at the ferromagnetic Curie temperature of 126K was found in single crystal $\text{La}_{1.8}\text{Sr}_{1.2}\text{Mn}_2\text{O}_7$ ⁷ - the saturation moment of $3 \mu_B$ with the moment direction in the xy plane has been confirmed by powder neutron diffraction¹⁴. A particularly interesting feature of this material from the point of view of applications is the low magnetic fields (less than 1T) required to produce magnetoresistance. The recent observation of low-field CMR in cation substituted perovskites⁴ with a manganese oxidation state close to +3.5, and an ordered array of the +III and +IV oxidation states in zero field, makes the behaviour of the $n = 2$ RP phases in this oxidation state range of interest.

EXPERIMENT

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The samples discussed in the paper are prepared by subsolidus reaction of the constituent oxides and SrCO_3 in alumina crucibles in air or flowing nitrogen at temperatures

between 1350 °C and 1500 °C: precise details of the synthesis conditions are given in 15. Magnetisation experiments were carried out with an MPMS SQUID magnetometer over the temperature range $5 \leq T/K \leq 300$ and $0.01 \leq B/T \leq 5$. High resolution X-ray powder diffraction data were recorded at room temperature with the Bragg-Brentano geometry diffractometer at station 2.3 at the Synchrotron Radiation Source, Daresbury Laboratory and at the X7A beamline at the NSLS, Brookhaven National Laboratory. Neutron powder diffraction data were recorded on the D1B and D2B neutron diffractometers at the Institut Laue-Langevin, Grenoble over the temperature range $1.5 \leq T/K \leq 300$.

RESULTS

Sr₂LaMn₂O₇

High resolution powder X-ray and neutron diffraction measurements show that this composition phase separates into two $n = 2$ Ruddlesden-Popper phases with lattice parameters of $a = 3.8748(1)\text{\AA}$, $c = 19.9984(8)\text{\AA}$ for the majority phase (~80%) and $a = 3.8753(3)\text{\AA}$, $c = 20.072(1)\text{\AA}$ for the minority phase (~20%). SQUID magnetisation measurements had suggested the presence of both antiferromagnetic and ferromagnetic ordering in this sample⁸, consistent with earlier measurements on materials of this composition.^{11,12} Variable temperature powder neutron diffraction measurements show that this is attributable to the onset of ferromagnetic order at 124K in the minority phase, whose properties are very similar to those of Sr_{1.8}La_{1.2}Mn₂O₇,^{7,10,14} while the majority phase is a previously uncharacterised antiferromagnet with a Neel temperature of 220K.¹⁶ Rietveld refinement yields phase fractions of the two phases which, in combination with the assumption that the ferromagnetic phase is Sr_{1.8}La_{1.2}Mn₂O₇, leads to the conclusion that the new antiferromagnetic phase has a composition of Sr_{2.04}La_{0.96}Mn₂O₇, corresponding to a manganese oxidation state of +3.52. This has implications for a comparison of the homologous phases in the Sr/La system as a function of perovskite block thickness - $n = \infty$ is metallic at all temperatures and ferromagnetic at the +3.5 oxidation state, whereas both $n = 1$ and $n = 2$ are antiferromagnets, although it appears that the precise composition is unstable in the $n = 2$ case. This may have consequences for the existence of commensurate charge ordering in the $n = 2$ phase, which has not been detected in the current experiments.

Sr_{2-x}Nd_{1+x}Mn₂O₇

High resolution diffraction experiments indicate that phase separation is also an important problem to be addressed in this system. The ease of single phase synthesis increases with x , and depends on the reaction temperature and time. Representative data collected on station 2.3 at Daresbury are shown in Figure 1. The $\{0\ 0\ 10\}$ reflection is especially sensitive to the existence of multiple phases. The example of Sr_{1.6}Nd_{1.4}Mn₂O₇ shows clearly the issues involved. Figure 1(a) shows data from a sample with a $\{0\ 0\ 10\}$ reflection which can be fitted with a single pseudo-Voigt function with an FWHM of $0.075(2)^\circ$ (only slightly broadened over the instrumental resolution of 0.05° in this angular range at a wavelength of 1.39937\AA). We judge that this is a single phase, and the magnetic data shown in Figure 2(a) show only a low temperature spin-glass freezing transition. The data in Figure 1(b) are from a second, larger sample with the same nominal composition and similar thermal treatment. The $\{0\ 0\ 10\}$ reflection now has an FWHM of $0.127(2)^\circ$, which we judge to be representative of a biphasic sample. The magnetic data shown in Figure 2(b) are a strong indication that our conclusion that $\{0\ 0\ 10\}$ widths much in excess of 0.08° identify inhomogeneities in the sample which are significant from the point of view of controlling the electronic properties. These data clearly show the existence of a high temperature feature in the magnetisation similar to that found for samples with slightly lower values of x (≤ 0.3),⁹ together with the lower temperature freezing transition attributable to a second phase. Samples of Sr₂NdMn₂O₇ prepared with different thermal treatments illustrate the problems involved in preparing single phases and identifying them with certainty. Samples prepared either in air at 1350 °C or with a Bi₂O₃ flux at 1500 °C¹⁰ have FWHM of $0.182(4)^\circ$, while extended annealing at 1400 °C, 1450 °C and 1500 °C give reflections with widths of $0.131(2)^\circ$, $0.131(3)^\circ$ and $0.113(2)^\circ$ still in excess of our single phase limiting width. This is consistent with the complex magnetism, suggestive of biphasic behaviour,⁹ and in agreement with two-phase Rietveld refinements of $x = 0.0$ and $x = 0.1$

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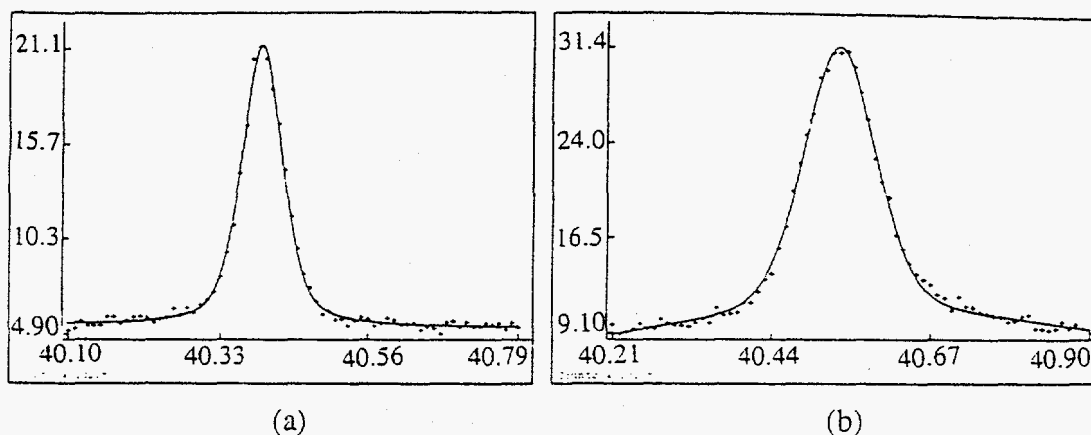


Figure 1: Synchrotron X-ray powder diffraction measurement of the {0 0 10} reflection of (a) single phase $\text{Sr}_{1.6}\text{Nd}_{1.4}\text{Mn}_2\text{O}_7$ (b) biphasic $\text{Sr}_{1.6}\text{Nd}_{1.4}\text{Mn}_2\text{O}_7$. Fits are to a single pseudo-Voigt function with widths quoted in the text.

samples.¹⁷ The $x = 0.2$ composition (prepared according to a recently published protocol¹⁰) has a {0 0 10} width of $0.103(3)^\circ$, which is again broader than our single phase criterion. These effects are hard to detect using a conventional laboratory diffractometer.

$\text{Sr}_2\text{LnMn}_2\text{O}_7$

At the 2:1 composition (which is phase-separated under all the subsolidus synthesis conditions we have investigated for $\text{Ln} = \text{Nd}, \text{La}$) changing the size of the lanthanide cation produces a transition to truly single phase behaviour beyond $\text{Sr}_2\text{EuMn}_2\text{O}_7$. The precise details of the synthetic procedure remain important in reproducibly preparing a single phase. In Figure 3, we show the {0 0 10} reflections of single phase samples of $\text{Sr}_2\text{YMn}_2\text{O}_7$ and $\text{Sr}_2\text{HoMn}_2\text{O}_7$ with FWHM of $0.0681(6)^\circ$ and $0.072(2)^\circ$ respectively. The electronic properties of both samples suggest that they are electronically homogeneous, with spin-glass like freezing below 20K signalled by a divergence between field cooled (FC) and zero field cooled (ZFC) magnetisations. Rietveld refinement of laboratory X-ray data indicates that the smaller 9 co-ordinate A cation site in the rock-salt layer of the structure is preferentially occupied by Ln^{3+} to an increasing extent as the size of the lanthanide cation decreases into this single phase region. In $\text{Sr}_2\text{DyMn}_2\text{O}_7$ this site is occupied by 94% of the Dy^{3+} cations while the larger 12 co-ordinate rock-salt layer site is almost exclusively occupied by Sr^{2+} cations. The site ordered single phases have a magnetic response which is quite different to that of the biphasic, larger lanthanide 2:1 compositions discussed earlier. In particular, there is no evidence for high temperature ordering or freezing of the manganese spins, and the magnetisation is non-hysteretic and obeys the Curie law well above 50K. Below approximately 30K, a divergence between the field-cooled (FC) and zero-field cooled (ZFC) magnetisations indicates a spin-glass like freezing of the manganese moments. The lower freezing temperature compared with $\text{Sr}_2\text{NdMn}_2\text{O}_7$ implies an increasing frustration of antiferromagnetic interactions as the size of the lanthanide cation decreases. This is particularly important as the low temperature spin-glass phase of $\text{Sr}_2\text{YMn}_2\text{O}_7$ does not display CMR at fields of up to 14T in the 5-300K temperature range, consistent with the absence of metamagnetic features in $M(H)$ isotherms measured for $5 \leq T/K \leq 300$.

CONCLUSIONS

We begin with a discussion of the implications of the phase separation at the $\text{Sr}_2\text{LaMn}_2\text{O}_7$ composition - in contrast to the $\text{Sr}_2\text{NdMn}_2\text{O}_7$ case, the cell volume differences between the two phases are large and different syntheses of this composition by different groups^{11,12,16} appear to give consistent results. In particular, reaction conditions which lead to single phase $\text{Sr}_{1.8}\text{La}_{1.2}\text{Mn}_2\text{O}_7$ yield for $\text{Sr}_2\text{LaMn}_2\text{O}_7$ a material whose electronic and diffraction properties can only be understood in terms of a separation into two distinct phases.

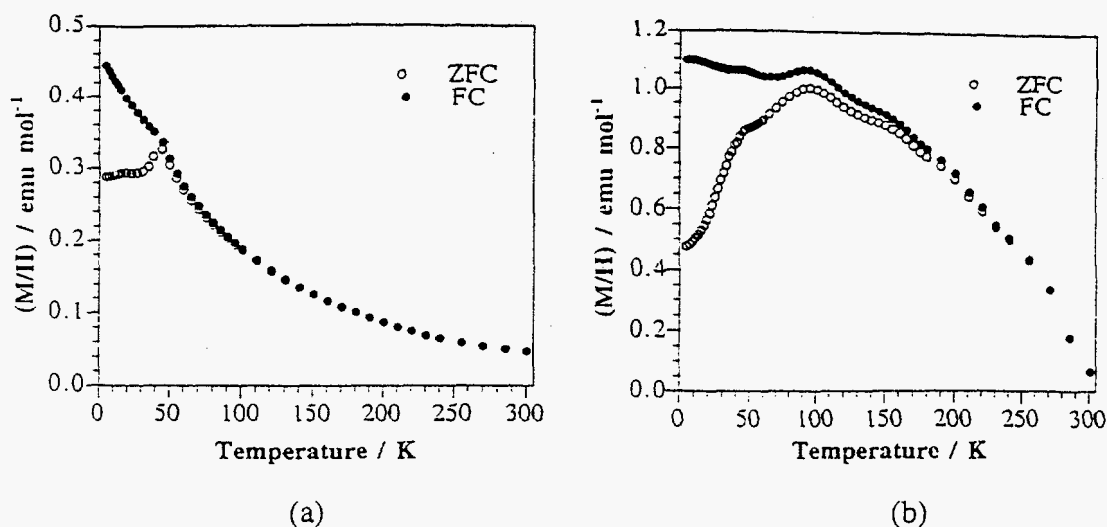


Figure 2: Magnetisation measurements on the (a) mono and (b) biphasic samples of $\text{Sr}_{1.6}\text{Nd}_{1.4}\text{Mn}_2\text{O}_7$ corresponding to the X-ray measurements in Figure 1.

The minority ferromagnetic component has already been well characterised from the electronic and diffraction point of view^{7,14}, but the new finding here is the existence of an antiferromagnetic phase close to the +3.5 oxidation state, where commensurate charge ordering is found in the $n = 1$ system $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ ^{18,19} but the $n = \infty$ $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ remains metallic and ferromagnetic.²⁰ The reduction in the bandwidth of the e_g carriers reduces the significance of the double exchange interaction sufficiently to suppress ferromagnetic order and leave the antiferromagnetic interactions dominant. The question of possible charge ordering in the $n = 2$ phase, where the carrier concentration is now no longer at the commensurate 1:1 +III/+IV value, is one that needs to be addressed by variable temperature electron diffraction measurements.

The behaviour of the Nd system is in sharp contrast to that of the La system and also that of other CMR systems: compositions $x = 0.0, 0.1$ and 0.2 in the $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ display CMR below 150K in fields of between 2T and 14T without any sign of bulk ferromagnetism.^{9,10} Magnetisation measurements show a sharp rise in magnetisation just below 300K: this corresponds to the onset of hysteresis in fields of less than 0.05T but not magnetic long range order (no magnetic Bragg peaks appear in the neutron diffraction pattern) or CMR. A further local maximum in M occurs at lower temperature and corresponds to the onset of long-range antiferromagnetic order. The Neel temperature decreases as the e_g electron concentration increases (from 137K at $x = 0.0$ to 100K at $x = 0.1$).¹⁷ The complete absence of even field-induced ferromagnetism in the field range over which CMR is observed suggests that this is a new type of CMR effect, which may in principle arise in either the spin-glass or the antiferromagnetic phase or at the interfaces between them. Further studies should concentrate on the preparation of both truly single phase powder samples, with close to resolution-limited reflection widths, and highly perfect single crystals to establish the possible role of grain boundaries³ in the unusual observation of CMR without ferromagnetism. Increased Mn(III) concentration into the single phase region for $x \geq 0.4$ reduces the Neel temperature due to increasing frustration of the antiferromagnetic interactions, and lead to the suppression of high temperature features (Neel ordering or spin-glass like freezing) in the magnetisation measurements. The magnetotransport properties of these single phases are currently unknown and promise to be particularly important for the interpretation of the behaviour of the earlier members of the series. The $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ series illustrates the difficulty of preparing single phase monophasic samples of the $n = 2$ RP phases and the utility of high resolution powder diffraction techniques in assessing the outcomes of syntheses and the electronic property measurements on the samples in question.

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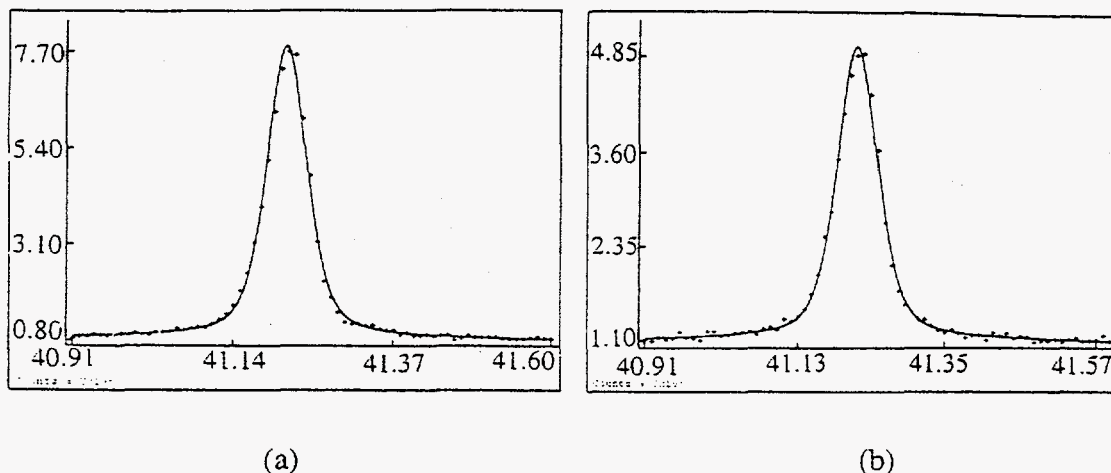


Figure 3: Synchrotron X-ray powder diffraction measurement of the {0 0 10} reflection of single phase $\text{Sr}_2\text{LnMn}_2\text{O}_7$ samples. (a) $\text{Sr}_2\text{Y Mn}_2\text{O}_7$ (b) $\text{Sr}_2\text{Ho Mn}_2\text{O}_7$. Fits are to a single pseudo-Voigt function with widths quoted in the text.

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