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Room temperature magnetoelectric coupling in intrinsic multiferroic Aurivillius phase textured ceramics

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Accepted 00th January 20xxZheng Li,^a Jing Ma,^{*b} Zhipeng Gao,^c Giuseppe Viola,^a Vladimir Koval,^d Amit Mahajan^a, Xuan Li,^a Chenglong Jia,^e Cewen Nan^b and Haixue Yan^{*a)}

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Spark Plasma Sintering was employed in order to obtain the textured Aurivillius phase ceramics exhibiting simultaneously ferroelectric and ferromagnetic properties at room temperature. The sintered multiferroics are layer-structured nearly single phase materials. Though, a small amount of the secondary phase consisting of magnetic Co and -Fe elements was detected by SEM/EDX, a majority of the observed ferromagnetic behaviour was attributed to the Aurivillius phase $\text{Bi}_{4.25}\text{La}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ based on the observed magnetic anisotropy. The ferroelectric switching was demonstrated to exist in the Aurivillius phase ceramics by measuring the current peaks upon electric field reversal. Piezoresponse microscopy at room temperature revealed substantial changes of the ferroelectric domain structure when the Aurivillius phase material is subjected to an external magnetic field.

Multiferroics with the coexistence of ferroelectricity (FE) and ferromagnetism (FM) have recently attracted great attention because of their potential applications in new types of sensors, actuators, data storage devices, etc.¹⁻⁴ However, only a few single-phase multiferroic materials, demonstrating magnetoelectric coupling at room temperature (RT) have been found due to the mutual repulsion of ferroelectric and magnetic ordering.⁵ Many investigations have concentrated on the well-known RT single-phase multiferroic BiFeO_3 (BFO), however BFO is G-type antiferromagnetic (AFM) at RT.⁶⁻⁸ Recently, bismuth layer-structured Aurivillius compounds with general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ (where m is the

number of octahedral layers in the perovskite slab)⁹ with addition of magnetic species in the B-site¹⁰⁻¹³ have been investigated in the search of single-phase multiferroic materials. The Aurivillius ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -based compounds were previously studied as candidates for non-volatile ferroelectric random access memory (FRAM) because of their good fatigue resistance and large FE spontaneous polarizations along the a-axis.¹⁴⁻¹⁶ By inserting BiMO_3 (M=Fe, Co, Mn, etc.) into $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, a typical $\text{Bi}_5\text{MTi}_3\text{O}_{15}$ Aurivillius phase with a four layered structure can be formed. The phase showed FE and weak FM properties at room temperature.^{12, 17} In Aurivillius phase $\text{Bi}_{4.25}\text{La}_{0.75}\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$ (BLFCT), La substitution is considered to reduce the electrical conductivity and decrease the ferroelectric coercive field, while Co and Fe co-substitution increases the magnetization.^{12, 18} Although BLFCT was reported to exhibit FM and FE properties at room temperature,¹⁹ the origin of its magnetic properties is still under debate because the net magnetization may originate from the presence of secondary phases which are not easily detected by laboratory XRD diffractometers.²⁰ Due to the structural anisotropy of Aurivillius phase materials, textured BLFCT ceramic is expected to show anisotropic FE and FM properties. Spark plasma sintering (SPS) is an efficient sintering process to fabricate high-density and textured materials.^{15, 21} In this work, SPS has been employed to produce highly grain-oriented BLFCT ceramics in order to study the anisotropy of ferroelectric and magnetic properties in Aurivillius phase materials. The study of the anisotropy of FE and FM enables clarifying whether the multiferroic behavior is intrinsic or it is due to secondary phases.

Figs. 1a and 1b show X-ray powder diffraction patterns of BLFCT powders and textured ceramics, respectively. Both materials are single phase Aurivillius structures (ICDD PDF-4 89-8545). Fig. 1(b) displays strong diffraction peaks for (0k0) crystallographic planes, so indicating the preferred orientation in the sample. To estimate the degree of orientation, the Lotgering factor²² f was calculated using the XRD data. For the textured BLFCT ceramics $f = 0.64$, which confirms a high degree of grain alignment in ceramic samples.

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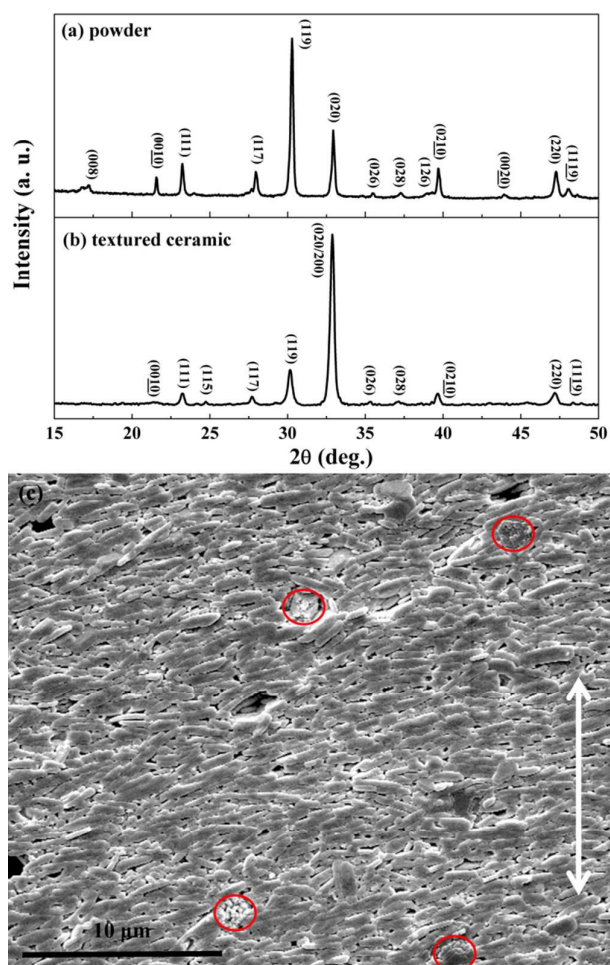


Fig.1 X-ray diffraction patterns of (a) the BLFCT powder, (b) textured ceramic sample prepared by SPS, and (c) SEM image of BLFCT textured ceramic. Pressure direction is marked by white arrow.

Fig. 1c shows morphology of the textured BLFCT ceramic sample. The grains are plate-like objects with their a - b axes orientated perpendicularly to the SPS pressure direction. A small amount of a secondary phase marked by red circles was observed by SEM (Fig. 1c). The secondary phase is represented by octahedral-like shaped particles with size within 1 - 3 μm . The amount of the secondary phase is approximately 1.7 vol. % (estimated from SEM micrographs, not shown here), which explains the absence of diffraction peaks of the secondary phase in the XRD patterns. According to the EDS analysis (line mode), the secondary phase consists of Fe, Co and O elements and Ti of a low concentration. To determine quantitatively the composition of the secondary phase, EDS data (spot scan) from different areas of the octahedral particles were collected and analysed. The results show that the atomic ratio $\text{Co}/(\text{Fe}+\text{Ti})$ is about 1. This suggests that the impurity particles are supposed to be Ti mixed Co_2FeO_4 or CoFe_2O_4 spinel ferrites. Similar observation on the presence of spinel-type impurities have been reported for Aurivillius phase multiferroics.^{20, 23, 24}

Fig. 2 shows the temperature dependence of the dielectric properties of BLFCT measured perpendicular to the SPS

pressure direction at three different frequencies. The peak of the dielectric permittivity at about 1100 K corresponds to the ferroelectric Curie temperature (FE T_c) of $\text{Bi}_{4.25}\text{La}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$. It is higher than that of Aurivillius $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ phase (T_c 1023 K).^{17, 25} The inset of fig. 2a shows a frequency independent peak in permittivity at about 775 K, which could be likely related to the ferromagnetic transition of spinel oxide CoFe_2O_4 (FM $T_c \sim 793\text{K}$).^{26, 27} The two anomalies observed at about 460 K and 380 K (Fig.2b) can be possibly connected to the ferromagnetic transition of spinel oxide Co_2FeO_4 (FM $T_c \sim 460\text{K}$)²⁸ and BLFCT, respectively. Figure 3a shows the zero field cooling (ZFC) and field cooling (FC) magnetization of BLFCT measured perpendicular [\perp] to the SPS pressure direction in temperature intervals of 5 - 300 K and 300 - 500 K at a magnetic field of 200 Oe. The discontinuity of the FC data in the figure is caused by two different furnace units, which were used for low-temperature and high-temperature magnetic measurements. Clearly, the BLFCT sample undergoes a ferromagnetic to paramagnetic transition at about 395 K (defined as the temperature of the peak of dM/dT) which is consistent with the ferromagnetic transition of Aurivillius phase BLFCT as observed in fig. 2b but far below the transition temperature of the secondary phase

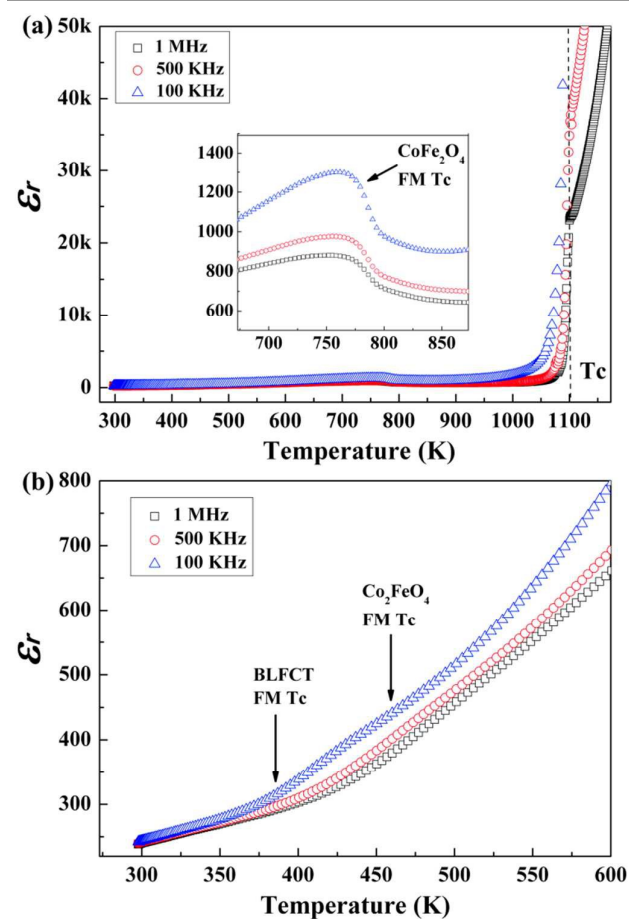


Fig. 2 The temperature dependence of the dielectric properties of the BLFCT ceramics measured perpendicular [\perp] to the SPS pressure direction over the range (a) 300 - 1100 K, inset shows the peak around 775 K, and (b) 300 - 600 K.

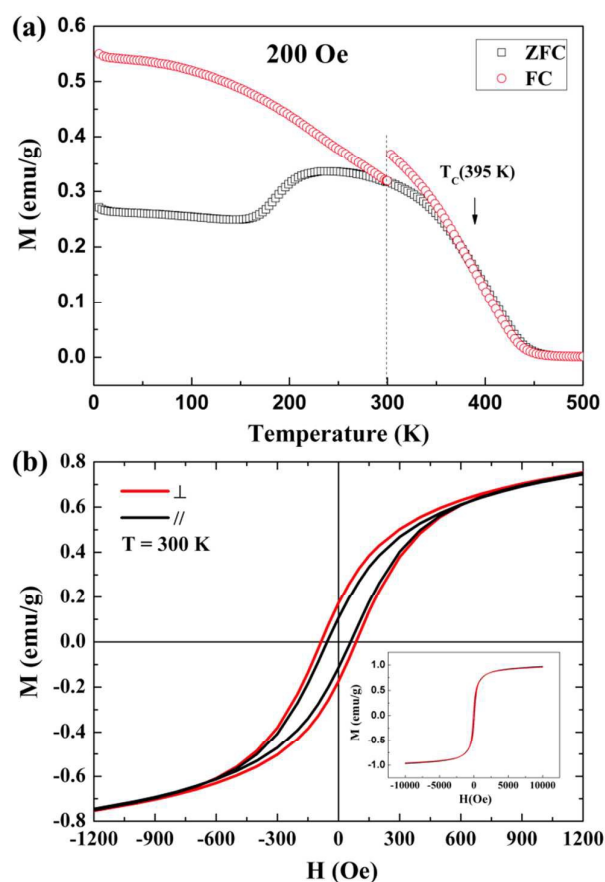


Fig. 3 (a) Temperature dependence of the magnetization for BLFCT ceramics [\perp] in the ZFC/FC modes measured in $H = 200$ Oe (measure in two different furnace units). (b) Field dependence of magnetization at 300K for the grain-orientated BLFCT samples in perpendicular [\perp] and parallel [\parallel]. The inset shows saturated MH loops at high magnetic field.

Co_2FeO_4 (FM $T_c \sim 460$ K). Furthermore, given that the spontaneous magnetization of Co_2FeO_4 is about 16 - 23.5 emu/g, the magnetic contribution of 1.7 Vol.% Co_2FeO_4 is estimated to be about 0.27 - 0.4 emu/g,²⁹ which is much smaller than the saturated magnetization of BLFCT at high magnetic field ($M_s = 0.8$ emu/g) in the inset of Fig. 3b. This indicates that the main ferromagnetic contribution in BLFCT is from main phase with Aurivillius structure. Moreover, the textured structure barely affects the magnetization of spinel oxide Co_2FeO_4 in different directions because it is a cubic phase material at room temperature and disorder distribution.³⁰ In Fig. 3b, the measured FM coercivities are approximately $H_c[\parallel] = 55$ Oe and $H_c[\perp] = 85$ Oe. The FM remnant magnetization $M_r[\parallel] = 0.1$ emu/g and $M_r[\perp] = 0.17$ emu/g. The larger value of $M_r[\perp]$ than that of $M_r[\parallel]$, is most likely due to the anisotropic exchange interaction between adjacent $\text{Fe}^{3+}/\text{Co}^{3+}$ magnetic ions in the Aurivillius phase structure $\text{Bi}_{4.25}\text{La}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$. Based on first principle calculations in Aurivillius phase materials,³¹ magnetic ions prefer to occupy B-site in the two middle layers of the perovskite slab, which gives rise to ferromagnetic coupling between neighbouring Fe^{3+} half-filled orbital and Co^{3+} either vacant or full-filled

orbital in the a - b plane. However, the Bi_2O_2 layer cuts off the exchange interactions between two pseudo-perovskite Fe/Co-O blocks layers along c -axis,³¹ which is consistent with the anisotropic magnetization in Aurivillius phase $\text{Bi}_{4.25}\text{La}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$.

Figure 4 shows the I-E and P-E hysteresis loops of the grain-oriented BLFCT ceramics measured in perpendicular and parallel direction to the SPS pressure direction at RT. The polarization of the sample measured in parallel direction to the SPS pressure is much smaller than that of the sample oriented perpendicularly. This ferroelectric feature can be attributed to the anisotropic nature of the structure. Although the FE hysteresis loops could not be saturated due to the dielectric breakdown under a high electric field, the presence of the current peaks in the I-E curves indicates the existence of ferroelectric domain switching³² in the a - b plane of the Aurivillius phase $\text{Bi}_{4.25}\text{La}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$.

To investigate a magnetoelectric coupling in the textured BLFCT ceramics, piezoelectric force microscopy (PFM) of the samples subjected to an external magnetic field was undertaken (Fig. 5). The vertical PFM scanning was performed on etched surface of [\perp] plane with roughness of about 260 nm. Some FE domains (yellow circles in Fig. 5) emerged under a positive magnetic field (+2000 Oe) applied in parallel direction to sample surface. Under the negative magnetic field of -2000 Oe, the areas of these domains decreased. The secondary phases $\text{Co}_2\text{FeO}_4/\text{CoFe}_2\text{O}_4$ are nonpolar ferromagnets showing no piezoelectric response. Therefore, the FE domain switching observed upon magnetic field reversal is believed to occur indeed in the main Aurivillius phase. Additionally, it should be noted that the density of secondary phase impurities is low and they appear on scale larger than $10 \mu\text{m}$ (Fig. 1c). These factors rule out a magnetostriction effect and magnetic dipole-dipole interaction of the secondary phase on the observed magnetoelectric coupling. Thus, the presence of magnetic impurities has no influence on the main results and conclusions of this work. The areas where the ferroelectric domain switching takes part are proposed to be the grains with highest concentrations of Fe/Co due to the random distribution of Fe/Co at B-site in

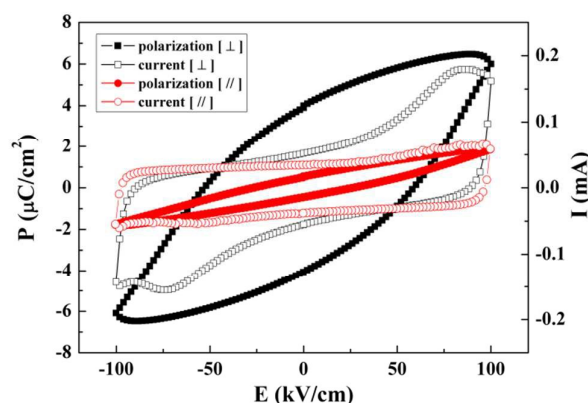


Fig. 4 P-E and I-E hysteresis loops of the textured BLFCT ceramics measured in the perpendicular and parallel direction to the SPS pressure direction.

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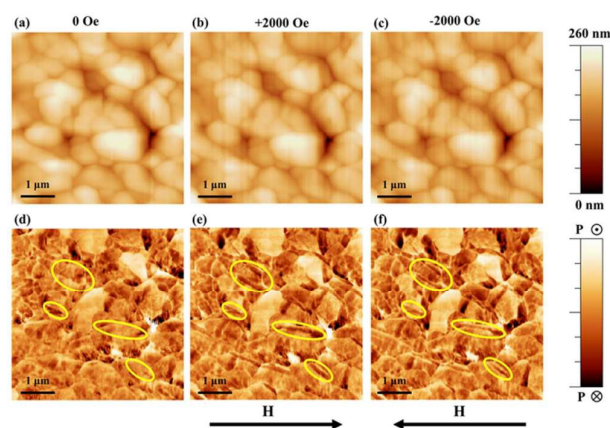


Fig. 5 ferroelectric domain switches under magnetic field of BFCT (a) topography and (d) vertical PFM phase under 0 Oe H field; (b) topography and (e) vertical PFM phase under +2000 Oe H field; (c) topography and (f) vertical PFM phase under -2000 Oe H field

Aurivillius phase.¹³ Such a magnetoelectric coupling confirms the intrinsic multiferroelectric character of the Aurivillius phase BLFCT.

In conclusion, the Aurivillius phase $\text{Bi}_{4.25}\text{La}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ is ferroelectric and ferromagnetic active at room temperature. Ferromagnetism is suggested to originate predominantly from the exchange interactions between neighbouring $\text{Fe}^{3+}\text{-O-Co}^{3+}$ ions. The textured Aurivillius phase ceramic was demonstrated to be an intrinsic room-temperature multiferroic material, where the B-site Co/Fe cations contribute simultaneously to the ferroelectric polarization and ferromagnetic moment.

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Notes and references

- W. Eerenstein, N. D. Mathur and J. F. Scott, *Nature*, 2006, **442**, 759-765.
- R. Ramesh and N. A. Spaldin, *Nature materials*, 2007, **6**, 21-29.
- J. Ma, J. Hu, Z. Li and C. W. Nan, *Advanced materials*, 2011, **23**, 1062-1087.
- J. F. Scott, *NPG Asia Materials*, 2013, **5**, e72.
- N. A. Hill, *The Journal of Physical Chemistry B*, 2000, **104**, 6694-6709.
- G. Catalan and J. F. Scott, *Advanced materials*, 2009, **21**, 2463-2485.
- Q.-H. Jiang, C.-W. Nan and Z.-J. Shen, *Journal of the American Ceramic Society*, 2006, **0**, 2123-2127.
- Q. Jiang, H. Ning, Q. Zhang, M. Cain, M. J. Reece and H. Yan, *Journal of Materials Chemistry C*, 2013, **1**, 5628.
- B. Aurivillius, *Arkiv for kemi*, 1950, **1**, 499-512.
- A. Srinivas, S. Suryanarayana, G. Kumar and M. M. Kumar, *Journal of Physics: Condensed Matter*, 1999, **11**, 3335.
- N. V. Prasad and G. S. Kumar, *Materials Science and Engineering: B*, 2004, **108**, 194-199.
- X. Mao, W. Wang, X. Chen and Y. Lu, *Applied Physics Letters*, 2009, **95**, 082901.
- L. Keeney, T. Maity, M. Schmidt, A. Amann, N. Deepak, N. Petkov, S. Roy, M. E. Pemble, R. W. Whatmore and D. Johnson, *Journal of the American Ceramic Society*, 2013, **96**, 2339-2357.
- Z. Shen, J. Liu, J. Grins, M. Nygren, P. Wang, Y. Kan, H. Yan and U. Sutter, *Advanced materials*, 2005, **17**, 676-680.
- G. Viola, K. Boon Chong, M. Eriksson, Z. Shen, J. Zeng, Q. Yin, Y. Kan, P. Wang, H. Ning, H. Zhang, M. E. Fitzpatrick, M. J. Reece and H. Yan, *Applied Physics Letters*, 2013, **103**, 182903.
- B. Park, B. Kang, S. Bu, T. Noh, J. Lee and W. Jo, *Nature*, 1999, **401**, 682-684.
- R. Singh, T. Bhimasankaram, G. Kumar and S. Suryanarayana, *Solid state communications*, 1994, **91**, 567-569.
- J. Liu, Z. Shen, H. Yan, M. J. Reece, Y. Kan and P. Wang, *Journal of Applied Physics*, 2007, **102**, 104107.
- X. Mao, H. Sun, W. Wang, X. Chen and Y. Lu, *Applied Physics Letters*, 2013, **102**, 072904.
- M. Palizdar, T. P. Comyn, M. B. Ward, A. P. Brown, J. P. Harrington, S. Kulkarni, L. Keeney, S. Roy, M. Pemble, R. Whatmore, C. Quinn, S. H. Kilcoyne and A. J. Bell, *Journal of Applied Physics*, 2012, **112**, 073919.
- Z. Shen, H. Peng and M. Nygren, *Advanced materials*, 2003, **15**, 1006-1009.
- W. Dollase, *Journal of Applied Crystallography*, 1986, **19**, 267-272.
- G. Ji, X. Lin, Y. Sun, S. A. Ali Trimizi, H. Su and Y. Du, *CrystEngComm*, 2011, **13**, 6451.
- S. Sun, Y. Huang, G. Wang, J. Wang, Z. Fu, R. Peng, R. J. Knize and Y. Lu, *Nanoscale*, 2014, **6**, 13494-13500.
- J. B. Li, Y. P. Huang, G. H. Rao, G. Y. Liu, J. Luo, J. R. Chen and J. K. Liang, *Applied Physics Letters*, 2010, **96**, 222903.
- A. Franco and F. C. e Silva, *Applied Physics Letters*, 2010, **96**, 172505.
- E. Y. Tsymbal and I. Zutic, *Handbook of spin transport and magnetism*, CRC press, 2011.
- S. Kawano, N. Achiwa, N. Yamamoto and S.-n. Higashi, *Materials Research Bulletin*, 1976, **11**, 911-916.
- I. P. Muthuselvam and R. N. Bhowmik, *Solid State Sciences*, 2009, **11**, 719-725.
- S. Monz, A. Tschope and R. Birringer, *Physical review. E, Statistical, nonlinear, and soft matter physics*, 2008, **78**, 021404.
- A. Y. Birenbaum and C. Ederer, *Physical Review B*, 2014, **90**.
- H. Yan, F. Inam, G. Viola, H. Ning, H. Zhang, Q. Jiang, T. A. O. Zeng, Z. Gao and M. J. Reece, *Journal of Advanced Dielectrics*, 2011, **01**, 107-118.