

Dependence of giant magnetoelectric effect on interfacial bonding for multiferroic laminated composites of rare-earth-iron alloys and lead–zirconate–titanate

Gang Liu, Ce-Wen Nan, Ning Cai, and Yuanhua Lin

Citation: *Journal of Applied Physics* **95**, 2660 (2004); doi: 10.1063/1.1645648

View online: <http://dx.doi.org/10.1063/1.1645648>

View Table of Contents: <http://aip.scitation.org/toc/jap/95/5>

Published by the *American Institute of Physics*

Articles you may be interested in

[Multiferroic magnetoelectric composites: Historical perspective, status, and future directions](#)

Journal of Applied Physics **103**, 031101 (2008); 10.1063/1.2836410

[Large high-frequency magnetoelectric response in laminated composites of piezoelectric ceramics, rare-earth iron alloys and polymer](#)

Applied Physics Letters **84**, 3516 (2004); 10.1063/1.1739277

[Influence of interfacial bonding on giant magnetoelectric response of multiferroic laminated composites of \$\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2\$ and \$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3\$](#)

Applied Physics Letters **83**, 4366 (2003); 10.1063/1.1630157

[A three-phase magnetoelectric composite of piezoelectric ceramics, rare-earth iron alloys, and polymer](#)

Applied Physics Letters **81**, 3831 (2002); 10.1063/1.1521247

[Coupled magnetic–electric properties and critical behavior in multiferroic particulate composites](#)

Journal of Applied Physics **94**, 5930 (2003); 10.1063/1.1614866

[Giant magnetoelectric effect of a hybrid of magnetostrictive and piezoelectric composites](#)

Journal of Applied Physics **93**, 9916 (2003); 10.1063/1.1577404

AIP | Journal of
Applied Physics

Save your money for your research.

It's now **FREE** to publish with us -

no page, color or publication charges apply.

Publish your research in the
Journal of Applied Physics
to claim your place in applied
physics history.

Dependence of giant magnetoelectric effect on interfacial bonding for multiferroic laminated composites of rare-earth-iron alloys and lead–zirconate–titanate

Gang Liu, Ce-Wen Nan,^{a)} Ning Cai, and Yuanhua Lin

State Key Laboratory of New Ceramics and Fine Processing, and Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

(Received 17 September 2003; accepted 12 December 2003)

The giant magnetoelectric effect of laminated composites of rare-earth-iron alloys (Terfenol-D) and lead–zirconate–titanate (PZT) is calculated by using the finite element method. Our simulations show that the magnetoelectric response of the laminated Terfenol-D/PZT composites is strongly dependent on interfacial bonding between Terfenol-D and PZT layers. The giant magnetoelectric effect and its dependence on the interfacial bonding predicted by the finite element method for the composites are in good agreement with predictions by a recent analytical method and recent experimental observations available. © 2004 American Institute of Physics.

[DOI: 10.1063/1.1645648]

I. INTRODUCTION

The magnetoelectric (ME) effect is characterized by the appearance of an electric polarization when applying a magnetic field on a material and/or by the appearance of a magnetization when applying an electric field. Although the ME effect was prophetically predicted by Curie early in 1894 on the basis of crystal symmetry consideration,¹ no further work was done until 1958 when Landau and Lifshitz proved the feasibility of the ME effect in certain crystals. Subsequently, the symmetry argument was applied by Dzyaloshinskii² to antiferromagnetic Cr_2O_3 and it was suggested that the ME effect could appear in Cr_2O_3 . This was followed by experimental confirmation.³ Since then, ME effects have been widely investigated in over ten different crystal families⁴ (e.g., yttrium iron garnets, boracites, rare-earth ferrites, and phosphates) due to their potential applications including magnetic-electric sensors in radioelectronics, optoelectronics, and microwave electronics and transducers in instrumentation. However, these monophasic ME materials do not exhibit a strong ME effect, and most of them have rather low Néel or Curie temperature far below room temperature, which makes such materials difficult to find any practical applications in technology.

Alternatively, some multiferroic composites made by combining ferroelectric and ferromagnetic substances together, such as $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ ^{5,6} and ferrite/lead–zirconate–titanate (PZT)^{7,8} have been found to exhibit an extrinsic ME effect, resulting from a coupling interaction between ferromagnetic and ferroelectric substances. Particularly, Nan and co-workers⁹ have recently predicted that the composites containing a giant magnetostrictive rare-earth-iron alloy [e.g., $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$ (Terfenol-D)],¹⁰ i.e., both particulate composites with Terfenol-D embedded in a piezoelectric matrix such as poly(vinylidene fluoride-

trifluorethylene) copolymer [P(VDF–TrFE)] and laminated composites of Terfenol-D/P(VDF–TrFE) or Terfenol-D/PZT, can exhibit a giant ME (GME) effect which is markedly larger than that in the best known ME materials (such as Cr_2O_3 and ferrite/piezoelectric ceramic composites). Sequentially, the laminated Terfenol-D/PZT composite made by stacking and bonding together the PZT and Terfenol-D disks with silver epoxy¹¹ and laminated Terfenol-D/PVDF composite made by gluing the polarized PVDF film on Terfenol-D disks with conductive epoxy¹² have been most recently found to exhibit such a GME sensitivity as predicted, which potentially makes such multiferroic composites particularly attractive for technological applications in sensor, actuators, and transducers. Obviously, the GME response of such laminated composites is dependent on interfacial bonding between the Terfenol-D and piezoelectric (e.g., PZT) layers because the conductive interfacial binder dominates the strain/stress transfer from the magnetostrictively deformed layer (Terfenol-D) to the piezoelectric layer (PZT). Thus, optimization of the conductive interfacial binder layers plays an important role in achieving an excellent ME response for these laminated composites.

For comprehensive understanding on such laminated composites, we take the laminated Terfenol-D/PZT composite as an example, and employ a finite element method (FEM) to calculate the GME effect in the laminated composites and to present the quantitative dependence of the GME response on the interfacial bonding. Our simulation results are also applicable to other systems such as the laminated composites of PVDF and Terfenol-D.

II. THEORETICAL FRAMEWORK

Consider a laminated Terfenol-D/PZT composite, as shown in Fig. 1. Its response involving the magneto-electro-elastic coupling effect can be described by the following general equations:⁹

^{a)} Author to whom correspondence should be addressed; electronic mail: cwnan@mail.tsinghua.edu.cn

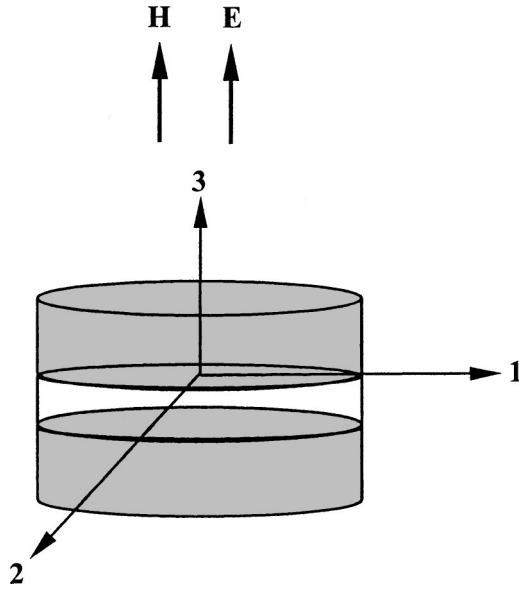


FIG. 1. Triplanar sketch and definition of the coordination axes for a disk-shaped composite of Terfenol-D and PZT.

$$\begin{aligned}\sigma_{kl} &= c_{kl ij}^{H,E} \epsilon_{ij} - e_{ikl}^H E_i - c_{kl ij}^{H,E} \epsilon_{ij}^s, \\ D_k &= e_{kij}^H \epsilon_{ij} + \kappa_{ki}^H E_i + \alpha_{ki} H_i, \\ B_j &= \mu_{ji}(\epsilon, E, H) H_i,\end{aligned}\quad (1)$$

where σ is the stress, ϵ is the strain, D is the electric displacement, E is the electric field tensor, B is the magnetic induction, and H is the magnetic field; c , κ , and μ , are, respectively, the stiffness at constant field, dielectric constant tensor at constant strain, and permeability constant tensor at constant strain; e is the piezoelectric coefficient tensor, α is the ME coefficient, and ϵ_{ij}^s is the magnetostrictive strain. The strain ϵ , electric field, and magnetic field are, respectively, defined by the displacement u , electric potential φ , and magnetic potential ϑ , i.e.:

$$\epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}), \quad E_i = -\varphi_{,i}, \quad H_i = -\vartheta_{,i}. \quad (2)$$

The magnetic flux density in the composites is dominantly induced by the externally applied magnetic field, and μ_{ji} in Eq. (1) is considered as being only dependent on H . Thus, the finite element formulation can be described as

$$\begin{bmatrix} [K_{uu}] & [K_{u\varphi}] \\ [K_{\varphi u}] & [K_{\varphi\varphi}] \end{bmatrix} \begin{Bmatrix} \{u\} \\ \{\varphi\} \end{Bmatrix} = \begin{Bmatrix} f - [K_{uu}]\{\epsilon^s\} \\ Q - [K_{\varphi\varphi}]\{\vartheta\} \end{Bmatrix} \quad (3)$$

where the submatrices K_{uu} , $K_{u\varphi}$, $K_{\varphi\varphi}$, and $K_{\varphi u}$ indicate the elastic, piezoelectric, permittivity, and magnetoelectric coefficient matrices, respectively. f and Q represent mechanical excitation vector and electric charge vector related to mechanical loads and electric displacement, respectively, i.e., $f = \int_V N_u^T P_v dV + \int_S N_u^T P_s dS$ and $Q = -\int_S N_\varphi^T D dS$, where P_v and P_s are body force and surface force, respectively, N_u and N_φ are corresponding nodal shape functions. The superscript of T means a transpose of a matrix. The left-hand side of Eq. (3) contains the unknown displacement and electric potential, and the right-hand side contains the excitation of the structure in terms of mechanical load, applied magnetic

TABLE I. Properties of Terfenol-D and PZT-5A used in the present FEM simulation.

Properties	Terfenol-D	PZT-5A
c_{11} (GPa)	82	121
c_{12} (GPa)	40	75.4
c_{13} (GPa)	40	75.2
c_{33} (GPa)	82	111
c_{44} (GPa)	38	21.1
ϵ_{11}/ϵ_0	6	916
ϵ_{33}/ϵ_0	6	830
μ_{33}/μ_0	5	1
e_{31} (C/m ²)	0	-5.4
e_{33} (C/m ²)	0	15.8
e_{15} (C/m ²)	0	12.3

load, and electric charge. Here, boundary conditions of open circuit and ends clamped in the polarization direction [e.g., the 3-direction in Fig. 1, i.e., $D_3=0$ and $\epsilon_{33}=0$, are considered for complying with experimental conditions].

III. NUMERICAL RESULTS AND DISCUSSION

On applying an external magnetic field H_3 alone along the symmetric X_3 axis of the composite specimen (Fig. 1), a ME output voltage E_3 is produced across the specimen along the X_3 direction. Thus, the ME sensitivity along the X_3 direction, α_{E33} , is

$$\alpha_{E33} = -E_3/H_3 = \alpha_{33}^*/\kappa_{33}^*, \quad (4)$$

where α_{33}^* and κ_{33}^* are the effective ME coefficient and dielectric constant of the composites, respectively. The engineering magnetostriction of a Terfenol-D polycrystalline disk, ϵ^s , should be practically determined for a special sample and may be variable from each other. Here we employ a ϵ^s-H behavior as presented previously,⁹ and the influence of ϵ^s-H behavior on the ME response will be discussed subsequently. Now for quantitative purposes, the properties of Terfenol-D and PZT used for calculations are presented in Table I. The saturation magnetostriction of $\epsilon_1^s = \epsilon_2^s = -530$ ppm and $\epsilon_3^s = 1060$ ppm at a high bias of $H_3 = 2500$ Oe is assumed for the Terfenol-D disk. The relative permeability and dielectric constant of the interfacial binder layers are both chosen as 6. Our FEM simulations showed that the calculated ME coefficients are quite insensitive to the permeability and dielectric constant of the interfacial layers, mainly due to two issues. One is that the ME response of the composites is due to *mechanical* coupling between Terfenol-D and PZT and thus is dominated by the interfacial contact status. The other is quite small thickness of the interfacial layers. The interfacial binder layers are just used to bond PZT and Terfenol-D for transferring magnetostrictive strain in Terfenol-D to PZT, and the elastic properties of the interfacial layers are far more vital than the relative permeability and dielectric constant in affecting the ME response. Thus, both the relative permeability and the dielectric constant of interfacial layers are chosen as 6 here for simplicity but without loss of generality.

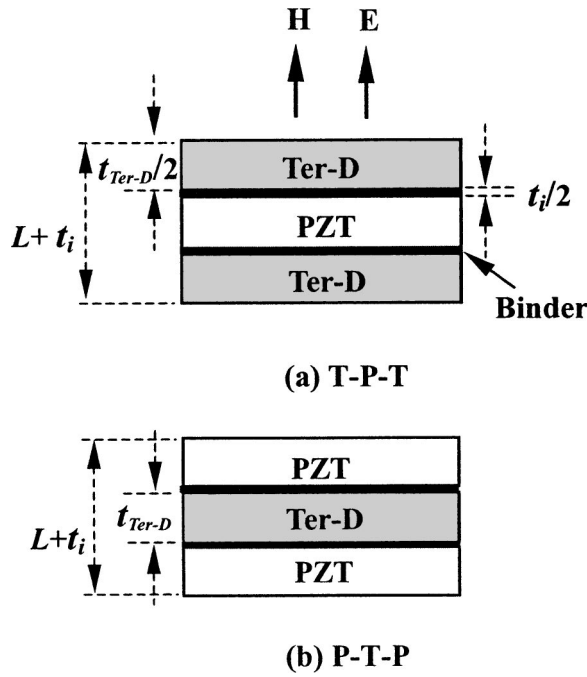


FIG. 2. Schematic illustration for (a) Terfenol-D/PZT/Terfenol-D (T-P-T) composite and (b) PZT/Terfenol-D/PZT (P-T-P) composite. All the Terfenol-D have a principal magnetostriction along the 3-direction and PZT is poled along the 3-direction.

A. The composites with different geometrical configurations

We first consider the influence of the interfacial binder layers on the ME response of the laminated composites with two different geometric configurations, i.e., disk-shaped composite of one PZT layer sandwiched between two Terfenol-D layers [denoted as T-P-T, Fig. 2(a)] and of one Terfenol-D layer sandwiched between two PZT layers [denoted as P-T-P, Fig. 2(b)]. The sizes of the samples are chosen as 12 mm in diameter and 3 mm in whole thickness as used in experiment.¹¹ By applying a magnetic field, the magnetostrictively induced strain in the Terfenol-D layers is passed to the PZT layers along the interfacial binder layer, thus resulting in an electric polarization. To estimate the effect of the interfacial bonding layer on the ME response of the composites, we focus on the relative thickness, t_i/L (see Fig. 2), and shear modulus, G_i , of the interfacial layer, since its thickness and shear modulus are most important for the strain/stress transfer from Terfenol-D to PZT.

As seen from Fig. 3, the ME response of the laminated composites is significantly dependent on both t_i/L and G_i . A thick layer (i.e., larger t_i/L) of interfacial binder with low G_i (i.e., softer binder) leads to a large decrease in the ME response of the composites. This is especially so at high $t_{\text{Ter-D}}/L$ (the relative thickness of Terfenol-D layers). This large decrease in the ME response is attributed to a loss in strain transfer at interface when the soft binder layers are introduced to bond the Terfenol-D and PZT layers.

Figure 3 also illustrates different ME response behaviors for these two different composites. The ME response of the T-P-T composite monotonically increases nearly up to extreme with increasing $t_{\text{Ter-D}}/L$, while the ME response of the

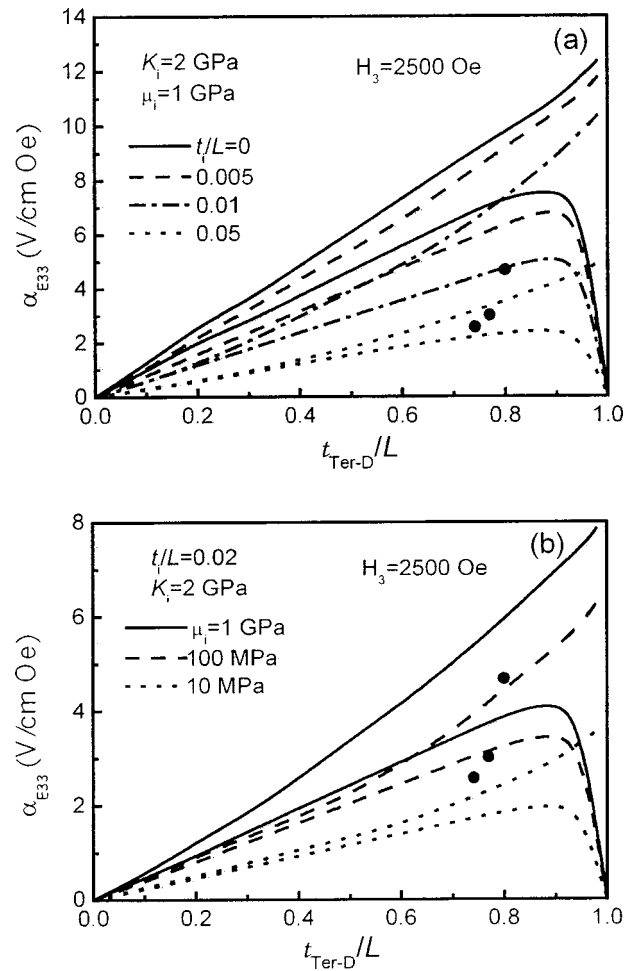


FIG. 3. Dependence of the ME sensitivity α_{E33} on (a) the relative thickness t_i/L , and (b) shear modulus G_i of the interfacial binder layers for the T-P-T and P-T-P laminated composites as a function of $t_{\text{Ter-D}}/L$ (see Fig. 2). Recent experimental data (solid dots) available for a T-P-T composite are also shown for comparison.

P-T-P composite is nonmonotonical with a peak at $t_{\text{Ter-D}}/L \approx 0.85$. Of interest is that a surprisingly large ME effect, i.e., a GME effect, is produced in these laminated composites with thick Terfenol-D layers but thin PZT layers. This trend is in an excellent agreement with that recent prediction by analytical Green's function technique,⁹ and such a GME effect has recently been experimentally observed in a disk-shaped T-P-T composite (e.g., a maximum $\alpha_{E33} \sim 5.90$ V/cm Oe at $t_{\text{Ter-D}}/L = 0.8$).¹¹ Comparison in Figs. 3(a) and 3(b) shows that the T-P-T composites possess a higher ME sensitivity than the P-T-P composites. In the T-P-T composites, the two outer Terfenol-D layers are also served as metal electrodes, and thus the effective dielectric constant κ_{33}^* of the T-P-T sample is equal to κ_{33}^{PZT} of PZT. For the P-T-P composites, the effective dielectric constant can be simply expressed as

$$\kappa_{33}^* = \kappa_{33}^{\text{PZT}} / (1 - t_{\text{Ter-D}}/L), \quad (5)$$

which is larger than κ_{33}^{PZT} . Thus, the T-P-T composites would exhibit a larger α_{E33} than the P-T-P composites with

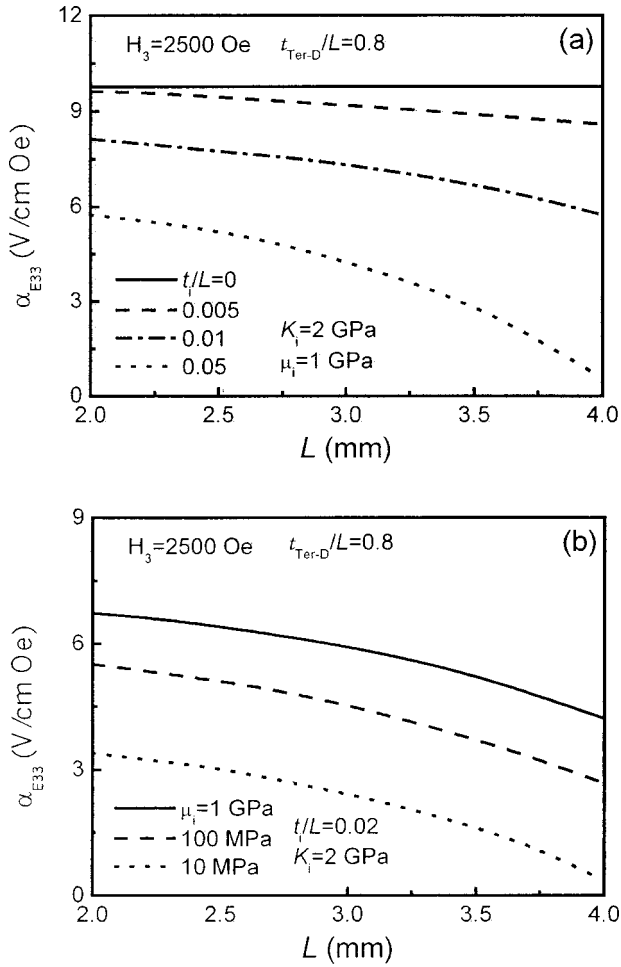


FIG. 4. Dependence of the ME sensitivity α_{E33} on the sample thickness of the T-P-T laminated composites with various (a) t_i/L and (b) G_i .

the same $t_{\text{Ter-D}}/L$. The FEM results shown in Fig. 3 are quite similar to those predicted recently by an analytical Green's function method.¹³

In the earlier simulations, the thickness of the laminated composite is fixed as 3 mm. In the case of the interfacial binder layers taken into account, the sample thickness has a remarked effect on the ME response of the composites, as shown in Fig. 4. The ME response of the composites decreases with increasing the sample thickness, and this size effect is more obvious for the case of a thick layer (i.e., large t_i/L) of softer interfacial binder (i.e., low G_i).

B. The composites with different magnetostrictive strains

In the earlier calculations, the applied magnetic field is kept constant as $H_3 = 2500$ Oe for simplicity. Now let us consider the dependence of the ME sensitivity on magnetostrictive strain or on the applied magnetic field. Two engineering magnetostriction behaviors,⁹ denoted as A and B in Fig. 5, are adopted for Terfenol-D polycrystals. Figure 6 shows the calculated dependence of α_{E33} on the magnetic field. When Terfenol-D follows the magnetostriction behavior A (see Fig. 5) where the magnetostriction gets saturation in the low field range, the ME sensitivity of the composites will change in a

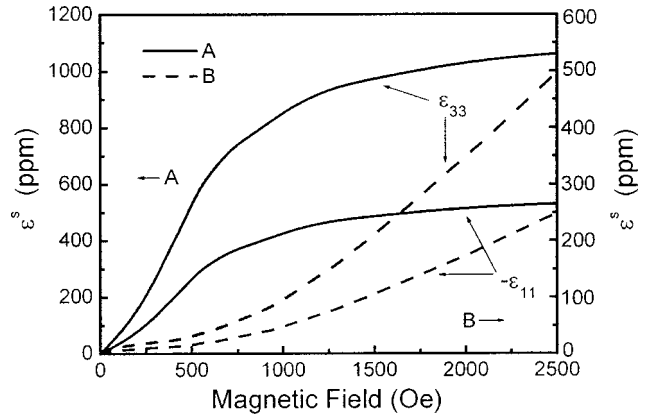


FIG. 5. Two kinds of magnetic-field-dependent magnetostrictions adopted for Terfenol-D polycrystals in the present simulation, denoted as A and B, respectively.

saddle shape with a maximum value in the low magnetic field range (Fig. 6). At high magnetic field, the magnetostriction becomes saturated, producing a nearly constant electric field, therefore α_{E33} decreases with increasing the magnetic field. When the Terfenol-D follows the magnetostriction behavior B (see Fig. 5) where the magnetostriction approaches saturation in high field range, the ME sensitivity of the composites monotonically increases (Fig. 6). Both trends have

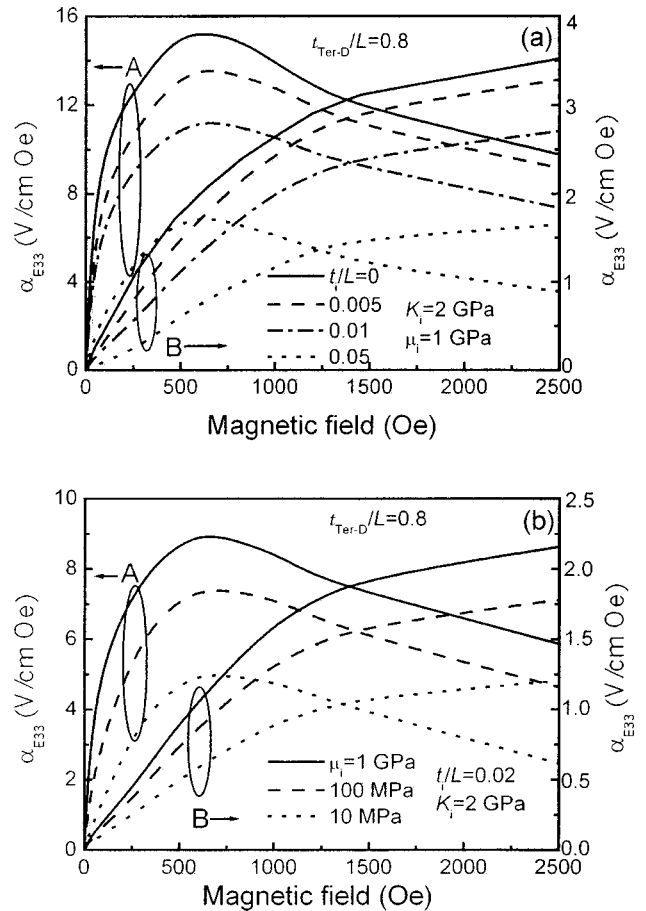


FIG. 6. Bias-dependent ME sensitivity for the T-P-T laminated composites with various (a) t_i/L and (b) G_i . The lines denoted by A and B are corresponding to the cases A and B shown in Fig. 5, respectively.

been observed in experiments and are consistent with those predicted by analytical Green's function techniques.⁹ The introduction of interfacial binder layers leads to a decrease in the ME sensitivity of the composites in the whole bias range, but has little effect on the bias dependence of the ME sensitivity. Thus, the magnetic field dependence of α_{E33} of the composites is dominated by the magnetic field dependence of magnetostriction of the Terfenol-D in the composites.⁹

IV. CONCLUSIONS

The GME response in the laminated composites of magnetostrictive Terfenol-D stacked and bonded with piezoelectric PZT by a conductive binder has been simulated by using a finite element method. The calculated GME effect of these sandwiched composites is reasonably agreeable with available experimental results reported recently and recent predictions by the analytical Green's function technique. The results reveal that the GME sensitivity of the laminated composites is strongly dependent on the thickness and shear modulus of the interfacial binder layers. Thinner and stronger interfacial binder layers are substantial preconditions for achieving an excellent GME effect. In addition, the relative thicknesses of the Terfenol-D and PZT layers are quantitatively found to exert marked influence on the ME response. The composites with thicker Terfenol-D layers but thinner PZT layers are favorable to produce a larger value of α_{E33} , and the T-P-T composites exhibit larger α_{E33} than the P-T-P composites. Such a GME sensitivity in the laminated composites with good interfacial bonding makes them important materials for magnetic-electric devices.

ACKNOWLEDGMENTS

This work was supported by the State Key Project of Fundamental Research of China (Grant Nos. 2002CB613303 and G2000067108) and from NSFC (Grant Nos. 50232030 and 50172026).

- ¹A. J. Freeman and H. Schmid, *Magnetoelectric Interaction Phenomena in Crystals* (Gordon and Breach, London, 1975).
- ²I. E. Dzyaloshinskii, Zh. Eksp. Teor. Fiz. **37**, 881 (1959). [Sov. Phys. JETP **10**, 628 (1960)].
- ³D. N. Astrov, Zh. Eksp. Teor. Fiz. **38**, 984 (1960); [Sov. Phys. JETP **11**, 708 (1961)]; V. J. Folen, G. T. Rado, and E. W. Stalder, Phys. Rev. Lett. **6**, 607 (1961).
- ⁴M. I. Bichurin, Proceedings of the 3rd International Conference on Magnetoelectric Interaction Phenomena in Crystals MEIPIC-3 (Novgorod, Russia, 1996) [Ferroelectrics **204**, 1 (1997)].
- ⁵G. Harshe, J. P. Dougherty, and R. E. Newnham, Int. J. Appl. Electromagn. Mater. **4**, 161 (1993).
- ⁶C. W. Nan, Phys. Rev. B **50**, 6082 (1994).
- ⁷M. I. Bichurin, I. A. Kornev, V. M. Petrov, and I. Lisnevskaya, Ferroelectrics **204**, 289 (1997).
- ⁸G. Srinivasan, E. T. Rasmussen, B. J. Levin, and R. Hayes, Phys. Rev. B **65**, 134402 (2002).
- ⁹C. W. Nan, M. Li, and J. H. Huang, Phys. Rev. B **63**, 144415 (2001); C. W. Nan, M. Li, X. Q. Feng, and S. W. Yu, Appl. Phys. Lett. **78**, 2527 (2001).
- ¹⁰G. Engdahl, *Handbook of Giant Magnetostrictive Materials* (Academic, New York, 2000).
- ¹¹J. Ryu, A. V. Carazo, K. Uchino, and H. E. Kim, Jpn. J. Appl. Phys., Part 1 **40**, 4948 (2001); J. Am. Ceram. Soc. **84**, 2905 (2001).
- ¹²K. Mori and M. Wattig, Appl. Phys. Lett. **81**, 100 (2002).
- ¹³C. W. Nan, G. Liu, and Y. Lin, Appl. Phys. Lett. **83**, 4366 (2003).