Competing magnetic ground states in the *A*-site layer-ordered manganite $La_{1-x}Ba_{1+x}Mn_2O_6$

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Using neutron and x-ray diffraction, we report the discovery of competing ground states near a multicritical point in *A*-site layer-ordered $La_{1-x}Ba_{1+x}Mn_2O_6$ materials. We demonstrate the dual effects of deliberate disorder on the system's stability, the freezing of the competing states, and the drastic reduction in magnetic fields required for the suppression of charge- and orbital-ordered phases. Our work suggests that quenched disorder is not the primary reason for phase separation and magnetoresistance and that increased doping leads to electronic phase separation.

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Phase separation and competition among various ferromagnetic (FM) and charge- or orbital-ordered antiferromagnetic (AFM) phases have recently taken center stage in research aimed at achieving a comprehensive understanding of the underlying mechanisms leading to the colossal magnetoresistance (CMR) phenomenon in manganites.[1–3] CMR and phase separation have typically been observed in *A*-site disordered manganite perovskites at boundary lines separating regions with significantly dissimilar physical and structural properties.[4–6] For many compositions, the spatially separated phases are noted to coexist over a wide temperature range and to remain remarkably stable in the presence of high external magnetic fields or other stimuli.[7–11] On the other hand, the charge-exchanged antiferromagnetic ordering, observed in many $A_{0.5}A'_{0.5}MnO_3$ CMR materials (A=La or rare earth; A'=Ca, Sr),[12–14] was demonstrated to withstand large external magnetic fields typically in the range of 10–60 T before melting.[6,15–19] In properly strained thin films, charge ordering could melt under significantly lower magnetic fields of $\sim 1-20$ T.[20–23]

Despite all progress made during the last decade, the successful use of manganites in advanced applications still faces many challenges largely due to the fact that high magnetic fields remain needed to achieve the CMR properties associated with the suppression of the metal to insulator transition that takes place when the material becomes phase separated or charge ordered. Most theoretical work thus far has been based on observations of properties arising from manganites exhibiting large Mn-O bond variations due to local *A*-site size and charge disorder. Hence, the need for a new class of materials that would exhibit smaller disorder to test theoretical predictions and allow the manipulation of transport and magnetic properties under significantly reduced external magnetic fields.

In recent work,[24] we have reported the formation of an unusually large and complex charge-ordered superstructure arising from the ordering of the *A*-site cations in $LaBaMn_2O_6$. Similar observations have also been reported for related *A*-site layer-ordered materials (e.g., $ABaMn_2O_6$ where A=Y, Sm, and Tb).[25–27] In these materials, two-dimensional Mn-O sheets are asymmetrically sandwiched between adjacent and alternating A^{3+} and Ba^{2+} layers, thus, giving rise to magnetic and transport properties that are significantly different from those of their three-dimensional *A*-site disordered $A_{0.5}Ba_{0.5}MnO_3$ counterparts. Hence, in this class of materials, cationic ordering adds another dimension to be accounted for in any theoretical work seeking to formulate the origin of CMR properties.

In this paper, we report the discovery of competing ground states in a lightly substituted *A*-site ordered $La_{0.96}Ba_{1.04}Mn_2O_6$ material with FM metallic and AFM insulating charge- and orbital-ordered properties. We demonstrate the suppression of charge ordering in magnetic fields as low as 1–2 T at 10 K and of the *A*-type orbital ordering in larger fields of $\sim 3-4$ T at 150–170 K. The low critical fields, the coexistence of three magnetically and energetically different phases within the same material, and the strong structure-property correlations make this class of layered materials an ideal candidate for further in-depth experimental and theoretical studies.

The structural properties of ordered $La_{1-x}Ba_{1+x}Mn_2O_6$ (x=0 and 0.04) are investigated as a function of temperature and magnetic field. Néel (T_N) and Curie (T_C) transition temperatures reported in this paper were extracted from previously published resistive and magnetic data.[24] High-resolution synchrotron x-ray data were collected at the Advanced Photon Source (Beamline 11-ID-C) with a wavelength λ=0.10772 Å. Field-dependent synchrotron x-ray diffraction data were collected at several temperatures. Time-of-flight neutron-diffraction data were collected at the Intense Pulsed Neutron Source (SEPD-ANL) at temperatures between 30 and 300 K.

In previous work, we reported phase separation in $LaBaMn_2O_6$ at ~ 200 K.[24] The high-temperature (HT) and low-temperature (LT) phases share similar structural traits but possess different magnetic properties. The HT phase remains present and ferromagnetic down to the lowest measured temperature while the LT phase accommodates long-range charge ordering below ~ 125 K. Our results have later been confirmed by Kawasaki *et al.*[28] who used ^{139}La and ^{55}Mn NMR probes to demonstrate a similar phase separation taking place in their $LaBaMn_2O_6$ sample.

On the other hand, the deliberate substitution of Ba for La in $La_{0.96}Ba_{1.04}Mn_2O_6$ appears to energetically favor the stabilization of a more robust orbital-ordered *A*-type AFM phase at a temperature below ~ 200 K. In both $LaBaMn_2O_6$ and $La_{0.96}Ba_{1.04}Mn_2O_6$, the HT and LT phases coexist at low temperatures with varying weight fractional amounts; thus,

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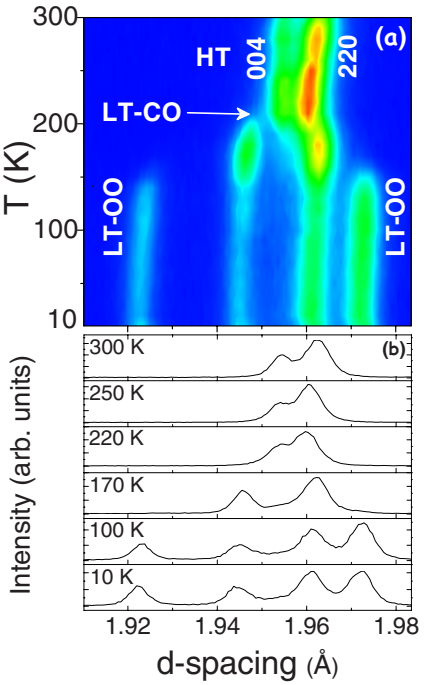

FIG. 1. (Color online) $La_{0.96}Ba_{1.04}Mn_2O_6$: (a) synchrotron data showing the HT-FM phase and the appearance of the LT-CO and LT-OO phases at 208 and 160 K, respectively. (b) Diffraction patterns at select temperatures showing the relative intensities and coexistence of the different phases.

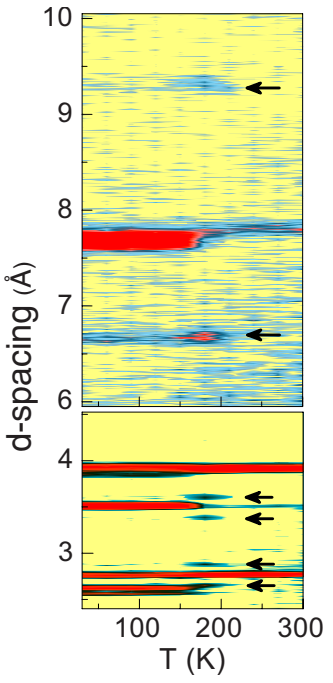

FIG. 2. (Color online) $La_{0.96}Ba_{1.04}Mn_2O_6$: portions of neutron-diffraction data showing weak OO and CO peaks.

resulting in pronounced kinks in the field-dependent magnetization loops and complex resistive properties as observed in Figs. 2 and 3 of Ref. 24. For $La_{0.96}Ba_{1.04}Mn_2O_6$, significant behavioral changes clearly take place at temperatures near 298 (T_C), 208, and 160 K.

The temperature-dependent synchrotron data for $La_{0.96}Ba_{1.04}Mn_2O_6$, Fig. 1, demonstrate a single HT phase above 208 K with only two tetragonal 220 and 004 diffraction peaks recorded. Below 208 K, new Bragg peaks are observed indicating the transformation of part of the sample into a new state (hereafter called LT-CO). Interestingly, a second partial transformation takes place below ~160 K into a third state (hereafter called LT-OO) and the three phases coexist at all temperatures between 10 and 160 K. We note the correspondence of the phase transformation temperatures to the observed resistivity kinks. Thus, we correlate the resistivity upturn at 208 K with the nucleation of the LT-CO phase and the change in slope near 160 K with the LT-OO phase.

To elucidate the nature of these phases, the analysis of neutron-diffraction data (Fig. 2) clearly demonstrates the coexistence of the three phases below ~160 K. We first note the weak LT-CO peaks appearing below 208 K with an overall intensity that significantly drops below ~150 K; thus, indicating the relative instability of this phase which partially gives way to the *A*-type LT-OO state. Our data provide a direct evidence for the coexistence of considerable amounts of ferromagnetic, charge-ordered, and orbital-ordered states within the same *A*-site layer-ordered material. Successful three-phase Rietveld refinements using data collected at 150 K are displayed in Fig. 3. The inset (b) of Fig. 3 shows the refined weight fractional amounts for the three phases as a function of temperature. Our results show the fractional percentages to remain constant below 120 K indicating the freezing of the different states in their respective domains. The different states are identified as a function of temperature and composition in the narrow range phase diagram shown in the inset of Fig. 3(c).

Magnetic-field-dependent synchrotron data are displayed

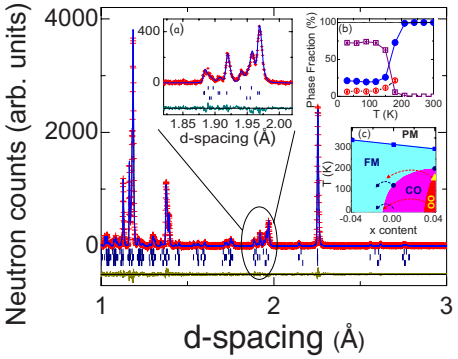

FIG. 3. (Color online) Best-fit three-phase Rietveld refinement for $La_{0.96}Ba_{1.04}Mn_2O_6$ at 150 K: tetragonal FM (low), monoclinic LT-OO (middle), and tetragonal LT-CO (upper ticks). Bottom curve shows the difference between observed and calculated intensities. Inset (a) shows the agreement between calculated and observed intensities in a narrow region dominated by 004 and 220 peaks. Inset (b) shows the weight fraction percentage of the HT (closed circles), LT-CO (open circles), and LT-OO (open squares) phases as a function of temperature and their freezing below 120 K. Inset (c) shows a limited phase diagram for $La_{1-x}Ba_{1+x}Mn_2O_6$ with $x=0$ and ± 0.04. Symbols represent measured T_C's and T_N's. Curved arrows show the phases observed in 0 T (starting points) and at $H=3$ or 6 T (ending points). See text for more details.

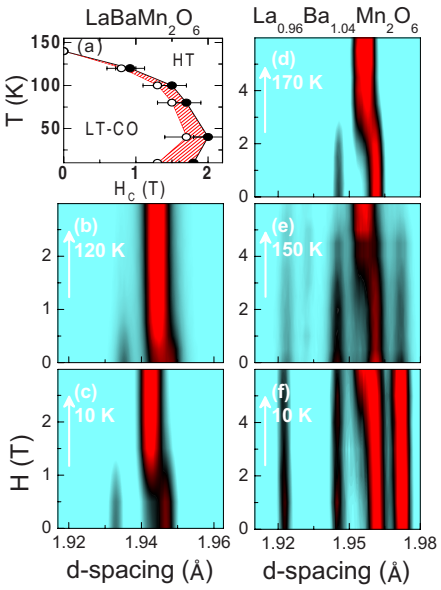

FIG. 4. (Color online) Synchrotron x-ray diffraction as a function of magnetic field for $LaBaMn_2O_6$ (left column) and $La_{0.96}Ba_{1.04}Mn_2O_6$ (right column). The figure shows low-field melting of the host nuclear phases for the [(b)–(d)] charge-ordered and (e) orbital-ordered states. (f) At 10 K, suppression of the OO phase is incomplete in fields up to 6 T. Panel (a) T-H_C phase diagram for $LaBaMn_2O_6$ extracted from the magnetic-dependent measurements.

in Fig. 4 for $LaBaMn_2O_6$ (left panels) and $La_{0.96}Ba_{1.04}Mn_2O_6$ (right panels). The data demonstrate the easy destabilization and suppression of the LT-CO phase under magnetic fields of not more than 1–2 T in agreement with the magnetization data (Fig. 2 in Ref. 24). We note the critical field needed to induce CO melting is an order of magnitude lower than that required for the common three-dimensional Mn perovskites. Hence, we speculate that properly strained $La_{1-x}Ba_{1+x}Mn_2O_6$ thin films could be tailored to have their critical fields further reduced to significantly less than 1 T. For $La_{0.96}Ba_{1.04}Mn_2O_6$, a field of 6 T field can only partially suppress the LT-OO phase at 10 K, Fig. 4(f). Nonetheless, at temperatures closer to the LT-CO and LT-OO phase transitions (i.e., 150–170 K), magnetic fields of 3–4 T are high enough to destabilize charge and orbital ordering and to establish the HT-FM metallic phase in the entire sample. It is useful here to note that a significant hysteresis behavior is observed showing lower critical fields obtained upon decreasing the magnetic field before phase separation is allowed to re-emerge, see Fig. 4(a).

Extensive theoretical models have been proposed to explain the unusual CMR effects and stability of coexisting phases in three-dimensional Mn-based perovskites. In Monte Carlo calculations, Dagotto and co-workers[2,29,30] demonstrated that a CMR peak in resistivity curves can be faithfully reproduced through the collaborative and/or competing effects of key parameters such as electron density (n), electron-phonon coupling (λ), quenched disorder (Δ), and superexchange coupling (J_{AF}). The quenched disorder term used by Dagotto and other groups[30–39] includes a wide range of disorders caused by a nonzero size variance of A- or B-site cations, local distortions, frozen clusters, as well as distorted Mn-O-Mn bond lengths and bond angles. Quenched disorder has frequently been emphasized as the main catalyst for CMR properties; however, further calculations proved that in the clean limit where $\Delta=0$, CMR properties and a first-order FM to AFM phase transition may still be observed by slightly increasing the magnitude of electron-phonon coupling and the system has to be fine tuned to be very close to the metal-insulator transition.[2,5]

To discuss the effects of quenched disorder on the properties of layered $La_{1-x}Ba_{1+x}Mn_2O_6$, we first note that, statistically, quenched disorder in $LaBaMn_2O_6$ is drastically minimized by the ordering of La and Ba on independent layers. Nonetheless, significant MR properties are still observed below T_C in the bulk material[24,40] as well as in thin films.[41]

With the deliberate inclusion of a small and symmetric disorder ($x=\pm 0.04$) at either the La or Ba sites $[La_{1-x}Ba_{1+x}(Mn^{3.5+x/2})_2O_6]$, one would expect an increase in the magnitude of quenched disorder and an asymmetric continuous change in the Mn oxidation state from $3.5-x/2$ to $3.5+x/2$ (in a linear manner). The La^{3+} substitution for Ba^{2+} (reduced doping—$Mn^{3.5-x/2}$) suppresses the CO state and stabilizes the high-temperature FM tetragonal phase down to 10 K.[24] On the other hand, the substitution of Ba^{2+} ions at the La^{3+} sites (increased doping—$Mn^{3.5+x/2}$) shifts the system's energy toward a phase-separation multicritical point. For a fixed disorder level (i.e., $x=\pm 0.04$), increased doping lowers T_C from 319 K ($x=0$) to 298 K ($x=+0.04$) while reduced doping increases it to 340 K ($x=-0.04$).[24] Therefore, in this system, the asymmetric properties' response to symmetric small disorder leads us to conclude that quenched disorder is not the primary factor for phase separation. Phase separation and coexistence brought about by the continuous charge doping appear to indicate that the electron-phonon coupling in the clean limit $\Delta\sim 0$ is sufficient to produce a first-order FM to AFM transition and the CMR behavior in the vicinity of a multicritical point.

When quenched disorder is strong enough, Dagotto[2,29] describes the opening of a glassy state "window" in which nanoscale mixtures of competing FM and charge-ordered AFM clusters can coexist. The size of the clusters could be regulated by disorder and proximity to the original first-order transition. The size could also be controlled by the increasing magnitude of strains as the clusters grow in size with decreasing temperature.[37] The presence of such a glassy state is demonstrated in our $La_{0.96}Ba_{1.04}Mn_2O_6$ sample with the freezing of the domains below 120 K but not in $La_{1.04}Ba_{0.96}Mn_2O_6$ which remains tetragonal and FM down to 10 K. Furthermore, a much more significant quenched disorder expected in A-site disordered $La_{1-x}Ba_xMnO_3$ ($x\sim 0.5$) does not result in any "long-range" phase separation.[24,42]

In conclusion, neutron and x-ray diffraction enabled the construction of temperature-composition and temperature-magnetic-field phase diagrams that demonstrate the strong competition between three magnetically different states in A-site layer-ordered $La_{1-x}Ba_{1+x}Mn_2O_6$ materials with reduced quenched disorder and the coexistence of the phases down to the lowest measured temperatures. The fragile character of the charge-ordered state in $LaBaMn_2O_6$ was demon-

strated by the low critical fields required to melting it. In $La_{0.96}Ba_{1.04}Mn_2O_6$, the charge-ordered state partially yields in favor of an *A*-type orbital-ordered state that can also be suppressed by relatively low critical magnetic fields. The strong interplay between the various magnetic states in two-dimensional Mn network systems should provide a unique opportunity to experimentalists and theorists to test and expand the validity of phase-separation models largely established from three-dimensional Mn perovskite networks with large quench disorder.

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