

## Magnetic-Field-Induced Electric Polarization in Multiferroic Nanostructures

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Magnetic-field-induced electric polarization in nanostructured multiferroic composite films was studied by using the Green's function approach. The calculations showed that large magnetic-field-induced polarization could be produced in multiferroic nanostructures due to enhanced elastic coupling interaction. Especially, the 1-3 type films with ferromagnetic nanopillars embedded in a ferroelectric matrix exhibited large magnetic-field-induced polarization responses, while the 2-2 type films with ferroelectric and ferromagnetic nanolaminates showed much weaker magnetoelectric coupling and lower magnetic induced polarization due to large in-plane constraint effect, which was in agreement with the recent observations.

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Multiferroic materials have drawn increasing interest due to their multifunctionality [1–3], which provides significant potentials for applications as the next-generation multifunctional devices. In these multiferroic materials, the coupling interaction between multiferroic orders could produce some new effects, such as magnetoelectric [1–3] or magnetodielectric effect [4]. The magnetoelectric response is the appearance of an electric polarization upon applying a magnetic field and/or the appearance of magnetization upon applying an electric field. This magnetic-field-induced electric polarization (MIEP) has been observed as an intrinsic effect at low temperature and high magnetic field in some natural material systems (e.g., in  $RMnO_3$  with  $R = Tb, Dy$  [5]). Alternatively and with greater design flexibility, multiferroic composites made by a combination of ferromagnetic and ferroelectric substances, such as combinations of piezoelectric ceramics [e.g.,  $BaTiO_3$  and lead-zirconate-titanate (PZT)] and ferrites or rare-earth-iron alloys (e.g., Terfenol-D), have been recently found to exhibit large magnetoelectric response at room temperature and low magnetic field [6–8]. The magnetoelectric behavior in these multiferroic composites is dependent on their microstructure and coupling interaction across ferromagnetic-ferroelectric interface [9].

Most recently, nanostructured  $BaTiO_3/CoFe_2O_4$  multiferroic composites have been deposited in a film-on-substrate geometry and magnetoelectric coupling has been observed for the first time in multiferroic nanostructures [10]. The coupling interaction between  $BaTiO_3$  and  $CoFe_2O_4$  in the multiferroic nanostructures has been found to be due to elastic interaction as was the case in bulk composites. However, the mechanical constraint arising from the film-on-substrate structures and the good bonding between the ferromagnetic and ferroelectric phases in the nanostructured films could significantly affect the coupling

interactions, thereby the magnetoelectric effect and/or MIEP. Currently, a theoretical description on such multiferroic nanostructured films is lacking. In this Letter, we calculate the magnetoelectric effect in the nanostructured ferroelectric-ferromagnetic composite films (e.g.,  $BaTiO_3/CoFe_2O_4$  films [10]) based on the Green's function approach which had been successfully applied to bulk multiferroic composites [2,7]. The present work provides the first phenomenological understanding of the MIEP in multiferroic nanostructures.

As the coupling interaction between ferroelectric and ferromagnetic phases in the multiferroic nanostructures is still an elastic interaction [10], the constitutive equations for the coupling magnetic-mechanical-electric interactions in the nanostructured films can be expressed by direct notation for tensors as

$$\begin{aligned}\sigma &= \mathbf{c}\boldsymbol{\varepsilon} - \mathbf{e}^T \mathbf{E} - \mathbf{c}\boldsymbol{\varepsilon}^{ms} - \sigma_s, \\ \mathbf{D} &= \mathbf{e}\boldsymbol{\varepsilon} + \kappa \mathbf{E} + \alpha \mathbf{H} + \mathbf{P}_s, \\ \mathbf{B} &= \mu(\boldsymbol{\varepsilon}, \mathbf{E}, \mathbf{H})\mathbf{H} + \mathbf{M}_s,\end{aligned}\quad (1)$$

where  $\sigma$ ,  $\boldsymbol{\varepsilon}$ ,  $\mathbf{D}$ ,  $\mathbf{E}$ ,  $\mathbf{B}$ , and  $\mathbf{H}$  are the stress, strain, electric displacement, electric field, magnetic induction, and magnetic field, respectively;  $\mathbf{c}$  and  $\kappa$  are, respectively, the stiffness at constant fields and the dielectric constant at constant strain; the permeability  $\mu$  strongly depends on  $\boldsymbol{\varepsilon}$  and electric and magnetic fields;  $\mathbf{e}$  ( $\mathbf{e}^T$  being the transpose of  $\mathbf{e}$ ) is the piezoelectric coefficient; and  $\boldsymbol{\varepsilon}^{ms}$  is the magnetostrictively induced strain related with the magnetic-field dependent magnetostriction constants (e.g.,  $\lambda_{001}$  and  $\lambda_{111}$  [11]) of the ferromagnetic phase;  $\alpha$  is the magnetoelectric coefficient. These are the same as the case for bulk multiferroic composites [2,7]. However, in comparison to the bulk composites, there exist remarkable residual stress

$\sigma_s$  (or residual strain  $\varepsilon_s$ ), spontaneous polarization  $\mathbf{P}_s$  and magnetization  $\mathbf{M}_s$  in the multiferroic films.

The effective properties (denoted by the starred quantities below) of the multiferroic films can still be defined as usual [7] in terms of the averaged fields (denoted by  $\langle \rangle$ ), e.g.,  $\langle \mathbf{D} \rangle = \mathbf{e}^* \langle \boldsymbol{\varepsilon} \rangle + \kappa^* \langle \mathbf{E} \rangle + \alpha^* \langle \mathbf{H} \rangle + \bar{\mathbf{P}}_s$ . We considered the MIEP of such nanostructured films. Under only applied magnetic field, the effective polarization in the mechanically clamped films is

$$\bar{\mathbf{P}} = \alpha^* \langle \mathbf{H} \rangle + \bar{\mathbf{P}}_s. \quad (2)$$

In a state of static equilibrium,

$$\begin{aligned} \partial \sigma_{ij}(\mathbf{x}) / \partial x_j &= 0, & \partial D_i(\mathbf{x}) / \partial x_i &= 0, \\ \partial B_i(\mathbf{x}) / \partial x_i &= 0. \end{aligned} \quad (3)$$

By solving the equilibrium equations (3) under the homogeneous magnetic-mechanical-electric ( $\mathbf{H}^0$ - $\boldsymbol{\varepsilon}^0$ - $\mathbf{E}^0$ ) boundary conditions in terms of the Green's function approach [7], the local fields within the composite films can be obtained as

$$\begin{aligned} \boldsymbol{\varepsilon} &= \boldsymbol{\varepsilon}^0 + \mathbf{G}^u(\mathbf{c} - \mathbf{c}^0)\boldsymbol{\varepsilon} - \mathbf{G}^u \mathbf{e}^T \mathbf{E} - \mathbf{G}^u(\mathbf{c} \boldsymbol{\varepsilon}^{ms} + \boldsymbol{\sigma}_s), \\ \mathbf{E} &= \mathbf{E}^0 + \mathbf{G}^\phi \mathbf{e} \boldsymbol{\varepsilon} + \mathbf{G}^\phi(\boldsymbol{\kappa} - \boldsymbol{\kappa}^0)\mathbf{E} + \mathbf{G}^\phi(\alpha \mathbf{H} + \mathbf{P}_s), \\ \mathbf{H} &= \mathbf{H}^0 + \mathbf{G}^\psi(\boldsymbol{\mu} - \boldsymbol{\mu}^0)\mathbf{H} + \mathbf{G}^\psi \mathbf{M}_s, \end{aligned} \quad (4)$$

where  $\mathbf{c}^0$ ,  $\boldsymbol{\kappa}^0$ , and  $\boldsymbol{\mu}^0$  represent the constitutive constants of a homogeneous reference medium;  $\mathbf{G}^u$ ,  $\mathbf{G}^\phi$ , and  $\mathbf{G}^\psi$  are the modified displacement, electric and magnetic potential Green's functions for the homogeneous medium [2,7,12]. Substitution of Eq. (4) into (1) directly gives explicit solutions for the local  $\boldsymbol{\sigma}$ ,  $\mathbf{D}$ , and  $\mathbf{B}$ , also as a function of  $\boldsymbol{\varepsilon}^0$ ,  $\mathbf{E}^0$ , and  $\mathbf{H}^0$ . By averaging these solutions for local field quantities and eliminating  $\boldsymbol{\varepsilon}^0$ ,  $\mathbf{E}^0$ , and  $\mathbf{H}^0$  from them, we can get the effective polarization in the mechanically clamped films as

$$\begin{aligned} \bar{\mathbf{P}} &= \langle \mathbf{P}_s + (\boldsymbol{\kappa} - \boldsymbol{\kappa}^*) \mathbf{T}^{33} \mathbf{G}^\phi [\mathbf{P}_s - \mathbf{e} \mathbf{T}^{66} \mathbf{G}^u(\mathbf{c} \boldsymbol{\varepsilon}^{ms} + \boldsymbol{\sigma}_s)] \\ &+ (\mathbf{e}^* - \mathbf{e}) \mathbf{T}^{66} \mathbf{G}^u(\mathbf{c} \boldsymbol{\varepsilon}^{ms} + \boldsymbol{\sigma}_s + \mathbf{e}^T \mathbf{T}^{33} \mathbf{G}^\phi \mathbf{P}_s) \rangle, \end{aligned} \quad (5)$$

where  $\mathbf{T}^{66}$  and  $\mathbf{T}^{33}$  are two so-called  $t$ -matrix tensors as given before [7,12]. This equation is quite general and independent of the models assumed for the topology of the phases in the composite film.

For the (00 $l$ )-oriented multiferroic nanostructures [10], only the volume average is necessary in Eq. (5). We take the ferroelectric phase as the homogeneous reference medium as usual, since the ferroelectric phase with high volume fraction is a matrix phase [10]. Further due to the fact that  $\mathbf{e}(\text{and } \mathbf{e}^T) = 0$  and  $\mathbf{P}_s = 0$  for the ferromagnetic phase,  $\boldsymbol{\varepsilon}^{ms} = 0$  and  $\mathbf{M}_s = 0$  for the ferroelectric phase, and  $\alpha = 0$  for both phases, Eq. (5) can be rewritten as

$$\begin{aligned} \bar{\mathbf{P}} &= (1 - f) \{ \mathbf{P}_s + (\boldsymbol{\kappa}^p - \boldsymbol{\kappa}^*) \mathbf{G}^\phi (\mathbf{P}_s - \mathbf{e}^p \mathbf{G}^u \boldsymbol{\sigma}_s^p) \\ &+ (\mathbf{e}^* - \mathbf{e}^p) \mathbf{G}^u (\boldsymbol{\sigma}_s^p + \mathbf{e}^T \mathbf{G}^\phi \mathbf{P}_s) \} \\ &+ f \mathbf{e}^* [\mathbf{I} - \mathbf{G}^u(\mathbf{c}^m - \mathbf{c}^p)]^{-1} (\mathbf{c}^m \boldsymbol{\varepsilon}^{ms} + \boldsymbol{\sigma}_s^m), \end{aligned} \quad (6)$$

where  $f$  is the volume fraction of the ferromagnetic phase,  $\mathbf{I}$  is the unit tensor; and the quantities denoted using the superscripts  $p$  and  $m$  refer to those for the ferroelectric and ferromagnetic phases. Here  $\mathbf{e}^*$  and  $\boldsymbol{\kappa}^*$  were given as before [12].

For the 1-3 type (using the terminology introduced by Cross and co-workers [13]) nanostructured composite films with (00 $l$ ) ferromagnetic nanopillars embedded in a ferroelectric matrix [Fig. 1(a)] [10], the effective electric polarization  $\bar{P}_3$  along the symmetric direction is easily obtained from Eq. (6) as

$$\bar{P}_3 = (1 - f) P_{s3} + \frac{2f(1 - f)e_{31}^p}{\bar{k} + c_{11}^p - c_{12}^p} (\sigma_{11}^p - \sigma_{11}^m), \quad (7)$$

in the case that the height of pillars is much larger than their diameter (e.g., 20–30 nm in diameter and  $\sim 400$  nm in height for nanopillars [10]), where  $\bar{k} = f(c_{11}^p + c_{12}^p) + (1 - f)(c_{11}^m + c_{12}^m)$ ;  $\sigma_{11}^p$  and  $\sigma_{11}^m$  are in-plane total stresses including residual stresses and magnetostrictively induced stresses, respectively, in the ferroelectric and ferromagnetic phases, and are expressed as

$$\sigma_{11}^{p(m)} = (c_{11}^{p(m)} + c_{12}^{p(m)}) \varepsilon_{11}^{p(m)} + c_{13}^{p(m)} \varepsilon_{33}^{p(m)}, \quad (8)$$

where  $\varepsilon_{11}^{p(m)}$  and  $\varepsilon_{33}^{p(m)}$  are in-plane and out-of-plane total strains including residual strains ( $\varepsilon_{s11}$  and  $\varepsilon_{s33}$ ) and magnetostrictively induced strains ( $\varepsilon_{ij}^{ms}$ ) upon applying the magnetic field, respectively, in the ferroelectric and ferromagnetic phases, e.g.,  $\varepsilon_{11}^m = \varepsilon_{11}^{ms} + \varepsilon_{s11}^m$  and  $\varepsilon_{33}^m = \varepsilon_{33}^{ms} + \varepsilon_{s33}^m$ . At zero magnetic field,  $\varepsilon_{ij}^p$  and  $\varepsilon_{ij}^m$  are equal to their residual strains, i.e.,  $\varepsilon_{ij}^p(H = 0) = \varepsilon_{sij}^p$  and  $\varepsilon_{ij}^m(H = 0) = \varepsilon_{sij}^m$ .

For the 2-2 type [13] nanostructured composite films with (00 $l$ ) ferroelectric and ferromagnetic nanolaminates as shown in Fig. 1(b), the effective electric polarization  $\bar{P}_3$  can also be directly obtained from Eq. (6) as

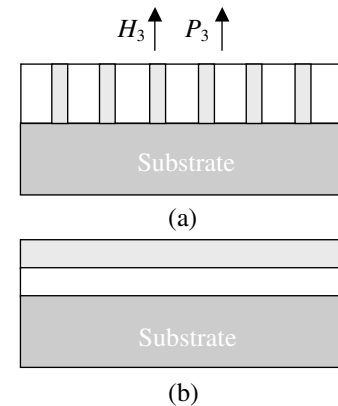


FIG. 1. Schematic illustration of the nanostructured multiferroic BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> films in (a) the 1-3 type where the CoFe<sub>2</sub>O<sub>4</sub> nanopillars (shaded) are embedded in the BaTiO<sub>3</sub> matrix, and in (b) the 2-2 type where the BaTiO<sub>3</sub> layer is first deposited on the substrate SrRuO<sub>3</sub> and then the CoFe<sub>2</sub>O<sub>4</sub> layer (shaded) on the piezoelectric layer.

$$\bar{P}_3 = (1-f) \frac{\kappa_{33}^m}{\bar{\kappa}_{33}} P_{s3} + \frac{f(1-f)e_{33}^p \kappa_{33}^m}{\bar{c}_{33} \bar{\kappa}_{33}} (\sigma_{33}^p - \sigma_{33}^m), \quad (9)$$

in the case that the thickness of a layer (e.g.,  $\sim 30$  nm [10]) is much less than the macroscopic size of the film plane, where  $\bar{c}_{33} = fc_{33}^p + (1-f)c_{33}^m$ ,  $\bar{\kappa}_{33} = f\kappa_{33}^p + (1-f)\kappa_{33}^m$ ;  $\sigma_{33}^p$  and  $\sigma_{33}^m$  are out-of-plane total stresses including residual stresses and magnetostrictively induced stresses, respectively, in the ferroelectric and ferromagnetic phases, and are expressed as

$$\sigma_{33}^{p(m)} = 2c_{13}^{p(m)} \varepsilon_{11}^{p(m)} + c_{33}^{p(m)} \varepsilon_{33}^{p(m)}. \quad (10)$$

At zero magnetic field,  $\varepsilon_{11}^{p(m)}(H=0) = \varepsilon_{s11}^{p(m)}$  and  $\varepsilon_{33}^{p(m)}(H=0) = \varepsilon_{s33}^{p(m)} = 0$ .

These explicit equations show that the effective electric polarization is sensitive to residual strains and spontaneous polarization in the films, materials constants of the two phases and the ways of their combination, and applied

magnetic field. For the 1-3 type films, after applying the magnetic field, the strains meet  $(1-f)\varepsilon_{11}^p + f\varepsilon_{11}^m = 0$  and  $\varepsilon_{33}^p = \varepsilon_{33}^m$  due to the constraint in the 1-3 film-on-substrate structures. However, for the 2-2 type films, the magnetostrictively induced in-plane strains are zero, i.e.,  $\varepsilon_{11}^p = \varepsilon_{11}^m = 0$ , due to gigantic constraint effect, and the out-of-plane strains also meet  $(1-f)\varepsilon_{33}^p + f\varepsilon_{33}^m = 0$ .

For quantitative comparison purposes, the effective electric polarization of the 1-3 and 2-2 type nanostructured multiferroic BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> films [(00*l*)-oriented films on SrTiO<sub>3</sub> substrate] [10] were calculated [14]. The magnetostrictive behavior of CoFe<sub>2</sub>O<sub>4</sub> is taken as shown in the inset of Fig. 2(b) [10,11]. For such (00*l*)-oriented films,  $\varepsilon_{33}^{ms} = \lambda_{001}$ . Figure 2(a) shows the MIEP, i.e.,  $\Delta\bar{P}_3 = \bar{P}_3 - \bar{P}_3(H=0)$ , calculated for the two multiferroic films with  $f = 0.35$  at room temperature.  $\Delta\bar{P}_3$  of the films nonlinearly increases with the magnetic field due to the nonlinear dependence of the magnetostriction of CoFe<sub>2</sub>O<sub>4</sub> on the applied magnetic field, and begins to approach its saturation at high magnetic fields where the magnetostriction gets saturated. Of particularly interesting to note is that a large MIEP is obtained in the 1-3 films at room temperature. When the applied magnetic field increases from zero up to 240 kA/m ( $\approx 0.3$  T), the MIEP of the 1-3 multiferroic BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> film is about 400  $\mu\text{C}/\text{m}^2$ , comparable with that in monophasic RMnO<sub>3</sub> observed at low temperature and high magnetic field [5]. In comparison, the MIEP in the 2-2 BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> film is quite low and much less than that in the 1-3 type. The main reason is attributed to the tremendous clamping effect in the 2-2 type film, where the in-plane gigantic constraint effect greatly inhibits the magnetostriction. In actual experiment [10], the 2-2 BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> film was indeed found to exhibit much weaker magnetoelectric coupling than the 1-3 type. For comparison, the 1-3 and 2-2 bulk composites [15] of BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> were calculated as well, as shown in Fig. 2(b), where the residual stress  $\sigma_s$  and the spontaneous polarization  $\mathbf{P}_s$  were neglected. As seen, the 1-3 bulk composites exhibit lower MIEP than the 1-3 nanostructured counterparts, and the 2-2 bulk composites also exhibit lower MIEP than the 1-3 type.

As shown in Fig. 2, the MIEP of the nanostructured composite films is closely related to the magnetostrictive behavior of the ferromagnetic phase. For further illustration, we take a few different values for the saturation magnetostriction  $\lambda_{001}$ . As seen from Fig. 2(c), the MIEP strongly depends on the magnetostriction. In the multiferroic composite films, the effective spontaneous polarization decreases with the increase in the volume fraction  $f$  of the ferromagnetic phase [Fig. 3(a)] as expected. The effective polarization degrades gradually with increasing  $f$  for the 1-3 film but sharply drops around  $f = 0.1$  for the 2-2 film. However, on the other hand, the MIEP increases from zero to the maxima with increasing  $f$  and then drops to zero at  $f = 1$ , as shown in Fig. 3(b). Especially, the variation in  $\Delta\bar{P}_3$  with  $f$  is remarkable for the 1-3 nano-

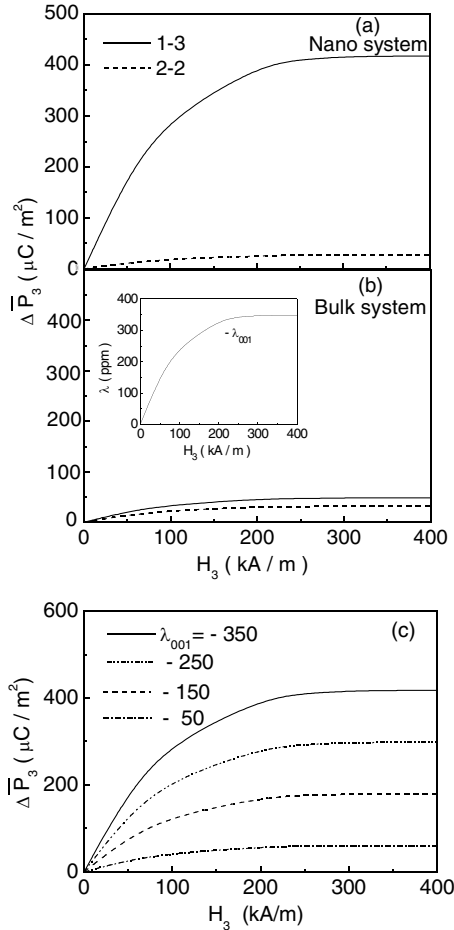


FIG. 2. Dependence of the magnetic-field-induced polarization  $\Delta\bar{P}_3$  on the magnetic field for (a) the nanostructured films and (b) the bulk composites of BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> with  $f = 0.35$  at room temperature. The inset in (b) is the magnetostrictive behavior taken for CoFe<sub>2</sub>O<sub>4</sub>. (c) Effect of the magnetostriction of the ferromagnetic phase on  $\Delta\bar{P}_3$  for this 1-3 type films.

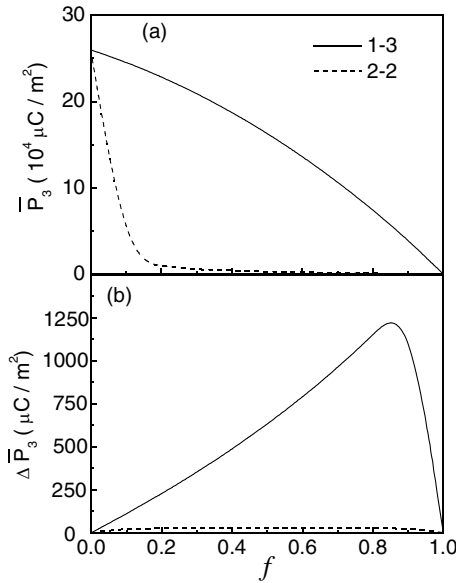


FIG. 3. The variation of (a) polarization  $\bar{P}_3$  and (b)  $\Delta\bar{P}_3$  with the volume fraction  $f$  of magnetostrictive phase at  $H_3 = 250$  kA/m for both the 1-3 and 2-2 type nanostructured films.

structured  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  films. Again, much smaller  $\Delta\bar{P}_3$  in the 2-2 nanostructured  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  films indicates a much weaker magnetoelectric coupling. As seen from Eqs. (7) and (9), the magnetically induced polarization in the 1-3 film is associated with the in-plane stresses while that in the 2-2 film is associated with the out-of-plane stresses. Thus much larger in-plane stresses and their variation with the applied magnetic field than the out-of-plane stresses in the film-on-substrate structures lead to much larger the magnetically induced polarization in the 1-3 film than in the 2-2 film. Moreover, the totally different constraint effect in these two nanostructures as discussed above also contributes to such a large difference between their MIEP results.

In summary, the explicit formula for the magnetic-field induced polarization in the nanostructured multiferroic films have been given based on the Green's function technique. The calculations showed that the 1-3 nanostructured films exhibit a large MIEP, but the 2-2 films exhibit much weaker magnetoelectric effect due to large in-plane constraint, which is in agreement with the observations. Large MIEP could be produced in multiferroic nanostructures due to enhanced elastic coupling interaction.

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- [1] N. A. Hill, *Annu. Rev. Mater. Res.* **32**, 1 (2002).
- [2] C. W. Nan, *Phys. Rev. B* **50**, 6082 (1994); C. W. Nan, Y. H. Lin, and J. H. Huang, *Ferroelectrics* **280**, 153 (2002).
- [3] J. Wang *et al.*, *Science* **299**, 1719 (2003).
- [4] G. Lawes, A. P. Ramirez, C. M. Varma, and M. A. Subramanian, *Phys. Rev. Lett.* **91**, 257208 (2003).
- [5] T. Kimura *et al.*, *Nature (London)* **426**, 55 (2003); T. Goto *et al.*, *Phys. Rev. Lett.* **92**, 257201 (2004); N. Hur *et al.*, *Nature (London)* **429**, 392 (2004).
- [6] J. van Suchtelen, *Philips Res. Rep.* **27**, 28 (1972); A. M. J. G. van Run *et al.*, *J. Mater. Sci.* **9**, 1710 (1974); G. Harshe *et al.*, *Int. J. Appl. Electromagn. Mater.* **4**, 145 (1993); M. I. Bichurin *et al.*, *Ferroelectrics* **204**, 289 (1997); K. K. Patankar *et al.*, *Mater. Chem. Phys.* **65**, 97 (2000); G. Srinivasan *et al.*, *Phys. Rev. B* **65**, 134402 (2002).
- [7] C. W. Nan, M. Li, X. Q. Feng, and S. Yu, *Appl. Phys. Lett.* **78**, 2527 (2001); C. W. Nan, M. Li, and J. H. Huang, *Phys. Rev. B* **63**, 144415 (2001).
- [8] J. Ruy *et al.*, *J. Am. Ceram. Soc.* **84**, 2905 (2001); K. Mori and M. Wuttig, *Appl. Phys. Lett.* **81**, 100 (2002); S. X. Dong, J. F. Li, and D. Viehland, *Appl. Phys. Lett.* **83**, 2265 (2003); S. X. Dong, J. R. Cheng, J. F. Li, and D. Viehland, *Appl. Phys. Lett.* **83**, 4812 (2003).
- [9] C. W. Nan, G. Liu, and Y. H. Lin, *Appl. Phys. Lett.* **83**, 4366 (2003); G. Liu, C. W. Nan, N. Cai, and Y. H. Lin, *J. Appl. Phys.* **95**, 2660 (2004).
- [10] H. Zheng *et al.*, *Science* **303**, 661 (2004).
- [11] V. J. Folen, in *Magnetic and Other Properties of Oxides and Related Compounds*, edited by K. H. Hellwege and A. M. Hellwege, Landolt-Bornstein Group III, Vol. 4, Pt. b (Springer, Berlin, 1970), p. 366.
- [12] C. W. Nan and F. Jin, *Phys. Rev. B* **48**, 8578 (1993); C. W. Nan, *J. Appl. Phys.* **76**, 1155 (1994).
- [13] R. E. Newnham, D. P. Skinner, and L. E. Cross, *Mater. Res. Bull.* **13**, 525 (1978).
- [14] The properties of  $\text{BaTiO}_3$  and  $\text{CoFe}_2\text{O}_4$  used in the numerical calculations were given as  $(c_{11}^p, c_{12}^p, c_{13}^p, c_{33}^p) = (166.2, 76.5, 77.4, 161.4)$  GPa,  $\kappa_{33}^p/\kappa_o = 1350$ ,  $(e_{31}^p, e_{33}^p) = (-4.22, 18.6)$  C/m<sup>2</sup>, and  $P_{s3} = 26$   $\mu\text{C}/\text{cm}^2$  for  $\text{BaTiO}_3$ , and  $(c_{11}^m, c_{12}^m, c_{13}^m, c_{33}^m) = (286.0, 173.0, 170.5, 269.5)$  GPa and  $\kappa_{33}^m/\kappa_o = 10$  for  $\text{CoFe}_2\text{O}_4$ . From Ref. [10], the out-of-plane residual strains in the 1-3 nanostructured film were given as  $\varepsilon_{s33}^p = -\varepsilon_{s33}^m = 0.8\%$ , and the in-plane residual strains were determined as  $\varepsilon_{s33}^p = -1\%$  and  $\varepsilon_{s33}^m = -1.89\%$  from the lattice constant mismatches between  $\text{BaTiO}_3$  and the substrate and between  $\text{CoFe}_2\text{O}_4$  and the substrate. In the 2-2 type film, however, there exists only the in-plane residual strains, and  $\varepsilon_{s11}^p = -1\%$  and  $\varepsilon_{s11}^m = -1.6\%$  estimated from the lattice constant mismatches.
- [15] The 1-3 and 2-2 type bulk composites of  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  are normal  $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$  ceramic composites, i.e.,  $\text{CoFe}_2\text{O}_4$  ceramic rods embedded in  $\text{BaTiO}_3$  ceramic matrix for the 1-3 type, and laminated  $\text{BaTiO}_3$  and  $\text{CoFe}_2\text{O}_4$  ceramic layers for the 2-2 composite [2].