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Defect-related lattice strain and the transition temperature in ferroelectric thin films

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We propose an extension to the phenomenological thermodynamic Landau-Devonshire theory to include the contribution of inhomogeneous strains caused by lattice defects to the Gibbs free energy. The model yields correction terms for dielectric and ferroelectric quantities as a function of both elastic misfit strain and defect-related strain that can be measured by x-ray-diffraction techniques. We compare the correction in Curie-Weiss temperature due to elastic and inhomogeneous strain in pristine, W and Mn 1% doped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films grown on the $LaAlO_3$ substrate. If the contribution of inhomogeneous strain is included, the agreement with measurements markedly improves.

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Thin-film ferroelectric materials have been widely investigated as materials for the microelectronic devices such as dynamic random access memories, bypass capacitors, infrared detectors, and tunable-microwave devices.[1] Perovskite oxide thin films are especially of interest because of the relatively high dielectric constant and are considered to be used in tunable-microwave devices. In particular, solid solutions of $Ba_xSr_{1-x}TiO_3$ (BST) are widely investigated because of their high tunability and Curie temperature that is easily controlled by adjusting chemical composition. It was determined that apart from the chemical composition, the type of the substrate, microstructure of the interface, and mechanical stresses within the thin films have an important impact on the physical properties of the ferroelectric thin films. In particular, the change in ferroelectric-transition temperature, electric permittivity, and dielectric losses at microwave frequencies can be severe and an understanding of its origins is therefore of a great interest.[2–4] The influence of stress was already investigated by Merz[5] who has found that hydrostatic pressure decreases the Curie-Weiss temperature due to a smaller unit cell. Forsbergh[6] has studied effects of biaxial pressure on the ferroelectric-transition temperature both experimentally and theoretically in terms of the thermodynamic theory. A comprehensive phenomenological thermodynamic theory for ferroelectric thin films, based on the contribution of the substrate-film elastic lattice misfit strain energy to the free energy, has predicted an entirely new phase diagram and shift of the Curie-Weiss transition temperature, and change of dielectric and related properties.[7]

Different authors have early recognized importance of strain coupling[8] and misfit dislocations[9–14] on phase transformations and domain formation in ferroelectric thin films. Recently, it was recognized that electric permittivity of ferroelectric thin films critically depends on residual stress resulting from a misfit substrate-layer strain and its relaxation due to introduction of misfit dislocations as a function of the thin-film thickness.[15–20] Canedy *et al.*[21] have associated significant changes in electric permittivity of BST thin films with high density of threading dislocations that were observed by TEM. Our previous work[22] on doped BST films indicates that both dielectric properties and the ferroelectric-transition temperature depend not only on the lattice-mismatch misfit strains but also inhomogeneous strains associated with crystalline defects, including both misfit and threading dislocations and point defects. The influence of defect-related lattice strain can be substantial and dominate elastic-strain contribution. Here, instead of considering influence of misfit dislocations indirectly through the estimates of misfit strain as a function of the thin-film thickness, we lay out the theoretical model in order to explain the observed shift in Curie-Weiss transition temperature directly in terms of observables: lattice parameters and inhomogeneous strain caused by crystalline defects (nonrandomly distributed point defects and both misfit and threading dislocations), as deduced from the diffraction-line broadening. The theory presented allows for a straightforward derivation of related dielectric properties, as well.

In the approximation of a single-domain two-dimensional thin film constrained by the substrate, the additional term to the Gibbs free energy G due to an elastic-strain contribution is given as[6,7]

$$G' = G + \sum_i e_i \sigma_i, \quad G = U - TS. \tag{1}$$

Here, U denotes the internal energy, T the absolute temperature, S the entropy, e_i and σ_i the elastic strain and stress tensors in condensed Voigt notation. The Gibbs free energy close to the transition temperature and appearance of polarization P is

$$\begin{aligned} G = {} & a_1\,(P_1^2 + P_2^2 + P_3^2) + a_{11}\,(P_1^4 + P_2^4 + P_3^4) + a_{12}\,(P_1^2 P_2^2 \\ & + P_1^2 P_3^4 + P_2^2 P_3^2) + a_{111}\,(P_1^6 + P_2^6 + P_3^6) + a_{112}[P_1^4(P_2^2 + P_3^2) \\ & + P_3^4(P_1^2 + P_2^2) + P_2^4(P_1^2 + P_3^2)] + a_{123} P_1^2 P_2^2 P_3^2 - Q_{11}\,(\sigma_1 P_1^2 \\ & + \sigma_2 P_2^2) - Q_{12}\,[\sigma_1\,(P_2^2 + P_3^2) + \sigma_2\,(P_1^2 + P_3^2)] \\ & - Q_{44}\,P_1 P_2 \sigma_6 - 1/2\,s_{11}\,(\sigma_1^2 + \sigma_2^2) - s_{12}\,\sigma_1 \sigma_2 \\ & - 1/2\,s_{44}\,\sigma_6^2. \end{aligned} \tag{2}$$

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Here, $a_{i,j,k}$ are dielectric stiffness coefficients, s_{ij} is the elastic compliance tensor, and Q_{ij} the electrostrictive tensor.

This expression considers only elastic strains. However, both line and point crystalline defects cause inhomogeneous strains and therefore increase crystal's internal energy for an amount

$$\Delta U = \frac{1}{2}\sum_{ij} c_{ij}\varepsilon_i\varepsilon_j, \tag{3}$$

where the elastic stiffness tensor is denoted by c_{ij}. The strain ε_i is inhomogeneous strain (so-called strain of the III kind) that influences the diffraction line width, for instance.

In ionic crystals, defects are charged and can effect the polarization of a ferroelectric. For defects on an acentric crystallite site, the polarization of a single domain changes,[23]

$$\Delta P = N\overline{\Delta\mu}, \quad \overline{\Delta\mu} = \Delta\mu_d + \sum_i q_i\Delta x_i, \tag{4}$$

where $\Delta\mu_d$ is the change of dipole moment at the defect site and Δx_i is the displacement of charge q_i in the surrounding lattice due to the defects of average density N in the domain. The associated change in polarization is relatively small and proportional to the polarization

$$\Delta P \approx \alpha P, \tag{5}$$

and we can write

$$\widetilde{G} = G(P) + \left(\frac{\partial G}{\partial P}\right)_P \Delta P. \tag{6}$$

Therefore, the defects will renormalize the original coefficients a_n in the development of the Gibbs free energy (2):

$$\widetilde{\widetilde{G}} = \sum_n \widetilde{a_n}P^n = \sum_n a_n(1+n\alpha)P^n \tag{7}$$

and α will be the function of strain ε_i.

Thus, we can add and additional term to the Gibbs free energy, which is caused by inhomogeneous strain due to defects as

$$G'' = G' + \sum_i \varepsilon_i\Sigma_i, \tag{8}$$

where Σ_i are the stresses of the III kind.

No tractions at the free surface of the thin film require all three perpendicular stress components to vanish at the surface and therefore everywhere else in the thin film in the homogeneous stress approximation. The inhomogeneous stresses can be balanced locally in the thin film and thus have all six nonvanishing components. Because strain fields around point defects are isotropic, we shall assume a macroscopic isotropy of inhomogeneous strain.

The complete equilibrium conditions are then

$$\partial G/\partial\sigma_1 = \partial G/\partial\sigma_2 = -e_m; \quad \partial G/\partial\sigma_6 = 0;$$

$$\sigma_3 = \sigma_4 = \sigma_5 = 0 \tag{9}$$

for the elastic strain[7] and

$$\partial G/\partial\Sigma_1 = \partial G/\partial\Sigma_2 = \partial G/\partial\Sigma_3 = -\varepsilon_m;$$

$$\partial G/\partial\Sigma_6 = 0; \quad \Sigma_4 = \Sigma_5 = 0 \tag{10}$$

for the inhomogeneous strain.[24]

One can then calculate the Gibbs free energy as

$$\begin{aligned} G'' = {} & a_1^*(P_1^2 + P_2^2) + a_3^*P_3^2 + a_{11}^*(P_1^4 + P_2^4) + a_{33}^*P_3^4 + a_{13}^*(P_1^2P_3^2 \\ & + P_2^2P_3^2) + a_{12}^*P_1^2P_2^2 + a_{111}(P_1^6 + P_2^6 + P_3^6) + a_{112}[P_1^4(P_2^2 \\ & + P_3^2) + P_2^4(P_3^2 + P_1^2) + P_3^4(P_1^2 + P_2^2)] + a_{123}P_1^2P_2^2P_3^2 \\ & + \frac{e_m^2}{s_{11}+s_{12}} + \frac{3}{2}\frac{\varepsilon_m^2}{s_{11}+2s_{12}}, \end{aligned} \tag{11}$$

where the renormalized coefficients are

$$\begin{aligned} a_1^* &= a_1 - e_m\frac{Q_{11}+Q_{12}}{s_{11}+s_{12}} - \varepsilon_m\frac{Q_{11}+2Q_{12}}{s_{11}+2s_{12}}, \\ a_3^* &= a_1 - e_m\frac{2Q_{12}}{s_{11}+s_{12}} - \varepsilon_m\frac{Q_{11}+2Q_{12}}{s_{11}+2s_{12}}, \\ a_{11}^* &= a_{11} + \frac{1}{2}\frac{s_{11}(Q_{11}^2+Q_{12}^2) - 2s_{12}Q_{11}Q_{12}}{s_{11}^2 - s_{12}^2} \\ & \quad + \frac{1}{2}\frac{s_{11}(Q_{11}^2+2Q_{12}^2) + s_{12}(Q_{11}^2 - 4Q_{11}Q_{12})}{(s_{11}+2s_{12})(s_{11}-s_{12})}, \\ a_{33}^* &= a_{11} + \frac{Q_{12}^2}{s_{11}+s_{12}} \\ & \quad + \frac{1}{2}\frac{s_{11}(Q_{11}^2+2Q_{12}^2) + s_{12}(Q_{11}^2 - 4Q_{11}Q_{12})}{(s_{11}+2s_{12})(s_{11}-s_{12})}, \\ a_{12}^* &= a_{12} - \frac{s_{12}(Q_{11}^2+Q_{12}^2) - 2s_{11}Q_{11}Q_{12}}{s_{11}^2 - s_{12}^2} + \frac{Q_{44}^2}{2s_{44}} \\ & \quad + \frac{s_{11}(Q_{12}^2 + 2Q_{11}Q_{12}) - s_{12}(Q_{11}^2 + 2Q_{12}^2)}{(s_{11}+2s_{12})(s_{11}-s_{12})}, \\ a_{13}^* &= a_{12} + \frac{Q_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}} \\ & \quad + \frac{s_{11}(Q_{12}^2 + 2Q_{11}Q_{12}) - s_{12}(Q_{11}^2 + 2Q_{12}^2)}{(s_{11}+2s_{12})(s_{11}-s_{12})}. \end{aligned} \tag{12}$$

The last term in these expressions is given by the inhomogeneous strain. Notice that the inhomogeneous strain is always positive by definition unlike the elastic strain that can be either positive or negative, depending whether the film is in tension or compression parallel to the interface. The paraelectric-ferroelectric phase transition in the BT and BST thin films is still of the second order as found by Pertsev *et al.*,[7] as compared to the first-order transition in the bulk BT and BST.

Similarly, the Curie-Weiss temperature shift from the value for the bulk material follows from Eq. (12):

TABLE I. Elastic in-plane strain e_m and inhomogeneous strain ε_m, as measured by x-ray diffraction.

Sample	e_m (10^{-3})	ε_m (10^{-3})
$Ba_{0.6}Sr_{0.4}TiO_3$	−1.1	0.62
$Ba_{0.6}Sr_{0.4}Ti_{0.99}Mn_{0.01}O_3$	−2.1	0.69
$Ba_{0.6}Sr_{0.4}Ti_{0.99}(Mn\text{-}W)_{0.01}O_3$	−0.65	1.1
$Ba_{0.6}Sr_{0.4}Ti_{0.99}W_{0.01}O_3$	−0.31	2.5

$$\Delta T_{c\text{-}w} = \max\left\{ 2C\varepsilon_0\left(\frac{2Q_{12}}{s_{11}+s_{12}}e_m + \frac{Q_{11}+2Q_{12}}{s_{11}+2s_{12}}\varepsilon_m\right), 2C\varepsilon_0\left(\frac{Q_{11}+Q_{12}}{s_{11}+s_{12}}e_m + \frac{Q_{11}+2Q_{12}}{s_{11}+2s_{12}}\varepsilon_m\right)\right\}. \quad (13)$$

Here, C and ε_0 are the Curie-Weiss constant and the permittivity of the vacuum, respectively.

In order to test the influence of both elastic misfit and inhomogeneous defect-related strains, we prepared four thin films by the pulsed-laser deposition: The pristine $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) and 1% Mn-doped, W-doped, and both Mn and W (co-doped) $Ba_{0.6}Sr_{0.4}Ti_{0.99}M_{0.01}O_3$ (M=Mn,W) films were deposited on pseudo-(001) $LaAlO_3$ (LAO) substrate, as it was reported that dielectric losses at microwave frequencies can be decreased by doping BST with small quantities of Mn, W, Ca, Mg, and Zr.[25] More details about experimental conditions and dielectric measurements are given elsewhere.[22] Both elastic and inhomogeneous strains were determined by x-ray diffraction. Reciprocal space maps of asymmetric (013) BST reflections were used to obtain lattice parameters both parallel and perpendicular to the film surface, which was used to calculate elastic strains. The films were in compression parallel to and in tension perpendicular to the interface, thus facilitating "*c*"-type ferroelectric domains.

Inhomogeneous strains were determined by the diffraction-line broadening analysis formalism that allows for the separation of coherent-domain size and strain-broadening effects.[26] Domain size obtained varies from 850 to 1550 Å,[22] and is close to the measured thickness of the films. The values differ because diffraction measures the dimension of grains perpendicular to the substrate and is therefore reduced because of grain tilts and possible extended defects parallel to the surface. Both elastic and inhomogeneous strains are included in Table I. Generally, there is a decrease in elastic strain and increase in inhomogeneous strain upon doping, in particular, for the W-doped sample. This can be explained by the effect of doping on the introduction of misfit dislocations at the growth temperature, which would decrease elastic misfit strain but increase inhomogeneous-strain component. The doping is known to affect the concentration of oxygen vacancies[2] and point defects were found to be essential to the dislocation reactions, as showed for the $BaTiO_3/SrTiO_3$ system.[27]

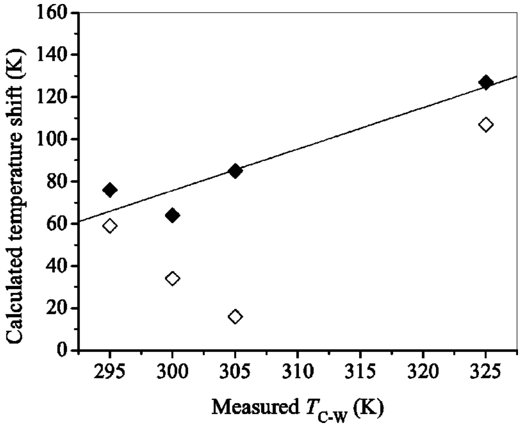

FIG. 1. Temperature shift in the Curie-Weiss temperature calculated from Eq. (13) as a function of the measured Curie-Weiss temperature. The values for two cases are plotted: (a) Only the elastic-strain contribution to Eq. (13) included (empty symbols); (b) Both elastic- and inhomogeneous-strain contribution to Eq. (13) included (full symbols). The straight line is a least-squares fit to the full symbols as a guide to the eye.

To investigate the influence of both elastic and inhomogeneous strain on the ferroelectric properties, we calculated the change in the Curie-Weiss temperature, from Eq. (13),[28] and plot it as a function of the measured Curie-Weiss temperature, as determined by the maximum in the electric permittivity as a function of temperature, in Fig. 1. A rather poor correlation in the case when only elastic-strain contribution to Eq. (13) is considered is markedly improved when both elastic and inhomogeneous strains are taken into account. This is especially evident in the case of W-doped sample. Therefore, the inhomogeneous strain potentially has a large influence on the Curie-Weiss temperature and it should not be neglected.

In summary, we report the evidence that the inhomogeneous defect-related lattice strain significantly affects ferroelectric and dielectric properties along with the elastic substrate-film lattice-misfit strain. As opposed to the current models that consider only the influence of misfit dislocation indirectly through the relief of misfit strain, we consider changes of ferroelectric and dielectric properties in terms of directly measurable properties, that is, lattice parameters and inhomogeneous strain, the latter depending on both misfit and threading dislocations and nonrandomly distributed point defects. We model the contribution of inhomogeneous strain and stress to the Gibbs free energy in the framework of the Landau-Devonshire thermodynamic theory and calculate the renormalized dielectric coefficients. As an example, we discuss the shift of the Currie-Weiss temperature in doped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films as a function of both elastic and inhomogeneous strain and show that the inclusion of the latter significantly improves the agreement with the measurements.

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