Abstract

In hybrid improper ferroelectric systems, polarization arises from the onset of successive nonpolar lattice modes. In this work, measurements and modeling were performed to determine the spatial symmetries of the phases involved in the transitions to these modes. Structural and optical measurements reveal that the tilt and rotation distortions of the MnO$_6$ or TiO$_6$ polyhedra relative to the high symmetry phases driving ferroelectricity in the hybrid improper Ca$_3$X$_2$O$_7$ system (X=Mn and Ti) condense at different temperatures. The tilt angle vanishes abruptly at $T_T \sim 400$ K for Ca$_3$Mn$_2$O$_7$ (and continuously for X=Ti) and the rotation mode amplitude is suppressed at much higher temperatures $T_R \sim 1060$ K. Moreover, Raman measurements in Ca$_3$Mn$_2$O$_7$ under isotropic pressure reveal that the polyhedral tilts can be suppressed by very low pressures (between 1.4 and 2.3 GPa) indicating their softness. These results indicate that the Ca$_3$Mn$_2$O$_7$ system provides a new platform for strain engineering of ferroelectric properties in film based systems with substrate induced strain.
I. Introduction

A broad range of mechanisms are known to produce ferroelectricity in solid materials including intrinsically atomic effects such as the lone pairs (e.g. 6s² in BiFeO₃ [1]) or ion size mismatch leading to off-center lattice distortions in the classical BaTiO₃ system [2]. From a microscopic perspective, these materials fall into two main classes having net electric polarization due to atomic displacement, such as the ABO₃ system, where an off-center B atom displacement is proposed. Alternatively, order-disorder transitions have also been proposed in these systems. In general, the microscopic mechanisms driving ferroelectric behavior are thought to cause a gamma point instability in the ordering of a polar mode of the parent structure. There is a direct connection between the polarization amplitude and the structural polar mode.

Distinct from these mechanisms above are a class of improper ferroelectrics in which the 
polarization is a secondary order parameter. Recently, the layered perovskites (n=2 Ruddelsen-Popper structure with double stacked MnO₆ polyhedra, A₃B₂O₇) was predicted to support ferroelectric induced by the introduction of a rotation pattern due to two independent nonpolar rotations of the BO₆ polyhedra [3] relative to the high symmetry I4/mmm (#139) phase at high temperature. The structure is characterized by an \(X_2^+\) rotation of the MnO₆ polyhedra in the high symmetry plane and a \(X_3^-\) tilt relative to the high symmetry (long) axis. The polarized state of this system is determined by the combined rotation and tilt structural modes. In these hybrid improper ferroelectrics, DFT calculations reveal that the symmetry of the phase exhibiting ferroelectricity has space group A₂ıam (#36, Cmc2₁ in standard setting). The rotations couple directly with the magnetic order of the Mn sites (having G type antiferromagnetic order) at low temperature [4].

The nature of the transition from the high-temperature I4/mmm phase to the low-temperature A₂ıam phase is not well understood. Determination of whether the rotation and tilt structural changes onset collectively or separately, the nature of the transitions (first or second order), and the appropriate long range and local symmetries present is essential to the development of accurate theoretical models.
Limited structural powder diffraction work suggests that the Ca$_3$Mn$_2$O$_7$ system undergoes a transition into an intermediate Acaa phase (#68, Ccca standard setting) [5]. In polycrystalline samples, the proximity of the Acaa and A$_2$am phase in energy was found to produce a broad mixed phase region. Additional symmetry possibilities of the intermediate state include the Acam, Amam and F2mm space groups. While clear switchable ferroelectric polarization has been observed in Ti and Sn-based systems (B site), the manganese perovskite system has not been seen to exhibit this critical behavior needed for device applications. A complex domain structure with the stacking of a and b domains along the c axis (long axis) has been found to suppress polarization in Ca$_3$Mn$_2$O$_7$ [6]. The primary difference between Ca$_3$Mn$_2$O$_7$ (with the coupling of magnetic order and structure but no finite electric polarization) and the Ca$_3$Ti$_2$O$_7$ (with large electric polarization, 8 $\mu$C/cm$^2$) [7] is the stability of A$_2$am low-temperature phase in the Ti-based system over a broad range of temperatures and its switchable room temperature electric polarization.

Systematic studies of the Ca$_3$Mn$_{2-x}$Ti$_x$O$_7$ mixed system have been initiated to understand the electric polarization domain structure and magnetic order in this system [5]. Recent Raman measurements up to 350 K on single crystals of Ca$_3$Mn$_2$O$_7$ indicate a significant softening of a mode near 107 cm$^{-1}$ which was assigned to be an antiphase tiling mode bases on phonon calculations utilizing classical interaction potentials [8]. Shifts in the modes corresponding to tilting and rotation were examined, and it is argued that reduction of the frequency of the tilting mode with temperature indicates that this is a transition from Cmc$2_1$ (A$_2$am) to an assumed Ccca (Acaa) intermediate phase is driven by a tilt rotation. An intermediate phase region with the coexistence of competing soft modes with distinct phases was found to be consistent with these measurements. However, no direct structural information was presented.

Neutron diffraction and laboratory based x-ray diffraction structural measurements on the B site (Ti or Mn) doped system Ca$_3$Mn$_{0.9}$Ti$_{0.1}$O$_7$ found antiphase tilting of the MnO$_6$ polyhedra decreases in amplitude while the rotation remains unchanged with increasing temperature and pressure [9]. The tilting was found to decrease smoothly (from ~8° to ~6.5°), going from ~10 K to ~375 K, with a kink near the
magnetic ordering temperature \( T_N \). In the analysis in that work, the single-crystal neutron scattering measurements reveal a polar Aba2 space group at 450 K. It was indicated that \( \text{Ca}_3\text{Ti}_2\text{O}_7 \), by contrast, would have enhancement of both antiphase tilt and in-plane distortion with increasing temperature.

To fully understand the nature of the transitions in this material, structural measurements on the endmember \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) and \( \text{Ca}_{2.4}\text{Sr}_{0.6}\text{Ti}_2\text{O}_7 \) (representing \( \text{CaTiO}_3 \)) were conducted over a broad temperature range. Samples derived from single crystals were used in all measurements. Heat capacity (2 K to 380 K) and differential scanning calorimetry (DSC, 300 K to 500 K) measurements were conducted. Local structural pair distribution function (PDF) measurements were conducted between 100, and 1100 K at the NSLS II XPD (28ID-2) Beamline and APS beamline 6-ID-D. X-ray absorption (XAFS and XANES) measurements were conducted with respect to the Mn site for the temperature range 300 K and 1100 K (at beamline 8-ID at NSLS II), and with respect the Ca site (at APS beamline 20 BM- for temperatures near the ~400 K transition). High-resolution synchrotron single crystal diffraction measurements were conducted between 100 K and 480 K (at APS beamline 15-ID-D). High-pressure Raman measurements were conducted at NSLS2 beamline 22-IR-1 to follow the changes in symmetry with pressure and determine the pressure ranges for the phase changes. Experimental and computation details are provided in the Supplementary Document.

Calorimetry measurements (differential scanning calorimetry (DSC) and heat capacity) reveal a second order transition near 110 K corresponding to the antiferromagnetic ordering temperature and a first-order transition near 367 K on cooling and near 405 K on warming in \( \text{Ca}_3\text{Mn}_2\text{O}_7 \). This first order transition is found in structural measurements corresponding to a loss of tilt angle (vanishing of \( X_3^- \) tilt amplitude) above this transition on warming and yields an nonpolar space group (I4/mmm or C2/m with split in-plane oxygen sites). The transition temperature is termed \( T_T \). Distinct domains with the same space group are found. These measurements are supported by Raman observations. Local structural measurements reveal enhanced Ca-Mn bond order on warming above \( T_T \) consistent with loss of electric polarization. No evidence of phase coexistence is found near \( T_T \). In this temperature region, thermal
measurements reveal no clear phase transitions in polycrystalline samples. PDF and XAFS measurements reveal a transition near 1060 K consistent with the loss of the $X_2^+$ rotation amplitude (termed $T_R$).

In this work, parallel structural and spectroscopic measurements, conducted on the corresponding Ti-based system $\text{Ca}_3\text{Sr}_x\text{Ti}_2\text{O}_7$ ($\text{Ca}_{2.4}\text{Sr}_{0.6}\text{Ti}_2\text{O}_7$), reveal the same trend. However the loss of the $X_3^-$ tilt amplitude is found to be a continuous transition. DFT calculations on both $\text{Ca}_3\text{Mn}_2\text{O}_7$ and $\text{Ca}_3\text{Ti}_2\text{O}_7$ indicate that the relevant self force constant for the O sites are significantly softer for a local tilt distortion compared to local twist or rotational local distortion, consistent with the measurements. The phonon density of states of both systems are qualitatively similar. The essential overview of the general $\text{Ca}_3\text{X}_2\text{O}_7$ system is that near $T_T$ ($\sim 400$ K) the tilt mode vanishes, while the rotational mode amplitude decrease continuously with increase temperature. High-pressure ramans measurements indicate loss of tilt angle for very low pressures (between 1.4 and 2.3 GPa) revealing the softness of the tilt mode. Preparing thin film samples with substrate strain values near this critical cross-over value in strain (near ferro/paraelectric transition will enable switching of polarization (on/off) using a piezoelectric substrate. The results also suggest that enhancement of the A-O bond strength will lift the temperate $T_T$ at which the polarization vanishes. Work on the X=Mn system is presented in the main text and the X=Ti system results are included in the supplementary document.

II. Qualitative Structure, Predicted Phonon Spectra and Raman Measurements

Figure 1(a) shows the crystal structure of $\text{Ca}_3\text{Mn}_2\text{O}_7$ with respect to the Cmc2$_1$ space group (#36, standard setting) with the long-axis along a. Note that there are three distinct types of O sites in this n=2 Ruddlesden-Popper perovskite system. There are apical O sites bonded only to one Mn site and weakly bonded to the Ca sites, apical interior sites shared by two Mn sites along the a-axis (a-axis, long axis for this space group setting) and planar O sites shared between two Mn site in the b-c plane. Fig. 1(b) shows
the MnO$_6$ polyhedral rotation about the long axis ($X_2^+$, black curved arrow) and the tilts ($X_3^-$, blue arrows) of the polyhedra normal to the long axis.

Calculation of the force constants by DFT methods enables computation of the phonon density of states. Fig. 1(c) shows the phonon density of states (DOS) projected onto the Mn, Ca and O sites exclusively. What can be seen is that although the Ca atoms are lower in mass than the Mn atoms, the main peak in the phonon DOS at low energy is primarily from the Ca site. The Mn contributions are broad and extend up to ~500 cm$^{-1}$ while the O DOS covers the full energy range. Hence Ca atom motions dominate the low-frequency phonon modes while oxygen contributes at all frequencies. The similarity of the force constants indicates similar phonon DOS for Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$. Indeed theoretical work on Ca$_3$Ti$_2$O$_7$ yield qualitatively similar phonon DOS [10] to that presented in Fig. 1(c).

Raman measurements were conducted on single crystal, and polycrystalline samples for temperatures between 100 and 500 K, covering the high end of any possible low-temperature transitions. In Fig. 2(a) we show spectra for the incident laser beam normal to the long axis (x-axis). Note the abrupt change in frequency in the peak near 615 cm$^{-1}$ on cooling below ~370 K (breathing mode of MnO$_6$ polyhedra, see below). Near the same temperature, the peak near 460 cm$^{-1}$ also vanishes. We note that a weak low-frequency peak near 146 cm$^{-1}$ in the spectrum is found to vanish with increasing temperature (see arrow in Fig. 2(a)). The area of this peak vs. temperature is given in Fig. 2(b) indicates the abrupt drop-off with temperature. For the same measurement geometry, the peak position of the main peak near 615 cm$^{-1}$ is shown on warming and cooling in Fig 2(c) and in Fig. S4(b). The abrupt transition is characteristic of first-order behavior. Measurement of a polycrystalline sample over the same temperature range reveals no step change, consistent with earlier measurements [4] on the same type of material suggesting mixed phase behavior. Fig. S1 (supplementary document) shows the calculated displacement modes from DFT for phonons near 129 cm$^{-1}$ and 142 cm$^{-1}$ (Fig. S1(a), Fig. S1(b) and Table S1.). The lowest energy mode (129 cm$^{-1}$) corresponds to the shear motion of the Ca ion near the apical O atoms. While the calculated mode at 142 cm$^{-1}$ corresponds to the combined planar motion of the Ca sites and tilt rotations of the MnO$_6$ polyhedra. For both modes, all Ca atomic motions are in the yz plane containing
the electric polarization vector. The main peak at 612 cm\(^{-1}\) (Fig. S1(c)) is characterized by a breathing mode of the MnO\(_6\) polyhedra. The full set of calculated phonon-frequencies at the gamma point are given in Table S1. The corresponding Raman spectra in a offset configuration for the laser beam normal to and along the long axis are given in Fig. S2. The measurements for the beam along the symmetry axis show suppression of the peak near 120 cm\(^{-1}\) with increasing temperature (Fig S3, and additional surface plots in Fig S4).

III. Calorimetric Measurements

Heat capacity and DSC measurements on crystals of Ca\(_3\)Mn\(_2\)O\(_7\) were used to identify the nature of the observed transitions. Low-temperature heat capacity measurements (Fig. S5) on both warming and cooling reveal a smooth transition near 110 K corresponding to the magnetic ordering temperature (T\(_N\)). The absence of hysteresis and the step-like shape indicates that the transition is second order. DSC measurements on crystals of at higher temperature (Fig. 3) reveal an abrupt structural transition at 405 K on warming and at 367 K on cooling the sample, indicating that the transition is first order in nature. No transition features are seen in the corresponding polycrystalline sample measurements (derived from solid state reaction, Fig.S6(a)).

DSC measurements for Ca\(_{2.4}\)Sr\(_{0.6}\)Ti\(_2\)O\(_7\) indicate a very weak feature with the characteristic step change observed for continuous or glass-like transitions (Fig. S6(b)). Raman measurements on single crystal Ca\(_{2.4}\)Sr\(_{0.6}\)Ti\(_2\)O\(_7\) (stabilized by Sr doping) between 100 and 500 K (Figs. S7 and S8) indicate low-frequency phonons near 93 and 112 cm\(^{-1}\) soften smoothly with temperature indicating a continuous transition. Similar behavior is seen in polycrystalline samples of Ca\(_3\)Ti\(_2\)O\(_7\) with low-frequency phonons near 121 cm\(^{-1}\) (Figs. S9 and S10). The combined results indicate that the transition at T\(_T\) is first order for the X=Mn system and continuous for the X=Ti system.
IV. Local Structural Measurements (X-Ray Absorption Spectroscopy)

Detailed structural measurements on Ca₃Mn₂O₇ were conducted to determine the changes in local and long-range structure with temperature. XAFS measurements relative to the Mn site were used to determine the changes in local structure between 300 and 1100 K (Fig. 4). Fits were made for Mn-O, Mn-Ca and Mn-Mn bond (covering the range up to ~ 4 Å, Fig S11). At high temperatures (Fig. 5(a) and 5(b)) the Mn-O and Mn-Ca bonds exhibit changes associated with ordering of the structure (near Tₚ). Examination of the structure-function over the full temperature range reveals stiff Mn-O bonds and stiff Mn-Mn correlation with weak changes in the peak amplitudes with temperature (See Fig. S11) as predicted by the DFT simulations (Table I). The largest changes with temperature occur in the Ca-Mn correlation peak between 300 and 600 K. The Mn lattice sites are seen to form a very rigid network with major changes corresponding to the angular motion of rigid MnO₆ polyhedra units and the Ca ions. In the temperature region between 300 and 700 K (Fig. S12), an enhancement of the Mn-O peak width is seen near 400 K on warming.

Examination of the Ca site (Ca-O, Ca-Mn and Ca-Ca bonds up to ~ 4 Å) near the vicinity of the transition at 400 K reveal an enhancement of Ca-Mn correlation (peak width of Ca-Mn distribution) on heating through Tₚ indicating an increase on local symmetry at this transition. This can be seen in Figs. S13 and Table S2, where the Gaussian width of the Ca-Mn are found to become narrow on going above the Tₚ.

To follow the local structure trends in the X=Ti system, Ti K-edge XANES spectra of crystal derived Ca₂.₄Sr₀.₆Ti₂O₇ samples were measured for temperatures between 300 and 540 K (Fig. S14(a)). It was found that the main pre-edge feature (feature B in Fig S14(b)) increases in intensity with increasing temperature. Simulated XANES spectra for perovskite systems (Fig. S14(b)) showed that the reduction of tiling amplitude relative to the long axis (called a-axis here) increases the amplitude of peak B while reduction of twisting about z-axis reduces the peak amplitude (dotted line). Hence the observed continuous increase the B feature amplitude for temperatures from 300 to 540 K is related to a continuous
loss of tilt angle with temperature. Hence, like the Ca$_3$Mn$_2$O$_7$ system, the Ca$_{2.4}$Sr$_{0.6}$Ti$_2$O$_7$ (representing X=Ti) system shows a reduction in tilt angle with increasing temperature.

V. Nanoscale Structural Measurements (X-Ray Pair Distribution Function Analysis)

More detailed structural information on Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$ type systems was obtained on an intermediate length scale by PDF measurements between 100 K and 1100 K (in real space taken over the range 1.3 to 20 Å (Fig. S15), single crystal based materials). To determine the space group in Ca$_3$Mn$_2$O$_7$ on this intermediate structural level on crossing the transition near 400 K (T$_T$), fits to unit cells with possible space groups suggested previously [3] were examined including the groups Cmc$_{21}$ (#36), Amm2 (#38), Amam (#63), Acam (#64), and Acaa (#68). The Rw parameter indicating the fit quality was compared over the temperature range 200 to 450 K for each space group (see Fig. S16(a)).

\[
R_w = \left\{ \frac{\sum_{i=1}^{N} w(r_i) [G_{obs}(r_i) - G_{calc}(r_i)]^2}{\sum_{i=1}^{N} w(r_i) [G_{obs}(r_i)]^2} \right\}
\]

was scaled by the number of independent parameters minus the number of free fitting parameters [11]). Additional, comparisons of the space group Cmc$_{21}$ (#36) with the nonpolar space group I4/mmm (#139) and C2/m (#12, see below), both with cells having ½ the volume of the Cmc$_{21}$ unit cell, were also conducted (Fig. S16(b)). The results indicate that below (T$_T$), Ca$_3$Mn$_2$O$_7$ crystals possess Cmc$_{21}$ space group symmetry on an intermediate structural range. While above it, the space group is closer to the C2/m space group on this intermediate length scale (1.3 to 20 Å used in fits). Examining the a/c ratio (Fig. S17) reveals an abrupt transition near 400 K on warming and near 370 K on cooling consistent with the DSC measurements (Fig. 3). The high temperature PDF measurement over the range 300 to 1100 K (Fig. S18) reveals an abrupt change in R$_w$ near 1060 K and smooth increase in the b/c ratio at this transition but no change along the c axis consistent with rotation of the MnO$_6$ polyhedra (T$_R$).

In Fig. 6, we examine the change in the structure of Ca$_3$Mn$_2$O$_7$ on this length scale in more detail (with respect to the cell Cmc$_{21}$ cell in Fig 1). In Fig. 6(a), the volume on cooling (3 K steps) reveals two
distinct regions of thermal expansion behavior. The volumetric thermal expansion coefficient \( \alpha_V \) takes on the value \( 3.5(1) \times 10^{-5} \text{ K}^{-1} \) above \( \sim 370 \text{ K} \) and the value \( 2.63(4) \times 10^{-5} \text{ K}^{-1} \) below it. Near 110 K evidence is seen for a negative thermal expansion corresponding to the onset of the magnetic ordering and spin lattice coupling. The inset of the figure reveal hysteresis behavior covering the region between \( \sim 350 \) and \( \sim 400 \text{ K} \). (Consistent with earlier published work on polycrystalline samples [4], our PDF data on polycrystalline samples (Fig. S19, inset) reveals hysteresis behavior covering a much broader region of temperature (\( \sim 250 \) to \( \sim 400 \text{ K} \)).) As indicated in Fig. 6(b), examination of the PDF refinement xyz data indicates that the Mn x position (long axis) show abrupt change both at \( T_N \) and at \( T_T \). However, the Ca x atomic position show changes only at \( T_T \). With the enhanced symmetry indicated by the XAFS results on the Ca local structure, this indicates a loss of polarization at \( T_T \). The exact nature of the structural change was qualitatively determined by looking at the atomic displacements of the 400 K PDF structure relative to the structure at 300 K. In Fig 6(c), we see that the major displacements are for axial O atoms leading to reduction of the MnO_6 tilt amplitude \( (X^-_3 \text{ amplitude}) \).

**VI. Single Crystal Diffraction Measurements (Space Group above \( T_T \))**

Accurate structural parameters of \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) were derived from detailed synchrotron single crystal diffraction measurements on \( \sim 20 \) microns crystals between 300 and 480 K on warming. A high count rate Pilatus 1M detector (\( 10^7 \) cps maximum/pixel) was utilized to obtain large signals for structure factors corresponding to scattering from both the light O atoms and heavy atoms (Mn/Ca). (Use of this detector with the high flux at a synchrotron beamline was found to enable the structural solution of atomic positions of B atoms in rare earth systems such as \( \text{HoAl}_3(\text{BO}_3)_4 \) yielding accurate B-O distances (see Ref. [12]).) For each temperature data set, a systematic space group search was conducted [13]. Fits of full diffractions data sets on the Cmc2_1 structure were found to be stable for the temperature range 300 (fit parameter \( R1 = 5.2\% \)) to 380 K (\( R1 = 5.6\% \)). At 400 K the best structural refinements were obtained for the nonpolar spacegroups I4/mmm (\( R1 = 5.6\% \)) and C2/m (\( R1 = 7.1\% \)). Fits to the polar Aba2 space
group at 400 K yielded $R1 = 10\%$ and large residual charge density. Measurements up to 480 K were taken, and the fits to I4/mmm and C2/m space groups yielded $R1= 4.2\%$ and $R1 = 4.8\%$, respectively.

The full structural data from the refinements of $\text{Ca}_3\text{Mn}_2\text{O}_7$ at 480 K are given in Tables S3 and S4 for I4/mmm and Table S5 for the C2/m space group (both with cells $\frac{1}{2}$ the Cmc$_2$1 cell). The room temperature structural data (Cmc$_2$1) are given in Tables S6 and S7. Tables S4 and S7 and Fig. S22 can enable comparison of the bond distribution difference between the 300 K and 480 K structures. The room temperature results reproduce the previously published work [14].

Using either of the high-temperature single crystal structure solutions (I4/mmm or C2/m), it is found that the tilt angle in $\text{Ca}_3\text{Mn}_2\text{O}_7$ vanishes above $T_T$. Quantifying the result of Fig. 4(c), the $X_3^-$ tilt amplitude vanishes and hence, the electric polarization determined by the existence of both $X_3^-$ and $X_2^+$ distortion is predicted to vanish abruptly near 400 K on heating. The single crystal results are consistent with the abrupt in-plane shift at the Ca site seen in the PDF measurement. Fig. 7 shows the 480 K structure (I4/mmm space group) while the corresponding figure for C2/m space group is given in Fig. S20. Note that in both structural solutions the rotation amplitude ($X_2^+$) is nonzero at 480 K. The in-plane O sites have double occupancy indicating the presence of 50/50 domains (by volume) with positive and negative in-plane rotations ($X_2^+$ mode) of the MnO$_6$ polyhedra but of the same magnitude (see structural results in Tables S3 and S5). It should be noted that the abrupt change in structure and loss of tilt seen in the single crystal measurements are consistent with first order behavior seen in the DSC and Raman measurements as well as with the abrupt changes in structure found in the PDF refinements. The electric polarization in $\text{Ca}_3\text{Mn}_2\text{O}_7$ is expected to vanish abruptly near $T_T$ while that in $\text{Ca}_3\text{Ti}_2\text{O}_7$ is expected to vanish continuously after passing through $T_T$.  


VII. High Pressure Raman Measurements

To understand the softness of the tilting configuration in the Ca$_3$Mn$_2$O$_7$ system quantitatively, high-pressure Raman scattering measurements were conducted. In Fig. 8, data are shown for the pressure range 1 to 13.4 GPa for the same crystal orientation as in Fig. 3. The feature near 140 cm$^{-1}$, labeled A (Fig. 8(a)), is seen to vanish between 1.4 and 2.3 GPa. In temperature-dependent ambient pressure Raman measurements (Fig. 2), this feature was associated with the loss of tilt and transition into a nonpolar phase as indicated by the combined structural and optical measurements. We find that at very low pressures, the system goes from the Cmc$_2$1 space group into a nonpolar space group (C2/m). Between 4.7 and 5.8 GPa (inset, Fig. 8(a)) the peak near 380 cm$^{-1}$ splits into two components and an additional feature near 190 cm$^{-1}$ onsets and grows larger as pressure rises (indicating symmetry reduction). Fig. 8(b) and the corresponding inset again shows the disappearance of the same feature between 1.4 and 2.3 GPa (near 460 cm$^{-1}$) which vanishes at $T_T$ in the ambient pressure data (Fig. 3).

VIII. Discussion of Combined Results

Development of an intuitive approach for the origin of the softness of the tilt mode is possible via simulations. The DFT derived self-force constants [15] (on site terms in force constant matrix which indicate the force on the isolated atom with respect unit displacements) are presented in Table I for each unique site the directions are labeled by the unit cell in Fig. 1 (for both Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$). The force constants of the Mn sites are seen to be the same for displacements along a, b, and c axis for the Mn sites. They are also significantly larger than those of any other atomic sites. Combined with typically strong Mn-O bonds, the results predict rigid MnO$_6$ polyhedra. For the apical O sites, the force constants in the yz plane are smaller than those for motion transverse to this plane ($k_x,k_z \approx \frac{1}{3} k_x$ (long axis)). The same holds for the apical interior O atoms. On the other hand, the planar (O3, O4) atoms have ($k_x,k_z \approx 2 k_x$). This predicts that local tilting (Fig. 1(b)) of the MnO$_6$ polyhedra corresponding mainly to y/z displacement of the apical O and displacement of the planar O atoms will be softer than rotation of the
polyhedra about the x-axis (long axis). In the case of the rotation, the planar O atoms have $k_x,k_z \sim 2k_x$ making this type of distortion relatively stiffer. The same trend in self-force constants is seen for the Ca$_3$Ti$_2$O$_7$ system. **Hence it is predicted that local tilting of single MnO$_6$ polyhedron in the lattice, as opposed to coherent long-range tilting of all MnO$_6$ polyhedra simulated in previous work [3], is a lower energy distortion than local rotation in both Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$.** Also, in contrast with the current work, Ref. [9] suggests a difference in behavior between Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$ with enhancement of both antiphase tilt and in-plane rotation occurring with increasing temperature in Ca$_3$Ti$_2$O$_7$, this is not observed in this work.

In addition to the possibility of local tilt or local rotation structural phases being the cause of the observed order of the transitions, we note that the relative stability of the $X_3^-$ and $X_2^+$ distortions is reversed by compressive biaxial strain of ~1.5 % [3] compared to the strain free or tensile strained systems under DFT+U. This strain value is at the level of accuracy for the determination of lattice parameters found in standard DFT simulations. It would be useful to explore more accurate methods than DFT+U to determine the stable structural phases.

**IX. Summary**

We note that the Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$ exhibit a transition near 400 K with verified loss of inversion center in the case of Ca$_3$Mn$_2$O$_7$ (for temperatures below ~400 K). The characteristic feature in these systems is the low energy **local tilting** of the Mn/Ti-O$_6$ polyhedra groups. To sustain the electric polarization at higher temperatures, it is necessary to strengthen the bond on the Ca site (A site) in these systems. We also note that the low isotropic pressure needed to suppress the polarization state (1-2 GPa) will be significantly reduced if uniaxial pressure is applied. This may make it possible to switch the electrical polarization on and off by depositing this material as a thin film on a piezoelectric substrate for films strained just below this critical strain value. The measurements also suggest that simulations beyond standard DFT+U may be needed to determine the ordering of the energetics of the distortions.
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Table I. $\text{Ca}_3\text{Mn}_2\text{O}_7$ and $\text{Ca}_3\text{Ti}_2\text{O}_7$ Self-Force Constants

| Ion Site                  | $k_x$ (long axis) (eV/Å$^2$) | $k_y$ (eV/Å$^2$) | $k_z$ (eV/Å$^2$) |
|---------------------------|-------------------------------|-----------------|-----------------|
| $\text{Ca}_3\text{Mn}_2\text{O}_7$ |                               |                 |                 |
| Mn                        | 26                            | 26              | 26              |
| Ca1                       | 8.6                           | 7.9             | 7.7             |
| Ca2                       | 11                            | 7.5             | 6.8             |
| O1 (apical interior)      | 21                            | 8.8             | 5.7             |
| O2 (apical)               | 17                            | 6.6             | 5.4             |
| O3                        | 7.2                           | 14              | 15              |
| O4                        | 7.6                           | 14              | 14              |
| $\text{Ca}_3\text{Ti}_2\text{O}_7$ |                               |                 |                 |
| Ti                        | 24                            | 19              | 19              |
| Ca1                       | 8.0                           | 6.8             | 6.3             |
| Ca2                       | 11                            | 7.8             | 6.7             |
| O1 (apical interior)      | 21                            | 8.1             | 6.0             |
| O2 (apical)               | 18                            | 6.8             | 5.2             |
| O3                        | 7.6                           | 13              | 15              |
| O4                        | 8.1                           | 13              | 13              |
Figure Captions

Fig. 1. (a) Low-temperature unit cell indicating unique O sites and (b) the MnO₆ polyhedral rotation about the long axis ($X^+_{2}$, black curved arrow) and the tilts ($X^-_{3}$, blue arrows) of the polyhedra normal to the long axis. (c) Partial density of states derived from DFT simulations showing the Mn, Ca and O site projected components. Note that the phonon DOS corresponding to the Ca sites vanishes for energies above ~ 350 cm⁻¹.

Fig. 2. (a) Raman spectra of single crystal for photon beam normal to the long axis for data taken between 100 and 500 K. Note that the weak peak near ~146 cm⁻¹ vanishes as temperature increases (measured on cooling from 500 K). The vertical line indicates the abrupt change in structure near 370 K. (b) The weak peak (arrow in (a) ) area vs. temperature is displayed showing that it disappears above ~370 K. (c) comparison of the peak position vs. temperature for the main Raman peak for powder and single crystal samples. Data are for cooling unless both warming and cooling results are shown.

Fig. 3. DSC curves for Ca₃Mn₂O₇ (cooling rate=20 K/min) from single crystal materials. Multiple scans reveal the high reproducibility of the transitions in both systems. The hysteresis in the complete loops (see offset transitions here at 405 K on warming and 367 K on cooling) reveal that the transition in Ca₃Mn₂O₇ is first order.

Fig. 4. XAFS structure function of Ca₃Mn₂O₇ measured between 320 K and 1100 K (in (a) and (b)) revealing that the Mn-Mn first and second nearest neighbor in plane correlations persist for the full temperature range. In (b) the inset shows that there is an abrupt reduction of the position of the Mn-O peak near 1060 K indicating the transition to the I4/mmm high symmetry structure.

Fig. 5. Local structure results derived from XAFS measurements. In the high-temperature region the (a) Mn-O and (b) Mn-Ca bond lengths reveal abrupt changes near 1060 K.
**Fig. 6.** Intermediate structure results derived from PDF measurements. (a) Temperature-dependent volume (cooling data) with b axis length shown as inset (warming and cooling). Clear transitions are seen near ~350 K on cooling and near ~400 on warming (b-axis). The volume data also reveal a transition near 105 K which is the magnetic ordering temperature (see also heat capacity data in Fig S1). (c) Position of the Ca2 and Mn ions vs. temperature revealing that only the Mn site position changes near 105 K and both Mn and Ca sites change near 370 K (cooling run). Motion of ions going from 300 K to 400 K. The arrows indicate exclusively a tilt rotation about an axis normal to the long axis exclusively.

**Fig. 7.** Crystal structure at 480 K derived from single crystal diffraction data. Note that the tilt angle vanishes. The planar oxygen atoms exist in two positions with 80% probability indicating multiple domain structure but the rotation about the local z-axis is nonzero relative to the cubic structure.

**Fig. 8.** High-pressure Raman measurements for the incident beam normal to (a) and parallel to (b) the long axis. High-pressure Raman data reveal a phase transition between 1.0 and 2.3 GPa indicated by suppression of features A and D in panels (a) and (b). The feature D is expanded in the inset to panel (b). Panel (a) shows a second transition onsetting near 5.8 GPa as feature labeled B also associated with the splitting of a peak near 380 cm\(^{-1}\) indicated as feature C.
Fig. 1. Liu et al.

(a)

(b)

(c)

Single Atom Projected DOS (Thz$^{-1}$)

Energy (cm$^{-1}$)

Mn DOS
Ca DOS
O DOS
Fig. 2  Liu et al.
Fig. 3. Liu et al.
Fig. 4. Liu et al.
Fig 5. Liu et al.
Fig 6. Liu et al.

(a)

(b)

(c)
Fig 7. Liu et al.
Fig. 8. Liu et al.
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Nature of the Structural Symmetries Associated with Hybrid Improper Ferroelectricity in Ca$_3$X$_2$O$_7$

(Supplementary Document)

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Samples of \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) and \( \text{Ca}_{3-x}\text{Sr}_x\text{Ti}_2\text{O}_7 \) were prepared in single crystal form as given in Ref. [1]. For powder sample measurements, the crystal samples were crushed in 500 mesh powders. Polycrystalline samples prepared by solid-state reaction were also examined for comparison, but the primary work is on materials derived from single crystal samples.

Specific heat measurements on single crystals were conducted on cooling from 390 K to 2 K and on warming from 60 K to 390 K using the relaxation method in a Quantum Design PPMS system. Temperature steps of 1 K were utilized, and each temperature point was measured three times, and the average result is reported (Fig. S1). Approximately 10 minutes was required to measure each temperature data point. Hence the system was never in a quenched state. Differential scanning calorimetry measurements were conducted under flowing \( \text{N}_2 \) using a Perkin Elmer DSC 6000. Ambient pressure Raman Spectra were measured with an excitation wavelength of 532 nm in backscattering geometry using a Thermo Scientific DXR Raman Microscope. A 50X objective was used with 10 mW power setting. The sample was found to be stable under this laser power after test were done on a range of laser powers (3 to 10 mW). The original spectra were recovered after warming and cooling cycles. Both the Raman and DSC measurements were conducted at the NJIT York Center.

High-pressure Raman measurements were conducted at National Synchrotron Light Source (NSLS2) beamline 22-IR-1 National. Measurements were conducted in a symmetric diamond cell with (100) oriented diamonds. The culet size was 500 \( \mu \text{m} \) and tungsten gaskets were used. The pressure medium utilized was methanol:ethanol:water in a 14:3:1 ratio by volume. Pressure calibration was conducted using both ruby fluorescence mainline shifts [2] and the changes in the diamond Raman edge (near \( \sim 1300 \text{ cm}^{-1} \)) [3]. Pressure calibration measurements were made before and after each Raman spectrum was collected. In addition, calibration measurements as a function of position at multiple points in the cell at the highest pressure showed variation below 0.1 GPa indicating a high level of hydrostatic behavior of the pressure medium. The custom micro-Raman system at beamline 22-IR-1 consisted of a 532 nm solid-state laser (Spectral-Physics Excelsior, 150 mW), a Princeton Instruments liquid-nitrogen cooled PyloN CCD detector, a PI Acton SpectraPro SP-2556 Imaging Spectrograph and a 50X objective.
Based on the ambient pressure laser power tests, a laser power was used which caused no change in sample spectra during the measurements. The accumulation time was 20 seconds and averaged 20 times. For all Raman measurements no change in the spectra was observed over time at a given pressure.

Diffraction measurements on ~20 μm diameter crystals were conducted at the Advanced Photon Source (Argonne National Laboratory) beamline 15-ID-B with a wavelength of 0.41328 Å. The data were collected with a PILATUS 1M detector (maximum count rate = 10^7 cps/pixel, counter depth =20 bit) between 300 K and 480 K. Refinement of the data was done using the program Olex2 [4] after the reflections were corrected for absorption. Anomalous scattering corrections were induced for all atoms.

To determine force constants and phonon DOS for Ca₃Mn₂O₇, spin density functional calculations in the projector augment wave approach [5] were carried out utilizing the VASP code. Full structural optimization was conducted for both lattice parameters and atomic positions and the LDA+U approximation was implemented to obtain the relaxed structure. The parameters U = 8.0 eV and J = 0.88 eV were used for the Mn on-site coulomb and exchange parameters (as done for YMnO₃ [6]). An energy cutoff of 500 eV was implemented. The ground state structure was optimized so that forces on each atom were below 1 x 10⁻⁵ eV/Å. Force constants were determined using density functional perturbation theory. Cells of dimension 1x1x1 (with 4 Ca₃Mn₂O₇ units) were utilized yielding DOS curves similar to the 1x2x2 cell used in reference [7] for the Ca₃Ti₂O₇ system. The code Phonopy was utilized to determine the phonon density of states and phonon displacement mode from the force constants (see Fig 1, Fig. S1, Table I and Table S1) [8].

Mn and Ti K-edge XAFS spectra were collected at NSLS2 beamline 8-ID (ISS). Reduction of the x-ray absorption fine-structure (XAFS) data was performed using standard procedures [9]. Measurements were done in fluorescence mode with 500 mesh powders held in 1 mm quartz capillaries with 10 mm walls. Data were corrected for self-absorption. In the XAFS refinements, to treat the atomic distribution functions on equal footing, the Mn and Ti K-edge spectra were modeled in R-space by optimizing the integral of the product of the radial distribution functions and theoretical spectra with respect to the measured spectra. To treat the atomic distribution functions on equal footing at all temperatures the
spectra were modeled in R-space by optimizing the integral of the product of the radial distribution functions and theoretical spectra with respect to the measured spectra. Specifically, the experimental spectrum is modeled by,

\[
\chi(k) = \int \chi_{th}(k, r) 4\pi r^2 g(r)dr
\]

where \(\chi_{th}\) is the theoretical spectrum and \(g(r)\) is the real space radial distribution function based on a sum of Gaussian functions (\(\chi(k)\) is measured spectrum) \[10\] at each temperature (as in Ref. \[11\]). For each shell fit, the coordination number (N) was held at the crystallographic value but the position (R) and Gaussian width (\(\sigma\)) was fit to the data. For the Mn K-Edge, the k-range \(2.50 < k < 12.1\ \text{Å}^{-1}\) and the R-range \(0.63 < R < 3.80\ \text{Å}\) were utilized. Coordination numbers for the atomic shells were fixed to the crystallographic values. For the Mn K-Edge \(S_0^2\) (accounting for electron loss to multiple excitation channels) value was fixed at 0.81. The Gaussian widths and positions were fit for each component. Additional Ca K-edge XAFS were collected at APS beamline 20 BM at Argonne National Laboratory. The measurements were done at 300 K, 350 K and 450 K. The k-range \(2.39 < k < 10.4\ \text{Å}^{-1}\) and the R-range \(1.02 < R < 3.40\ \text{Å}\).

The theoretical Ti K-edge x-ray near edge spectra (XANES) presented were computed, as in Ref. \[12\] using the RELXAS programs \[13\]. The potentials were computed for cubic perovskite structures, based on clusters containing the first 118 atoms surrounding the Ti site. A simple cluster based on CaTiO\(_3\) was used to determine the changes in the XANES pre-edge structure on tilting and rotation of the TiO\(_6\) polyhedra.

Pair distribution function experiments for all solid state reaction prepared powder samples were conducted at beamline the XPD (28 ID) beamline at Brookhaven National Laboratory’s National Synchrotron Light Source II using a wavelength \(\lambda = 0.18372\ \text{Å} (67.486\ \text{keV})\). For the samples derived from single crystal Ca\(_3\)Mn\(_2\)O\(_7\), measurements between 90 K to 450 K were conducted at APS beamline 6 ID-D at Argonne National Laboratory (\(\lambda = 0.12368\ \text{Å} (100.25\ \text{keV})\)). A high-temperature measurement set on crystal derived Ca\(_3\)Mn\(_2\)O\(_7\) powder between 300 K and 1100 K was conducted at NSLS2 beamline 28 ID. All measurements utilized Perkin Elmer Area detectors with a sample to detector distance of \(~200\ \text{mm}\). Exact detector to sample distances were derived by fit to Ni powder calibration standards. The
range \( Q_{\text{min}} = 0.23 \ \text{Å}^{-1} \) and \( Q_{\text{max}} = 25.1 \ \text{Å}^{-1} \) was used in data reduction. The methods utilized for analysis of the PDF data are described in detail in Refs. [1,14]. For the fits in R-space covered the range: \( 1.3 < r < 20 \ \text{Å} \). The time interval between temperature points was \( \sim 7 \) minutes. Combined with the small temperature steps, the approach kept the samples from being in quenched states.

**Fig. S1.** Atomic motion for phonon modes from DFT simulations of \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) for energies (a) 129, (b) 142 and (c) 612 cm\(^{-1}\). The black, grey and red symbols correspond to Mn, Ca and O atoms. Note that the low-frequency modes involve motion of the Ca and O ions only. The arrows indicated the atomic displacement directions for one half of the motion cycle (arrows change direction on second half of cycle) with lengths indicating the corresponding amplitudes. The full set of phonon energies are given in Table S1.
Table S1. Computed Phonon Energies for Ca$_3$Mn$_2$O$_7$ (Cmc2$_1$ Space Group)*

| Energy(cm$^{-1}$) | Irreducible Rep. | Energy(cm$^{-1}$) (cont.) | Irreducible Rep. |
|------------------|------------------|---------------------------|------------------|
| 125.7            | A1               | 333.2                     | A2               |
| 128.5            | A1               | 338.5                     | B2               |
| 141.6            | B2               | 344.3                     | B1               |
| 161.0            | A2               | 350.1                     | A1               |
| 161.1            | B2               | 370.2                     | A2               |
| 169.1            | A1               | 372.6                     | A1               |
| 169.5            | B1               | 385.1                     | B2               |
| 173.5            | B2               | 402.6                     | B1               |
| 179.1            | A2               | 414.5                     | A2               |
| 191.5            | B1               | 422.5                     | B2               |
| 193.7            | A2               | 434.7                     | A1               |
| 197.8            | A1               | 436.7                     | B1               |
| 211.6            | B2               | 437.2                     | B2               |
| 224.6            | B1               | 446.1                     | A2               |
| 229.7            | A2               | 451.7                     | B2               |
| 232.8            | B1               | 456.1                     | A1               |
| 236.5            | A1               | 465.8                     | B1               |
| 237.1            | B2               | 485.8                     | A2               |
| 239.0            | A1               | 492.6                     | A1               |
| 241.0            | A2               | 493.2                     | B2               |
| 244.6            | A1               | 540.6                     | A2               |
| 245.7            | B2               | 546.0                     | B1               |
| 254.4            | B1               | 555.0                     | B2               |
| 261.6            | A2               | 576.9                     | A2               |
| 274.9            | B2               | 590.1                     | B1               |
| 275.6            | A1               | 595.2                     | A1               |
| 277.5            | A2               | 604.4                     | B1               |
| 279.8            | A1               | 604.7                     | A2               |
| 290.5            | B1               | 605.4                     | A1               |
| 296.6            | B2               | 611.3                     | B2               |
| 297.1            | B1               | 615.2                     | A1               |
| 312.6            | A1               | 644.9                     | B1               |
| 319.6            | B2               | 683.3                     | B2               |
| 322.5            | A1               | 695.8                     | A2               |
| 324.1            | A1               |                            |                  |

*The table shows that the calculation yielded 18 A1, 17 A2, 16 B1 and 18 B2 Modes.
Fig. S2. Full Raman spectra for Ca₃Mn₂O₇ single crystal for beam normal to (a) and along (b) the long axis (in-plane). The full spectrum is given in (a). Note the reduction in amplitude of the feature near 130 cm⁻¹ indicated by the arrow. Data are from cooling curves.
**Fig. S3.** Expanded low energy region Raman spectra for Ca$_3$Mn$_2$O$_7$ single crystal for beam along the long axis (in-plane). Note the reduction in amplitude of the feature near 120 cm$^{-1}$ indicated by the arrow.
Fig. S4. (a) Surface plot for warming from 200 K to 500 K for incident beam normal to long axis. In (b), a surface plot is given for the intensity of the main peak vs. temperature for warming and cooling. As in Fig. 2, note the abrupt changes in the position of this peak near 370 K during cooling and near 400 K during warming.
Fig. S5. The heat capacity of Ca₃Mn₂O₇ single crystal revealing the magnetic transition near ~108 K (see inset). Note that no additional clear features are seen up to the maximum temperature of 390 K indicating that any transition must be soft and/or continuous.
Fig. S6. (a) DSC curves for Ca$_3$Mn$_2$O$_7$ (cooling rate=20 K/min) from a polycrystalline sample (solid state synthesis) indicating no clear transition. Upper and lower curves have the same meaning as in (a). (b) Cooling curve DSC measurement for Ca$_{2.4}$Sr$_{0.6}$Ti$_2$O$_7$ crystals indicating a very weak feature characteristic with step change characteristic of a continuous or glass-like transition. Note that no background subtraction (of Al container) was done for samples.
Fig. S7. Raman spectra for Ca_{2.4}Sr_{0.6}Ti_2O_7 single crystal (beam direction with respect to crystal not known). The full spectrum is given in (a). Note the reduction in amplitude of the features near 120 cm\(^{-1}\) and 200 cm\(^{-1}\) which are expanded in (b). Both peak are suppressed at \(\sim 420\) K. This behavior is similar to that seen in Ca_3Mn_2O_7. Data are from cooling curves.
Fig. S8. Extracted parameters for 93 and 112 cm\(^{-1}\) peaks for Ca\(_{2.4}\)Sr\(_{0.6}\)Ti\(_2\)O\(_7\) single crystal. Note the decay of the 112 cm\(^{-1}\) peaks amplitude by 300 K in (a), and the softening of the 93 and 112 cm\(^{-1}\) peaks above 400 K. Data are from cooling curves.
Fig. S9. Raman spectra for Ca$_3$Ti$_2$O$_7$ polycrystalline sample. Note the reduction in amplitude of features near 120 cm$^{-1}$ and 200 cm$^{-1}$ have the same behavior as the temperature increases up to ~420 K (vanish) as the Ca$_{2.4}$Sr$_{0.6}$Ti$_2$O$_7$ single crystal sample. Hence there is a common type of structural transition near ~ 400 K in the Ti and Mn-based systems. Data are from warming curves.
Fig. S10. Extracted parameters for 108 and 121 cm\(^{-1}\) peaks for Ca\(_3\)Ti\(_2\)O\(_7\) powder sample. Note the decay of the 121 cm\(^{-1}\) peaks amplitude with temperature in (a). The phonon modes harden with increasing temperature. Data are from warming curves.
Fig. S11. (Left Panel) Fit to Ca$_3$Mn$_2$O$_7$ Mn K-edge data at 880 K showing the single scattering $g(r)$ Gaussian peaks for the Mn-O shell and the Mn-Ca shell and both single and multiple scattering contributions for the nearest neighbor in plane Mn-Mn peak. The full R-space fit over the same three shells also given (Right Panel). The peak near 4.0 Å (left panel) includes multiple scattering contributions.
Fig. S12. XAFS structure function of Ca$_3$Mn$_2$O$_7$ measured between 320 K and 700 K (in (a) and (b)) revealing that the Mn-O and Mn-Ca Correlations. Note the change in the Mn-O correlation near 400 and 500K.

Fig. S13. Fit to Ca K-edge XAFS of Ca$_3$Mn$_2$O$_7$ in R-space for data (crystal derived powder) taken at 350 K. Extracted structural parameters are given in Table S2 at multiple temperatures (300, 350 and 450 K).
Table S2. Ca K-Edge XAFS Derived Structural Parameters

| Average Bond Distance (Å) | Gaussian Width (Å) |
|---------------------------|--------------------|
| **300 K**                 |                    |
| Ca-O 2.30(1)              | 0.007(1)           |
| Ca-Mn 3.13(1)             | 0.009(1)           |
| Ca-Ca 3.62(1)             | 0.003(1)           |
| **350 K**                 |                    |
| Ca-O 2.35(2)              | 0.008(2)           |
| Ca-Mn 3.15(1)             | 0.007(1)           |
| Ca-Ca 3.63(2)             | 0.004(2)           |
| **450 K**                 |                    |
| Ca-O 2.34(2)              | 0.011(2)           |
| Ca-Mn 3.17(1)             | 0.008(2)           |
| Ca-Ca 3.64(2)             | 0.006(2)           |
Fig. S14. (a) Ti K-edge XANES spectra of Ca$_{2.4}$Sr$_{0.6}$Ti$_2$O$_7$ between (crystal ground into powder sample) for temperatures between 300 and 540. In the inset, note that the pre-edge peak B intensity increase with increasing temperature. (b) Simulated spectra for a CaTiO$_3$ cluster for 119 atoms centered on Ti. Note that reduction of tiling relative to the long axis (called x here, Fig. 1(a)) increases the amplitude of peak B while reduction of twisting about the z-axis reduces the peak amplitude (dotted line). Hence the observed continuous enhancement of the B feature with temperature indicates continuous reduction of the tilting of the TiO$_6$ polyhedra with increasing temperature in Ca$_{2.4}$Sr$_{0.6}$Ti$_2$O$_7$. 
Fig. S15. R-Space PDF fit between 1.3 and 20 Å for the Cmc2 model for typical data taken at 399 K. The lower curve is the difference between the model (solid red line) and the data (open circles). Fits were conducted with PDFgui [15].
Fig. S16. (a) Rw fitting parameters for Ca$_3$Mn$_2$O$_7$ from PDF fits show that the Cmc2$_1$ space group gives the best model up to ~400 K while a possible space group for higher temperatures is the polar Amm2 space group. (b) Utilizing the space group (unit cell) results from single crystal measurements, it is seen that the best model above the first order transition is the C2/m cell with volume ½ that of the low-temperature Cmc2$_1$ cell. Data are from cooling curves.
Fig. S17. Ratio of a to c lattice parameter Ca$_3$Mn$_2$O$_7$ (based on single crystal sample) during warming and cooling based on PDF fits.
**Fig. S18.** (a) Fit of the parameter (for single crustal derived Ca$_3$Mn$_2$O$_7$ power) for short range structure PDF data covering same r-range as in Fig. S15 (1.3 to 20 Å). The local structure is consistent with the C2/m space group for the full temperature range. (b) b/a ratio (C2/m space group) near the high-temperature transition at ~1050 K. Measurements were made on warming.
Fig. S19. Volume and b lattice parameter vs. temperature for polycrystalline Ca$_3$Ti$_2$O$_7$. Note broad range of separation for the b parameter (inset) for warming and cooling. The broad hysteresis is due to defects in powder prepared samples. Data in the main figure are from PDF cooling curves.
Table S3. Structural Parameters from Single Crystal Solution for Ca₃Mn₂O₇ at 480 K (I4/mmm)

| Atoms                      | x     | y     | z     | Ueq (Å²)×10³ |
|----------------------------|-------|-------|-------|--------------|
| Mn                         | 5000  | 5000  | 4018.7(6) | 6.6(4)       |
| Ca1                        | 5000  | 5000  | 1865.3(9) | 13.3(5)      |
| Ca2                        | 0     | 0     | 5000   | 13.7(6)      |
| O1 (apical interior)       | 5000  | 5000  | 5000   | 20.0(16)     |
| O2 (apical)                | 5000  | 5000  | 3040(3) | 14.3(10)     |
| O3 (in-plane)*             | 4188(12) | 0    | 4031(2) | 14.2(11)     |

| Atom | U₁₁(Å²)×10³ | U₂₂(Å²)×10³ | U₃₃(Å²)×10³ | U₁₂(Å²)×10³ | U₁₃(Å²)×10³ | U₂₃(Å²)×10³ |
|------|-------------|-------------|-------------|-------------|-------------|-------------|
| Mn   | 6.0(5)      | 6.0(5)      | 7.7(6)      | 0           | 0           | 0           |
| Ca1  | 14.5(6)     | 14.5(6)     | 10.7(8)     | 0           | 0           | 0           |
| Ca2  | 13.2(7)     | 13.2(7)     | 14.6(10)    | 0           | 0           | 0           |
| O1   | 28(2)       | 28(2)       | 3(2)        | 0           | 0           | 0           |
| O2   | 17.0(14)    | 17.0(14)    | 8.9(16)     | 0           | 0           | 0           |
| O3   | 12(2)       | 6.8(18)     | 24(2)       | 0           | -4.3(13)    | 0           |

Space Group: I4/mmm (Z=2) Tetragonal Cell
a = 3.7054 (3) Å, c = 19.585 (3) Å, Dx = 4.225 g/cm³
Measurement Temperature: 480 K
Crystal Dimensions: ~20 µm (diameter)
Wavelength: 0.41328 Å,
Absorption Coefficient: 1.783 mm⁻¹
F(000) = 333.4
Reflections Collected: 5325
20 Range : 2.42° to 40.2°
-6≤ h ≤6, -6≤ k ≤5, and -31 ≤ l ≤32,
Number of Measured Reflections: 5325
Number of Independent Reflections: 241
Number of fitting parameters: 20
Restraints = 0
Max and Min Peak in Final Difference Map: 3.1/-1.0 e-/Å³
R₁ = 4.42 %, wR₂ = 18.8 %, Goodness of Fit = 1.63 (I>2σ (I))
R₁ = 4.56 %, wR₂ = 19.0 % (all data)

\[
R₁ = \frac{\sum ||F₀| - |F_{c}||}{\sum |F₀|}
\]

\[
wR₂ = \frac{\sum w(F₀² - F_{c}²)²}{\sum w(F₀²)²}
\]

* O3 atoms have 50% occupancy of two sites.
Table S4. Bond Distances in Ca$_3$Mn$_2$O$_7$ at 480 K

| Atoms   | Distance (Å)          |
|---------|-----------------------|
| Mn-O3   | 1.8771(7) x 4         |
| Mn-O2   | 1.922(1)              |
| Mn-O2   | 1.916(6)              |
| Ca1-O2  | 2.301(6)              |
| Ca1-O3  | 2.344(4) x 2          |
| Ca1-O2  | 2.6266(5) x 4         |
| Ca1-O2  | 2.779(5) x 2          |
| Ca2-O3  | 2.451(4) x 4          |
| Ca2-O2  | 2.6201(4) x 4         |
| Ca2-O3  | 2.870(4) x 4          |
| Mn-Ca1  | 3.1405(9) x 4         |
| Mn-Ca2  | 3.2494(7) x 4         |

$\langle R_{\text{Mn-O}} \rangle = 1.89$ Å, Standard Dev = 0.02 Å
$\langle R_{\text{Ca-O}} \rangle = 2.61$ Å, Standard Dev = 0.18 Å
$\langle R_{\text{Mn-Ca}} \rangle = 3.19$ Å, Standard Dev = 0.05 Å
Table S5. Structural Parameters from Single Crystal Solution for Ca$_3$Mn$_2$O$_7$ at 480 K (C2/m low symmetry solution)

| Atoms          | x     | y     | z     | Ueq ($\text{Å}^2$)$\times10^3$ |
|----------------|-------|-------|-------|-------------------------------- |
| Mn             | 5983.5(10) | 5000  | 8035.1(8) | 7.1(3)            |
| Ca1            | 8135.4(19) | 5000  | 3731.0(12) | 14.1(3)          |
| Ca2            | 5000   | 0     | 10000  | 14.4(4)          |
| O1 (apical)    | 5000   | 5000  | 10000  | 21.5(11)         |
| O2 (apical)    | 6960(6) | 5000  | 6081(4) | 14.0(7)          |
| O3             | 3870(16) | 2103(17) | 8060(6) | 15.2(16)         |
| O3P            | 3052(18) | 2917(17) | 8064(7) | 14.6(16)         |

| Atom | U$_{11}$(Å$^2$)$\times10^3$ | U$_{22}$(Å$^2$)$\times10^3$ | U$_{33}$(Å$^2$)$\times10^3$ | U$_{12}$(Å$^2$)$\times10^3$ | U$_{13}$(Å$^2$)$\times10^3$ | U$_{23}$(Å$^2$)$\times10^3$ |
|------|----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Mn   | 6.6(4)                     | 6.7(4)                      | 8.2(4)                      | -0                          | -2.2(3)                     | 0                           |
| Ca1  | 15.1(5)                    | 15.5(6)                     | 11.7(5)                     | -0                          | -3.6(4)                     | 0                           |
| Ca2  | 13.3(6)                    | 14.5(7)                     | 15.4(7)                     | -0                          | -3.6(5)                     | 0                           |
| O1   | 27(3)                      | 31(3)                       | 5.9(18)                     | -0                          | -3.5(19)                    | 0                           |
| O2   | 12.4(14)                   | 20.5(17)                    | 7.8(12)                     | -0                          | -0.1(10)                    | 0                           |
| O3*  | 11(3)                      | 13(3)                       | 21(2)                       | -1(2)                       | -3.5(19)                    | -4.3(19)                    |
| O3P  | 12(3)                      | 10(3)                       | 25(3)                       | -3(2)                       | -10(2)                      | 2(2)                        |

Space Group: C2/m (Z=2) Monoclinic Cell
a = 5.2404(7) Å, 5.2401(7) Å, c = 10.1369(14) Å, Dx = 4.225 g/cm$^3$
b= 75.024(3)$^\circ$
Measurement Temperature: 480 K
Crystal Dimensions: ~20 µm (diameter)
Wavelength: 0.41328 Å,
Absorption Coefficient: 1.783 mm$^{-1}$
F(000) = 333.4
Reflections Collected: 5325
20 Range: 2.42$^\circ$ to 40.2$^\circ$
-8≤h≤8, -8≤k≤7, and -16≤l≤16
Number of Measured Reflections: 5325
Number of Independent Reflections: 687
Number of fitting parameters: 46
Restraints = 0
Max and Min Peak in Final Difference Map: 3.1/-1.7 e-/Å$^3$
R$_1$ = 4.77 %, wR$_2$ = 15.5 %, Goodness of Fit = 1.53 (I>=2σ (I))
R$_1$ = 5.60 %, wR$_2$ = 19.7 % (all data)
\[
R_1 = \frac{\sum |F_0| - |F_c|}{\sum |F_0|}
\]
\[
wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}
\]

* O3 and O3P atoms have 50% occupancy of the two sites (derived from fit).
**Fig. S20.** Unit cell for the low symmetry solution (C2/m) to 480 K data for Ca$_3$Mn$_2$O$_7$. Note (as in I4/mmm solution) that there is a 50/50 split occupancy at the O3 site in-plane due to domain formation.
### Table S6. Structural Parameters from Single Crystal Solution of Ca$_3$Mn$_2$O$_7$ at 300 K

| Atoms | x       | y       | z       | Ueq ($\AA^2$)×10$^3$ |
|-------|---------|---------|---------|-------------------|
| Mn    | -4018.5(5) | -7504.8(13) | -2684.3(19) | 5.8(2)           |
| Ca1   | -3136.9(7)  | -7453(2)   | -7846(2)   | 9.5(3)           |
| Ca2   | 5000     | -2507(4)  | -2487(3)  | 10.9(4)          |
| O1    | 5000     | -7948(11) | -2709(14) | 12.5(12)         |
| O2    | -3040(2)  | -7208(8)  | -2627(10) | 9.5(8)           |
| O3    | -4112(2)  | -4623(6)  | -4780(10) | 11.2(7)          |
| O4    | -3943.2(19) | -9641(7)  | -5515(11) | 12.0(7)          |

| Atom | U11($\AA^2$)×10$^3$ | U22($\AA^2$)×10$^3$ | U33($\AA^2$)×10$^3$ | U12($\AA^2$)×10$^3$ | U13($\AA^2$)×10$^3$ | U23($\AA^2$)×10$^3$ |
|------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Mn   | 6.2(4)            | 7.0(4)            | 4.1(4)            | 0.05(15)          | 1.6(3)            | -0.19(16)         |
| Ca1  | 8.5(5)            | 12.2(5)           | 7.7(6)            | -0.5(3)           | 0.3(5)            | 1.2(3)            |
| Ca2  | 10.6(7)           | 12.3(6)           | 9.7(9)            | -0                | -0                | -2.1(5)           |
| O1   | 4.8(18)           | 16(3)             | 17(3)             | -0.9(10)          | -2(2)             | 0.1(15)           |
| O2   | 7.2(13)           | 9.9(15)           | 11(2)             | -0.9(10)          | -2(2)             | 0.1(15)           |
| O3   | 15.1(15)          | 8.1(16)           | 10.3(15)          | -1.1(12)          | 0.1(13)           | 0.9(13)           |
| O4   | 15.4(14)          | 8.9(15)           | 11.6(17)          | -0.6(11)          | 0.7(14)           | -3.0(16)          |

Space Group: Cmc$_2_1$ (Z=4) Orthorhombic Cell

a = 19.4387(12) Å, b = 5.2493(3) Å, c = 5.2433(3) Å, Dx = 4.247 g/cm$^3$

Measurement Temperature: 300 K

Crystal Dimensions: ~20 μm (diameter)

Wavelength: 0.41328 Å,

Absorption Coefficient: 1.792 mm$^{-1}$

F(000) = 666.8

Reflections Collected: 10565

2θ Range: 2.44° to 40.3°

-32 ≤ h ≤ 32, -7 ≤ k ≤ 8, -8 ≤ l ≤ 8

Number of Measured Reflections: 10,565

Number of Independent Reflections: 1296

Number of fitting parameters: 58

Restraints = 1

Flack Parameter = 0.4(3)

Max and Min Peak in Final Difference Map: 3.2/-2.7 e-/Å$^3$

R$_1$ = 5.23 %, wR$_2$ = 14.7 %, Goodness of Fit = 1.54 (I>=2σ(I))

R$_1$ = 7.15 %, wR$_2$ = 21.3 % (all data)

$$R_1 = \frac{\sum |F_0| - |F_c|}{\sum |F_0|}$$

$$wR_2 = \frac{\sum w(F_0^2 - F_c^2)^2}{\sum w(F_0^2)^2}$$
### Table S7. Bond Distances in Ca$_3$Mn$_2$O$_7$ at 300 K

| Atoms   | Distance (Å) |
|---------|--------------|
| Mn-O1   | 1.9221(12)   |
| Mn-O2   | 1.9084(4)    |
| Mn-O3   | 1.8975(5)    |
| Mn-O3   | 1.8794(4)    |
| Mn-O4   | 1.8875(5)    |
| Mn-O4   | 1.8665(5)    |
| Ca1-O2  | 2.2984(4)    |
| Ca1-O2  | 2.4574(4)    |
| Ca1-O2  | 2.5176(6)    |
| Ca1-O2  | 2.8114(4)    |
| Ca1-O3  | 2.4574(4)    |
| Ca1-O3  | 2.4104(4)    |
| Ca1-O4  | 2.2955(5)    |
| Ca1-O4  | 2.5975(5)    |
| Ca2-O1  | 2.7488(8)    |
| Ca2-O1  | 2.5178       |
| Ca2-O1  | 2.8595(5)    |
| Ca2-O1  | 2.3965(5)    |
| Ca2-O3  | 2.3795(5)    |
| Ca2-O3  | 2.6965(5)    |
| Ca2-O3  | 2.3795(5)    |
| Ca2-O3  | 2.6965(5)    |
| Ca2-O4  | 2.5614(4) x 2|
| Mn-Ca1  | 3.0617(15)   |
| Mn-Ca1  | 3.1171(14)   |
| Mn-Ca1  | 3.1543(13)   |
| Mn-Ca1  | 3.2032(12)   |
| Mn-Ca2  | 3.2457(18)   |
| Mn-Ca2  | 3.2473(18)   |
| Mn-Ca2  | 3.1596(19)   |
| Mn-Ca2  | 3.3264(18)   |

$<R_{Mn-O}> = 1.89$ Å, Standard Dev =0.02 Å
$<R_{Ca-O}> = 2.55$ Å, Standard Dev =0.18 Å
$<R_{Mn-Ca}> = 3.19$ Å, Standard Dev =0.08 Å
Fig. S21. Distribution of atoms about Ca at 300 K (a) and at 480 K (b) taken from the single crystal structure solution. Note the strong sharpening of the Ca-Mn distribution (pink blocks) at high temperature.
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