Structures and Magnetism of La$_{1-x}$Sr$_x$MnO$_{3-(0.5+x)/2}$ (0.67 ≤ x ≤ 1) Phases

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ABSTRACT: Topotactic reduction of La$_{1-x}$Sr$_x$MnO$_3$ (0.67 ≤ x ≤ 1) phases with sodium hydride yields a series of isoelectronic materials of composition La$_{1-x}$Sr$_x$MnO$_{3-(0.5+x)/2}$. Lanthanum rich members of the series (0.67 ≤ x ≤ 0.83) adopt anion deficient perovskite structures with a 6-layer -OTOO-T′O- stacking sequence of sheets of octahedra/square-based pyramids (O) and sheets of tetrahedra (T). The strontium rich members of the series (0.83 ≤ x ≤ 1) incorporate "step defects" into this 6-layer structure in which the OTOOT′O stacking sequence is converted into either OOTOOT′ or TOOT′OO at a defect plane which runs perpendicular to the [201] lattice plane. The step defects appear to provide a mechanism to relieve lattice strain and accommodate additional anion deficiency in phases with x > 0.83. Magnetization and neutron diffraction data indicate La$_{1-x}$Sr$_x$MnO$_{3-(0.5+x)/2}$ phases adopt antiferromagnetically ordered states at low-temperature in which the ordered arrangement of magnetic spins is incommensurate with the crystallographic lattice.

KEYWORDS: topotactic reduction, manganate, magnetism

INTRODUCTION

There has been extensive interest in mixed valent manganese oxides since the observation of large magnetoresistive effects in these phases.1–3 Subsequent intense study has revealed the presence of strong coupling between spin, charge, and lattice degrees of freedom, which has further sustained interest in these materials.4,5 The vast majority of investigations have focused on Mn$^{3+/4+}$ phases with cubic perovskite or Ruddlesden–Popper type structures, because of their relative ease of preparation and their ability to incorporate a large variety of dopants. In contrast relatively few studies have investigated the analogous Mn$^{2+/3+}$ materials as these generally cannot be prepared directly at high temperature.

Recently we have utilized low-temperature reduction with metal hydrides to prepare topotactically reduced manganese oxide phases with significant concentrations of Mn$^{2+}$. Thus for example the reduction of the Ruddlesden–Popper manganates YSr$_2$Mn$_2$O$_7$ and LaSrMnO$_4$ yield the Mn$^{2+}$ phases YSr$_2$Mn$_2$O$_{5.5}$ and LaSrMnO$_{3.5}$, respectively,6,7 while the reduction of the hexagonal perovskites 4H-BaMnO$_3$–x and 4H-Ba$_2$Sr$_2$Mn$_2$O$_{7.4}$ yield 4H-BaMnO$_2$ and 4H-Ba$_2$Sr$_2$Mn$_2$O$_{7-x}$, respectively.6,9 All of these Mn$^{2+}$ phases adopt antiferromagnetically ordered states at low temperature, consistent with simple superexchange between centers with d$^9$ electronic configurations.

In an attempt to induce ferromagnetic behavior we have turned our attention to the preparation of materials with Mn$^{2+/3+}$ mixed valency, synthesized via the low-temperature reduction of La$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr, Ba) perovskite phases. Reduction of lanthanum-rich La$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr, Ba) phases with sodium hydride (NaH) leads to the formation of materials with anion-vacancy ordered 4-layer brownmillerite structures (Figure 1).10,11 However, the low-temperature
redox of lanthanum-poor \( \text{La}_{1-x} \text{A}_{x} \text{MnO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \)) phases yields materials with structures which depend on the identity of the A-cation. Reaction of \( \text{La}_{1-x} \text{Ca}_{x} \text{MnO}_3 \) with NaH yields Mn\(^{2+}/3+\) containing phases of composition \( \text{La}_{1-x} \text{Ca}_{x} \text{MnO}_3 \).\(^{12}\) In contrast reaction of \( \text{La}_{0.33} \text{Sr}_{0.67} \text{MnO}_3 \) with NaH yields the mixed valent Mn\(^{2+}/3+\) phase, \( \text{La}_{0.33} \text{Sr}_{0.67} \text{MnO}_3 \cdot \text{O}_{1.42} \), which adopts an anion-vacancy ordered structure related to that of brownmillerite, but with a 6-layer stacking sequence as shown in Figure 1.\(^{3}\) In anion-vacancy ordered structure related to that of brownmillerite, La\(^{3+}\) mixed valent Mn\(^{2+}/3+\) phase, \( \text{La}_{0.33} \text{Sr}_{0.67} \text{MnO}_2.42 \), which adopts an anion-vacancy ordered structure related to that of brownmillerite, but with a 6-layer stacking sequence as shown in Figure 1.\(^{3}\) In this manuscript we extend our study of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \)\(^{1+}\) phases and report the structures, compositions and magnetic behavior of materials prepared by the low temperature reduction of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) (0.67 \( \leq \) \( x \) \( \leq \) 1) perovskite phases.

**EXPERIMENTAL SECTION**

**Preparation of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) Phases.** Five gram samples of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) (\( x = 0.67, 0.7, 0.75, 0.83, 0.9, 1 \)) phases were prepared using a standard ceramic route as described previously.\(^{14}\) Appropriate stoichiometric ratios of \( \text{La}_2 \text{O}_3 \) (99.999\%, dried at 900 °C), \( \text{SrCO}_3 \) (99.994\%), and \( \text{MnO}_2 \) (99.999\%) were thoroughly mixed and then heated at 900 °C in air to decompose the carbonate. The resulting black powders were reground, pressed into 13 mm pellets and then heated at 1350 °C for 3 periods of 48 h under flowing argon with intermittent rerinding. Finally, the powders were heated to 500 °C under flowing oxygen for 12 h and then cooled to room temperature at 1 °C min\(^{-1}\) to ensure full oxygen stoichiometry was achieved. X-ray powder diffraction data collected from these materials were indicative of single phase samples with lattice parameters consistent with those previously reported for the \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) series.\(^{14}\)

**Reduction of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) Phases.** The reduction of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) (0.67 \( \leq \) \( x \) \( \leq \) 1) phases was performed using NaH (>95\%) as a solid-state reducing agent in a manner similar to that described for \( \text{La}_{0.33} \text{Sr}_{0.67} \text{MnO}_3 \). 5 g samples of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) were mixed with two mole-equivalents of NaH in an argon-filled glovebox (\( \text{O}_2 \) and \( \text{H}_2 \text{O} \) < 1 ppm). The resulting mixtures were then sealed under vacuum in Pyrex tubes and heated for 12 h at 180 °C and then for a further 24 h at 210 °C. The sample was then reground and resealed and heated at 210 °C for a further 3 periods of 48 h with intermittent rerinding. Finally the sample was washed under a nitrogen atmosphere with 4 \( \times \) 100 mL of methanol to remove sodium containing phases (\( \text{NaOH} \) and \( \text{NaH} \)) before being dried under vacuum. On the basis of our previous experience of preparing \( \text{La}_{0.33} \text{Sr}_{0.67} \text{MnO}_3 \cdot \text{O}_{1.42} \), the \( x = 0.7 \) and \( x = 0.75 \) samples were annealed at 400 °C for 48 h in sealed, evacuated silica ampules to improve their crystallinity.\(^{13}\)

**Characterization.** X-ray powder diffraction data were collected using a PANalytical Xpert X-ray diffraction, incorporating an Xcelerator position sensitive detector (monochromatic Cu K\(_\alpha\) radiation). Neutron powder diffraction data were collected from samples contained within vanadium cans sealed under an argon atmosphere with an in situ swash. Data were collected at room temperature using the D1A diffractometer (\( \lambda = 1.90 \) Å) and at low temperature using the D1B diffractometer (\( \lambda = 2.52 \) Å) at the ILL neutron source, Grenoble. Rietveld refinement was performed using the GSAS suite of programs.\(^{15}\) Electron diffraction (ED) data and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were collected from finely ground samples supported on holey carbon grids (deposited from suspension in ethanol) using a Tecnai G2 transmission electron microscope. Thermogravimetric reoxidation measurements were performed by heating powdered samples under flowing oxygen using a Netsch STA 409PC balance. Magnetization measurements were collected from powdered samples using a Quantum Design MPMS SQUID magnetometer.

**RESULTS**

**Chemical Characterization.** Thermogravimetric data collected during the reoxidation of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) (0.7 \( \leq \) \( x \) \( \leq \) 1) phases to the corresponding \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \cdot \text{O}_{3} \) perovskite phases (confirmed by X-ray powder diffraction) are summarized in Table 1. Full thermogravimetric traces, shown in the Supporting Information, reveal complete oxidation occurs below 300 °C for all compositions, consistent with samples being topotactically reduced perovskite phases. The oxygen stoichiometries derived from these data indicate average manganese oxidation states of Mn\(^{2+}/3+\), within error, for all the reduced phases in the series such that the empirical stoichiometries can be approximately expressed as \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \cdot (0.5+3\times/2) \)

**Structural Characterization.** X-ray powder diffraction data collected from samples of composition \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) (0.5\( +3\times/2 \) (\( x = 0.7, 0.75, 0.83, 0.9, 1 \)) are shown in Figure 2. Examination of these data reveal the \( x = 0.7 \) and 0.75 data sets are very similar, while those of the \( x = 0.83, 0.9 \), and 1 samples are clearly related, but have broader diffraction reflections than the samples with smaller values of \( x \) (Table 2). We will therefore describe the structural characterization of the \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \cdot (0.5+3\times/2) \) series in two parts: the lanthanum-rich phases (\( x = 0.7, 0.75 \)) and the strontium-rich phases (\( x = 0.83, 0.9, 1 \)).

**Structural Characterization of \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \) (0.5\( +3\times/2 \) (\( x = 0.7, 0.75 \)). X-ray and neutron powder diffraction data collected from \( \text{La}_{1-x} \text{Sr}_{x} \text{MnO}_3 \cdot (0.5+3\times/2) \) phases with \( x = 0.7 \) or 0.75 could be readily indexed using unit cells based on a \( \sqrt{2a_p} \times 6a_p \times 2\sqrt{2a_p} \) expansion relative to the unit cell of a simple cubic perovskite as detailed in Table 2, in a manner directly analogous to that previously reported for \( \text{La}_{0.33} \text{Sr}_{0.67} \text{MnO}_3 \cdot 4.2 \).\(^{13}\) Electron diffraction data (not shown) collected from the \( x = 0.7 \) and \( x = 0.75 \) samples confirm the doubling of the crystallographic \( c \)-axis and are consistent with \( P \text{mnb} \) spacegroup symmetry, suggesting these phases adopt structures analogous...
This document discusses the structural refinements of La1−xSrMnO3−y phases and peak widths of [040] reflection. It is described that the La0.33Sr0.67MnO2.42 was also employed in the current refinements. The ordered layer excess is equal to the fraction of (0.5+x) twisted chains of tetrahedra minus the fraction of "incorrectly" twisted chains (occupancy of O3 − occupancy of O3’). To further confirm the structural assignments of the (x = 0.7, 0.75, 0.83) phases, the samples exhibited streaking parallel to b*, indicating interlayer disorder. The lattice parameters of the x = 0.7, 0.75, 0.83 phases are given in the Supporting Information, Tables S2, S3, with selected bond lengths and other data shown in Tables 3 and 4.

**Table 2. Refined Lattice Parameters of La1−xSrMnO3−y Phases and Peak Widths of [040] Reflection**

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>volume (Å³)</th>
<th>[040] fwhm (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>5.5849(2)</td>
<td>23.4734(9)</td>
<td>11.2275(5)</td>
<td>1471.8(1)</td>
<td>0.110(2)</td>
</tr>
<tr>
<td>0.75</td>
<td>5.5902(3)</td>
<td>23.4817(7)</td>
<td>11.1795(7)</td>
<td>1467.4(1)</td>
<td>0.119(3)</td>
</tr>
<tr>
<td>0.83</td>
<td>5.5906(6)</td>
<td>23.5204(1)</td>
<td>11.1548(1)</td>
<td>1466.7(1)</td>
<td>0.128(2)</td>
</tr>
<tr>
<td>0.9</td>
<td>5.5230(20)</td>
<td>23.6024(23)</td>
<td>11.0573(32)</td>
<td>1444.3(6)</td>
<td>0.239(4)</td>
</tr>
<tr>
<td>1</td>
<td>5.4882(25)</td>
<td>23.6775(32)</td>
<td>10.9464(26)</td>
<td>1422.4(7)</td>
<td>0.377(3)</td>
</tr>
</tbody>
</table>

“The lattice parameters of the x = 0.9 and x = 1 phases are described with √2ap × 6ap × 2√2ap units cells for consistency.”

**Table 3. Selected Bond Lengths and Angles from the Refined Structures of La1−xSrMnO3−(0.5+x)/2 (x = 0.7, 0.75, 0.83) Phases**

<table>
<thead>
<tr>
<th>cation</th>
<th>anion</th>
<th>x = 0.7</th>
<th>x = 0.75</th>
<th>x = 0.83</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1) octahedral/pyramidal</td>
<td>O(1)</td>
<td>1.925(23)</td>
<td>1.925(23)</td>
<td>1.925(23)</td>
</tr>
<tr>
<td>O(2)</td>
<td>2.020(33)</td>
<td>2.052(33)</td>
<td>2.036(33)</td>
<td></td>
</tr>
<tr>
<td>O(5)</td>
<td>1.964(33)</td>
<td>1.980(22)</td>
<td>2.060(13)</td>
<td></td>
</tr>
<tr>
<td>O(6)</td>
<td>2.015(36)</td>
<td>2.012(13)</td>
<td>1.960(13)</td>
<td></td>
</tr>
<tr>
<td>O(9)</td>
<td>1.995(34)</td>
<td>1.987(20)</td>
<td>1.925(13)</td>
<td></td>
</tr>
<tr>
<td>O(10)</td>
<td>1.984(36)</td>
<td>1.982(15)</td>
<td>2.031(13)</td>
<td></td>
</tr>
<tr>
<td>Mn(4) octahedral/pyramidal</td>
<td>MN+3.34/+2.70</td>
<td>MN+3.24/+2.60</td>
<td>MN+2.62</td>
<td></td>
</tr>
<tr>
<td>BVS</td>
<td>Mn+3.34/+2.70</td>
<td>Mn+3.24/+2.60</td>
<td>Mn+2.62</td>
<td></td>
</tr>
<tr>
<td>Mn(2) tetrahedral</td>
<td>O(3)</td>
<td>2.125(8)</td>
<td>2.275(8)</td>
<td>2.260(8)</td>
</tr>
<tr>
<td>O(4)</td>
<td>2.179(15)</td>
<td>2.003(15)</td>
<td>2.089(23)</td>
<td></td>
</tr>
<tr>
<td>O(7) × 2</td>
<td>1.926(23)</td>
<td>1.975(23)</td>
<td>1.935(23)</td>
<td></td>
</tr>
<tr>
<td>Mn(3) tetrahedral</td>
<td>O(3)</td>
<td>2.223(15)</td>
<td>1.981(15)</td>
<td>2.115(15)</td>
</tr>
<tr>
<td>O(4)</td>
<td>1.941(8)</td>
<td>2.158(8)</td>
<td>2.205(8)</td>
<td></td>
</tr>
<tr>
<td>O(2) × 2</td>
<td>2.056(23)</td>
<td>2.018(15)</td>
<td>1.969(23)</td>
<td></td>
</tr>
<tr>
<td>O(3)−O(4)−O(3) angle (deg)</td>
<td>112.1(2)</td>
<td>110.7(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4. Crystallographic Parameters Extracted from the Refined Structures of La1−xSrMnO3−(0.5+x)/2 Phases**

<table>
<thead>
<tr>
<th>x</th>
<th>O(3)−O(4)−O(3) (deg)</th>
<th>tetrahedral layer separation (Å)</th>
<th>O(1)/O(8) occupancy</th>
<th>ordered layer excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>112.6(8)</td>
<td>11.7052(4)</td>
<td>0.25</td>
<td>52(2)%</td>
</tr>
<tr>
<td>0.75</td>
<td>112.2(2)</td>
<td>11.7367(5)</td>
<td>0.23</td>
<td>26(2)%</td>
</tr>
<tr>
<td>0.83</td>
<td>110.2(2)</td>
<td>11.7406(4)</td>
<td>0.14</td>
<td>12(2)%</td>
</tr>
</tbody>
</table>

The ordered layer excess is equal to the fraction of "correctly" twisted chains of tetrahedra minus the fraction of "incorrectly" twisted chains (occupancy of O3 − occupancy of O3’).

To further confirm the structural assignments of the (x = 0.7, 0.75, 0.83) phases, the samples exhibited streaking parallel to b*, indicating interlayer disorder. The lattice parameters of the x = 0.7, 0.75, 0.83 phases are given in the Supporting Information, Tables S2, S3, with selected bond lengths and other data shown in Tables 3 and 4.
meaning that the manganese cations are located in tetrahedral and square-based pyramidal coordination sites. Details of the statistical fits for the refinement of the different 6-layer models against data collected from La₀.₁₇Sr₀.₈₃MnO₂.₃₆ and a complete description of the refined structure in Pnmb symmetry are listed in the Supporting Information, Tables S1 and S4, respectively, with selected bond lengths and other data shown in Tables 3 and 4.

Despite good refinement statistics, close inspection of the refined fit to the neutron diffraction data collected from La₀.₁₇Sr₀.₈₃MnO₂.₃₆ reveals poorly fitted regions, most obviously at 2θ ~ 50° and 58°, compared to the analogous fit for the La₀.₃₅Sr₀.₇₅MnO₂.₃₈ sample as shown in Figure 3. Analogous refinement of La₀.₁₇Sr₀.₈₃MnO₂.₃₆. A 3-layer repeat sequence can also be seen in this image corresponding to the STS stacking of layers of tetrahedra (T) and square-based pyramids (S) observed in the structure refined from neutron powder diffraction data. However, close inspection reveals that the dark lines, corresponding to layers of tetrahedra, do not extend continuously across the whole image. Instead there are step defects which shift the STSTS 6-layer stacking repeat either up or down to form STSTST or TSSTSS sequences respectively. This can be seen clearly by observing the white boxes in Figure 4b which mark the 11.76 Å STS 3-layer stacking repeats. Compared to the left-most box, the white box in the center of the image has been shifted down by ~1/6 of a unit cell (~1/3 of a 3-layer repeat) due to a “step” defect. In addition the right-most box has been shifted up ~1/6 of a unit cell relative to the central region. Thus on moving from left to right across the image, the STSTS stacking sequence is converted to TSSTSS and then back to STSTS as shown in Figure 4b. The “step” defects appear to occur with varying frequency and no obvious structural periodicity. In addition, there appears to be no long-range order to the direction of the “step” in the stacking sequence, with “up” and “down” steps appearing at random.

Examination of the x = 0.₉ and x = 1 samples (shown respectively in Figure 5 and Figure 4c) reveals similar step defects. Although it is difficult to quantify exactly, it appears that the frequency of the defect steps increases with increasing x, consistent with the observed increase in neutron and X-ray diffraction peak widths with increasing strontium content. Figure 4f shows a typical electron diffraction pattern of the [201] zone of SrMnO₂.₂₂. Within this figure it can be seen that the reflections corresponding to the perovskite subcell are sharp. However at the positions where, according to the defectless 6-layer structure there should be the reflections with hkl:k±3n, there are instead displaced and smeared out diffraction features. This spreading and displacement of diffraction features is in agreement with the step defects observed on the HAADF-STEM images. Within the electron diffraction pattern shown in Figure 4 these smeared features are also present turned by a 90° angle, as nanoscale twinning is
present. However, a pure, non-twinned Fourier transform can be achieved as seen in Figure 5 (La0.1Sr0.9MnO2.32), which is taken from the untwinned HAADF-STEM image shown there. The close-up of the area indicated by a white rectangle in Figure 5 clearly shows a wavy aspect in the brightest dots corresponding to the La/Sr cations, because of differences in the distances between consecutive La/SrO layers, being larger when separated by the tetrahedra (the darkest rows) than by the square based pyramids.

Magnetic Characterization. Low temperature neutron powder diffraction data collected from La1−xSr×MnO3−(0.5+x)/2 (x = 0.67, 0.7, 0.75, 0.83) phases exhibit additional diffraction features compared to analogous data collected at room temperature, indicative of magnetic order. Diffraction data measured as a function of temperature (Figure 6) reveal that on cooling to T ∼ 75 K all samples exhibit a broad diffraction feature at 2θ ∼ 27° (d ∼ 5.4 Å) which sharpens and increases in intensity on cooling below 65 K. On further cooling a further additional diffraction feature appears at 2θ ∼ 38° (d ∼ 3.8 Å). The additional low-temperature diffraction features cannot be readily indexed using simple expansions of the crystallographic unit cells, suggesting the magnetic repeat unit is incommensurate with the crystallographic lattice. This view is reinforced by the observation that the magnetic diffraction features shift significantly and systematically to shorter d-spacing as a function of increasing strontium content (Figure 7) in a manner that cannot be accounted for by the small changes in the structural lattice parameters across the La1−xSr×MnO3−(0.5+x)/2 series (Table 5). Unfortunately the small number of observed magnetic diffraction reflections prevents the unambiguous indexation of the magnetic cell or the determination of the magnetic structure. Magnetization data collected from La1−xSr×MnO3−(0.5+x)/2 (x = 0.67, 0.7, 0.75, 0.83) phases indicate samples contain small quantities of a ferromagnetic impurity (presumably La1−xSr×MnO3 perovskite phases) so data were collected using the "ferromagnetic subtraction" technique described previously and detailed in the Supporting Information. Figure 6 shows the paramagnetic susceptibility of La1−xSr×MnO3−(0.5+x)/2 (x = 0.67, 0.7, 0.75, 0.83) samples as a function of temperature. All samples show a significant anomaly at 65 K, coincident with the strengthening of the 2θ ∼ 28° magnetic diffraction peaks (Figure 6) which we take to indicate the onset of antiferromagnetic order. In addition magnetization-field isotherms are symmetric about the origin for T > 40 K and asymmetric below T ∼ 40 K, suggesting the appearance of the 2θ ∼ 39° magnetic diffraction peak is associated with the onset of glassy magnetic behavior.

DISCUSSION

Crystal Structure. Topotactic reduction of La1−xSr×MnO3 (0.67 ≤ x ≤ 1) perovskite phases with NaH yields the corresponding anion-deficient materials of composition La1−xSr×MnO3−(0.5+x)/2. Lanthanum rich members of the series (x = 0.67, 0.7, 0.75, 0.83) adopt anion-vacancy ordered structures consisting of 6-layer -OTOOTO- stacking sequences of sheets
The twisted chains of MnO₄ tetrahedra within the reduced phases adopt complex ordering schemes. If the structures of the La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) (x = 0.67, 0.7, 0.75, 0.83) phases are considered as a series, it can be seen that the ordering of the twisted tetrahedral chains can be separated into two components: intralayer order and interlayer order. Following this classification procedure, examination of the refined structures of the La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) (x = 0.67, 0.7, 0.75, 0.83) phases reveals all 4 phases exhibit intralayer LRLR order (where L and R refer to the twisting direction of the chains of tetrahedra¹¹), with the degree of interlayer order decreasing with increasing strontium content (Table 4).

Previous studies of brownmillerite structures have revealed the tetrahedral-chain twist ordering scheme adopted by a particular phase can be rationalized on the basis of the cancellation of dipole moments which arise from the twisting of the tetrahedral chains, with the particular brownmillerite structural variant adopted being dependent on the chain dipole strength (degree of chain distortion) and the distance separating adjacent layers of tetrahedra.¹¹,¹⁸,¹⁹ This same logic can be applied to rationalize the tetrahedral-chain twist ordering patterns in the 6-layer La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) phases. As shown in Table 4 the O(4)–O(3)–O(4) chain-twist angle of the La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) phases decreases from 112.6(8)° for x = 0.67 to 110.7(2)° for x = 0.83 indicating that the tetrahedral-chain distortion angle increases from 67.4(8)° to 69.3° across the series (the distortion angle is equal to 180° minus the twist angle). Comparing these tetrahedral chain distortion angles with those plotted on the brownmillerite structure map (created by plotting the tetrahedral distortion angle against tetrahedral layer separation for a large number of reported brownmillerite phases)¹¹ it can be seen that the La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) (x = 0.67, 0.7, 0.75, 0.83) phases have some of the most distorted tetrahedral chains yet reported. These large distortion angles correspond to large tetrahedral-chain dipole moments which strongly favor the efficient dipole cancellation offered by LRLR intralayer chain order. Indeed, from the brownmillerite structural map it can be seen that the LRLR intralayer ordered La₁₋ₓAₓMnO₃₋(0.5ₓ+1/2) (A = Ba, Sr, Ca) brownmillerite phases all have tetrahedral-chain distortion angles greater than 62.5°.¹¹ Thus the tetrahedral-chain distortion angles observed for La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) (x = 0.67, 0.7, 0.75, 0.83) phases are entirely consistent with the observed LRLR intralayer tetrahedral chain twist order.

The interlayer ordering interactions are rather more complex. The "perfect" Pnma 6-layer structure of the La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) phases has a rigorous interlayer stacking sequence in which the LRLR intralayer ordered sheets of tetrahedra are stacked with a stacking vector that has an alternating sequence: 1/2[111/2], 1/2[111/2], 1/2[111/2], ... as shown in Figure 8a. However "real" La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) Phases exhibit a degree of interlayer disorder (Table 4) which is attributed to the presence of stacking disorder,¹³ such that the rigorous alternation of the stacking vector

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**Table 5. Lattice Parameters of La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) Phases at 5 K and the d-Spacings of the Observed Magnetic Reflections**

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>d_{magtetra} (Å)</th>
<th>d_{maghedral} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66</td>
<td>5.550(2)</td>
<td>23.287(3)</td>
<td>11.195(2)</td>
<td>5.48(1)</td>
<td>3.89(1)</td>
</tr>
<tr>
<td>0.7</td>
<td>5.566(1)</td>
<td>23.337(2)</td>
<td>11.183(2)</td>
<td>5.44(1)</td>
<td>3.79(1)</td>
</tr>
<tr>
<td>0.75</td>
<td>5.582(2)</td>
<td>23.361(2)</td>
<td>11.089(2)</td>
<td>5.32(1)</td>
<td>3.68(3)</td>
</tr>
<tr>
<td>0.83</td>
<td>5.571(2)</td>
<td>23.385(2)</td>
<td>11.087(2)</td>
<td>5.28(1)</td>
<td>3.66(3)</td>
</tr>
</tbody>
</table>

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Figure 6. Magnetization data (left) and variable temperature neutron diffraction data (right) collected from La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) phases.

Figure 7. Neutron diffraction data collected from La₁₋ₓSrₓMnO₃₋(0.5ₓ+1/2) phases at 5 K.
of a “perfect” Pmnb type lattice is intergrown with “faults” which break the rigid alternation as shown in Figure 8b. Analogous stacking faults have been observed in the brownmillerite phase Sr2Fe2O5.20 The brownmillerite structural map indicates that the stacking faults have been observed in the brownmillerite phase Sr2Fe2O5. Thus at O(1) and O(8) sites declines this coupling also declines leading to an increase in the concentration of stacking defects. Hence at O(1) and O(8) sites, respectively. These step defects have a number of distinct features: (i) The direction (up or down) of a particular step defect appears random, (ii) The frequency of defect planes appears to increase with increasing x (strontium content) and the spatial separation between defect planes is irregular, (iii) Defect planes are sharp when viewed parallel to the [010] zone axis and appear to occur over a single Mn—O—Mn repeat length.

As noted above, the oxygen stoichiometry of La1−xSr0.83−xMnO3+δ(x) indicates that the bridging O(1) and O(8) anion sites are completely empty for this phase, as confirmed by the refined structure. Thus to maintain the La1−xSrMnO3+(0.5x)/2 composition in phases with x > 0.83, oxide ions must be removed from other anion sites within the 6-layer framework. The appearance of step defects in phases with x ≥ 0.83 and the increase in defect concentration with increasing x suggests that these step defects are associated with the incorporation of this further anion deficiency in strontium-rich phases. Figure 9 shows a representation of our proposed model of the step defects present in La1−xSrMnO3+(0.5x)/2 phases. As shown in Figure 9 the SST stacking sequence in section A (left-hand side) is converted into a STS sequence in section B (right-hand side). Thus at the defect plane sheets of unlike polyhedra are joined. As shown in layer 1 and layer 2 of Figure 9, joining sheets of tetrahedra and square-based pyramids naturally leads to a lowering of the oxygen content, if the 4-coordination of the tetrahedra is maintained at the expense of the 5-coordination of the square base pyramids, by introducing additional anion vacancies at the defect place (marked with black circles in Figure 9). The additional anion vacancies mean that the model of the step defect shown has a composition of (La/Sr)3Mn3O6.5 (La/Sr)MnO3+δ(x) rather than the (La/Sr)3MnO6 ((La/Sr)MnO3) composition of the nondefective bulk.

It should be noted that to achieve the oxygen stoichiometries observed for strontium-rich La1−xSrMnO3+(0.5x)/2 phases using the defect model shown in Figure 9, defect frequencies of 1 in 5 and 1 in 2 would be required for the x = 0.9 and x = 1 phases, respectively. These defect frequencies are clearly much higher than those observed in Figures 4 and 5, suggesting additional anion vacancies are present, either in the bulk material or more likely at the step defects within layer 3.

It can be seen from the HAADF-STEM images of the [201] zones of La1−xSrMnO3+(0.5x)/2 phases (Figure 4 and 5) that the step defects are “sharp”, occurring within a single Mn—O—Mn repeat, and run perpendicular to the [100] direction. An explanation for this unusual behavior can be reached by observing that these sharp step defect planes seen in La1−xSrMnO3+(0.5x)/2 phases are reminiscent of the sharp 90° twinning defects observed in the isostructural phase YSr2CoCu2O7,21 suggesting that the step defects are associated with a similar twinning plane. Thus in the proposed model of the step defect shown in Figure 9 it can be seen that the chains of tetrahedra in section A propagate parallel to [001] while those in section B propagate at 90° parallel to [001].

Microstructure. HAADF-STEM images collected from strontium-rich members of the La1−xSrMnO3+(0.5x)/2 series (x ≥ 0.83) reveal these phases exhibit “step” defects in which the 6-layer OTOOT’ stacking sequence is either shifted up or down to yield OTOOT’ or TOOT’OO sequences, respectively. These step defects have a number of distinct
Figure 9. Proposed model for the step defects present in La$_{1-x}$Sr$_x$MnO$_3$ (0.5 ≤ x ≤ 1) viewed down the [010] direction (top). The red spheres represent oxide ions and the gray spheres La/Sr cations. The bottom part of the figure shows a view along [010] of three stacked layers. Open circles indicate the position of anion vacancies in the defect plane.

A rather unexpected feature of the reduction of La$_{1-x}$Sr$_x$MnO$_3$ (0.5 ≤ x ≤ 1) phases is that reaction with sodium hydride leads to the formation of an isoelectronic series, La$_{1-x}$Sr$_x$MnO$_3$$_{(0.5+x)/2}$ in which the oxygen content evolves with x to maintain a constant manganese oxidation state (Mn$^{2.5}$). Usually the extent to which anions can be topotactically deintercalated from complex oxide hosts can be thought to be under the control of either crystallographic considerations (lattice energy, anion vacancy ordering) or electrochemical considerations ("reducing power" of reductant). Thus the formation of a series isosctructural La$_{1-x}$A$_x$MnO$_{3.5}$ (A = Ca, Sr, Ba; 0.3 ≤ x ≤ 0.5) brownmillerite phases via the reduction of the corresponding La$_{1-x}$A$_x$MnO$_3$ perovskite phases with NaH$^{11}$ can be attributed to the stability of the A$_2$B$_2$O$_5$ brownmillerite structure, while the formation of the La$_{1-x}$Sr$_x$MnO$_{3.3/2}$ (0 ≤ x ≤ 0.3) series of phases, via the reduction of La$_{1-x}$Sr$_x$MnO$_3$ phases with a zirconium getter, is attributed to the reducing power of this technique being limited to the formation of Mn$^{2+}$.$^{22}$

However, neither of these guiding features provides a convincing explanation for the formation of the isoelectronic La$_{1-x}$Sr$_x$MnO$_3$$_{(0.5+x)/2}$ series, as it is hard to see that the disordered oxygen vacancies present in the 6-layer structures described above provide much stoichiometric control, or that the reducing power of NaH is limited to preparing phases with manganese oxidation states of Mn$^{2.5}$ given that Mn$^{2+}$ phases such as YSr$_2$Mn$_2$O$_{5.5}$ have been prepared by an analogous route.$^6$ This suggests the electronic state of phases prepared is particularly favorable in some way. Bond valence sums (BVS) calculated for the MnO$_4$ tetrahedra in La$_{1-x}$Sr$_x$MnO$_3$$_{(0.5+x)/2}$ phases are consistent with the presence of Mn$^{2+}$ on these sites. As a result the average manganese oxidation state of the octahedral layers is Mn$^{2.75}$. However, detailed electron diffraction studies show no evidence for Mn$^{2+}/3+$ charge order which might be expected to stabilize the observed oxygen stoichiometries. It is therefore likely that the isoelectronic series forms as a result of a number of complex factors.

**Magnetic Behavior.** The complex magnetic behavior of La$_{1-x}$Sr$_x$MnO$_3$$_{(0.5+x)/2}$ phases can be rationalized by considering the competing magnetic superexchange interactions which exist between the manganese centers in these materials. Bond valence sums (Table 3) indicate that the MnO$_4$ tetrahedral sites are occupied by Mn$^{2+}$ centers, with the remaining octahedral/ square based pyramidal manganese sites occupied by a disordered 3:1 ratio of Mn$^{3+}$ and Mn$^{2+}$ centers, as shown in Figure 10. If we take a localized electron view, the elongation of the apical bonds of the MnO$_{5/6}$ centers in the “octahedral” layers suggests that the manganese d$_{yz}$ orbitals will be aligned parallel to the crystallographic stacking direction (y-axis) and that they will be of lower energy than the d$_{x^2-y^2}$ orbitals which reside in the xy-plane, as shown in Figure 10. Furthermore, within this orbital framework we would expect Mn$^{3+}$ and Mn$^{2+}$ centers to have orbital occupancies of (d$_{yz}$)$^2$(d$_{xz}$)$^2$(d$_{xy}$)$^1$(d$_{xy}$)$^1$(d$_{xz}$)$^0$ and (d$_{xy}$)$^2$(d$_{yz}$)$^2$(d$_{xz}$)$^1$(d$_{xy}$)$^1$(d$_{xz}$)$^1$, respectively. Thus according to the Goodenough–Kanamori rules,$^{23}$ we would expect strong 180° Mn(d$_{x^2-y^2}$)–O(2p)–Mn(d$_{x^2-y^2}$) antiferromagnetic superexchange coupling between adjacent MnO$_4$ and MnO$_{5/6}$ centers along the crystallographic y-axis (Figure 10a). We would also expect strong antiferromagnetic coupling between adjacent MnO$_{5/6}$ centers located on either side of the anion deficient layer. This coupling will be mediated either by 180° Mn(d$_{xy}$)–O(2p)–Mn(d$_{xy}$) superexchange when a bridging oxide ion is present or by direct 180° Mn(d$_{xy}$)–Mn(d$_{xy}$) exchange in the absence of a bridging anion (Figure 10b).
The magnetic coupling in the $xz$-plane is more complex. As noted above the manganese centers in the "octahedral" layers have an average oxidation state on Mn$^{2+}$.75. There are therefore three possible 180° Mn($d_{x^2}$)−O(2p)−Mn($d_{x^2}$) superexchange couplings possible: Mn$^{2+}$-Mn$^{3+}$, Mn$^{2+}$-Mn$^{4+}$, and Mn$^{3+}$-Mn$^{4+}$. As shown in Figure 10c the first two combinations are expected to be antiferromagnetic and the third ferromagnetic. Thus in the absence of Mn$^{4/III}$ charge order we would expect the magnetic interactions within the $xz$-planes of the octahedral layers to be frustrated. However rather than exhibiting the expected spin-glass behavior in which local pairwise magnetic interactions dominate, the La$_{1-x}$Sr$_x$MnO$_3$-$\text{perovskite phases}$ adopt an antiferromagnetically ordered state, albeit one which is incommensurate with the structural lattice.

The competition between antiferromagnetic and ferromagnetic couplings described above for the mixed valent Mn$^{2+/3+}$ phases has direct parallels to the magnetic couplings present in Mn$^{3+/4+}$ perovskite phases. The electronic configuration of Mn$^4+$ centers is $(d_{x^2})^3(d_{y^2})^1(d_{z^2})^0$; thus, the superexchange coupling between Mn$^{4+}$-Mn$^{4+}$ is antiferromagnetic and those between Mn$^{3+}$-Mn$^{4+}$ and Mn$^{3+}$-Mn$^{3+}$ are antiferromagnetic or ferromagnetic depending on orbital orientation. Thus both Mn$^{3+/4+}$ and Mn$^{2+/3+}$ systems have mixtures of antiferromagnetic and ferromagnetic couplings which depend on orbital order.

Given these similarities, it is striking that the magnetic behavior observed for Mn$^{2+/3+}$ phases is dominated by antiferromagnetic order, while that of the Mn$^{3+/4+}$ materials has strong ferromagnetism in some regions of the phase diagram. This difference in behavior can be explained by observing that ferromagnetism is generally accompanied by metallic conductivity in Mn$^{3+/4+}$ phases. For example La$_{1-x}$Ca$_x$MnO$_3$ perovskite phases exhibit a low-temperature coupled metallic-ferromagnetic state for compositions in the range 0.2 $\leq x \leq$ 0.5. This coupled metallic-ferromagnetic behavior observed for Mn$^{3+/4+}$ phases is generally attributed to the operation of the Zener double exchange mechanism, in which the transfer of itinerant $e_g$ electrons from Mn$^{3+}$ centers to Mn$^{4+}$ centers aligns the localized manganese $t_{2g}$ electrons ferromagnetically.24 The presence of itinerant conduction electrons is therefore a prerequisite for the operation of this mechanism.

All the Mn$^{2+/3+}$ phases prepared in this study are electronic insulators. The insulating behavior of Mn$^{2+/3+}$ phases compared to Mn$^{3+/4+}$ phases can be rationalized by considering two factors: (i) On reduction the electron count of Mn$^{2+/3+}$ phases rises, increasing the on-site repulsion (U) and favoring electron localization. (ii) Topotactic reduction of complex manganese oxides leads to an extension of the average Mn−O bond length. As the host structure is generally unable to expand to accommodate these longer Mn−O bonds, this drives a decrease in the average Mn−O−Mn bond angle, which leads to a reduction in orbital overlap and a narrowing of the conduction bandwidth (W) which also favors electron localization. Thus we would expect almost all topotactically reduced Mn$^{2+/3+}$ oxides to have localized valence electrons and thus be unable to participate in Zener double exchange, explaining the prevalence of antiferromagnetic behavior rather than ferromagnetic behavior in these materials.

In summary, we have prepared a series of La$_{1-x}$Ca$_x$MnO$_3$-$\text{perovskite phases}$ which adopt 6-layer anion-vacancy order structures. While these mixed valent Mn$^{2+/3+}$ phases have magnetic coupling interactions which are analogous to those in Mn$^{3+/4+}$ phases, high on-site electron−electron repulsions and highly distorted Mn−O−Mn bond angles suppress the appearance of metallic-ferromagnetic behavior and magnetoresistance.

## ASSOCIATED CONTENT

## Supporting Information

Thermogravimetric reoxidation data collected from La$_{1-x}$Sr$_x$MnO$_3$-$\text{(0.5$\times$0.5)/2}$ phases. Fitting statistics for the refinement of 6-layer models against neutron powder diffraction data collected from La$_{0.3}$Sr$_{0.6}$MnO$_{2.4}$ and La$_{0.25}$Sr$_{0.75}$MnO$_{2.38}$. Structural parameters refined for La$_{1-x}$Sr$_x$MnO$_3$-$\text{(0.5$\times$0.5)/2}$ ($x = 0.7, 0.75, 0.83$). A description of the magnetic measurement procedure for samples containing ferromagnetic impurities (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.
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Notes
The authors declare no competing financial interest.

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