Double-Bilayer Polar Nanoregions and Mn antisites in $(\text{Ca,Sr})_3\text{Mn}_2\text{O}_7$

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Article

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Abstract

The layered perovskite $\text{Ca}_3\text{Mn}_2\text{O}_7$ (CMO) is a hybrid improper ferroelectric (HIF) candidate proposed for room temperature multiferroicity, which also displays negative thermal expansion behavior due to a competition between coexisting polar and nonpolar phases. However, little is known about the atomic-scale structure of the polar/nonpolar phase coexistence, or the underlying physics of its formation and transition. In this work, we report the first direct observation of double bilayer polar nanoregions (db-PNRs) in $\text{Ca}_{2.9}\text{Sr}_{0.1}\text{Mn}_2\text{O}_7$ using aberration-corrected scanning transmission electron microscopy (S/TEM). In-situ TEM heating experiments show that the db-PNRs can exist up to 650°C. Electron energy loss spectroscopy (EELS) studies coupled with first-principles calculations demonstrate that the stabilization mechanism of the db-PNRs is directly related to a Mn oxidation state change (from 4+ to 2+), which is linked to the presence of Mn antisite defects. These findings open the door to manipulating phase coexistence and achieving exotic properties in HIFs.

Full Text

The development of multiferroic materials aims to realize direct electric-field controlled switching of magnetization at room temperature.^{1,2} However, identifying stable and single-phase multiferroic materials to achieve this objective has been challenging, because electrical polarization and magnetization must be strongly coupled together in such systems.^{1–6} Recently, a new class of materials, called hybrid improper ferroelectrics (HIFs), was theoretically proposed as a potential room-temperature multiferroic system.² The principle of the HIF mechanism is to induce ferroelectricity, ferromagnetism, and magnetoelectricity simultaneously with the same set of lattice instabilities.^{2,7} In particular, oxygen octahedron rotations and tilts, which are ubiquitous in perovskite materials and couple strongly to magnetism, combine with a layered crystal structure to induce polarization.^{8,9} Hybrid improper ferroelectricity at room temperature was first experimentally confirmed in the $n=2$ Ruddlesden-Popper material $\text{Ca}_3\text{Ti}_2\text{O}_7$ ¹⁰ and was subsequently observed in $\text{Sr}_3\text{Sn}_2\text{O}_7$ and other layered perovskites.^{11–13}

$\text{Ca}_3\text{Mn}_2\text{O}_7$ (CMO) is another HIF candidate, which was the first theoretically proposed system for achieving room temperature multiferroicity.² $\text{Ca}_3\text{Mn}_2\text{O}_7$ is an $n=2$ member of the Ruddlesden Popper layered perovskite family with a general formula $(\text{ABO}_3)_n(\text{AO})$ or $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$. The CMO crystal structure consists of double CaMnO_3 perovskite blocks stacked along the $[001]$ direction, with an extra CaO rocksalt sheet inserted after each double perovskite block. At room temperature, CMO crystallizes in the polar $A2_1am$ space group. The condensation of an out-of-phase ($a^-a^-c^0$ in Glazer notation¹⁴) octahedral tilting distortion and an in-phase ($a^0a^0c^+$) octahedral rotation distortion establish the $A2_1am$ symmetry and induce a polarization.² Figure 1(a) shows schematic views of the $A2_1am$ crystal structure viewed along the a ($[100]_{\text{ortho}}$) and b ($[010]_{\text{ortho}}$) projections, with the polarization (P) pointing along $[00]$. The polarization arises primarily from a two-against-one displacement of the Ca ions along the a -axis in each

perovskite block (Figure 1a, right). In addition, the $a^-a^0c^0$ octahedral tilting distortion involves alternating left/right displacements along the b-axis of the Ca ions in each layer (Figure 1a, left).

Several studies have revealed the complex domain structure and phase transition sequence of CMO. Early transmission electron microscopy (TEM) studies showed twin variants of the $A2_1am$ phase with an (001) interface.¹⁵ In addition, Gao et al. observed irregular orthorhombic twins with curved boundaries and further demonstrated the rearrangement of the oxygen octahedral tilts and rotations during a complex phase transition from $I4/mmm$, to an intermediate nonpolar phase $Acaa$ ($a^0a^0c^-$), and finally to the polar $A2_1am$ ($a^-a^0c^+$) phase.⁷ This transition leads to a degeneracy of polarization orientations along either the a-axis ($[100]_{\text{orth}}$) or b-axis ($[010]_{\text{orth}}$) of the CMO crystal, and a large number of 90° ferroelectric domain walls perpendicular to the c-axis.⁷ Liu et al. experimentally demonstrated ferroelectric switching by measuring the ferroelectric hysteresis loop, but this could only be accomplished at a very low temperature ($T < 28\text{K}$) due to the relatively high electrical conductivity of CMO.¹⁶ On the other hand, the complex domain morphology of CMO leads to many novel physical properties.^{16,17} Most notably, negative thermal expansion (NTE) behavior was observed in both CMO and $\text{Ca}_{3-x}\text{Sr}_x\text{Mn}_2\text{O}_7$ (CSMO) crystals and was closely related to the coexistence of competing polar $A2_1am$ and nonpolar $Acaa$ phases over a large temperature range.^{18,19} It was further demonstrated that NTE can be tuned by controlling the phase competition between the polar $A2_1am$ and nonpolar $Acaa$ phase with different levels of Sr doping.¹⁹

Although several studies have focused on understanding the macroscale properties of CMO, little has been done to uncover the structure of the polar-nonpolar phase coexistence at the atomic scale.

In this work, for the first time, we uncover polar nanoregions (PNRs) in a nonpolar matrix of a layered perovskite at the atomic scale using scanning/transmission electron microscopy (S/TEM) imaging and quantify its structure with picometer precision. We further explore the underlying physics and chemistry of the phase competition transition dynamics as a function of temperature using in-situ high-resolution TEM and monochromated electron energy loss spectroscopy (EELS) techniques. We observe that the formation of Mn antisites drives the phase competition, which is a mechanism that may stabilize similar polar/nonpolar phase competition in other layered perovskite crystals and beyond.

This study explores Sr-doped CMO because the presence of the Sr cation promotes the coexistence of the $A2_1am$ and $Acaa$ phases at room temperature. The addition of 3% Sr is expected to decrease the ferroelectric transition temperature of $\text{Ca}_{2.9}\text{Sr}_{0.1}\text{Mn}_2\text{O}_7$ to below room temperature, and thus at room temperature, we expect a small fraction of the $A2_1am$ polar phase region to be embedded in a nonpolar matrix with $Acaa$ symmetry, as indicated by previous X-ray measurements.¹⁹

Figures 1b and c show the annular dark-field (ADF) and annular bright-field (ABF) STEM micrographs of the CSMO crystal with the nonpolar $Acaa$ space group, respectively. The ADF-STEM shows the contrast from heavier atomic species, Ca, Sr, and Mn. The presence or absence of Ca/Sr displacements can be used to distinguish between the $A2_1am$ phase where displacements are expected (Figure 1a) and the

Acaa phase, where such displacements are not allowed by symmetry. The Ca/Sr atoms in the image do not exhibit displacement with regard to the unit cell center, which is expected since the matrix should belong to the nonpolar *Acaa* space group. On the other hand, we observe many nanometer-sized features along the (001) interface distributed randomly all across the sample on the low magnification TEM micrograph taken from $[100]_{\text{orth}}$ zone axis (Figure 1d). To determine the crystal structure, we obtain the selected area electron diffraction (SAED) patterns from the same sample (Figure 1e). A row of weak spots at $(0, \frac{1}{2}, \frac{1}{2})$ (with $\frac{1}{2} = 2n+1$) connected with near-continuous streaks is observed in the SAED patterns, suggesting the formation of a superstructure along the (001) interfacial planes, similar to the features in the electron diffraction study reported in an undoped $\text{Ca}_3\text{Mn}_2\text{O}_7$ crystal with a polar $A2_1am$ space group.¹⁵ High-resolution transmission electron microscopy (HREM) images taken in this region confirm that the weak spots and the streaks in the SAED pattern arise from the linear features within the crystalline matrix (Figure S1).

To directly observe the linear features at the atomic scale, we perform aberration-corrected high-resolution scanning transmission electron microscopy (AC-STEM). Numerous linear features (bright lines) along the (001) interface are observed in the ADF-STEM image in Figure 2a. The high-resolution ADF-STEM image of the linear features reveals two distinct types of double bilayer polar nanoregions (a-type and b-type db-PNRs), as shown in Figures 2b and 2c, respectively. Both types of db-PNRs consist of two adjacent double perovskite blocks (a double bilayer). Importantly, this is the first observation of db-PNRs in a layered perovskite system. In the a-type db-PNRs (Fig. 2b), we observe alternating left/right displacements of the Ca/Sr atoms in the rocksalt sheet between two double perovskite blocks. In the b-type db-PNRs (Fig. 2c), the Ca/Sr atoms all displace in the same direction. The a-type and b-type db-PNRs show displacement patterns similar to those of the CMO $A2_1am$ polar ground state structure viewed from the $[010]$ and $[100]$ zone axis, respectively (Figure 1a). To quantify the structural distortions, we use an atom position refinement algorithm to accurately assess the atom positions and measure the center Ca/Sr atomic displacements in the double perovskite blocks.^{20,21} The displacement measurement is presented in Figure 2b and 2c as colored vector maps superimposed on the ADF-STEM images of the db-PNRs. The left panel of Figure 2b shows the a-type db-PNRs with a relative displacement of the Ca/Sr atoms of close to 40 pm, and the left panel of Figure 2c shows the b-type db-PNRs with an alternating left/right displacement of the Ca/Sr atoms of approximately 20 pm. Additionally, as illustrated in the vector map, the center Ca/Sr atoms exhibit much larger displacements than the matrix of the crystal (close to 0 pm as indicated by purple color, also see Figure S2). The strain mapping from our geometric phase analysis (GPA) overlaid on the ADF-STEM image (Fig. 2b and 2c, right panel) shows a large strain of around 5-10% along the $[001]$ direction. This local strain is likely the cause of the diffraction contrast in the lower magnification ADF-STEM image in Figure 2a.

To investigate the possibility of oxygen vacancies^{22,23} as well as to quantify the magnitude of the octahedral tilts, we make use of ABF-STEM. The ABF-STEM mode has been widely used for imaging light elements in a wide range of materials and is especially useful in visualizing oxygen octahedral distortions in oxide materials.^{24–26} In this work, our ABF-STEM images uncover the oxygen atom columns

in CSMO, and show an intact crystal structure at and away from the db-PNRs regions, as shown in Figure 2d. There is no clear indication of oxygen vacancy ordering as it would modulate the intensity of the oxygen atom columns locally. Additionally, the ABF-STEM images clearly illustrate a negligible tilt of the oxygen octahedra in the matrix as expected in the nonpolar *Acaa* phase, whereas significant octahedral tilting is observed at the vicinity of the db-PNRs. We measure the oxygen octahedra tilting angle to be 158 degrees on average with a standard deviation of 4.7 degrees locally in the vicinity of the db-PNRs, as opposed to approximately 180 degrees in the matrix.

To further understand the dynamics and stabilization of polar nanoregions in CSMO, we perform in-situ heating experiments inside the TEM column. Figure 3 shows the TEM micrographs of the morphology in the CSMO sample at different temperatures during heating. Initial heating of the sample starts from room temperature and goes to 200 °C, as shown in Figure 3a. As discussed previously, the densely populated, nanometer-sized features are the db-PNRs. During heating from 200 °C to 450 °C, the location and the density of the db-PNRs are relatively stable and do not show much change as shown in Figure 3a-c. Within this temperature range, the sample undergoes strain relaxation, and the diffraction contrast induced by strain is reduced. As the temperature is further raised to 550 °C, the db-PNRs start to disappear in the nonpolar phase (Figure 3d). By 600-650 °C, most of the db-PNRs undergo a phase transition into the nonpolar *Acaa* phase (Figure 3e-f). However, there are still a small number of db-PNRs remaining at 650 °C. This observation indicates a gradual transition between the polar and nonpolar phases in CSMO, but the mechanism that stabilizes db-PNRs at high temperatures is still unknown.

To understand the underlying physics of the db-PNR stabilization mechanism, we use monochromated EELS to determine the local chemical environment of the Mn ions in the db-PNRs. The L ionization edges of the transition metal elements (Mn in this case) reflect the electronic transition from 2p to 3d levels, with the L_3 and L_2 edges showing the transition from $2p^{3/2}$ to $3d^{3/2}$ $3d^{5/2}$ levels and from $2p^{1/2}$ to $3d^{3/2}$ levels respectively.²⁷⁻³⁰ By performing monochromated EELS, the energy loss near edge structure (ELNES) of Mn $L_{2,3}$ is resolved for fingerprinting the oxidation states across the db-PNRs in the crystal. Since the ELNES for the same Mn oxidation state in different compounds is very similar, it has been successfully demonstrated that mixed Mn oxidation states can be determined with very high resolution by fitting the experimental Mn ELNES spectra with the existing reference ELNES spectra.³¹⁻³³ Figure 4a is a plot of a line-scan EELS data overlaid on the ADF-STEM image indicating the spatial location of the electron probe, and Figure 4b shows the averaged EELS Mn L edge spectra from the db-PNRs (red) and nonpolar phase (blue). We perform linear combination fitting on our line-scan EELS data set; fitting of the averaged spectra from the polar and nonpolar regions is shown in Figure 4b. We use the ELNES spectra from MnO (Mn^{2+}) and $SrMnO_3$ (Mn^{4+}) collected by Garvie et al. as the reference spectra.³² The fitting results indicate that the ELNES of the Mn L-edge at the db-PNRs shows more similarity to the Mn^{2+} reference spectra. These fitting results are plotted and overlaid on the simultaneously acquired ADF-STEM image (Figure 4c) and indicate that the Mn^{2+} percentage is approximately 90% at the center of the db-PNRs.

To confirm this result, we also determine the integrated intensity ratio of the L_3/L_2 edges of the line-scan dataset acquired from another region near the db-PNRs and obtain a ratio of approximately 2.6 and 2 at polar and nonpolar regions respectively (Figure S3). The L_3/L_2 edge intensity ratio confirms that the oxidation state of Mn ions at the db-PNRs changes from the Mn^{4+} state to either Mn^{3+} or a mixture of Mn^{2+}/Mn^{4+} states.²⁷ Additionally, we observe a much stronger Mn L edge intensity from the center rocksalt layer of the db-PNRs compared to the perovskite layer. Energy-dispersive X-ray spectroscopy (EDX) mapping of the same region confirms a higher Mn ion and lower Ca ion content in these rocksalt sheets (Figure S4 and S5). Our observations indicate that Mn antisite defects form at the rocksalt layer Ca site of the Ruddlesden-Popper structure. The multi-valent Mn ions change oxidation states when forming antisite defects on the Ca sites.

To validate our hypothesis that Mn antisite defects stabilize the db-PNRs in CSMO, we perform density functional theory (DFT)+U calculations on $Ca_{3-x}Mn_{2+x}O_7$ for a range of x . We do not include the Sr dopants in our calculations to keep our computational cell to a reasonable size. The main effect of this choice is that $A2_1am$ is the ground state structure for all Mn dopant concentrations that we consider, however, the energy difference can still inform us about how the substitution of Mn for some Ca cations impacts the relative energy of the two phases. Figure 5(a) shows as a function of Mn-dopant concentration x for $Ca_{3-x}Mn_{2+x}O_7$, obtained from DFT+U structural relaxations. As the dopant concentration x increases, the energy difference grows, indicating that the $A2_1am$ structure is further stabilized with respect to $Acaa$. This result supports the interpretation of the experimental data that regions with Mn dopants stabilize the polar structure with $A2_1am$ -symmetry.

Figure 5(b-g) show the Mn-O-Mn bond angles for several Mn-dopant concentrations, obtained from our DFT+U structural relaxations. The structures in Figure 5(b-g) depict the lowest energy dopant configuration for each doping level. Other Mn-dopant configurations are shown in Figures S7-S8. The $n=2$ Ruddlesden-Popper $A_3B_2O_7$ structure contains two symmetry-distinct A-sites: a larger A-site situated in the center of the perovskite bilayer, and a smaller A-site located in the rock salt layer. Our DFT calculations show that it is always energetically favorable to place the smaller Mn^{2+} dopants in the rocksalt A-sites, which agrees with prior experimental observations. Interestingly, when more than one dopant is present in the supercell (Figure 4c-f), we find that it is energetically favorable for the Mn^{2+} dopants to cluster in a single rocksalt layer. We also find that as the Mn-dopant concentration increases, the bond angles bend further from 180° . This effect can be rationalized by considering the tolerance factor: a decrease in the A-site cation ionic radius decreases the tolerance factor, which leads to increased octahedral rotation angles.^{34,35} The Shannon radii of Ca^{2+} and Mn^{2+} (in 8-fold coordination) are 1.12 and 0.96 respectively. Thus, as the Mn^{2+} dopant concentration increases, the tolerance factor decreases, and the octahedral tilting increases (more bending of the Mn-O-Mn bond). We further notice that the bond angles closest to the Mn^{2+} dopants change the most compared to their values in the undoped compound in Figure 5b, whereas the bond angles further away from the dopant change a smaller amount.

We also use our DFT+U calculations to probe the charge state of the Mn dopants substituted on the Ca sites. In $\text{Ca}_3\text{Mn}_2\text{O}_7$, the Mn cations have a formal charge of 4+, whereas we expect a formal charge of 2+ if Mn substitutes onto a Ca site. Mn^{2+} can adopt high- or low-spin states, which would correspond to magnetic moments of 5 and 0.5 respectively. Table 1 reports the magnetic moments of the Mn-dopants obtained from our DFT+U calculations. We find that for all dopant concentrations, the moment of the Mn dopants is 4.3-4.4 μ_B , which is consistent with the Mn^{2+} charge state in the high-spin configuration. This agrees with the experimental observation of the existence of the Mn^{2+} oxidation state in the polar region. Overall, the DFT calculations exhibit excellent agreement with our experimental observations from atomic resolution STEM combined with EELS.

In conclusion, our study uncovers that the coexistence of polar $A2_1am$ and nonpolar $Acaa$ phases in CSMO leads to the formation of db-PNRs. PNRs are widely viewed as the embryo of the ferroelectric phase and are critical to the relaxor properties of ferroelectrics in ultrasonic applications due to their superior piezoelectric properties³⁶, and the discovery of db-PNRs in a hybrid improper ferroelectric system is unprecedented. The interpretation of the origin of the polar nanoregions in the relaxor ferroelectric materials has been challenging because of the heterogeneity over different time and length scales.^{37–39} By employing atomic-resolution STEM imaging in combination with EELS and DFT calculations, this study demonstrates the polar $A2_1am$ phase stabilization mechanism of db-PNRs in CSMO to be the formation of the Mn antisites on the Ca sites that increases the octahedral tilting amplitudes. This study utilizes an in-situ heating experiment to further explore the polar/nonpolar phase transition as a function of temperature and observed the presence of the db-PNRs at temperatures as high as 650 °C. Both previous studies¹⁹ and our in-situ heating experiment show that the polar $A2_1am$ and nonpolar $Acaa$ phases in CSMO exhibit a competition over a large temperature range, but the stabilization mechanism has not been clear until now. The stabilization mechanism of db-PNRs in CSMO due to Mn antisites is similar to Ti antisites producing PNRs and a switchable polarization in SrTiO_3 ^{40,41}, as well as the recent report of Y antisites leading to room temperature ferroelectricity in yttrium orthoferrite YFeO_3 .⁴² Our work shows that antisite defects play an important role in stabilizing polar nanoregions in the family of layered perovskite crystals and beyond. This study provides a path toward engineering polar nanoregions and designing novel lead-free relaxor ferroelectrics in hybrid improper ferroelectric materials by tuning the stoichiometry during growth for sophisticated defect engineering.

Table 1. The magnetic moment of Mn-dopant atoms in $\text{Ca}_{3-x}\text{Mn}_{2+x}\text{O}_7$ for structures with symmetry $A2_1am$ and $Acaa$ calculated with DFT+U. For compositions with more than one dopant atom in the supercell, the reported magnetic moment is obtained by averaging the moments of all the dopant atoms in that cell. The magnetic moment of the B-site Mn atoms

(that is, those within the oxygen octahedra) is for all structures, which is consistent with a Mn^{4+} charge state.

Material	x	Magnetic moment, $A2_1am$ (μB)	Magnetic moment, $Acaa$ (μB)
$\text{Ca}_{2.75}\text{Mn}_{2.25}\text{O}_7$	0.25	4.40	4.45
$\text{Ca}_{2.5}\text{Mn}_{2.5}\text{O}_7$	0.5	4.37	4.43
$\text{Ca}_{2.25}\text{Mn}_{2.75}\text{O}_7$	0.75	4.37	4.42
$\text{Ca}_2\text{Mn}_3\text{O}_7$	1.0	4.35	4.41
CaMn_4O_7	2.0	4.34	4.41

Methods

Computational Details:

We perform density functional theory (DFT) calculations using the Vienna ab initio Simulation Package (VASP).^{43,44} We employ the PBEsol exchange-correlation functional and a plane-wave basis with an energy cutoff of 600 eV.⁴⁵ All calculations are performed in a 48-atom computational cell with a Monkhorst-Pack k-point mesh to sample the Brillouin zone. For structural relaxations, a force convergence tolerance of 2 meV/Å is used, and both lattice parameters and atomic positions are optimized. We make use of the Liechtenstein formulation of the DFT+U method⁴⁶ to treat the Mn on-site Coulomb interaction and set the Coulomb and exchange parameters to be $U = 4.5$ eV and $J = 1.0$ eV, respectively. We impose G-type antiferromagnetic order in the perovskite bilayers, which is the known ground state magnetic structure of $\text{Ca}_3\text{Mn}_2\text{O}_7$.² For compositions with Mn dopants substituted on some Ca sites, the Mn dopant spins are placed in a ferromagnetic order. The DFT+U-relaxed lattice parameters of all $\text{Ca}_{3-x}\text{Mn}_{2+x}\text{O}_7$ compositions discussed in the main text are reported in Table S1. We note that due to the ordered nature of the Mn dopant atoms in the periodic computational supercell, for most dopant concentrations the symmetry of the crystal structure is lower than the $A2_1am$ or $Acaa$ symmetry of $\text{Ca}_3\text{Mn}_2\text{O}_7$. However, for simplicity we choose to refer to these Mn-doped structures by the symmetry of the corresponding $\text{Ca}_3\text{Mn}_2\text{O}_7$ structure ($A2_1am$ or $Acaa$) throughout the text. We use the ISOTROPY Software Suite⁴⁷ for group-theoretic analysis and VESTA⁴⁸ to visualize crystal structures.

Sample Preparation:

Single-crystalline CSMO were grown by using optical floating zone methods grown as described elsewhere (see ref 7 and 19). The TEM samples were prepared using the Thermo Scientific Helios NanoLab Dual-Beam Focused Ion Beam (FIB) system. Before mounting the CSMO crystal into the

FIB/SEM column, a thin layer of carbon was deposited for better electron conductivity and preventing charging. The regular TEM samples were prepared by first lifting out the 1-2 μm lamella from the crystal surface and mounting the lamella onto the copper V-post TEM grid. The mounted lamella was then thinned down using the 30 kV Ga ion beam to around 400 nm and subsequently to around 100 nm (electron transparent) using the 5 kV Ga ion beam. Later, 2 kV and 1 kV ion beams were applied to gently reduce the amorphization and Ga ion implantation caused by Ga ion bombardment.

The in-situ TEM samples were prepared by an ex-situ lift-out method. First, we created a trench at the crystal surface with the lamella sitting vertically in the center. Second, the lamella was thinned down to around 100 nm using the 30 kV and 5 kV ion beam. Third, we used the 2 kV ion beam to mill the sample surface for final cleaning. Then, the arms of the lamella that attaches to the trench were cut off and this step makes the electron transparent sample left free-standing in the trench. Subsequently, the crystal was carefully taken out of the SEM column and transferred to the EXpressLO workstation. Lastly, we used a glass needle with a very fine tip to lift out the sample using electrostatic force and placed the sample flat onto the windows in the SiC membrane of the Protochips heating E-chip.

Transmission electron microscopy:

The aberration-corrected scanning transmission electron microscopy (STEM) images and the electron energy loss spectroscopy (EELS) spectra were both collected using the Thermo Scientific Titan³ S/TEM equipped with a spherical aberration corrector, a monochromator, and a Gatan imaging filter (GIF). The STEM imaging was operated at the acceleration voltage of 300 kV with the probe convergence angle of 30 mrad. The ADF/ABF STEM images are acquired using HAADF and ABF detectors, respectively. The collection angle for the ADF detector is 44–244 mrad while for the ABF detector is 9–51 mrad. During the STEM-EELS data acquisition, the acceleration voltage is reduced to 80 kV for alleviating the beam damage. The EELS data was acquired in dual-EELS mode, in which each EELS data set consists of the low-loss spectra containing the zero-loss peak (ZLP) and the high-loss spectra with the core-loss edges. The collection angle for EELS data acquisition is 9.2 mrad. After activating the monochromator, the aberration correction is performed to enhance spatial resolution. The energy resolution is approximately 0.15 eV by measuring the FWHM of the ZLP. The exposure time for each probe position is 4 seconds.

The in-situ heating experiment was performed inside the Thermo Scientific Talos F200X TEM. The Protochips heating E-chip was first mounted onto the Protochips Fusion Select holder with the double tilt capability. After the holder was inserted into the TEM column, we first used the double tilt function to find the correct zone axis for the observation, and then start the heating process at the rate of 10 °C per minute until the temperature reached set goals. Several TEM images were captured during the heating process. After the sample reached a certain temperature, the sample position and tilt angles were adjusted to ensure the image to be acquired from relatively the same region, and then the temperature was held for around 10-15 minutes for the potential dynamics to take place. Multiple TEM images were taken at different magnifications every one to two minutes.

STEM and EELS analysis:

Each STEM image analyzed and presented in this work is drift corrected with a non-linear drift correction algorithm, with the input being a pair of sequentially acquired STEM images with perpendicular scanning directions.⁴⁹ The atom position analysis and displacement measurement were performed using the customized Matlab code.^{21,50} The atom positions in ADF/ABF STEM images were determined by fitting a 2D-gaussian over the atomic columns and we defined the refined atomic positions as the center of the Gaussian peak. The atomic displacement was calculated by measuring the distance from the displaced atoms to the unit cell center positions. The GPA strain measurement was performed using Strain++ software.^{51,52} Prior to the analysis, a Hann window was applied on the STEM image input to reduce the fast Fourier transform (FFT) artifact. Then we applied FFT to the input image and obtained the power spectrum. Afterward, the Bragg-filtered images were generated by first applying two gaussian masks over the first Brillouin zone of two reciprocal lattice vectors and then perform an inverse Fourier transform. Later the phase images can be extracted from the Bragg-filtered images and the strain field can be determined from the phase images.

Before analyzing the EELS line-scan data, all energy loss axes in the high-loss spectra were first corrected according to the shift in the ZLP positions measured in the simultaneously collected low-loss spectra. The corrected high-loss EELS spectra were then denoised by employing the principal component analysis method and select the first five principal components to reconstruct the line-scan EELS data.⁵³ For the EELS white-line ratio calculation, we first subtract the continuum contribution using a Hartree–Slater cross-section and determined L_3/L_2 intensity by fitting Gaussian peaks and integrating the intensity within the fitted Gaussian peaks (Figure S8).²⁷ The ELNES fitting was performed on monochromated EELS spectra and the oxidation state was obtained by fitting the Mn L edges as a linear combination of two reference spectra of different oxidation states. The spectra are adjusted to accommodate the different calibration of the drift tube in different TEM instrument.

Declarations

ASSOCIATED CONTENT

The Supporting Information is available free of charge at:

Experimental methods including computational details, sample preparation, transmission electron microscopy, and STEM and EELS analysis (PDF)

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Author Contributions

L.M. designed the study in consultation with N.A. L.M. carried out the in-situ TEM, STEM/EELS experiments and data analysis. P.M., D.M. and K.W contributed to the TEM data collection. K.H. and E.A.N. carried out the DFT simulations and S.W.C carried out the crystal synthesis. The manuscript was drafted by L.M. and edited by N.A. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Ethics declarations

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

(a) Schematics of the $A2_1am$ crystal structure for hybrid improper ferroelectric $Ca_3Mn_2O_7$ viewed along the $[100]$ and $[010]$ projections. The gray arrows indicate the alternating left/right and parallel displacements of the Ca atoms in each layer along $[010]$ and $[100]$, respectively. The alternating displacements along $[010]$ arise from the $a^-a^+c^0$ octahedral tilting distortion, whereas the parallel displacements along $[100]$ give rise to the polarization. (b, c) The ADF-STEM and ABF-STEM images of $Ca_{2.9}Sr_{0.1}Mn_2O_7$ in the $Acaa$ non-polar space group, along the $[100]$ zone axis. The insets show the magnified micrographs with the crystal structure overlaid. (d) a TEM image of the $Ca_{2.9}Sr_{0.1}Mn_2O_7$ sample along the $[100]$ zone axis. Numerous and randomly distributed nano-meter sized features are observed. (e) The selected area electron diffraction (SAED) pattern along the $[100]$ zone axis. The contrast of the SAED pattern is reversed to better visualize the weak extra diffraction spots. The red arrows point out the rows of weak spots at $(0, \frac{1}{2}, \frac{1}{2})$, with $\frac{1}{2} = 2n+1$, connected with near-continuous streaks.

Figure 2

(a) The ADF-STEM image at lower magnification shows numerous linear structures at the [001] interface (bright lines) embedded and scattered randomly in the crystal. (b) and (c) left panel: The displacement measurement of the center Ca atom in the double perovskite blocks in a- and b-type db-PNRs in CSMO, respectively. The measurement is presented as colored vector maps superimposed on the ADF-STEM images of the db-PNRs, with the purple and yellow colors indicating displacements of 0 and 45 pm, respectively. (b) and (c) right panel: the GPA ϵ_{yy} strain mapping of the db-PNR. (d) ADF-STEM image of the db-PNR in CSMO, with the overlaid color map on the micrograph indicating the measured oxygen octahedra tilting angles. (e) Enlarged image from (d) highlighting the oxygen octahedra tilting at the db-PNR. The zig-zag shape shows the opposite tilting directions for any two adjacent octahedra.

Figure 3

The TEM micrographs taken from [100] zone axis of the morphology of the CSMO sample at different temperatures during the in-situ heating experiment. The [001] direction of the sample is labelled using the white arrow. The polar nanoregions can be seen as the randomly distributed, linear features that are perpendicular to the [001] direction. (a-f) The TEM image acquired at the temperature of 200 °C, 320 °C, 450 °C, 550 °C, 600 °C, and 650 °C, respectively. The white scale bar is 50 nm.

Figure 4

(a) a plot of a line-scan EELS data overlaid on the ADF-STEM image. The crosses and different colors of the spectra indicate different electron probe spatial locations on the ADF-STEM image. The red and blue brackets on the right indicate the spectra from polar and non-polar regions respectively. (b) The averaged EELS Mn L edge spectra from the polar nanoregions (red) and non-polar matrix (blue), as indicated in (a). The reference Mn^{2+} and Mn^{4+} spectra are also plotted as black solid and dashed lines. The height of the reference spectra is plotted based on the ELNES fitting results on both averaged spectra. (c) The results of the ELNES fitting results. The upper panel shows the electron probe locations scattered on the simultaneously acquired ADF-STEM image. The color of the circles indicates the percentage of the Mn^{2+} as calculated by the ELNES fitting. The lower panel shows the plot of Mn^{2+} percentage versus the probe positions. A spike in Mn^{2+} percentage is indicated in the center of the polar region by this plot.

Figure 5

(a) Energy difference between the nonpolar Acaa and polar $A2_1am$ phases of $\text{Ca}_{3-x}\text{Mn}_{2+x}\text{O}_7$ as a function of Mn dopant concentration x calculated with DFT+U. For Mn concentrations where there is more than one possible configuration of Mn dopants, we report the energy of the lowest energy configuration (the energies of other configurations are shown in the SI). (b-g) Mn-O-Mn bond angles for a range of $\text{Ca}_{3-x}\text{Mn}_{2+x}\text{O}_7$ compositions. For each composition, the lowest energy dopant configuration is shown. Blue, green, magenta, and red balls represent calcium, Mn^{4+} , Mn^{2+} , and oxygen atoms, respectively.

Supplementary Files

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