Structural, magnetic, and dielectric properties of charge-order phases in manganite \( \text{La(Ca}_{0.8}\text{Sr}_{0.2})_2\text{Mn}_2\text{O}_7 \)

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ABSTRACT

Charge-ordered layered manganites \( \text{ReA}_2\text{Mn}_2\text{O}_7 \) (\( \text{Re} = \text{rare-earth species} \) and \( \text{A} = \text{Ca, Sr, Ba, etc.} \)) are believed to offer a number of fascinating electronic and magnetic properties, including the long-time claimed but not yet confirmed ferroelectricity associated with charge-ordering. Experimental observations of the charge-order induced transport and electrically polar behaviors have been insufficient. In this work, we synthesize the \( \text{La(Ca}_{0.8}\text{Sr}_{0.2})_2\text{Mn}_2\text{O}_7 \) (LCSMO) single crystal and investigate its structural, magnetic, and dielectric properties. It is revealed that LCSMO undergoes two consecutive charge-ordering transitions upon decreasing temperature \( T \) before entering an antiferromagnetic state in the low-\( T \) range. The first charge-order transition occurs at temperature \( T_{\text{CO1}} \sim 314 \text{ K} \) from the high-\( T \) paramagnetic state. This charge-order state (CO1 state) is transferred into another charge-order state (CO2 state) by a sequence starting from \( \sim 290 \text{ K} \), and the resultant CO2 state is dynamic and polar-like. The dynamic behaviors of this polar-like CO2 state is confirmed by the remarkable dielectric relaxation associated with this state. The present work provides a connection between the charge-ordering and electrically polar response in LCSMO, while ferroelectricity remains yet to be an issue.

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I. INTRODUCTION

Perovskite-based manganites, in which rich emergent phenomena associated with the charge, spin, orbital, and lattice degrees of freedom are available, have been attracting much attention because of their significance in fundamental physics and promising applications.1-3 For example, the coexistence and coupling between ferroelectricity and magnetism, i.e., multiferroicity, were demonstrated in various manganites (e.g., \( \text{TbMnO}_3 \) and \( \text{ThMn}_2\text{O}_3 \)) and have become the research forefront of condensed matter physics.4-6 So far, those promising multiferroic materials can be roughly categorized into two types. Type-I multiferroics include materials in which ferroelectricity and magnetism are only weakly coupled. Type-II multiferroics, typically manganites, have ferroelectricity to be generated from a specific spin order and thus strong magnetoelectric coupling. Consequently, perovskite-based manganites become highly attractive for designing and discovering multiferroics.

Along this line, in one aspect, promising mechanisms such as hybrid improper multiferroicity were proposed, raising interest in those well-known 327 manganites and titanates (\( \text{Ca}_3\text{Ti}_2\text{O}_7 \))7,8 \( \text{Ca}_3\text{Mn}_2\text{O}_7 \),9-11 etc.). In these materials, a combination of two non-polar lattice modes, e.g., the rotation mode \( X_2 \) and tilt mode \( X_3 \) of the oxygen octahedra, is necessary for generating weak ferromagnetism and ferroelectricity simultaneously. In the other aspect, attention has also been paid to possible ferroelectricity caused by different charge-order (CO) forms.12 These proposed CO states are associated with half-doped perovskite manganites and ferrites, while evidence with the electrically polar-like behaviors has not yet been sufficient although second harmonic generation (SHG) signals in \( \text{Pr(Ca, Sr)}_2\text{Mn}_2\text{O}_7 \), one of the 327 manganites, were detected.
The CO state is rather ubiquitous in mixed-valent transition metal oxides, and the mechanism for local electric dipole generation is schematically drawn in Fig. 1 while a detailed description was given in the literature. Here, one considers the one-dimensional chain where equal charge (zero) and equivalent bonds are situated on each site. If charge-ordering and dimerization occur simultaneously, the initial homogeneous ion chain will evolve into two sets: one set of ions has a larger charge and the other set has a smaller charge. The two sets of ions alternate along the chain direction, generating a site-centered CO state, as shown in Fig. 1(b). On the other hand, a dimerization of the two sets of ions can make the strong bonds and weak bonds to align alternatively, constituting the bond-centered CO state. Certainly, the coexisting site-centered and bond-centered charge states, if properly aligned, will lead to the spatial inversion symmetry breaking and thus to the generation of ferroelectric polarization.

In spite of this theoretical prediction, experimental realization of such CO-induced ferroelectricity has not yet been evidenced. In some cases, whether the consequent lattice structure is polar or not remains yet unclear, not to mention the ferroelectricity. The first observation was made on LuFe2O4 rather than manganites, while subsequent verifications gave somewhat negative results. In spite of these problems, the CO physics of ferroelectricity in manganites remains attractive enough simply because the charge-ordering occurs at high temperature, and the CO state can also be easily destroyed by external stimuli, two advantages absent but crucial for most of the type-II multiferroics. Therefore, substantial effort is being made.

In fact, layered manganites are under continuous focus far beyond ferroelectricity alone, since the work of Tokunaga et al. on Pr(Ca0.9Sr0.1)2Mn2O7 (PCSMO). The resistivity, magnetization, optical SHG, and synchrotron x-ray oscillation measurements confirmed two distinct CO states (CO1 and CO2 states) appearing at temperature and thus to the generation of ferroelectric polarization. In proceeding, one considers the A-site size of these 327 manganites. On one hand, it is found that the MnO6 octahedra network would be less distorted when the A-site size is larger. A large A-site may drive the shifting of the oxygen O1 ion connecting the neighboring two oxygen octahedra. While no clear correlation between the polar distortion and octahedra tilting has been claimed, the O1 ion shifting would be benefitting to the polar distortion. On the other hand, it is still a question whether a 327 manganite with large A-site size promotes the CO stability or not. Along this line, we consider another 327 manganite La(Ca0.8Sr0.2)2Mn2O7 (LCSMO). It has a larger A-site size than Pr-based 327 manganites. An investigation of the charge-ordering, magnetism, and dielectric responses of this 327 manganite would be appreciated to check the polar-like state if any, which is a topic of this work. We report the synthesis of LCSMO single crystals and investigations of the structure, transport, magnetic, and dielectric properties. Indeed, LCSMO does undergo two consequent CO events, respectively, with decreasing T. More importantly, dielectric relaxation features associated with the polar-like behavior in the CO2 state is identified, suggesting that this CO2 state is dynamic without a clear indication of the long-range ferroelectric order.

II. EXPERIMENTAL DETAILS

Species La3+ has its ionic radius of 136 pm, larger than 129 pm, the ionic radius of Pr3+. The average A-site size for LCSMO is ~136 pm and that for Pr(Ca0.8Sr0.2)2Mn2O7 (PCSMO) is ~133 pm, given that the (Ca0.8Sr0.2)2+ average ionic size is 136 pm. Therefore, LCSMO would exhibit less octahedra tilting than PCSMO. Following earlier reports on the synthesis of LaCa2Mn2O7, LCSMO polycrystalline powder was prepared by the solid-state reaction method. High-purity powder of La2O3 (99.95%), SrCO3 (99.99%), CaCO3 (99.9%), and Mn2O3 (99.9%)
were mixed, ground, pelletized, and sintered at 1350 °C for totally 90 h with several intermediate grindings to ensure a complete reaction. The as-prepared powder was submitted to the standard processing of polycrystalline bars for subsequent single crystal growth using the floating-zone method based on a light furnace equipped with double-elliptical mirrors (Cyberstar, MF-2400, France). The growth was run in the atmosphere of 8.0 atm O2 ambient with the seeding and feeding speed of 4 mm/h and 4.5 mm/h, respectively.

It should be mentioned that some of the as-prepared single crystals contain local twin-like regions. In order to exclude the possible influence from these twin-like structures, the samples for the subsequent measurements were carefully chosen and only those crystals without twin-like contrast in the optical microscopy were took for measurement. The crystallinity of the as-grown crystals was characterized by x-ray diffraction (XRD) in two different ways: single crystal and polycrystalline powder crushed from the single crystals, using the Bruker D8 Advance x-ray diffractometer with Cu Kα radiation (wavelength \( \lambda = 0.15406 \) nm). For the single crystal, the bar was cut into typical size of 2.5 × 2 × 0.5 mm\(^3\). For the polycrystalline powder, the XRD data were fitted with the Rietveld structural refinement using the GSAS program.\(^{21}\) It was shown that the powder exhibits the single-phase crystallinity, fitting well to the orthorhombic symmetry. The chemical composition distributions of the as-grown single crystals were detected using scanning electron microscopy with the energy dispersive x-ray spectroscopy (EDX) unit.

The electric resistivity along the c-axis (\( \rho_c \)) and along the a/ b-axis (\( \rho_a \) and \( \rho_b \)) as functions of temperature \( T \) in the cooling and heating sequences, respectively, were measured using the Quantum Design physical property measurement system (PPMS) under the zero magnetic field condition. The dc magnetic moments along the c-axis and b-axis as functions of \( T \), respectively, were measured using the Quantum Design superconducting quantum interference device magnetometer (SQUID). The resistivity data were obtained using the conventional four-probe method. The heat capacity \( (C_p) \) was measured by PPMS in a standard procedure over the temperature range from 16 K to 200 K. Despite no reliable data were obtained from the second harmonic generation (SHG) experiment, it is still necessary to describe the SHG experimental procedure. It was performed in a home-made measuring system where an amplified mode-locked Ti:Sapphire laser (spectra Physics Hurricane, 1.41 eV) with a pulse width of 100 fs and a repetition rate of 1 kHz was used for excitation. The energy per pulse was 15 \( \mu \)J focused on a spot of 0.5 mm diameter on the selected surface of the single crystals under measurement. The second harmonic signals were detected in the reflection geometry with a ~5° incident angle of the laser beam, while the second harmonic signals at an energy of 2.82 eV was selected by color filters and detected using a photomultiplier.

The dielectric constant along the b- and c-axis as functions of \( T \) and ac signal frequency \( f \) was measured in the in-plane interdigital electrode mode and plane-parallel capacitor mode on a sample of 2.5 × 2.0 × 0.5 mm\(^3\), using the HP4294A impedance analyzer in the frequency range of 1.0 kHz–1 MHz at a measuring voltage \( V_{dc} = 0.1 \) V. This measurement was based on the assumption that electric polarization, if any, would be aligned along the b-axis. Furthermore, due to the large leakage of the samples due to the relatively small bandgap, the measured dielectric signals may contain some contribution from the carrier motion, and thus we also measured the dielectric response along the c-axis for a comparison. The interdigital electrodes were sputtered using the simple evaporation method, and careful calibration was made so that the probed signals are intrinsic.

III. RESULTS AND DISCUSSION

A. Microstructural characterizations

First of all, a schematic of the lattice structure is plotted in Fig. 2(a) only for a guide of eyes. The XRD 0–20 data for single crystal plates are plotted in Fig. 2(b) where the optical image of one plate-like crystal is inserted. The well-defined (00L) reflections from \( L = 4 \) to \( L = 16 \) are detected with the full-width at half-height (FWHH) of ~0.3° for the (0010) peak, evidencing the good quality of the single crystals. Given the relatively remarkable difference between these lattice constants (a, b, c), the absence of any peak splitting in the XRD spectrum seems to be a hint that the out-of-plane (c-axis) twinning structure if any should be little although there likely exists an in-plane twinning structure. Furthermore, we check the composition homogeneity of the as-grown single crystals, and the EDX in-plane images of the spatial distributions of La, Ca, Sr, Mn, and O are presented in Figs. 3(a)–3(c), while the EDX determined atomic ratios are La/(Ca0.8Sr0.2)2.0Mn2.0O6.5 agreeing roughly with the nominal composition.

It is believed that LCSMO belongs to the Ruddlesden–Popper (RP) series, whose crystal structure can be viewed as the alternative...
stacking of double-layered pseudo-cubic (La,Ca,Sr)MnO$_3$ and rock salt sheets like (La,Ca,Sr)O along the c-axis. To the best of our knowledge, no report on the crystal structure of La(Ca$_{1-x}$Sr$_x$)Mn$_2$O$_7$ is available until now, but it is believed that La(Ca$_{1-x}$Sr$_x$)Mn$_2$O$_7$ shares the same lattice symmetry as LaCa$_2$Mn$_2$O$_7$ with the Cmcm space group. For further checking of the crystallinity, the single crystals were ground into powder and the 0–2θ data are plotted in Fig. 2(c) with the structure fitting. In our data fitting, the Amam space group has been used as the initial model for our Rietveld refinement of the room temperature XRD data, according to an earlier literature study.\(^20\) Indeed, the Amam structure can be well fitted with LCSMO. Here, it should be mentioned that both the Cmcm symmetry and Amam one belong to the same group number (No. 63) although they have the different setting coordinates. In the Cmcm setting, as used in the Rietveld refinement of LaCa$_2$Mn$_2$O$_7$ in the literature, the axis with the largest lattice constant is defined as the a-axis with $a > b > c$, where $(a, b, c)$ are the lattice constants. However, as used in the present work and others,\(^17\) for the Amam setting, the axis with the largest lattice constant is the c-axis with $c > b > a$. In order to avoid this inconsistency, in our Rietveld refinement of the XRD data, we performed the coordinate transform from the Cmcm setting to the Amam setting by rotating the lattice by 90° clockwise around the b-axis. Therefore, the results and conclusion are the same.

While the fitting data are highly reliable, evidenced with the squared fit goodness $\chi^2 = 2.529$, agreement factor $R_p = 4.54\%$, and weighted agreement factor $R_{wp} = 6.72\%$, it is confirmed that the lattice structure does belong to the Amam point group. The as-obtained lattice constants and ionic coordinates are listed in Table I. For the site occupation, it is found that the A-sites prefer the highly ordered occupation. In detail, the A-site at coordinates ($-0.75, y, 0.50$) is occupied by the La\(^{3+}\), Ca\(^{2+}\), and Sr\(^{2+}\) ions at a probability of 0.612, 0.264, and 0.124, respectively, suggesting that La\(^{3+}\) ions prefer to take the perovskite layers while most Ca\(^{2+}/\)Sr\(^{2+}\) ions take the rock salt sheets, similar to the cases of Pr(Ca$_{0.8}$Sr$_{0.2}$)Mn$_2$O$_7$\(^19\) and LaCa$_2$Mn$_2$O$_7$.\(^25\) In our samples, the Mn–O bond lengths of the perovskite units are different, and the average in-plane Mn–O bond length is 1.9316 Å while the length along the c-axis is 1.954 Å, suggesting a length ratio of 1.0116. This ratio is larger than 0.996, the value for LaCa$_2$Mn$_2$O$_7$,\(^25\) indicating that the Sr substitution of Ca makes the lattice to expand along the c-axis.

For a better illustration of the lattice distortion, we plot in Fig. 4(a) the a-axis projection of the lattice. The shifting of oxygen ions along the b-axis is clearly illustrated. The two oxygen ions O1 and O2 in identical octahedral shift in the same b-axis direction, while either O1 or O2 in the neighboring octahedra shift along the opposite directions. The shifting of O1 ion along the b-axis in LCSMO is remarkably larger than that in LaCa$_2$Mn$_2$O$_7$, suggesting more serious distortion along the b-axis, noting that this shifting benefits to the polar state formation. The project plot along the c-axis is shown in Fig. 4(b) where the in-plane Mn–O–Mn bond angle is ~176°. All these data suggest that the in-plane lattice distortion is relatively weak while the out-of-plane distortion (c-axis lattice expansion and large shifting of O1 and O2 along the b-axis) becomes strong.

All we have discussed above are the room temperature data. It is known that the high-symmetry Pr(Ca$_{0.8}$Sr$_{0.2}$)Mn$_2$O$_7$ belongs to the Amam space group, and a sequence of two consecutive charge-order transitions lowers the symmetry from the high-T Pmmm group to the low-T Am2m group.\(^17\) It is expected that LCSMO would undergo symmetry transition with decreasing $T$ since similar charge-ordering and orbital-ordering transitions occur here too. The conventional XRD technique is insufficient to detect such transitions while high-resolution diffraction, for example, high revolution synchrotron radiation (SR) x-ray diffraction, may be needed for such a clarification.

**B. Magnetism, specific heat, and transport**

Now, we look at the magnetic and thermodynamic behaviors along the in-plane a- and b-axes (IP) and c-axis (OP), respectively. The dc magnetic susceptibility ($\chi = M/H$) at $H = 1.0$ kOe as a...
function of $T$ in the three major axes are plotted in Figs. 5(a) and 5(b) with the zero-field-cooling (ZFC) and field-cooling (FC) modes respectively. While the three sets of $\chi(T)$ curves are different in quantitative sense, they are qualitatively similar and on the same order of magnitude, suggesting the absence of serious orientation anisotropy of magnetism in terms of the anomalies in the $\chi(T)$ curves. Basically, for LCSMO, similar to other 327 manganites, the magnetic transition sequence upon decreasing $T$ is complicated.

### Table I

<table>
<thead>
<tr>
<th>Space group</th>
<th>Crystal system</th>
<th>Lattice parameters</th>
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<tr>
<td>Amam</td>
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<td>$a = 5.45272$ Å</td>
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<td></td>
<td></td>
<td>$\alpha = 90^\circ$</td>
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<tr>
<td></td>
<td></td>
<td>$b = 5.46058$ Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 19.54296$ Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\gamma = 90^\circ$</td>
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<tr>
<th>Atom</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>Occ</th>
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<td>La1</td>
<td>−0.750 000</td>
<td>0.2448(13)</td>
<td>0.500 000</td>
<td>0.612(3)</td>
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<tr>
<td>La2</td>
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<td>0.2622(10)</td>
<td>0.685 45(9)</td>
<td>0.127(2)</td>
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<tr>
<td>Ca1</td>
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<td>0.500 000</td>
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<td>0.685 45(9)</td>
<td>0.745(2)</td>
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<td>Sr1</td>
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<td>Sr2</td>
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<td>0.685 45(9)</td>
<td>0.128(2)</td>
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<tr>
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<td>0.7536(15)</td>
<td>0.599 53(12)</td>
<td>1.063(3)</td>
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<td>O1</td>
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<td>0.500 000</td>
<td>0.773(15)</td>
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<tr>
<td>O2</td>
<td>−0.750 000</td>
<td>0.7024(29)</td>
<td>0.6949(4)</td>
<td>1.08(20)</td>
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<td>O3</td>
<td>0.000 000</td>
<td>0.000 000</td>
<td>0.4025(8)</td>
<td>0.905(15)</td>
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<tr>
<td>O4</td>
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<td>0.5942(9)</td>
<td>0.825(15)</td>
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### Table II

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<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
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<td>Mn−O1</td>
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<tr>
<td>Mn−O2</td>
<td>1.924(8)</td>
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<td>Mn−O3 × 2</td>
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<td>Mn−O4 × 2</td>
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<tr>
<td>Mn−Ca1</td>
<td>3.3523(13)</td>
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<tr>
<td>Mn−Ca2</td>
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<tr>
<td>Mn−La2</td>
<td>3.242(8)</td>
</tr>
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</table>

**FIG. 4.** The bc-plane and ab-plane projected lattice structure, obtained from the Rietveld refinement. The O1/O2 shifting along the b-axis is clearly illustrated.
Just referring to the data plotted in Fig. 5, one does see this complexity. We take the curves along the c-axis shown in Fig. 5(b) as an example. Upon decreasing T from 400 K down to the lowest T in this experiment, two consecutive peaks and then a broad valley can be identified at temperatures $T_1$ ($T_{CO1}$), $T_2$, and $T_3$ ($T_{AF}$), respectively, where definitions in the parenthesis will be discussed subsequently.

First, we look at the peak at $T_1 \sim 314$ K, which is obviously the character for the first charge-ordering sequence (CO1) and thus we assign $T_1 = T_{CO1}$. Above $T_{CO1}$, the $\chi(T)$ curves in the IP and OP geometries can be well fitted by the Curie–Weiss law $\chi(T) = C/(T + \Theta)$, where the Curie constant $C = N_A \cdot \mu_B^2 / 3k_B$ and $\Theta$ is the Weiss temperature, $N_A$ is the Avogadro constant, $k_B$ is the Boltzmann constant, and $\mu_B$ is the effective magnetic moment. By fitting the data above $T_{CO1}$, the $b$-axis effective moment of 4.18$\mu_B$ and the $c$-axis moment of 4.31$\mu_B$ are obtained. The two evaluated moments both fall in between the calculated moment for Mn$^{4+}$, 4.9$\mu_B$, and the moment for Mn$^{3+}$, 4.0$\mu_B$. The corresponding Weiss temperatures $\theta_a = -123.47$ K and $\theta_c = -113.59$ K. It is thus indicated that the system exhibits strong antiferromagnetic interactions along all major axes.

Second, we discuss the valley at $T_2$ which is $\sim 90$ K for $\chi(T)$ along the $c$-axis and $\sim 30$ K for $\chi(T)$ along the $a$-axis and $b$-axis. To clarify the nature of this valley, we plot the measured specific heat $C_p(T)$ data in Fig. 5(c). Clearly, a relatively big bump peaked at $T_3 \sim 90$ K can be observed, and no more anomalies below this temperature were detected. Certainly, this peak marks another antiferromagnetic re-ordering along the $c$-axis since the peak location is consistent with the valley point of the $\chi(T)$ curve along the $c$-axis ($T_3 = T_{AF}$). The upturn of $\chi(T)$ below $T_{AF}$ may be related to weak spin canting while details of this canting deserve further investigation.

Third, we come back to the event occurring around $T_3$. The peak at $T_3 \sim 200$ K is not easily assigned. In analogy again to the 327 manganites, this peak should be related to the second charge-ordering (CO2) event. For Pr-based 327 manganites, this CO2 event is actually a consequence of a thermally driven 90° rotation of the orbital stripes from the alignment along the $a$-axis (CO1 state) to that along the $b$-axis (CO2 state). Two features for this CO1–CO2 transition are expected. First, this transition is thermally driven and thus a clear thermal hysteresis would be expected. Second, the CO2 state was predicted to be ferroelectric but the CO1 state is not, and thus it will be highly concerned. To check the two features, we present in Fig. 6 the measured magnetization (M) data along the $b$-axis and $c$-axis, each as a function of $T$ in the cooling-heating cycle, where the black arrows indicate the measuring path. At the same time, the measured $dc$ resistivities along the three main axes ($\rho_a$, $\rho_b$, and $\rho_c$) in the same cycle are also plotted. On one hand, clear $M(T)$ hysteresis loops along the $b$-axis and $c$-axis exist in between $T_{CO1}$ and $T_3$, suggesting the CO1–CO2 transition, the first feature mentioned above. However, the $M(T)$ hysteresis along the $b$-axis expands the gap from $T_{CO1}$ to $T_2$, while the hysteresis along the $c$-axis is slightly narrower than that along the $b$-axis. On the other hand, the three $\rho(T)$ loops all start at $T_{CO1}$ from the high-$T$ side. The loop along the $c$-axis ends at $\sim 230$ K from the low-$T$ side, but the loops along the $a$-axis and $b$-axis do not close until $T < T_2$ from the low-$T$ side. These behaviors suggest that the CO1–CO2 transition seems to expand over a broad $T$ range, e.g., from a temperature right below $T_{CO1}$ ($\sim 290$ K) downward some temperature above $T_2$ ($\sim 230$ K). In other words, one may argue that, different from Pr(Ca, Sr)Mn$_2$O$_4$ [17,22] here LSMO does not have a clear CO1–CO2 transition point $T_{CO2}$ and this transition most likely covers a broad $T$ range. It is thus suggested that no long-range CO2 state can be developed in LCSMO, and thus no long-range ferroelectric order can be generated if this CO2 phase is ferroelectric. For convenience, one may assign $T_{CO2}$ as a $T$ range instead of a clear temperature, as marked in Figs. 5 and 6.
This itineration becomes localized with decreasing stripes are developed in the MnO$_2$ plane. Upon further cooling from $T_{CO1}$ through $T_{CO2}$ until $T_{AF}$. This steep variation is the consequence of charge-ordering, accompanied with well-known $\rho(T)$ hysteresis in the cooling-warming cycle. In correspondence, magnetization $M$ decreases with decreasing $T$ from $T_{CO1}$ due to the antiferromagnetic nature of the CO state. The slight upturn of the $M(T)$ curves around $T_{CO2}$ with clear $M(T)$ hysteresis in the cooling-warming cycle indicates the well-believed $90^\circ$ rotation of the orbital stripes from the $a$-axis to the $b$-axis. It was claimed that the two CO states below $T_{CO1}$ and $T_{CO2}$ are both the electronic polar states. Third, the antiferromagnetic order is sufficiently established below $T_{AF}$ after the two charge-ordering transitions at $T_{CO1}$ and $T_{CO2}$, evidenced by the further steep increasing of $\rho(T)$ and decreasing of $M(T)$ with decreasing $T$.

These magnetotransport behaviors are qualitatively similar to those observed for Pr(Ca, Sr)$_2$Mn$_2$O$_7$ and other 327 manganites, suggesting the similar lattice and magnetic structures of the present LCSMO. With this similarity, one has reason to look into the electrically polar properties. In fact, the existence of $\rho(T)$ and $M(T)$ hysteresis loops between $T_{CO1}$ and $T_{AF}$ reflects the dynamic character of the CO phases, an advantage for checking the dielectric behaviors associated with polar state of LCSMO if any.

C. Dielectric response

As mentioned, the predicted electric polarization, if any, should be aligned along the $b$-axis. Referring to the resistivity data shown in Fig. 6, one sees that the samples are highly conductive at $T > 360$ K and the measured high frequency dielectric constant becomes negative $T > 400$ K due to the high conductivity. Therefore, we only discuss the dielectric data below 360 K, as shown in Figs. 7(a) and 7(b) where dielectric constants $\varepsilon_a(T)$ and $\varepsilon_b(T)$ over the frequency range from 1.0 kHz to 1.0 MHz are plotted. It is seen that in the $b$-axis all the $\varepsilon_b(T)$ curves show a broad peak around $T_{CO1}$, and this peak does not shift much with varying frequency although the peak height does fall down gradually with increasing frequency. On the contrary, in the non-polar $c$-axis, these peaks shift with varying frequency, especially in high frequency range. Therefore, we can conclude that the broad peaks in $\varepsilon_b(T)$ curves should be a consequence of the polar charge-ordered state developed below $T_{CO2}$ along the $b$-axis and the frequency-dependent broad peaks in $\varepsilon_c(T)$ curves is a consequence of thermally trapped charges.

It was claimed that spontaneous polarization in Pr(Ca, Sr)$_2$Mn$_2$O$_7$, as probed by SHG, emerges at $T_{CO2}$ instead of $T_{CO1}$. The polar state actually emerges at $T_{CO2}$ below which the local polarization is generated. Upon the transition at $T_{CO2}$ corresponding to the $90^\circ$ rotation of the orbital stripes, the local polarizations may be well ordered, and then a net polarization may emerge at $T_{CO2}$. This scenario would be expected to apply to the LCSMO crystals here, and the appearance of a dielectric peak at $T_{CO2}$ is understandable. Nevertheless, we cannot observe any reliable SHG signals over the whole $T$ range. In the low-frequency range (1.0 kHz–30 kHz), we observe a weak kink of $\varepsilon_a(T)$ around $T_{CO2}$, as indication of the dominant three-dimensional character over the two-dimensional one associated with the layered structure. Second, the gradual increasing $\rho$ with decreasing $T$ in the paramagnetic state at $T > T_{CO1}$ is observed and followed by a further and steep enhancement with further decreasing $T$ from $T_{CO1}$ through $T_{CO2}$ until $T_{AF}$.

Based on the assignment of the CO1 state, CO2 state, and low-$T$ AFM transition at $T_{AF}$, we can now discuss the possible physics related to the magnetism and transport. It is understood that for $T > T_{CO1}$, Mn$^{3+}$ and Mn$^{4+}$ ions are randomly distributed in the $ab$-plane, allowing the itineration of $\varepsilon_q$ electrons in the lattice. This itineration becomes localized with decreasing $T$ down to $T_{CO1}$ ~ 314 K, where Mn$^{3+}$ and Mn$^{4+}$ ions are ordered and form the checkerboard-type CO state. At the same time, ordered orbital stripes are developed in the MnO$_2$ plane. Upon further cooling from $T_{CO1}$, similar to Pr(Ca$_{0.85}$Sr$_{0.15}$)$_2$Mn$_2$O$_7$, another charge-ordering occurs inside the $T_{CO2}$ range, accompanied with the $90^\circ$ rotation of ordered orbital stripes. This CO2 state may not be homogeneous but droplet-like, embedded in the matrix of the CO1 phase. Therefore, the CO2 phase is most likely dynamic in nature without the long-range order and accommodates both the site-central and bond-central configurations. One says it is polar-like. Here, it should be mentioned that no identifiable difference in the $\gamma(T)$ curve between the ZFC and FC modes is observed, suggesting the absence of glassy-like feature often observed in perovskite manganites.

With the above knowledge, one comes to look at the magnetic and transport behaviors plotted in Fig. 6. Several major features deserve highlighting regarding the $\rho(T)$ and $M(T)$ dependences. First, the resistivity along the $b$-axis is smaller than the out-of-plane resistivity over the whole $T$ range. This is understandable for such 327 manganites due to the layered lattice structure. In correspondence, the in-plane magnetic moment ($b$-axis moment) is slightly smaller than the out-of-plane moment due to the strong in-plane antiferromagnetic interaction and alignment. In spite of these delicate differences, one sees that the in-plane and out-of-plane resistivities and moments show quite similar $T$-dependences, a clear indication of the dominant three-dimensional character over the two-dimensional one associated with the layered structure. Second, the gradual increasing $\rho$ with decreasing $T$ in the paramagnetic state at $T > T_{CO1}$ is observed and followed by a further and steep enhancement with further decreasing $T$ from $T_{CO1}$ through $T_{CO2}$ until $T_{AF}$. This steep variation is the consequence of charge-ordering, accompanied with well-known $\rho(T)$ hysteresis in the cooling-warming cycle. In correspondence, magnetization $M$ decreases with decreasing $T$ from $T_{CO1}$ due to the antiferromagnetic nature of the CO state. The slight upturn of the $M(T)$ curves around $T_{CO2}$ with clear $M(T)$ hysteresis in the cooling-warming cycle indicates the well-believed $90^\circ$ rotation of the orbital stripes from the $a$-axis to the $b$-axis. It was claimed that the two CO states below $T_{CO1}$ and $T_{CO2}$ are both the electronic polar states. Third, the antiferromagnetic order is sufficiently established below $T_{AF}$ after the two charge-ordering transitions at $T_{CO1}$ and $T_{CO2}$, evidenced by the further steep increasing of $\rho(T)$ and decreasing of $M(T)$ with decreasing $T$.
indicated by the coarse arrow in Fig. 7(a). This kink shifts slightly toward the high-\(T\) side with increasing frequency. A plot of the kink coordinates (\(T, f\)) in Fig. 7(c) suggests that the dynamic response can be well described by the Arrhenius equation \(f = f_0 \cdot \exp(-E_a / k_B T)\), where \(f_0\) is the characteristic frequency prefactor, \(E_a\) is the activation energy, and \(k_B\) is the Boltzmann constant. A fitting produces \(E_a = 0.9487\ \text{eV}\). This value fits typically the oxygen vacancy migration mechanism, suggesting that this kink is more or less related to the defect migrations associated with polar dynamics.

D. Absence of ferroelectricity and discussion

In fact, so far, our measurements on ferroelectricity of our crystals using the \(P-E\) loop probes in the positive-up-negative-down (PUND) mode, the pyroelectric current method, and the SHG technique all suggest the absence of spontaneous electric polarization. This absence is an indication of ferroelectric ordering, which is of long-range, but it may not exclude the possible existence of a local polar state due to the charge-ordering. The absence of ferroelectricity would have several possible sources. First, no intrinsic ferroelectricity exists, or the ferroelectric order cannot be established via the proposed mechanism of charge-ordering. This is most unlikely because so far there have been quite a few reports supporting the existence of a polar state or ferroelectricity in similar 327 manganites. Second, the ferroelectric state cannot be maintained due to the seriously large leakage. This is however most likely the reason why one cannot obtain high-quality \(P-E\) hysteresis and the conventional technique does not work for such leaky samples. Third, no long-range charge-ordering is established due to the high degree of disorder in the samples even if they are single crystals. In this case, the intrinsic inhomogeneity for manganites makes the charge-order state between \(T_{CO1}\) and \(T_{AF}\) likely dynamic, as confirmed by the remarkable hysteresis in \(ρ(T)\) and \(M(T)\). Fourth, as mentioned above, in the present system, the electronic polar state can be established by the superposition of bond alternation inherent to the underlying chemical lattice (e.g., the alternate tilting of MnO\(_6\) octahedra along the \(b\)-axis) and the site alternation (commensurate charge-order) in the \(ab\)-plane. If the charge sector in the \(ab\)-plane deviates from the commensurate order, the phase mismatch between bond and site alternations can be introduced and the electric polar state will be suppressed. Therefore, a checking of the commensurate charge-order by means of, for example, TEM is highly needed for this possibility.

Further evidence can be seen regarding the dielectric response. The dielectric peak at \(\sim T_{CO1}\) is very broad, distinctly different from the sharp peak for normal ferroelectric or antiferroelectric transition. This broad peak should be associated with the inhomogeneous charge-order regions between \(T_{CO1}\) and \(T_{AF}\). These regions are not strongly correlated but each such region is polar-like, contributing to the as-measured dielectric responses shown in Fig. 7.

IV. CONCLUSION

In summary, we have successfully grown high-quality La(Ca\(_{0.8}\)Sr\(_{0.2}\))\(_3\)Mn\(_2\)O\(_7\) single crystals using the optical float zone method and performed a series of structural, magnetic, transport, and dielectric properties along the in-plane \(b\)-axis and out-of-plane \(c\)-axis directions. It is revealed that La(Ca\(_{0.8}\)Sr\(_{0.2}\))\(_3\)Mn\(_2\)O\(_7\) exhibits the highly ordered \(A\)-site occupation and \(Aam\) lattice symmetry. The O1 ion shifting along the \(b\)-axis is found to be larger in La(Ca\(_{0.8}\)Sr\(_{0.2}\))\(_3\)Mn\(_2\)O\(_7\) than Pr(Ca\(_{0.8}\)Sr\(_{0.2}\))\(_3\)Mn\(_2\)O\(_7\), suggesting the higher stability of the polar-like state in La(Ca\(_{0.8}\)Sr\(_{0.2}\))\(_3\)Mn\(_2\)O\(_7\). The magnetic and electrical measurements indicate the consecutive charge-ordering sequence at \(T_{CO1} \sim 314\) K and then the CO1 to CO2 transition. This late transition may cover a \(T\) range starting from a temperature below \(T_{CO1}\) and terminating at \(T \sim 230\) K, evidenced with the magnetization and electric resistivity hysteresis loops. A broad dielectric peak at the charging ordering point \(T_{CO1}\).
event, which is frequency-independent, is observed, indicating the emergence of a polar-like state associated with the charge-ordering. Our measurements do not show any evidence with the long-range ferroelectricity. The ferroelectricity associated with the charge-ordered systems remains to be an issue for future investigation.

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