Asymmetric Character of the Ferroelectric Phase Transition and Charged Domain Walls in a Hybrid Improper Ferroelectric

Mads C. Weber,* Yannik Zemp, Morgan Trassin, Arkadiy Simonov, Jakob Schaab, Bin Gao, Sang-Wook Cheong, Thomas Lottermoser, and Manfred Fiebig

In improper ferroelectrics, the spontaneous ordering is typically driven by a structural distortion or a magnetic spin alignment. The induced electric polarization is only a secondary effect. This dependence is a rich source for unusual phenomena and ferroelectric domain configurations for proper, polarization-driven ferroelectrics. This study focuses on the polar domain structure and the hysteretic behavior at the ferroelectric phase transition in Ca₃Mn₁.₉Ti₀.₁O₇ as a representative of the recently discovered hybrid improper ferroelectric class of multiferroics. Combining optical second harmonic generation and Raman spectroscopy gives access to the spontaneous structural distortion and the resulting improper electric polarization. This study shows that hybrid improper ferroelectrics contrast proper and improper ferroelectrics in several ways. Most intriguingly, adjacent ferroelectric domains favor head-to-head and tail-to-tail domain walls over charge-neutral configurations. Furthermore, the phase transition occurs in an asymmetric fashion. The regime of phase coexistence of the nonpolar and polar phases shows a clear and abrupt upper temperature limit. In contrast, the coexistence toward low temperatures is best described as a fade-out process, where 100-nm-sized islands of the nonpolar phase expand deep into the polar phase.

1. Introduction

Ferroelectric functionalities are tightly bound to domains, that is, regions with different, yet uniform direction of the spontaneous polarization. In ferroelectric memory devices, domains can be considered as logic bits in which the polarization direction represents a binary information. The domains are separated by domain walls, which themselves may add further functionalities because they can possess non-bulk-like properties. These properties depend strongly on the crystallographic orientation of the walls. For instance, if the spontaneous polarization in neighboring ferroelectric domains points perpendicular to the domain wall,[1,2] so-called head-to-head or tail-to-tail walls form. These configurations can lead to a non-bulk-like conductivity of the domain walls because of charge-screening effects.[9]

Understanding and controlling the configuration of the domains is at the heart of functionalizing ferroelectrics. The criteria that determine this configuration strongly depend on the origin of the ferroelectric state. In proper ferroelectrics, where the polarization represents the primary order parameter, the domains typically arrange such that the energetically costly head-to-head or tail-to-tail walls are avoided. In improper ferroelectrics, however, where the polarization is only a byproduct of another, leading order, other criteria are driving the domain formation. Therefore, improper ferroelectrics are an abundant source for unconventional domain structures.[3–7]

A novel contribution to this class of materials are the so-called hybrid improper ferroelectrics. Here, the ferroelectric state originates from two modes with different symmetries. These modes are not polar themselves. In their combination, however, they activate an electric polarization; hence the denomination as hybrid improper ferroelectric.[8]

Much research on hybrid improper ferroelectrics focuses on compounds like (Ca,Sr)₇(Ti,Mn)₂O₁₅. These compounds crystallize in a Ruddlesden–Popper structure built from double perovskite-type layers separated by rock-salt-like (Ca,Sr)O sheets (Figure 1a).[8,9] A plethora of tilt systems of the (Ti,Mn)O₆ octahedra as central building blocks of this structure gives rise to a rich phase diagram of competing states.[10–15] While structural analyses based on X-ray and neutron diffraction were applied to a large variety of compounds of the (Ca,Sr)₈(Ti,Mn)₂O₁₅-family, investigations of the domain structure were mostly restricted to the titanium-rich compounds. Here, studies bring domain configurations with
In the manganese-rich compounds, however, attempts to visualize ferroelectric domains have been unsuccessful so far. Leakage currents impede piezo-response or conductive force microscopy. Therefore, they belong to the class of multiferroics, which are of great current interest for their potential magneto-electric functionality. Before this aspect can be addressed any further, we must first gain an understanding of the ferroelectric state and its domains.

In the present work, we therefore investigate the domain configuration in the manganese-rich hybrid improper ferroelectric Ca$_3$Mn$_{1.9}$Ti$_{0.1}$O$_7$ with a focus on the role of the ferroelectric phase transition. We can only get to these results through a combination of experimental techniques, namely optical second harmonic generation (SHG) and Raman spectroscopy (RS). SHG, that is, frequency doubling of a light wave in a material, is extremely sensitive to the loss of inversion symmetry and thus a probe for emerging ferroelectricity. RS is based on the inelastic scattering of light and is an excellent technique for probing tilt-driven phase transitions and subtle structural distortions. With the sensitivity of SHG and RS to polar and distortive properties, respectively, we gain access to structurally driven ferroelectricity and the associated domain structure.

We find that the ferroelectric behavior in hybrid improper ferroelectrics can contrast not only proper but also other improper ferroelectrics. Specifically, the polar 180° domains in Ca$_3$Mn$_{1.9}$Ti$_{0.1}$O$_7$ prefer head-to-head and tail-to-tail rather than charge-neutral domain walls. Furthermore, the ferroelectric phase transition shows an asymmetric character. While the phase coexistence of the nonpolar and polar phases has a clear upper temperature limit $T_C$, the region of phase coexistence expands far below $T_C$ without a clear lower temperature limit.

2. Results and Discussion

2.1. Ferroelectric Phase Transition

The prototype space-group symmetry of Ca$_3$Mn$_{1.9}$Ti$_{0.1}$O$_7$ is tetragonal, I4/mmm. From this, a phase transition to the orthorhombic Ccce phase takes place at, presumably, 1100 K. It consists of an anti-phase rotation of the oxygen octahedra of X$_1$ symmetry around the former fourfold axis of the tetragonal prototype phase; subsequently, a first-order phase transition from the nonpolar Ccce to the polar Cmc2$_1$ phase takes place at 364 and 380 K in cooling and heating runs, respectively. The associated $a' a' b$ tilt system of the octahedra is intriguing since it is composed of two nonpolar modes, that is, an in-phase rotation mode $X_2^+ (a' d' b')$ and an anti-phase rotation mode $X_1^- (a' a' b')$. In their combination, these modes activate a spontaneous electric polarization through Ca$^{2+}$ displacement along the z direction. A mechanism of this type is termed hybrid improper ferroelectricity. We now aim to understand the ferroelectric phase transition from a microscopic perspective. We begin by investigating the transition between the Ccce and Cmc2$_1$ phases in SHG measurements. Centrosymmetric phases like Ccce do not allow for the leading-order all-electric-dipole-type SHG process. Phases without inversion symmetry, however, such as the polar Cmc2$_1$ state permit this contribution, for further information see Supporting Information 3. Figure 2a shows...
define the temperatures of zero SHG signal for heating and cooling runs, respectively. T_c^\text{heating} = 387 K, the SHG signal shows a kink and vanishes in a staircase-like descent across a range of 3 K (Regime 2). During re-cooling, the inverse process takes place, yet now with T_c^\text{cooling} = 358 K. The pronounced hysteresis with a width of 30 K confirms the first-order nature of the transition.[18, 23] In Figure 2b, we track the hysteretic behavior by spatially resolved SHG imaging. We find that a Barkhausen-like transition of clearly demarcated sample areas causes the staircase-like progression of the SHG signal in Regime 2. The sequence of abrupt changes is likely caused by pinning defects. Furthermore, the discontinuous nature of this first-order phase transition may play a role: The change between the out-of-phase tilts $a^0a^0b^0$ in the CcCe phase and the in-phase tilts $a^0a^0b^0$ in the Cmcm2 phase requires every second octahedron along the z direction of the tetragonal prototype phase to change its sense of rotation. The associated major atomic displacement might be particularly susceptible to structural inhomogeneities resulting in pinning effects.

Let us now turn to the pronounced, yet continuous change of the SHG signal with temperature in Regime 1. Two different scenarios may be responsible for the observed evolution: an extended region of phase coexistence of the nonpolar CcCe phase and the polar Cmcm2 phase below T_c (Scenario 1) or a conventional thermal decrease of the spontaneous polarization toward T_c (Scenario 2). In the former case, the change in signal would point to a change of the volume of the polar phase rather than of the polarization itself.

To identify if one of these options prevails or if both contribute to the signal change in Regime 1, we perform temperature-dependent micro-RS. For Scenario 1, the phase coexistence, the Raman spectra of both phases would be detected simultaneously but both spectral contributions would exhibit different evolutions with temperature.[23] For Scenario 2, the change in polarization, one would expect a change of the vibrational frequencies of the tilt modes, which couple linearly to the ferroelectric mode.[8]

Figure 3a shows the temperature-dependent Raman spectra during a heating run (for the selection rules of the Raman-active modes refer to Supporting Information 2). At 298 and 413 K, we find a spectral dependence that is characteristic for the Cmcm2 and the CcCe phase, respectively.[26] The two spectra differ significantly in number and frequencies of the observed modes. In a heating run, the signal of the CcCe phase gives rise to new spectral features complementing the spectral signature of the Cmcm2 phase (see Figure 3a, green shaded areas). With further increasing temperature, the contribution of the CcCe phase to the spectrum increases until at T_c^\text{heating} = 390 K, analogous to the SHG data, the sample abruptly transfers into the pure CcCe phase. We therefore find a substantial temperature interval of phase coexistence in Regime 1 in agreement with Scenario 1. T_c^\text{heating} as transition temperature marks the limit of the polar Cmcm2 phase and, hence, the high-temperature boundary of the region of phase coexistence.

Figure 3b illustrates this evolution by the normalized weight of both spectra extracted from their fits. For the spectral features of the CcCe phase, converging fits are obtained starting from at 358 K. We therefore show the data points down to this value, even though the region of phase coexistence is likely to extend to even lower temperature. Note that the normalized weight of the spectral intensity is no measure for the volumetric ratio of the two phases since their scattering probabilities are most likely different.
We estimate the size of the inclusions of the Ccce phase below $T_C$ to be in the 100-nm range because with a spot size of the Raman probe of 1 μm, we already obtain a homogeneous Raman signal throughout the sample. Note that to identify this hierarchical structure of large ferroelastic domains with embedded tens-of-micrometer-sized ferroelectric domains, which are infused by nanometric nonpolar islands, we need the combination of both SHG measurements and RS. Because of the substantially smaller laser spot size of Raman measurements in comparison with SHG measurements (270 μm), the staircase-like transition process of Regime 2 is not observed in the former. From the SHG measurements in Figure 2a, we find that aside from the hysteretic temperature shift of $T_C$ the behavior in heating and cooling runs is the same.

In the next step, we examine if the phase coexistence (Scenario 1) alone is responsible for the temperature dependence of the SHG signal in Regime 1, or if a change in polarization also plays a role (Scenario 2). Figure 3c shows the temperature-dependent evolution of the phonon-mode frequencies extracted from Figure 3a. We find that the modes show no sign of softening toward $T_C$ heating. To access the (Ti,Mn)O$_6$ tilt angles, which are proportional to the polar displacement, we trace the tilt vibrations toward $T_C$ heating. Thanks to a recent mode assignment, we identify the $A_1$(TO) modes at 142 and 87 cm$^{-1}$ as in-phase and out-of-phase tilt modes, respectively. Figure 3d shows the evolution of both modes with rising temperature. Between room temperature and $T_C$ heating, the in-phase rotation mode (142 cm$^{-1}$) exhibits a shift by 1 cm$^{-1}$. The out-of-phase rotation mode (87 cm$^{-1}$) shifts by 8 cm$^{-1}$. Making use of the linear relation between the vibrational frequency and the tilt angle (the magnitude of the order parameter is approximately proportional to the frequency of the associated mode, and by comparison with neutron diffraction data, we can approximate the tilt-related frequency shifts as 17.1 and 12.5 cm$^{-1}$ deg$^{-1}$ for the in-phase and the out-of-phase rotations, respectively. This is in good agreement with data obtained for the related perovskite-type compounds CaTiO$_3$ and CaMnO$_3$. With about 0.06°, the modification of the angle of the in-phase rotation mode is therefore negligible. For the out-of-phase rotation, we estimate a rotation change of about 0.6°, in good agreement with neutron diffraction data. This corresponds to a change of the out-of-phase rotation by 10%. Therefore, the related change in polarization is minor in comparison to the one at proper ferroelectric phase transitions, which is also consistent with reports by Senn and co-workers. With the relation $P_s = E (2\omega) \propto I_{SHG}^{1/2}$, where $P_s$ is the spontaneous polarization of the material and $E(2\omega)$ and $I_{SHG}$ are the electric field and intensity of the SHG light, respectively, the polarization change thus can only account for 20% of the variation of the SHG signal in Regime 1.

We therefore conclude that the polarization (Scenario 2) change plays a secondary role in Regime 1, which is instead dominated by a wide region of phase coexistence (Scenario 1) in the form of 100-nm-sized regions of the Ccce phase below $T_C$. In an asymmetric fashion, this phase coexistence prevails below $T_C$ only. The crystalline structure remains rigid around the phase transition at $T_C$. The transition is, therefore, best described as an abrupt event, during which the in-phase tilts ($a^*a^*b^*$, Cmc2$_1$) transfer into out-of-phase tilts ($a^*a^*b^*$, Ccce

---

**Figure 3.** a) Evolution of the Raman spectra in x(yz) configuration (for further information on the Raman selection rules see Supporting Information 2) with increasing temperature across the phase transition. The spectra of the Ccce and of the (predominantly) Cmc2$_1$ phase are given in green and black, respectively. Emergent spectral features of the nonpolar phase within the polar phase are shaded green. b) Onset and decline of the $A_1$(TO) (Cmc2$_1$, black triangles) mode frequencies with increasing temperatures (see Supporting Information 2.1 for the evolution of TO modes). d) Evolution of the frequencies of the $A_1$(TO) soft modes in the Cmc2$_1$ phase. As illustrated, the vibrational patterns of the soft modes relate directly to the in-phase and out-of-phase tilts of the octahedra that represent the order parameters of the system. The dotted lines in (b–d) mark $T_C$-heating.
2.2. Ferroelastic and Ferroelectric Domain Configuration

We now scrutinize the domain configuration in the ferroelectric phase. With $I4/mmm$ as prototype symmetry, the $Cmc2$, phase has two ferroelastic domain states with mutually exchanged $y$ and $z$ axes. Each of these hosts two ferroelectric domain states with opposite direction of the spontaneous polarization parallel to the $z$ axes, giving rise to four polarization domain states in total. (For an in-depth discussion of the resulting domain-wall configurations see Ref. [9].)

First, we image the ferroelastic domains by RS. We use the differences in the signatures of the Raman spectra for differently oriented ferroelastic domains to map the domain configuration (see Supporting Information 2.2). Since every image point represents an entire spectrum, this method, unlike photographic microscopy techniques, is very robust against intensity changes due to surface imperfections. Figure 4a shows the domain configuration as a distribution of bright and dark regions representing the two ferroelastic domain states, to which we refer as FA-1 and FA-2. The ferroelastic domains are $100 \mu$m in size, comparable to earlier findings.\[23\] To identify the orientation of the polar axis within the ferroelastic domains, we measure the anisotropy of the SHG signal (see Supporting Information 3.1). In accordance with the allowed SHG tensor components in the $Cmc2$ space group (Supporting Information 3), we find as expected the polar axes in FA-1 and FA-2 perpendicular to each other as indicated in Figure 4a. Hence, the ferroelastic domain walls roughly align with $x$ and $y$ axes of the tetragonal prototype phase, which are oriented at $45^\circ$ to the orthorhombic $y$ and $z$ axes.

In the next step, we investigate the ferroelectric 180° domains within the ferroelastic domains by spatially resolved SHG imaging. Figure 4b shows the SHG image of the center part of Figure 4a with FA-1 and FA-2 appearing as bright and dark, respectively (for a visualization of FA-2 see Supporting Information 3.3). The ferroelastic domain configurations obtained by SHG and RS imaging are in striking agreement. This agreement of the reflection-based SHG image and the spectrum-based RS image allows us to exclude optical artifacts in the SHG images. For example, areas of altered surface roughness, which therefore emit reduced SHG intensity could be falsely interpreted as different ferroelastic domain, but the spectrum-based RS imaging allows for an unambiguous identification of the domain state. Within the probed FA-1 area, we observe regions of different brightness. These results from domains stacked parallel to the surface so that the passing laser beam leads to interfering SHG contributions.

Furthermore, we identify black lines within $yz$ plane. The lines result from the destructive interference occurring at the boundary between the ferroelectric domains and hence indicate the position of the ferroelectric 180° domain walls near the surface.\[34\] The ferroelectric domains have a lateral extension on the order of tens of micrometers. This is comparable to the lateral expansion observed in the related compound $Ca_3Ti_2O_7$.\[9,35\]

For clarity, Figure 5a illustrates the distribution of the different domain and domain-wall types. To describe the relation between a ferroelectric domain wall and the direction of the spontaneous polarization, we introduce the angle $\theta$ as defined in Figure 5a. $\theta = 0^\circ, 180^\circ$ means that the domain walls are oriented parallel to the polarization and are thus electrically neutral. For $\theta = 90^\circ$ and $270^\circ$, the domain walls are perpendicular to the polarization, indicating charged head-to-head and tail-to-tail walls, respectively. In Figure 5b, we show the integrated length of the domain walls against the angle $\theta$. Strikingly, the domain walls preferentially align perpendicular to the local polar axis as indicated by the maxima for $\theta = 90^\circ$ and $270^\circ$. In other words, $Ca_3Mn_{1.9}Ti_{0.1}O_7$ favors maximal head-to-head and tail-to-tail walls over neutral walls.

This is a remarkable and very unexpected observation. In proper ferroelectrics, such as Pb(Zr,Ti)O$_3$, LiNbO$_3$, or...
3. Conclusion

Using the unique combination of SHG measurements and Raman spectroscopy, we observe an unusual phase transition between the nonpolar Cc̅c̅c̅ and the polar Cmc21 phases in the hybrid improper ferroelectric material Ca3Mn1.9Ti0.1O7. This phase transition is characterized by a highly asymmetric behavior of phase coexistence. While there is a clear upper temperature boundary Tc of the phase coexistence of the Cc̅c̅c̅ and Cmc21 phases, there is no such boundary toward the low temperature side. 100-nm-sized islands of the nonpolar phase expand deep into the polar phase. These nonpolar inclusions within the polar phase may be the reason why the ferroelectric poling was so far observed at cryogenic temperatures only.[7] This behavior contrasts most proper and improper ferroelectrics, where the switching is easiest close to the Curie temperature.

Furthermore, the ferroelectric domains favor a counterintuitive formation of head-to-head and tail-to-tail boundaries even in the as-grown state. This typically avoided configuration is a source for charged domain walls with a conductivity substantially different from the bulk. The charged, possibly conductive domain walls in combination with the in-plane ferroelectricity and the layered structure of Ca3Mn1.9Ti0.1O7 make this compound very promising for the functionalization of ferroelectrics. In particular, a recent study showed that layered perovskite-type ferroelectrics can be switched fatigue free.[43]

Unlike other hybrid improper ferroelectrics, Ca3Mn1.9Ti0.1O7 also exhibits magnetic order. The combination of magnetism and uncommon ferroelectric behavior may open up perspectives for unusual magnetoelectric coupling phenomena in hybrid improper ferroelectrics. Just like the ferroelectric order, the magnetic order is linked to the tilts of the octahedra. Therefore, the magnetic domains must follow the same domain hierarchy as the ferroelectric domains—forming 90° walls with ferroelastic walls and magnetic 180° walls only interior ferroelastic domains.

4. Experimental Section

Ca3Mn1.9Ti0.1O7 crystals were grown by the floating-zone method as described elsewhere.[23] We perform SHG and RS experiments on a single-crystalline sample in near-normal or normal incidence to the optically flat cleavage planes, which lie orthogonal to the x axis, as confirmed by single-crystal X-ray diffraction.

For our SHG measurements, we used a Coherent Elite Duo laser system (central wavelength 800 nm, pulse width 125 fs, 8 mJ pulse energy, repetition rate 1 kHz) to pump an optical parametric amplifier, which, supplemented by frequency mixing stages, generates laser light between 0.41 and 4.96 eV. The polarization of the incident and the detected light was set by a half-wave plate and a Glan–Taylor prism, respectively. Long-pass filters were mounted in front of the sample to suppress higher harmonics generated in the optical components. Behind the sample, short-pass filters cut off the fundamental light. A photomultiplier tube detects the SHG light. Spectral resolution is provided by a monochromator. Alternatively, a long-working-distance microscope objective with a magnification of 20 and a liquid-nitrogen-cooled Jobin Yvon Back Illuminated Deep Depletion CCD camera were used to image the domain structure at a fixed photon energy with a spatial resolution of 1 μm. A heating plate and a self-made furnace based on resistive heating allowed for measurements above room temperature.

BiFeO3, charged domain walls are avoided because of the resulting Coulomb forces and the energetic costs for their screening. Hence, charged domain walls usually occur only through strain, in thin films, by poling or as slightly inclined walls.[2,36–38] In improper ferroelectrics, the tendency to avoid head-to-head and tail-to-tail walls is less dominant.[4,6,9,39,40] Hybrid improper ferroelectrics further detach from this guideline. In the related compounds (Ca,Sr)3Ti2O7, the Coulomb forces appear insignificant with domain walls forming arbitrarily angles of 0°, 45°, 90°, 135°, etc. with the polarization to avoid distortions of the octahedra. Ca3Mn1.9Ti0.1O7 even goes to the extreme and prefers a domain configuration with charged head-to-head (90°) and tail-to-tail walls (270°) in the as-grown state.

The explicit preference for the ferroelectric head-to-head and tail-to-tail walls is likely linked to the layered structure. For instance, out-of-phase boundaries that are structural defects inherent to the layered perovskite-type materials lead to charge accumulations as reported for Aurivillius-type compounds.[45] The stabilization of head-to-head and tail-to-tail walls may compensate for these defects and be energetically favorable despite their nominally charged character.
An inVia Renishaw Reflex Raman microscope in micro-Raman mode with a 633-nm He-Ne laser and a spectral cut-off of 70 cm⁻¹ was used. During the RS experiments, crystals were heated using a Linkam THMS600 stage. We limited the laser power to reduce the sample heating to ≤2 K. Intensities and frequencies of the phonon modes were obtained by fitting the Raman spectra with Lorentzian functions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors are grateful to J. Kreisel (University of Luxembourg) and I. Burgert and T. Keplinger (ETH Zurich) for allowing the use of Raman spectroscopy facilities. The authors thank T. Weber and the D-MATL X-Ray Service Platform for experimental support. This work was financially supported by SNSF (Grant No. 200021_178825/1) and European Research Council (Advanced Grant 694955-INSEETO). M.T. acknowledges financial support by the Swiss National Science Foundation under Project 200021_188414. A.S. acknowledges financial support through the SNF Ambizione PZ00P2_180035 grant. The work at Rutgers University was supported by the DOE under Grant No. DOE: DE-FG02-07ER46382. Open Access Funding provided by Eidgenössische Technische Hochschule Zurich.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
charged domain walls, hybrid improper ferroelectric, multiferroic, phase transition

Received: April 26, 2021
Revised: July 9, 2021
Published online: September 12, 2021

[1] D. Meier, J. Phys.: Condens. Matter 2015, 27, 463003.
[2] P. S. Bednyakov, B. I. Sturman, T. Sluka, A. K. Tagantsev, P. V. Yudin, npj Comput. Mater. 2018, 4, 65.
[3] M. Lilienblum, T. Lottermoser, S. Manz, S. M. Selbach, A. Cano, M. Fiebig, Nat. Phys. 2015, 11, 1070.
[4] D. Meier, J. Seidel, A. Cano, K. Delaney, Y. Kumagai, M. Mostovoy, N. A. Spaldin, R. Ramesh, M. Fiebig, Nat. Mater. 2012, 11, 284.
[5] T. Choi, Y. Horibe, H. T. Yi, Y. J. Choi, W. Wu, S.-W. Cheong, Nat. Mater. 2010, 9, 253.
[6] M. Matsubara, S. Manz, M. Mochizuki, T. Kubacka, A. Iyama, N. Aliouane, T. Kimura, S. L. Johnson, D. Meier, M. Fiebig, Science 2015, 348, 1112.
[7] D. Meier, M. Maringer, T. Lottermoser, P. Becker, L. Bohatý, M. Fiebig, Phys. Rev. Lett. 2009, 102, 107202.
[8] N. A. Benedek, C. J. Fennie, Phys. Rev. Lett. 2011, 106, 107204.
[9] Y. S. Oh, X. Luo, F.-T. Huang, Y. Wang, S.-W. Cheong, Nat. Mater. 2015, 14, 407.
[10] F. Pomiro, C. Ablitt, N. C. Bristowe, A. A. Mostofí, C. Won, S.-W. Cheong, M. S. Senn, Phys. Rev. B 2020, 102, 014101.
[11] M. S. Senn, A. Bombardi, C. A. Murray, C. Vecchini, A. Scherillo, X. Luo, S.-W. Cheong, Phys. Rev. Lett. 2015, 114, 035701.
[12] M. S. Senn, C. A. Murray, X. Luo, L. Wang, F.-T. Huang, S.-W. Cheong, A. Bombardi, A. A. Mostofí, N. C. Bristowe, J. Am. Chem. Soc. 2016, 138, 5479.
[13] F.-T. Huang, B. Gao, J.-W. Kim, X. Luo, Y. Wang, M.-W. Chu, C.-K. Chang, H.-S. Sheu, S.-W. Cheong, npj Quantum Mater. 2016, 1, 16017.
[14] M. Kratochvílova, F.-T. Huang, M.-T. F. Diaz, M. Klicpera, S. J. Day, S. P. Thompson, Y.-S. Oh, B. Gao, S.-W. Cheong, J.-C. Park, J. Appl. Phys. 2019, 125, 244102.
[15] M. V. Lobanov, M. Greenblatt, E. a. N. Caspi, J. D. Jorgensen, D. V. Sheptyakov, B. H. Toby, C. E. Botez, P. W. Stephens, J. Phys.: Condens. Matter 2004, 16, 5339.
[16] F. T. Huang, F. Xue, B. Gao, L. H. Wang, X. Luo, W. Cai, X. Z. Lu, J. M. Rondinelli, L. Q. Chen, S. W. Cheong, Nat. Commun. 2016, 7, 11602.
[17] M. Liu, Y. Zhang, L.-F. Lin, L. Lin, S. Yang, X. Li, Y. Wang, S. Li, Z. Yan, X. Wang, X.-G. Li, S. Dong, J.-M. Liu, Appl. Phys. Lett. 2018, 113, 022902.
[18] F. Ye, J. Wang, J. Sheng, C. Hoffmann, T. Gu, H. J. Xiang, W. Tian, J. J. Molaison, A. M. dos Santos, M. Matsuda, B. C. Chakoumakos, J. A. Fernandez-Baca, X. Tong, B. Gao, J. W. Kim, S.-W. Cheong, Phys. Rev. B 2018, 97, 041112.
[19] T. Lottermoser, D. Meier, R. V. Pisarev, M. Fiebig, Phys. Rev. B 2009, 80, 100101.
[20] D. Meier, N. Leo, G. Yuan, T. Lottermoser, M. Fiebig, P. Becker, L. Bohatý, Phys. Rev. B 2010, 82, 155112.
[21] J. F. Scott, Rev. Mod. Phys. 1974, 46, 83.
[22] M. C. Weber, M. Guennou, N. Díx, D. Pesquera, F. Sánchez, G. Herranz, J. Fontcuberta, L. López-Conesa, S. Estrade, F. Peiró, J. Íñiguez, J. Kreisel, Phys. Rev. B 2016, 94, 014118.
[23] B. Gao, F.-T. Huang, Y. Wang, J.-W. Kim, L. Wang, S.-J. Lim, S.-W. Cheong, Appl. Phys. Lett. 2017, 110, 222906.
[24] A. M. Glazer, Acta Crystallogr. B 1972, 28, 3384.
[25] O. N. Shebanova, P. Lazor, J. Raman Spectrosc. 2003, 34, 845.
[26] A. Glamazda, D. Wulfertding, P. Lemmens, B. Gao, S.-W. Cheong, K.-Y. Choi, Phys. Rev. B 2018, 97, 094104.
[27] W. Hayes, R. Loudon, Scattering of Light by Crystals, John Wiley & Sons, New York 1978.
[28] M. C. Weber, M. Guennou, H. J. Zhao, J. Íñiguez, R. Vilarinho, A. Almeida, J. A. Moreira, J. Kreisel, Phys. Rev. B 2016, 94, 214103.
[29] M. Guennou, P. Bouvier, B. Krikler, J. Kreisel, R. Haumont, G. Garbarino, Phys. Rev. B 2010, 82, 134101.
[30] K. Poepplmeier, M. Leonowicz, J. Scanlon, J. Longo, W. Yelon, J. Solid State Chem. 1982, 43, 71.
[31] M. V. Abrashev, J. Bäckström, L. Börjesson, V. N. Popov, R. A. Chakalov, N. Kolev, R.-L. Meng, M. N. Iliev, Phys. Rev. B 2002, 65, 184301.
[32] A. von Hippel, Rev. Mod. Phys. 1950, 22, 221.
[33] K. J. Choi, M. Biegsals, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schom, C. B. Eom, Science 2004, 306, 1005.
[34] M. Fiebig, D. Fröhlich, T. Lottermoser, M. Maat, Phys. Rev. B 2002, 66, 144102.
[35] M. H. Lee, C.-P. Chang, F.-T. Huang, G. Y. Guo, B. Gao, C. H. Chen, S.-W. Cheong, M.-W. Chu, Phys. Rev. Lett. 2017, 119, 157601.
[36] M. Schröder, A. Haußmann, A. Thiessen, E. Soergel, T. Woike, L. M. Eng, Adv. Funct. Mater. 2012, 22, 3936.
[37] J. Seidel, L. W. Martin, Q. He, Q. Zhan, Y.-H. Chu, A. Rother, M. E. Hawkridge, P. Maksymovych, P. Yu, M. Gajek,
N. Balke, S. V. Kalinin, S. Gemming, F. Wang, G. Catalan, J. F. Scott, N. A. Spaldin, J. Orenstein, R. Ramesh, Nat. Mater. 2009, 8, 229.

[38] C.-L. Jia, S.-B. Mi, K. Urban, I. Vrejoiu, M. Alexe, D. Hesse, Nat. Mater. 2008, 7, 57.

[39] P. Chu, Y. L. Wang, L. Lin, S. Dong, J. M. Liu, IEEE Trans. Magn. 2013, 49, 3117.

[40] N. Leo, A. Bergman, A. Cano, N. Poudel, B. Lorenz, M. Fiebig, D. Meier, Nat. Commun. 2015, 6, 6661.

[41] M. Campanini, M. Trassin, C. Ederer, R. Erni, M. D. Rossell, ACS Appl. Electron. Mater. 2019, 1, 1019.

[42] E. Gradauskaite, M. Campanini, B. Biswas, C. W. Schneider, M. Fiebig, M. D. Rossell, M. Trassin, Adv. Mater. Interfaces 2020, 7, 2000202.