Giant magnetoelectric effects in multilayered composites of cobalt ferrite and lead magnesium niobate titanate

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Abstract. The magnetoelectric (ME) coupling responses of [CoFe₂O₄/(1-x)Pb(Mg₁/₃Nb₂/₃)O₃-xPbTiO₃]ₙ, represented as (CFO/PMNT)ₙ, multilayered composites were theoretically investigated by using an average method. It is found that a stronger interface coupling could be obtained in multilayers than in bilayers if the number of layers (n) is reasonably increased. Using an empirical dependence of the interface coupling parameter on the number of layers n, it is theoretically estimated that the ME coupling effect is first enhanced and then deteriorated with the gradual increase in n. The best ME response is estimated to occur at n=15, where the transverse ME voltage coefficient \( \alpha_{E31} \) reaches as high as 658 mV·cm⁻¹·Oe⁻¹. Moreover, it is theoretically found that the ME coupling effect in (CFO/PMNT)ₙ multilayered composites is strongly dependent on the volume fraction of the piezoelectric (or magnetostrictive) phase, and the ME voltage coefficient for transverse field orientation \( \alpha_{E31} \) is estimated to be roughly 90% higher than that for the longitudinal case \( \alpha_{E33} \), revealing a large anisotropy in the ME coupling effect of (CFO/PMNT)ₙ multilayered composites. These findings pave the way for experimental achievement of strong ME coupling responses, and provide important implications for the design and performance optimization of related devices comprising this kind of multiferroic magnetoelectric materials.

1. Introduction
Multiferroic magnetoelectric (ME) materials, which simultaneously exhibit ferroelectricity and ferromagnetism, have recently become the focus of research because of their scientific interest and significant technological promise in the novel multifunctional devices. Natural multiferroic single-phase compounds are rare, 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 ferri-/ferromagnetic phases, typically yield giant magnetoelectric coupling responses above room temperature, making them ready for technological applications, such as applications in magnetic field sensors, transducers, magnetoelectric memories and microwave devices (filters, oscillators, phase shifters, etc) [1,2]. The magnetoelectric effect is defined as the dielectric polarization of a material in an applied magnetic field or an induced magnetization in an external electric field. That is, the induced polarization \( \mathbf{P} \) is related to the magnetic field \( \mathbf{H} \) by the expression, \( \mathbf{P}=\alpha\mathbf{H} \), where \( \alpha \) is the second rank ME-susceptibility tensor. A parameter of importance is the ME voltage coefficient \( \alpha_{E}=\delta E/\delta H \) with \( \alpha=\varepsilon_\alpha,\sigma_\alpha \). A multilayer structure is expected to be far superior to bulk composites since the leakage current problem can be avoided and the piezoelectric layer can

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easily be poled electrically to enhance the piezoelectricity and the ME effect [3]. In particular, multilayered magnetoelectric composites with cobalt ferrite (CoFe$_2$O$_4$, abbreviated as CFO) have attracted great interest due to the very high magnetostriction in CFO [4-7]. Moreover, the material system of lead magnesium niobate titanate [(1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$, abbreviated as PMNT] is known to possess very high piezoelectric coefficients with composition near the morphotropic phase boundary (x: 0.3-0.4) [8-10]. As a consequence, the combination of highly magnetostrictive CFO and highly piezoelectric PMNT is a good choice for studying the magnetoelectric effect in multilayered composites. Until now, however, very few results have been reported in literature for multilayered composites composed of CFO and PMNT.

In this work, the magnetoelectric coupling responses of (CFO/PMNT)$_n$ multilayered composites were theoretically investigated by using an average method derived by Bichurin et al. [11,12]. In this model, an interface coupling parameter $k$ that describes the actual boundary conditions is introduced. It is theoretically demonstrated that a stronger interface coupling could be obtained in multilayers than in bilayers if the number of layers is reasonably increased; moreover, the ME coupling effect in (CFO/PMNT)$_n$ multilayered composites is strongly dependent on the volume fraction of the piezoelectric (or magnetostrictive) phase, and there is a large anisotropy in the ME coupling effect of (CFO/PMNT)$_n$ multilayered composites.

2. Theoretical model

An averaging method was used for deriving the effective material parameters of CFO-PMNT composites and was performed in two stages [11,12]. In the first stage, the composite is considered as a bilayer consisting of magnetostrictive CFO and piezoelectric PMNT phases. It is noted that we consider only symmetric extensional deformation in this model and ignore any asymmetric flexural deformations of the layers. The magnetostrictive phase with a cubic symmetry can be expressed by the following equations:

\[ mS_i = m_{ij}^{s} mT_j + m_{ki}^{s} mH_k, \]
\[ mB_k = m_{ki}^{s} mT_i + m_{kn}^{s} mH_n, \]  

where $mS_i$ and $mT_j$ are strain and stress tensor components of the magnetostrictive phase, $mH_k$ and $mB_k$ are the vector components of magnetic field and magnetic induction, $m_{ij}^{s}$ and $m_{ki}^{s}$ are compliance and piezomagnetic coefficients, and $m_{kn}^{s}$ is the magnetic permeability matrix. For the polarized piezoelectric phase with the symmetry $\infty m_\perp$, the strain and electric displacement can be written as

\[ pS_i = p_{ij}^{s} pT_j + p_{ki}^{s} pE_k, \]
\[ pD_k = p_{ki}^{s} pT_i + p_{kn}^{s} pE_n, \]  

where $pS_i$ and $pT_j$ are strain and stress tensor components of the piezoelectric phase, $pE_k$ and $pD_k$ are the vector components of electric field and electric displacement, $p_{ij}^{s}$ and $p_{ki}^{s}$ are compliance and piezoelectric coefficients, and $p_{kn}^{s}$ is the dielectric permittivity matrix. Then, the ME voltage coefficients can be obtained from Eqs. (1) and (2) assuming in-plane mechanical connectivity between the two phases. In order to describe the actual boundary conditions, an interface coupling parameter ($k$) is introduced, which takes the form

\[ k = (pS_i - pS_{i0}) / (mS_i - mS_{i0}) , \]  

where $pS_{i0}$ is strain tensor components with no friction between layers. The $k$ factor depends on the interface quality and is a measure of differential deformation between piezoelectric and magnetostrictive layers. The coupling factor $k=1$ is for an ideal interface and zero for the case with no
friction. In the second stage, the bilayer is considered as homogeneous and the behaviour is described by

\[
\begin{align*}
S_i &= s_{ij} T_j + d_{ik} E_k + q_{ik} H_k, \\
D_k &= d_{ik} T_i + \varepsilon_{kn} E_n + \alpha_{kn} H_n, \\
B_k &= q_{ik} T_i + \alpha_{kn} E_n + \mu_{kn} H_n,
\end{align*}
\tag{4}
\]

where \(\alpha_{kn}\) is the ME coefficient. Effective parameters of the composite are obtained by solving Eq. (4), taking into account the solutions of Eqs. (1) and (2), for which the electric and magnetic vectors are determined using open- and closed-circuit conditions.

For detailed description, a coordinate system is assumed with the sample in the (1,2) plane. The sample is poled with an electric field \(E\) along the direction 3. ME coupling is estimated from the induced field \(\delta E\) across the sample that is subjected to an ac magnetic field \(\delta H\) in the presence of a bias field \(H\). Basic relations for ME coefficients are obtained for two orientations of \(H\) and \(\delta H\): along direction 3 (longitudinal to \(\delta E\)) or along direction 1 (transverse to \(\delta E\)), as depicted in Fig. 1. Therefore, the longitudinal ME voltage coefficient is given by

\[
\begin{align*}
\alpha_{E,33} &= \frac{-2\mu_0 k v (1-v)^p d_{31}^m q_{31}}{2(p d_{31})^2 (1-v) k + p \varepsilon_{33}[(p s_{11} + s_{12})(v-1) - kv(m s_{11} + m s_{12})]} \times \frac{[(p s_{11} + s_{12})(v-1) - kv(m s_{11} + m s_{12})]}{[\mu_0 (v-1) - n \mu_3 v][kv(m s_{11} + m s_{12}) - (p s_{11} + p s_{12})(v-1)] + 2(m q_{31})^2 k v^2}.
\tag{5}
\end{align*}
\]

where \(v = p v/(p v + m v)\), representing the volume fraction of piezoelectric phase; \(p v\) and \(m v\) denote the volume of piezoelectric phase and magnetostrictive phase, respectively. The transverse ME voltage coefficient is given by

\[
\begin{align*}
\alpha_{E,31} &= \frac{-k v (v-1)^p d_{31}^m q_{31}}{(m s_{11} + m s_{12}) p \varepsilon_{33} k v + (p s_{11} + p s_{12}) p \varepsilon_{33} (1-v) - 2(p d_{31})^2 k (1-v)}.
\tag{6}
\end{align*}
\]

Figure 1. Schematic diagram showing a bilayer of piezoelectric and magnetostrictive phases in the (1,2) plane. Field orientations for longitudinal (3,3) and transverse (3,1) ME effects are also depicted.

The difference between ME coefficients for bilayer and multilayer is due primarily to an imperfect bonding of layers. As a result, the aforementioned \(k\) factor should be strongly dependent on the number of layers \(n\) in multilayered composites. Using an empirical formula extracted from experimental data for NiFe\(_2\)O\(_4\)-Pb(Zr,Ti)O\(_3\) composites [13,14]:

\[
k = 1 - (n - 15)^2 / 225,
\tag{7}
\]

we can estimate the dependence of ME coupling effect on the number of layers in (CFO/PMNT)\(_n\) multilayered composites.

3. Results and discussion
Let us now use the theoretical model for the calculation of ME coupling in \((\text{CFO/PMNT})_n\) multilayered composites. The following sample parameters were used: for PMNT, the composition was selected as \(0.68\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.32\text{PbTiO}_3\), then \(s_{11}=47.7\times10^{-12} \text{m}^2/\text{N}, s_{12}=-13.1\times10^{-12} \text{m}^2/\text{N}, d_{31}=-686\times10^{-12} \text{C/N}\) and \(e_{33}/\varepsilon_0=4970\) \([15]\); for CFO, \(s_{11}=6.48\times10^{-12} \text{m}^2/\text{N}, s_{12}=-2.73\times10^{-12} \text{m}^2/\text{N}, q_{11}=-1880\times10^{-12} \text{m/A}, q_{12}=556\times10^{-12} \text{m/A}, q_{31}=556\times10^{-12} \text{m/A}\) and \(\mu_3/\mu_0=2\) \([16]\).

Since the strength of the ME coupling depends sensitively on the concentration of the two phases, we estimate the ME voltage coefficients as a function of the piezoelectric volume fraction \(v\). Figure 2 shows the calculated dependence of longitudinal \((\alpha_{E,33})\) and transverse \((\alpha_{E,31})\) ME coefficients on \(v\) for \((\text{CFO/PMNT})_n\) multilayered composites with a series of \(k\) values. Both \(\alpha_{E,33}\) and \(\alpha_{E,31}\) coefficients first increase and then decrease with the increase in the piezoelectric volume fraction \(v\), reaching a maximum at \(v_m\). It can also be seen from the figure that the decrease in \(k\) value leads to a significant lowering of the strength of ME coupling. This is because the ME coupling weakens with decreasing \(k\). As a consequence, with increasing \(k\), both the maximum \(\alpha_{E,33}\) and \(\alpha_{E,31}\) display a trend of near-linear increase. The ME coupling, however, reaches a maximum at progressively decreasing \(v_m\) with the increase in \(k\). In other words, as \(k\) value increases, \(v_m\) shifts to CFO-rich compositions. These results are summarized and plotted in Fig. 3.

Figure 2. Dependence of the transverse \((\alpha_{E,31})\) and longitudinal \((\alpha_{E,33})\) magnetoelectric voltage coefficients on the volume fraction \(v\) of the piezoelectric phase in \((\text{CFO/PMNT})_n\) multilayered composites. Theoretical estimates are shown as a function of the interface coupling parameter \(k\).
Figure 3. Variation with $k$ of maximum $\alpha_{E,31}$ (a) and $\alpha_{E,33}$ (b) and the corresponding $v_m$ for (CFO/PMNT)$_n$ multilayered composites.

It is shown in Fig. 4 that the transverse and longitudinal ME voltage coefficients depend drastically on the number of layers in (CFO/PMNT)$_n$ multilayered composites. For a given $v$ value, the maximum ME coupling is obtained at $n=15$ for both $\alpha_{E,33}$ and $\alpha_{E,31}$, where the strongest interface coupling is achieved. This implies that the number of layers should be optimized in multilayered magnetoelectric composites in order to obtain a strong interface coupling and thus a strong ME coupling effect. Similarly, it is experimentally verified that the ME coupling effect could be enhanced in multilayered composites if the number of layers is reasonably increased [14,17,18]. It is pointed out that the volume fraction of the two phases also has a remarkable effect on the ME coupling, especially for the longitudinal ME response. In the case of (CFO/PMNT)$_n$ multilayered composites, the maximum ME coupling occurs at $n=15$ and $v=0.6$. Hence, both the number of layers and the volume fraction of piezoelectric phase should be carefully taken into consideration in the design of high-performance multilayered magnetoelectric composites.

Figure 4. Peak transverse (a) and longitudinal (b) ME voltage coefficients as a function of the number of layers in (CFO/PMNT)$_n$ multilayered composites with different piezoelectric volume fractions.

4. Conclusions
The magnetoelectric coupling responses of (CFO/PMNT)$_n$ multilayered composites were theoretically investigated by using an average method. It is found that the ME coupling effect in (CFO/PMNT)$_n$ multilayered composites is strongly dependent on the volume fraction of the piezoelectric phase ($v$), and the ME voltage coefficient for transverse field orientation ($\alpha_{E,31}$) is estimated to be roughly 90%
higher (nearly double) than that for the longitudinal case \( (a_{E,33}) \), revealing a large anisotropy in the ME coupling effect of (CFO/PMNT)_n multilayered composites. It is also found that a stronger interface coupling and thus a stronger ME coupling effect could be obtained in multilayers than in bilayers if the number of layers \( (n) \) is reasonably increased. Using an empirical dependence of the interface coupling parameter on the number of layers, it is theoretically estimated that the ME coupling effect is first enhanced and then deteriorated with the gradual increase in \( n \). The best ME response is estimated to occur at \( n=15 \) and \( v=0.6 \), where the transverse ME voltage coefficient \( a_{E,31} \) reaches as high as 658 mV·cm\(^{-1}\)·Oe\(^{-1}\). These findings pave the way for experimental achievement of strong ME coupling responses, and provide important implications for the design and performance optimization of related devices comprising this kind of multiferroic magnetoelectric materials.

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