Microstructure of bilayer manganite PrCa$_2$Mn$_2$O$_7$ showing charge/orbital ordering

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The strongly correlated electronic systems of perovskite manganites have received great attention because of their fascinating physical properties such as colossal magnetoresistance and high spin polarity, which could find potential applications in spintronics or magnetic tunnel junction.1–9 The physical mechanism of these properties was ascribed to the complicated interplays between the four degrees of freedom of lattice, charge, orbital, and spin, and the consequent ordering as well as possible phase separation.6,10–12 Recently, two distinct charge/orbital ordering (CO/OO) states were found in the Ruddlesden-Popper (RP) compound Pr(Sr$_{1-x}$Ca$_x$)$_2$Mn$_2$O$_7$.13 Pr(Sr$_{1-x}$Ca$_x$)$_2$Mn$_2$O$_7$ has a layer structure (AO) (ABO$_3$)$_n$ ($n = 2$), where two (ABO$_3$) perovskite layers are separated by a AO rock salt layer along the long axis. The two reported CO/OO phases in Pr(Sr$_{0.5}$Ca$_{0.5}$)$_2$Mn$_2$O$_7$ are the high-temperature phase CO1 and CO2 phase.14 Therefore, it is particularly important to reveal the different aspects of the microstructure. The phases and micro domains viewed along the [001] zone axis are discussed. The heavy Pr atoms were found to locate in-between the bilayer MnO$_6$ octahedra.

Bulk PrCa$_2$Mn$_2$O$_7$ samples were synthesized using a transmission electron microscopy along the [001] direction by the appearance of satellite spots for both the CO1 and CO2 phase.14 Therefore, it is particularly important to reveal the microstructure along this direction. The CO1/CO2 phases and crystallographic orientation (as marked) in different domains are deduced from the selected-area ED patterns, insetted in the schematic diagram in Fig. 1(b). The orientation of the orbital stripes in different domains is schematically illustrated by heavy arrows according to the orientation of the lines of satellite spots found in the ED patterns. The domains B to D have the same height and are well aligned from left to right. Different from the common straight domain boundaries in this system, the domain boundary between the domains C and D is curved, as marked by some small dots. The phases in A, B, C, and G exhibit the CO1 phase, which is a high temperature phase in the previous reports,13 but a room temperature
phase in our samples. The CO2 phase in the D and E domains
has almost the same crystallographic orientation, similar to
that of the CO1 phase in the B and C domains.

The domain boundary between B and A (or F) is
deduced as (1–10)\textit{A} and the crystallographic orientation
between them is rotated by $\frac{90}{\sqrt{C24}}$ around the [001] axis, as
deduced from ED patterns, implying a (1–10)\textit{A} twin relation-
ship between them. The twin domains were believed to be
duced by the phase transition from the parent phase with a
higher symmetry\textsuperscript{19} and generally generates a splitting of
some diffraction spots in the [001] zone axis.\textsuperscript{20,21} The [00-1]
HRTEM image in Fig. 2(a) further reveals the characteristics
of this kind of twin. The two adjacent domains are connected
with each other through the (1–10)\textit{A} twin boundary (TB).
The lattice fringes with a width of 0.54 nm (corresponding to
the magnitude of $a_{\text{CO1}}$) are nearly perpendicular to each
other in both domains. A careful measurement, however,
indicates that the angle between both $b$ axes in the two
domains is not exactly $90^\circ$, but different by $0.9^\circ$ (as shown
by the thin white and black lines).

The crystallographic orientation between domains B and
C is almost the same, as seen from their similar orientation
of their [001] ED patterns in Fig. 1(b). A slight difference,
however, is found from the fast Fourier transform (FFT)
(Fig. 2(d)) of the HRTEM image including B and C domain
boundaries (Fig. 2(b)). Compared to the FFT of the HRTEM
image from one single domain (Fig. 2(c)), some of the high-
index diffraction spots in Fig. 2(d) are evidently split, e.g.,
the $(h\ h\ 0)$ spots in the red circles, suggesting a small rotation
of the lattice around the [001] axis occurred in the adjacent
B and C domains, e.g., $0.8^\circ$ deviation for the (110) plane in
both domains, the same as that deduced from the split of the
diffraction spots in the red circles.

In order to study the change of domains and orbital
stripes when the CO2 phase is clamped by the CO1 phase,
we carried out an \textit{in situ} heating TEM experiment. Fig. 3(a)
is the bright-field TEM image of the areas in Fig. 1(a), but
taken at 333 K. The mass loss during the \textit{in situ} observation
can be ignored because the sample is stable in that range of
temperatures. All phases in each domain are determined as
CO1 by selected-area ED patterns, as indicated in Fig. 3(b).
The thermally induced $90^\circ$ rotation of the orbital stripes was
observed only in the domains D and E (highlighted by green
circles), as revealed by the $90^\circ$ rotation of the lines of satel-
lite spots in their [001] ED patterns, in agreement with
previous observations. However, the orientation of the orbital stripes of the CO1 phase is conserved during the increase of temperature. Consequently, all the domains are the CO1 phase and the orientation of both orbital stripes and lattice from B to E is nearly the same. The twin relationship between B (or C, D, E) and A (or F) domains is also the same as that of the B and A domains at room temperature. Furthermore, the straight boundaries between them are maintained and domains from B to E are still clamped by A and F. However, the curved boundary between C and D domains in Fig. 1(a) disappeared and is replaced by a straight boundary after the phase transition. The disappearance of the curved boundary between C and D implies its lower energy.

HRTEM image is a widely used technique to analyze the microstructure of perovskite-based manganites, and CO/OO stripes. Fig. 4(a) is a [001] HRTEM image of the CO1 phase. The stripes of CO/OO with a modulation period of 1.08 nm are running along the b-direction, as marked by short line segments. The intensity of the bright spots in the HAADF-STEM image of Fig. 4(b) is constant and homogeneous, implying the superlattice is not caused by A-site cation ordering, concordant with the observation in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, but different from the observed A-site cation ordering in La$_{0.75}$Ca$_{0.25}$MnO$_3$. Fig. 4(c) is a [001] HRTEM image of the CO2 phase, where the superlattice with a period of $\sim$1.08 nm runs along the a-direction. It is difficult to distinguish between the CO1 and CO2 phase from [001] HRTEM images because they have similar structure blocks and modulation period. However, the difference is clearly seen from the insetted FFT of the HRTEM images. Comparing to the FFT of the CO2 phase in Fig. 4(c), there is one more line of weak spots in-between the lines of the main diffraction spots for the CO1 phase, as indicated by short white segments in the insetted FFT image in Fig. 4(a).

In addition to the CO1 and CO2 phase, the third CO/OO phase with two orthogonal modulations, named CO3, is also found at room temperature, as seen in Fig. 4(d). After carefully checking the [001]$_{CO2}$ HRTEM images, some areas show two sets of mutually perpendicular structural modulations, also verified by the satellite spots with two modulation vectors $q_1 = \frac{1}{2} a^*_0$, and $q_2 = \frac{1}{2} b^*_0$, as clearly seen from the FFT insetted in Fig. 4(d). The two superlattices in the HRTEM image, along the vertical and horizontal directions, respectively, have almost the same period of $\sim$1.08 nm, equal to that of $b_{CO1}$ (or $a_{CO2}$). The intensity of line scans along two perpendicular directions in the middle of Fig. 4(d) shows the difference of the two sets of superlattices. On the one hand, the intensity of the red profile from the horizontal atomic line shown in the bottom has a higher symmetry than the green one from the vertical atomic line in the right part. A mirror m perpendicular to the b-axis within one superlattice period could be deduced from the red profile, while no mirror could be found in the green profile. On the other hand, the deeper grooves in the green profile (as indicated by arrows at the right part) were arranged periodically along the a-axis, while no periodically darker contrast was found along the b-direction (see the red profile). The difference of intensity profile of the two sets of superlattice could be caused by various origins and the reasons need to be further clarified. More importantly, the CO3 phase might be an intermediate state of the 90° rotation of the OO stripes between the phase transition of the CO1 and CO2 phase, as observed by the ED patterns with two perpendicular modulations.
FIG. 5. (a) [110] HRTEM image of PrCa$_2$Mn$_2$O$_7$ with the $n = 2$ RP structure, showing a perfect stacking of layers along the $c$ axis. The [110] ED pattern is insetted. (b) The HAADF-STEM image demonstrates that the white dots (corresponding to heavy Pr atoms) locate in-between the bilayer of MnO$_6$ octahedra, as evidenced by the structure model in (c). The insetted simulated HAADF-STEM image at the right of (b) is in good agreement with the experimental results.

The bilayer structure of PrCa$_2$Mn$_2$O$_7$ is demonstrated from observations along the [110] orientation. The [110] HRTEM image in Fig. 5(a) shows the alternating bilayer MnO$_6$ octahedron blocks and the AO rock salt layer stacking along the $c$ axis, indicating a well-ordered $n = 2$ RP structure, quite similar to the structure projection of Ca$_3$Mn$_2$O$_7$ (with a similar unit cell) along the same direction. The number $n$ of (AO) (ABO)$_{3n}$, namely, the perovskite thickness, could be also determined directly from ED patterns containing $c^*$ as $n = N/2$, where $N$ is the number of diffraction spots between the central spot and the (002) reflection of cubic perovskite. The $n = 2$ is found from the [110] ED pattern insetted in Fig. 5(a) because of 4 spots between the central spot and (002)p. No diffuse scattering along $c^*$ was found, suggesting a perfect stacking along the $c$-direction. The [110] HAADF-STEM image in Fig. 5(b) is characterized by white spots arranged in line (emphasized by arrows in the right) and located in the middle of the two adjacent dark lines (rock salt layers), implying that the heavy Pr atoms (the whiter spots) locate in-between the bilayer MnO$_6$ layers, which is not concordant with the results by X-ray diffraction. A structural model of PrCa$_3$Mn$_2$O$_7$ with Pr atoms only located in-between the bilayer MnO$_6$ layers is therefore proposed in Fig. 5(c). The simulated HAADF-STEM image based on this model (as insetted in the right of Fig. 5(b)) shows a good agreement with the experimental results, in contrast to the disordered phase of Pr(Ca$_{0.9}$Sr$_{0.1}$)$_2$Mn$_2$O$_7$, where both Ca and Pr atoms locate at the cages of the MnO$_6$ octahedra and also in the AO layers.

In summary, the microstructure of the CO/OO Ruddleden-Popper bilayer manganite PrCa$_2$Mn$_2$O$_7$ was studied by electron microscopy along both [001] and [110] zone axes. Three CO/OO phases, namely CO1, CO2, and CO3, were found to coexist at room temperature, where the CO3 phase has two orthogonal superlattices with a similar modulation period of 1.08 nm along the $a$ and $b$ axis, respectively. The $in situ$ heating TEM experiment indicates that the CO2 phase, clamped by the CO1 domains, can change into the CO1 phase by heating, inducing a 90° rotation of the OO stripes. A perfect bilayer MnO$_6$ perovskite block stacking along the $c$ axis is observed along the [110] orientation. However, the Pr atoms were found to locate in-between the bilayer MnO$_6$ octahedra from [110] HAADF-STEM image and simulation, which is different from previous reports from X-ray diffraction.

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