The Effect of Substrate Clamping on Laminated Magnetoelectric Composite

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A theory model was established to calculate the magnetoelectric voltage coefficient of piezoelectric/piezomagnetic laminated composites on silicon or magnesium oxide substrates. The magnetoelectric voltage coefficient is calculated as function of interface coupling factor k, volume ratio of piezoelectrics to piezomagnetic, and volume ratio of substrates to composite. It was found that the magnetoelectric voltage coefficient decreases as the interface coupling factor k weakens, while the volume ratio of piezoelectrics to piezomagnetic $v_{\max}$ shifts to lead-rich compositions. The magnetoelectric voltage coefficient of laminated composites decreases sharply with increasing substrates thickness ratio, which shows strong substrate clamping effect to the magnetoelectric composite.

Key words: Magnetoelectric; ME Voltage Coefficient; Clamping.

1. Introduction

In recent years, multiferroic magnetoelectric (ME) materials, which simultaneously exhibit ferroelectricity and ferromagnetism, have drawn increasing interest due to their potential for applications as multifunctional devices, such as magnetic sensors, transformers, gyrators, microwave devices, and so on [1 – 3].

Usually, the natural multiferroic single-phase compounds are rare [4 – 7], and their magnetoelectric responses are either relatively weak or occur at temperatures too low for practical applications. In contrast, multiferroic composites, which incorporate both ferroelectric and ferromagnetic phases [8 – 10], typically yield giant magnetoelectric coupling response above room temperature, which makes them ready for technological applications [11, 12]. Numerous research results indicated that the ferroelectric and ferromagnetic behaviours of multiferroic composites are affected by many factors, including thicknesses of the respective constituent layers, thin films annealing temperature, structure design, thin film orientation, and so on [13 – 15]. The enhanced ferroelectric and ferromagnetic behaviour may lead to the larger ME effect. The strongest ME coupling was expected in a layered structure due to the absence of leakage current and ease of poling to align the electric dipoles. Many researchers have investigated the ME coupling behaviour in the piezoelectric/ferrite ceramic composites both in the experimental [16 – 19] and theoretical [20 – 22] fields.

The laminated magnetoelectric composites were fabricated a lot for their low leakage current and strength of electric dipoles. In this paper, we focus on the theoretical understanding of Si/MgO substrates clamping effect and interface coupling coefficient k on ME voltage coefficient α_E of $PbZrTiO_3/CoFe_2O_4$ (PZT/CFO) and $PbZrTiO_3/NiFe_2O_4$ (PZT/NFO) laminated composites. The dependence of the $\alpha_{E,33}$ on layer number was obtained for PZT/NFO multilayer composites.The relative mechanism was also discussed.

2. Theoretical Consideration

Consider a simple bilayered composite of piezoelectric layer $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PMN-PT) and magnetic layer (CFO) on a substrate as shown in Figure 1. The polarization direction coincides with the axis 3.The piezoelectric phase is ∞m symmetrical, and the magnetostrictive phase is cubic symmetrical. We assume that the bilayer composites are homoge-

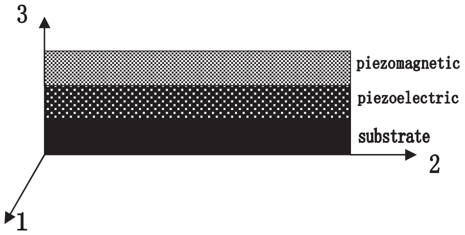

Fig. 1. Schematic illustration of the piezomagnetic/piezoelectric/substrate laminated composites in the (1,2) plane on substrate.

neous and the behaviour is described by

$$\begin{aligned} S_i &= s_{ij}T_j + d_{ki}E_k + q_{ki}H_k, \\ D_k &= d_{ki}T_i + \varepsilon_{kn}E_n + \alpha_{kn}H_n, \\ B_k &= q_{ki}T_i + \alpha_{kn}E_n + \mu_{kn}H_n, \\ S_i^{\mathrm{s}} &= s_{ij}^{\mathrm{s}}T_j^{\mathrm{s}}, \end{aligned} \tag{1}$$

where S_i and T_j are strain and stress tensor components, E_k and D_k are the vector components of electric field and electric displacement, H_k and B_k are the vector components of magnetic field and magnetic induction, s_{ij}, d_{ki}, and q_{ki} are effective compliance, piezoelectric, and piezomagnetic coefficients, and ε_{kn}, μ_{kn}, α_{kn}, are effective permittivity, permeability, and ME coefficient, respectively.

For the solution of the set of equations (1), we assume (1,2) as the laminated composite plane (as shown in Figure 1) and the direction 3 perpendicular to the sample plane. The laminated composite is poled with an electric field E along direction 3. We consider the interface coupling parameter k between magnetic and piezoelectric phases for characterizing actual bonding conditions at the interface, and perfect interface between substrates and piezoelectric phases was also assumed. Then the following boundary conditions are used:

$$\begin{aligned} &S_i^{\mathrm{p}} = \kappa S_i^{\mathrm{m}} = S_i^{\mathrm{s}}, \\ &T_i^{\mathrm{p}}v^{\mathrm{p}} + T_i^{\mathrm{m}}v^{\mathrm{m}} + T_i^{\mathrm{s}}v^{\mathrm{s}} = 0, \\ &T_3^{\mathrm{p}} + T_3^{\mathrm{m}} + T_3^{\mathrm{s}} = 0, (i = 1,2), \end{aligned} \tag{2}$$

where v^{p}, v^{m}, and v^{s} are the volume of piezoelectric, magnetostrictive phase, and substrate, respectively. The superscripts p, m, s correspond to piezoelectric and piezomagnetic phases and substrate, respectively. The third term in (2) corresponds to the equilibrium condition (the total force projections on 1 and 2 axes are equal to zero). Using continuity conditions for magnetic and electric fields and open- and closed-circuit conditions, the expressions for transverse and longitudinal ME coefficient could be obtained as follows [23–26]:

$$\begin{aligned} a_{E,31} = {} & (q_{11}^{\mathrm{m}} + q_{21}^{\mathrm{m}})d_{31}^{\mathrm{p}}kv^{\mathrm{p}}v^{\mathrm{m}} \times \Bigg\{ (v^{\mathrm{p}} + v^{\mathrm{m}}) \\ & \times \Bigg\{ \Bigg[(s_{11}^{\mathrm{m}} + s_{12}^{\mathrm{m}})kv^{\mathrm{p}} + (s_{11}^{\mathrm{p}} + s_{12}^{\mathrm{p}})v^{\mathrm{m}} \\ & + (s_{11}^{\mathrm{m}} + s_{12}^{\mathrm{m}}) \times \frac{(s_{11}^{\mathrm{p}} + s_{12}^{\mathrm{p}})}{s_{11}^{\mathrm{s}} + s_{12}^{\mathrm{s}}}kv^{\mathrm{s}} \Bigg] \varepsilon_{33}^{\mathrm{p}} \\ & - \frac{2(d_{31}^{\mathrm{p}})^2}{s_{11}^{\mathrm{s}} + s_{12}^{\mathrm{s}}}(s_{11}^{\mathrm{m}} + s_{12}^{\mathrm{m}})v^{\mathrm{s}} - 2(d_{31}^{\mathrm{p}})^2 v^{\mathrm{m}} \Bigg\} \Bigg\}^{-1}, \end{aligned} \tag{3}$$

$$\begin{aligned} a_{E,33} = {} & -2q_{31}^{\mathrm{m}}d_{31}^{\mathrm{p}}kv^{\mathrm{p}}v^{\mathrm{m}} \times \Bigg\{ (v^{\mathrm{p}} + v^{\mathrm{m}}) \\ & \times \Bigg\{ \Bigg[(s_{11}^{\mathrm{m}} + s_{12}^{\mathrm{m}})kv^{\mathrm{p}} + (s_{11}^{\mathrm{p}} + s_{12}^{\mathrm{p}})v^{\mathrm{m}} \\ & + (s_{11}^{\mathrm{m}} + s_{12}^{\mathrm{m}}) \times \frac{(s_{11}^{\mathrm{p}} + s_{12}^{\mathrm{p}})}{s_{11}^{\mathrm{s}} + s_{12}^{\mathrm{s}}}kv^{\mathrm{s}} \Bigg] \varepsilon_{33}^{\mathrm{p}} \\ & - \frac{2(d_{31}^{\mathrm{p}})^2}{s_{11}^{\mathrm{s}} + s_{12}^{\mathrm{s}}}(s_{11}^{\mathrm{m}} + s_{12}^{\mathrm{m}})kv^{\mathrm{s}} - 2(d_{31}^{\mathrm{p}})^2 v^{\mathrm{m}} \Bigg\} \Bigg\}^{-1}. \end{aligned} \tag{4}$$

3. Results and Discussion

In this model, we suppose that the epilayer thickness is sufficiently large to neglect the influence of strain relaxation on average stresses in the structures that determine the ME voltage coefficient. We now estimate the parameter for a bilayer magnetoelectric composite with the following material parameters [26]:

PZT: $s_{11} = 15.3 \cdot 10^{-12}\ \mathrm{m^2/N}$,
$s_{12} = -5 \cdot 10^{-12}\ \mathrm{m^2/N}$,
$d_{31} = -175 \cdot 10^{-12}\ \mathrm{m/A}$,
$\varepsilon_{33}/\varepsilon_0 = 1750$.

CFO: $s_{11} = 6.5 \cdot 10^{-12}\ \mathrm{m^2/N}$,
$s_{12} = -2.4 \cdot 10^{-12}\ \mathrm{m^2/N}$,
$q_{11} = -1880 \cdot 10^{-12}\ \mathrm{m/A}$,
$q_{21} = q_{31} = 566 \cdot 10^{-12}\ \mathrm{m/A}$.

NFO: $s_{11} = 6.5 \cdot 10^{-12}\ \mathrm{m^2/N}$,
$s_{12} = -2.4 \cdot 10^{-12}\ \mathrm{m^2/N}$,

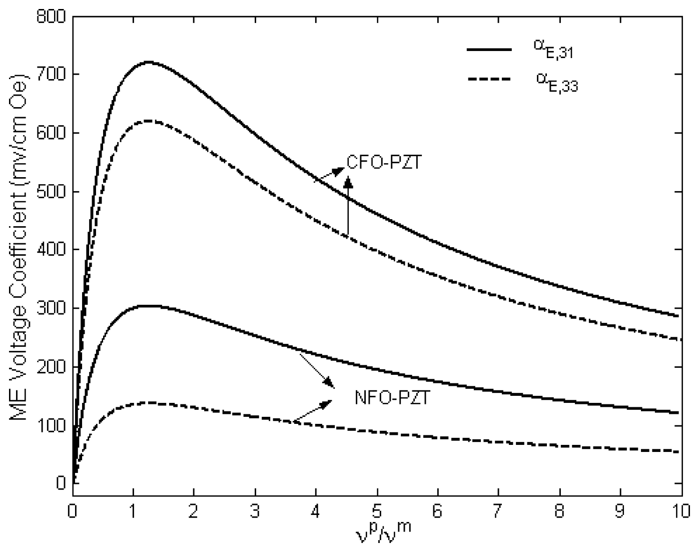

Fig. 2. Dependence of ME voltage coefficient on piezoelectric-to-piezomagnetic volume ratio v^p/v^m for the different laminated composites.

$$q_{11} = -680 \cdot 10^{-12}\ \mathrm{m/A},$$
$$q_{21} = q_{31} = 125 \cdot 10^{-12}\ \mathrm{m/A}.$$
$$\text{Si:}\quad s_{11} = 7.67 \cdot 10^{-12}\ \mathrm{m^2/N},$$
$$s_{12} = -2.14 \cdot 10^{-12}\ \mathrm{m^2/N}.$$
$$\text{MgO:}\quad s_{11} = 4 \cdot 10^{-12}\ \mathrm{m^2/N},$$
$$s_{12} = 0.96 \cdot 10^{-12}\ \mathrm{m^2/N}.$$

Using the material parameters, piezoelectrics-to-piezomagnetic volume ratio dependence of ME voltage coefficient of PZT/CFO and PZT/NFO without substrate are shown in Figure 2. It was found that for ideal interface coupling ($k = 1$), α_E increases dramatically with the increasing of v^p/v^m, and attain a peak corresponding to a value of $(v^p/v^m)_{max}$, then drop gradually with increasing of v^p/v^m. Pure piezoelectrics and pure piezomagnetics do not reveal the ME effect. And the transverse ME voltage coefficient $\alpha_{E,31}$ is larger than the longitudinal ME coefficient $\alpha_{E,33}$, which indicates a stronger transverse coupling than that of the longitudinal case in such laminate composites. Otherwise, NFO is a soft ferrite with a much smaller anisotropy and magnetostriction than CFO, so the ME effect of PZT/NFO is much weaker than that of PZT/CFO.

Next, the longitudinal ME effect in bilayers of PZT/CFO on different substrates and with different substrate-to-composite volume ratio (with $v_s = 0, 1, 3$; $v_s = v^s/(v^m + v^p)$) estimates are shown in Figure 3. The curves for $v_s = 0$ mean no substrate, corresponding to the curves in Figure 2. And with increasing value of v_s, the longitudinal ME coefficient $\alpha_{E,33}$ decrease sharply, which shows a strong clamping effect of the substrate. Meanwhile, the $(v^p/v^m)_{max}$ shifts to lead-lack compositions. For larger volume of substrate, this clamping effect is more evident. Comparing silicon with magnesium oxide substrates to the ME effect for the PZT/CFO composite, we conclude that the silicon substrate has a weaker ME clamping effect, and is more suitable for a substrate to prepare a composite.

Figure 4 shows an example calculated from the laminate composites with piezoelectric-to-piezomagnetic volume ratio v^p/v^m and interface coupling coefficient k for the PZT/CFO bilayer on the silicon substrate (with $v_s = 1$). The strength of $\alpha_{E,33}$ decreases as the coupling factor k weakens, while $(v^p/v^m)_{max}$ shifts to lead-rich compositions. Besides, $\alpha_{E,33}$ decreased rapidly with the increase of v^p/v^m, and the $\alpha_{E,33}$ of the systems are almost equally when v_s arrived at 10 or more.

Figure 5 shows the dependence of $\alpha_{E,33}$ on substrate-to-composite volume ratio v_s and interface coupling coefficient k for the PZT/CFO bilayer on the silicon substrate (with $v^p/v^m = 1.5$). $\alpha_{E,33}$ initially shows a rapid decrease, then a linear decrease with increasing substrate volume. With the gradually diminishing of the interface coupling coefficient k, $\alpha_{E,33}$ becomes smaller and smaller corresponding to the same value of v^p/v^m.

From experimental data for NFO/PZT, we utilize an empirical dependence of k on the number of lay-

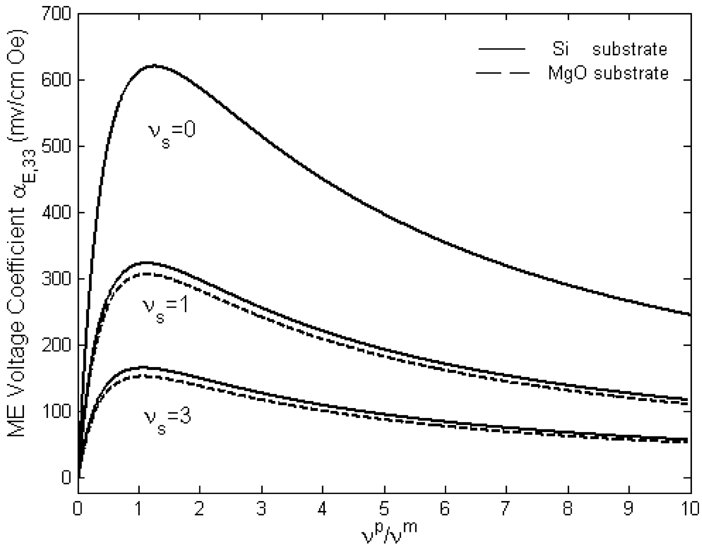

Fig. 3. Dependence of $\alpha_{E,33}$ on piezoelectric-to-piezomagnetic volume ratio v^p/v^m and substrate-to-composite volume ratio $v_s = 0$, 1, and 3 for the PZT/CFO bilayer on Si and MgO substrates.

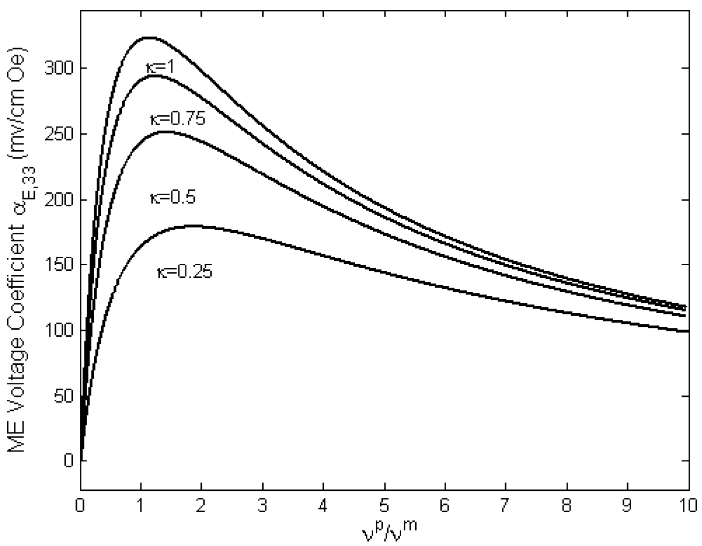

Fig. 4. Dependence of $\alpha_{E,33}$ on piezoelectric-to-piezomagnetic volume ratio v^p/v^m and interface coupling coefficient k for the PZT/CFO bilayer on Si substrate (with $v_s = 1$).

ers n as: $k = 1-(n-1)^2/225$ [24]. Substituting this expression for k in basic equations, it is possible to obtain expressions for the longitudinal ME voltage coefficient as a function of the number of layers n. Figure 6 shows the variation of $\alpha_{E,33}$ with the number of layers and substrate-to-composite volume ratio v_s for the PZT/NFO multilayer on silicon substrate (with $v^p/v^m = 1.5$). Unlike in Figures 2 and 3, the relation curves of $\alpha_{E,33}$ and v^p/v^m are all approximately symmetrical. Furthermore, there is a maximum for the longitudinal ME voltage coefficient with a corresponding number of layers about 15. For the different v_s values, the relation curves also express the strong substrate clamping effect of the ME composite.

In conclusion, the substrate has compressive stress on the piezoelectrics in plane, and piezomagnetics have tensile stress on the piezoelectrics in plane. The tensile stress enhances with the increasing thickness of piezomagnetics, which change the lattice constant of piezoelectrics, and then influence the property of the composite. Otherwise, the piezoelectrics also have compressive stress on the piezomagnetics. The stress release with the increasing thickness of piezomagnetics. Therefore, we can control interfacial stress through

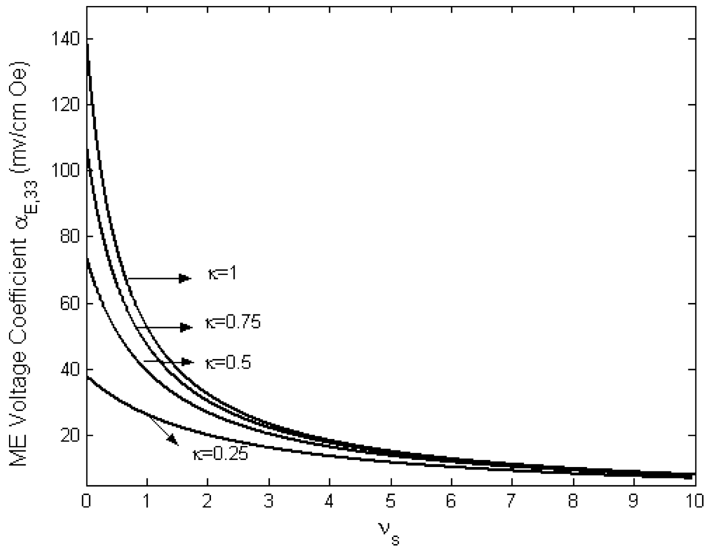

Fig. 5. Dependence of $\alpha_{E,33}$ on substrate-to-composite volume ratio v_s and interface coupling coefficient k for the PZT/CFO bilayer on Si substrate (with $v^p/v^m = 1.5$).

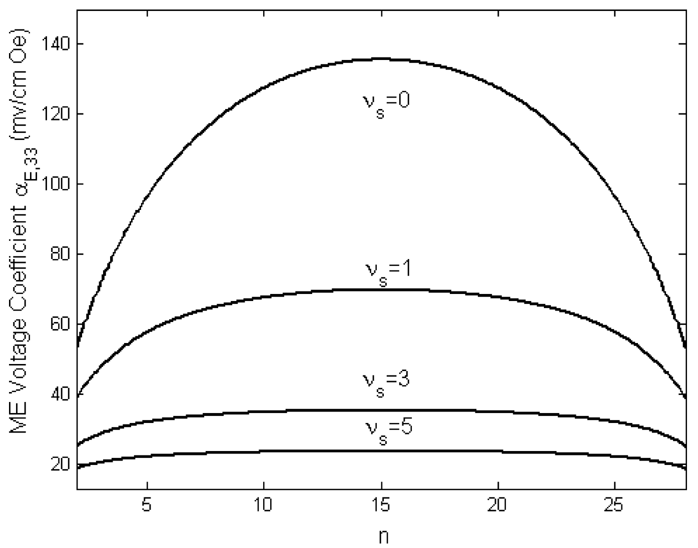

Fig. 6. Dependence of $\alpha_{E,33}$ on number of layers and substrate-to-composite volume ratio v_s for the PZT/NFO multilayer on Si substrate (with $v^p/v^m = 1.5$).

controlling the thickness of piezoelectrics or piezomagnetics, selecting a thinner substrate to dominate the ME coupling of the composite. In addition, improving the interface coupling is also an approach to enhance the ME effect.

4. Summary and Conclusions

A theorical model of piezoelectric/piezomagnetic laminated composite on Si/MgO substrates was established. Although the estimates here are based on bulk material parameters, it can easily be refined to take into account parameters for bilayer CFO/PZT and NFO/PZT. It was found that the ME effect of PZT/CFO is much stronger than that of PZT/NFO. The strength of ME interactions is weaker with the Si/MgO substrate increasing, which ascribe to the strong clamping effects of the substrate. On the other hand, the strength of $\alpha_{E,33}$ decreases as the coupling factor k weakens, while $(v^p/v^m)_{max}$ shifts to lead-rich compositions. The dependence of $\alpha_{E,33}$ on v_s and k for the PZT/CFO bilayer on the silicon substrate are also considered. Dependence of $\alpha_{E,33}$ on the layer number was obtained for PZT/NFO multilayer composites. By this model, we can understand the ME response of ferroelectric/ferromagnetic/substrate laminated composites well, and get an approach to promote the ME response by artificially controlling the influencing factors. Nonetheless, the model is based on the assumption of perfect elastic and symmetry. The residual stress and shear stress in both the transverse and longitudinal directions were not in consideration, which must reduced the ME convertion. However, the method proposed here was simple for numerical calculations and expected to be able to study the substrate clamping effect on the ME laminated composite. We hope that these results may provide some useful information for theoretical and experimental work on ferroelectric/ferromagnetic/substrate composites with the developments of the experimental techniques in this field.

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