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Magnetic properties of insulating $R\mathrm{TiO_3}$ thin films

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Abstract The magnetic properties of epitaxial $R\mathrm{TiO_3}$ (R=Y, Eu) thin films are reported. The films were grown on various substrates with different lattice mismatches using the pulsed laser deposition technique. Ferromagnetic $\mathrm{YTiO_3}$ thin films could only be grown on $\mathrm{LaAlO_3}$ (110) substrates, while $\mathrm{EuTiO_3}$ films could be grown on various substrates. The magnetic properties of the grown films are discussed in light of the structural characterization.

Keywords Ferromagnetism · PLD · Multiferroic

1 Introduction

Perovskite oxide materials have attracted a great deal of attention because of their remarkable physical properties, such as high-temperature superconductivity and colossal magnetoresistance [1, 2]. Furthermore, multiferroic materials that show both ferromagnetic and ferroelectric behavior have recently become an active area of research. The control of electric polarization by a magnetic field has been reported in rare earth manganites, such as $\mathrm{TbMnO_3}$ and $\mathrm{TbMn_2O_5}$ [3, 4]. Research regarding these materials is important, as the strong coupling of both the magnetic and electric properties could lead to applications of these materials in multinary memory devices.

The multiferroic behaviors of various manganite materials have been investigated [5], while there have been few studies regarding titanates. It seems hardly possible that two distinct order parameters—polarization and magnetization—could exist simultaneously in transition metal oxides. This is because magnetism is usually attributed to the excess electrons in transition metals and their ordering, and the interesting electric properties, such as ferroelectricity, are attributed to the d^0-ness of transition metal oxides. However, the well-known Mott insulators, which have excess *d*-electrons, could be candidates for dielectric materials with a magnetic order parameter.

In this study, the well-known ferromagnetic insulator, $\mathrm{YTiO_3}$ (YTO) [6, 7], and the recently proposed multiferroic, $\mathrm{EuTiO_3}$ (ETO) [8], were investigated as new candidate multiferroic materials. YTO is a well-known Mott insulator that shows insulating behavior, even though there is one *d* electron at the site of the transition metal, Ti. The large correlation energy between electrons is attributed to the insulating behavior of these Mott insulators. Although most Mott insulators show antiferromagnetic behavior, YTO is a rare example that shows ferromagnetism below 30 K. The origin of ferromagnetism in YTO is quite complicated, and the most likely explanation seems to be the t_{2g} orbital ordering of Ti^{3+} ions [6]. The epitaxial growth of YTO on $\mathrm{LaAlO_3}$ (110) substrate has been reported, where the ferromagnetic behavior of orthorhombic YTO thin films was attributed to the anisotropic substrate strain [7].

ETO is known as an incipient ferroelectric material and shows typical G-type antiferromagnetic ordering of Eu

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spins [9]. The coupling between the magnetic and electric subsystems has been reported [9, 10]. These studies demonstrated the magnetic influence on the frequency of soft-phonon mode and the dielectric constant anomaly along the magnetic field. The localized spin in $EuTiO_3$ may influence the conduction of electricity under the influence of an external magnetic field. Under these conditions, the inherent ferroelectricity of ETO can be controlled by a magnetic field. Furthermore, oxygen-deficient ETO exhibits ferromagnetism below 6 K [11]. This indicates that ETO thin films could exhibit strong coupling due to the large magnetic moment seen in bulk $EuTiO_3$.

Here, it was demonstrated that YTO deposited on $LaAlO_3$ (110) substrate exhibited clear ferromagnetic behavior similar to that of bulk $BiMnO_3$, while ETO thin films grown epitaxially showed ferromagnetic behavior. These results were in agreement with those of previous studies on YTO and ETO thin films [7, 11].

2 Experimental procedures

YTO and ETO thin films were grown on various oxide single crystals using the pulsed laser deposition technique. Substrates of $SrTiO_3$ (STO) (110), $(La,Sr)(Al,Ta)O_3$ (LSAT) (110), $YAlO_3$ (YAO) (010), and $LaAlO_3$ (LAO) (110) were used for YTO films and (001) substrates of STO, LSAT, $LaSrGaO_4$ (LSGO), and LAO were used for ETO films. During thin film growth, the growth mode was monitored using in situ reflection high-energy electron diffraction (RHEED). Ceramic $Y_2Ti_2O_7$ and $Eu_2Ti_2O_7$ targets were ablated using a KrF excimer laser with fluence of 0.5–3 J/cm^2. The temperature of the substrate during film growth was varied from 700 to 950 °C. The electric properties were measured using the conventional four-probe method. The dependencies of the magnetic moment on the magnetic field and on the temperature were measured using a superconducting quantum interference device (Quantum Design, MPMS*XL*).

3 Results and discussion

Figure 1(a) shows the x-ray diffraction patterns of $YTiO_3$ thin films grown on STO (110), LSAT (110), YAO (010), and LAO (110) single crystals. These substrates generally caused an anisotropic in-plane stress to be applied to the thin film. YTO has a highly distorted orthorhombic crystal structure with lattice constants of a=5.679 Å, b=5.316 Å, and c=7.611 Å. The surfaces of STO (110), LSAT (110), YAO(010), and LAO (110) substrates had in-plane lattice constants of 3.905×5.522 Å, 3.867×5.481 Å, 5.273×7.308 Å, and 3.789×5.358 Å, respectively. The STO (110), LSAT (110), YAO(010) substrates could not stabilize the YTO epitaxial phase, and the YAO(010) substrate also resulted in other impurity phases. Only the LAO (110) substrate, which had the smallest lattice mismatch, produced an epitaxial YTO phase with a thickness of 57 nm. Figure 1(b) shows that the partial pressure of oxygen (P_{O2}) and the lattice mismatch were crucial factors for successful growth of the YTO phase. When P_{O2} increased, the x-ray diffraction peaks of YTO (200) decreased and the peaks of the other phases, including the$Y_2Ti_2O_7$ phase, increased.

To understand the electrical and magnetic properties of the YTO thin film, the temperature dependence of its

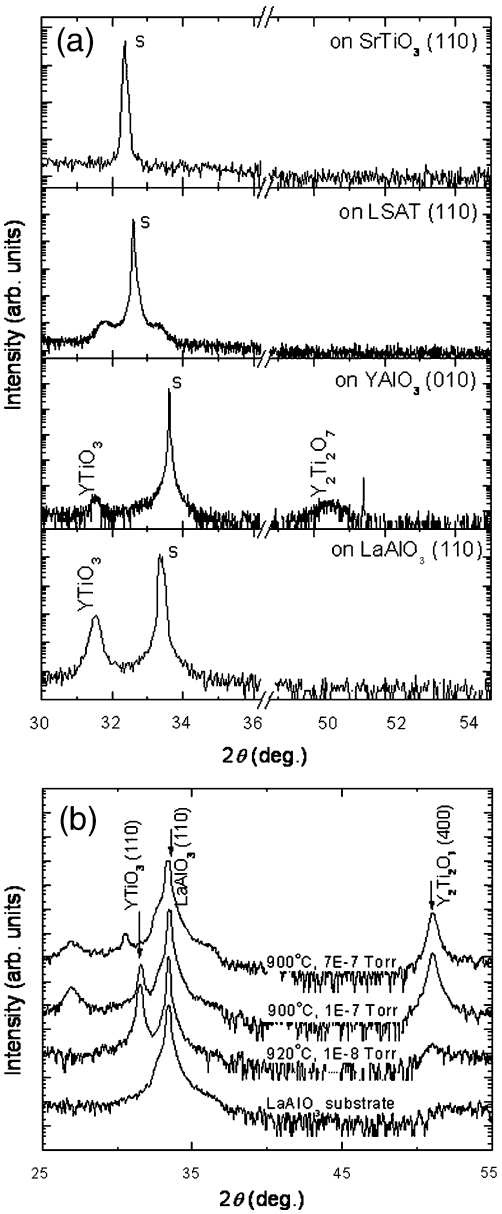

Fig. 1 (**a**) X-ray diffraction patterns of $YTiO_3$ thin films grown on $SrTiO_3$ (110), LSAT (110), $YAlO_3$ (010), and $LaAlO_3$ (110) single-crystal substrates. (**b**) X-ray diffraction patterns of $YTiO_3$ thin films grown on (**a**) $LaAlO_3$ (110) at differnt pressure

electrical resistivity and the dependence of the magnetic moment on the magnetic field were investigated. Figure 2(a) shows that the electrical resistivity is relatively small, around 200 Ωcm, at room temperature. However, as the temperature decreases, the resistivity shows insulating behavior, i.e., an increase in resistivity, which is comparable with the reported value for YTO single crystals [12]. Figure 2(b) and (c) show the dependence of the magnetic moment on the magnetic field in both the bare LAO substrate and the YTO thin film grown on the LAO substrate. The magnetic fields were applied parallel to the substrate, i.e., in the in-plane direction. The magnetic moments were estimated by subtracting the diamagnetic signal from the LAO substrate. Compared to the magnetic moment signal of the bare substrate, the YTO thin film showed an enhanced magnetic moment with clear ferromagnetic hysteresis. The saturated moment is estimated to be 0.7 μB/Ti, a value comparable to that of bulk YTO [13].

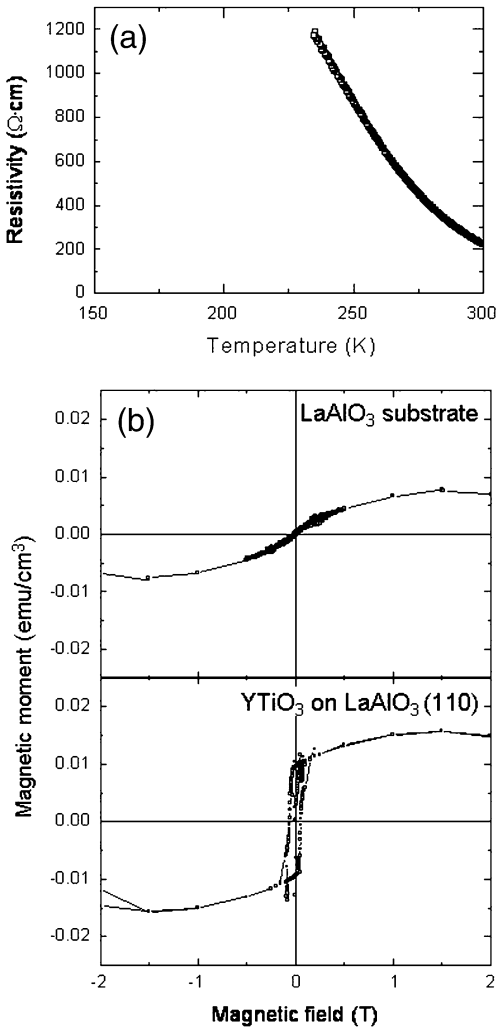

Fig. 2 (**a**) Temperature dependence of resistivity of $YTiO_3$ thin film on $LaAlO_3$ substrate, (**b**) Dependence of the magnetic moment on the magnetic field of bare $LaAlO_3$ substrate and the $YTiO_3$ thin film on $LaAlO_3$ substrate

ETO thin films with a thickness of 150 nm were grown on STO, LSAT, LSGO, and LAO single crystals with (001) orientation. Figure 3 shows the x-ray diffraction patterns of ETO thin films on various oxide substrates with the ETO (001) diffraction peaks. No impurity phases were observed. Bulk ETO has a cubic perovskite structure with a lattice constant of 3.905 Å. The in-plane lattice constants of STO, LSAT, LSGO, and LAO substrates are 3.905, 3.867, 3.843, and 3.789 Å, respectively. For these substrates, the lattice mismatches with ETO are 0%, 0.7%, 1.6%, and 3.1%, respectively. However, the out-of-plane lattice constants of the ETO film grown on the four substrates were larger than the lattice constant of bulk ETO. For example, the *c*-axis lattice constant of ETO film on STO was about 3.973 Å, 2% larger than the lattice constant of 3.905 Å.

The reciprocal space mappings of the (103) pseudo-cubic substrate lattice were determined to clarify the origin of the abnormal out-of-plane lattice expansion in the x-ray θ–2θ scan and the relation between the magnetic properties and the structural properties. Figure 4 shows the reciprocal space mappings of the ETO thin films. As the lattice mismatch increased, the in-plane lattice constants relaxed. The ETO films grown on STO and LSAT substrates, both of which have relatively small lattice mismatches of 0% and 0.7%, respectively, showed almost coherent growth, while the ETO films on LSGO and LAO substrates showed relaxed in-plane lattice constants. The estimated volume expansion of ETO from the x-ray θ–2θ scans and reciprocal space mapping suggests that the abnormal expansion in

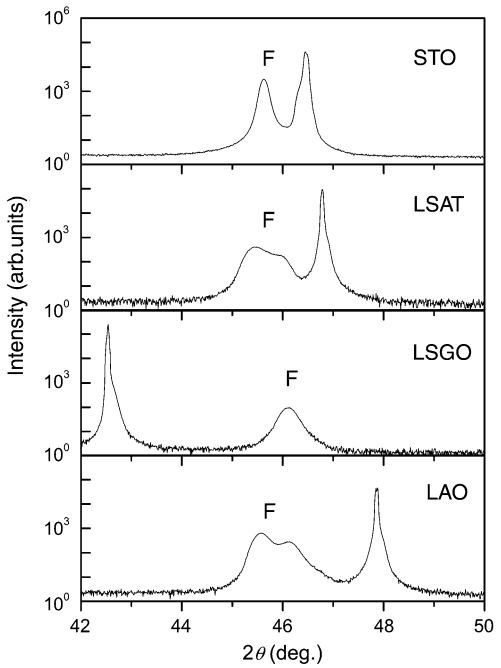

Fig. 3 X-ray diffraction pattern of $EuTiO_3$ thin films grown on $SrTiO_3$ (001), LSAT (001), $LaSrGaO_4$ (001), and $LaAlO_3$ (001) single-crystal substrates

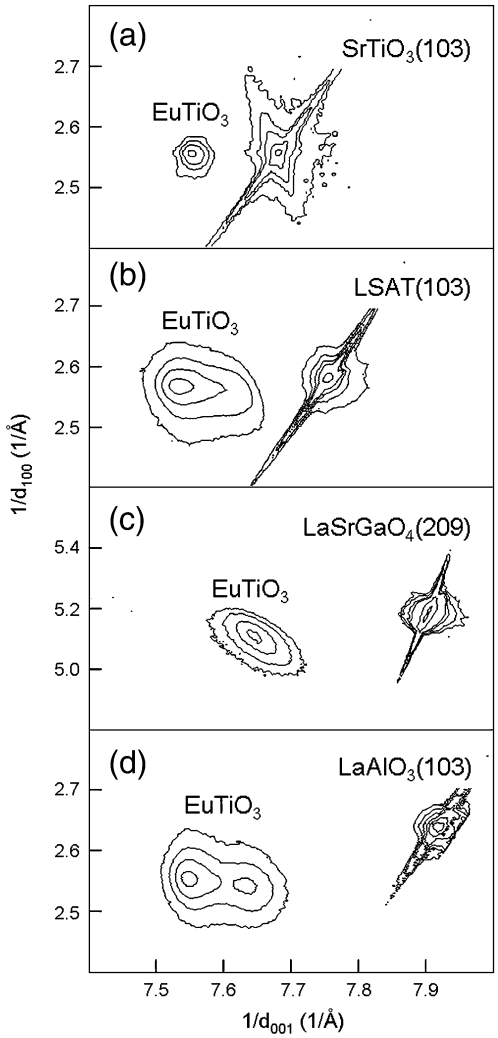

Fig. 4 Reciprocal space mapping of $EuTiO_3$ thin films grown on (**a**) $SrTiO_3$ (001), (**b**) LSAT (001), (**c**) $LaSrGaO_4$ (001), and (**d**) $LaAlO_3$ (001) single-crystal substrates

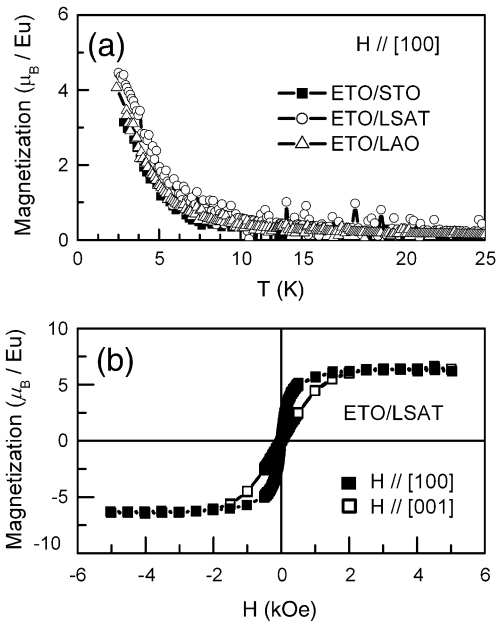

Fig. 5 (**a**) The temperature dependence of the magnetic moment of $EuTiO_3$ grown on $SrTiO_3$ (001), LSAT (001), and $LaAlO_3$ (001) single-crystal substrates. (**b**) The dependence of the magnetic moment on the magnetic field of $EuTiO_3$ grown on LSAT (001). The magnetic fields were applied in both the vertical and parallel directions, denoted by *solid* and *open squares*, respectively

out-of-plane lattice constants could be attributed to oxygen vacancies. Structural data, including x-ray θ–2θ scans and reciprocal space mapping, also indicate that the film shows a gradual lattice relaxation for the ETO film on LSAT substrate and the possible existence of twins for the ETO film on the LAO substrate.

The temperature dependence and the dependence of the magnetic moment on the magnetic field of ETO thin film were investigated, and the results are shown in Fig. 5. Bulk ETO is known to be an antiferromagnetic material with a Néel temperature of 6 K [14]. Figure 5(a) shows an increase in magnetic moment below 7 K without any cusp, which is a hallmark of antiferromagnetism [15]. This ferromagnetic-like behavior was also observed in the dependence of the magnetic moment on the magnetic field, as shown in Fig. 5(b). The saturated magnetic moment was estimated to be about 6.5 μ_B/Eu. Unfortunately the coercive field was much less than 1 Oe. This ferromagnetic behavior with Curie temperature of around 7 K and magnetic moment of 6.5 μ_B/Eu is in good agreement with the value reported previously [11].

The ferromagnetic properties of ETO thin films can be attributed to the strain effect from the substrate and/or oxygen vacancies [8]. Reciprocal space mapping of ETO showed that the in-plane lattice constants remain close to the substrate in-plane lattice constant except in the case of growth on the LAO substrate. Recently, the boundary between the ferromagnetic–ferroelectric phase and antiferromagnetic–paraelectric phase was calculated, and shown to be a biaxial compressive strain of about 1.2% in ETO film, which results in the freezing-in of a soft polar phonon by spin phonon coupling [8]. However, considering the lattice mismatch of 0.7% between ETO and LSAT, our results cannot be explained by the theoretical prediction [9].

Ruderman–Kittel–Kasuya–Yoshida interactions could also be a cause of ferromagnetism [14]. The x-ray θ–2θ scan patterns also showed the enormous additional expansion of out-of-plane lattice constant shown in Fig. 3. This volume expansion can be attributed to the oxygen vacancies of ETO thin films. The electron doping by oxygen vacancies results in the ordering of localized 4*f* spins of Eu^{2+} ion mediated by itinerant 3*d* electrons of the Ti site. The ferromagnetism of epitaxial $EuTiO_{3-\delta}$ thin film grown on STO substrate was also reported [11]. In the case of $(Eu^{2+}Ln^{3+})TiO_3$, where electron doping is done by A-site doping, the magnetic properties was similar to that of our

films, while the resistivity showed metallic behavior with a decrease in temperature [14].

4 Conclusions

The magnetic properties of epitaxial $R\mathrm{TiO_3}$ (R=Y, Eu) thin films grown on various oxide single-crystal substrates with different lattice mismatches using the pulsed laser deposition technique were investigated. YTO thin films, which showed clear ferromagnetic behavior, could only be grown on LAO (110) substrates. The temperature dependence of resistivity was similar to that of bulk $\mathrm{BiMnO_3}$, an example of a multiferroic material, showing good insulating behavior at temperatures far above the ferromagnetic transition temperature. ETO films could be grown on various substrates. The observed ferromagnetic-like behavior was discussed with reference to the presence of oxygen vacancies and the lattice strain.

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