論文内容の要旨

論文題目　Coupling between magnetic and dielectric properties in $EuTiO_3$ epitaxial thin films

（$EuTiO_3$エピタキシャル薄膜における磁性 - 誘電性結合）

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Introduction

$EuTiO_3$ (ETO) is quite unique material because magnetic Eu^{2+} and dielectric Ti^{4+} ions coexist in the same material. ETO with simple cubic perovskite structure is an incipient ferroelectric and exhibits quantum paraelectric behavior. Eu spins show G-type antiferromagnetic (AFM) ordering at Neel temperature (T_N) of 5-5.5 K and dielectric constant (ε_r) drops sharply below T_N. When an external magnetic field is applied to ETO, a ferromagnetic (FM) state appears, and ε_r below T_N simultaneously increases. This coupling between magnetic and dielectric properties is known as magnetodielectric (MD) coupling. Recent first principle calculations have predicted that magnetic and dielectric properties of ETO are quite sensitive to cell parameters. It is expected that hydrostatic expansion of cell volume switches from AFM to FM ground state, and that biaxial strain may divergently enhance MD coupling. Furthermore, multiferroic behavior is also expected in strained ETO. For studying magnetic and dielectric properties of ETO as a function of cell parameters, epitaxial thin films are suitable. Strain can be introduced through lattice mismatch between the film and the substrate in a controlled manner. In addition, thin films, in general, have different cell volume from bulk, even if they are fabricated on a substrate without lattice mismatch. Such variation of cell volume would significantly affect the physical properties, particularly magnetic properties of ETO through anisotropic exchange interaction, which also may have influence on MD coupling. However, there have been only a few reports of the epitaxial growth of ETO films, especially on dielectric properties. This is mainly because it is difficult to fabricate high quality ETO films. Divalent Eu is stabilized relatively reducing condition, while tetravalent Ti in relatively oxidizing condition. In my doctor thesis, I have investigated magnetic and dielectric properties of ETO as influenced by cell parameters, using high quality ETO epitaxial films.

Experimental

ETO thin films were grown on Nb (0.05wt%)-doped $SrTiO_3$ (NSTO) (100) substrates, which have no lattice mismatch with ETO, by pulsed laser deposition (PLD) at substrate temperature (T_s) of 650 - 1250 ^oC and oxygen pressures (Po_2) in a range of 10^{-5} – 10^{-8} Torr. Laser pulses with a fluence of 700 -1000 mJ / (cm^2 shot) and a frequency (f_l) in the range of 0.3 - 10 Hz were supplied by a KrF excimer laser (λ=248 nm). As a PLD target, a pyrochlore $Eu_2Ti_2O_7$ polycrystalline pellet were employed. Crystallinity and surface morphology of the films were characterized by in situ reflection high-energy electron diffraction (RHEED), X-ray diffraction (XRD), and atomic force microscopy. Magnetic and dielectric properties were measured using a SQUID susceptometer and a LCR meter, respectively. In LCR measurements, probe voltage E of 250mV was applied perpendicular to the film surfaces. As a top electrode, Ag was deposited by resistive heating, and Nb-doped (0.05wt%) STO substrates were used as a bottom electrode.

Epitaxial growth of ETO thin films

To find an optimized growth condition for high quality ETO films, I first constructed a growth phase diagram of $EuTiO_x$ film as shown in Fig. 1, where T_s was fixed at 650^{o}C and Po_2 and laser frequency were varied. The diagram clearly reveals a tendency that lower Po_2 and higher f_l conditions, that is, relatively reducing conditions are necessary for stabilizing the perovskite ETO phase, which consist of divalent Eu. In these conditions, ETO film growth proceeds in layer-by-layer mode, as seen from RHEED intensity oscillation in Fig.2(a), and atomically flat surface can be obtained. XRD measurement revealed that in-plane lattice constant of ETO films is completely locked to STO substrate ($a = b$ = 3.905Å), while the out-of-plane lattice constant is longer than that of bulk ETO (3.933 Å $\leq c \leq$ 3.988Å, 1.007 $\leq c/a \leq$ 1.021). In higher Po_2 and lower f_l conditions in Fig.1, that is, in relatively oxidizing conditions, layered perovskite $Eu_2Ti_2O_7$ with trivalent Eu, and amorphous phase appeared.

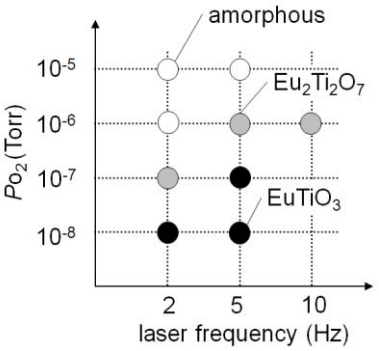

Fig1. Growth phase diagram of $EuTiO_x$ at T_s = 650^{o}C

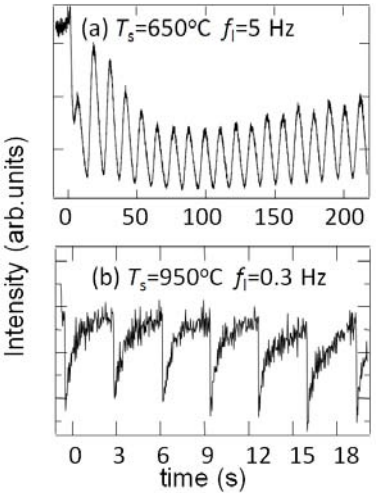

Fig2. RHEED specular spot intensity during ETO film deposition

On increasing T_s beyond 920 ^{o}C, growth mode of ETO film changed from layer-by-layer mode to step-flow mode. Fig. 2(b) depicts a RHEED intensity profile monitored during step-flow growth (T_s = 950^{o}C, Po_2=1x10^{-7} and f_l = 0.3 Hz). In this condition where step-flow growth mode is dominant, ETO films with $a = c$ = 3.905Å (c/a = 1) were obtained. At such higher T_s, surface morphology of ETO films was quite sensitive to Po_2, partly due to the formation of layered perovskite $Eu_2Ti_2O_7$ phase. At higher T_s, oxygen atoms easily defuse into perovskite ETO through the film surfaces, resulting in generation of trivalent Eu. As a consequence, I have determined T_s = 1250 ^{o}C, Po_2 = 3x10^{-8}

Torr, and f_l = 2 Hz as an optimized film growth condition. To compensate oxygen vacancies generated in such a strongly reducing growth condition, conductive NSTO capping layer, which protects ETO form surface oxidation, were deposited on ETO films and annealing in air at 400°C for 24hours were performed. By careful tuning of growth condition as is mentioned above, high quality ETO films with systematically different cell parameters ($1 \leq c/a \leq 1.021$) were successfully fabricated.

Magnetic properties of epitaxial ETO thin films

Fig. 3(a) and (b) show magnetization vs. temperature (M–T) curves of an ETO films with different cell parameter (c/a) under different magnetic field. In fig. 3(a), where external magnetic field perpendicular to the film surface ($H_\perp$) was applied, all the films with different c/a showed characteristic cusp structure at 4.2-5.4 K, which correspond to T_N and indicate that all the films undergo antiferromagnetic (AFM) transition. On the other hand, in fig. 3(b), where parallel magnetic field ($H_{//}$) applied, cusp structure clearly depend on c/a. Fig. 4 depict the correlation between magnetization at 2 K under $H_{//}$ and c/a and cell volume (c^2/a). This implies that larger c/a or cell volume lead to destabilize AFM ordering, or in other word, prefer FM ordering. These results demonstrate that the antiferromagnetism in ETO is quite sensitive to cell parameter, which is in good agreement with the recent band calculation.

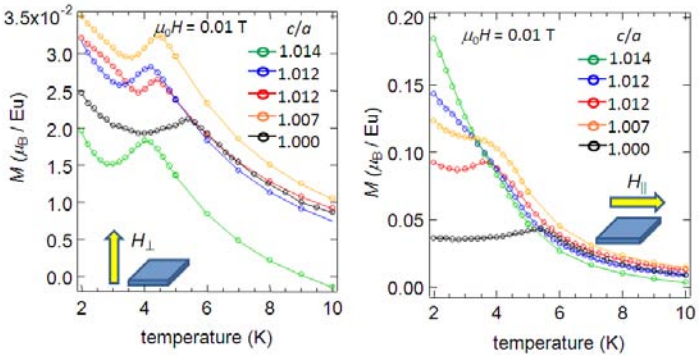

Fig.3. M - T curve of the ETO film under (a) perpendicular magnetic field ($H_\perp$) and (b) parallel magnetic field ($H_{//}$)

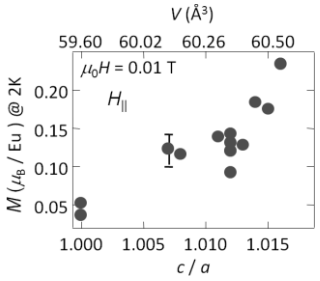

Fig.4. Magnetization at 2K under $H_\perp$ vs. c/a and cell volume ($V = c^2/a$) curve

Dielectric properties and coupling between magnetic and dielectric properties

Fig. 5 shows ε_r vs temperature (ε_r -T) curves measured under various magnetic fields ($H_\perp$). Notably, the ETO film with c/a=1.011 exhibits quantum paraelectric behavior and sharp drop of ε_r at T_N under zero magnetic field. Fig. 6 (a) is a close-up view of the low temperature part (2-10 K) of Fig. 5. Fig. 6 (b) plots magnetization in the same temperature region. With increasing external magnetic field, the cusp in M-T curve in Fig. 6(b) tends to be suppressed and completely disappears at 5 T, corresponding to the evolution of FM ordering. In synchronization with the FM ordering, ε_r increases. This is the first observation of MD coupling in ETO thin films. For observation of quantum paraelectricity and magnetodielectric effect in thin film samples, dielectric loss factor (D), which determines leakage current, must be as low as possible. The typical D value of our samples is evaluated to be 10^{-3} at 2 K. Such low D is a consequence of high quality of the present ETO samples.

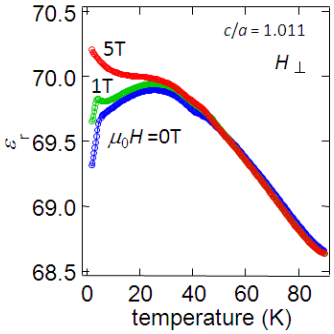

Fig.5 ε_r vs temperature curve under various magnetic field

The shape of ε_r - T curves was found to be insensitive to the direction of magnetic field ($H_\perp$ and $H_{//}$) and cell parameters (c/a). On the contrary, ε_r - H curves shows clear dependence on the direction of magnetic field and c/a. Fig.7 shows $\Delta\varepsilon_r(H)$ vs H curves of ETO films with different c/a, where $\Delta\varepsilon_r(H)$ represents $[\varepsilon_r(H)- \varepsilon_r(0)]/\varepsilon_r(0)$ and corresponds the degree of MD response. Evidently, under both $H_\perp$ and $H_{//}$, larger c/a weakens MD coupling. At the same time, each sample exhibits anisotropic MD coupling depending on magnetic field direction. To clarify this anisotropy, $\Delta\varepsilon_r(H_\perp)/\Delta\varepsilon_r(H_{//})$ vs H curve were plotted in Fig.8. Surprisingly, all the samples with different c/a show the same value, $\Delta\varepsilon_r(H_\perp)/\Delta\varepsilon_r(H_{//}) = 1.2$ at higher H. In bulk ETO, it has been reported that ε_r as a function of temperature and magnetic field can be expressed by an empirical formula $\varepsilon_r(T,H) = \varepsilon_0(T)[1+\alpha\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle_H]$, where $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle_H$ is the Eu spin pair correlation, and α is the spin-phonon coupling constant, related to the derivative of exchange interaction[ref.1,2]. The anisotropic behavior of $\Delta\varepsilon_r(H)$, as shown in Fig. 8, suggests that the α parameter is dependent on the direction of spin pairs. Here I further assume that α is the product of c/a dependent term, $\alpha_{c/a}$, and spin-pair-direction-dependent term, α_{ij}. Then, the MD coupling in ETO films is given as

$\Delta\varepsilon_r(H_\perp)/\Delta\varepsilon_r(H_{//}) = [\alpha_{c/a}\alpha_{ij(5T,H\perp)}+\alpha_{c/a}\alpha_{ij(0T)}]/[\alpha_{c/a}\alpha_{ij(5T,H//)}+\alpha_{c/a}\alpha_{ij(0T)}] = [\alpha_{ij(5T,H\perp)}+\alpha_{ij(0T)}]/[\alpha_{ij(5T,H//)}+\alpha_{ij(0T)}] = 1.2$,

where $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle_{5T,H\perp} = \langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle_{5T,H//} = -\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle_{0T}$ in the mean field approximation at 2 K[ref.1]. For better understanding of microscopic mechanism of MD coupling, the spin-pair-direction-dependence of α should be considered.

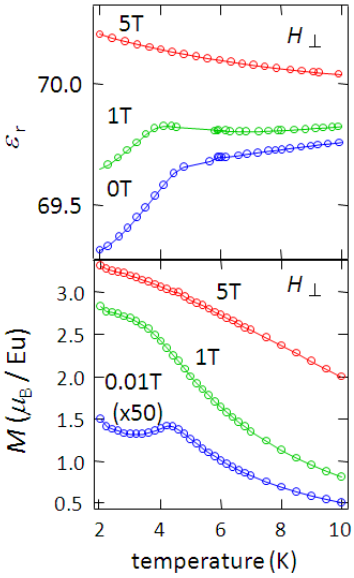

Fig.6 temperature dependence of ε_r and magnetization

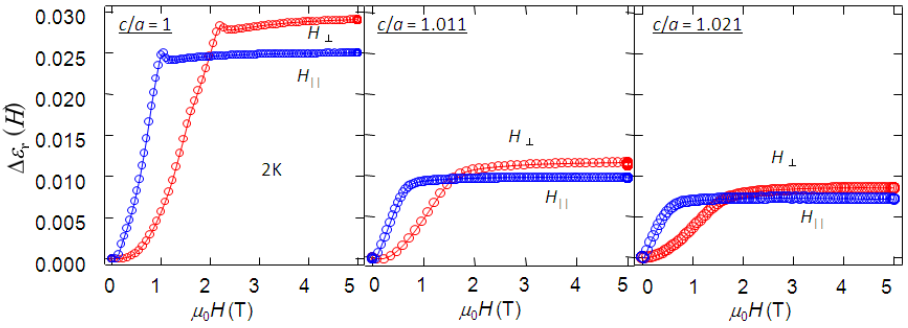

Fig.7. $\Delta\varepsilon_r(H)$- H curve of the ETO film under $H_\perp$ and $H_{//}$ at 2K

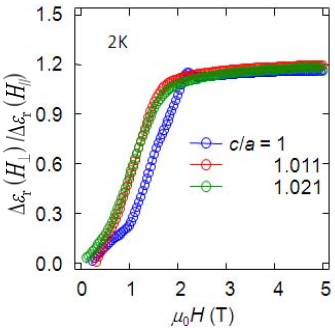

Fig.8 $\Delta\varepsilon_r(H_\perp)/\Delta\varepsilon_r(H_{//})$ - H curve at 2K

Summary

I have investigated magnetic and dielectric properties of ETO films as functions of cell parameters. As a result, I observed that the increase of cell volume destabilizes the AFM ordering, being consistent with the result of band calculation. I also found that anisotropy in MD coupling, i.e., spin-pair-direction-dependence of $\Delta\varepsilon_r(H)$, which seems to be a key phenomenon for better understanding of microscopic mechanism of MD coupling.

Ref.1 T. Katsufuji et al., Phys. Rev. B 64 (2001) 054415

Ref.2 W. Baltensperger et al., Helv. Phys. Acta 41 (1968) 668; C. J. Fennie et al., Phys. Rev. Lett. 96 (2006) 205505