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Strain-driven phase transitions and associated dielectric/piezoelectric anomalies in BiFeO₃ thin films

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Strain-driven phase transitions and related intrinsic polarization, dielectric, and piezoelectric properties for single-domain films were studied for BiFeO₃ using phenomenological Landau–Devonshire theory. A stable and mixed structure between tetragonal and rhombohedral-like (monoclinic) phases is predicted at a compressive misfit strain of $u_m = -0.0382$ without an energy barrier. For a tensile misfit strain of $u_m = 0.0272$, another phase transition between the monoclinic and orthorhombic phases was predicted with sharply high dielectric and piezoelectric responses.

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Normal functional materials could become excellent electromechanical systems by the formation of morphotropic phase boundary (MPB) as in the examples of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ and $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$,^{1–3} since they have piezoelectric coefficients more than one order of magnitude larger than the commonly used piezoelectrics such as quartz. Piezoelectric and dielectric phenomena in ferroelectrics are well known to stem from both intrinsic and extrinsic sources. The intrinsic contribution corresponds to the lattice contribution from the ionic/electronic displacements while the extrinsic contribution arises from domain wall motion or the change in domain volume fraction due to the phase competition. It is reported that the intrinsic dielectric response in the MPB $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) thin film is the largest in comparison with those in rhombohedral (R), orthorhombic (O) or tetragonal (T) phases. However, the room temperature permittivity in PZT films is dominated largely by extrinsic domain wall motion contributing up to 75% of its total relative permittivity.⁴

A great deal of work has been reported on fundamental and technological aspects of the misfit strain dependent BiFeO₃ (BFO) structures and related properties.^{5–11} The lead-free BFO thin film deposited on LaAlO₃ (LAO) demonstrated a large piezoelectric response recently near the strain-driven, tetragonal to rhombohedral-like phase transition, besides the chemical composition driven phase transitions mentioned above.¹² In contrast to the traditional Pb-based ferroelectrics, BFO thin film is an environmentally friendly material and is considered to be a promising candidate for realizing multiferroic properties for spintronic devices. Notwithstanding the dramatic progress in the development of strain dependent properties in BFO thin films,^{6–13} there are still many unanswered questions such as the stable domain structure and related ferroelectric, piezoelectric, and ferro-

magnetic properties in the different strain-driven polymorphic phases.

In the present letter, we report a study of the misfit strain on phase stability, spontaneous polarization, dielectric, and piezoelectric properties of BFO thin films. Two mixed structure between T and M, M and O phases are predicted based on thermodynamic theory. Moreover, the stable mixed structures between the T and M phases, driven by the large compressive misfit strain, were investigated theoretically and compared with experimental results.¹² Finally, we propose the anomalous peaks in dielectric and piezoelectric responses near the M and O phase boundary.

In constructing the misfit strain-temperature phase diagram for BFO thin film, we assume that a single domain (001) BFO film epitaxially grows on the thick cubic substrate under short-circuit electrical boundary conditions. The thermodynamic potential of the pseudocubic BFO film is expressed as a function of polarization P_i ($i=1-3$) temperature T and misfit strain $u_m = (a_s - a_f)/a_s$, where a_s is the in-plane lattice parameter for the substrate and a_f is the equivalent cubic lattice constant of the free standing film. The expression of thermodynamic potential follows as:¹⁰

$$F = a_1^*(P_1^2 + P_2^2) + a_3^*P_3^2 + a_{11}^*(P_1^4 + P_2^4) + a_{33}^*P_3^4 + a_{13}^*(P_1^2P_3^2 + P_2^2P_3^2) + a_{12}^*P_1^2P_2^2 + \frac{u_m^2}{s_{11} + s_{22}},$$

with the following renormalized coefficients:

$$a_1^* = a_1 - u_m \frac{Q_{11} + Q_{12}}{S_{11} + S_{12}}, \quad a_3^* = a_1 - u_m \frac{2Q_{12}}{S_{11} + S_{12}},$$

$$a_{11}^* = a_{11} + \frac{1}{2} \frac{1}{S_{11}^2 - S_{12}^2} [(Q_{11}^2 + Q_{12}^2)S_{11} - 2Q_{11}Q_{12}S_{12}],$$

$$a_{33}^* = a_{11} + \frac{Q_{12}^2}{S_{11} + S_{12}}, \quad a_{13}^* = a_{12} + \frac{Q_{12}(Q_{11} + Q_{12})}{S_{11} + S_{12}},$$

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$$a_{12}^* = a_{12} - \frac{1}{2} \frac{1}{S_{11}^2 - S_{12}^2} [(Q_{11}^2 + Q_{12}^2)S_{11} - 2Q_{11}Q_{12}S_{12}] + \frac{Q_{44}^2}{2S_{44}},$$

where a_1 is the dielectric stiffness, a_{ij} and a_{ijk} are the higher order stiffness coefficients at constant stress, Q_{ij} are the electrostrictive coefficients, and S_{ij} are the elastic compliances of the film. The parameters and coefficients used for calculation are collected from previous papers.^{10,12,13} Four misfit-strain-dependent, potentially stable phases at room temperature, were considered in our numerical calculation with different free energies F and spontaneous polarizations P , they are as follows: cubic (F_C , $P=0$), tetragonal (F_T , $P_1=P_2=0$, $P_3=P_T \neq 0$), monoclinic (F_M , $P_1=P_2=P_{M1} \neq 0$, $P_3=P_{M3} \neq 0$), and orthorhombic (F_O , $P_1=P_2=P_O \neq 0$, $P_3=0$), which correspond to paraelectric phase, c phase, r phase and aa phase in Ref. 14, respectively.

The misfit strain-temperature phase diagram and related properties of BFO thin films have been reported previously but the aim of this paper is different.^{9,13} Similar strain-dependent results have been obtained by first principles method but only the effect of negative misfit strain arising from a compressive substrate, on the polarization and stable phase structure was considered. Moreover, an energy gap still exists between the T and R-like phases near the strain-driven coexistence range which is not consistent with the reported experimental observation of coexistence of T and R-like phases in the BFO/LAO system.⁹ Due to the small range of absolute misfit strain considered in the previous calculations,¹³ the mixed T and O phases found to be stable at high absolute strains and reported in this study were not revealed. From the Landau phenomenological theory, we can obtain the stable phase by minimizing the total energies among the different phases. Figure 1 shows the calculated total free energies and spontaneous polarizations for different phases as a function of misfit strain at room temperature. Two mixed phase structures near the T/M and M/O boundaries can be deduced from Fig. 1 due to the very close free energy for the different misfit strains of about $u_m = -0.038$ and $u_m = 0.0272$. With reduction in misfit strain in Fig. 1(b), the stable phase changes from O to M and finally to T phase with increase in spontaneous polarization, and switch in its direction from in-plane to out-of-plane. At the compressive misfit strain of $u_m = -0.038$ in Fig. 1(a), a mixed T and M phase structure could be predicted as the free energies for the T and M phases overlap implying that they can coexist at this misfit strain. The characteristic intrinsic dielectric constants ϵ_{33} and piezoelectric coefficients d_{33} under compressive strain are shown in Fig. 2 based on the single domain model. The calculated intrinsic d_{33} increases from 25 pm/V to 40 pm/V with increase in compressive misfit strain. In contrast to the reported total piezoelectric response ($d_{33}^t = 120$ pm/V),¹⁵ the intrinsic d_{33} in T and M mixed phase is much smaller and thus we infer that the extrinsic contribution is dominant for the mixed T and M phase structure. This implies that the change in phase fraction via phase boundary motion contributes more to the total piezoresponse in the mixed structure.¹² Despite the experimental observation of the mixed T-like and M phase stripes in BFO/LAO system by high-resolution atomic force microscopy and transmission electron microscopy (TEM),¹² detailed information on the

FIG. 1. (Color online) (a) The total free energy F and (b) the spontaneous polarization P as a function of misfit strain for different phases at room temperature.

equilibrium phase boundary structure is still not available. According to our thermodynamic calculation following the idea of a mixture of T and R phases in PZT's MPB,¹⁶ the stable mixed T and M (R-like) phases structure in BFO is shown in Fig. 3. Note that m_0 is the normal to the interface between T and R-like phases in BFO thin film. In order to accommodate a stable mixed phase structure, both principal axes of T and R-like lattices rotate 1.65° from the corresponding free standing lattices. The angle Φ corresponding to the direction of the phase interface is calculated to be 52° . Here we only considered a mixed T/R structure with a fixed geometry for simplicity, and obtained quantitatively the stable configuration which agrees with the observed results

FIG. 2. (Color online) Misfit strain dependent intrinsic dielectric constant ϵ_{33}/ϵ_0 and piezoelectric coefficient d_{33} for single domain BiFeO₃ thin films.

FIG. 3. (Color online) (a) The schematic of the mixed structure between tetragonal and rhombohedral-like phases for BFO film and (b) an equilibrium state of the mixed structure between T and R-like phases from calculation (up) and published experimental results (see Ref. 12) (down).

($\Phi=48.4^\circ$ and $\theta=3.23^\circ$) shown by TEM images. Thus, it is reasonable to forecast the phase boundary interface as the (101) plane. The most recent experimental results however show that this mixed T and R-like phase structure can be more complicated than the current simple model, even though the current model can explain some key experimental findings. There could be many extra “phases” such as the parent phases, transitional phases, etc., in mixed phase structures when the film is subjected to large compressive misfit strains. These structures vary quasiperiodically with complex behavior of nanoscale twinlike structures. The experimental results of these will be reported in subsequent papers.

Additionally, it could be noted in Fig. 1 that there is another strain-induced phase transition subject to tensile strain where a stable coexisting region is evident between M and O phases due to their equal free energies at $u_m=0.0272$. The dielectric response for this strain exhibits a sharp anomaly which corresponds to an excellent piezoelectric response d_{33} near the mixed M and O phase boundary. This intrinsic d_{33} is even larger than the total piezoelectric response d_{33}^t (about 120 pm/V) reported for the mixed T and M phases in BFO/LAO systems.^{12,15} For the well-known traditional T/R MPB in PZT, the ultrahigh electromechanical response is attributed to the lower symmetrical, intermediate monoclinic phase that connects the tetragonal and rhombohedral phases. But this anomalous behavior at $u_m=0.0272$ is linked a change in phase structure from M phase to O phase. We propose that there might be some other low symmetrical phases linking M and O phases to induce the anomalous dielectric/piezoelectric responses near the proposed M/O boundary, which can be developed in the higher-order terms in Landau–Devonshire free energy expansion.¹⁷ For ex-

ample, an anomalous dielectric response was reported between an orthorhombic phase of the $Pbma$ space group and another orthorhombic phase of the $Pbnm$ space group in the $(1-x)\text{NaNbO}_3-x\text{CaTiO}_3$ system.¹⁸

In summary, we have studied the misfit strain-driven phase transitions of single domain BFO thin films. The spontaneous polarization, dielectric, and piezoelectric coefficients are calculated as a function of misfit strain at room temperature for T, M, and O phases. A stable geometric mixed structure between T and M (R-like) phases is investigated theoretically, and we suggest that the phase interface is along the (101) planes with certain distortions to accommodate large strains. Our theoretical results also indicate the possibility of another gigantic out-of-plane dielectric and piezoelectric responses between the M and O phases. This is even larger than the total dielectric and piezoelectric responses of the mixed T and M phases.

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