

# Order–Disorder Phenomena in New LaBaMn<sub>2</sub>O<sub>6–x</sub> CMR Perovskites. Crystal and Magnetic Structure

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Three new perovskites in the LaBaMn<sub>2</sub>O<sub>6–x</sub> family have been synthesized by controlling the oxygen pressure, during both synthesis and postannealing. Structural determination from powder neutron diffraction (PND) data shows that one form of LaBaMn<sub>2</sub>O<sub>6</sub> is cubic ( $a = 3.906 \text{ \AA}$ ), with a disordered distribution of La<sup>3+</sup> and Ba<sup>2+</sup> cations, whereas a second form of LaBaMn<sub>2</sub>O<sub>6</sub> is tetragonal ( $a = 3.916 \text{ \AA}$ ;  $c = 7.805 \text{ \AA}$ ), with an alternate stacking of lanthanum and barium layers along  $c$ . The same La/Ba cation order is observed for the ordered, oxygen-deficient perovskite LaBaMn<sub>2</sub>O<sub>5</sub>, which is also tetragonal ( $a = 5.650 \text{ \AA}$ ;  $c = 7.808 \text{ \AA}$ ) and adopts a YBaCuFeO<sub>5</sub>-related structure. Elucidation of the magnetic structure of LaBaMn<sub>2</sub>O<sub>5</sub>, from low-temperature PND data, leads to a G-type antiferromagnetic model; the superimposed Mn<sup>2+</sup>/Mn<sup>3+</sup> charge order results in ferrimagnetic behavior for this phase and explains its magnetic properties, as obtained from susceptibility measurements. In both forms of LaBaMn<sub>2</sub>O<sub>6</sub>, the PND data show a ferromagnetic contribution. The CMR properties of the “O<sub>6</sub>” forms exhibit a remarkable feature:  $T_C$  is increased from 270 K for the disordered phase to 335 K for the ordered one, probably owing to the La/Ba ordering.

## 1. Introduction

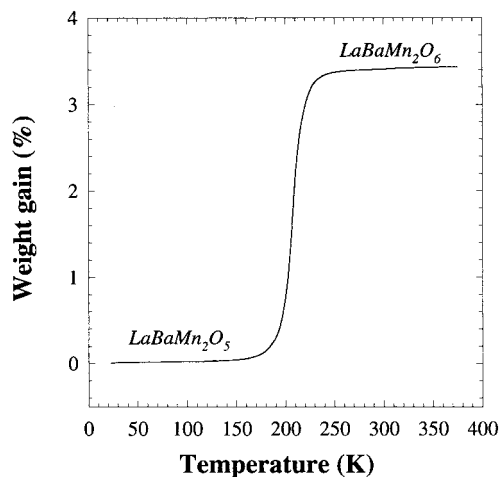
Among the numerous manganese oxides with colossal magnetoresistance (CMR) properties, the manganites La<sub>1–y</sub>Ba<sub>y</sub>MnO<sub>3</sub> offer a particular interest in that they exhibit large resistance ratios above room temperature. Several perovskite-based phases have been isolated for the lanthanum-rich compositions La<sub>1–y</sub>Ba<sub>y</sub>MnO<sub>3</sub>,  $y < 0.4$ .<sup>1–5</sup> For instance, bulk of La<sub>0.65</sub>Ba<sub>0.35</sub>MnO<sub>3</sub> has a  $T_C$  of 362 K.<sup>5</sup> Such high  $T_C$ 's are a result of the relatively large average size of the A-site cation, since it has been shown that  $T_C$  increases as  $\langle r_A \rangle$  increases.<sup>6,7</sup> However, there exists an antagonist effect, called “mismatch”, owing to the size difference between the A-site cations (La and Ba) which opposes the increase of  $T_C$ .<sup>8</sup> The latter effect results from local lattice distortions due to the disorder of the A-site cations. These observations suggest that it should be possible to suppress the

mismatch effect in the perovskites La<sub>1–y</sub>Ba<sub>y</sub>MnO<sub>3</sub> by inducing an ordering between the La<sup>3+</sup> and Ba<sup>2+</sup> cations. While several perovskite-based phases have been isolated for the lanthanum-rich compositions La<sub>1–y</sub>Ba<sub>y</sub>MnO<sub>3</sub>, the perovskite La<sub>0.5</sub>Ba<sub>0.5</sub>MnO<sub>3</sub> has never been synthesized owing to the formation of the hexagonal related perovskite BaMnO<sub>3–ε</sub>.<sup>9,10</sup> for  $x > 0.4$ . Recently, through the use of a two-step synthesis method, the composition corresponding to  $x = 0.5$  has been investigated. The cubic perovskite La<sub>0.5</sub>Ba<sub>0.5</sub>MnO<sub>3</sub> is of great interest, although it exhibits a  $T_C$  of only 270 K. For this manganite, which will be formulated as LaBaMn<sub>2</sub>O<sub>6</sub> herein, we have considered the possibility of ordering the La<sup>3+</sup> and Ba<sup>2+</sup> cations in the form of layers, as in the oxygen-deficient perovskite YBaCuFeO<sub>5</sub><sup>11,12</sup> or YBaMn<sub>2</sub>O<sub>5</sub>.<sup>13</sup> For this purpose, we successfully synthesized the ordered, oxygen-deficient perovskite LaBaMn<sub>2</sub>O<sub>5</sub> and then, in a second step, we obtained the ordered, stoichiometric perovskite LaBaMn<sub>2</sub>O<sub>6</sub> by annealing at low temperature in an oxygen

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**Figure 1.** TG weight gain versus temperature under an oxidizing atmosphere ( $\text{O}_2$ ) for the ordered, oxygen-deficient perovskite  $\text{LaBaMn}_2\text{O}_5$ .

flow. Attfield et al.<sup>13</sup> have reported that  $\text{YBaMn}_2\text{O}_5$  decomposes irreversibly into  $\text{YMnO}_3$  and  $\text{BaMnO}_3$  above  $220^\circ\text{C}$  in air or oxygen. In the present paper, we report on the synthesis and the crystal and magnetic structures of two stoichiometric perovskites,  $\text{LaBaMn}_2\text{O}_6$  (ordered and disordered), and the ordered, oxygen-deficient perovskite  $\text{LaBaMn}_2\text{O}_5$ .

## 2. Experimental Section

The purity of the samples (whose synthesis is described in 3.1 below) was first verified from X-ray diffraction data registered with a Philips diffractometer using  $\text{Cu K}\alpha$  radiation. The ordered-phase  $\text{LaBaMn}_2\text{O}_5$  was subsequently registered on the D1a high-resolution neutron powder diffractometer at Institut Laue-Langevin with a wavelength of  $1.907 \text{ \AA}$  at three

temperatures: 1.7 and 70 K and room temperature. The sample was contained in a vanadium can. The high-flux powder diffractometer D1b was used to investigate the thermal dependence of the magnetic structure in the temperature range of 70–100 K. The ordered form of the stoichiometric phase  $\text{LaBaMn}_2\text{O}_6$  was registered on D1a at 1.7 and 400 K and room temperature, while the cubic form of  $\text{LaBaMn}_2\text{O}_6$  was registered on the high-resolution diffractometer D2b using a wavelength of  $1.594 \text{ \AA}$ . The nuclear and magnetic refinements were performed using the profile fitting program Fullprof<sup>14</sup> ( $b_{\text{La}} = 0.824 \times 10^{-12} \text{ cm}$ ;  $b_{\text{Ba}} = 0.525 \times 10^{-12} \text{ cm}$ ;  $b_{\text{Mn}} = -0.373 \times 10^{-12} \text{ cm}$ ;  $b_{\text{O}} = 0.58 \times 10^{-12} \text{ cm}$ ).<sup>15</sup>

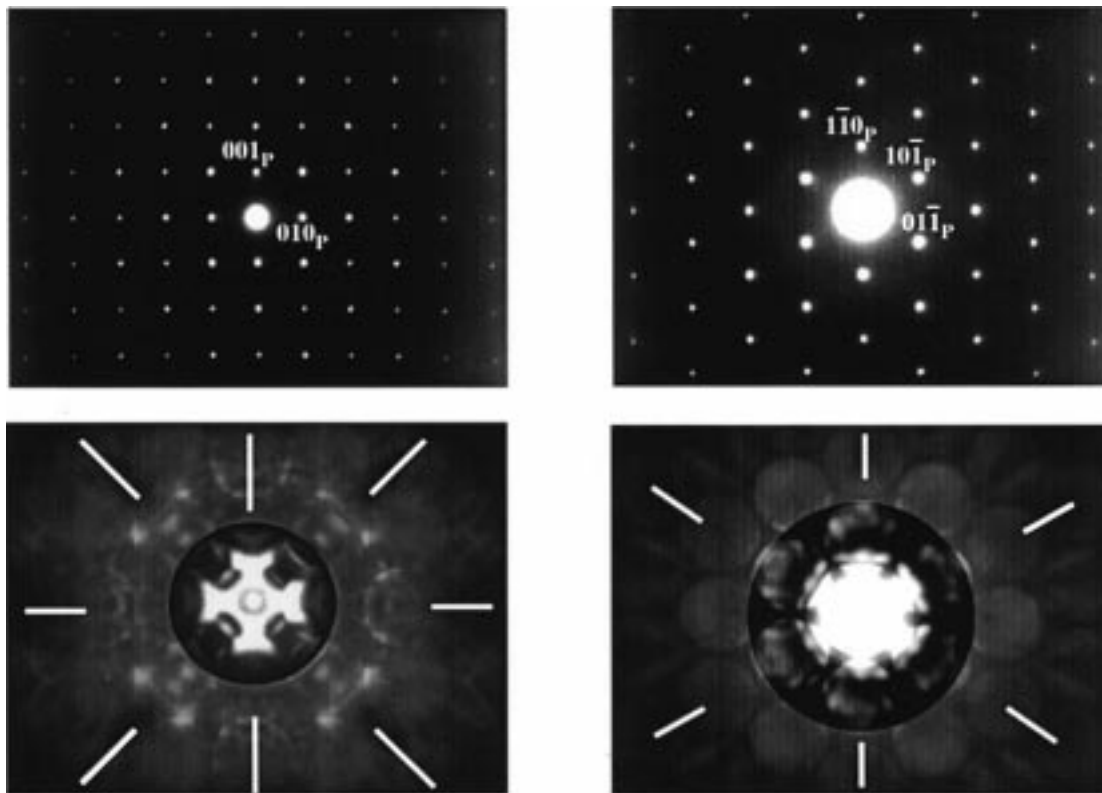
Samples for electron microscopy were crushed in n-butanol, and the microcrystals were deposited on a holey carbon-coated film (copper grid). The electron diffraction (ED) study was carried out with a JEM 200CX fitted with a tilting-rotating sample holder ( $\pm 60^\circ$ ). The high-resolution electron microscopy (HREM) and the convergent beam electron diffraction (CBED) studies were performed with a TOPCON 002B microscope having a point resolution of  $1.8 \text{ \AA}$ . Both microscopes were equipped with EDS, which allows confirmation of the cationic composition and the homogeneity within the crystals.

Magnetization measurements were made with a SQUID (MPMS Quantum Design) magnetometer. These DC susceptibility measurements were carried out at low field (100 G) with increasing temperature after the samples were either zero field cooled (ZFC) or field cooled (FC).

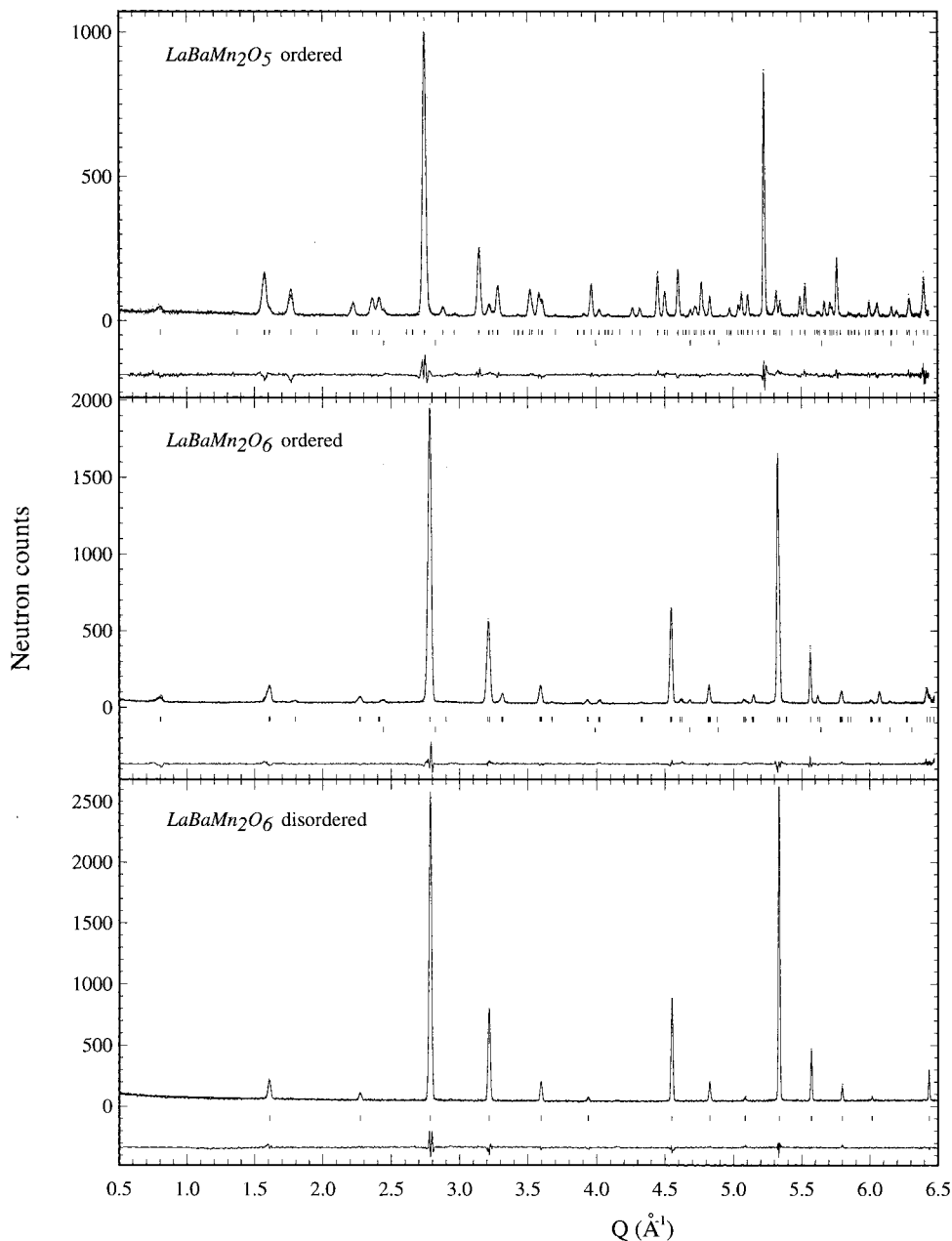
AC susceptibilities were measured with a Lake Shore 7000 susceptometer ( $8 \leq f \leq 666 \text{ Hz}$ ;  $5 \leq T \leq 320 \text{ K}$ ;  $10^{-2} \leq h_{\text{AC}} \leq 10 \text{ G}$ ).

Resistivities were measured between 5 and 400 K, on bars with the approximate dimensions of  $0.2 \times 0.2 \times 1 \text{ cm}^3$ , using a standard four-points method. Magnetoresistance measurements were performed using applied magnetic fields up to 7 T, with temperatures ranging from 5 to 400 K.

The thermogravimetric (TG) analysis was realized with a Setaram microbalance under an oxygen flow.



**Figure 2.** [100] and [111] SAED and CBED patterns index to an  $a_p \times a_p \times a_p$  cell and are in agreement with a  $Pm\bar{3}m$  space group.



**Figure 3.** Rietveld refinement plot of the neutron diffraction data. The ticks are given for nuclear structure peaks (top row) and MnO impurity nuclear peaks (bottom row). Top: Ordered  $\text{LaBaMn}_2\text{O}_5$  at room temperature. Middle: Ordered  $\text{LaBaMn}_2\text{O}_6$  at  $T = 400$  K. Bottom: Disordered  $\text{LaBaMn}_2\text{O}_6$  at room temperature.

### 3. Results and Discussion

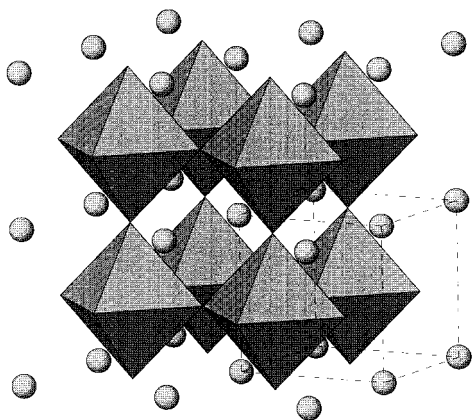
#### 3.1. Synthesis of Three New Perovskites: $\text{LaBaMn}_2\text{O}_6$ (Ordered and Disordered) and $\text{LaBaMn}_2\text{O}_5$ (Ordered)

The synthesis of the perovskites  $\text{LaBaMn}_2\text{O}_6$  and  $\text{LaBaMn}_2\text{O}_5$  is partially hindered by the formation of the hexagonal related perovskite  $\text{BaMnO}_{3-\epsilon}$ .<sup>10</sup> To avoid the formation of the latter, both the partial oxygen pressure and the temperature had to be carefully controlled during the synthesis.

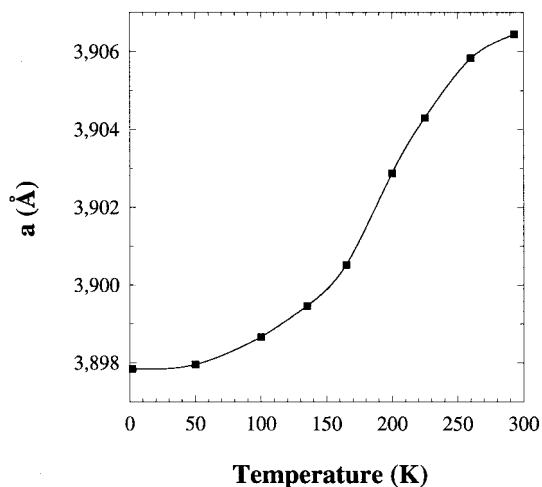
The disordered cubic perovskite  $\text{LaBaMn}_2\text{O}_6$  was prepared by reacting appropriate mixtures of  $\text{La}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{BaCO}_3$ . The reagent powders were ground and calcined in a mixed  $\text{Ar}/\text{O}_2$  flow at  $1500^\circ\text{C}$  to avoid the complete oxidation of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$ , which would

favor the formation of  $\text{BaMnO}_{3-\epsilon}$ . The products were cooled to  $800^\circ\text{C}$  in the same atmosphere and finally cooled slowly to room temperature in an oxidizing atmosphere ( $\text{O}_2$ ) to optimize the oxygen content of the sample. When the products are oxidized below  $800^\circ\text{C}$ , the formation of  $\text{BaMnO}_{3-\epsilon}$  is never observed. Iodometric titration indicates that the oxygen stoichiometry is close to  $\text{O}_6$ .

The ordered, oxygen-deficient tetragonal perovskite  $\text{LaBaMn}_2\text{O}_5$  was also prepared by mixing the oxides  $\text{La}_2\text{O}_3$  and  $\text{MnO}_2$  with the carbonate  $\text{BaCO}_3$ , in stoichiometric proportions. But after a preliminary decarbonation at  $900^\circ\text{C}$ , the powders were sintered at  $1500^\circ\text{C}$  in a pure argon flow to avoid any oxidation of  $\text{Mn}^{3+}$  into  $\text{Mn}^{4+}$ . The products were then slowly cooled in the same atmosphere to room temperature. Using these conditions, an oxygen-deficient perovskite of the formula



**Figure 4.** Structure of the disordered perovskite LaBaMn<sub>2</sub>O<sub>6</sub>.



**Figure 5.** Evolution of the cell parameter and the magnetic moment versus temperature for the disordered perovskite LaBaMn<sub>2</sub>O<sub>6</sub>.

LaBaMn<sub>2</sub>O<sub>5+ε</sub> was obtained with a very small oxygen excess (ε) with respect to the ideal formula, O<sub>5</sub>. Removal of this excess oxygen was achieved by annealing the obtained powder at 600 °C in an evacuated silica ampule in the presence of zirconium–titanium alloy chips for 12 h. The oxygen content of the sample was then determined by iodometric titration and was found to be very close to the ideal stoichiometry, O<sub>5</sub>.

To isolate the ordered stoichiometric tetragonal perovskite LaBaMn<sub>2</sub>O<sub>6</sub>, we annealed the ordered, oxygen-deficient phase at low temperature in the presence of oxygen. Thermogravimetric analysis (Figure 1) revealed that the oxidization begins at very low temperature, ~210 °C; finishes near 230 °C; and occurs in a single step. The weight gain of the thus-obtained sample determined from the TG analysis clearly shows that the oxygen content is close to O<sub>6</sub>. It is worth pointing out that the oxygen content of all of these perovskites was further confirmed by the neutron diffraction refinements.

### 3.2. Nuclear and Magnetic Structure of the Perovskites LaBaMn<sub>2</sub>O<sub>6</sub> and LaBaMn<sub>2</sub>O<sub>5</sub>

#### 3.2.1. The Disordered Cubic Perovskite LaBaMn<sub>2</sub>O<sub>6</sub>

Both the reconstruction of reciprocal space from the selected area electron diffraction (SAED) patterns and the convergent beam electron diffraction studies for the

cubic form of LaBaMn<sub>2</sub>O<sub>6</sub> confirmed the absence of reflection conditions (Figure 2) and lead to the space group *Pm3m*, with  $a = a_p$ ; [111] and [100] zero-order Laue zone (ZOLZ) CBED patterns show *3m* and *4mm* two-dimensional symmetry, respectively.<sup>16–18</sup> The quality of the CBED patterns, even at room temperature, indicates good crystallinity of the samples, which is also confirmed by the evenness of the contrast in the HREM images.

The refinement of this structure was first undertaken in the paramagnetic domain using the room-temperature neutron diffraction data. All of the observed diffraction peaks could be indexed in the space group *Pm3m* with the unit cell parameter  $a_p = 3.9065$  Å. The observed, calculated, and difference profiles are plotted in Figure 3. The refinement converges to give an agreement factor  $R_{wp} = 7.41\%$  and  $\chi^2 = 1.66$ . The cubic symmetry is in agreement with the complete disordering of lanthanum and barium on the same site of the perovskite cell (Figure 4). The evolution of the lattice parameter versus temperature is shown in Figure 5. At room temperature, one observes a Mn–O distance of 1.953 Å which is in agreement with the ionic radii of the Mn<sup>3+</sup>/Mn<sup>4+</sup> (1:1) and O<sup>2-</sup> ions. The neutron diffraction data collected at various temperatures show a ferromagnetic contribution. At 1.7 K, the Mn moment is almost 3.5 μ<sub>B</sub>, i.e., exactly the expected spin value for the Mn<sup>3+</sup>/Mn<sup>4+</sup> ratio (1:1).

**3.2.2. The Ordered, Oxygen-Deficient Tetragonal Perovskite LaBaMn<sub>2</sub>O<sub>5</sub>.** For the ordered, oxygen-deficient perovskite LaBaMn<sub>2</sub>O<sub>5</sub>, ED observations on more than 20 crystals showed the existence of extra reflections indicative of the supercell  $a_p\sqrt{2} \times a_p\sqrt{2} \times 2a_p$ , with the reflection conditions  $hk0$ ,  $h + k = 2n$ ;  $h0l$ , none; and  $hhl$ , none (Figure 6). In the ED pattern of the latter zone, i.e., [100]<sub>p</sub> diffraction, it is the observation of a high-order Laue zone (HOLZ) that confirms the doubling of the cell volume: the first-order Laue zone (FOLZ) is translated by  $\frac{1}{2}a_p^*$  as compared to the zero-order Laue zone (ZOLZ) reflections, and the measurement of the FOLZ diameter allows evaluation of the reciprocal perpendicular distance between the FOLZ and the ZOLZ as closed to  $\frac{1}{2}a_p$  Å<sup>-1</sup>. From the ED investigations, the deduced space group is *P4/nmm*.

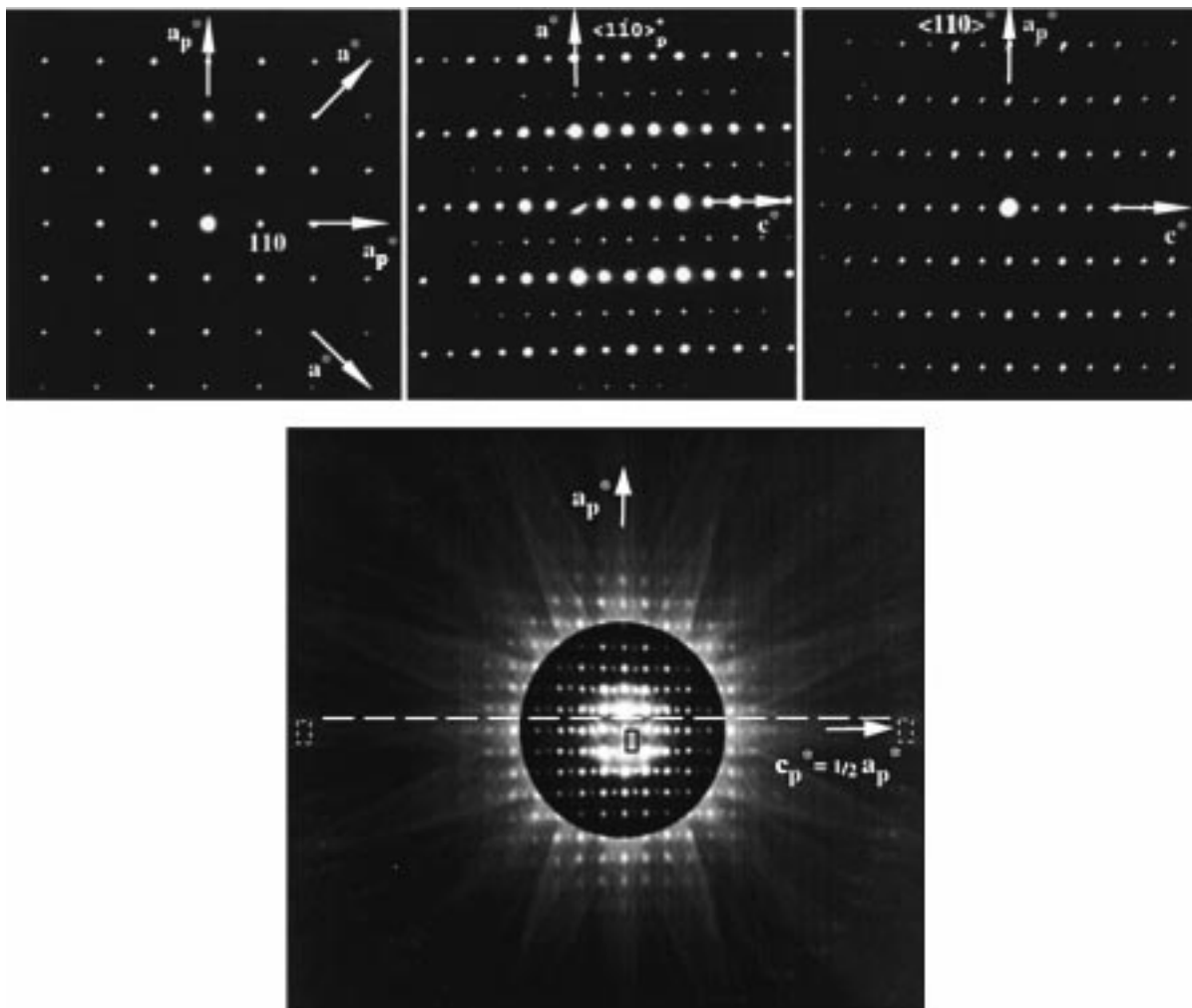
While the iodometric titration results indicate the oxygen content to be near O<sub>5</sub>, the ED investigations show that complete deoxygenation is not always reached. Indeed, a few crystals have different ED patterns from that discussed above. Two distinct kinds of microcrystals have been characterized. In the first type, [001]<sub>p</sub> ED patterns show starlike reflections and associated microdiffraction observations, as well as reciprocal reconstruction, leading to an  $a_p \times a_p \times 2a_p$  cell (Figure 7). The corresponding dark-field [001] image shows a tweed-like contrast. Such a phenomenon could be interpreted as microdomains having different oxygen contents close to O<sub>5+ε</sub>. In the second type, the ED patterns show very weak extra spots which index to an

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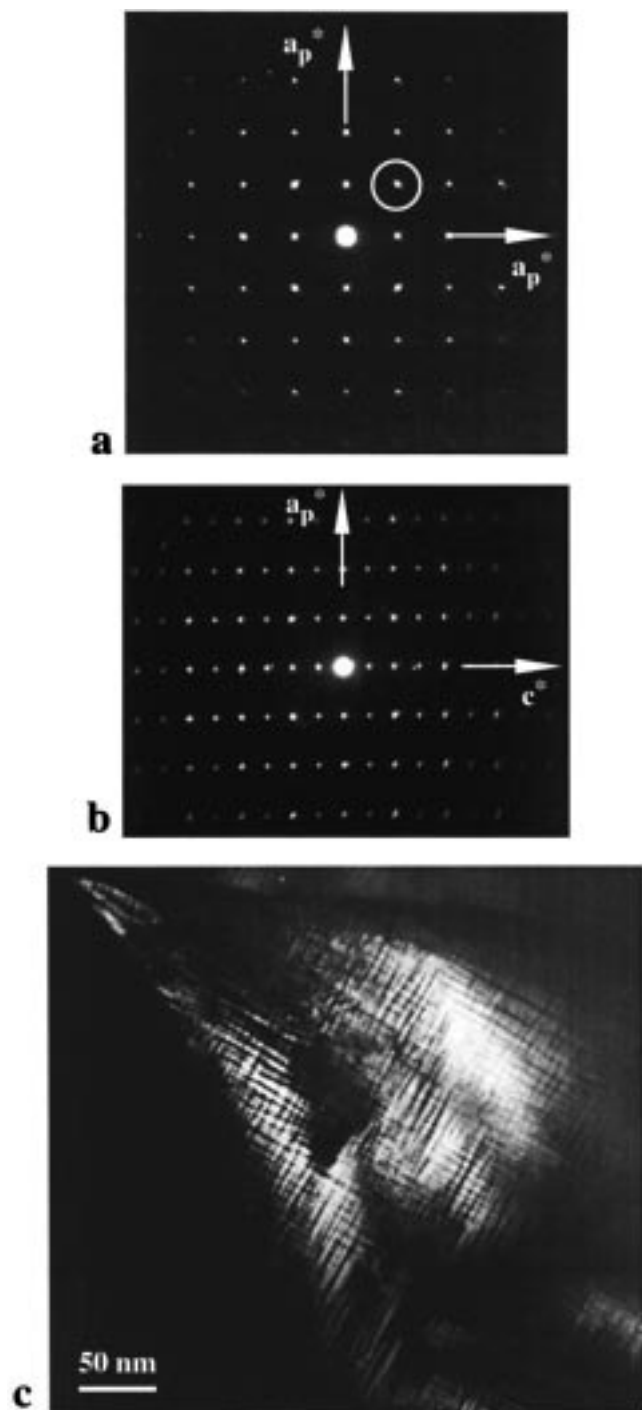
**Figure 6.** [001], [010], and [110] SAED patterns index to an  $a_p\sqrt{2} \times a_p\sqrt{2} \times 2a_p$  cell and show reflection conditions  $hk0$ ,  $h+k = 2n$ ;  $h0l$ , none; and  $hhl$ , none. The [110] microdiffraction shows the doubling of the cell by translation of the FOLZ with respect to the HOLZ; the two-dimensional reciprocal array is materialized through a black rectangle in both the HOLZ and the FOLZ.

$a_p \times 2a_p \times 4a_p$  supercell (Figure 8), similar to that of the partially deoxygenized compound  $\text{LaBaMn}_2\text{O}_{5.5}$ .<sup>19</sup> This superstructure effect is not always as well established. In Figure 8b, the SAED pattern only shows a splitting of dots in parallel to the  $[110]^*$  direction indicative of the coexistence of domains showing a slightly distorted framework. The corresponding HREM image shows a  $[110]$  typical  $\text{LaBaMn}_2\text{O}_5$  contrast ( $a_p \times 2a_p$  periodicity), but some domains can be distinguished which show modulation of contrast typical of  $\text{LaBaMn}_2\text{O}_{5.5}$  structure ( $2a_p \times 4a_p$  centered periodicity). The  $b/2$  parameter of the  $\text{LaBaMn}_2\text{O}_{5.5}$  structure and the  $d_{110}$  distance of the  $\text{LaBaMn}_2\text{O}_5$  structure being close to 4.09 and 3.99 Å, respectively, this phenomenon is probably responsible for the dot splitting on the SAED pattern. These observations suggest that deoxygenation in a few crystals is only partially achieved, but nonetheless would occur in an ordered fashion (as deduced from synthesis conditions of  $\text{LaBaMn}_2\text{O}_{5.5}$  compound).<sup>19</sup>

The powder neutron diffraction pattern of this phase, collected at room temperature in the paramagnetic domain, was indexed with a tetragonal cell, space group  $P4/nmm$  with  $a = 5.6501$  Å and  $c = 7.8083$  Å, in agreement with the ED results. The data were first analyzed with a "whole pattern fitting" algorithm to determine accurately the profile shape function, back-

ground, and cell parameters. This preliminary study provided good estimates of  $R_{wp}$  and  $\chi^2$  that could be reached during the structure refinement. This whole pattern fitting led to  $R_{wp} = 8.98\%$  and  $\chi^2 = 2.25$ . One hundred and two Bragg peaks were used to refine 5 positional parameters and 5 isotropic temperature factors. The refinement converged to give an agreement factor  $R_{wp} = 10.0\%$  and  $\chi^2 = 2.82$ . An impurity was identified as MnO and represented less than 1% of the mass of the sample. The observed, calculated, and difference profiles are plotted in Figure 3. Because the ionic radii of  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  are not too different, it is possible to have a statistical occupation of the same site by these two cations. However, refinement of the site occupancies showed that the 2b site is fully occupied by  $\text{La}^{3+}$  cations (in the oxygen deficient layer), while the 2a site is fully occupied by  $\text{Ba}^{2+}$  cations.

The structure of  $\text{LaBaMn}_2\text{O}_5$  is quite similar to that of  $\text{YBaCuFeO}_5$ <sup>11,12</sup> or  $\text{YBaMn}_2\text{O}_5$ .<sup>13</sup> Double layers of apex-sharing  $\text{MnO}_5$  pyramids, containing the  $\text{Ba}^{2+}$  cations, are interleaved with the oxygen-free lanthanum layers. The resultant order of the  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  cations forms layers parallel to (001). The most important difference between the structures of  $\text{LaBaMn}_2\text{O}_5$  and  $\text{YBaCuFeO}_5$  concerns the ordering of the B-site cations; the existence of two distinct sites for manganese is



**Figure 7.** (a, b) [001] and [100] SAED patterns index to an  $a_p \times a_p \times 2a_p$  cell. (c) The star-like shape on the [001] SAED pattern is imaged through a tweed-like contrast on a dark-field image obtained from 110 reflection (circled on the SAED pattern).

observed in the former, while the Cu–Fe is of some debate in the latter.<sup>11,12</sup> The final atomic coordinates for  $\text{LaBaMn}_2\text{O}_5$  are listed in Table 1, and the interatomic distances are given in Table 2. The Mn1 and Mn2 sites exhibit average Mn–O distances of 1.965 Å and 2.079 Å, respectively. Taking into consideration the ionic radii of  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions, it can be assumed that the Mn1 sites are occupied by  $\text{Mn}^{3+}$  ions and that the Mn2 sites are occupied by the  $\text{Mn}^{2+}$  ions. Each  $\text{Mn}^{2+}\text{O}_5$  pyramid is linked to five  $\text{Mn}^{3+}\text{O}_5$  pyramids (Figure 9). For the pyramidally coordinated  $\text{Mn}^{3+}$ ,

considering the Mn–O bond lengths (four equatorial Mn1–O1 distances of 1.949 Å and one apical Mn1–O2 distance of 2.027 Å), the occupied  $d_z^2$  orbital extends along [001], whereas the unoccupied  $d_{x^2-y^2}$  orbital extends along [110] and  $[1\bar{1}0]$ . Considering the Mn–O bond lengths of the Mn2 site, an orbital order similar to that of the Mn1 site can be assumed for this site, but both the  $d_z^2$  and the  $d_{x^2-y^2}$  orbitals are occupied for the high-spin  $\text{Mn}^{2+}$  cation.

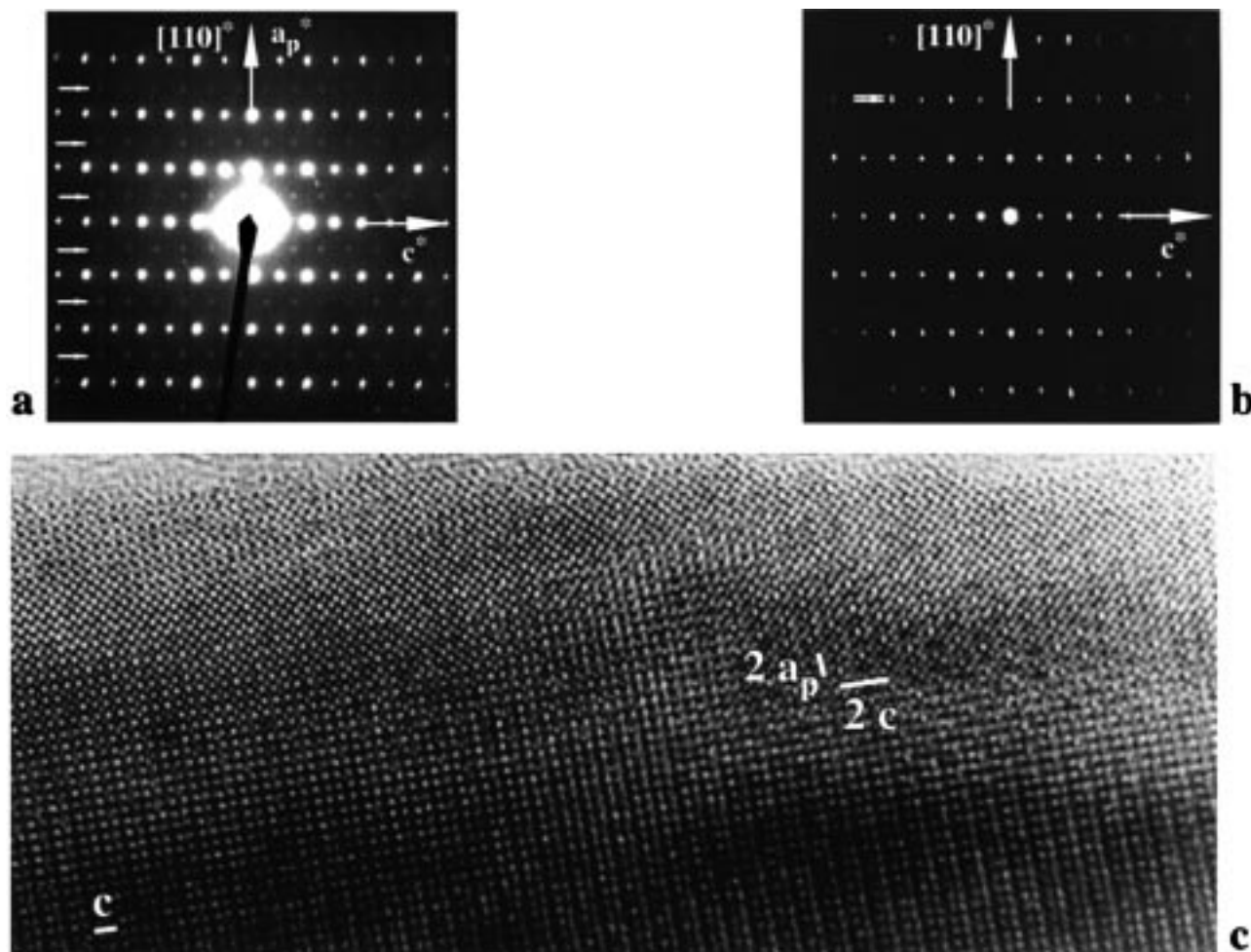
A comparison between the low- and room-temperature neutron diffraction data (Figure 10) reveals an increase of the intensity of several reflections. These reflections can be indexed on the basis of the nuclear cell, i.e., the magnetic unit cell is  $a_p\sqrt{2} \times a_p\sqrt{2} \times 2a_p$ . These magnetic peaks correspond to  $hkl$  with  $h+k=2n+1$  and  $l$  odd. The first extinction condition implies an antiparallel orientation of the spins within the  $(a_p, a_p)$  plane. The second extinction condition implies that, along the  $c$ -axis, two magnetic atoms separated by  $d/2$  have antiparallel magnetic moments. This leads to a G-type antiferromagnetic model (Figure 11). The spin of the magnetic ions is parallel to the  $c$ -axis ( $R_{\text{mag}} = 5.96\%$ ;  $\chi^2 = 2.93$  at  $T = 1.5$  K). The magnetic moments of the two sites are  $2.7(1) \mu_B$  for Mn1 and  $3.2(1) \mu_B$  for Mn2. Each  $\text{Mn}^{2+}$  cation is linked via a Mn–O–Mn bridge to five  $\text{Mn}^{3+}$  cations, and vice versa. Thus, the order is ferrimagnetic as observed by the susceptibility measurement.

If one considers the Goodenough–Kanamori rules<sup>20</sup> for magnetic interactions in manganese oxides, the expected magnetic order would be A-type. This arises from superexchange interactions between occupied  $d_{x^2-y^2}$  orbitals on the  $\text{Mn}^{2+}$  site with empty  $d_{x^2-y^2}$  orbitals on the  $\text{Mn}^{3+}$  site. Owing to the charge order, each  $\text{Mn}^{2+}$  site has four  $\text{Mn}^{3+}$  neighbors in the plane leading to an expected ferromagnetic layer. The interactions between the occupied  $d_z^2$  orbitals in the  $c$ -direction should be, as observed experimentally, antiferromagnetic. However, as discussed above, the in-plane interactions are also antiferromagnetic, despite the ferromagnetic expectations. This is most likely due to a large distortion of the Mn–O–Mn angles away from the ideal  $180^\circ$  interactions assumed in the Goodenough–Kanamori scenario. This distortion can strongly influence the magnetic interactions, and it is evidently large enough to drive the expected ferromagnetic interactions to become antiferromagnetic; thus, the resultant G-type structure.

**3.2.3. The Ordered Stoichiometric Tetragonal Perovskite  $\text{LaBaMn}_2\text{O}_6$ .** The ED study of the ordered stoichiometric perovskite  $\text{LaBaMn}_2\text{O}_6$  shows that it has tetragonal symmetry with the cell parameters  $a_p \times a_p \times 2a_p$ . It can be noticed that the extra spots which imply the doubling of the  $a_p$  parameter along the  $c$ -direction are very weak. As will be shown from the structure determination, this observation is not surprising since the cell doubling is only due to La–Ba order and involves almost no distortion of the oxygen framework. This leads to a  $d/a$  ratio, for the ordered phase, of almost exactly 2, and therefore,  $90^\circ$  oriented domain phenomena are very often observed (Figure 12).

For the refinement of the ND data of this compound, we started from the hypothesis that the cation ordering

(20) Goodenough, J. B. *Magnetism and Chemical Bond*; Interscience Publishers: New York, 1966.



**Figure 8.** (a)  $\langle 100 \rangle_p$  SAED pattern showing weak extra dots which index to the centered two-dimensional array  $2a_p \times 4a_p$  similar to the  $\langle 100 \rangle$  ED pattern of  $\text{LaBaMn}_2\text{O}_{5.5}$  compound. (b)  $\langle 110 \rangle$  SAED pattern showing a splitting of dots parallel to the  $[110]^*$  direction. (c) Corresponding HREM image showing contrast-modulated domains.

**Table 1. Refined Structural Parameters of Ordered  $\text{LaBaMn}_2\text{O}_5$  (Space Group  $P4nmm$ )**

		$T = 1.5 \text{ K}$	$T = 293 \text{ K}$
La	2b	$B_{\text{iso}}^a = 0.22(9)$	$B_{\text{iso}} = 0.41(9)$
Ba	2a	$B_{\text{iso}} = 0.21(9)$	$B_{\text{iso}} = 0.45(9)$
Mn1 = Mn <sup>III</sup>	2c	$z = 0.2637(9)$	$z = 0.2632(9)$
		$B_{\text{iso}} = 0.46(9)$	$B_{\text{iso}} = 0.59(9)$
Mn2 = Mn <sup>II</sup>	2c	$z = -0.2489(9)$	$z = -0.2495(9)$
		$B_{\text{iso}} = 0.46(9)$	$B_{\text{iso}} = 0.59(9)$
O1	8j	$x = 0.4908(6)$	$x = 0.4913(6)$
		$z = 0.2999(3)$	$z = 0.3002(3)$
		$B_{\text{iso}} = 0.60(7)$	$B_{\text{iso}} = 0.95(9)$
O2	2c	$z = 0.0061(9)$	$z = 0.0035(9)$
		$B_{\text{iso}} = 0.96(9)$	$B_{\text{iso}} = 1.09(9)$
$a$ (Å)		5.6386(2)	5.6501(2)
$c$ (Å)		7.7799(4)	7.8083(4)
$\mu_B$	Mn1	2.7(1)	
	Mn2	3.2(1)	
$R_p$		7.58%	8.26%
$R_{\text{wp}}$		9.02%	10.0%
$\chi^2$		2.93	2.82

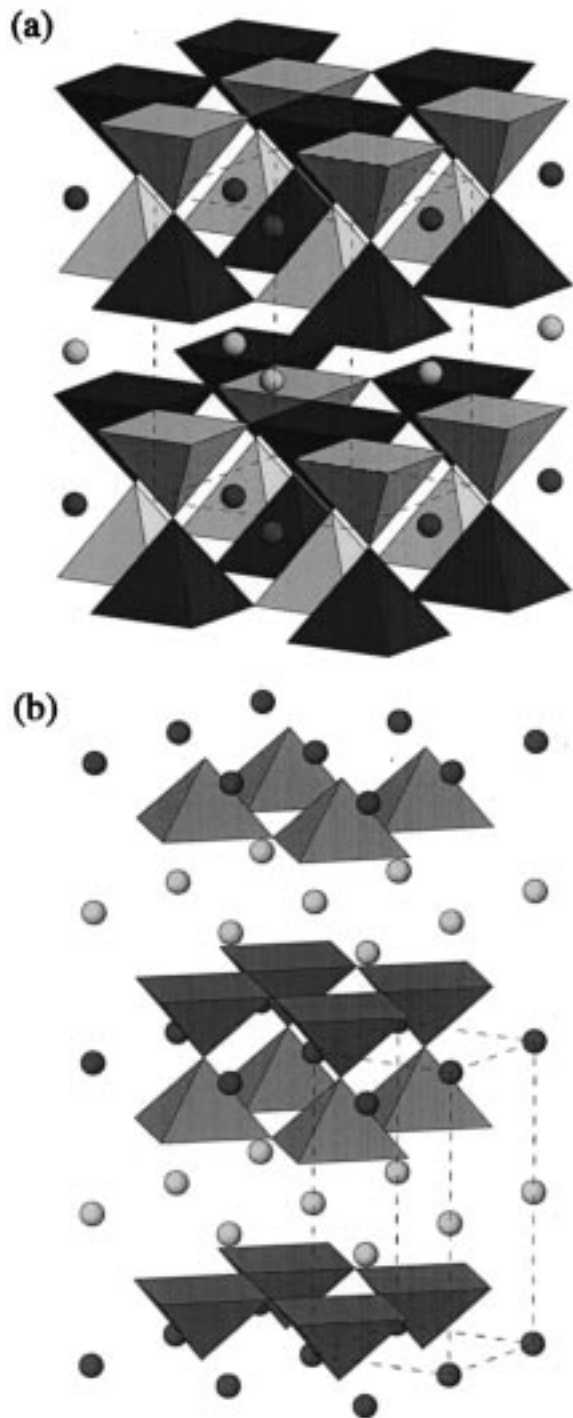
<sup>a</sup> Å<sup>2</sup>.

observed in the parent phase  $\text{LaBaMn}_2\text{O}_5$  is not strongly affected, because the oxidization is performed at low temperature. Then, the additional oxygen (with respect to  $\text{O}_5$ ) was distributed on the parent phase vacant second apical site (in the lanthanum layer), to transform the  $\text{MnO}_5$  pyramids of  $\text{LaBaMn}_2\text{O}_5$  into  $\text{MnO}_6$  octahedra for  $\text{LaBaMn}_2\text{O}_6$ . The neutron diffraction data at 400 K

**Table 2. Selected Interatomic Distances and Angles of Ordered  $\text{LaBaMn}_2\text{O}_5$**

	$T = 1.5 \text{ K}$	$T = 293 \text{ K}$	multiplicity
La–O1 (Å)	2.530(3)	2.536(3)	×8
Ba–O1 (Å)	3.070(3)	3.081(3)	×8
Ba–O2 (Å)	2.820	2.825	×4
Mn1–O1 (Å)	1.941(4)	1.949(4)	×4
Mn1–O2 (Å)	2.004(9)	2.027(9)	×1
Mn2–O1 (Å)	2.105(5)	2.105(5)	×4
Mn2–O2 (Å)	1.985(9)	1.976(9)	×1
Mn1–O1–Mn2 (deg)	160.8(6)	160.6(8)	
Mn1–O2–Mn2 (deg)	180	180	

were first analyzed with a whole pattern fitting algorithm. All of the observed diffraction peaks could be indexed in the space group  $P4/mmm$  with unit cell parameters  $a = 3.9160 \text{ Å}$  and  $c = 7.8054 \text{ Å}$ . This preliminary fit converged to  $R_{\text{wp}} = 6.47\%$  and  $\chi^2 = 1.61$ ; which could be reached during the final structure refinement. The refinement converged to give an agreement factor  $R_{\text{wp}} = 7.30\%$  and  $\chi^2 = 2.06$ . The observed, calculated, and difference profiles are plotted in Figure 3. The final atomic coordinates are listed in Table 3, and the interatomic distances are given in Table 4. These results clearly establish that the structure of the ordered stoichiometric  $\text{LaBaMn}_2\text{O}_6$  perovskite (Figure 13) consists of a pure octahedral  $[\text{MnO}_6]$  framework, wherein the layered order of the  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  cations along the  $c$ -axis of the parent-phase  $\text{LaBaMn}_2\text{O}_5$  is

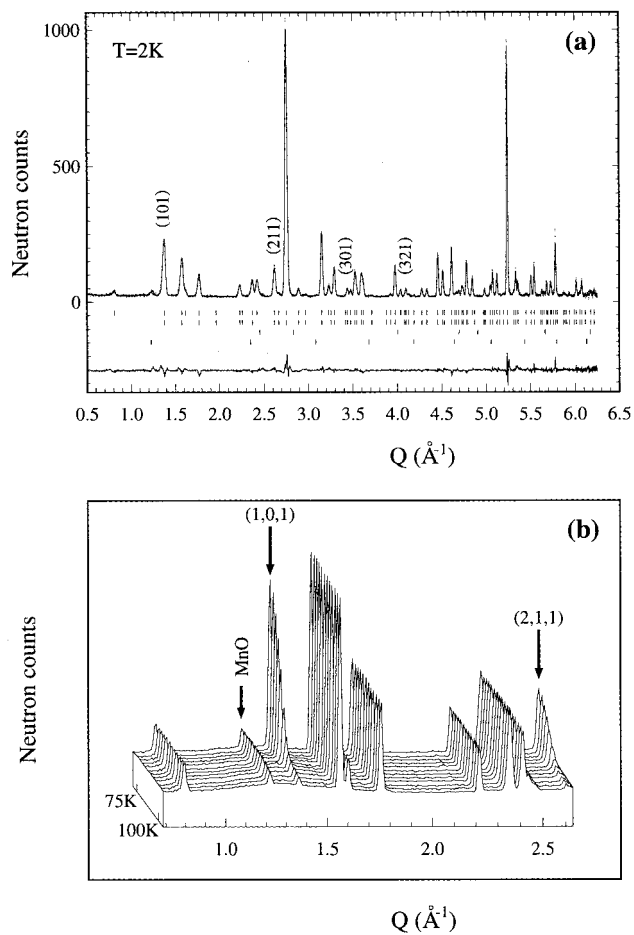


**Figure 9.** Structure of the perovskites  $\text{LaBaMn}_2\text{O}_5$  (a) and  $\text{YBaCuFeO}_5$  (b).

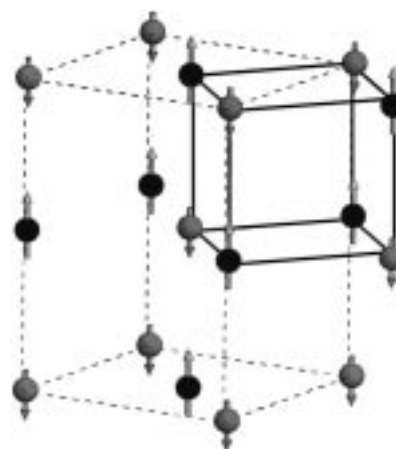
preserved. As seen for the cubic-phase  $\text{LaBaMn}_2\text{O}_6$ , one observes a ferromagnetic contribution to the powder neutron diffraction data registered at 1.7 K; in contrast to the disordered phase, ferromagnetic contributions are also observed for the room-temperature data of the ordered stoichiometric phase.

### 3.3. Magnetic and Transport Properties

$\text{LaBaMn}_2\text{O}_5$ , owing to its Mn(II)–Mn(III) mixed valence state and to the order of its Mn(III) and Mn(II) species, exhibits very different magnetic properties from the  $\text{LaBaMn}_2\text{O}_6$  perovskites. The AC and DC suscep-



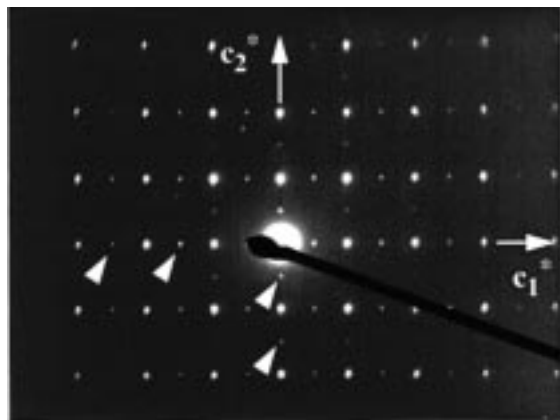
**Figure 10.** (a) Rietveld refinement plot at 2 K of the neutron diffraction data of the ordered perovskite  $\text{LaBaMn}_2\text{O}_5$ . (b) Thermal dependence of the magnetic structure in the temperature range 70–100 K.



**Figure 11.** G-type structure of the perovskite  $\text{LaBaMn}_2\text{O}_5$ .

tibility measurements (Figure 14) are easily explained by considering the Mn(II)/Mn(III) order. One observes a magnetic transition at 100 K, and a ferromagnetic component is clearly revealed by the peak in the imaginary part of the susceptibility. However, the saturated moment obtained from the DC measurement at 5 K is only  $0.35 \mu_B/\text{Mn}$  (i.e.,  $0.7 \mu_B$  per  $\text{LaBaMn}_2\text{O}_5$  formula unit), which can be compared to the total moment of  $4.5 \mu_B/\text{Mn}$  (i.e.,  $9 \mu_B$  per  $\text{LaBaMn}_2\text{O}_5$ ) that would result from a ferromagnetically ordered array of  $S = 5/2 \text{Mn}^{2+}$  and  $S = 4/2 \text{Mn}^{3+}$  spins. The neutron results





**Figure 12.**  $\langle 100 \rangle$  SAED pattern typical of the ordered perovskite  $\text{LaBaMn}_2\text{O}_6$ . Two  $90^\circ$  oriented domains can be distinguished. Dots introducing the doubling of the  $a_p$  parameter along the  $c$ -direction (arrowheads) are rather weak compared to the  $a_p$  subcell array.

**Table 3. Refined Structural Parameters of Ordered  $\text{LaBaMn}_2\text{O}_6$  (Space Group  $P4mmm$ )**

		$T = 1.5 \text{ K}$	$T = 293 \text{ K}$	$T = 400 \text{ K}$
La	1b	$B_{\text{iso}}^a = 0.41(9)$	$B_{\text{iso}} = 0.65(9)$	$B_{\text{iso}} = 0.71(9)$
Ba	1a	$B_{\text{iso}} = 0.29(9)$	$B_{\text{iso}} = 0.51(9)$	$B_{\text{iso}} = 0.94(9)$
Mn	2h	$z = 0.2528(9)$ $B_{\text{iso}} = 0.33(9)$	$z = 0.2519(9)$ $B_{\text{iso}} = 0.48(9)$	$z = 0.2514(9)$ $B_{\text{iso}} = 0.53(9)$
O1	4i	$z = 0.2655(6)$ $B_{\text{iso}} = 0.38(9)$	$z = 0.2649(6)$ $B_{\text{iso}} = 0.94(9)$	$z = 0.2645(6)$ $B_{\text{iso}} = 1.21(9)$
O2	1c	$B_{\text{iso}} = 1.14(9)$	$B_{\text{iso}} = 1.52(9)$	$B_{\text{iso}} = 1.60(9)$
O3	1d	$B_{\text{iso}} = 1.11(9)$	$B_{\text{iso}} = 1.34(9)$	$B_{\text{iso}} = 1.80(9)$
$a$ (Å)		3.9018(1)	3.9090(1)	3.9160(1)
$c$ (Å)		7.7919(2)	7.7958(2)	7.8054(2)
$\mu_B$		2.879(4)	1.287(5)	
$R_p$		7.77%	6.72%	5.61%
$R_{\text{wp}}$		11.2%	8.93%	7.30%
$\chi^2$		4.62	1.46	2.06

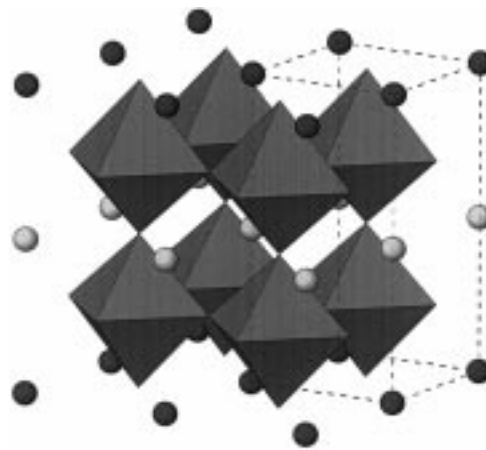
<sup>a</sup> Å<sup>2</sup>.

**Table 4. Selected Interatomic Distances and Angles of Ordered  $\text{LaBaMn}_2\text{O}_6$**

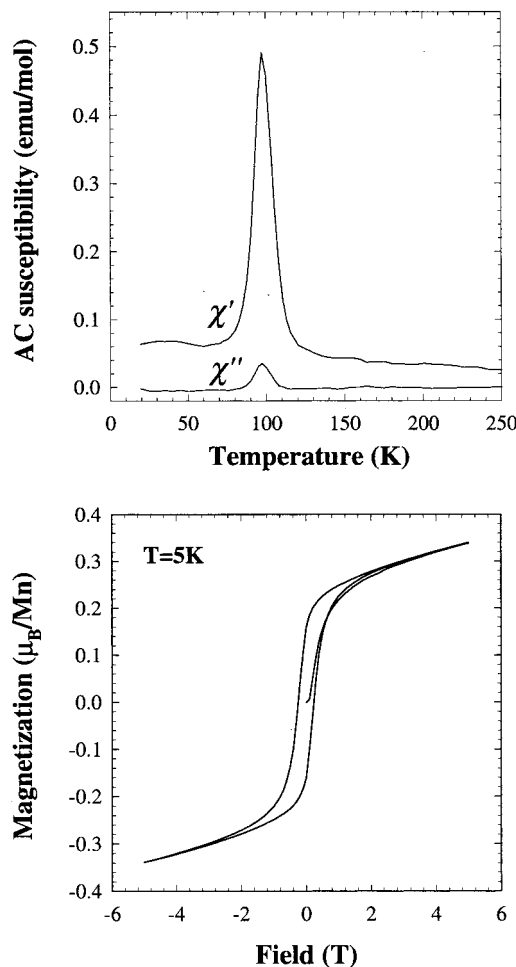
	$T = 1.5 \text{ K}$	$T = 293 \text{ K}$	$T = 400 \text{ K}$	multiplicity
La–O1 (Å)	2.673(2)	2.679(1)	2.686(1)	$\times 8$
La–O3 (Å)	2.759	2.764	2.769	$\times 4$
Ba–O1 (Å)	2.843(1)	2.844(1)	2.845(1)	$\times 8$
Ba–O2 (Å)	2.759	2.764	2.769	$\times 4$
Mn–O1 (Å)	1.953(1)	1.957(1)	1.961(1)	$\times 4$
Mn–O2 (Å)	1.970(5)	1.964(4)	1.962(3)	$\times 1$
Mn–O3 (Å)	1.926(5)	1.934(4)	1.940(3)	$\times 1$
Mn–O1–Mn (deg)	174.19(1)	174.06(1)	174.04(1)	
Mn–O2–Mn (deg)	180	180	180	
Mn–O3–Mn (deg)	180	180	180	

show that the order is ferrimagnetic, with a small ferromagnetic component due to the incomplete compensation of antiferromagnetically ordered sublattices.<sup>13</sup> If all of the  $S = 5/2 \text{ Mn}^{2+}$  spins are antiparallel to the  $S = 4/2 \text{ Mn}^{3+}$  spins, a saturated moment of  $1 \mu_B$  per  $\text{LaBaMn}_2\text{O}_5$  formula unit is expected. This is consistent with the observed value of  $0.7 \mu_B$ . As expected from the observed ordered arrangement of the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  species,  $\text{LaBaMn}_2\text{O}_5$  is an insulator.

In contrast to the oxygen-deficient perovskite  $\text{LaBaMn}_2\text{O}_5$ , the two stoichiometric  $\text{LaBaMn}_2\text{O}_6$  perovskites are metallic at low temperature. In fact, the  $R(T)$  curves of these oxides registered in a zero magnetic field (Figures 15 and 16) and the  $M(T)$  curves registered under 100 G show that both of them exhibit a transition

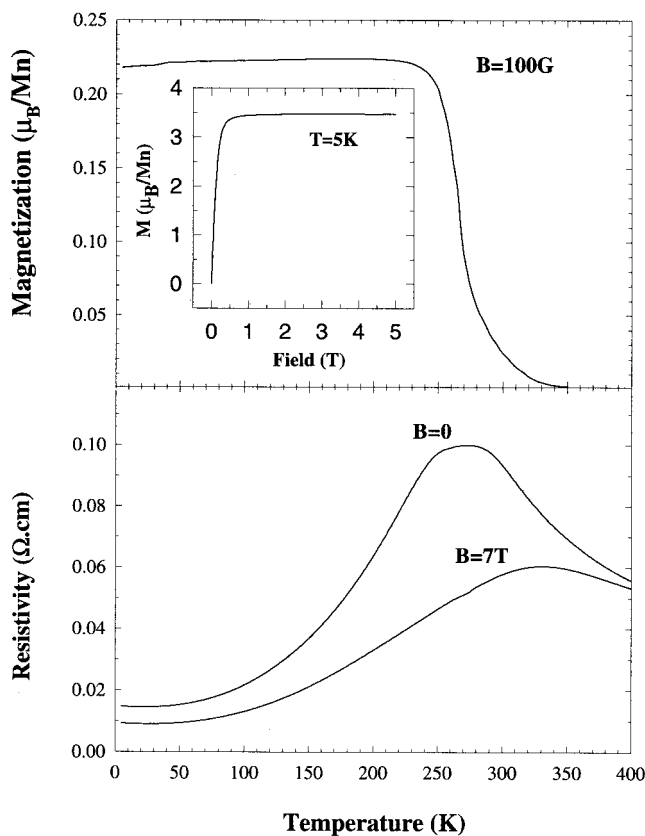


**Figure 13.** Structure of the ordered perovskite  $\text{LaBaMn}_2\text{O}_6$ .



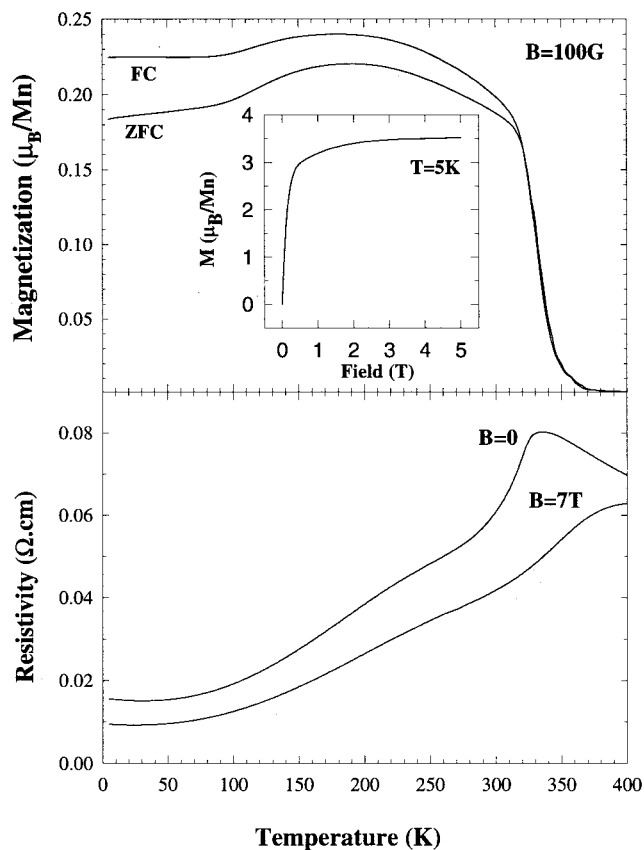
**Figure 14.** AC and DC susceptibility of  $\text{LaBaMn}_2\text{O}_5$ .

from a paramagnetic insulating state to a ferromagnetic metallic state as  $T$  decreases. The magnetic moment deduced from the  $M(H)$  curves (see Figure 15 (inset) and Figure 16) is  $3.5 \mu_B$  at 3.5 K, in agreement with the neutron diffraction data. The behavior of  $\text{LaBaMn}_2\text{O}_6$  can be compared with that of both the insulator  $\text{LaMnO}_3$  and the CMR manganite  $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ .  $\text{LaMnO}_3$  is an antiferromagnetic insulator, wherein the antiferromagnetism arises from  $\text{Mn}^{3+}-\text{O}-\text{Mn}^{3+}$  superexchange in-



**Figure 15.** Physical properties of the disordered perovskite LaBaMn<sub>2</sub>O<sub>6</sub>. Top: Magnetisation curve versus  $T$ . The inset shows the magnetization curve registered with increasing magnetic field at  $T = 5$  K. Bottom: Resistivity curves versus  $T$  for  $B = 0$  and  $7$  T.

teractions. In La<sub>0.5</sub>Ba<sub>0.5</sub>MnO<sub>3</sub> (i.e., LaBaMn<sub>2</sub>O<sub>6</sub>), the superexchange is diluted by hole doping: Ba<sup>2+</sup> substitution on the La<sup>3+</sup> sites results in a concomitant formation of Mn<sup>4+</sup> cations. Thus, the magnetic properties of both forms of the O<sub>6</sub> compounds can be understood, to a first approximation, as a result of the double exchange mechanism,<sup>21</sup> leading to a ferromagnetic state at low temperature. As seen in other mixed-valent manganese oxides, a simultaneous transition to a metallic state at  $T_C$  (Curie point) leads to a large CMR effect. However, the interesting difference between the two forms of O<sub>6</sub> compounds is that the order on the perovskite A-site lattice plays an important role in determining the value of  $T_C$ .  $T_C$  is indeed increased from 270 K for the disordered stoichiometric perovskite to 335 K for the ordered perovskite. While the average A-site ionic radius and the mismatch between these radii<sup>8</sup> have been shown to be important chemical considerations in controlling  $T_C$ , it is evident that the cationic order also plays an important role. In this case, La/Ba cation order in every other (001) layer leads to an important enhancement of  $T_C$ . Since the current compound is the only case where such order is observed, owing to the unique synthetic approach, it is impossible to ascertain completely the effects of this order on the manganese–oxygen interactions which drive the electronic/magnetic properties. Further research on other ordered A-site compounds will undoubtedly yield interesting insights into these chemical and physical phenomena.



**Figure 16.** Physical properties of the ordered perovskite LaBaMn<sub>2</sub>O<sub>6</sub>. Top: Magnetization curve versus  $T$ . The inset shows the magnetization curve registered with increasing magnetic field at  $T = 5$  K. Bottom: Resistivity curves versus  $T$  for  $B = 0$  and  $7$  T.

#### 4. Concluding Remarks

Using a reducing-type synthesis, we have shown that the  $x$  value in the La<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> system could be increased to  $x = 0.5$ . Moreover, in a synthetic atmosphere which favors the Mn<sup>2+</sup>/Mn<sup>3+</sup> couple, we were able to synthesize the ordered, oxygen-deficient perovskite LaBaMn<sub>2</sub>O<sub>5</sub>. This compound has several unique crystal chemical features, including La/Ba order in every other (001) plane; oxygen vacancies ordered in every La layer; Mn<sup>2+</sup>/Mn<sup>3+</sup> order even at room temperature, such that these cations alternate along each direction of the unit cell; and ferrimagnetic order below 100 K. Low-temperature oxidation of this compound leads to an A-cation-ordered oxygen stoichiometric material, LaBaMn<sub>2</sub>O<sub>6</sub>, which differs from the disordered compound directly synthesized in both the cation order and magnetic properties. The  $T_C$  of the ordered A-site O<sub>6</sub> compound increases, indicating that cation order plays an important role in directing the electronic/magnetic properties in CMR materials. Coupling between A-site order, oxygen vacancy order, manganese valence state, and orbital order controls the final properties of these materials, and more work is required to elucidate the individual effects of these complex interactions.

**Acknowledgment.** The authors would like to thank Paul Salvador for helpful discussions.