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Strain Induced Metastable Phase and Phase Revolution in $\text{PbTiO}_3\text{-CoFe}_2\text{O}_4$ Nanocomposite Film *

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An inter-component epitaxial strain-induced PbTiO_3 metastable phase is observed in a $\text{PbTiO}_3\text{-CoFe}_2\text{O}_4$ epitaxial composite film, corresponding to the dielectric anomaly reported previously. High-resolution synchrotron radiation X-ray diffraction and first principles calculation demonstrate the coexistence of different PbTiO_3 phases, even a possible morphotropic phase boundary in the film, elucidating the underlying microscopic mechanism of the formation of PbTiO_3 metastable phase. This sheds light on the design and manipulation of electromechanical properties of epitaxial films, through the strain engineering.

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Strain engineering, which makes use of the elastic strain induced by lattice mismatch, is an appealing route to manipulate the ferroelectricity,^[1–3] ferromagnetism,^[4] superconductivity^[5] and structural properties^[6,7] of epitaxial films. However, conventional film/substrate lattice mismatch induced epitaxial strain usually relaxes when film thickness reaches tens of nanometers,^[8,9] which makes it impractical since most film devices require much thicker films.

Recently, the strain effect in epitaxial nanocomposite films has been highlighted because a large strain could be maintained in these films, even to hundreds of nanometers, which meets the need for potential practical device applications. Harrington *et al.* found that the ferroelectric Curie temperature of $\text{Sm}_2\text{O}_3\text{-BaTiO}_3$ (BTO) epitaxial nanocomposite can be increased to $\sim 330^\circ\text{C}$, in contrast to that of bulk BTO ($\sim 130^\circ\text{C}$).^[10] Electric field-controllable nanoscale magnetization switching was revealed in 200-nm-thick BiFeO_3 (BFO)- CoFe_2O_4 (CFO) epitaxial columnar composite.^[11] Moreover, the large strain presented in these epitaxial composites could even lead to structural transition and multiphase coexistence state in some materials, as reported for highly-strained BFO.^[7,12]

For ferro/di/piezo-electric materials, especially with morphotropic phase boundary (MPB), multiphase coexistence is crucial to their electrical properties.^[13–15] For instance, in the famous PbTiO_3 (PTO)- PbZrO_3 piezoelectric solid solutions with compositions near the MPB, the coexistence

of rhombohedral, tetragonal and other ferroelectric phases with similar free energies were found. The symmetry allowed ferroelectric polarization rotation from pseudocubic $\langle 111 \rangle$ directions (rhombohedral phase) to pseudocubic $\langle 001 \rangle$ directions (tetragonal phase) under applied external electric field, which is thought to be responsible for the outstanding electric-mechanical coupling (piezoelectric effect) of the compounds.^[16] Meanwhile, the multiple possible directions of polarization result in a remarkable dielectric response.^[17] Therefore, exploring tunable multiphase coexistence state of ferroelectric materials is a promising route for novel functionals and devices.

Previously, we have reported a dielectric anomaly in a $\text{PTO}_{(1-x)}\text{-CFO}_x$ ($0 \leq x \leq 1$) epitaxial composite film deposited on a $\text{MgO}(100)$ single crystal substrate, where an unexpected peak was observed around $x = 0.20$ in the dielectric and nonlinear dielectric constant curves as a function of composition x .^[18,19] Such a dielectric anomaly is quite similar to the dielectric response of Pb-based solid solutions with MPB, suggesting that an MPB-like PTO multiphase coexistence state appears in the composite film. However, low-resolution conventional X-ray diffraction (XRD) is not ready to provide clear microstructure evidence for the PTO multiphase coexistence state, which leaves this question still open. In this Letter, through a detailed study of their structure using synchrotron radiation XRD, an unreported strain-induced PTO metastable phase and, thus, PTO multiphase coexistence state are revealed in the $\text{PTO}_{(1-x)}\text{-CFO}_x$ epitaxial compos-

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ite film around $x = 0.20$. This observation, which is consistent with first principles calculation, is claimed to be the origin of the dielectric anomaly previously found in this composition.

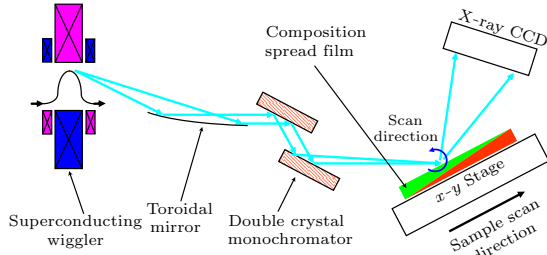


Fig. 1. Configuration of beamline U7B at NSRL. X-ray from a superconducting wiggler was focused by a toroidal mirror and monochromated by a double crystal monochromator. The spot size was limited to $3(\text{H}) \times 0.15(\text{V})$ mm by the exit slit and the flux is about 1.5×10^9 ph/s.

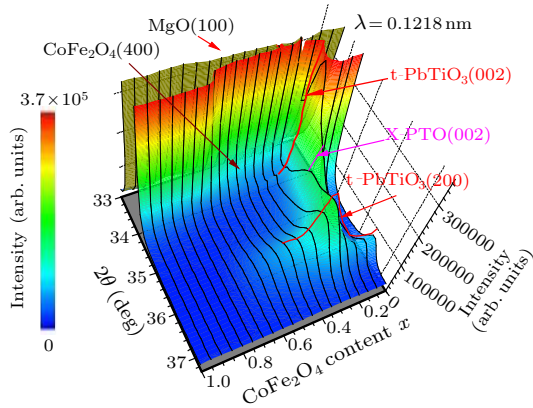


Fig. 2. Compositional dependence of the XRD pattern of $(\text{PbTiO}_3)_{1-x}(\text{CoFe}_2\text{O}_4)_x$ epitaxial composite film. With the increase in CFO content x , t-PTO(002) and t-PTO(200) peaks shift centripetally. A small peak (marked as X-PTO(002)) appears at 34.8° , indicating the formation of a new metastable phase.

In order to probe the phase evolution in the PTO-CFO epitaxial composite film, a high-resolution synchrotron radiation XRD was carried on beamline U7B at National Synchrotron Radiation Laboratory (NSRL). During the measurements, the film was mounted on a motorized translation stage that was moved along the spread direction to shift the irradiated area from pure CFO to pure PTO. The experimental configuration is illustrated in Fig. 1. Figure 2 presents the diffraction patterns as a function of the composition x . At the pure PTO end ($x = 0.0$), two tetragonal peaks, t-PTO(002) and t-PTO(200), were observed, indicating that the majority of tetragonal PTO domains orient their c -axis perpendicular (referred to as the out-plane phase) or parallel (the in-plane phase) to the substrate, which is consistent with other reports.^[9,20,21] With increasing CFO proportions, t-PTO(002) shifts to a higher angle while t-PTO(200) shifts to a lower angle, suggesting that cubic strain develops inside the PTO domains. Due to the high resolution of synchrotron radiation XRD,

an unreported small peak at 34.8° was identified in the composite with $x = 0.20$, implying the formation of a new phase. Since this composition is almost the same as that of the dielectric anomaly, this novel phase is probably the key for dielectric tunability.

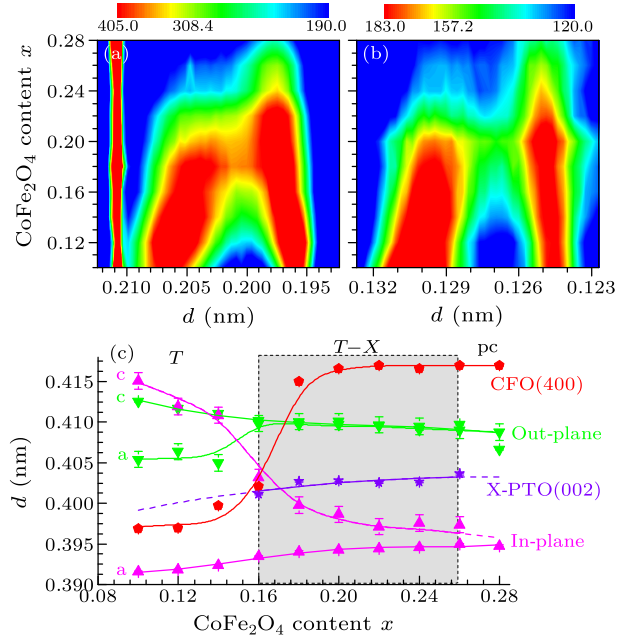


Fig. 3. (a) Symmetric and (b) asymmetric XRD patterns. (c) Lattice parameters and phase evolution with respect to CFO content from $x = 0.1$ to $x = 0.28$. For $x < 0.14$, only the tetragonal (T) PTO exists while only the pseudo-cubic (pc) PTO shows up in the $x > 0.26$ region. Between them (shadow region), the T- and X-PTO coexist.

To access precise information of the new phase, both symmetric and asymmetric high resolution XRDs were implemented on beamline U7B at National Synchrotron Radiation Laboratory and beamline BL14B1 at Shanghai Synchrotron Radiation Facility (SSRF). Figures 3(a) and 3(b) present the diffraction patterns around PTO(002) and PTO(103), respectively, in the composition range of $x = 0.10$ – 0.28 . To calculate the in-plane lattice parameters, the fitting of these diffraction patterns were carried out with assumption of Gaussian peak profile and continuous evolution of peak width with composition. The resulting lattice constants are depicted in Fig. 3(c) as a function of the composition x . With an increase in CFO content, CFO keeps the cubic symmetry while its strain gradually relaxes from the compressive state ($x < 0.12$) to the full-relaxed state ($x > 0.20$). We also found that the tetragonality of both in-plane and out-plane PTO phases decreases with increasing CFO content. The c/a ratio for in-plane and out-plane PTO approaches the unit at about $x = 0.28$ and 0.16 , respectively; that is, transforming to a pseudo-cubic phase. This indicates that a new metastable PTO phase (referred to as X-PTO) develops in the range $x = 0.16$ – 0.26 .

To further study the phase evolution with temper-

ature, one $\text{PTO}_{0.8}\text{-CFO}_{0.2}$ composite film was fabricated under the same conditions as that for the composite spread and then temperature-dependent high-resolution synchrotron radiation XRD was carried out on it. Peak fitting was performed for these patterns and the induced temperature-dependent evolution of peak positions are presented in Fig. 4. It is obvious that the metastable X-PTO phase coexists with the parent t-PTO phases at room temperature, implying that X-PTO is a new phase other than cubic-PTO since generally it is hard for t-PTO and cubic-PTO to coexist due to the large free energy difference. With the increasing temperature, the t-PTO(002), t-PTO(200) and X-PTO(002) merge into cubic-PTO(002) at 400°C, while t-PTO(103), t-PTO(301) and X-PTO(103) into cubic-PTO(103), indicating a tetragonal-to-cubic phase transition at $\sim 400^\circ\text{C}$, which is consistent with the reduced Curie temperature for the PbTiO_3 film. Although the peak position of X-PTO(002) is close to that of cubic-PTO(002), and almost does not shift with the increasing temperature, the peak intensity of X-PTO decreases with the increasing temperature and becomes invisible at $\sim 300^\circ\text{C}$, which also indicates that X-PTO is not cubic-PTO. Furthermore, the dielectric anomaly observed in PTO-CFO epitaxial composite film indicates that the X-PTO is not a mixture of tetragonal and cubic PTO because the mixture of tetragonal and cubic phase domains usually cannot result in such a large dielectric anomaly.

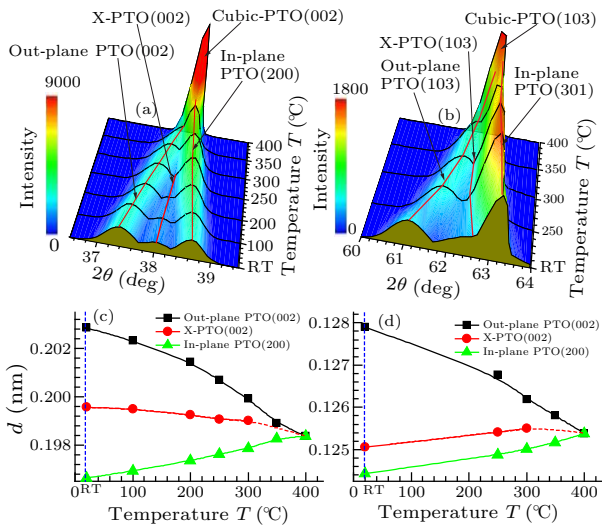


Fig. 4. Phase evolution of $(\text{PbTiO}_3)_{0.8}\text{-(CoFe}_2\text{O}_4)_{0.2}$ composite film with temperature: (a) (002)–(200) diffraction peaks, (b) (103)–(301) diffraction peaks, (c) and (d) lattice parameters versus temperature. Profiles displayed in Figs. 3(a) and 3(b) are the best fittings of the experimental data.

A first principles calculation was used to elucidate the microscopic mechanism of the formation of X-PTO. The enthalpy difference for different PTO phases was obtained, under the constrain of experimental lattice constants and tetragonal symmetry, from density functional calculations within the

generalized-gradient approximation (GGA), using the projector augmented wave (PAW) method^[22] as implemented in the Vienna *ab initio* simulation package (VASP)^[23] and depicted in Fig. 5. Experimental lattice constants were obtained from the peak fitting of diffraction patterns. The enthalpy of the X-PTO for $x < 1.6$ and $x > 0.26$ (dashed line in Fig. 5) was obtained from the lattice constants of X-PTO for $x < 1.6$ and $x > 0.26$ extrapolated from experimental data between $x = 0.16\text{--}0.26$ (dashed line in Fig. 3(c)). We found that the enthalpy of the X-PTO crosses that of the out-plane phase around $x = 0.16$, and is about 25 meV higher than that of the in-plane PTO between $x = 0.16\text{--}0.26$. Since the kT at room temperature is 26 meV, we conclude that X-PTO coexists with tetragonal PTO in this composition range. The enthalpy surface in pure PTO is believed to be softer under high pressure.^[24,25] Similarly, inside the composite film, inter-component strain weakens the enthalpy barrier between different phases, and a new metastable phase arises. From the above analyses, the phase diagram for PTO-CFO composite film can be plotted in Fig. 3(c): for $x < 0.14$, tetragonal PTO exists (T); between $x = 0.16\text{--}0.26$ (shadow region), tetragonal PTO coexists with X-PTO (T-X); when $x > 0.26$, only pseudo-cubic PTO is left (pc).

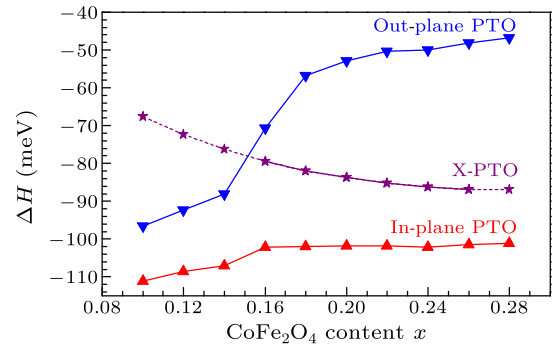


Fig. 5. Enthalpy differences (ΔH) with respect to the cubic phase of the in-plane, out-plane and X-PTO phases versus CFO content x .

The dielectric anomaly in PTO-CFO epitaxial composite film is similar to the dielectric response in usual Pb-based piezoelectric solid solutions. Consequently, it is likely to have a similar mechanism with that in these Pb-based systems. In usual Pb-based systems, near the MPB, free energy difference for polarization along different directions is so small that polarization can be easily rotated by an applied external electric field. In PTO-CFO epitaxial composite film, the metastable X-PTO was confirmed around $x = 0.20$, corresponding to the composition of dielectric anomaly, indicating that X-PTO is closely related to the dielectric anomaly. This strongly suggests a microscopic mechanism in the phase transition between metastable X-PTO and existing PTO results in the dielectric anomaly. The first principles calculation shows that metastable X-PTO and existing

PTO have almost equal enthalpy. Therefore, an external electric field could alter the balance among them. The relative dielectric constant of a multi-phase material can be expressed as the partial differential of the total polarization to the electric field. Considering that different phases have different spontaneous polarizations, the relative dielectric constant of PTO-CFO composite film probably shows anomalous enhancement around $x = 0.20$, resulting from the subtle rebalance of metastable X-PTO and existing PTO under applied electric field. Moreover, the coexistence of metastable X-PTO and parent PTO even indicates a possible MPB induced by inter-component strain in the composite film. Further detailed study is required to verify this possible MPB. In comparison, the strain-induced MPB behavior found in highly strained BFO/LAO films has been recently extensively studied, and the subsequently obtained crystal/domain structural details and their evolution with temperature, film thickness and external field could be used to successfully reveal the structural origin for the property anomaly found there. The literature^[7,12,26–29] and references therein are useful for comprehensive understanding of the content of this study.

In summary, an inter-component strain-induced metastable phase has been confirmed in PTO-CFO epitaxial composite films with direct microstructure evidence. The first principles calculation shows that X-PTO has substantial probability in certain composition range at room temperature. In addition, the phase evolution with temperature is investigated to support our observation. The inter-component strain used in our approach allows the film remaining in the fully strained state up to several hundreds of nanometer. This feature may be used in search for potential applications in electromechanical devices where thick piezoelectric films are usually needed. Furthermore, our finding of strain-induced metastable phase in the composite film can trigger a search for similar control in other composite perovskite thin films.

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