New Mechanism for Ferroelectricity in the Perovskite Ca$\textsubscript{2-x}$Mn$\textsubscript{x}$Ti$\textsubscript{2}$O$\textsubscript{6}$ Synthesized by Spark Plasma Sintering

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ABSTRACT: Perovskite oxides hosting ferroelectricity are particularly important materials for modern technologies. The ferroelectric transition in the well-known oxides BaTiO$\textsubscript{3}$ and PbTiO$\textsubscript{3}$ is realized by softening of a vibration mode in the cubic perovskite structure. For most perovskite oxides, octahedral-site tilting systems are developed to accommodate the bonding mismatch due to a geometric tolerance factor $t = (A$–$O)/(\sqrt{2(B$–$O)}) < 1$. In the absence of cations having lone-pair electrons, e.g., Bi$^{3+}$ and Pb$^{2+}$, all simple and complex A-site and B-site ordered perovskite oxides with a $t < 1$ show a variety of tilting systems, and none of them become ferroelectric. The ferroelectric CaMnTi$\textsubscript{2}$O$\textsubscript{6}$ oxide is, up to now, the only one that breaks this rule. It exhibits a columnar A-site ordering with a pronounced octahedral-site tilting and yet becomes ferroelectric at $T_c \approx 650$ K. Most importantly, the ferroelectricity at $T < T_c$ is caused by an order–disorder transition instead of a displacive transition; this character may be useful to overcome the critical thickness problem experienced in all proper ferroelectrics. Application of this new ferroelectric material can greatly simplify the structure of microelectronic devices. However, CaMnTi$\textsubscript{2}$O$\textsubscript{6}$ is a high-pressure phase obtained at 7 GPa and 1200 °C, which limits its application. Here we report a new method to synthesize a gram-level sample of ferroelectric Ca$_2$–Mn$_x$Ti$_2$O$_6$ having the same crystal structure as CaMnTi$_2$O$_6$ and a similarly high Curie temperature. The new finding paves the way for the mass production of this important ferroelectric oxide. We have used neutron powder diffraction to identify the origin of the peculiar ferroelectric transition in this double perovskite and to reveal the interplay between magnetic ordering and the ferroelectric displacement at low temperatures.

1. INTRODUCTION

The cubic ABO$_3$ perovskite structure consists of corner-shared BO$_6$ octahedra with B atoms at the corner and A atoms in the body center of the unit cell. A tolerance factor $t = (A$–$O)/(\sqrt{2(B$–$O)})$ is a measure of the mismatch between the equilibrium A–O and B–O bond lengths. A $t < 1$ is accommodated by a cooperative rotation of the BO$_6$ octahedra that lowers the crystal symmetry; a $t > 1$ is accommodated by the formation of a hexagonal polymorph or by a ferroelectric (or antiferroelectric) displacement that creates asymmetric B–O and/or A–O bonds if B is a d$^0$ transition-metal cation, and/or A has an s$^2$ core of lone-pair electrons, e.g., Bi$(\text{III})$ or Pb$(\text{II})$.

The relationship between the t-factor and ferroelectricity is well-illustrated by the ATiO$\textsubscript{3}$ family in which A = Ca has $t < 1$, A = Sr has $t \approx 1$, and A = Ba has a $t > 1$ at room temperature. BaTiO$\textsubscript{3}$ undergoes ferroelectric distortions. SrTiO$\textsubscript{3}$ normally exhibits a cooperative rotation of the TiO$_6$ octahedra at low temperature, but substitution of $^{18}$O for $^{16}$O can trigger a low-temperature ferroelectric distortion. Ferroelectric antisymmetric cation–anion bonds have not been found in perovskite oxides without the s$^2$ core A-site cations where the BO$_6$ octahedra undergo cooperative rotations.

Benedek and Fennie have performed very interesting computer experiments. The frequency of the ferroelectric mode has been calculated as a function of the t-factor for

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perovskite oxides with the cubic Pn3m and the orthorhombic Pbnn symmetries. Their results show that the ferroelectric transition is essentially suppressed in the Pbnn perovskites, independent of the tilting magnitude. The a′ a′ c′ tilting system of the Pbnn structure can be decomposed into two sub systems labeled a′ a′ c′ and a′ a′ c′, which allows illustrating the rotation-wise ferroelectric instability. Whereas ferroelectricity is more easily obtained in the cubic phase than in the subgroups of a′ a′ c′ and a′ a′ c′, a ferroelectric instability becomes achievable in the phase with the a′ a′ c′ tilting system as the octahedral tilting along the c axis increases. It is the A-site displacement associated with the a′ a′ c′ tilting mode that suppresses the ferroelectric mode strongly. The A-site antipolar displacements and associated tilting can be suppressed in a heterogeneous structure, such as an La2NiMnO6 film on a SrTiO3 substrate and in a NdNiO3 film on a LaAlO3 substrate where ferroelectricity has indeed been found.

Double perovskites with a more general formula AA′BB′O6 can show even more complicated tilting systems and A-site environments. Cations at both the A site and B site can be ordered into a rock-salt, columnar, or layered structure. Among these double perovskites, few of them adopt a polar structure like NaRMnWO6 (R = La, Nd, Tb) with a P21 phase caused by layered ordering of A-site cations and rock-salt ordering of the B-site cations, which has the a′ a′ c′ tilting system. Density functional theory (DFT) calculations have predicted that double perovskites with this structure are ferroelectric. However, switchable ferroelectricity was not found experimentally for any of these three double perovskites.

CaMnTi2O6 is the only switchable ferroelectric double perovskite that is Pb2+ or Bi3+ free. The columnar ordering of A-site cations found in CaFeTi2O6 is a rare case. The octahedral-site tilting in the tilt system a′ a′ c′ (P42/mmc) places Ca2+ in columns along the c-axis; every Ca column is surrounded by Fe columns consisting of alternating FeO4 tetrahedra and coplanar FeO4. Although the space group allows Fe2+ to be displaced off the plane of the coplanar FeO4 units, Fe2+ stays perfectly in the plane formed by four oxygen; this compound is not ferroelectric as determined by a measurement of second harmonic generation at room temperature. The double perovskite CaMnTi2O6 adopts the same crystal structure as CaFeTi2O6 at high temperatures. The only difference is that the Mn2+ is displaced off the MnO4 plane, which is allowed by symmetry, but it is randomly displaced along the c-axis above Tc, shown in Figure 1(a). At T < Tc, however, all the displacements of Mn2+ at the coplanar sites are in the same direction along the c-axis. Correspondingly, Mn cations in tetrahedra and Ti in octahedra are polarized, as shown in Figure 1(b). The polarization is switchable under an external electric field. Since the nonpolar CaFeTi2O6 has the identical tilting system, ferroelectricity in CaMnTi2O6 is clearly driven by manganese, most likely by the Mn ions in the coplanar coordination. The disorder—order type of ferroelectric transition is rare and offers a fundamentally different mechanism from the well-discussed cases of proper, improper, hybrid improper ferroelectricity and may find potentially new applications. Gaining a fundamental understanding of the mechanism triggering the ferroelectric transition is critically important for applications of the new ferroelectric oxide and for designing new ferroelectric materials. To this end, a thorough structural study by neutron diffraction is needed. Moreover, since the ferroelectric CaMnTi2O6 is a high pressure phase, it is necessary to explore an alternative approach to synthesize the material in larger quantities.

2. EXPERIMENTAL SECTION

Synthesis. A mixture of xMnO, xTiO2 and (2 − x)CaTiO3 was used as the starting materials. The sintering was performed with a SPS system model 10–3 from Thermal Technology LLC at 1350 °C under 90 MPa for 1 min within a 20 mm diameter graphite die.

Structural Characterization. The obtained pellets with orange color were crushed into powders for the characterization by X-ray diffraction. Rigaku Miniflex 600 with Cu Kα radiation was used to determine the phase purity. Neutron powder diffraction experiments were performed in the temperature range of 1.5 to 340 K with wavelength 2.52 Å and from 393 to 703 K with wavelength 1.59 Å at Institut Laue-Langevin (ILL), France. Neutron powder diffraction measurements on a different batch of the SPS sample were performed with POWGEN located at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. All diffraction patterns are refined by the Rietveld method with the FullProf software. The actual Mn concentration x in the SPS products was determined by measuring the temperature dependence of paramagnetic susceptibility with a Physical Property Measurement System (PPMS) (Quantum Design).

Ferroelectric Characterization. A well-polished bulk sample was used to measure the temperature dependence of the optical Second Harmonic Generation (SHG). Ti:sapphire laser at 780 nm wavelength (76 MHz repetition rate, 150 fs pulse width) was incident on the sample at 45°. A photomultiplier tube (PMT) detected 390 nm s-polarized SHG generated by s-polarized incoming light that is insensitive to the surface, but is sensitive to centrosymmetry-breaking in a crystal structure caused by a ferroelectric transition. For dielectric property measurements, the polycrystalline sample was polished to a thickness of 0.29 mm for permittivity and 0.18 mm for the E hysteresis loop measurement at 200 Hz with an aixACCT Easy Check and TF Analyzer 2000 ferroelectric tester at room temperature.
DFT Calculation. Spin polarized DFT calculations were performed with the projector augmented wave method,\textsuperscript{23,24} as implemented in the Vienna Ab Initio simulation package.\textsuperscript{25−28} Electron exchange and correlation was described within the generalized gradient approximation by using the Perdew–Burke–Ernzerh functional. A Hubbard term was added to the d orbitals of Mn and Ti with an effective U value of 3.8 and 4.36 eV, respectively. A 5 × 5 × 5 k-point mesh, a plane wave cutoff of 600 eV, and a force convergence tolerance of 2.5 meV Å were employed for structural relaxation. Phonon frequencies were calculated with density functional perturbation theory.

3. RESULTS AND DISCUSSION

Double Perovskites and Spark Plasma Sintering (SPS). For the double perovskites AA′B′B″O6′ or the A-site ordered perovskites AA′A′2B′B″3O12, whether the perovskite phase is stable depends on the global instability index (GII) in addition to the t factor; GII is defined as the difference between the bond valence sum (BVS) and the formal valence of cations and anions in a complex oxide. A survey in the literature on this issue indicates that high-pressure synthesis is normally required if GII is larger than 0.02 for a given complex oxide formula.\textsuperscript{29–30} A calculation using the software SPuDS gives a GII = 0.219 for CaMnTi2O6 which is why high-pressure synthesis is required to stabilize this double perovskite. However, high-pressure synthesis is not the only way to obtain a complex oxide with a high GII. For example, an A-site ordered perovskite CaCu3Fe2Sb2O12 with a GII = 0.033, which has been obtained previously with high-pressure synthesis,\textsuperscript{29} can be synthesized at ambient pressure through a designed chemical procedure.\textsuperscript{31} The same procedure, however, did not work to synthesize the double perovskite CaMnTi2O6. The issue for us to consider is whether the SPS synthesis could help to overcome the barrier of the GII.

The SPS process starts with an initial activation by applying a pulsed current while the powder is placed under pressure. The on−off DC current in this stage generates the spark discharge and rapid Joule heating between grains. Ionized elements from the particle’s surface can be transformed into a plasma in some cases. The spark and plasma vaporize the contact area between particles, which cleans up the surface and draws together particles to create necks. The intensified Joule heating up to thousands of degrees Celsius and pressure make these necks develop and grow. The radiant Joule heating between particles also causes plastic deformation on the surface of the particles, which in turn enhances the consolidation. These features can enable completion of the material sintering in a very short period of time, even within 1 min in the case of the double perovskite presented in this work.

A direct reaction by firing the starting components of CaCO3, MnO, and TiO2 at ambient pressure gives rise to a mixture of perovskite CaTiO3 and ilmenite Mn3TiO5. Mn3TiO5 will convert into MnTi2O6 at higher temperatures. By changing the tilting group from a′a′c′′ of perovskite CaTiO3 into the a′a′c′, the insertion of Mn2+ at the A-site of CaTiO3 can be achieved under high temperatures and a very modest pressure in a SPS synthesis, which also favors a columnar ordering of Ca and Mn columns along the c axis. The ilmenite Mn3TiO5 and spinel Mn3TiO5 have lower melting temperatures than that of perovskite CaTiO3. A prolonged sintering of CaTiO3 + Mn3TiO5 will result in a phase segregation between a solid phase and a liquid phase, which minimizes the Mn concentration in the perovskite. The pressure used in SPS is too small to influence the tolerance factor of the perovskite phase, but it helps to confine the oxides during the reaction. By taking advantage of the nearly instant reaction with SPS, a significantly high concentration of Mn can enter into the A-site of the double perovskite without phase segregation; the maximum x ≈ 0.6 in perovskite Ca2−xMnTi2O6 can be obtained at 100 MPa. Moreover, the graphite die used in SPS provides some reduction effect, which prevents Mn2+ from further oxidation during the reaction. The final manganese concentration in the product is determined by the measurement of magnetic susceptibility on the assumption of Mn2+ in the perovskite. The calculated valence based on the BVS from the structural data is also consistent with the amount of Mn2+ in the structure. As shown in the following paragraph, the manganese concentration in the samples made with SPS is sufficiently high to make the perovskite ferroelectric. The synthetic results are mapped out in the pressure−temperature phase diagram shown in the Supporting Information.

One of the significant findings in this work is that the SPS sintering lowers the GII value of the double perovskite formula, so that a high pressure phase can be stabilized under a very modest pressure. Ionized elements from the particle’s surface during SPS appear to change the dynamics of chemical reaction to form a bonding structure with a higher GII. This finding may make potentially the SPS method applicable to stabilize new metastable phases in a broader range of materials.

Crystal Structure through the Refinement of Neutron Powder Diffraction. Neutron powder diffraction experiments have been performed on Ca2−xMn3Ti2O6 (x = 0.6) in the temperature range of 1.5 to 700 K; patterns and the refinement results at selected temperatures are shown in Figure 2. More detailed information about the refinement can be found in Supporting Information. A structural transition at 570 K is marked by an anomaly in the temperature dependence of lattice parameters of Figure 3(a); a and c start to be separated at T < 570 K. The neutron diffraction pattern can be fit well by the structural models of nonpolar double perovskite P4_2/mmc at T > Tc and polar double perovskite P4_2/nmc at T < Tc. These structural models have been used to fit XRD patterns of the double perovskite CaMnTi2O6 made under high pressure as

![Figure 2](image-url)

Figure 2. Neutron powder diffraction pattern and results of the refinement of Ca1.4Mn0.6Ti2O6. These patterns have been collected with the neutron beam (λ = 1.59 Å) at D2B. ILL, France.
illustrated in Figure 1. Although Ca apparently occupies partially the 2c site for Mn in addition to the 2a and 2b sites in the SPS product, the disorder does not destroy the columnar ordering of A-site cations in the double perovskite structure. The space group $P4_2/mmc$ allows Mn$^{2+}$ on the coplanar site to move out of the square plane formed by four oxygen, but the moving direction remains random along the $c$ axis in this nonpolar structure, which is why a finite displacement on the Mn site is obtained even at $T > T_c$, see Figure 3(b). The displacement shows no noticeable change on crossing the nonpolar to polar structural transition. However, right below $T_c$, Mn on the tetrahedral-site is polarized in the opposite direction to that of the coplanar Mn; the polarization gradually changes sign as temperature decreases. Given nearly canceling electric dipoles from two Mn sites right below $T_c$, the net dipole moment comes from the TiO$_6$ array. A clear displacement of Ti occurs on cooling through $T_c$ as is shown in Figure 3(c). The Ti displacement in an octahedral-site with the $a'a'e'$ tilting system is highly unusual and it must be induced by the A-site displacement. We will come back to this point in the following discussion.

The polar displacements of Mn and Ti ions create interesting changes of interatomic distances and bonding angles. While the changes of Mn–O bond length in the coplanar and in the tetrahedra sites of Figure 3(d) are consistent with the Mn displacement, the coplanar oxygen exhibit an unusual change from a square into a rectangle of Figure 3(e) on cooling through $T_c$. The MnO$_4$ tetrahedra also become distorted, i.e., they are elongated along the $c$ axis, see Figure 3(f). The TiO$_6$ octahedra are no longer regular; the basal plane of an octahedron becomes rectangular below $T_c$. Since coplanar MnO$_4$ units share the apical oxygen and tetrahedral MnO$_4$ units share the oxygen in the basal plane of an octahedron, these local structural changes on cooling through $T_c$ lead to corresponding changes in the Ti–O–Ti bonding angles of Figure 3(e); the bond angle increases along the $a$ axis and decreases for the bonding along the direction 90° from the $a$ axis in the basal plane. There is no change of the bond angle along the $c$ axis. Calculations of BVS for each cation based on the structural data show that the Mn$^{2+}$ at coplanar and tetrahedral sites have BVS values of 1.18 and 1.30, respectively, while the BVS value of the Ti$^{4+}$ is 4.20, indicating that Mn–O is slightly under-bonded and Ti–O is slightly overbonded. We have further calculated the temperature dependence of GII for the whole structure. Presented in the Supporting Information, the GII increases slightly below $T_c$, which means that the ferroelectric transition further enlarges the degree of under-bonding and overbonding at different cation sites in the structure.

Physical Properties of the SPS Product. We have used the same SPS procedure to synthesize a series of perovskites $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$ ($0 < x \leq 0.6$). While XRD shows a single phase for all these compositions, it is difficult from the refinement alone to determine whether the phases are simple perovskite or have the polar double perovskite structure at room temperature, especially for compositions with the lower Mn concentration. We used the SHG microscopy to probe ferroelectricity, which is particularly useful in the cases where the structural distortion associated with a ferroelectric transition is too small to be detected by diffraction technique. Figure 4(a) shows the temperature dependence of the SHG intensity for $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$ samples with different Mn concentrations. The polarized SHG detected is generated by s-polarized incident beam. Green dashed line indicates the background noise level, which is close to zero. (b) The phase diagram of $\text{Ca}_{2-x}\text{Mn}_x\text{Ti}_2\text{O}_6$. $T_c$ of the SPS samples is defined from temperature-dependent measurements of SHG, where the SHG vanishes. The data for high-pressure sample are after ref 16.
In comparison with the structural data of CaMnTi$_2$O$_6$ synthesized under high pressure, $T_c$ appears to be related to the magnitude of the Mn displacement on the coplanar site in the nonpolar phase. We have also performed polarization measurements on the SPS samples, as presented in Supporting Information. Due to the leaking problem caused by residual carbon in the SPS samples, the polarization curves look slightly different from typical ones by the conventional method. However, a normal polarization curve can be obtained by the PUND method. The results indicate that the double perovskites Ca$_{2-x}$Mn$_x$Ti$_2$O$_6$ obtained by the SPS method are switchable ferroelectrics.

**Magnetism and Ferroelectricity.** Like the double perovskite CaMnTi$_2$O$_6$ synthesized under high pressure, the SPS samples exhibit a magnetic ordering at $\sim$5 K as indicated by specific heat measurement. Neutron powder diffraction at low temperatures also detect reflections from the manganese sublattice. Due to the substitution of Ca on the Mn sites in the SPS samples, the intensity of magnetic-order-related reflections is rather weak and peaks looks broader. The refinement converges only if the type-C antiferromagnetic model is used. The refinement, however, cannot distinguish the easy axis of magnetic moments at Mn sites. The higher order term of spin–orbit coupling for the Mn at the coplanar sites prefers a moment normal to the oxygen square plane. Our DFT calculations also show that the ground state with the type-C magnetic ordering has the lowest energy. More detailed information about the calculated results can be found in the Supporting Information. The electron configuration $t^5$ of the high-spin Mn$^{2+}$ is compatible with a weak antiferromagnetic Mn$^{2+}$–O–O–Mn$^{2+}$ superexchange interaction between Mn$^{2+}$ columns; the superexchange spin–spin interaction between tetrahedral and coplanar Mn$^{2+}$ along a column is antiferromagnetic and extremely weak. The overall ferromagnetic intracolumn coupling must be from magnetic dipole–dipole interactions. An important finding is that the Mn$^{2+}$ displacement of the coplanar site of Figure 3(b) is further enhanced while the magnetic moment at the same site becomes ordered. This finding is opposite the conventional wisdom that magnetism and ferroelectric displacements do not coexist on the same site. Hill has argued that the superexchange interaction facilitating magnetism tends to optimize the local bonding structure so as to maximize the orbital overlap integral, which is always against the displacement required for ferroelectricity at octahedral sites. In the case of double perovskite Ca$_{2-x}$Mn$_x$Ti$_2$O$_6$, however, the intracolumn coupling is dominated by the magnetic dipole–dipole interaction, which appears to be compatible with the electric dipole associated with the Mn displacement at the coplanar site. The observation that the Mn displacement is enhanced in the AF state is consistent with the DFT calculations. By relaxing the Mn displacement, our calculations indicate that the Mn displacement increases by 0.009 Å in the type-C ordered phase relative to the nonmagnetic phase.

**The Driving Force for the Ferroelectric Transition.** For proper ferroelectricity, a double-well potential is formed due to a large gain of the orbital hybridization at the expense of elastic energy associated with the atomic displacements, which leads to a soft-mode transition to polar structures. From the point of view of structural symmetry, a variety of octahedral-site tilting modes in the perovskite structure do not give rise to a polar structure since a rotation at one site is accompanied by an opposite rotation at adjacent sites, for example, in the $a'$-$a$-$c$-tilting system of the double perovskite CaFeTi$_2$O$_6$. At $T > T_c$, Ca$_{2-x}$Mn$_x$Ti$_2$O$_6$ oxides share the same nonpolar double perovskite structure as that of CaFeTi$_2$O$_6$. However, there is a distinct difference between these two perovskites. Allowed by symmetry in the nonpolar $P4_2$/mnc structure, Mn at coplanar sites in Ca$_{2-x}$Mn$_x$Ti$_2$O$_6$ moves out of the plane, but the direction of the movement is random between sites. In contrast, Fe at the same position in CaFeTi$_2$O$_6$ stays in the plane even though Mn$^{2+}$ and Fe$^{2+}$ cations have similar sizes. To understand why the coplanar Mn$^{2+}$ move off the plane whereas the coplanar Fe$^{2+}$ does not, a DFT calculation was done, which takes into account the second nearest neighbors of oxygen atoms. Figure 5(a) illustrates that the orbital occupation number of $d$ electrons is a key to the displacement of the Mn$^{2+}$. The coplanar symmetry stabilizes the $z'$ orbital and destabilizes the antibonding $xy$ orbital. Moving the cation out of the plane lowers the $xy$-orbital energy, but it increases the energies of the $z'$ and $yz \pm izx$ orbitals; the net energy change still favors a Mn$^{2+}$ ion moving out of the plane, as can be seen from the total energy change for Mn$^{2+}$ at the center versus off-center provided in the Supporting Information. In contrast, the occupation of the $z'$ orbital by an extra electron in Fe$^{2+}$ ion costs more energy for the displaced Fe$^{2+}$ relative to that within the plane, as illustrated in Figure 5(b). While the consideration of the orbital occupation can justify the displacement of Mn$^{2+}$, it is not directly related to the transition to a polar structure. The $a'a'c'$-tilting system of the $P4_2$/mnc structure creates the MnO$_4$ square planes that share the apical oxygen of the adjacent four TiO$_4$ octahedra. The tilting system changes from the $a'a'c'$ to the $a'b'c'$ at the phase transition to the polar $P4_2/mc$ structure as reflected in the temperature dependence of the Ti–O–Ti bond angles in Figure 3(h) on cooling through
As a result, the coplanar MnO4 changes from a square in the nonpolar phase to a rectangle in the polar phase. The longer edge of the rectangle causes a reduction of the octahedral-site tilting around the axis normal to the longer edge of the rectangle. At $T > T_c$, since the Mn displacement is random at coplanar sites, the local tilting pattern must be a mixture of the $a'b'c'$ and $b'a'c'$. It is impossible to detect the local tilting system by diffraction technique, so that the $a'a'c'$ is used as the global tilting system in the refinement of diffraction pattern at $T > T_c$. Since TiO4 octahedra share corners to form a 3D network in the perovskite structure, a mixture of the $a'b'c'$ and $b'a'c'$ in the local tilting system would create significant bond length mismatch and stresses and raise the system elastic energy as illustrated in Figure 6. One obvious change from the nonpolar to the polar structural transition is to increase the cooperativity of the octahedral-site tilting in the structure, which lowers the system energy. Starting with the nonpolar structure having the coplanar Mn in up-and-down positions and allowing the lattice to be relaxed, our DFT calculation always gives a ground state having ordered Mn displacement at the coplanar sites. The distortion of the Mn displacement direction and associated rectangle orientation at $T > T_c$ destroys the cooperativity of the octahedral-site rotation and increases the elastic energy of the structure. The tendency to lower the elastic energy is the driving force for ordering the displacement direction at Mn sites and therefore the ferroelectric transition.

Figure 6. Structural models projected along the $a$ axis. Only the Mn at coplanar sites and Ti at octahedral site are shown in the drawing. Arrows point to the direction of oxygen displacement associated with the rotation of O$_4$ plane. For the oxygen moves toward the Mn, the longer axis of the O$_4$ rectangle is parallel to the $a$ axis. It is along the $b$ axis for oxygen moves away from the Mn. The cooperative octahedral-site rotation requires a uniform reduction of the O$-$O distance at coplanar sites. The disorder of the Mn displacement direction and associated rectangle orientation at $T > T_c$ destroys the cooperativity of the octahedral-site rotation and increases the elastic energy of the structure. The tendency to lower the elastic energy is the driving force for ordering the displacement direction at Mn sites and therefore the ferroelectric transition.

In summary, we have developed a new procedure to synthesize gram-level new ferroelectric $\text{Ca}_3\text{Mn}_2\text{Ti}_2\text{O}_9$. By using neutron powder diffraction and first-principles calculations, we have identified the origin causing the ferroelectric transition. Unlike proper ferroelectricity where dipoles are generated directly from the displacement associated with softening of a polar mode in the high symmetry paraelectric phase, the order−disorder transition at the coplanar Mn$^{2+}$ site leads to a polar structure in which dipoles are created at Ti$^{4+}$ sites, the Mn$^{2+}$ tetrahedral sites, and Mn$^{2+}$ at the coplanar sites. The Curie temperature for the ferroelectric transition is about 560 K and this new type of ferroelectricity has the potential to overcome the critical thickness problem experienced in the proper ferroelectric materials for practical applications. The new mechanism of ferroelectricity and the method for the material synthesis presented in this work provide an exciting new direction to the search for new ferroelectric materials.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b11219.

Further structural refinement results, electronic calculation results, the results of polarization measurement, and the pressure−temperature phase diagram of $\text{Ca}_{1.4}\text{Mn}_{0.6}\text{Ti}_2\text{O}_6$ (PDF)

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### Notes

The authors declare no competing financial interest.

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