A-site driven ferroelectricity in strained ferromagnetic La$_2$NiMnO$_6$ thin films

R. Takahashi,1 I. Ohkubo,2,3 K. Yamauchi,4 M. Kitamura,2 Y. Sakurai,5 M. Oshima,2,5 T. Oguchi,3,6 Y. Cho,7 and M. Lippmaa1
1Institute for Solid State Physics, University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
2Department of Applied Chemistry, School of Engineering, University of Tokyo, 7-3-1 Hongo, Tokyo 113-8656, Japan
3National Institute for Materials Science, Tsukuba 305-0044, Japan
4Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan
5Synchrotron Radiation Research Organization, University of Tokyo, Tokyo 113-8656, Japan
6JST-CREST, Kawaguchi, Saitama, 332-0012, Japan
7Research Institute of Electrical Communication, Tohoku University, Sendai, 980-8577, Japan

(Dated: April 21, 2015)

We report on theoretical and experimental investigation of A-site driven ferroelectricity in ferromagnetic La$_2$NiMnO$_6$ thin films grown on SrTiO$_3$ substrates. Structural analysis and density functional theory calculations show that epitaxial strain stretches the rhombohedral La$_2$NiMnO$_6$ crystal lattice along the [111]$_{\text{cubic}}$ direction, triggering a displacement of the A-site La ions in the double perovskite lattice. The lattice distortion and the A-site displacements stabilize a ferroelectric polar state in ferromagnetic La$_2$NiMnO$_6$ crystals. The ferroelectric state only appears in the rhombohedral La$_2$NiMnO$_6$ phase, where MnO$_6$ and NiO$_6$ octahedral tilting is inhibited by the 3-fold crystal symmetry. Electron localization mapping showed that covalent bonding with oxygen and 6s orbital lone pair formation are negligible in this material.

PACS numbers: 75.47.Lx, 77.80.bn, 77.55.Px, 77.55.Nv
Keywords: Multiferroic, epitaxial strain, ferroelectric ferromagnet

I. INTRODUCTION

The likelihood of a symmetry-breaking ferroelectric atomic displacement occurring at the B-site of an ABO$_3$ perovskite can generally be predicted by evaluating the Goldschmidt tolerance factor, $t = (r_O + r_A)/\sqrt{2}(r_O + r_B)$, where $r_O$, $r_A$, and $r_B$ are the ionic radii of the oxygen anion, and the A- and B-site cations [1, 2]. 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. Conversely, if $t < 1$, an A-site displacement would be preferred over a B-site shift, as has been predicted theoretically for K$_{0.5}$Li$_{0.5}$NbO$_3$ [1] and LaLuNiMnO$_6$ [2]. Experimentally, Ba$_{1-x}$Ca$_x$TiO$_3$ (0.02 < x < 0.34) single crystals have been shown to exhibit off-center displacements of the smaller Ca ions at the A-site [4]. However, smaller A-site ions generally lead to rotations and tilting of the BO$_6$ octahedra, which preserves the inversion symmetry by doubling the unit cell [1, 2]. For this reason, A-site driven proper ferroelectricity is usually negligible in perovskites.

Well-known exceptions are the Bi- and Pb-containing A-site ferroelectric perovskites Pb(Ti,Zr)O$_3$, BiFeO$_3$, and Bi$_2$NiMnO$_6$ [3, 4]. The Pb and Bi ions in those compounds form covalent bonds with oxygen and contain 6s orbital lone pairs, stabilizing a distorted structure and breaking the inversion symmetry. For other A-site ions, like Ba and La, it is exceedingly rare to form a covalent bond with oxygen and 6s orbital lone pairs in the perovskite lattice. Exceptions can be found in short-period PbTiO$_3$/SrTiO$_3$ A-site ordered superlattices [10] and in A-site ordered double perovskites [11, 12]. A combination of A-site ordering and BO$_6$ octahedral rotation in epitaxially-strained heterostructures has been shown to give rise to improper ferroelectricity.

In this work, we have investigated the possibility of A-site driven ferroelectricity in B-site ordered ferromagnetic La$_2$NiMnO$_6$ crystals. Based on Kanamori-Goodenough rules [13, 14], La$_2$NiMnO$_6$ has been theoretically predicted and experimentally reported to show ferromagnetic order due to the presence of 180° Ni$^{2+}$–O–Mn$^{4+}$ superexchange bonding between an empty Mn$^{4+}$ $e_g$ orbital and a half-filled d orbital on a neighboring Ni$^{2+}$ site. The average tolerance factor of La$_2$NiMnO$_6$ is 0.97, suggesting the possibility of A-site driven ferroelectricity. However, in bulk crystals, the BO$_6$ octahedra are tilted and rotated, forming non-polar rhombohedral (R3) and monoclinic (P2$_1$/n) structures [15, 16].

La$_2$NiMnO$_6$ thin films can be grown epitaxially on LaAlO$_3$, (LaAlO$_3$)$_{0.5}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.5}$ (LSAT), and SrTiO$_3$ substrates [18]. Epitaxial strain always shrinks or expands the crystal lattice of a thin film along a certain direction, possibly stabilizing a phase that is different from a strain-free bulk crystal. Even when no strain-related symmetry changes occur in the film, it is common to see Curie temperature shifts in ferroelectrics and ferromagnets [19]. For example, epitaxial strain has been shown to induce ferroelectricity in paraelectric SrTiO$_3$ [20], SrMnO$_3$ [21], and EuTiO$_3$ [22]. In the case of La$_2$NiMnO$_6$ films on LaAlO$_3$(001) substrates, polar-
ized Raman measurements have revealed that the rhombohedral (R\(3\)) and monoclinic (P2\(_1/\)n) phases coexist at room temperature \[23\], even though in bulk La\(_2\)NiMnO\(_6\) crystals the rhombohedral and monoclinic phases are stabilized at high and low temperatures, respectively \[13,16\]. Here, we theoretically and experimentally investigate the epitaxial strain effect on the dielectric properties of La\(_2\)NiMnO\(_6\) thin films and show that epitaxial strain induces ferroelectricity in La\(_2\)NiMnO\(_6\)/SrTiO\(_3\) heterostructures.

II. FIRST-PRINCIPLES DENSITY FUNCTIONAL CALCULATIONS

The effect of epitaxial strain on the crystal symmetry and polar instability of La\(_2\)NiMnO\(_6\) films was studied by density functional theory (DFT) simulations using the Vienna Ab-initio Simulation Package (VASP) within the generalized gradient approximation to the exchange correlation potential \[24,25\]. The electronic correlation effects were considered by using the generalized gradient approximation (GGA)+\(U\) method with \(U = 3\) eV for the Mn and Ni \(d\) states \[26\]. It has been reported that La\(_3\)NiMnO\(_6\) crystallizes in the rhombohedral structure (R\(3\)) at high temperature and transforms to the monoclinic structure (P2\(_1/\)n) at low temperature. In fact, these two structures coexist over a wide temperature range \[12,18\]. The strain effect on the polar instability was studied for both structures. For the rhombohedral structure, the unit cell volume was constrained to the experimentally observed value, \(V = 353.33\) Å\(^3\), and converted to a hexagonal structure for the calculation. The \(c/a\) ratio was tuned to simulate the strain effect. The cutoff energy for the plane waves was set at 400 eV, whereas the \(k\)-point sampling was done using a \(4 \times 4 \times 2\) grid in the hexagonal lattice. The Mn and Ni atoms were aligned alternately along the [110] cubic direction with the spins set in a ferromagnetic configuration. The ferroelectric polarization was calculated by using the Berry phase method and comparing the ferroelectric structure and the paraelectric (centrosymmetric) reference structure.

The monoclinic structure did not show spontaneous polarization under any strain field, corroborating the recent work by Zhao et al. \[12\]. In contrast, the rhombohedral La\(_2\)NiMnO\(_6\) crystal structure, schematically illustrated in the inset of Fig. \(\text{II(a)}\), presented a clear polar state under moderate strain. Fig. \(\text{II(a)}\) shows the strain dependence of the spontaneous polarization along the [111]\(_{\text{cubic}}\) direction in a rhombohedral La\(_2\)NiMnO\(_6\) crystal. The inset plot shows the relationship between the rhombohedral lattice parameter and the rhombohedral angle. Increasing the tensile strain lowers the rhombohedral angle of the La\(_2\)NiMnO\(_6\) crystal and ultimately leads to a polar state when the lattice parameter exceeds 5.7 Å, which corresponds to 4.2% tension with respect to the experimental bulk value of 5.47 Å. A comparison of the partial density of states plots (not shown) of the paraelectric and a 5.9% stretched (\(a = 5.79\) Å) ferroelectric phases indicated that the empty La 6s state is very slightly shifted by the structural distortion, whereas the Ni and Mn 3d states remain essentially unaffected.

The crystal structures of the unstrained paraelectric and the +5.9% stretched ferroelectric rhombohedral La\(_2\)NiMnO\(_6\) phases are compared in Figs. \(\text{II(b)}\) and \(\text{II(c)}\). The structural model plots have been oriented along the [110]\(_{\text{cubic}}\) and [001]\(_{\text{cubic}}\) directions. The B-site Ni and Mn ions are alternately aligned along the [111]\(_{\text{cubic}}\) direction. The relaxed structural parameters of the paraelectric and ferroelectric La\(_2\)NiMnO\(_6\) phases are listed in Table \(\text{II}\). In the paraelectric R\(3\) structure, the A-site La lat-
TABLE I. Energy-minimized structural parameters of the paraelectric (top) and the ferroelectric (bottom) La$_2$NiMnO$_6$ structure under 5.9% tension.

|                  | Paraelectric phase: R̅3 | Ferroelectric phase: R3, 5.9% tension |
|------------------|-------------------------|-------------------------------------|
| $a$ (Å)          | 5.475 60.671            | 5.253 53.997                        |
| $\alpha$ (°)     | 0.243 0.243 0.243       | 0.272 0.272 0.272                   |
| $x$              | Ni 0 0 0                | La 0.773 0.773 0.773                |
| $y$              | Mn 0.500 0.500 0.500    | Ni 0.505 0.505 0.505                |
| $z$              | O 0.787 0.701 0.273     | O 0.247 0.794 0.704                 |

![Calculated electron localization functions for the ferroelectric NiMnO$_6$ structure](image)

**FIG. 2.** Calculated electron localization functions for the ferroelectric R3 structure of La$_2$NiMnO$_6$. The La ions are shown in dark red, the Ni ions in gray, the Mn ions in dark blue, the oxygen in white and the electron localization in pink. The black lines mark the rhombohedral unit cell.

The La lattice develops a sizable La displacement along the [111]$_{\text{cubic}}$ direction. The mechanism responsible for the La lattice shift is fundamentally different from the Bi lone pair mechanism seen in ferroelectric BiFeO$_3$ and Bi$_2$NiMnO$_6$. The calculated electronic localization function is mapped in Fig. 2 for the R3 symmetry of ferroelectric La$_2$NiMnO$_6$. No unbalanced charge distributions were found around the La ions, unlike the ferroelectric Bi perovskites that have been reported to exhibit localized lobe-shaped charge distributions surrounding the Bi ions. This indicates that the strain-induced ferroelectricity in rhombohedral La$_2$NiMnO$_6$ cannot be attributed to either a 6s orbital lone pair of La or covalent bonding between La and oxygen. The DFT calculation suggests that ferroelectricity and ferromagnetism coexist in the rhombohedral La$_2$NiMnO$_6$ lattice when the crystal is stretched along the [111]$_{\text{cubic}}$ direction.

### III. EXPERIMENT

To verify the DFT calculation results experimentally, La$_2$NiMnO$_6$ films were grown on SrTiO$_3$ (c = 3.905 Å) and LSAT (c = 3.87 Å) substrates by pulsed laser deposition (PLD). A polycrystalline stoichiometric La$_2$NiMnO$_6$ target, fabricated by conventional solid state reactions, was ablated with a KrF excimer laser ($\lambda = 248$ nm) at a repetition rate of 5 Hz. During deposition, the SrTiO$_3$ substrates were kept at temperatures between 600 and 700°C and pure oxygen gas was continuously supplied into the growth chamber to maintain an ambient pressure of 500 mTorr. After growth, the films were cooled to 500°C at a rate of 15°C/min. The growth chamber was then filled to 760 Torr of pure oxygen gas and the films were cooled down to room temperature.

Basic room-temperature structural analysis was done by x-ray diffraction (XRD) and reciprocal space mapping. As it is difficult to determine the crystal symmetry of La$_2$NiMnO$_6$ films by XRD, Raman spectroscopy was used to determine the presence of different crystallographic phases and to look for structure changes below room temperature. A He-Ne laser (633 nm, 17 mW) was focused on the La$_2$NiMnO$_6$ film surface through a ×50 objective lens with N.A.=1.0 for room-temperature measurements and 0.5 for low-temperature measurements. The scattering spectra were collected by a charge-coupled device detector (RAMASCOPE, Renishaw). As the film surface was parallel to the (001)$_{\text{cubic}}$ plane, polarized Raman spectra could be taken in exact $XX'Y'$ scattering configurations, where $X \parallel [110]_{\text{cubic}}$, $X' \parallel [100]_{\text{cubic}}$, $Y \parallel [\overline{1}0]_{\text{cubic}}$, and $Y' \parallel [010]_{\text{cubic}}$. The sample temperature was controlled with a He flow cryostat (Microstat, Oxford Instruments).

The degree of B-site order in La$_2$NiMnO$_6$ films can be estimated from the saturation magnetization. The magnetic properties of the films were measured with a superconducting quantum interference device (SQUID) magnetometer.

The presence of ferroelectric order was measured by several complementary techniques to show that the ferroelectricity is indeed an intrinsic feature of the films and not an artefact of temperature- or bias-dependent leak current or interface capacitance changes. For traditional ferroelectric $P - E$ hysteresis measurements, interdigitated Au electrodes were formed on the La$_2$NiMnO$_6$ film surfaces by e-beam evaporation and photolithographic lift-off. The Au electrode thickness was 100 nm, the finger width and length were 10 µm and 200 µm, respectively, and the electrode gap was 10 µm. Electrical contacts were made by ultrasonic wire bonding of aluminum wires to the Au pads. The electrical polarization was deduced by measuring the displacement current during a bipolar 15 V triangular bias voltage sweep at 1 Hz.

Positive-Up-Negative-Down (PUND) measurements...
were performed for detecting the displacement current during ferroelectric domain reversal by an applied bias voltage and eliminate the possibility that the $P - E$ loop measurements might be affected by a bias-dependent interface capacitance change. At first, all ferroelectric domains were poled by a trapezoidal 20 V pulse. Subsequently, two positive and two negative trapezoidal pulses were applied to the La$_2$NiMnO$_6$ films. The displacement current was converted to a voltage signal with a current-voltage converter and measured with a digitizer.

Determining the temperature dependence of polarization from $P - E$ measurements can be complicated in thin films by changes in the magnitude of leak currents that may completely mask small displacement currents. A useful technique for measuring the polarization of a thin film sample without having to apply a bias voltage during the measurement is the Chynoweth method of dynamic pyroelectric detection of dielectric polarization. For the pyroelectric measurements,[32–35] a 100-nm thick Pd top electrode was deposited on the polarization. For the pyroelectric measurements[32–35], the sample current was converted to a voltage signal with a current-voltage converter and measured with a digitizer.

In double perovskite thin films, the nanoscale spatial distribution of ferroelectric polar order can be tuned by varying the film growth temperature and the oxygen pressure, leading to various different magnetic phases, including ferromagnetic, ferrimagnetic, and antiferromagnetic films.[29, 32]. In this work, ordered and disordered La$_2$NiMnO$_6$ films were grown on SrTiO$_3$(001) substrates at 700°C and 600°C, respectively. In Fig. 3(a), a reciprocal space map of a La$_2$NiMnO$_6$/SrTiO$_3$ sample grown at 700°C shows a single (206) film reflection in addition to the strong substrate (103) peak. All samples used in this study presented similar coherent growth of La$_2$NiMnO$_6$ on both SrTiO$_3$(001) and LSAT(001) substrates. The in-plane and out-of-plane lattice parameters of the strained La$_2$NiMnO$_6$/SrTiO$_3$ film were 3.91 Å and 3.89 Å, respectively. In contrast, the lattice parameters of a La$_2$NiMnO$_6$/LSAT sample were 3.87 Å and 3.88 Å along the in-plane and out-of-plane directions. The SrTiO$_3$ substrate thus induced tensile strain, stretching the La$_2$NiMnO$_6$ lattice along the in-plane direction. The ordering of the B-site Ni and Mn ions was determined from $\theta$/$2\theta$ XRD measurements performed with a four-circle diffractometer along the [111]$_{\text{cubic}}$ direction, as shown in Fig. 3(b). In addition to the SrTiO$_3$ (ill) substrate peaks, all La$_2$NiMnO$_6$ (ill) reflections can be clearly seen. Small peaks of odd-l La$_2$NiMnO$_6$ (ill) reflections correspond to the ordered B-site superlattice of Ni and Mn ions along the [111]$_{\text{cubic}}$ direction. The inset shows details of the La$_2$NiMnO$_6$(333) reflection. The red line marks the expected peak position of a non-strained bulk La$_2$NiMnO$_6$ crystal, showing that the B-site ordered La$_2$NiMnO$_6$ film on the SrTiO$_3$ substrate was stretched by +1.1% along the [111]$_{\text{cubic}}$ direction by the epitaxial strain.

Rhombohedral and monoclinic phases have been reported to coexist in La$_2$NiMnO$_6$ at room temperature.[23] Even in a phase-pure rhombohedral La$_2$NiMnO$_6$ film grown on a SrTiO$_3$(001) substrate, four reflection peaks should be visible in a reciprocal space map around the SrTiO$_3$(103) reflection. The overlapping diffraction peaks of multiple domains of two possible phases make detailed structural analysis difficult with a laboratory x-ray source. Due to this, the reciprocal space map Fig. 4(a) shows only a single peak originating from the La$_2$NiMnO$_6$ film. In order to accurately analyze the La$_2$NiMnO$_6$ film structure, polarized Raman measurements were performed on the ordered La$_2$NiMnO$_6$/SrTiO$_3$ films at room temperature, as shown in Fig. 4(a). The main benefit of the Raman measurement is the ability to distinguish between the rhombohedral and monoclinic phases in the film.

Except for small differences in phonon line parameters, the spectra and their variation with scattering configuration closely resemble those reported for La$_2$NiMnO$_6$/LaAlO$_3$(001) films.[23] indicating that rhombohedral and monoclinic phases coexist in our La$_2$NiMnO$_6$/SrTiO$_3$ films as well. In particular, the presence of three peaks in a $XY'$ spectrum can be used to detect the presence of the rhombohedral phase, because the monoclinic phase should not exhibit any $XY'$ scattering peaks.

In order to investigate the stability of the rhombohedral and monoclinic phases at low temperature, the temperature dependence of $XX$ and $XY$ Raman spectra was investigated from 5 K to 300 K, as shown in Figs. 4(b) and 4(c). The spectra show that both rhombohedral and monoclinic phases coexist over the whole temperature...
The SrTiO$_3$ substrate crystal undergoes an antiferrodistortive structural transition from a high-temperature cubic phase to a low-temperature tetragonal phase at 105 K, resulting in a 0.015% in-plane lattice parameter change $\Delta a/2a = 0.30\%$. The epitaxial strain imposed on the film by the SrTiO$_3$ substrate thus changes slightly at this temperature, resulting in a discontinuous temperature dependence of the Raman spectra in La$_2$NiMnO$_6$ samples. The reduction of the crystal symmetry of a La$_2$NiMnO$_6$ film can therefore be expected to enhance the ferroelectric polarization at temperatures below 105 K.

The level of $B$-site order can be quantified by looking at the magnetization of the films, as shown in Fig. 5(a). The magnetization hysteresis loops were measured at 10 K for ordered and disordered La$_2$NiMnO$_6$/SrTiO$_3$ samples. By comparing the observed saturation magnetizations of the films with the theoretical magnetization of 2.5 $\mu_B$ for a perfectly ordered La$_2$NiMnO$_6$ crystal $^{13,14}$, the fraction of $B$-site order in the ordered and disordered La$_2$NiMnO$_6$ films can be estimated to be 80% and 26%, respectively. Fig. 5(b) presents the temperature dependence of the field-cooled and zero-field-cooled magnetizations at 0.75 T for the same samples. The magnetic Curie temperature is 280 K in both cases, matching reported values $^{13}$. The magnetization data suggests that the ordered (80%) and disordered (26%) La$_2$NiMnO$_6$/SrTiO$_3$ films were ferromagnetic and ferrimagnetic, respectively.

B. Ferroelectric properties of La$_2$NiMnO$_6$ films

The presence of spontaneous polarization was determined in ordered and disordered La$_2$NiMnO$_6$/SrTiO$_3$ films, as well as an ordered La$_2$NiMnO$_6$/SrTiO$_3$/LSAT sample by measuring the ferroelectric polarization and the displacement current in the in-plane direction at 10 K as shown in Fig. 6. Both films grown on SrTiO$_3$ substrates were verified to exhibit ferroelectric domain reversal under an external electric field, while the La$_2$NiMnO$_6$/LSAT sample showed no hysteresis behavior at all, revealing the importance of strain in the formation of a ferroelectric state in the La$_2$NiMnO$_6$/SrTiO$_3$ films. There is little difference in ferroelectric polarization between the ordered and disordered La$_2$NiMnO$_6$/SrTiO$_3$ films. This is consistent with the calculation results in Fig. 1 which showed that the $B$-site Ni and Mn ions do not have a significant effect on the $A$-site driven ferroelectricity in La$_2$NiMnO$_6$ films. Moreover, this data can rule out improper ferroelectricity originating from bond- and site-centered charge ordering, as happens in Fe$_2$O$_3$ crystals $^{22,32}$, and the $E$-type antiferromagnetic order that can be found in Y$_2$CoMnO$_6$ and Lu$_2$CoMnO$_6$ crystals $^{41,43}$.

We note that when measuring the ferroelectric polarization in thin films grown on SrTiO$_3$ substrates, it is important to verify that the substrate material does not contribute to the observed signal $^{52}$. It has been reported that an electric field of 700 V/mm can in-

![Graphical Image](image-url)
FIG. 4. (Color online) (a) Polarized Raman spectra of an ordered La$_2$NiMnO$_6$/SrTiO$_3$ film obtained at room temperature, showing that rhombohedral and monoclinic phases coexist. Temperature dependence of $XX$ (b) and $XY$ (c) Raman spectra of a $B$-site ordered La$_2$NiMnO$_6$/SrTiO$_3$ film between 5 K and 300 K. The red arrow in (c) marks the 457 cm$^{-1}$ peak that appears below 105 K.

FIG. 5. (Color online) (a) Magnetization hysteresis loops at 10 K for ordered and disordered La$_2$NiMnO$_6$ films on SrTiO$_3$ substrates. (b) Temperature dependence of the magnetic moment at 0.75 T, showing that the magnetic Curie temperature is close to 280 K, corresponding to the reported bulk value.

FIG. 6. (Color online) Ferroelectric polarization (left axis) and displacement current (right axis) as a function of applied voltage at 10 K for ordered (a) and disordered (b) La$_2$NiMnO$_6$/SrTiO$_3$ films, an ordered La$_2$NiMnO$_6$/LSAT film (c), and a non-ferroelectric SiO$_x$/SrTiO$_3$ (d) reference sample. The hysteresis loop and displacement current of a SiO$_x$/SrTiO$_3$ film for comparison with the ordered and disordered La$_2$NiMnO$_6$/SrTiO$_3$ films. The SiO$_x$/SrTiO$_3$ sample did not show a hysteresis loop, proving that the hysteresis loops obtained for the ordered and disordered La$_2$NiMnO$_6$/SrTiO$_3$ films originated from ferroelectricity in the films.

Successful observation of ferroelectric hysteresis loops means that leakage currents in the La$_2$NiMnO$_6$ films were low compared to the displacement current that arises when the ferroelectric polarization is reversed by an applied bias. However, this type of direct hysteresis mea-
measurements is generally not a reliable method for measuring the spontaneous polarization in ferroelectric oxide thin films because the measured current consists of several components due to switching of the ferroelectric domains, the linear dielectric response, and leakage current of the material. Particularly for La$_2$NiMnO$_6$ films, the intermixed non-ferroelectric monoclinic phase would produce a linear dielectric response when an electric field is applied, resulting in an increase of the background current. To suppress the linear dielectric behavior during hysteresis measurements, PUND measurements were performed for the ordered La$_2$NiMnO$_6$/SrTiO$_3$ sample, as shown in Fig. 7(a).

Only the first and third pulses showed domain reversal displacement currents, proving that the La$_2$NiMnO$_6$/SrTiO$_3$ film was indeed ferroelectric. The advantage of PUND measurements is to eliminate the linear dielectric current contribution by subtracting the second (fourth) cycle current from the first (third) cycle one. Fig. 7(b) presents the ferroelectric hysteresis loop measured in this way, exhibiting a fully saturated loop with a spontaneous polarization of 3.8 µC/cm$^2$. The PUND measurement shows that the spontaneous polarization of the La$_2$NiMnO$_6$ layer is slightly lower than the remnant polarization seen in the standard hysteresis measurements in Fig. 6(a), which include a linear dielectric response component.

The temperature dependence of ferroelectric hysteresis loop shapes is presented in Fig. 8(a), together with the temperature dependence of the remanent polarization in Fig. 8(b). The remanent polarization of ordered and disordered La$_2$NiMnO$_6$/SrTiO$_3$ films were estimated to be 4.2 µC/cm$^2$ and 3.2 µC/cm$^2$, respectively, from the hysteresis loops measured at 10 K, and gradually decreased to zero at around 50 to 60 K as the temperature was increased.

To precisely evaluate the polar state in La$_2$NiMnO$_6$/SrTiO$_3$ films, dynamic pyroelectric measurements were performed for the ordered and disordered La$_2$NiMnO$_6$/Nb: SrTiO$_3$(001) samples, as shown in Fig. 9. In this case, the temperature derivative of the spontaneous polarization was measured along the out-of-plane direction. Below 250 K, the pyroelectric response increased for both samples with decreasing temperature. The maximum pyroelectric signal amplitude was observed at 100 to 150 K, below which the pyroelectric response decreased. A clear kink can be seen in the pyroelectric current amplitude at 105 K, as marked by arrows in Fig. 9. This is related to the abrupt change observed in the Raman measurements in Fig. 4(c). The 105 K structural transition in the SrTiO$_3$ substrate crystal causes a stepwise 0.015% change in the epitaxial strain on the La$_2$NiMnO$_6$ film lattice, resulting in a discontinuous temperature dependence of the pyroelectric responses in both samples. This result is a clear indication that ferroelectricity in La$_2$NiMnO$_6$/SrTiO$_3$ films is very sensitive to epitaxial strain.

The ferroelectric domain structure of the films was determined by acquiring SNDM images at room temperature. Fig. 10(a) shows a typical SNDM image for an ordered La$_2$NiMnO$_6$/Nb: SrTiO$_3$ film. The observation of a uniform SNDM frequency shift signal indicates
that the La$_2$NiMnO$_6$/SrTiO$_3$ film was spontaneously polarized at room temperature. The histogram in Fig. 10(b) shows that most areas were polarized with a negative charge at the top surface, matching the polarization direction determined by the pyroelectric analysis. Some regions exhibited a zero frequency shift, indicating that there was no vertical spontaneous polarization in these parts of the La$_2$NiMnO$_6$/Nb:SrTiO$_3$ film, probably due to the intermixing of the non-polar monoclinic phase that was detected in the Raman measurements.

According to the DFT calculations, a ferroelectric distortion appears only in the rhombohedral La$_2$NiMnO$_6$ phase when the crystal is stretched along the $[111]_\text{cubic}$ direction. The monoclinic structure lacks the 3-fold rotation, allowing anti-phase tilting of the MnO$_6$ and NiO$_6$ octahedra, which suppresses the La polar distortion and results in a paraelectric state. In contrast, the rhombohedral structure preserves the 3-fold rotation symmetry that does not allow MnO$_6$ and NiO$_6$ octahedral tilting but allows polar ionic shifts of La. Therefore, ferroelectricity is induced only in a strained La$_2$NiMnO$_6$/SrTiO$_3$ film and cannot appear in bulk La$_2$NiMnO$_6$.

V. CONCLUSION

We have theoretically and experimentally demonstrated the presence of strain-induced ferroelectricity in ferromagnetic La$_2$NiMnO$_6$ films. Theoretical calculations and tolerance factor analysis indicated the presence of A-site driven ferroelectricity along the $[111]_\text{cubic}$ direction in epitaxially strained La$_2$NiMnO$_6$ crystals. A polar state was shown to exist in epitaxial La$_2$NiMnO$_6$ films even at room temperature. The observation of A-site ferroelectricity in epitaxially-strained La$_2$NiMnO$_6$ films highlights the potential of strain engineering for tailoring the properties of complex oxides and extending their functionalities for new device applications.

ACKNOWLEDGMENTS

This study was partly supported by JSPS KAKENHI (Grant Nos. 26105002, 25706022, 24740235, and 23226008). This work was also partly supported by the Kurata Memorial Hitachi Science and Technology Foundation and the Iketani Science and Technology Foundation. MK acknowledges the financial support from the Japan Society for the Promotion of Science for young scientists. The authors would like to thank N. Chinone for technical support in using the SNDM.

[1] D. I. Bilc and D. J. Singh, Phys. Rev. Lett., 96, 147602 (2006).
[2] N. A. Benedek and C. J. Fennie, J. Phys. Chem. C, 117, 13339 (2013).
[3] D. J. Singh and C. H. Park, Phys. Rev. Lett., 100, 087601 (2008).
[4] D. Fu, M. Itoh, S.Y. Koshihara, T. Kosugi, and S. Tsuneyuki, Phys. Rev. Lett., 100, 227601 (2008).
[5] R. E. Cohen, Nature, 358, 136 (1992).
[6] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaitiyanathan, D. G. Schrom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science, 299, 1719 (2003).
[7] N. A. Hill, J. Phys. Chem. B, 104, 6694 (2000).
[8] J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, Phys. Rev. B, 71, 014113 (2005).
[9] M. Azuma, K. Takata, T. Saito, S. Ishiwata, Y. Shimakawa, and M. Takano, J. Am. Chem. Soc., 127, 8889 (2005).
[10] E. Bousquet, M. Dawber, N. Stuck, C. Lichtensteiger, P. Hermet, S. Gariglio, j. M. Triscone, and P. Ghosez, Nature, 452, 732 (2008).
[11] J. M. Rondinelli and C. J. Fennie, Adv. Mater., 24, 1961 (2012).
[12] H. J. Zhao, W. Ren, Y. Yang, J. Iniguez, X. M. Chen, and L. Bellaiche, Nat. Commun., 5, 4021 (2014).
[13] J. B. Goodenough, Phys. Rev., 100, 564 (1955).
[14] J. Kanamori, J. Phys. Chem. Solids, 10, 87 (1959).
[15] N. S. Rogado, J. Li, A. W. Sleight, and M. A. Subramanian, Adv. Mater., 17, 2225 (2005).
[16] C. L. Bull, D. Gleeson, and K. S. Knight, J. Phys. Condens. Matter., 15, 4927 (2003).
[17] H. Das, U. V. Waghmare, T. Saha-Dasgupta, and D. D. Sarma, Phys. Rev. Lett., 100, 186402 (2008).
[18] M. Hashisaka, D. Kan, A. Masuno, M. Takano, Y. Shimakawa, T. Terasshima, and K. Mibu, Appl. Phys. Lett., 89, 032504 (2006).
[19] D. G. Schlom, L. Q. Chen, C. J. Fennie, V. Gopalan, D. A. Muller, X. Pan, R. Ramesh, and R. Uecker, MRS Bulletin, 39, 118 (2014).
[20] N. A. Pertsiev, A. K. Tagantsev, and N. Setter, Phys. Rev. B, 61, R825 (2000).
[21] J. H. Lee and K. M. Rabe, Phys. Rev. Lett., 104, 207204 (2010).
[22] J. H. Lee, L. Fang, E. Vlahos, X. Ke, Y. W. Jung, L. F. Kourkoutis, J. W. Kim, P. J. Ryan, T. Heeg, M. Roeckermann, V. Goian, M. Bernhagen, R. Uecker, P. C. Hammel, K. M. Rabe, S. Kamba, J. Schubert, J. W. Freeland, D. A. Muller, C. J. Fennie, P. Schiffer, V. Gopalan, E. Johnston-Halperin, and D. G. Schlom, Nature, 466, 954 (2010).
[23] M. N. Iliev, H. Guo, and A. Gupta, Appl. Phys. Lett., 90, 151914 (2007).
[24] G. Kresse and J. Furthmuller, Phys. Rev. B, 54, 11169 (1996).
[25] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., 77, 3865 (1996).
[26] Y. M. Zhu, D. Ke, R. Yu, Y. H. Hsieh, H. J. Liu, P. P. Liu, Y. H. Chu, and Q. Zhan, Appl. Phys. Lett., 100, 062406 (2012).
[27] B. Silvi and A. Savin, Nature, 371, 683 (1994).
[28] P. Baettig, C. F. Schelle, R. LeSar, U. V. Waghmare, and N. A. Spaldin, Chem. Mater., 17, 1376 (2005).
[29] M. Kitamura, I. Ohkubo, M. Kubota, Y. Matsumoto, H. Koinuma, and M. Oshima, Appl. Phys. Lett., 94, 132506 (2009).
[30] M. Kitamura, I. Ohkubo, M. Matsunami, K. Horiba, H. Kumigashira, Y. Matsumoto, H. Koinuma, and M. Oshima, Appl. Phys. Lett., 94, 262503 (2009).
[31] Y. Sakurai, I. Ohkubo, Y. Matsumoto, H. Koinuma, and M. Oshima, J. Appl. Phys., 110, 063913 (2011).
[32] R. Takahashi, Y. Cho, and M. Lippmaa, J. Appl. Phys., 117, 014104 (2015).
[33] R. Takahashi, T. Tybell, and M. Lippmaa, J. Appl. Phys., 112, 014111 (2012).
[34] R. Takahashi, H. Misumi, and M. Lippmaa, Phys. Rev. B, 86, 144105 (2012).
[35] R. Takahashi, M. Katayama, O. Dahl, J. K. Grepstad, Y. Matsumoto, and T. Tybell, Appl. Phys. Lett., 94, 232901 (2009).
[36] Y. Cho, A. Kirihara, and T. Saeki, Rev. Sci. Instruments, 67, 2297 (1996).
[37] Y. Cho, J. Mater. Res., 26, 2007 (2011).
[38] M. Kitamura, I. Ohkubo, M. Kubota, Y. Matsumoto, H. Koinuma, and M. Oshima, Appl. Phys. Lett., 94, 132506 (2009).
[39] J. Brink and D. I. Khomskii, J. Phys.: Condens. Mater, 20, 434217 (2008).
[40] G. Sharma, J. Saha, S. D. Kaushik, V. Siruguri, and S. Patnaik, Appl. Phys. Lett., 103, 012903 (2013).
[41] M. N. Iliev, M. V. Abrashev, A. P. Litvinchuk, V. G. Hadjiev, H. Guo, and A. Gupta, Phys. Rev. B, 75, 104118 (2007).
[42] A. Okazaki and M. Kawaminami, Mater. Res. Bull., 8, 545 (1973).
[43] J. Hemberger, P. Lunkenheimer, R. Viana, R. Bohmer, and A. Loidl, Phys. Rev. B, 52, 13159 (1995).