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Abstract
Recent experimental results (Zheng et al 2004 Science 303 661) have shown that a 1-3-type BaTiO$_3$–CoFe$_2$O$_4$ composite film exhibited a strong coupling between the ferroelectric and ferromagnetic order parameters. The coupling interaction in the nanostructured multiferroic film could be different from that in a bulk composite because there exists a giant residual stress/strain in the film. In this paper, by considering the influence of the three-dimensional residual strain in the film, the magnetically induced polarization of the nanostructured BaTiO$_3$–CoFe$_2$O$_4$ multiferroic films has been studied using the Landau–Ginsberg–Devonshire thermodynamic theory. The calculation results show that the 1-3-type nanostructured composite film could produce a ferroelectric–ferromagnetic coupling larger than that of its bulk counterpart which is in broad agreement with the experimental results. The 2-2-type nanostructured composite films were found to produce much less coupling interaction in comparison with the 1-3-type film. The dependence of multiferroic coupling on composition and temperature was analysed on the basis of the calculated results.

1. Introduction
Multiferroic materials have attracted great interest owing to their multi-functionality [1–3], which provides significant potential for application as next-generation multi-functional devices. In these multiferroic materials, the coupling interaction between the multiferroic orders could produce some new effects, such as the magnetoelectric [1–3] and/or the magnetodielectric effect [4]. The magnetoelectric response is the appearance of an electric polarization on applying a magnetic field and/or the appearance of magnetization on applying an electric field. This magnetically induced ferroelectric polarization has been observed in TbMnO$_3$ at a low temperature of $\sim$20 K and a high magnetic field of $\sim$9 T [5]. More importantly, the multiferroic composites formed by the combination of the ferromagnetic and the ferroelectric substances, such as combinations of piezoelectric ceramics (e.g. BaTiO$_3$, lead–zirconate–titinate PZT) and ferrite or rare-earth-iron alloys (e.g. Terfenol-D), have been recently found to exhibit a large magnetoelectric response at room temperature [6–8]. The magnetoelectric behaviour in these multiferroic composites is dependent on their microstructure and the coupling interaction across the ferromagnetic–ferroelectric interface [9].

More recently, nanostructured BaTiO$_3$/CoFe$_2$O$_4$ multiferroic composites have been deposited in a film-on-substrate geometry [10]. The coupling interaction between BaTiO$_3$ and CoFe$_2$O$_4$ in the multiferroic nanostructures is still found to be due to elastic interaction as in the bulk composites. However, the mechanical constraint arising from the film-on-substrate and the good bonding between the ferromagnetic and the ferroelectric phases in the nanostructured films could significantly affect the coupling interactions, thus resulting in a magnetoelectric effect and/or magnetically induced polarization at room temperature. Therefore, the theoretical and experimental study of these multiferroic nanostructures has been of significant interest.

For the bulk ferroelectric/ferromagnetic multiferroic systems, several theoretical methods or approaches have been
suggested to describe the coupling magnetic–mechanical–electric interactions, including the Green’s function technique [7,9,11], the finite element method [12] and the simple averaging method [13]. Recently, a theoretical description of such multiferroic nanostructured films has been proposed by using the Green’s function technique to estimate the magneto-electric effect or the magnetically induced polarization, which takes account of the influence of spontaneous polarization and the constraint effect by the substrate and present a new set of constitutive equations for the multiferroic nanostructured films [14]. In this paper, a phenomenological model based on the Landau–Ginsberg–Devonshire (LGD) thermodynamic theory is used to investigate multiferroic BaTiO3/CoFe2O4 nanostructure films. The calculated results by the present thermodynamic method are in good agreement with those using the Green’s function technique [14] and the available experimental results from Zheng et al [10].

2. Theoretical framework

According to the LGD thermodynamic theory, which has been extensively and successfully used to understand the ferroelectric behaviours of perovskite films [15–17], the Gibbs free energy of the ferroelectric BaTiO3 could be written as follows:

$$\Delta G = \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}(P_1^2 P_2^4 + P_2^4 P_3^2 + P_3^4 P_1^2) + \alpha_{122}(P_1^2 P_2^2 P_3^2 - \frac{1}{2} s_1(X_1^2 + X_2^2 + X_3^2) - s_2(X_1 X_2 X_3 + X_1 X_3 + X_2 X_3) - \frac{1}{2} s_{24}(X_1^2 X_2^2 + X_2^2 X_3^2 + X_3^2 X_1^2) - Q_{11}(X_1 P_1^2 + X_2 P_2^2 + X_3 P_3^2)) - Q_{12}(X_1(P_2^2 P_3^4 + X_2 P_1^2 P_3^2) + X_2(P_1^2 P_2^4 + X_3 P_1^2 P_3^2) + X_3 P_1^2 P_2^2) - Q_{44}(P_1 P_3 X_1 + P_1 P_2 X_3 + P_2 P_3 X_1),$$

(1)

where $\Delta G$ is Gibbs free energy function for unit area of BaTiO3, $\alpha_i$, $\alpha_{ij}$ and $\alpha_{ijk}$ the dielectric stiffness and higher-order stiffness coefficients at constant stress; $X_i$ the stress in the BaTiO3; $s_i$ the elastic compliance coefficient and $Q_{ij}$ the electrostrictive constant in polarization notation. The first partial derivatives of the energy with respect to the components of $P$ and $X$ give the conjugate parameters of the electric field $E$ and the negative of the strain $-\varepsilon$, respectively,

$$\frac{\partial \Delta G}{\partial P_i} = E_i, \quad \frac{\partial \Delta G}{\partial X_{ij}} = -\varepsilon_{ij}.$$  

(2)

We consider three types of nanostructured BaTiO3/CoFe2O4 multiferroic films, i.e. (1) 1-3-type film with CoFe2O4 nanoparticles (shaded) embedded in the BaTiO3 matrix (figure 1(a)); (2) BaTiO3/CoFe2O4 2-2-type (P/M) with the BaTiO3 layer (white) deposited first on the substrate of SrRuO3 and then the CoFe2O4 layer (shaded) deposited on the BaTiO3 layer (figure 1(b)); and (3) CoFe2O4/BaTiO3 2-2-type (M/P) with the CoFe2O4 layer (shaded) deposited first on the substrate and then the BaTiO3 layer (white) on the CoFe2O4 layer (figure 1(c)). The mechanical boundary conditions for BaTiO3 in the M/P-2-type films are essentially the same as those proposed by Pertsev et al [15], i.e. $\partial \Delta G/\partial X_1 = \partial \Delta G/\partial X_2 = -\varepsilon_{11}, \partial \Delta G/\partial X_3 = 0$, $X_3 = X_4 = X_5 = 0$ and $\varepsilon_{11} = \varepsilon_{11}^{m} + \varepsilon_{11}^{p}$, where $\varepsilon_{11}^{p}$ is the in-plane residual constraint strain in piezoelectric BaTiO3 layer that results from a lattice mismatch with the substrate and the magnetostrictive layer and $\varepsilon_{11}^{m}$ is the magnetically induced strain in the external magnetic field that should be passed from the CoFe2O4 layer to the BaTiO3 layer. In comparison, in the 1-3-type films, there also exists a strain along the 3-direction or the epitaxial direction besides the in-plane strains. Correspondingly, the mechanical boundary conditions for the BaTiO3 phase in the 1-3-type composite film are $\partial \Delta G/\partial X_1 = \partial \Delta G/\partial X_2 = -\varepsilon_{11}^{p}, \partial \Delta G/\partial X_3 = -\varepsilon_{33}^{p}, \partial \Delta G/\partial X_4 = \partial \Delta G/\partial X_5 = \partial \Delta G/\partial X_6 = 0$; $\varepsilon_{11}^{p} = \varepsilon_{11}^{m}$ and $\varepsilon_{33}^{p} = \varepsilon_{33}^{m} + \varepsilon_{33}^{m}$, where the superscript p and m refer to the piezoelectric BaTiO3 phase and magnetostrictive CoFe2O4 phase, respectively. As for the P/M 2-2-type films, the CoFe2O4 layer is clamped by the substrate directly and thus on applying the magnetic field the magnetostrictive behaviour in the CoFe2O4 layer is restricted almost completely.

Based on the above mechanical boundary conditions, the polarization of the epitaxially grown c-phased BaTiO3 ($P_1 = P_2 = 0, P_3 \neq 0$) or the nanostructured multiferroic films could be calculated from the following stationary electric equilibrium condition:

$$\frac{\partial \Delta G}{\partial P_3} = E_3 = 0.$$  

(3)
of not only the residual strain but also the magnetically which will be discussed in the next section.

After applying the external magnetic field, \( \varepsilon \) depends on the temperature and the composition as well as the lattice mismatch both between BaTiO3 and the substrate and between BaTiO3/CoFe2O4 films and \((\frac{b}{2})\) the bulk BaTiO3/CoFe2O4 composites \((f = 0.35)\) at room temperature. The inset in \((\frac{b}{2})\) is the magnetostriuctive behaviour for CoFe2O4.

\( 3.1. \) \textbf{Ferroelectric properties of the nanostructured films}

According to the LGD phenomenological thermodynamic theory, the relative dielectric constant \( \kappa_{33} \) of the tetragonal BaTiO3 phase is related to the inverse of the second derivative of \( \Delta G \) (equation (1)) with respect to the polarization component \( P_3 \) and is given by the following:

\[
\kappa_{33} = \frac{\partial^2 \Delta G}{\partial P^2} \left( \frac{\partial P_3}{\partial X_3} \right)^{-1}
\]

with \( \kappa_0 \) being the vacuum dielectric permittivity. Also, the piezoelectric strain coefficients \( d_{ij} \) are defined as follows [19]:

\[
d_{31} = b_{31} \kappa_{33}, \quad d_{33} = b_{33} \kappa_{33},
\]

where \( b_{ij} \) are the piezoelectric polarization-related coefficients

\[
b_{ij} = -\frac{\partial^2 \Delta G}{\partial P_i \partial X_j}.
\]

Using equation (1) and (5)–(7), the spontaneous polarization and the dielectric and piezoelectric constants can be calculated.
as \( P_1^f \) = 12.6 \( \mu \) C cm\(^{-2}\), \( \kappa_{33}/\kappa_0 \) = 650, \( d_{33} \) = 18.0 pm V\(^{-1}\), and \( d_{31} \) = -7.1 pm V\(^{-1}\) for the nanostructured P/M 2-2-type films; and \( P_1^f \) = 17.5 \( \mu \) C cm\(^{-2}\), \( \kappa_{33}/\kappa_0 \) = 270, \( d_{33} \) = 12.5 pm V\(^{-1}\) and \( d_{31} \) = -5.0 pm V\(^{-1}\) for the nanostructured 1-3-type film under no applied magnetic field (table 2). These calculations for the nanostructured 1-3-type film are in good agreement with the measured values of \( P_3^f \) \( \approx \) 16.7 \( \mu \) C cm\(^{-2}\), \( \kappa_{33}/\kappa_0 \) < 330, \( d_{31} \) \( \approx \) 10 pm V\(^{-1}\) [10].

In addition, when an external electric field \( \hat{E}_3 \) is applied, the total Gibbs free energy \( G \) is given as follows:

\[
G = \Delta G - \hat{E}_3 P_3. \tag{8}
\]

The stability condition of the dielectric stiffness \( \chi_{33} = \partial^2 G/\partial P_3^2 > 0 \) for the ferroelectric phase makes it possible to calculate the minimum polarization which can exist in an antiparallel electric field [20]. From the condition of \( \chi_{33} = 0 \), the critical polarization \( P_3^c \) could be obtained in a similar form to equation (8), and as a result the coercive field \( \hat{E}_c \) is given from \( \partial G/\partial P_3 = 0 \) as follows:

\[
\hat{E}_c = \frac{\partial \Delta G}{\partial P_3} \bigg|_{P_3 = P_3^c}. \tag{9}
\]

For comparative purposes, the \( \hat{E}_c \) value is calculated as \( \approx 11.2 \) MV m\(^{-1}\) for BaTiO\(_3\) in the nanostructured 1-3-type BaTiO\(_3\)-CoFe\(_2\)O\(_4\) composite film, also in agreement with the measured value of \( \approx 9.1 \) MV m\(^{-1}\) [10].

### 3.2. Magnetically induced polarization in the multiferroic films

With the application of an external magnetic field, the polarizations of the multiferroic films will vary correspondingly. Figure 2(a) shows the calculated \( \Delta P_3 \) in these three types of multiferroic films with \( f = 0.35 \) at room temperature. \( \Delta P_3 \) of the 1-3-type and P/M 2-2-type films increases nonlinearly with the magnetic field owing to the nonlinear dependence of the magnetostriction of CoFe\(_2\)O\(_4\) on the applied magnetic field, while \( \Delta P_3 \) of the M/P 2-2-type film is almost equal to zero regardless of the application of the magnetic field. The reason for the latter result is that the CoFe\(_2\)O\(_4\) layer in the M/P 2-2-type film is fully constrained by the substrate so that the magnetostrictive capability is destroyed almost completely. It is particularly interesting to note that a large magnetically induced polarization is obtained in the 1-3-type films at room temperature. When the applied magnetic field increases from zero to 5000 Oe (0.5 T), the magnetically induced polarization in the 1-3-type film increases up to 420 \( \mu \) C m\(^{-2}\), on an equal level with that of TbMnO\(_3\) at a low temperature (\( \approx 20 \) K) and a high magnetic field (\( \approx 9 \) T) [5]. In contrast, the magnetically induced polarization in the P/M 2-2-type BaTiO\(_3\)/CoFe\(_2\)O\(_4\) composite film is quite low and much less than that in the 1-3-type. This could be attributed mainly to the tremendous clamping effect in the 2-2-type film, where the in-plane constraint effect greatly inhibits the magnetostriction of the CoFe\(_2\)O\(_4\) layer. In the actual experiment [10], the 2-2-type BaTiO\(_3\)/CoFe\(_2\)O\(_4\) film is indeed found to exhibit far weaker magnetoelastic coupling than the 1-3-type one. For comparison, the cases in bulk 1-3 and 2-2-type BaTiO\(_3\)/CoFe\(_2\)O\(_4\) composites are also calculated by assuming the absence of residual strain, as shown in figure 2(b). The mechanical boundary condition of (1 – \( f \))\( e_{11}^m + f e_{11}^m = 0 \) for the 1-3-type nanostructured multiferroic films should be revised as \( e_{11}^m = e_{11}^m \) for the 1-3-type bulk systems because the in-plane constraint will be released completely in bulk case. As seen in figure 2(b), the 1-3-type bulk composites exhibit a lower magnetically induced polarization than the 1-3 nanostructured counterparts, and the 2-2-type bulk composites also exhibit lower magnetically induced polarization than the 1-3-type. The present calculations are quite agreeable with those recently calculated by using the Green’s function technique [14].

As shown in figure 2, the magnetically induced polarization of the nanostructured composite films is closely dependent on the magnetostrictive behaviour of the ferromagnetic phase. For further illustration, we take a few different values for the saturation magnetostriction \( \lambda_{001} \) (figure 3). As seen in figure 3, the magnetically induced polarization depends strongly on the magnetostriction. With the decrease in the saturation magnetostriction of the magnetostrictive phase, the magnetically induced polarization decreases monotonously. The comparison of figure 3 with figure 2(b) indicates that the magnetostrictive phase with \( \lambda_{001} = -50 \) ppm in the 1-3-type nanostructured multiferroic films could produce an almost equally magnetically induced polarization to that caused by the magnetostrictive phase with \( \lambda_{001} = -350 \) ppm in bulk systems.

The entire discussion above is based on an assumption of \( f = 0.35 \) [10]. For 1-3-type composite films, the volume fraction of the magnetostrictive phase will exert a significant influence on the magnetically induced polarization as shown in figure 4(a). On the contrary, the magnetically
induced polarization in 2-2-type composite films is insensitive to the constituent content, which proves again that the elastic coupling in 2-2-type composite films is very weak. For further illustration, figure 4(b) shows the variation of the magnetically induced polarization with $f$ as a function of the saturation magnetostriction, from which the coupled influence from both $f$ and the magnetostrictive behaviour on the magnetically induced polarization is quantitatively presented for 1-3-type composite films.

As mentioned above, the magnetically induced polarization is also dependent on the temperature, $T$. Although the spontaneous polarization of the BaTiO$_3$ phase increases with decreasing $T$, the magnetically induced polarization decreases at a lower temperature, as shown in figure 5(a). This contrary variation trend may be attributed to the larger spontaneous polarization at lower $T$, which makes further increases in polarization more difficult and so the magnetically induced polarization will decrease. However, the less the saturation magnetostriction, the less is the magnetically induced polarization sensitive to the temperature (figure 5(b)). In this sense, a lower $f$ or a higher volume fraction of the BaTiO$_3$ should produce a magnetically induced polarization less sensitive to the test temperature. It is particularly interesting to note that at room temperature the calculated spontaneous polarization for the 1-3-type nanostructured BaTiO$_3$/CoFe$_2$O$_4$ composite film with $f = 0.35$ is about 17.5 $\mu$C/cm$^2$ (figure 5(a)), close to that measured by Zheng et al. [10] of ~16.0 $\mu$C/cm$^2$.

4. Conclusions

The magnetically induced polarization in the nanostructured BaTiO$_3$/CoFe$_2$O$_4$ multiferroic films has been calculated using the LGD thermodynamic theory. The calculation results show that the 1-3-type nanostructured BaTiO$_3$/CoFe$_2$O$_4$ composite films exhibit a large magnetically induced polarization, but the 2-2-type films exhibit a much weaker magnetoelastic effect because of large in-plane constraint, which is in agreement with the experimental observations. The dependences of magnetically induced polarization on the composition and the temperature have also been revealed explicitly.

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