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Epitaxial growth of hexagonal GdFeO₃ thin films with magnetic order by pulsed laser deposition

Jun Kasahara¹, Tsukasa Katayama^{2,3*}, Akira Chikamatsu¹, Yosuke Hamasaki⁴ and Tetsuya Hasegawa¹

¹Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

²Research Institute for Electronic Science, Hokkaido University, N20W10, Kita, Sapporo 001-0020, Japan.

³JST-PRESTO, Kawaguchi, Saitama 332-0012, Japan

⁴Department of Applied Physics, National Defense Academy, Yokosuka 239-8686, Japan

*Corresponding author: katayama@es.hokudai.ac.jp

Abstract

Hexagonal rare-earth iron oxides, h -RFeO₃, are promising multiferroic materials. The ferroic properties of h -RFeO₃ can be controlled by varying R . However, h -RFeO₃ exists in a metastable phase, resulting in a limit of available range of R . In this study, we fabricated h -GdFeO₃ phase via epitaxial stabilization. The h -GdFeO₃ epitaxial film with c -axis orientation was deposited on an indium tin oxide (ITO(111)) layer as the bottom electrode via pulsed laser deposition. The metastable hexagonal phase was obtained in a narrow range of deposition parameters. High-crystalline h -GdFeO₃ film was obtained at substrate temperature of 780 °C and oxygen pressure of 13 Pa. The a -axis of the h -GdFeO₃ phase is parallel to the [11-2] directions of ITO(111) layer. The h -GdFeO₃ film exhibited weak ferromagnetism with a Néel temperature of 43 K, which was lower than that of the previously reported h -RFeO₃ films (R = Dy–Lu, Y and Sc) owing to the longer a -axis.

Keywords

Pulsed laser deposition; Gadolinium ferrite; Metal oxide; Thin film; Ferromagnetism; Multiferroics

Introduction

Rare-earth iron oxides ($R\text{FeO}_3$) exhibit fascinating electronic and electrochemical properties, such as water splitting photocatalysis [1], high oxygen ion conductivity [2], ferroelectricity [3-7], and magnetoelectric coupling [8,9]. Their properties can be customized by appropriately selecting the R^{3+} ion and crystal structure. The most stable structure of $R\text{FeO}_3$ is the orthorhombic (o -) perovskite phase comprising FeO_6 octahedra (Fig. 1(a)). o - $R\text{FeO}_3$ is a promising multiferroic material with strong magnetoelectric couplings [8,9]. For example, o - $\text{Dy}_{0.75}\text{Gd}_{0.25}\text{FeO}_3$ shows electric-field-induced generation and a reversal of a macroscopic ferromagnetic moment [10]. A ferroelectric phase can be induced by a magnetic field in o - DyFeO_3 [11]. However, the polarization of o - $R\text{FeO}_3$ induced by the magnetic field is small ($< 0.5 \mu\text{C}/\text{cm}^2$) and occurs only at low temperature ($< 10 \text{ K}$) [8-10]. Hexagonal (h -) $R\text{FeO}_3$ has been intensively studied as a promising multiferroic material (Fig. 1(b)) [11]. In contrast to o - $R\text{FeO}_3$, h - $R\text{FeO}_3$ exhibits large spontaneous polarization ($\sim 10 \mu\text{C}/\text{cm}^2$) along the c -axis, even at the room temperature [3,4]. In addition to the ferroelectricity, h - $R\text{FeO}_3$ exhibits weak ferromagnetism with a spontaneous magnetization along the c -axis [12,13].

The ferroelectric properties of h - $R\text{FeO}_3$ considerably depend on the ionic size of R^{3+} (r_R). For example, h - YbFeO_3 undergoes a temperature-induced transition between the two ferroelectric phases ($P6_3cm$, $P6_3mc$) [5], while only a $P6_3cm$ ferroelectric phase exists in h - LuFeO_3 [3]. On the other hand, antiferroelectric behavior can be observed when r_R becomes large [14]. The r_R value also affects the strength of the magnetic interaction in conjunction with a change in the Fe–O–Fe bond length in the a - b plane [15]. Thus, both magnetic and ferroelectric properties of h - $R\text{FeO}_3$ can be controlled by varying R ; thus, researchers have been conducting numerous studies to expand the available range of R . However, h - $R\text{FeO}_3$ exists in a metastable phase owing to the instability of the $3d_{z^2}$ orbital of high-

spin Fe^{3+} ($3d^5$) ions in the FeO_5 trigonal bipyramid. In particular, at large r_R , the $h\text{-RFeO}_3$ phase becomes unstable. Although $h\text{-GdFeO}_3$ ($h\text{-GFO}$) has not been synthesized till date, the synthesis of $h\text{-RFeO}_3$ with smaller r_R ($R = \text{Dy-Lu}$, Y and Sc) has already been reported [3-7,16,17].

One of the most promising methods to synthesize metastable $h\text{-RFeO}_3$ is by epitaxial thin-film growth. For practical application of $h\text{-RFeO}_3$ to multiferroic and/or ferroelectric devices, c -axis oriented $h\text{-RFeO}_3$ films must be grown on bottom electrodes. To date, three kinds of bottom electrodes have been used for the $h\text{-RFeO}_3$ films: $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ on $\text{SrTiO}_3(111)$ substrate (for $R = \text{Sc}$ [7]), Pt deposited on $\text{Al}_2\text{O}_3(001)$ substrate (for $R = \text{Y}$, Lu, Yb, Tm [3-6]), and indium tin oxide (ITO) on yttria-stabilized zirconia (YSZ(111)) substrate (for $R = \text{Dy}$ and Er [14,18]). Among them, ITO(111) on the YSZ(111) substrate (ITO(111)/YSZ(111)) demonstrates the best lattice matching to $h\text{-RFeO}_3$ with larger R [14]. Herein, we report the synthesis of $h\text{-GFO}$ epitaxial films on ITO(111)/YSZ(111) using pulsed laser deposition (PLD). High-quality single crystal $h\text{-GFO}$ films with c -axis orientation were synthesized by optimizing the substrate temperature (T_s) and oxygen pressure (P_{O_2}) during the deposition. The $h\text{-GFO}$ film exhibited weak ferromagnetism with a Néel temperature (T_N) of 43 K.

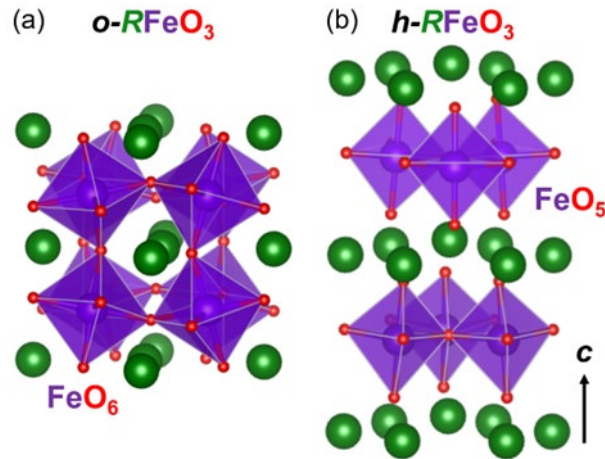


Figure 1. Crystal structure of (a) $o\text{-RFeO}_3$ and (b) $h\text{-RFeO}_3$.

Experimental

ITO(111) conductive layers and GFO films were deposited on the YSZ(111) substrate via PLD. As the PLD targets, 10 wt% SnO₂-doped In₂O₃ and *o*-GdFeO₃ ceramic pellets were used. During the PLD deposition, T_s and P_{O_2} were kept at 600 °C and 13 Pa for ITO, while they were kept at 600–780 °C and 7–27 Pa for GFO. KrF laser ($\lambda = 248$ nm) was used with a frequency of 5 Hz and laser energy of 4–5 J cm⁻² shot⁻¹ for both ITO and GFO layers. Thickness of the ITO and GFO layers were ~40 and 60–100 nm, respectively, which was measured by a stylus surface profiler. Before the film deposition, the YSZ substrates (purchased from K&R Creation. Co., Ltd., Japan) were ultrasonically cleaned with acetone and ethanol for 10 minutes each. The typical thickness of these GFO films was 70 nm. The crystal structures of the films were determined using high-resolution X-ray diffraction (XRD) with Cu- $K\alpha_1$ radiation (Bruker, D8 DISCOVER). Out-of-plane magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL).

Results and discussion

Figure 2(a) shows the out-of-plane 2θ - θ XRD patterns of the GFO films obtained at various T_s ($P_{O_2} = 7$ Pa). All the films showed ITO 222 diffraction peaks at $2\theta = 30.8^\circ$, confirming that the ITO(111) conductive layers were produced on the YSZ(111) substrates. At $T_s \leq 700$ °C, no peaks originating from *h*-GFO were detected. At a higher temperature, $T_s = 780$ °C, the *h*-GFO 002 diffraction peak was observed at 15.2° , although its intensity was weak, and the *o*-GFO 112 diffraction peak was observed at 32.9° . These results indicate that a high T_s is required for obtaining *h*-GFO.

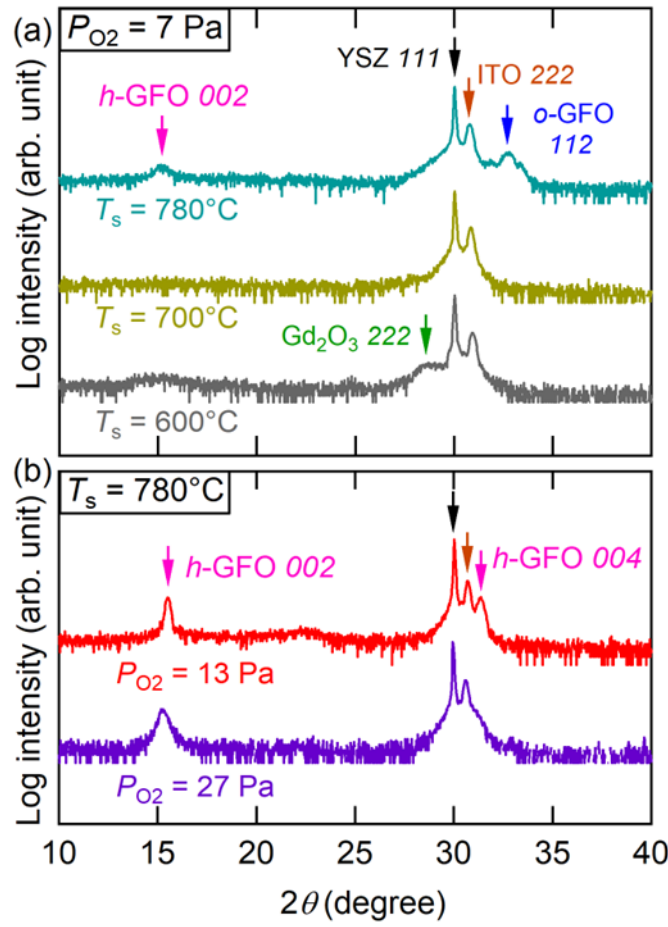


Figure 2. Out-of-plane 2θ - θ XRD patterns for the GFO films obtained (a) at various T_s ($P_{O_2} = 7$ Pa) and those obtained (b) at $P_{O_2} = 13$ Pa and 27 Pa ($T_s = 780$ °C).

Figure 2(b) shows the out-of-plane 2θ - θ XRD patterns of the GFO films obtained at $T_s = 780$ °C and $P_{O_2} = 13$ Pa and 27 Pa. At $P_{O_2} = 13$ Pa, the film showed h -GFO 002 and 004 diffraction peaks at 15.5° and 31.4° , respectively, without impurities such as o -GFO and Gd_2O_3 . At $P_{O_2} = 27$ Pa, these peaks were more broadened than those at $P_{O_2} = 13$ Pa. The crystal phases of the films as a function of T_s and P_{O_2} are summarized in Fig. 3, showing that high-quality c-axis-oriented h -GFO film was obtained in a narrow range of deposition parameters ($T_s = 780$ °C and $P_{O_2} = 13$ Pa).

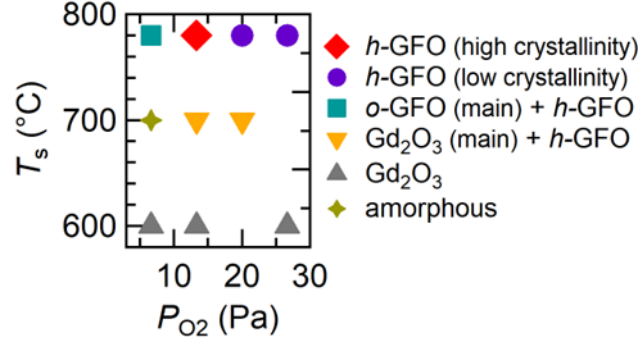


Figure 3. Crystal phases observed in the GFO films as a function of T_s and P_{O_2} .

To determine the in-plane orientation of the *h*-GFO phase, ϕ -scan measurements were performed for the optimized *h*-GFO film. Figure 4(a) shows the ϕ -scan pattern of the *h*-GFO film around the *h*-GFO {114}, ITO {440} and YSZ {220} diffraction peaks. The *h*-GFO {114} peaks had six-fold symmetry, reflecting the hexagonal structure of the *h*-GFO phase. The ϕ values of the ITO {440} and YSZ {220} peaks were the same as those of the *h*-GFO {114} peaks, indicating that the *a*-axis of the *h*-GFO phase is along the [11-2] directions of the ITO layer and YSZ substrate. From the 2θ values of the *h*-GFO 002, 004, and 114 diffraction peaks, the *a*- and *c*-axis lattice constants were calculated to be 6.36 and 11.35 Å, respectively.

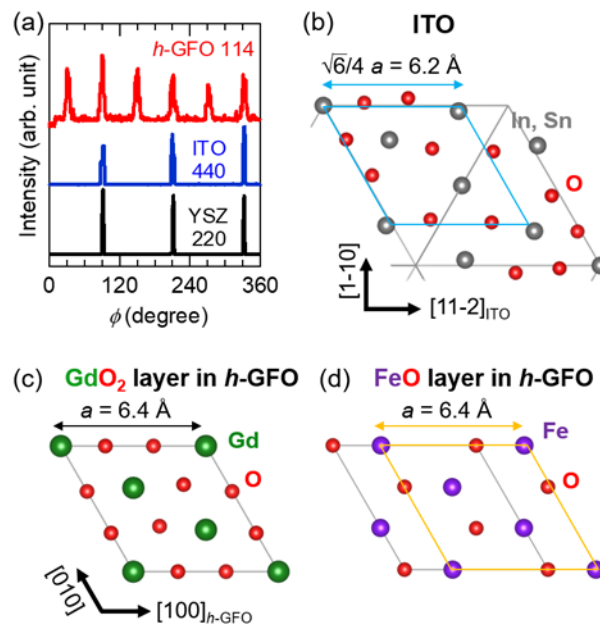


Figure 4. (a) ϕ -scan patterns of the h -GFO film. Plan-view ionic arrangement images for (b) one of the ITO(111) planes and (c) GdO₂ and (d) FeO layers in the h -GFO(001) film.

Figures 4(b-d) show the plane view ionic arrangements of the ITO conductive layer and h -GFO film. The cationic arrangement of the ITO layer is similar to those of both Gd and Fe in the h -GFO film (Fig. 4(c and d)). In contrast, the a value of the h -GFO film (6.4 Å) was 3.0% greater than the $\sqrt{6}/4$ a value of the ITO layer (6.2 Å). This suggests that the similarity of the in-plane ionic arrangements is more important for obtaining h -GFO rather than the lattice matching.

Finally, the magnetic properties of the h -GFO film were analyzed. Figure 5(a) shows the out-of-plane magnetization versus temperature (M - T) curve of the h -GFO film under a magnetic field (H) of 80 kA/m. At low T , M abruptly increased with decreasing T . The M - H curve at 5 K was a good fit with the Brillouin function, suggesting the existence of a paramagnetic component in the film. The h -GFO film has two types of magnetic moments: Fe³⁺ 3d and Gd³⁺ 4f spins. Since the magnetic interaction between the R ions is significantly weaker than the antiferromagnetic interaction between the Fe ions in h -RFeO₃ [3-6,14], it is natural to assume that the paramagnetic component originates from the Gd³⁺ ions. On the other hand, magnetic hysteresis loop was observed in the M - H curve at 20 K (Fig. 5(b)), indicating the weak ferromagnetism of the h -GFO film.

As shown in the inset of Fig. 5(a), the M - T curve shows a weak kink at 43 K. Similar kink structures have been observed in the M - T curves of other h -RFeO₃ thin films; the weak ferromagnetic to paramagnetic transition in these films has been attributed to the presence of the aforementioned kinks [3,10,14,15]. Accordingly, it was observed that the h -GFO film exhibited weak ferromagnetism with T_N of 43 K. Figure 5(c) shows the a -axis length dependence of T_N for various h -RFeO₃ [3-7,14,15,18,19]. The T_N values tend to decrease linearly with increasing a . This is derived from the reduction of the orbital overlap between the Fe ions in the a - b plane [15]. The (a , T_N) values of the h -GFO film primarily fall on the linear fitted line, thus confirming that the kink temperature in the M - T

curve corresponds to T_N . The T_N value of the h -GFO film is lower than those of the others, reflecting the longer a -axis length owing to the larger ionic radius of Gd^{3+} .

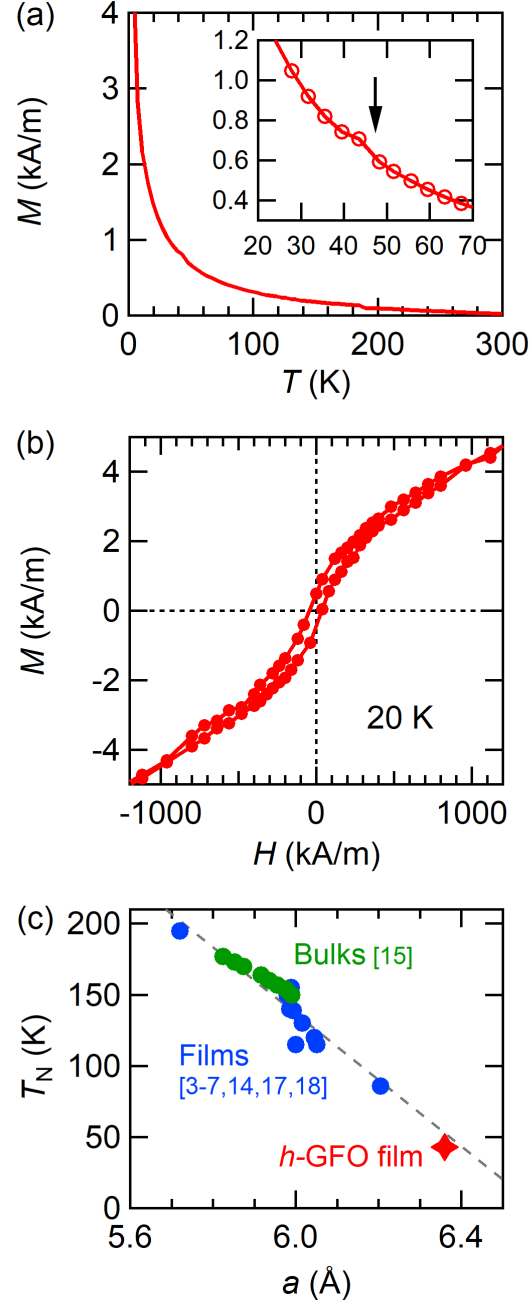


Figure 5. (a) M – T curve of the h -GFO film with H of 80 kA/m and (b) M – H curve at 20 K. (c) T_N of h -RFeO₃ as a function of a . The inset shows the magnified image at approximately 40 K.

Conclusion

In summary, we fabricated the *h*-GFO epitaxial film on the YSZ(111) substrate with an ITO conductive layer using a PLD method. The metastable hexagonal phase was obtained at $T_s = 780$ °C and $P_{O_2} = 13$ Pa. The [100] and [001] directions of the *h*-GFO phase are parallel to the [11-2] and [111] directions of the ITO layer and YSZ substrate, respectively. The *h*-GFO film exhibited weak ferromagnetism with a T_N of 43 K, which was lower than that of the previously reported *h*-RFeO₃ owing to the longer *a*-axis.

Acknowledgments

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References

- [1] K.M. Parida, K.H. Reddy, S. Martha, D.P. Das, N. Biswal, Fabrication of nanocrystalline LaFeO₃: An efficient sol–gel auto-combustion assisted visible light responsive photocatalyst for water decomposition, Int. J. Hydrog. Energy **35**, 12161 (2010). <https://doi.org/10.1016/j.ijhydene.2010.08.029>
- [2] A. J. Jacobson, Materials for Solid Oxide Fuel Cells, Chem. Mater. **22**, 660 (2010). <https://doi.org/10.1021/cm902640j>
- [3] Y. K. Jeong, J.-H. Lee, S.-J. Ahn, H. M. Jang, Epitaxially Constrained Hexagonal Ferroelectricity and Canted Triangular Spin Order in LuFeO₃ Thin Films, Chem. Mater. **24**, 2426 (2012). <https://doi.org/10.1021/cm300846j>
- [4] S.-J. Ahn, J.-H. Lee, Y. K. Jeong, E.-H. Na, Y. M. Koo, H. M. Jang, Artificially imposed hexagonal ferroelectricity in canted antiferromagnetic YFeO₃ epitaxial thin films, Mater. Chem. Phys. **138**, 929 (2013). <https://doi.org/10.1016/j.matchemphys.2012.12.086>

- [5] Y. K. Jeong, J. H. Lee, S. J. Ahn, S. W. Song, H. M. Jang, H. Choi, J. F. Scott, Structurally Tailored Hexagonal Ferroelectricity and Multiferroism in Epitaxial YbFeO₃ Thin-Film Heterostructures, *J. Am. Chem. Soc.* **134**, 1450 (2012). <https://doi.org/10.1021/ja210341b>
- [6] S. J. Ahn, J. H. Lee, H. M. Jang, Y. K. Jeong, Multiferroism in hexagonally stabilized TmFeO₃ thin films below 120 K, *J. Mater. Chem. C.* **2**, 4521 (2014). <https://doi.org/10.1039/C4TC00461B>
- [7] Y. Hamasaki, T. Katayama, S. Yasui, A. Shiraishi, A. Akama, T. Kiguchi, T. Taniyama, M. Itoh, Switchable third ScFeO₃ polar ferromagnet with YMnO₃-type structure, *J. Mater. Chem. C.* **8**, 4447 (2020). <https://doi.org/10.1039/C9TC07006K>
- [8] Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T. Arima, Y. Tokura, Electric-field-induced generation and reversal of ferromagnetic moment in ferrites, *Nat. Phys.* **8**, 838 (2012). <https://doi.org/10.1038/nphys2405>
- [9] U. Chowdhury, S. Goswami, D. Bhattacharya, J. Ghosh, S. Basu, S. Neogi, Room temperature multiferroicity in orthorhombic LuFeO₃, *Appl. Phys. Lett.* **105**, 52911 (2014). <https://doi.org/10.1063/1.4892664>
- [10] Y. Tokunaga, S. Iguchi, T. Arima, and Y. Tokura, Magnetic-Field-Induced Ferroelectric State in DyFeO₃, *Phys. Rev. Lett.* **101**, 097205 (2008). <https://doi.org/10.1103/PhysRevLett.101.097205>
- [11] M. Fiebig, T. Lottermoser, D. Frohlich, A. V. Goltsev, R. V. Pisarev, Observation of coupled magnetic and electric domains, *Nature* **419**, 818 (2002). <https://doi.org/10.1038/nature01077>
- [12] H. Das, A. L. Wysocki, Y. Geng, W. Wu, C. J. Fennie, Bulk magnetoelectricity in the hexagonal manganites and ferrites, *Nat. commun.* **5**, 2998 (2014). <https://doi.org/10.1038/ncomms3998>
- [13] M. Li, H. Tan and W. Duan, Hexagonal rare-earth manganites and ferrites: a review of improper ferroelectricity, magnetoelectric coupling, and unusual domain walls, *Phys. Chem. Chem. Phys.* **22**, 14415 (2020). <https://doi.org/10.1039/D0CP02195D>

- [14] J. Kasahara, T. Katayama, S. Mo, A. Chikamatsu, Y. Hamasaki, S. Yasui, M. Itoh, T. Hasegawa, Room-Temperature Antiferroelectricity in Multiferroic Hexagonal Rare-Earth Ferrites, *ACS Appl. Mater. Interfaces* **13**, 4230 (2021). <https://dx.doi.org/10.1021/acsami.0c20924>
- [15] A. Masuno, A. Ishimoto, C. Moriyoshi, H. Kawaji, Y. Kuroiwa, H. Inoue, Expansion of the Hexagonal Phase-Forming Region of $\text{Lu}_{1-x}\text{Sc}_x\text{FeO}_3$ by Containerless Processing, *Inorg. Chem.* **54**, 9432 (2015). <https://doi.org/10.1021/acs.inorgchem.5b01225>
- [16] A. R. Akbashev, A. S. Semisalova, N. S. Perov, A. R. Kaul, Weak ferromagnetism in hexagonal orthoferrites $R\text{FeO}_3$ ($R = \text{Lu}, \text{Er-Tb}$), *Appl. Phys. Lett.* **99**, 122502 (2011). <https://doi.org/10.1063/1.3643043>
- [17] B. Chen, T. Hasegawa, H. Ohta, and T. Katayama, Antiferroelectric-to-ferroelectric phase transition in hexagonal rare-earth iron oxides, *J. Mater. Chem. C* **10**, 5621 (2022). <https://doi.org/10.1039/D1TC05944K>
- [18] H. Yokota, T. Nozue, S. Nakamura, H. Hojo, M. Fukunaga, P.-E. Janolin, J.-M. Kiat, A. Fuwa, Ferroelectricity and weak ferromagnetism of hexagonal ErFeO_3 thin films, *Phys. Rev. B* **92**, 054101 (2015). <https://doi.org/10.1103/PhysRevB.92.054101>
- [19] S. M. Disseler, J. A. Borchers, C. M. Brooks, J. A. Mundy, J. A. Moyer, D. A. Hillsberry, E. L. Thies, D. A. Tenne, J. Heron, M. E. Holtz, J. D. Clarkson, G. M. Stiehl, P. Schiffer, D. A. Muller, D. G. Schlom, W. D. Ratcliff, Magnetic Structure and Ordering of Multiferroic Hexagonal LuFeO_3 , *Phys. Rev. Lett.* **114**, 217602 (2015). <https://doi.org/10.1103/PhysRevLett.114.217602>