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Influence of interfacial bonding on giant magnetoelectric response of multiferroic laminated composites of $Tb_{1-x}Dy_xFe_2$ and $PbZr_xTi_{1-x}O_3$

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The influence of interfacial bonding on the magnetoelectric response in multiferroic laminated composites of $Tb_{1-x}Dy_xFe_2$ (Terfenol-D) and lead-zirconate-titanate (PZT) by using the recent Green's function technique was studied. Numerical results demonstrate that a giant magnetoelectric response is produced in the simple sandwiched composites of thick Terfenol-D layers and thin PZT layers. The interfacial epoxy binders used for bonding PZT and Terfenol-D together are very critical to the giant magnetoelectric response of the composites. A thicker interfacial epoxy film and, in particular, a sliding interfacial bonding by a very flexible epoxy would result in a significant drop in the magnetoelectric response. © 2003 American Institute of Physics.
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Multiferroic materials, made by combining ferroelectric and ferromagnetic substances, have drawn significant interest in recent years due to their multifunctionality in which the coupling interaction between ferroelectric and ferromagnetic substances could produce another effect.¹ These multiferroic materials provide opportunities for potential applications as transducers, actuators, and sensors. These kinds of such multiferroic composites are ferrite/piezoelectric ceramic composites, such as $CoFe_2O_4/BaTiO_3$ and ferrite/lead-zirconate-titanate (PZT) composites, made by a solid-state sintering procedure.¹ In addition to simultaneous ferroelectricity and ferromagnetism in these ceramic composites, they have been found to exhibit an extrinsic magnetoelectric (ME) effect characterized by the appearance of an electric polarization (ME_H output) upon applying a magnetic field. The ME_H response observed above room temperature is known as a product property resulting from the interaction between the ferrite and piezoelectric ceramic phases, since neither phase is magnetoelectric.² More importantly, the ME_H response of these multiferroic ceramic composites is larger than that observed in ferroic crystal families³ currently available (e.g., antiferromagnetic Cr_2O_3 ,⁴ yttrium iron garnets, boracites, rare-earth ferrites, and phosphates).³

Recently, by developing the Green's function technique,⁵⁻⁷ we have predicted that both particulate composites with $Tb_{1-x}Dy_xFe_2$ (Terfenol-D)⁸ embedded in a piezoelectric matrix [such as a polyvinylidene fluoride (PVDF)-based polymer or PZT] and the laminated composites of Terfenol-D/PVDF or Terfenol-D/PZT can exhibit a giant ME (GME) effect which is about 10^2 – 10^3 times larger than that in the ME materials (e.g., Cr_2O_3 and ferrite/piezoelectric ceramic composites).⁹ Subsequently, the laminated Terfenol-D/PZT composite, made by stacking and bonding the PZT and Terfenol-D disks with silver epoxy¹⁰ and a laminated Terfenol-D/PVDF composite made by gluing the polarized PVDF film on Terfenol-D disks with conductive epoxy,¹¹ have been most recently found to exhibit such a GME sen-

sitivity as predicted. This potentially makes such multiferroic composites particularly attractive for technological applications. Among the multiferroic composites found so far, Terfenol-D/PZT [and Terfenol-D/P(VDF-TrFE) (or PVDF)] possess an extremely high ME sensitivity. However, it is hard to prepare the Terfenol-D/PZT composite by a conventional sintering method. Thus, the direct bonding of PZT and Terfenol-D disks with conductive epoxy¹⁰ is one of the most effective approaches to achieve a GME response, which raises a very important issue as to how the GME response depends on the interfacial bonding between two layers by gluing together. In this letter, taking the laminated PZT/Terfenol-D composite as an example, we quantitatively treat the influence of the interfacial bonding on the GME response of the multiferroic composites by using the recent Green's function technique.⁹ The results are also applicable to other systems, such as laminated Terfenol-D/PVDF composites.

We consider two kinds of sandwiched composites of Terfenol-D and PZT, i.e., PZT/Terfenol-D/PZT and Terfenol-D/PZT/Terfenol-D and let the PZT be poled along the x_3 axis of the composite specimen, as shown in Fig. 1. The aspect ratio of the sample is 0.2 (e.g., 2 mm in thickness and 10 mm in diameter). Upon only applying an external magnetic field

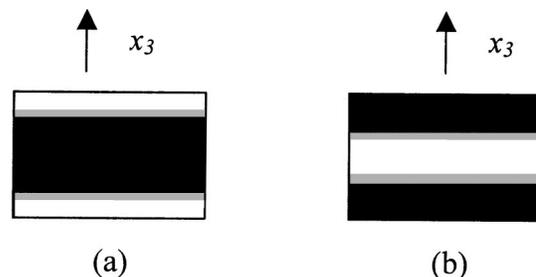


FIG. 1. Schematic illustration of (a) PZT/Terfenol-D/PZT and (b) Terfenol-D/PZT/Terfenol-D sandwiched composites. The white, black, and gray layers represent PZT, Terfenol-D, and interfacial binder layers, respectively. The polarization direction in the PZT is parallel to the x_3 axis of the composites, along which an external magnetic field (H_3) is applied.

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$\langle H_3 \rangle$ along the symmetric x_3 axis of the composite sample (Fig. 1), the ME_H output voltage \bar{E}_3 developed a cross the sample along the x_3 direction is

$$\bar{E}_3 = -\alpha_{33}^* \langle H_3 \rangle / \kappa_{33}^* = -\alpha_{E33} \langle H_3 \rangle, \quad (1)$$

where α_{E33} is the ME_H voltage coefficient or ME_H sensitivity which is a figure of merit used to assess the performance of a ME material for a magnetic device, and κ_{33}^* and α_{33}^* are, respectively, the effective dielectric constant and ME coefficient of the composite. Furthermore, the Green's function technique gives the ME coefficient of a composite in terms of the tensor representation as⁹

$$\alpha^* \langle \mathbf{H} \rangle = f \mathbf{e}^* \langle [\mathbf{I} - \mathbf{G}^u(\mathbf{c} - \mathbf{c}^o)]^{-1} \mathbf{G}^u \mathbf{c} \epsilon^{ms} \rangle_{\text{orient}}, \quad (2)$$

where f is the volume fraction of Terfenol-D, \mathbf{e}^* is the effective piezoelectric coefficient of the composite, \mathbf{c} and \mathbf{c}^o are respectively the stiffness of Terfenol-D and matrix, \mathbf{I} is the unit tensor, and \mathbf{G}^u is the modified displacement Green's functions, $\langle \rangle_{\text{orient}}$ denotes averaging over all possible orientations of Terfenol-D in the composite, and ϵ^{ms} is the magnetostrictively induced strain related to the magnetic field dependent magnetostriction constants, λ_{100} and λ_{111} ,⁸ of Terfenol-D. Equation (2) is a general formula for the extrinsic ME_H coefficient resulting from the coupling interaction between the *nonlinear magnetostrictive* (ϵ^{ms}) and *linear piezoelectric* (\mathbf{e}^*) effects.

For the sandwiched PZT/Terfenol-D/PZT composite with the interfacial binders, the matrix is the PZT, and Eq. (2) is rewritten as

$$\alpha^* \langle \mathbf{H} \rangle = \frac{t_{\text{Ter}} + t_i}{L} \mathbf{e}^* \langle [\mathbf{I} - \mathbf{G}^u(\bar{\mathbf{c}} - \mathbf{c}^p)]^{-1} \mathbf{G}^u \bar{\mathbf{c}} \epsilon^{ms} \rangle_{\text{orient}}, \quad (3)$$

where \mathbf{c}^p is the stiffness of the PZT, t_i , t_{Ter} , and L are, respectively, the thicknesses of the interfacial binder layers, Terfenol-D disk, and the whole sample. $\bar{\mathbf{c}}$ and $\bar{\epsilon}^{ms}$ are, respectively, the equivalent stiffness and magnetostrictively induced strain of the epoxy binder/Terfenol-D/epoxy binder composite system, and can be easily calculated.⁷ The matrix properties involved in the calculations⁹ of \mathbf{e}^* and \mathbf{G}^u are taken as those for the PZT.

For the sandwiched Terfenol-D/PZT/Terfenol-D composite with the interfacial binders, the matrix is the Terfenol-D, i.e., $\mathbf{c}^o = \mathbf{c}$. Two conductive Terfenol-D disks are electrically active and serve as electrodes. Thus, Eq. (2) can be simplified as

$$\alpha^* \langle \mathbf{H} \rangle = \frac{t_{\text{Ter}}}{L} \bar{\mathbf{e}} \langle \mathbf{G}^u \mathbf{c} \epsilon^{ms} \rangle_{\text{orient}}, \quad (4)$$

where $\bar{\mathbf{e}}$ is the equivalent piezoelectric coefficient of the epoxy binder/PZT/epoxy binder composite system and can also be easily obtained;⁵ but the matrix properties involved in the calculations of \mathbf{G}^u are now taken as those for Terfenol-D.

Figure 2 shows our numerical results^{12,9} (at room temperature) for these two sandwiched composites with perfect interfacial bonding between PZT and Terfenol-D disks with two different magnetic orientations, i.e., isotropic Terfenol-D polycrystal and optimally magnetic [111]-growth Terfenol-D crystal (i.e., [111] crystallographic direction of the Terfenol-D disks being parallel to the x_3 axis). For the sand-

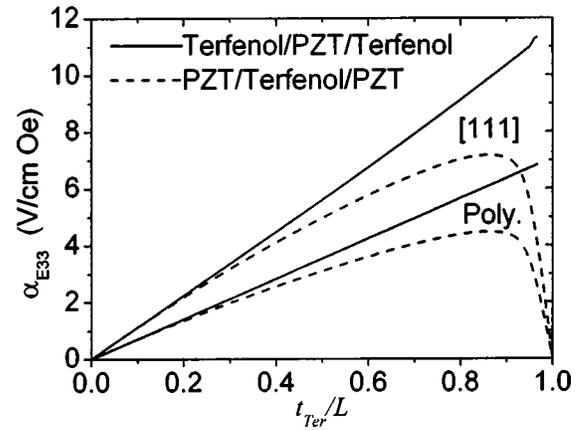


FIG. 2. ME sensitivity α_{E33} at high-field saturation of these sandwiched composites with two different magnetic orientations of the Terfenol-D, as a function of the thickness ratio t_{Ter}/L of the Terfenol-D.

wiched PZT/Terfenol-D/PZT composite, the ME effect non-monotonically depends on t_{Ter}/L with a maximum at $t_{\text{Ter}}/L \cong 0.85$, as predicted previously,⁹ while the ME effect of the sandwiched Terfenol-D/PZT/Terfenol-D composite nearly linearly increases with t_{Ter}/L . Of particular interest is that a surprisingly large ME effect, i.e., a GME effect, is produced in these two laminated composites with thick Terfenol-D layers but thin PZT layers. The ME effect of the composite in the preferred [111] orientation case of the

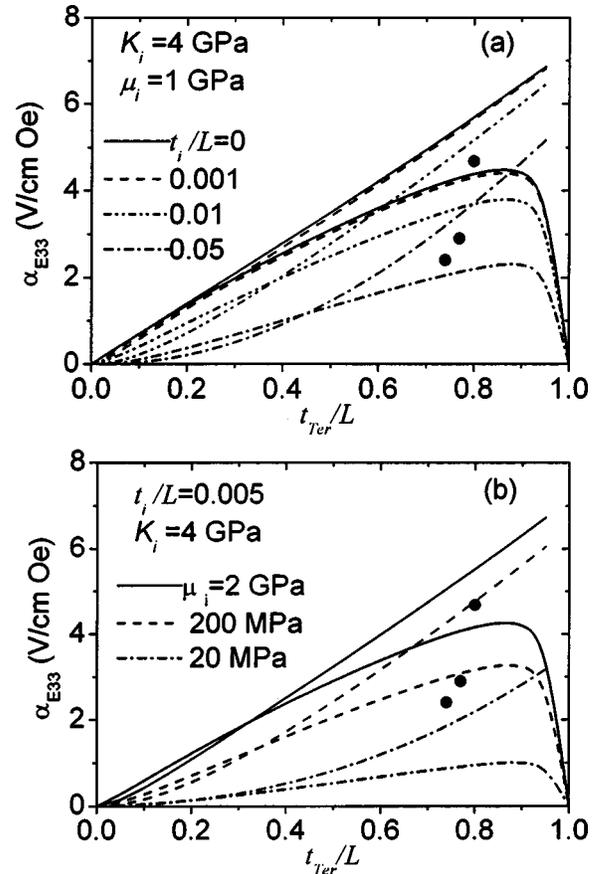


FIG. 3. Effect of (a) relative thickness t_i/L and (b) shear modulus μ_i of the interfacial epoxy binder layers on ME sensitivity α_{E33} at high-field saturation of these sandwiched composites. Recent experimental data (see Ref. 10) available for a Terfenol-D/PZT/Terfenol-D composite are also shown for comparison.

Terfenol-D disks is larger than in the case of the isotropic polycrystalline Terfenol-D disks.

In order to treat the interfacial bonding effect, we change the shear modulus μ_i and the relative thickness t_i of the conductive epoxy (see Fig. 1) used for gluing the PZT and Terfenol-D disks. Figure 3 shows the influence of interface properties on the ME response of the laminated composites with isotropic polycrystalline Terfenol-D disks. The comparison in Fig. 3 shows that the predictions are in reasonable agreement with experimental data available,¹⁰ though the interfacial bonding status in the experiment is not clear.

The increase in the thickness t_i of the conductive epoxy films between the PZT and Terfenol-D leads to a decrease in the α_{E33} values [Fig. 3(a)], since the conductive epoxy films are inert, i.e., not magnetostrictive and piezoelectric. Figure 3(a) shows that a very thin epoxy film (e.g., $t_i/L \leq 0.001$) with bonding capability is good enough for producing the GME response. The elastic modulus of the inert epoxy films have a significant effect on the α_{E33} values [Fig. 3(b)]. By decreasing the shear modulus μ_i of the thin epoxy films, i.e., using a very flexible epoxy as the binder, the interfacial bonding between the PZT and Terfenol-D becomes weak due to the formation of a sliding interface. The weak interfacial contact would lead to appreciable losses of transferring elastic strain/stress from Terfenol-D to PZT, and thus the decrease in the shear modulus μ_i of the thin interfacial epoxy films results in a large decrease in the ME response of the composites.

In summary, the GME response can be produced in the simple sandwiched composites of thick Terfenol-D layers and thin PZT layers, especially in the sandwiched Terfenol-D/PZT/Terfenol-D samples. However, the conductive epoxy binders used for bonding the PZT and Terfenol-D are very critical to the GME response of the samples. The thicker

interfacial epoxy binder films (e.g., $t_i/L > 0.001$) leads to a decrease in the ME effect. In particular, a sliding interfacial bonding, by a very flexible epoxy with low shear modulus, results in a significant drop in the ME response. Any imperfect interfacial bonding produced by the epoxy binders would decrease the displacement transfer capability, thereby leading to a decrease in the ME response of the composites.

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¹²The properties of the Terfenol-D and PZT-5A used in the numerical calculations were given before, i.e. $(c_{11}, c_{12}, \text{ and } c_{44}) = (82, 40, \text{ and } 38)$ GPa, and $(\lambda_{111} \text{ and } \lambda_{100}) = (1700 \text{ and } 100)$ ppm at the saturation for Terfenol-D, and $(c_{11}^m, c_{12}^m, c_{13}^m, c_{33}^m, \text{ and } c_{44}^m) = (121, 75.4, 75.2, 111, \text{ and } 21)$ GPa, $\kappa_{33}^m/\kappa_o = 830$, $\mu_{33}^m/\mu_o = 1$, and $(e_{31}^m, e_{33}^m, \text{ and } e_{15}^m) = (-5.4, 15.8, \text{ and } 12.3)$ C/m² for PZT-5A.