Pressure-induced large enhancement of Néel temperature and electric polarization in the hexagonal multiferroic \( \text{Lu}_{0.5}\text{Sc}_{0.5}\text{FeO}_3 \)

Fengliang Liu,1,2 Changsong Xu,3 Shoudong Shen,1 Nana Li,2 Hangwen Guo,4,5 Xujie Lu,2 Hongjun Xiang,1,5 L. Bellaiche,3 Jun Zhao,4 Liteng Yin,1,4,5 Wenge Yang,2,* Wenbin Wang,4,5,† and Jian Shen1,4,5

1State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China
2Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China
3Physics Department and Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville, Arkansas 72701, USA
4Institute for Nanoelectronic Devices and Quantum Computing, Fudan University, Shanghai 200433, China
5Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China

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Hexagonal ferrites (\( h\)-FeO\(_3\)) have attracted great attention for their high ferroelectric transition temperature, strong magnetoelectric couplings, and tunable Néel temperature (\( T_N \)) and electric polarization. While introducing structural distortion has been previously found to be effective to raise \( T_N \) and polarization in \( h\)-FeO\(_3\), it is generally difficult to create sizable structural distortion by common approaches including substrate-induced epitaxial strain and chemical doping. Here, we use high-pressure x-ray-diffraction measurements to show that pressure can generate large structural distortion and \( R \)-layer displacement of \( h\)-FeO\(_3\), resulting with dramatically enhancement of polarization and \( T_N \). Density-functional theory calculations reveal that the enlarged \( c/a \) ratio results in an \( \sim 70 \text{ K} \) increase of \( T_N \) along with a significant enhancement of ferroelectric polarization. Our results suggest that pressure is effective to tune structural distortions and related multiferroicity of the \( h\)-FeO\(_3\) system, making \( h\)-FeO\(_3\) a promising material for spintronic applications.

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Recently, multiferroicity of the hexagonal \( R\text{MO}_3 \) (\( h\)-RMO\(_3\)) with \( R = \text{Y}, \text{Sc}, \) rare-earth \( \text{Lu-Dy} \) and \( M = \text{Fe, Mn} \) materials has attracted great interest [1–3], especially for hexagonal \( R\text{FeO}_3 \) (\( h\)-RFeO\(_3\)) that have relatively high magnetic transition temperatures [4–9]. The coexisting spontaneous electric polarization and magnetization, along with the spin reorientation transition, render \( h\)-RFeO\(_3\) compounds promising materials for multiferroic applications. In the \( h\)-RFeO\(_3\) family, LuFeO\(_3\) has the highest Néel temperature \( (T_N) \) of 147 K [5–9], which is still too low for room-temperature spintronic applications.

Numerous approaches have been pursued to enhance \( T_N \) [9,10]. In particular, it was proposed that increasing \( c/a \) ratio is an effective way to increase \( T_N \) [10,11]. As a matter of fact, increasing the \( c/a \) ratio in \( h\)-RMO\(_3\) system results in a large structural distortion that enhances the superexchange interaction between transition-metal atoms (Fe or Mn), which is beneficial for high magnetic transition temperature [10,11]. For instance, partial substitution of Mn atoms by Fe atoms in \( h\)-LuMnO\(_3\) leads to an increase of the \( c/a \) ratio from 1.885 up to 1.925 and yields an increase of \( T_N \) from 100 to 130 K [10].

Moreover, an enlarged \( c/a \) ratio and structural distortion is closely related to an enhancement of ferroelectric polarization in \( h\)-RFeO\(_3\), which arises from the displacements of \( R \)-atom \((R = \text{Y}, \text{Sc, rare-earth Lu-Dy})\) layers and tilting in FeO\(_3\) bipyramid [11]. As reported by previous first-principles studies, applying chemical or hydrostatic pressure to hexagonal rare-earth ferrites leads to an enhanced “\( K_3\)”-mode distortion, which further results in the increase of the \( c/a \) ratio, as well as enhanced ferroelectric polarization [12]. It is highly desirable to experimentally achieve largest possible \( c/a \) ratio and thus the highest temperature at which multiferroicity can occur in \( h\)-RMO\(_3\) materials.

Several methods have been utilized to tune the structure of \( h\)-RMO\(_3\) systems. The substrate-induced epitaxial strain has been proven to have limited effects, due to the weak interfacial bonding between substrates and layered \( h\)-RMO\(_3\) [9]. Chemical doping appears to be effective in increasing the \( c/a \) ratio of \( h\)-RMO\(_3\), ranging from 1.885 in \( h\)-LuMnO\(_3\) up to 1.997 in \( h\)-Lu\(_{0.5}\text{Sc}_{0.5}\text{FeO}_3 \) (\( h\)-LSFO) [10]. The highest \( T_N \) in the \( h\)-RMO\(_3\) family has been achieved in \( h\)-LSFO, which is 172 K [10]. In the present work, we show experimentally that hydrostatic pressure can further dramatically increase the \( T_N \) and ferroelectric polarization in \( h\)-LSFO system. \textit{In situ} high-pressure powder x-ray-diffraction (XRD) measurements unveil that (i) the hexagonal crystal structure of \( h\)-LSFO is stable up to 35.1 GPa and (ii) The hydrostatic pressure can not only increase the \( c/a \) ratio, but also increases the displacement in \( R \)-layer atoms and the tilting angle of the FeO\(_3\) trigonal bipyramid, which is the main reason for the dramatically enhanced polarization and \( T_N \). Density-functional theory (DFT) calculations show that such distortions yield a large increase in \( T_N \) and ferroelectric polarization [13]. Our study of the pressure effects on \( h\)-LSFO thus provides a powerful solution
FIG. 1. Structural information of pressurized hexagonal Lu$_{0.5}$Sc$_{0.5}$FeO$_3$, revealed from high pressure XRD. (a) X-ray diffraction patterns collected during the compressing process, with the incident x-ray wavelength of 0.3263 Å. (b) GSAS refinement of XRD patterns at pressures 2.9, 18.7, and 35.1 GPa. (c) Lattice constant $a$ (red) and $c$ (blue) evolutions under pressure, with the measured data in dots, and the dashed black lines are the fitted curves. The measured lattice constants ($a = 5.8735$ Å, $c = 11.7098$ Å) at ambient conditions are also shown here. (d) $c/a$ ratio vs pressure.

for tuning structural and physical properties of $h$-RMO$_3$ materials.

I. METHODS

The hexagonal Lu$_{0.5}$Sc$_{0.5}$FeO$_3$ ($h$-LSFO) single crystal was grown using the floating-zone technique. First, polycrystalline samples were prepared by a standard solid-state reaction technique. Lu$_2$O$_3$ was heated at 800 °C for 10 h before use. Stoichiometric ratios of Lu$_2$O$_3$, Sc$_2$O$_3$, and Fe$_2$O$_3$ were mixed and thoroughly ground in a mortar. The mixture was pelletized and then sintered at 1350 °C for 2 d. The resulting powder was packed into latex tubes and pressed into rods of ~5 mm in diameter and ~12 cm in length under ~300-MPa hydrostatic pressure. The obtained rods were sintered at 1380 °C for 10 h in a vertical furnace. A single crystal of Lu$_{0.5}$Sc$_{0.5}$FeO$_3$ was grown in flowing O$_2$ atmosphere at a pressure of 40 bar using a vertical optical image furnace (model HKZ, SciDre, GmbH, Dresden) equipped with a 3-kW Xenon arc lamp. During growth, the gas flow rate was 0.1 L/min and the upper and lower rods were counter-rotated at 23 and 29 rpm, respectively, to maintain a homogeneous melt. The crystal was grown at a speed of 1 mm/h.

Powder lab-based x-ray diffraction measurements were performed on the well-crystallized compound on a Bruker D8 Discover diffractometer ($\lambda = 1.5405$ Å) at ambient conditions. Rietveld refinement was conducted on the XRD pattern collected during the compressing process with the incident x-ray wavelength of 0.3263 Å. (b) GSAS refinement of XRD patterns at pressures 2.9, 18.7, and 35.1 GPa. (c) Lattice constant $a$ (red) and $c$ (blue) evolutions under pressure, with the measured data in dots, and the dashed black lines are the fitted curves. The measured lattice constants ($a = 5.8735$ Å, $c = 11.7098$ Å) at ambient conditions are also shown here. (d) $c/a$ ratio vs pressure.

High-pressure synchrotron powder XRD measurements were conducted at room temperature at sector 16BM-D, the Advanced Photon Source (APS), Argonne National Lab (ANL) by using the monochromatic incident x-ray with the wavelength of 0.3263 Å. The powder sample was first grinded into micrometer size, and then loaded into the sample chamber shaped by rhenium gasket in the Mao-Bell diamond-anvil cell [16]. Silicone oil was used as the pressure-transmission medium for providing better hydrostatic pressure condition [17], and ruby fluorescence was used to determine the hydrostatic pressure in the sample chamber [18]. The high-pressure XRD data were collected with compression range from 0.2 up to 35.1 GPa, and decompression from 35.1 down to 0.1 GPa. The diffraction image was collected by a two-dimensional x-ray detector (MAR345) at each pressure point. Each diffraction pattern was converted into one-dimensional raw data by using the DIOPTAS software [19]. Rietveld refinement [20] analysis was performed on each pattern to get the structure information by using the GSAS software [21]. The lattice parameters were collected from GSAS refinement.

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [22]. The generalized gradient approximation and the Perdew-Burke-Ernzerhof functions for solids [23] were employed. A 500-eV plane-wave cutoff energy was used for all calculations along with the projector-augmented wave method [24], with the Lu (5p, 5d, and 6s), Sc (3p, 3d, and 4s), Fe (3d and 4s), and O (2s and 2p) electrons being treated as valence electrons. A
FIG. 2. DFT calculation results of some properties in pressurized \( h \)-LSFO. (a) 3D view of the crystal structure for the \( P\bar{6}mc \) hexagonal space group. The red arrows are related to the tilting of \( \text{FeO}_3 \) bipyramids associated with the \( K_3 \) mode, while the black arrows indicate the displacement of the Lu/Sc atoms within this \( K_3 \) mode. The tilting angle of \( \text{FeO}_3 \) bipyramids is denoted as \( \theta \). (b) High-pressure evolution of the displacement of Lu/Sc atoms in the Lu(Sc)-O layers and (c) tilting angle in the FeO\(_3\) bipyramids, with the lattice parameters obtained from XRD results, while the atomic positions are optimized until all Hellman-Feynman forces are smaller than 0.01 eV/Å on each ion. Inset of (b), (c), experiment results of displacement (b) and tilting angle (c) extracted from GSAS refinement. The values along the \( x \) axis represent the pressure, labeled as \( P \) (GPa). The values along the \( y \) axis in the inset represent the experimental value of the relative [value(high pressure)-value(ambient)] displacement [(b), marked as \( \Delta d \)] and tilting angle [(c), marked as \( \Delta \theta \)]. The DFT results and the GSAS refinement results both show consistent trends of pressure-induced enhancement of displacement and tilting angle. (d) Predicted electrical polarization vs pressure (inset, polarization vs. \( c/a \) ratio).

The ambient XRD measurements show that LSFO crystallizes in the \( P\bar{6}mc \) space group (see Sec. S1 and Fig. S1 in Supplemental Material [27]) as reported before [25,28,29]. Figure 1(a) shows the diffraction patterns of \( h \)-LSFO cells. The experimental lattice parameters extracted from high-pressure XRD measurement at each pressure point are adopted, while the atomic positions are optimized until all Hellman-Feynman forces are smaller than 0.01 eV/Å on each ion. Particularly, we worked on a specific (Lu, Sc) configuration that has the highest reported \( c/a \) ratio to 2.015 [Fig. 1(c)]. Note that this is among the highest reported \( c/a \) ratios among the hexagonal rare-earth ferrites [9,10]. The large pressure-induced \( c/a \) ratio may be attributed to several factors: (1) The \( Fe \ 3d-O \ 2p \) hybridization prefers to be along the \( c \) axis, and therefore the out-of-plane lattice constant is much more stable against pressure [30]. (2) Structural distortion of \( \text{FeO}_3 \) bipyramids may also play a significant role, as the tilting angle \( [\theta \ \text{angle demonstrated in Fig. 2(a)] increases under pressure, which is discussed in detail in Sec. S3 of Supplemental Material [27].

Previous studies demonstrated that hexagonal \( \text{Lu}_5\text{Sc}_0\text{Fe}_3 \) exhibits an electric polarization that is induced by geometrical displacements [25,29], which originates from the buckling of Lu/Sc atoms (one up/two down) and the tilting of \( \text{FeO}_3 \) bipyramids associated with the so-called \( K_3 \) mode. Such \( K_3 \) mode is a zone-boundary mode located at \( \frac{2\pi}{a} (\frac{1}{2}, \frac{1}{2}, 0) \), where the atomic displacement of \( \text{FeO}_3 \) include the two apical oxygen atoms with opposite

typical effective Hubbard \( U = 4 \) eV was also used to treat the localized \( 3d \) electrons of Fe ions [25]. Moreover, a \( 5 \times 5 \times 3 \) \( k \)-point mesh was employed for the 30-atom \( h \)-LSFO cells. The experimental lattice parameters extracted from high-pressure XRD measurement at each pressure point are adopted, while the atomic positions are optimized until all Hellman-Feynman forces are smaller than 0.01 eV/Å on each ion. Particularly, we worked on a specific (Lu, Sc) configuration that has the displacement patterns of \( \text{(Lu}_{\text{up}}, \text{Lu}_{\text{down}}, \text{Sc}_{\text{down}}) \) in one layer and \( \text{(Lu}_{\text{up}}, \text{Sc}_{\text{down}}, \text{Sc}_{\text{down}}) \) in the other layer. Such configuration has been proven to have the lowest energy among five considered possibilities in a previous work [25]. Polarizations are calculated using the Berry phase method [26].

II. RESULTS

The ambient XRD measurements show that LSFO crystallizes in the \( P\bar{6}mc \) space group (see Sec. S1 and Fig. S1 in Supplemental Material [27]) as reported before [25,28,29]. Figure 1(a) shows the diffraction patterns of \( h \)-LSFO under pressure, evidencing that the crystal structure is robust up to 35.1 GPa (see Sec. S2 in Supplemental Material [27] for detailed discussion of phase stability of \( \phi \) phase and \( h \) phase of \( \text{RFeO}_3 \)). Upon increasing pressure, all the Bragg diffraction peaks move towards higher angles, indicating the shrinkage of lattice constants under pressure [Fig. 1(a)]. Rietveld refinement reveals that each XRD pattern within the pressure range of 35.1 GPa can be well indexed by the original hexagonal structure \( P\bar{6}cm \), as shown in Fig. 1(b), which further demonstrates that the Y\( \text{MnO}_3 \)-type hexagonal structure is preserved under pressure up to 35.1 GPa.

Rietveld refinement analysis further reveals that \( h \)-LSFO is nonuniformly compressed along the \( a \)- and \( c \)-axes directions. As shown in Fig. 1(c), the lattice constant \( a \) decreases by 4.8% from 5.8735 to 5.5915 Å while the lattice constant \( c \) decreases by 3.8% from 11.7098 to 11.2683 Å, resulting in an increase of the \( c/a \) ratio to 2.015 [Fig. 1(d)]. Note that this is among the highest reported \( c/a \) ratios among the hexagonal rare-earth ferrites [9,10]. The large pressure-induced \( c/a \) ratio may be attributed to several factors: (1) The \( Fe \ 3d-O \ 2p \) hybridization prefers to be along the \( c \) axis, and therefore the out-of-plane lattice constant is much more stable against pressure [30]. (2) Structural distortion of \( \text{FeO}_3 \) bipyramids may also play a significant role, as the tilting angle \( [\theta \ \text{angle demonstrated in Fig. 2(a)] increases under pressure, which is discussed in detail in Sec. S3 of Supplemental Material [27].

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FIG. 3. Density-functional theory calculation results of the magnetic transition temperature \( T_N \) in \( h\)-RFeO\(_3\) under chemical doping or hydrostatic pressure. (a) The nearest-neighbor (NN) superexchange interactions between in-plane Fe atoms \((J)\), the spin structure used for the calculation is consistent with Refs. \([10,34]\). (b) \( T_N \) vs the \( c/a \) ratio. Calculated \( T_N \) are shown via blue dots for hexagonal HoFeO\(_3\) (HFO), TmFeO\(_3\) (TFO), LuFeO\(_3\) (LFO), and \( \text{Lu}_{5}\text{Sc}_{2}\text{FeO}_3 \) (LSFO) using the experimental lattice parameters for HFO \([4]\), TFO \([35]\), LFO \([36]\) as inputs, while experimental results of \( T_N \) are shown via red dots for HFO \([4]\), LFO \([5–8]\), and LSFO (our experiment result). The calculated \( T_N \) of hexagonal \( \text{Lu}_{5}\text{Sc}_{2}\text{FeO}_3 \) under pressure is also displayed via magenta dots. (c) The calculated \( T_N \) vs tilting angle for \( h\)-RFeO\(_3\) (blue dots) and \( h\)-\( \text{Lu}_{5}\text{Sc}_{2}\text{FeO}_3 \) (magenta dots), with the tilting angle vs \( c/a \) ratio being shown in the inset.

Directions in the \( ab \) plane, and the three equatorial oxygen atoms with two up/one down along the \( c \) direction \([11,31]\), which is indicated by the red arrows in Fig. 2(a). According to previous studies of RFeO\(_3\) and \( R\text{MnO}_3 \) \([12,32]\), it softens under pressure. Here, the GSAS (General Structure Analysis System software) refinement on the XRD patterns further shows that the LuSc layers prefer to buckle under pressure, leading to a pressure-induced displacement enhancement [see inset of Fig. 2(b)]. Moreover, the GSAS refinement also suggests that the \( \theta \) tilting angle [Fig. 2(a)] of nearest-neighbor interlayer FeO layers increases under pressure [see inset of Fig. 2(c)]. Therefore, the XRD data clearly indicate a pressure-induced enhancement of electric polarization in \( h\)-LSFO, as a result of this increase of the tilting angle and displacement.

DFT calculations are performed here to simulate the hydrostatic pressure effects on structural properties and electric polarization of \( h\)-LSFO. Figure 2(a) schematizes the relative displacements of Lu/Sc layers and the tilting of FeO\(_5\) bipyramids, which constitute the so-called \( K_3 \) mode. As pressure is increased up to 35.1 GPa, the displacement of Lu/Sc layers increases by 11% [Fig. 2(b)], and the tilting angle of FeO\(_5\) bipyramids is enhanced by 34% [Fig. 2(c)] in \( h\)-LSFO, as found from our DFT calculations. These results agree well with the GSAS refinement results of the XRD measurements (inset of Figs. 2(b) and 2(c); see Sec. S3 of Supplemental Material for details [27]). Such enhancement indicates that the strength of \( K_3 \) mode increases with increasing pressure, which is consistent with previous calculations on RFeO\(_3\) and \( R\text{MnO}_3 \) \([12,32]\). The polarization, which is coupled with the \( K_3 \) mode, is determined to increase accordingly by 23%, from 12.0 \( \mu \)C/cm\(^2\) at ambient pressure up to 14.8 \( \mu \)C/cm\(^2\) at 35.1 GPa [Fig. 2(d)]. Such pressure-induced polarization enhancement originates from the improper nature of the ferroelectricity in hexagonal \( \text{YMnO}_3\)-type ferroelectrics. Therefore, in hexagonal ferrites and other improper ferroelectrics, the pressure can not only increase the \( c/a \) ratio, but also increases the displacement in \( R \)-layer atoms and the tilting angle of the FeO\(_3\) trigonal bipyramid, which is the main reason for the dramatically enhanced polarization.

Besides the electric polarization, the evolution of \( T_N \) of \( h\)-LSFO under pressure is also calculated by DFT calculations and mean-field approximation. We adopt here the magnetic Hamiltonian \( H = \sum_i \sum_j J_{ij} S_i \cdot S_j \), where the summation runs over all nearest-neighbor Fe-Fe pairs. The interlayer couplings are neglected, since previous studies show that they are much weaker than intralayer couplings \([25]\). The coupling coefficient, \( J \), can be extracted from the total energies of ferromagnetic and antiferromagnetic configurations. \( T_N \) can then be estimated using the equation \( T_N = \frac{2J \langle S \rangle}{k_B S} \), where \( k_B \) is the Boltzmann constant, \( S = 5/2 \) is the spin quantum number of Fe\(^{3+}\), and \( g = 6 \) is the number of the nearest neighbors \([33]\). Note that \( J \) parameters under all pressures are rescaled by the same constant, which ensures the predicted \( T_N \) of the hexagonal LuFeO\(_3\) to be consistent with the experimental value \([5–8]\). In addition, the spin structure used in the DFT calculation is shown in Fig. 3(a) and is consistent with the previous reported experiment results \([10,34]\). As shown in Fig. 3(b), the predicted \( T_N \) of the \( h\)-LSFO is 160 K at ambient pressure, which is quite close to our measured 167 K, testifying the accuracy of our calculations (once adopting the aforementioned rescaling). The calculated \( T_N \) increases monotonically with increasing pressure and reaches 228 K at 35.1 GPa, which is nearly 70 K higher than \( T_N \) at ambient condition. Moreover, Fig. 3(b) also shows that pressure has a much larger effect on \( T_N \) than chemical doping since the pressure-induced slope of \( T_N \) with increasing \( c/a \) ratio [the magenta dots and lines represent the calculated \( T_N \) of pressurized \( h\)-LSFO in Fig. 3(b)] is over 6 times larger than that induced by chemical doping [see Fig. 3(b), where the blue dots represent the calculated \( T_N \) of \( h\)-RFeO\(_3\) but for which the lattice parameters are extracted from measurements \([4,35,36]\) while the red dots display experimental results \([4–8]\)]. The dramatic enhancement of \( T_N \) can be understood from the analysis of structural distortion and tilting angle of the FeO\(_5\) bipyramids. As pressure increases to 35.1 GPa, the
calculated tilting angle increases from 5.3° to 7.1° for h-LSFO [Fig. 2(c)], which is over 6 times larger than the increase of tilting angle induced by chemical doping [from 5.1° for TmFeO$_3$ to 5.3° for h-LSFO at ambient pressure, as shown in the inset of Fig. 3(c)]. As a summary of Fig. 3, it can be intuitively figured out that instead of increasing the c/a ratio, the remarkably enhanced tilting angle under pressure does matter for the dramatically $T_N$ enhancement among the hexagonal ferrites.

We now turn to discuss the correlation between the enhanced $T_N$ of h-LSFO and the structural distortion revealed by both DFT calculations and XRD measurements. As pressure increases, the distances between Fe atoms and the bond length between Fe and O atoms both decrease (see Fig. S2 [27]), leading to a stronger exchange interaction, and thus giving rise to an enhanced $T_N$. Besides, as pressure increases, the $K_3$ distortion is also enhanced, contributing to an enhancement of magnetic properties in h-LSFO [Fig. 3(c)], which is in line with the theory analysis proposed by Das et al. in hexagonal RMO$_3$ systems [11]. In addition, Sinha et al. also reported that $T_N$ can be increased by enhancing structural distortion in hexagonal ScFeO$_3$ films grown on Al$_2$O$_3$ (001) substrate [37]. Moreover, the structural distortion can be much more dramatically enhanced at the case of applying hydrostatic pressure rather than the chemical doping [Fig. 3(c)] or strains arising from substrates, leading to a much more remarkable enhancement of $T_N$. In fact, the effectiveness of pressure to increase $T_N$ reflects the fact that pressure has a more pronounced effect on structural distortion than previous methods (strain and chemical doping). As the crystal structure will go back to the ambient phase (see Fig. S3 [27]), and thus the $T_N$ is also expected to go back to its value in the ambient phase. Therefore, further investigation of searching a quenchable high-pressure hexagonal phase with enhanced structural distortion and reduced Fe-Fe distance is also deserved to be done among the hexagonal ferrites and systems alike.

In conclusion, we report that, and explain why, pressure can be an effective method to enhance multiferroicity of hexagonal ferrites. In particular, pressure can lead to a large increase of $T_N$ as well as an enhancement of the polarization in hexagonal Lu$_{0.5}$Sc$_{0.5}$FeO$_3$. According to our calculation, similar behaviors are also expected in other hexagonal systems such as RFeO$_3$ ($R = Y$, Sc, rare-earth Lu-Dy), and this behavior should also be valid for other hexagonal ferrites and other improper ferroelectrics.

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[13] Note that the fully optimized $c/a$ ratio from simulations follows the same trend with our experimental one that the $c/a$ ratio increases when increasing pressure.