Research Article

Strain-Dependence of the Structure and Ferroic Properties of Epitaxial NiTiO_3 Thin Films Grown on Different Substrates

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Polarization-induced weak ferromagnetism has been predicted a few years back in perovskite MTiO_3 ($M = \text{Fe}, \text{Mn}, \text{and Ni}$). We set out to stabilize this metastable perovskite structure by growing NiTiO_3 epitaxially on different substrates and to investigate the dependence of polar and magnetic properties on strain. Epitaxial NiTiO_3 films were deposited on Al_2O_3 , Fe_2O_3 , and LiNbO_3 substrates by pulsed laser deposition and characterized using several techniques. The effect of substrate choice on lattice strain, film structure, and physical properties was investigated. Our structural data from X-ray diffraction and electron microscopy shows that substrate-induced strain has a marked effect on the structure and crystalline quality of the films. Physical property measurements reveal a dependence of the weak ferromagnetism and lattice polarization on strain and highlight our ability to control the ferroic properties in NiTiO_3 thin films by the choice of substrate. Our results are also consistent with the theoretical prediction that the ferromagnetism in acentric NiTiO_3 is polarization induced. From the substrates studied here, the perovskite substrate LiNbO_3 proved to be the most promising one for strong multiferroism.

1. Introduction

There has been a recent wave of interest in the MTiO_3 ($M = \text{Fe}, \text{Mn}, \text{and Ni}$) compounds as a result of a theoretical prediction that their polymorph crystallizing in space group $R3c$ exhibits multiferroic properties and may enable switching of the direction of magnetization by the application of an electric field [1, 2]. The one-atmosphere, equilibrium structure of these compounds is the ilmenite (ILM) structure with space group $R3^-$ [3]. The ILM phase is nonpolar, hence paraelectric, and nonferromagnetic. The acentric, polar $R3c$ phase, also known as the LiNbO_3 -type (LNO) structure, can be stabilized in the bulk under high-pressure, high-temperature conditions, as reported for FeTiO_3 [4, 5] and MnTiO_3 [6, 7]. LNO-type NiTiO_3 is expected to form under similarly extreme conditions [8], although its synthesis in the bulk has not been reported. The demonstration of coupling between the ferromagnetic and ferroelectric order parameters required for multiferroic switching will demand

either bulk single crystals or epitaxial films. Thin film deposition by molecular beam epitaxy (MBE) or pulsed laser deposition (PLD) is often the methods of choice to prepare high-quality epitaxial films because they allow for the stabilization of otherwise metastable structures and tuning material properties by the introduction of lattice strain. Thin film deposition also eliminates the need for specialized high-pressure apparatus needed for growing crystals of the above MTiO_3 compounds in the LNO-type structure.

Recently, we have demonstrated that epitaxial NiTiO_3 films can be grown on sapphire substrate by PLD [9] and that such films exhibit both lattice polarization and weak ferromagnetism [10]. Furthermore, the properties of $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ films were successfully manipulated by applied strain [11]. While the latter reports confirmed that our epitaxial NiTiO_3 films were indeed of the LNO-type structure, the lattice mismatch between the film(s) and the sapphire substrate resulted in less-than-high-quality films in terms of crystallinity, most likely affecting the observed physical properties

adversely. Al_2O_3 exerts a large compressive strain on NiTiO_3 , which may promote the stabilization of the metastable LNO-type structure, but the effect of smaller and/or tensile strains on LNO-type MTiO_3 films is still unknown. Both compressive and tensile strains are known to promote multiferroic properties in the same compound [12]. In this work, the choice of substrate was extended by adding hematite Fe_2O_3 (001) (a very close lattice match) and LiNbO_3 (001) substrates (>2% tensile strain) to the list, and the influence of the strain on film structure and properties was investigated. Based on high-resolution X-ray diffraction (HRXRD) and transmission electron microscopy (TEM), we describe the effect of strain from lattice mismatch on the structure of the films. From our complimentary physical property characterization by DC magnetization and second harmonic generation (SHG), we infer that our $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ and $\text{NiTiO}_3/\text{LiNbO}_3$ films exhibit polarization-induced weak ferromagnetism and that the choice of substrate can be employed to control the ferroic properties of these potentially multiferroic films.

2. Experiment

Epitaxial NiTiO_3 films were grown on Al_2O_3 (001), LiNbO_3 (001) (MTI Corporation, Richmond, CA 94804), and Fe_2O_3 (001) substrates (SurfaceNet GmbH, 48432 Rheine, Germany) by offaxis PLD. The substrates were ultrasonically cleaned in acetone and isopropanol for 10 minutes each prior to loading in the PLD chamber. NiTiO_3 films on the different substrates were synthesized using identical deposition conditions with similar different deposition times to achieve similar film thicknesses. The commercially purchased NiTiO_3 (Plasmaterials, Inc., Livermore, CA 94550) and NiO targets (Kurt J. Lesker, Co., Livermore, CA 94551) were 2-inch diameter and used as received. The NiO target was used to adjust the Ni/Ti ratio in the films to achieve stoichiometric films. In a typical two-target growth procedure, each target was irradiated with a few laser pulses, followed by closing the shutter and moving the second target into the ablation position. These "layer sequences" were repeated as many times as necessary to achieve NiTiO_3 films of typically ~30–50 nm thickness. A repetition rate of 2 Hz was used for the KrF laser ($\lambda = 248$ nm). The laser energy as measured at the laser was 315 mJ. Prior to growth, the targets were ablated for 15 minutes at a laser repetition rate of 10 Hz in 10 mTorr O_2 in order to eliminate carbonaceous surface contamination. The substrate temperature was held constant during growth at 600°C and the O_2 partial pressure in the chamber was 10 mTorr during deposition. Substrates were cooled to room temperature in 10 mTorr O_2 following growth, with no postgrowth annealing. The combination of the offaxis geometry and a relatively high oxygen pressure to reduce molten droplet incorporation in the films has been shown to result in high-quality oxide films [13–15].

Film composition and thickness were verified by Rutherford backscattering spectrometry (RBS) measurements carried out using 2 MeV helium (He^+) ions. Backscattered He^+ ions were collected at the scattering angle of 150° using a surface barrier detector. The SIMNRA [16] simulation

program was used to model experimental RBS spectra, yielding the elemental ratios and thicknesses of the films.

Lattice parameters, crystal quality, and lattice strain were investigated using high-resolution X-ray diffraction (HRXRD) with a Philips X'Pert Materials Research Diffractometer (MRD) equipped with a fixed Cu anode operating at 45 kV and 40 mA. A hybrid monochromator, consisting of four-bounce double crystal Ge (220) and a Cu X-ray mirror, were placed in the incident beam path to generate monochromatic $\text{Cu } K_\alpha$ X-rays ($\lambda = 1.54056 \text{ \AA}$) with a beam divergence of 12 arc seconds. Grazing-incidence diffraction (GIXRD) measurements to verify epitaxial character of the films before the HRXRD and X-ray reflectivity (XRR) for film thickness and roughness determination were carried out on a Philips X'Pert Multipurpose Diffractometer (MPD) also equipped with a fixed Cu anode operating at 45 kV and 40 mA. The lattice parameters for the NiTiO_3 films were determined by simultaneously fitting the (006) and (0012) out-of-plane peaks (for parameter c) and the (104), (116), and (1010) in-plane peaks (a and b) using the software TOPAS 4.2 (Bruker AXS GmbH, 76187 Karlsruhe, Germany).

Transmission electron microscopy (TEM) and high angle annular dark field scanning TEM (HAADF-STEM) images were collected on a probe-corrected Titan 80–300 TEM operated at 300 kV. HAADF-STEM images were acquired with an annular inner angle greater than 50 mrad. Cross-sections were prepared using a focused ion beam- (FIB-) based liftout approach on an FEI Helios FIB/SEM, with final cleaning at 2 kV.

High-resolution X-ray photoelectron spectroscopy (XPS) measurements using a Phi 5000 VersaProbe with a monochromatic focused $\text{Al-K}\alpha$ X-ray (1486.68 eV) source and a hemispherical analyzer were used to verify the film composition as well as for the determination of the oxidation state from the lineshape and chemical shift. The XPS spectra were referenced to an energy scale with binding energies for $\text{Cu } 2p_{3/2}$ at $932.67 \pm 0.05 \text{ eV}$ and $\text{Au } 4f$ at $84.0 \pm 0.05 \text{ eV}$. Low energy electrons at ~1 eV, 40 μA and low energy Ar^+ ions were used to minimize the surface charging. The Ti 2p, Ni 2p, and O 1s XPS peaks were charge corrected to the adventitious C 1s peak taken to be 284.8 eV. The oxidation states of Ni and Ti in the films were found to be +2 and +4, respectively.

Field-dependent magnetization (hysteresis) curves for the films were measured on a Quantum Design Physical Property Measurement System (PPMS). Optical SHG mapping was performed with a fundamental wave generated from a coherent Chameleon tunable Ti-sapphire laser with 100 fs pulses of wavelength 872 nm incident normal to the sample surface. Two-dimensional mapping of the signal was done using a Zeiss LSM 710 multiphoton microscope with a 40x NA0.75 air objective. A nondescanned detector was used to maximize the detection efficiency. An emission band pass filter at 436 nm was used to collect SHG signal and reject any fluorescence signal.

3. Results and Discussion

3.1. Influence of Strain on the Structural and Morphological Properties of the Films. It has been demonstrated that the

FIGURE 1: (Color online) Predicted effect of in-plane strain on NiTiO₃ exerted using epitaxy. (a) Schematic epitaxial phase diagram of NiTiO₃ strained from 6% (in-plane compression) to 2.5% (in-plane tension). Regions with polar/ferroelectric (FE) and ferromagnetic (FM) behavior are shown. (b) Lattice parameter (in-plane) versus strain from mismatch for the three substrates used in this study. (c) Crystal structure of unstrained bulk NiTiO₃ in the desired R3c structure. Grey octahedra: NiO₆, blue octahedra: TiO₆. (d) Schematic of the in-plane straining (compression/expansion) of thin-film NiTiO₃ on the substrate (here, the structure of the LiNbO₃ substrate is shown, green octahedra are NbO₆, blue octahedra are LiO₆).

structure and physical properties of electric and magnetic materials in thin film form can be modified or controlled by substrate-exerted strain [17–23]. Biaxial strain was used to increase the transition temperature in high- T_C superconductors [17, 18] and ferroelectric materials [19–21]. The saturation magnetization in ferromagnets [22] and the spontaneous polarization in ferroelectrics were also shown to be affected by strain [20, 23]. Our goal was to investigate substrate-exerted strain as a way to stabilize the desired multiferroic phase in the films and manipulate their physical properties. As cited in Section 1, the transition from $R3^-$ to $R3c$, which is quite subtle [4, 5], can be brought about by compression in the bulk. This phase change in bulk FeTiO₃ results in a volume reduction of 1.1% (from $V = 315.93 \text{ \AA}^3$ in ILM to $312.53 \text{ \AA}^3$) [5, 24]. In our attempt to stabilize the $R3c$ structure in epitaxial thin film form, three different substrates providing different epitaxial strain were used, all c -axis cut and (001) oriented: sapphire Al₂O₃, hematite Fe₂O₃, and LiNbO₃. Using the formula $\epsilon_{\text{substrate}} = (a_{\text{film}} - a_{\text{substrate}})/a_{\text{substrate}}$, where ϵ is the strain in the in-plane direction and a is the corresponding lattice parameter in Å, the in-plane strain was estimated to be $\epsilon_{\text{ALO}} = -5.7\%$ for Al₂O₃, $\epsilon_{\text{FEO}} = 0.1\%$ for Fe₂O₃, and $\epsilon_{\text{LNO}} = 2.3\%$ for LiNbO₃. The bulk lattice parameters used for the calculation were $a = 5.030 \text{ \AA}$ for NiTiO₃ [25], $a = 4.759 \text{ \AA}$ for Al₂O₃ [26], $a = 5.036 \text{ \AA}$ for Fe₂O₃ [27], and $a = 5.151 \text{ \AA}$ for LiNbO₃ [28]. The in-plane lattice parameter versus strain from mismatch for the three substrates is plotted

in Figure 1, and a schematic of the predicted effect of in-plane strain exerted using epitaxy on the physical properties of NiTiO₃ is also depicted. Al₂O₃ substrate was chosen as a nonmagnetic, nonpolar alternative with lattice parameters close to those of NiTiO₃, but still providing a large positive (5.7%) lattice mismatch and thus compressive strain. Sapphire substrates have been used previously to grow epitaxial FeTiO₃ films [29] and, more recently, epitaxial NiTiO₃ films [9, 11, 30]. The potential benefit to using sapphire substrate may be the considerable compressive strain it provides, which may mimic a high-pressure compression employed in the synthesis of bulk LNO-type FeTiO₃ [5] and MnTiO₃ [7]. The in-plane distortion may result in strong polarization, which, in turn, may induce ferromagnetism, as predicted for the bulk [1]. Fe₂O₃ was considered as substrate due to its very closely matching lattice parameter (0.1% strain) and being nonpolar. It was expected that biaxial strain will be necessary to achieve sufficient lattice distortion to make polar NiTiO₃, and the lack of strain, as in the NiTiO₃/Fe₂O₃ samples, may not promote the growth of a polarized lattice in NiTiO₃. Ferroelectric nonmagnetic LiNbO₃, of the $R3c$ structure itself, exhibits a significant tensile strain (2.3%) to NiTiO₃. Stretching the NiTiO₃ lattice in the in-plane direction may result in distortion to help stabilize the desired polar $R3c$ structure. Due to its strong ferroelectric polarization [31], the ferroelectric response of NiTiO₃ films grown on LiNbO₃ will be dominated by the substrate and can only be probed by

methods that discriminate between the film and substrate (e.g., in reflection mode with soft X-rays). Strain regions corresponding to the three substrates in this study, with the expected polar/ferroelectric (FE) and ferromagnetic (FM) behavior, are shown in the diagram of Figure 1.

The list of the films prepared, substrates used, film thicknesses, and lattice parameters are provided in Table 1. As suggested by XRD and TEM, all of the films discussed here were epitaxial and consisted of a single phase, $\text{Ni}_{1-x}\text{Ti}_{1-y}\text{O}_3$ (representing small deviations from the 1:1:3 stoichiometry). For this study, we assume that no oxygen vacancies are present. Figure 2(a) shows representative 2θ - θ HRXRD patterns of NiTiO_3 films grown on each substrate. They suggest that all films exhibit the expected (001) oriented rhombohedral structure (only the (006) and (0012) film peaks detected) with no evidence of secondary phase formation. The lack of (009) reflections in the patterns (45–75° range omitted as it had no peaks) suggests the presence of $R3c$ -type NiTiO_3 , where the (009) peak should be extinct, as opposed to ordered $R3^-$ -type structure, which should exhibit the (009) peak [29]. Figure 2(b) shows in-plane rocking curves around the (116) reflection of NiTiO_3 deposited on each substrate. The peak breadth and intensity in these rocking curves carry information about the crystalline quality (crystallite size and mosaic spread) in the material. The decreasing peak width and increasing intensity going from sapphire to hematite (peak full width at half maximum, FWHM, changes from 2.024° to 1.651°) and to LiNbO_3 substrate (FWHM = 0.024°) suggest improved NiTiO_3 crystallinity, with the improvement being quite drastic for the $\text{NiTiO}_3/\text{LiNbO}_3$ film. The broader curves for the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ and $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$ samples indicate relatively poorly aligned crystallites of a maximum of few tens of nanometers in size. The widths of these curves suggest that the structural quality of the films is most likely not limited by the structural quality of the substrate. At the same time, the LiNbO_3 substrate seems to promote the growth of >100 nm NiTiO_3 crystallites with a high degree of in-plane alignment. Representative reciprocal space maps (RSM) collected around the (1010) reflection of films on each substrate are shown in Figure 2(c). For NiTiO_3 on Al_2O_3 , the RSM indicates a film in-plane parameter very different from that of the substrate and suggests that the film is relaxed (mostly free of epitaxial strain). For NiTiO_3 on Fe_2O_3 and LiNbO_3 , the films appear strained, with an in-plane parameter closer to that of the substrate, in agreement with the lattice parameter values in Table 1.

The lattice parameters of the three films overall are quite similar to that of bulk NiTiO_3 (Table 1). The in-plane parameters track those of the substrates, with NiTiO_3 on Al_2O_3 being the smallest (5.021 Å) and $\text{NiTiO}_3/\text{LiNbO}_3$ being the largest (5.039 Å). The in-plane parameters clearly reflect the effect of substrate strain; compressive strain results in smaller, tensile strain larger cell parameters. The out-of-plane parameters are greater for the two high-strain films; for both $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ and $\text{NiTiO}_3/\text{LiNbO}_3$ c values are similar (13.84 Å), while that of the $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$ film is 13.79 Å. In the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ samples, greater strain from mismatch is accompanied by a larger out-of-plane parameter suggesting that lattice compression in the a -axis direction causes the

lattice to relax in the other (c -axis). This argument does not seem to apply for the $\text{NiTiO}_3/\text{LiNbO}_3$ film, where the strain is smaller and compressive.

The TEM micrographs in Figure 3 reveal films grown epitaxially on the (001) substrates with the expected NiTiO_3 (001) [001]//substrate (001) [001] relationship. STEM analysis confirmed that the films were crystalline having a high degree of epitaxy, in agreement with the XRD. In the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ sample, misfit dislocations and buckling at the interface were evident from the STEM, and these defects are a result of the large lattice mismatch between NiTiO_3 and Al_2O_3 and the presumably columnar growth. Atomic resolution images of the interface (see Figure 3(a)) reveal a structurally distinct, ~2 nm layer between the substrate and the well-oriented film. Buckling of layers at the film-substrate interface has been observed earlier in $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ films from XRD data [9]. Some of the flawed regions near the interface may be due to the formation of strained islands to release strain energy as observed in other large or moderate mismatch systems [33]. The high-resolution image of the $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$ sample (Figure 3(b)) shows a significantly smoother interface between the substrate and the film, and the Fe_2O_3 seemed to alleviate buckling and misfit dislocations due to the close lattice match to NiTiO_3 (0.1%). The $\text{NiTiO}_3/\text{LiNbO}_3$ sample exhibits an imperfect interface due to the 2.3% mismatch (Figure 3(c)), and interfacial coherence lies somewhere between those in the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ and $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$ films. Our high-resolution HAADF-STEM imaging exhibits a rhombohedral arrangement consistent with the $R3c$ structure, as overlaid on the image of the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ sample in Figure 3(d). No evidence of Ni/Ti segregation was found in any of these samples.

3.2. Influence of Strain on Magnetism and Lattice Polarization.

The theory suggests that the ferromagnetism is induced by the lattice polarization in MTiO_3 ($M = \text{Fe, Mn, and Ni}$) compounds in the LNO-type structure [1]. We expect that the polarization is dependent on the substrate-exerted strain in the films. For this reason, we investigated the ferromagnetic behavior of our film samples by performing field-dependent DC magnetization measurements on them using a Quantum Design PPMS in an attempt to correlate their magnetism to epitaxial strain. Figure 4 shows isothermal magnetization curves measured in the three films: $\text{NiTiO}_3/\text{Al}_2\text{O}_3$, $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$, and $\text{NiTiO}_3/\text{LiNbO}_3$. The film grown on Al_2O_3 substrate exhibits an S-shape magnetization measured at 10 K (well below the measured Néel temperature of 110 K) indicative of a residual magnetization, also called weak ferromagnetism (WFM). After subtracting the diamagnetic portion, we calculated a magnetic moment of $0.28 \mu_B/\text{Ni}$ saturating by ~6 kOe. Stronger ferromagnetism was observed in the film grown on LiNbO_3 resulting in a hysteresis curve recorded at 90 K and a moment of $1.35 \mu_B/\text{Ni}$ saturating by ~20 kOe. While this moment is significantly greater than that of the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ sample and the value predicted for bulk multiferroic NiTiO_3 [1], it is not large enough to suspect that it is from a ferromagnetic impurity. No discernible ferromagnetic (S-shaped) component is observed in the field-dependent magnetization curves for the film on

FIGURE 2: (Color online) (a) Representative high-resolution 2θ - θ XRD pattern of $\text{NiTiO}_3/\text{Al}_2\text{O}_3$, $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$, and $\text{NiTiO}_3/\text{LiNbO}_3$ films showing (001)-oriented epitaxial films. (b) Representative in-plane (116) rocking curves for $\text{NiTiO}_3/\text{Al}_2\text{O}_3$, $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$, and $\text{NiTiO}_3/\text{LiNbO}_3$ films. (c) (1010) Reciprocal space maps for $\text{NiTiO}_3/\text{Al}_2\text{O}_3$, $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$, and $\text{NiTiO}_3/\text{LiNbO}_3$ films. Data collected using Cu $K\alpha$ (1.54056 $\text{\AA}$) radiation.

FIGURE 3: High magnification HAADF-STEM images of the (a) $\text{NiTiO}_3/\text{Al}_2\text{O}_3$, (b) $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$, and (c) $\text{NiTiO}_3/\text{LiNbO}_3$ interface. (d) Comparison of a high-resolution STEM image of NiTiO_3 grown on Al_2O_3 with an overlay of its theoretical LNO-type structure (space group $R3c$).

TABLE 1: Summary of the reported lattice parameters for bulk ILM-type NiTiO_3 , sapphire Al_2O_3 , hematite Fe_2O_3 , LiNbO_3 , and the measured parameters of NiTiO_3 films in the present study.

Material	Comment	a, b (Å)	c (Å)
ILM- NiTiO_3	bulk, reported [25]	5.030	13.790
Al_2O_3	bulk, reported [26]	4.759	12.991
Fe_2O_3	bulk, reported [32]	5.038	13.772
LiNbO_3	bulk, reported [28]	5.151	13.865
$\text{NiTiO}_3/\text{Al}_2\text{O}_3$ film	measured, this study; thickness: 50 nm	5.021(4)	13.840(4)
$\text{NiTiO}_3/\text{Fe}_2\text{O}_3$ film	measured, this study; thickness: 60 nm	5.030(3)	13.787(3)
$\text{NiTiO}_3/\text{LiNbO}_3$ film	measured, this study; thickness: 50 nm	5.039(1)	13.836(1)

FIGURE 4: (Color online) Field-dependent magnetization curves correlated with the schematic strain diagram showing the % amount of mismatch exhibited by the three substrates Al₂O₃, Fe₂O₃, and LiNbO₃, in the in-plane direction: magnetization curves for epitaxial NiTiO₃/Al₂O₃ film at 10 K, below the Néel temperature indicating residual magnetization, for epitaxial NiTiO₃/Fe₂O₃ film at 50 K showing no ferromagnetism, and for epitaxial NiTiO₃/LiNbO₃ film at 90 K showing ferromagnetism.

Fe₂O₃ substrate. The M-H curves recorded for NiTiO₃/Fe₂O₃ samples at several temperatures in the 50–300 K range showed some nonlinearity, but any measurable moment was below the noise level. When we consider this magnetic data in the context of strain, we find a clear dependence of the ferromagnetic behavior on strain. While the NiTiO₃ film deposited on Fe₂O₃ with only 0.1% mismatch shows no significant ferromagnetism, as we move to greater strains, we start to observe residual magnetization in the films deposited on Al₂O₃ (5.7% compressive strain) and LiNbO₃ (2.3% tensile strain). This dependence of the ferromagnetism on the substrate-exerted strain is consistent with the theory that it is the ferroelectric polarization that induces the WFM [1] and suggests that we can control the magnetic behavior by tuning the strain. As schematically illustrated in Figure 4, both the Al₂O₃ and the LiNbO₃ substrates strain the film to such degree that sufficient lattice polarization (FE) is created, which, in turn, may induce the ferromagnetism (FM) we observe. The measured moment does not appear to scale with the absolute value of the strain, which may be due to the different nature of the strain (compressive *versus* tensile) and/or experimental uncertainty on the calculated magnetic moments.

We have explored the polar properties of the NiTiO₃ films using optical second harmonic generation (SHG). Optical SHG involves the conversion of light at a given frequency into an optical signal of double the frequency by a nonlinear medium (here, the film + substrate sample) through the creation of a nonlinear polarization. SHG occurs only in the absence of inversion symmetry (in this case

for the acentric *R3c* structure), which is also a necessary condition for a polar medium such as a ferroelectric. It should not occur for a nonpolar substance such as the sapphire substrate or ILM-type NiTiO₃. First, we demonstrated that the nonpolar sapphire substrate shows no signal, therefore, any observed SHG contrast comes from the film and that a strong ferroelectric substrate, such as LiNbO₃, shows a strong SHG signal. Next, we performed optical SHG on three NiTiO₃ samples (NiTiO₃/Al₂O₃, NiTiO₃/Fe₂O₃, and NiTiO₃/LiNbO₃). By qualitatively comparing the three images (Figure 5), we find a correlation between strain and polarization; the NiTiO₃/Fe₂O₃ sample shows essentially no SHG signal (mostly noise detected), while the NiTiO₃/Al₂O₃ sample exhibits significant SHG signal indicating that the film is polar. The strong SHG response of the NiTiO₃/LiNbO₃ sample should be dominated by the ferroelectric substrate; therefore, it is not indicative of the substrate strain. As mentioned before, ferroelectric polarization of NiTiO₃ on LiNbO₃ may only be successfully probed by a method that discriminates between the film and substrate. Nevertheless, the comparison of NiTiO₃/Al₂O₃ and NiTiO₃/Fe₂O₃ samples supports the assumption that the polarization in our NiTiO₃ films is strain induced.

4. Conclusions

We have successfully stabilized the metastable LNO-type structure (acentric space group *R3c*) of NiTiO₃ in epitaxial thin film form on different substrates (Al₂O₃, Fe₂O₃, and LiNbO₃) and investigated the dependence of structural,

FIGURE 5: (Color online) Optical SHG images of $\text{NiTiO}_3/\text{Al}_2\text{O}_3$, $\text{NiTiO}_3/\text{Fe}_2\text{O}_3$, and $\text{NiTiO}_3/\text{LiNbO}_3$ films of similar thicknesses. Images for strongly ferroelectric single crystalline LiNbO_3 and nonpolar Al_2O_3 are shown as reference.

magnetic, and polar properties on strain. X-ray diffraction and electron microscopy show that substrate-exerted strain has a marked effect on the structure and crystalline quality of the films. Physical property measurements reveal a dependence of the weak ferromagnetism and lattice polarization on strain and highlight LiNbO_3 as the substrate of choice to grown NiTiO_3 thin films with potentially multiferroic properties on. Our results are also consistent with the theory prediction that the ferromagnetism in acentric NiTiO_3 is polarization-induced. Experiments at probing the coupling of the polar and magnetic orders in $\text{NiTiO}_3/\text{LiNbO}_3$ thin films are underway and will be reported upon success.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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