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Pyroelectric detection of ferroelectric polarization in magnetic thin films

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We review the performance of the pyroelectric measurement method in the context of polar states in multiferroic materials in which ferroelectricity coexists with ferromagnetism. The unique point of pyroelectric measurement is the ability to determine the presence of dielectric polarization without having to apply a bias voltage during the measurement. The convenience of the zero-bias technique is illustrated by summarizing experiments on measuring the pyroelectric hysteresis loops of leaky ferroelectric BaTiO₃ and PbTiO₃ thin film capacitors. This technique was also employed for detecting a polar state in magnetic materials, proving that the electronic polarization in ferrimagnetic Fe₃O₄ appears at the Verwey transition temperature at 120 K and to discover A-site-driven ferroelectricity in epitaxially strained ferromagnetic La₂NiMnO₆ films. © 2018 The Japan Society of Applied Physics

1. Introduction

Ferroelectricity is a characteristic of materials with switchable spontaneous dielectric polarization. The underlying mechanism of the appearance of a polar state in a material and the switchability of the direction of the polarization are important questions in basic materials science and solid-state physics, and are also important for device applications such as memories and piezoelectric or pyroelectric micro-electromechanical sensor devices.¹⁻³⁾ Bulk ferroelectricity has traditionally been associated with insulating dielectric materials, but the group of materials where ferroelectricity may exist is much wider. A new era of ferroelectricity research started with the discovery of the coexistence of ferroelectricity and magnetism in BiFeO₃ crystals.⁴⁾ The coupling between magnetization and polarization in a single-phase material has attracted great attention due to possible applications in highly sensitive magnetic sensors operating close to room temperature⁵⁾ and multiferroic memories.⁶⁾ However, although a large number of ferroelectric materials have been characterized, the coexistence of ferromagnetism and ferroelectricity in a single material is still exceedingly rare.⁷⁾ Typical ferroelectric materials are composed of d⁰ ions, such as Ti⁴⁺ or Zr⁴⁺, where covalent bonding with oxygen stabilizes a distorted unit cell structure.⁸⁾ In contrast, the d-orbitals of magnetic oxide materials are partially occupied, as in Mn or Fe, where covalent bonding with oxygen is negligible.⁹⁾ As we discuss in this review, despite this contradiction, there are a number of materials where polar and ferromagnetic states can coexist and we look at some such materials from the viewpoint of detecting the polar state.

From a technical point of view, quantitative analysis of spontaneous polarization by conventional polarization–electric field (*P*–*E*) hysteresis measurement can be ineffective for finding new materials that exhibit both ferroelectricity and ferromagnetism, when potentially ferroelectric samples have high leakage currents that mask weak displacement currents associated with ferroelectric domain switching. For example, the magnitude of the ferroelectric polarization in BiFeO₃ crystals reported initially in 1970 was $3.5 \,\mu\text{C/cm}^{2.10}$ Over 30 years later, it was found that the high leakage current of BiFeO₃ crystals veiled a much larger actual spontaneous polarization of over $50 \,\mu\text{C/cm}^{2.4}$ Inappropriate measurement methods may thus be especially misleading in high-

throughput screening experiments aimed at finding a ferroelectric polar state in previously unknown material systems.

Several methods can be used to measure P-E hysteresis loops of leaky ferroelectric capacitors such as the positiveup-negative-down (PUND),¹¹⁾ dynamic leakage current compensation,¹²⁾ and double-wave Sawyer–Tower methods.¹³⁾ In these measurements, the dynamic leakage current is compensated by performing several measurements at different frequencies,¹²⁾ or by applying short bias pulses with different amplitudes.^{11,13)} These methods have been used to observe ferroelectric domain reversal in multiferroic Fe₃O₄¹¹⁾ and ErMn₂O₄,¹³⁾ and in ferroelectric Pt/Pb(Zr,Ti)O₃/IrO₂ capacitors.¹²⁾

Moreover, several new measurement techniques with unique capabilities have become available for detecting a polar state in a material instead of P-E hysteresis measurements, such as piezoresponse force microscopy (PFM),14,15) scanning nonlinear dielectric microscopy (SNDM),^{16,17)} and second-harmonic generation (SHG).^{18,19)} The PFM technique is useful for imaging nanoscale polarization patterns in polar and ferroelectric materials. It has been used successfully to reveal a size effect of ferroelectric polarization¹⁴) and for determining the relationship between ferroelectric and magnetic domains.¹⁵⁾ However, for the purpose of investigating thin film materials and for screening materials for ferroelectricity, the PFM technique may give false positive results. This can happen when the surface of the sample becomes strongly charged by the bias applied on a sample by the conducting PFM tip.¹⁴⁾ The PFM signals from the surface charge, which can persist for an extended period of time, can be mistaken for true piezoelectricity. In such cases, a nonferroelectric sample may exhibit a ferroelectric-like behavior.

The SNDM technique is useful for nanoscale imaging of the dielectric polarization distribution in ferroelectric thin films, similarly to PFM. One of the merits of SNDM is higher spatial resolution than PFM when using frequencies in the GHz range, which limits the penetration depth to nm order. The high resolution of SNDM may enable ferroelectric data storage at densities above 1 Tbit/inch².¹⁷

The SHG technique is convenient for investigating polar states in crystalline thin films and has the additional advantage of sensing the crystal symmetry directly. A limiting factor for SHG detection is the symmetry breaking that always occurs at the interface between a film and a substrate,



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which also produces an SHG response. It may thus be difficult to distinguish the SHG signals that originate from the film and from the substrate interface.

Another technique that can detect polarity and ferroelectricity and is particularly useful for high-throughput screening of materials for the presence of intrinsic ferroelectric polarization is based on the pyroelectric effect. Since the polarization of a polar material is temperature-dependent, a pyroelectric current is generated when the temperature of a ferroelectric capacitor is varied. By integrating the pyroelectric current during a sweep of the measurement temperature, the polarization amplitude can be quantitatively estimated. The static pyroelectric approach has been used for quantitative analysis of ferroelectric polarization in magnetic TbMnO₃²⁰⁾ and LuFe₂O₄ crystals.²¹⁾

Dynamic pyroelectric measurement was originally reported by Chynoweth in 1956.^{22,23} Pulsed light illumination is used to modulate the temperature of a planar capacitor sample, triggering a pyroelectric current in an external circuit connected to the capacitor. The technique is not appropriate for accurate quantitative evaluation of spontaneous polarization, but a major benefit is that the presence of ferroelectric polarization can be detected at zero applied bias.^{24,25)} Compared with the static pyroelectric measurement, it is thus particularly useful for fast hysteresis loop measurements to test for ferroelectricity in leaky dielectric films. For example, pyroelectric detection has been used to investigate the size effect of ferroelectric properties in ultrathin poly(vinylidene fluoride) (PVDF) films,²⁶⁾ to detect the presence of a polar state in amorphous BaZrO₃ and SrTiO₃ films,²⁷⁾ and to test the switchability of domains in ultrathin PbTiO₃ films.^{28–30)} Here we review our recent work on the pyroelectric analysis of ferroelectricity in PbTiO₃ and BaTiO₃ films as well as the application of pyroelectric detection to the measurement of spontaneous polarization in thin films of the leaky magnetic materials Fe₃O₄ and La₂NiMnO₆.

2. Experiments

Figure 1(a) schematically illustrates the pyroelectric measurement setup. A thin film sample was sandwiched between top and bottom electrodes, forming a planar capacitor. For room-temperature measurements of ferroelectric PbTiO₃ and $BaTiO_3$ films, a top electrode with a typical diameter of 200 to 400 µm was deposited by electron beam evaporation through a metal stencil mask. Electrical contact was made with prober needles in air. For low-temperature measurements of magnetic Fe₃O₄ and La₂NiMnO₆ films, aluminum wires were attached to Pd top electrode pads with silver paste. For convenience, the top electrode pad diameter was increased to 1 mm to simplify the silver pasting of contact wires. The film sample was placed in a vacuum chamber and cooled using a two-stage cryocooler. The sample temperature was controlled between 9 and 300 K by thermal conduction from the cryocooler and a heater mounted on the sample stage.

In order to generate a pyroelectric current in a polar film, a diode laser was focused on the top electrode. The laser light was chopped by modulating the diode laser feed current with a rise time of $\sim 3 \,\mu s$ and focused to a spot with a diameter of approximately 50 μm . The laser spot position was optimized with an *x*-*y* stage to maximize the pyroelectric current. The wavelength of the diode lasers can be selected to match the



Fig. 1. (Color online) (a) Schematic illustration of the pyroelectric measurement circuit. (b) Sequences of the bias voltage generation, discharging, data acquisition, and relay switching during a pyroelectric hysteresis loop measurement.

material being measured. We used a diode laser with wavelength of 658 nm for PbTiO₃, 1.06 µm for BaTiO₃, 1.31 µm for Fe₃O₄, and 1.63 µm for La₂NiMnO₆. The wavelength was selected to minimize the risk of generating carriers in the dielectric sample by photoexcitation.³¹⁾ The laser focus spot position of the diode laser needs to be positioned on a particular top electrode pad for the pyroelectric measurement. This can be done with the help of a small digital camera but the use of a silicon-based camera sensor means that the diode laser wavelength cannot be much longer than about $1.2 \,\mu m$. Since longer wavelength laser light cannot be detected with a camera, an additional pointer laser is necessary, complicating the optical setup. For most pyroelectric measurements, the most suitable wavelength was found to be 1.06 µm. Furthermore, to avoid photoexciting carriers in the sample film, the top electrode thickness was set at about 100 nm. The generated pyroelectric current was converted to a voltage signal with a current-voltage converter at a transconductance of 10^8 V/A or higher and recorded with a digital oscilloscope or detected with a lock-in amplifier.

For pyroelectric hysteresis loop measurements, a relay circuit was connected to the top electrode, switching between a constant bias source for poling of the film and the pyroelectric current detection circuit. Figure 1(b) shows the timing sequence of a ferroelectric hysteresis loop measurement. The poling bias source, discharge delay timing, data acquisition, and relay switching were controlled with a data acquisition card in a computer. The relay circuit was used to apply 1 s voltage pulses, interleaved with periods where no bias was applied, but the pyroelectric signal strength and polarity were detected at zero bias. The hysteresis loop can be



Fig. 2. (Color online) Transient profiles of the heating laser power (a) and pyroelectric currents from positively (b) and negatively (c) polarized $Pd/BaTiO_3/Sr_2RuO_4$ capacitors. The sketches on the right schematically illustrate the ferroelectric domain configuration of the BaTiO_3 film.³²⁾

obtained by successively increasing the applied bias pulse amplitude from 0 V to a maximum value of V_{max} , decreasing to $-V_{\text{max}}$, and increasing again to V_{max} , usually in 0.2 V steps.³¹⁾ A 1.5 s delay was used after a poling pulse to allow any poling-related current transients to subside before performing pyroelectric polarization detection. Chopped laser light was used to modulate the sample temperature during the 1 s measurement period.

The chopping frequency of the laser light for PbTiO₃, Fe_3O_4 , and La_2NiMnO_6 films was 35 Hz, and it was 173 Hz for BaTiO₃. Relatively low frequencies were employed for the transient current profile measurements in order to separate the pyroelectric current from the residual photocurrent caused by the laser illumination.³¹⁾

3. Pyroelectric analysis of conventional ferroelectric capacitors

The performance of the pyroelectric measurement setup was validated by characterizing conventional ferroelectric capacitors consisting of BaTiO₃ (125 nm)/Sr₂RuO₄ (20 nm) heterostructures that were epitaxially grown on SrTiO₃(001) substrates by pulsed laser deposition (PLD).³²⁾ Figure 2 shows the time-dependent profiles of the chopped laser power (a) and the transient pyroelectric current signals for positively (b) and negatively (c) polarized capacitors of $Pd/BaTiO_3/$ Sr₂RuO₄ heterostructures. When the laser illumination starts and ends, the temperature of the thin film capacitor increases and decreases exponentially, resulting in the generation of positive and negative pyroelectric spike currents, respectively, as shown in Fig. 2(b) for a positively polarized capacitor. The current spike is caused by the temperature dependence of the spontaneous polarization of the BaTiO₃ film close to room temperature. Since the temperature modulation caused by the pulsed laser light is small, the current spike amplitude is proportional to the temperature derivative of the spontaneous polarization at the measurement temperature. In contrast, negatively polarized domains generate a



Fig. 3. (Color online) Pyroelectric current phase (a), amplitude (b) and the calculated pyroelectric current (c) as a function of the applied voltage for a Pd/BaTiO₃/Sr₂RuO₄ capacitor. The red and green data points mark the measurement points for the data shown in Fig. 2.³²⁾

pyroelectric current with the opposite polarity, consistent with the reversal of the ferroelectric domain state.

For pyroelectric hysteresis loop measurements, the pyroelectric current signal was integrated with a 300 ms time constant with a lock-in amplifier. The sample was poled with voltage pulses varying in amplitude between -6 and +6 V, while the pyroelectric response was monitored at zero applied bias between the poling pulses. Figure 3 shows the pyroelectric current phase (a) and amplitude (b) as a function of the applied voltage. There is a 180° phase shift between the positively and negatively poled domains in Fig. 3(a). The amplitude variation of the pyroelectric current signals presents a butterfly curve as shown in Fig. 3(b). The total pyroelectric current was calculated from the amplitude and phase signals, resulting in the hysteresis loop shown in Fig. 3(c).

Pyroelectric measurements are particularly useful for analyzing the hysteresis loops of leaky ferroelectric samples because the pyroelectric analysis is performed at zero applied bias.³¹⁾ To demonstrate the benefit of hysteresis loop measurement by pyroelectric detection in leaky ferroelectric samples, epitaxial PbTiO₃ films were grown on conducting 0.5 wt % Nb:SrTiO₃(001) substrates by off-axis radio frequency magnetron sputtering.^{33–35} Figure 4(a) shows a standard ferroelectric polarization hysteresis loop and the displacement current versus electric field for a Pt/PbTiO₃ (14 nm)/Nb:SrTiO₃ capacitor, measured with a conventional ferroelectric tester at 2 kHz. No saturation was observed due to a high leakage current and rectifying behavior of the filmsubstrate junction. High leakage currents are often present in ferroelectric thin films grown on Nb:SrTiO₃ substrates. Figure 4(b) shows a pyroelectric hysteresis loop measurement of the same sample. The sample was poled with voltage pulses varying in amplitude between -8 and +3 V, while the pyroelectric response was monitored at zero applied bias between the poling voltage pulses. The polarity of the pyroelectric charge was verified to be switchable by an



Fig. 4. (Color online) Ferroelectric polarization loop (blue, left axis) and leakage current (red, right axis) of a Pt/PbTiO₃ (14 nm)/Nb:SrTiO₃ capacitor, measured with a conventional ferroelectric tester at 2 kHz. (b) Hysteresis loop of current generated by pulsed temperature modulation and pyroelectric detection of the same sample, measured between 1 s poling pulses varying in amplitude from -8 to +3 V.³¹

applied electric field. In contrast to a standard ferroelectric bias sweep measurement, the pyroelectric hysteresis loop is fully saturated, showing the benefit of the pyroelectric approach to measuring the ferroelectric properties of nm-thick films.^{28,29,34)}

4. Pyroelectric analysis of magnetic materials

4.1 Ferroelectricity in ferrimagnetic Fe₃O₄ films

Pyroelectric analysis of PbTiO₃ and BaTiO₃ films showed that zero-bias pyroelectric measurement is effective for detecting the presence of spontaneous polarization in capacitors where leakage is caused primarily by lattice defects. We now turn our attention to magnetic materials where low resistivity is an intrinsic property of the material, rather than related to defects. The first target material is magnetite, Fe₃O₄, which is a common ferrite with ferrimagnetic spin order and a magnetic moment per formula unit (f.u.) close to $4.05 \,\mu_{\rm B}$ and a high Curie temperature of 860 K.^{36,37)} A unique feature of Fe₃O₄ is the well-known metal-insulator Verwey transition at 120 K.³⁸⁾ At room temperature, Fe₃O₄ is metallic, since electrons can hop within the *B*-site lattice between Fe^{2+} and Fe^{3+} ions. In contrast, the charges of Fe²⁺ and Fe³⁺ ions become ordered below 120 K and Fe₃O₄ crystals become insulating. A remarkable feature of the insulating Fe₃O₄ phase is the appearance of electronic ferroelectricity.³⁹⁾

Figures 5(a)–5(d) schematically illustrate the mechanism of electronic ferroelectricity in Fe₃O₄ crystals, following the model suggested by Brink and Khomskii.³⁹⁾ Figure 5(a) illustrates a homogeneous crystal with zero charge on each lattice site. Adding alternating charges to lattice sites [Fig. 5(b)] produces a site-centered charge-ordered state



Fig. 5. (Color online) Schematic illustrations of the mechanism of the ferroelectric phase in Fe₃O₄ crystals: (a) symmetric crystal, (b) site-centered charge ordering, (c) bond-centered charge ordering, and (d) combination of bond- and site-centered charge ordering. The arrows indicate the magnitude and direction of local polarization, which averages to zero in (a)–(c) but has a finite value in (d).

where neighboring sites are inequivalent with +e and -e charges, as in NaCl, but the inversion symmetry is not broken and the spontaneous polarization of the whole crystal remains zero. Another type of charge order is illustrated in Fig. 5(c), known as bond-centered charge order, which is related to the dimerization of bonds. However, in a centrosymmetric structure, the local dipoles cancel each other and no macroscopic polar state appears. In contrast, when site-centered charge order is combined with bond-centered order, as shown in Fig. 5(d), the total dipole moment is not canceled, and a macroscopic net dipole moment develops. Recent X-ray and neutron diffraction studies on Fe₃O₄ crystals below the Verwey transition temperature suggest that the charge ordering is site- and bond-centered, implying an electronic ferroelectric phase.⁴⁰⁻⁴²)

To investigate ferroelectric properties in Fe₃O₄ crystals, Fe₃O₄ thin films were grown on SrTiO₃(001) substrates by PLD.⁴³⁻⁴⁵⁾ A Pd film was deposited on the Fe₃O₄ surface by electron beam evaporation and interdigitated Pd electrodes were formed by standard lithography.⁴⁶⁾ The ferroelectricity of a 270 nm thick Fe₃O₄ film was characterized by conventional *P*–*E* hysteresis measurements at 8 K, as shown in Fig. 6(a). A clear ferroelectric polarization loop was observed together with the corresponding displacement current. When the polarity of the applied bias was changed, a clear displacement current was observed, showing that the polarity of the ferroelectric domains in the film was reversed. The remanent polarization was calculated by integrating the displacement current, yielding $3 \mu C/cm^2$, which is of the same order of magnitude as that in earlier reports.¹¹

The temperature dependence of the calculated remanent polarization is shown in Fig. 6(b). With increasing temperature, up to 20 K, the polarization gradually dropped. Above 20 K, the leakage current increased to a level where it exceeded the displacement current, resulting in overestimated ferroelectric polarization values, essentially setting a maximum measurement temperature of 20 K.

In order to investigate the relationship between the Verwey transition and the ferroelectric phase, the pyroelectric measurement technique was employed to detect the polarization signal in a leaky $Pd/Fe_3O_4/Nb$:SrTiO₃ capacitor.^{46,47}



Fig. 6. (Color online) (a) Ferroelectric polarization (left axis) and displacement current (right axis) as a function of applied bias at 8 K for an $Fe_3O_4/SrTiO_3$ thin film capacitor with interdigitated Pd electrodes. (b) Temperature dependence of the ferroelectric polarization estimated by integrating the displacement current. Above 20 K, the leakage current became larger than the displacement signal, resulting in an unrealistic overestimation of the polarization values.⁴⁶

Figures 7(a) and 7(b) show the temperature dependence of two-point resistance of the capacitor and the detected pyroelectric current. Figure 7(a) shows a discontinuous change in resistance at 120 K, corresponding to the Verwey transition temperature.³⁸⁾ Below this temperature, the pyroelectric response increased rapidly with decreasing sample temperature. The maximum pyroelectric signal was observed at 70 K, below which the pyroelectric response was reduced. The inset of Fig. 7(b) shows a pyroelectric hysteresis measurement result for a Pd/Fe₃O₄/TiN capacitor at 9K. The pyroelectric current polarity was switched by an applied electric field, indicating the presence of electronic ferroelectricity in the Pd/Fe₃O₄/TiN capacitor. The temperature dependence of the spontaneous polarization was estimated by integrating the pyroelectric current, as shown on the right axis of Fig. 7(b). It is thus clear that spontaneous polarization appears at the Verwey transition temperature. These experiments demonstrate that pyroelectric measurement is a useful tool for detecting the spontaneous polarization in intrinsically leaky thin films.

4.2 Ferroelectricity in ferromagnetic La₂NiMnO₆ films High-throughput screening using pyroelectric measurements was performed to discover a new multiferroic material with coexisting ferroelectricity and ferromagnetism. The pyroelectric approach successfully found a ferroelectric phase in ferromagnetic La₂NiMnO₆ thin films.⁴⁸⁾ La₂NiMnO₆ is a *B*-site-ordered double perovskite in which, based on Kanamori–Goodenough rules, ferromagnetic order can be



Fig. 7. (Color online) Temperature dependences of resistance (a) and dynamic pyroelectric current amplitude (b) for a Pd/Fe₃O₄/Nb:SrTiO₃ capacitor. The Verwey transition is visible at 120 K. The right axis in (b) corresponds to the integrated pyroelectric current, showing the temperature dependence of polarization in the Fe₃O₄ film. The inset in (b) shows a hysteresis loop for a Pd/Fe₃O₄/TiN junction measured at 9 K. The polarization was switchable by an applied electric field, proving that the films were ferroelectric.⁴⁷⁾

expected to occur due to the presence of 180° Ni²⁺–O–Mn⁴⁺ superexchange bonding between an empty Mn⁴⁺ e_g orbital and a half-filled d orbital on a neighboring Ni²⁺ site.^{49,50)} The bulk crystal symmetry can be either rhombohedral ($R\bar{3}$) or monoclinic ($P2_1/n$), which are both nonpolar.

For pyroelectric analysis, La₂NiMnO₆ thin films were deposited on Nb:SrTiO₃(001) substrates at 600 and 700 °C by PLD.⁵¹⁻⁵³⁾ Reciprocal space mapping analysis by X-ray diffraction showed that the La2NiMnO6 films were coherently grown on SrTiO₃(001). The level of B-site order was quantified by examining the magnetization of the La₂NiMnO₆ films, as shown in Fig. 8(a). The magnetization hysteresis loops were measured at 10K for ordered and disordered La2NiMnO6/Nb:SrTiO3 samples, which were deposited at 700 and 600 °C, respectively. The observed saturation magnetization of the films was estimated to be $2.0 \mu_{\rm B}/B$ -site for the ordered film and $0.65 \,\mu_{\rm B}/B$ -site for the disordered film. Compared with the theoretical magnetization of 2.5 $\mu_{\rm B}/B$ -site for a perfectly ordered La₂NiMnO₆ crystal, the fraction of *B*-site order in Fig. 8(a) can be estimated to be 80 and 26%for the ordered and disordered samples, respectively. The temperature dependence of magnetization showed that the magnetic Curie temperature was 280 K in both cases, matching earlier reported values for bulk La₂NiMnO₆ polycrystalline samples.

The presence of ferroelectric polarization in La_2NiMnO_6 was characterized by pyroelectric measurements for ordered and disordered La_2NiMnO_6 films grown on Nb:SrTiO₃ substrates. The temperature dependence of the amplitude of the pyroelectric current is shown in Fig. 8(b). Below 250 K, pyroelectric current was generated by the temperature



Fig. 8. (Color online) (a) Magnetization hysteresis loops at 10 K for ordered (red) and disordered (blue) $La_2NiMnO_6/SrTiO_3$ films. (b) Temperature dependence of the pyroelectric response for ordered (red) and disordered (blue) $La_2NiMnO_6/SrTiO_3$ films. The gray dashed circles mark the discontinuities in the pyroelectric response at 105 K. (c) Lattice parameters of the SrTiO_3 substrate as a function of temperature.^{48,54)}

modulation caused by the pulsed infrared laser illumination, indicating that a polar phase exists in the ferromagnetic La_2NiMnO_6 films. With decreasing temperature, the pyroelectric response increased for both samples. The pyroelectric current amplitude reached a maximum between 100 and 150 K and decreased at lower temperatures.

At 105 K, both ordered and disordered La₂NiMnO₆ films show a discontinuity in the pyroelectric signal amplitude. This temperature corresponds to a structural cubic-to-tetragonal symmetry reduction of the SrTiO₃ substrate crystal as shown by the substrate lattice parameter plots in Fig. 8(c).⁵⁴⁾ It is clear that the phase transition in the substrate affects the epitaxial strain in the La₂NiMnO₆ film and the pyroelectric response. Such a kink at 105 K was not seen in the temperature dependence of a Pd/Fe₃O₄/Nb:SrTiO₃ capacitor, as shown in Fig. 7(b), suggesting that the spontaneous polarization in La₂NiMnO₆ originates from epitaxial strain.

To investigate the epitaxial strain effect on the polar state in La₂NiMnO₆ films, P-E hysteresis loop measurements were performed at 10 K for the ordered and disordered La₂NiMnO₆/SrTiO₃, and ordered La₂NiMnO₆/LSAT films, as shown in Fig. 9. Both films on SrTiO₃ exhibited ferroelectric domain reversal under an external electric field, while the La₂NiMnO₆/LSAT films sample showed no hysteresis behavior at all, proving that the ferroelectricity in La₂NiMnO₆



Fig. 9. (Color online) Ferroelectric polarization hysteresis loops at 10 K for ordered (red) and disordered (blue) La₂NiMnO₆ on SrTiO₃ and ordered La₂NiMnO₆ on LSAT (green), with interdigitated Au electrodes.⁴⁸⁾

films is triggered by the epitaxial strain. Moreover, no significant difference was observed between the ordered and disordered La_2NiMnO_6 films grown on SrTiO₃, leading to the conclusion that *B*-site ordering of the double perovskite structure is not related to ferroelectricity in La_2NiMnO_6 crystals.

Bulk La₂NiMnO₆ has been reported to crystallize in the rhombohedral structure $(R\overline{3})$ at a high temperature and transform to the monoclinic structure $(P2_1/n)$ at a low temperature.^{55,56)} These crystal symmetries should not be ferroelectric. Indeed, recent density functional theory (DFT) simulations of monoclinic La2NiMnO6 crystals found no ferroelectricity under any strain field.⁵⁷⁾ To understand the origin of a polar phase in La₂NiMnO₆ thin films, the epitaxial strain effect on the crystal symmetry and polar instability of rhombohedral La₂NiMnO₆ crystals was studied by DFT simulations. Figure 10(a) shows the strain dependence of the spontaneous polarization along the [111]_{cubic} direction in a rhombohedral La₂NiMnO₆ crystal, which is illustrated in the inset of Fig. 10(a). The inset plot shows the relationship between the rhombohedral lattice parameter and the rhombohedral angle, under the assumption that the crystal volume is constrained to the experimentally observed value of V =353.33 A³. Increasing the tensile strain lowers the rhombohedral angle of the La₂NiMnO₆ crystal and ultimately leads to a polar state when the lattice parameter exceeds 5.7 Å, which corresponds to 4.2% tensile strain with respect to the experimental bulk value of 5.47 Å.

Figure 10(b) illustrates the distortions caused by strain in the crystal structure of the ferroelectric rhombohedral La₂NiMnO₆ phase stretched at +5.9% along the [111]_{cubic} direction. The *B*-site Ni and Mn ions are alternately aligned along the [111]_{cubic} direction. In the relaxed $R\bar{3}$ structure, the *A*-site La lattice shows no displacement. By applying a tensile strain field, the crystal symmetry drops from $R\bar{3}$ to R3and La ions develop a sizable displacement along the [111]_{cubic} direction.

It is common to see a symmetry-breaking ferroelectric atomic displacement occurring at the *B*-site of most common ferroelectric materials. The reason for this can be understood by considering the perovskite tolerance factor, $t = (r_{\rm O} + r_{\rm A})/\sqrt{2}(r_{\rm O} + r_{\rm B})$, where $r_{\rm O}$, $r_{\rm A}$, and $r_{\rm B}$ are the ionic radii of the oxygen anion and the *A*- and *B*-site cations, respectively.^{58,59}



Fig. 10. (Color online) (a) Calculated strain dependence of the spontaneous polarization along the [111]_{cubic} direction in the rhombohedral La₂NiMnO₆ lattice. The arrows in the plot mark the experimental bulk (5.47 Å) and strained (5.79 Å) film lattice constants. The relationship between the rhombohedral lattice parameter and the rhombohedral angle α is shown in the inset. A schematic illustration of the rhombohedral La₂NiMnO₆ crystal structure is also shown. The *B*-site Ni (red) and Mn (blue) atoms are alternately aligned along the [111]_{cubic} direction. (b) Schematic illustration of the ferroelectric crystal structure under 5.9% tensile strain. The black solid lines denote the rhombohedral La₂NiMnO₆ unit cell. A displacement of the *A*-site La ions is clearly visible along the [111]_{cubic} direction in the ferroelectric phase of the strained rhombohedral La₂NiMnO₆ lattice.⁴⁸)

When t > 1, the *B*-site cation in the perovskite lattice has sufficient space to be displaced from the center of a BO_6 octahedron, which occurs in BaTiO₃ and PbTiO₃. Conversely, if t < 1, an A-site displacement is preferred over a B-site shift. However, smaller A-site ions generally lead to rotation and tilting of the BO_6 octahedra, preserving the inversion symmetry by doubling the unit cell. For this reason, A-site-driven ferroelectricity is quite unusual in perovskites. Some other known examples of A-site-driven ferroelectricity are $K_{0.5}Li_{0.5}NbO_3$,⁵⁸⁾ LaLuNiMnO₆,⁵⁹⁾ and Ba_{1-x}Ca_xTiO₃ (0.02 < x < 0.34).⁶⁰⁾ The tolerance factor of La₂NiMnO₆ is 0.97, suggesting the possibility of A-site-driven ferroelectricity. However, in bulk crystals, the BO₆ octahedra are tilted and rotated, forming nonpolar rhombohedral $(R\bar{3})$ and monoclinic $(P2_1/n)$ structures. The important difference between the two symmetries is the presence of threefold crystal symmetry, which can inhibit the MnO₆ and NiO₆ octahedral tilting and stabilize the A-site displacement in the rhombohedral structure under tensile epitaxial strain.

In this paper, we have presented some of the advantages of pyroelectric analysis to determine the presence of spontaneous polarization in ferroelectric thin films that are not necessarily good insulators, such as PbTiO₃, BaTiO₃, Fe₃O₄, and La₂NiMnO₆. However, we should also draw attention to potential pitfalls. As has been reported for LuFe₂O₄ crystals, a thermally induced current that is generated in a pyroelectric measurement of a ferroelectric material may also arise due to an electrode contribution if a Schottky-type depletion layer is present and the temperature modulation affects the charge

distribution in the space-charge region of the junction.^{61,62} This means that it may be impossible to experimentally prove a polar state in a thin film grown on a conducting electrode layer or substrate only by pyroelectric analysis. Furthermore, in the Chynoweth method, the laser light used for temperature modulation may photoexcite carriers in the sample film, as discussed above. The combination of pyroelectric analysis with other techniques, such as a conventional P-E hysteresis measurement, PFM, SNDM, and SHG, may be needed for quantitative analysis of the ferroelectric state in thin film capacitors. However, for qualitative screening purposes, the pyroelectric detection method has a clear advantage.

5. Conclusions

We have demonstrated the advantages of pyroelectric measurements of ferroelectric thin films, including PbTiO₃, BaTiO₃, Fe₃O₄, and La₂NiMnO₆. Pyroelectric analysis is a powerful measurement tool for investigating leaky ferroelectric capacitors as well as rapidly screening materials for the presence of spontaneous polarization. In particular for high-throughput screening of new multiferroic thin films, this technique is useful for investigating the temperature dependence of the pyroelectric response and determining the strain effect on ferroelectricity, which was demonstrated by the study of ferroelectric analysis has clear advantages for characterizing basic phenomena in ferroelectric materials and for finding novel polar materials for multiferroic applications.

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