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The effective magnetoelectric coefficients of polycrystalline multiferroic composites

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Abstract

In this paper, we develop a self-consistent approach using effective medium approximation to calculate the macroscopic magnetoelectric (ME) coefficients of polycrystalline multiferroic composites, emphasizing the effects of shape, volume fraction, and orientation distribution of particles of both phases. This approach is especially suitable for composites with volume fractions of each phase close to 50%, in which there may not be a matrix phase present and thus mean field Mori–Tanaka model is not applicable. It is observed from the numerical calculations that the aligned particles result in highest ME coefficients and coupling factors, while randomly oriented particles lead to essentially zero ME coupling, even though the ME coefficient is an even rank tensorial property. In addition, it is observed that lamellar particles are optimal for ME coefficient a_{11}, while fibrous particles are optimal for a_{33}. We also postulate that the large discrepancy between theoretical calculations and experimental measurements for ME coefficients of multiferroic composites previously reported is partly due to the orientation distribution of particles that has rarely been considered. When our calculations took the orientation distribution of particles of both phases into account, good agreement with experimental data is observed.

Keywords: Multiferroic composite; Magnetoelectric effect; Effective medium approximation; Self-consistent approach

1. Introduction

The magnetoelectric (ME) effect was first predicted by Landau and Lifshitz in 1957 [1,2], and was later confirmed in an antiferromagnetic single crystal Cr_2O_3 [3–5]. Subsequently, observations of ME effect in more crystals have been reported, including $BiFeO_3$ [6] and $YMnO_3$ [7]. Use of these so-called multiferroic materials, which possess two or more types of orders simultaneously, is envisioned in a wide range of applications, including electrically controlled microwave phase shifters or ferromagnetic resonance devices, magnetically controlled electro-optic or piezoelectric devices, broadband magnetic field sensors, and ME memory devices. For the materials to be technologically viable, however, large ME coupling must be demonstrated, and thus there is great effort devoted to developing multiferroic composites that possess higher ME coupling than single phase materials.

Since the first multiferroic composite consisting of a piezoelectric phase $BaTiO_3$ and a ferromagnetic phase $CoFe_2O_4$ was reported in the 1970s [8,9], a variety of multiferroic composites have been fabricated, with piezoelectric phases including $BaTiO_3$, PZT, and PVDF, and ferromagnetic phases including $CoFe_2O_4$ and TbDyFe [10–18]. Recently, a self-assembled multiferroic nanocomposite has also been reported [19], with hexagonal arrays of $CoFe_2O_4$ nanopillars embedded in a $BaTiO_3$ matrix. Despite this progress, the experimentally

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observed ME coefficients in most of those composites are usually much smaller than the theoretical predictions. This suggests that there is a great deal of room for improvement in materials processing, but it also calls for more reliable theoretical models that approximate the composite microstructures better. We intend to address modeling issues related to multiferroic composites in this paper.

A variety of models have been proposed in the last 10 years to predict the effective magnetoelectroelastic moduli of multiferroic composites. For example, Nan [20] used the Green's function method combined with perturbation theory to study a fibrous composites consisting of $CoFe_2O_4$ and $BaTiO_3$. For such fibrous composites, exact connections among the effective magnetoelectroelastic moduli were derived by Benveniste [21]. Multilayered laminate was studied by Avellaneda and Harshe [22], and Mori–Tanaka model has been generalized to multiferroic composites by Li and Dunn [23], among others. Very recently, the authors generalized this Mori–Tanaka model to study the effects of orientation distribution of second phase particles in a matrix based multiferroic composites, which shows good agreement between theoretical predications and experimental measurements [24]. This demonstrates the importance of orientation distribution of particles, which has not been accounted for in previous modeling efforts. Yet such orientation distribution is inevitable in composites because it is usually very difficult to align all the particles during composite processing.

Our recent study also reveals another weakness of previous models. Virtually all the theoretical models suggest that the ME coefficient reaches its maximum when the volume fraction of each phase is approximately 50%, where the interaction between the ferroelectric phase and ferromagnetic phase is maximized. On the other hand, all the models assume that the composite is matrix based, while at around 50% volume fraction, it is often difficult to decide which phase is matrix and which is the second phase. In other words, the composites often demonstrate a granular polycrystalline type of microstructure and simply do not possess a distinct matrix phase. We intend to address this deficiency in this paper and study the effect of polycrystalline microstructure on the ME coefficients of multiferroic composites. In particular, we will generalize a self-consistent model to polycrystalline multiferroic composites to study the effects of shape, orientation distribution, and volume fraction of both phases, with the objective of identifying the optimal shapes and textures for the ME coupling.

The paper is organized as following. The basic equations and notations regarding the magnetoelectroelasticity are given in Section 2, and a micromechanical model for the polycrystalline multiferroic composites will be derived in Section 3. Numerical results and discussions will then be presented in Section 4.

2. Governing equations of magnetoelectroelasticity

We consider the linear magnetoelectroelastic effect, where the static magnetic, electric, and elastic fields are coupled through the following constitutive equations:

$$\begin{aligned} \sigma_{ij} &= C_{ijkl}\varepsilon_{kl} + e_{ijl}(-E_l) + q_{ijl}(-H_l), \\ D_i &= e_{ikl}\varepsilon_{kl} - \kappa_{il}(-E_l) - a_{il}(-H_l), \\ B_i &= q_{ikl}\varepsilon_{kl} - a_{il}(-E_l) - \mu_{il}(-H_l). \end{aligned} \tag{1}$$

Here, σ_{ij} and ε_{ij} are the elastic stress and strain; D_i and E_i are the electric displacement and field; B_i and H_i are the magnetic intensity and field. C_{ijkl}, κ_{il}, and μ_{il} are the elastic stiffness, the dielectric, and magnetic permeability tensors. These tensors directly connect like fields, e.g., stresses to strains. Elastic field is coupled to the electric and magnetic fields through the piezoelectric coefficient e_{ijl} and piezomagnetic coefficient q_{ijl}, respectively, while electric and magnetic fields are coupled through the ME coefficient a_{il}. In addition, we can define the ME coupling factors k_{11} and k_{33},

$$k_{11}^2 = \frac{a_{11}^2}{\kappa_{11}\mu_{11}}, \quad k_{33}^2 = \frac{a_{33}^2}{\kappa_{33}\mu_{33}}. \tag{2}$$

In the constitutive equations, we use $-E_i$ and $-H_i$ rather than E_i and H_i, as they will enable the construction of a symmetric matrix of constitutive moduli.

The constitutive equations are complemented by gradient equations and equilibrium equations, where the strain, electric, and magnetic fields are derived from vector or scalar potential,

$$\begin{aligned} \varepsilon_{ij} &= \tfrac{1}{2}(u_{i,j} + u_{j,i}), \\ E_i &= -\phi_{,i}, \\ H_i &= -\psi_{,i}, \end{aligned} \tag{3}$$

and the stress, electric displacement, and magnetic intensity are divergence free in the absence of body force and free charge,

$$\begin{aligned} \sigma_{ij,i} &= 0, \\ D_{i,i} &= 0, \\ B_{i,i} &= 0. \end{aligned} \tag{4}$$

In those equations, u_i is elastic displacement, ϕ and ψ are electric and magnetic potential, respectively, and subscript comma is used to denote partial differentiation with respect to x_i.

For conciseness, we generalize a notation introduced by Barnett and Lothe [25] for piezoelectricity, where both upper and lower case subscripts are used. Upper case subscript ranges from 1 to 5 and lower case subscript ranges from 1 to 3. Repeated subscripts are summed. As a result, the constitutive, gradient, and equilibrium equations can be rewritten as

$$\Sigma_{iJ} = L_{iJKl} Z_{Kl}, \quad Z_{Kl} = U_{K,l}, \quad \Sigma_{iJ,i} = 0, \tag{5}$$

with the field variables given by

$$\Sigma_{iJ} = \begin{cases} \sigma_{ij}, \\ D_i, \\ B_i, \end{cases} \quad Z_{Ji} = \begin{cases} \varepsilon_{ij}, \\ -E_i, \\ -H_i, \end{cases} \quad U_J = \begin{cases} u_j, & J = 1,2,3, \\ \phi, & J = 4, \\ \psi, & J = 5 \end{cases}$$

and constitutive moduli given by

$$L_{iJKl} = \begin{cases} C_{ijkl}, & J,K = 1,2,3, \\ e_{ijl}, & K = 4,\ J = 1,2,3, \\ q_{ijl}, & K = 5,\ J = 1,2,3, \\ e_{ikl}, & J = 4,\ K = 1,2,3, \\ -\kappa_{il}, & J = 4,\ K = 4, \\ -a_{il}, & J = 4,\ K = 5, \\ q_{ikl}, & J = 5,\ K = 1,2,3, \\ -a_{il}, & J = 5,\ K = 4, \\ -\mu_{il}, & J = 5,\ K = 5. \end{cases} \tag{6}$$

$$\mathbf{T}^{-1} = \begin{bmatrix} \cos\psi\cos\theta\cos\phi - \sin\psi\sin\phi & \sin\psi\cos\theta\cos\phi + \cos\psi\sin\phi & -\sin\theta\cos\phi \\ -\cos\psi\cos\theta\sin\phi - \sin\psi\cos\phi & -\sin\phi\cos\theta\sin\phi + \cos\psi\cos\phi & \sin\theta\sin\phi \\ \cos\psi\sin\theta & \sin\psi\sin\theta & \cos\theta \end{bmatrix}.$$

When the standard matrix notation for tensors is adopted [26], the constitutive equation can be written as

$$\mathbf{\Sigma} = \mathbf{LZ}, \tag{7}$$

with

$$\mathbf{\Sigma} = \begin{bmatrix} \boldsymbol{\sigma} \\ \mathbf{D} \\ \mathbf{B} \end{bmatrix}, \quad \mathbf{Z} = \begin{bmatrix} \boldsymbol{\varepsilon} \\ -\mathbf{E} \\ -\mathbf{H} \end{bmatrix}, \quad \mathbf{L} = \begin{bmatrix} \mathbf{C} & \mathbf{e} & \mathbf{q} \\ \mathbf{e}^{t} & -\boldsymbol{\kappa} & -\mathbf{a} \\ \mathbf{q}^{t} & -\mathbf{a}^{t} & -\boldsymbol{\mu} \end{bmatrix}, \tag{8}$$

where superscript t is used to denote the matrix transpose.

3. Polycrystalline multiferroic composites

3.1. Orientation distribution function and orientational averaging

We now consider a multiferroic composite consisting of several phases, where the particles of each phase have identical shape, but may have certain orientation distributions. As such, two different kinds of coordinate systems have to be established, one is global fixed on the composite, and the other is local fixed on particles of different orientations. The orientations of different particles can then be described by three Euler angles (θ, ψ, ϕ) [27]. Due to the anisotropy of material properties, particles of different orientations will have different constitutive moduli in the global coordinate system, and as a result, the constitutive equation for a particle of phase r at orientation (θ, ψ, ϕ) is given by

$$\mathbf{\Sigma}_r(\theta, \psi, \phi) = \mathbf{L}_r(\theta, \psi, \phi)\mathbf{Z}_r(\theta, \psi, \phi) \tag{9}$$

in the global coordinate system, where $\mathbf{L}_r(\theta, \psi, \phi)$ can be obtained from their principal values in local coordinate using transformation rules for second, third, and fourth rank tensors,

$$a_{ij}(\theta, \psi, \phi) = T_{ik}T_{jl}a_{kl}, \quad e_{ijk}(\theta, \psi, \phi) = T_{il}T_{jm}T_{kn}e_{lmn}, \quad C_{ijkl}(\theta, \psi, \phi) = T_{im}T_{jn}T_{ko}T_{lp}C_{mnop}, \tag{10}$$

with

We are interested in determining the macroscopic properties of the multiferroic composites in terms of their microstructures, which requires the evaluation of an averaging field in the composite. Due to the polycrystalline microstructure we are considering, the averaging has to be carried out in two steps. First, for each phase r, we have to carry out orientational averaging, which averages a physical quantity over particles of phase r at all orientations. We then average the orientationally averaged quantity over all phases. For example, in order to average a physical variable H in the composite, we first average $H_r(\theta, \psi, \phi)$ over all orientations,

$$\langle H_r(\theta, \psi, \phi) \rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} H_r(\theta, \psi, \phi) W_r(\theta, \psi, \phi) \times \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\psi \, \mathrm{d}\phi, \tag{11}$$

where $\langle \cdot \rangle$ is used to denote orientational averaging, and $W_r(\theta, \psi, \phi)$ is the orientation distribution function (ODF) for phase r, which gives the probability of locating a particle of phase r at orientation (θ, ψ, ϕ). After the orientational averaging for each phase is carried out, the volume averaging over all phases will be performed, resulting in

$$\bar{H} = \sum_{r=1}^{N} f_r \langle H_r(\theta, \psi, \phi) \rangle, \tag{12}$$

where overhead bar is used to denote the averaging quantity in the composite, f_r is the volume fraction of phase r, and N is the number of phase in the composite.

In this work, we adopt a Gaussian distribution function for ODF,

$$W_r(\theta,\psi,\phi) = \frac{1}{\mu_r\sqrt{2\pi}} e^{-\frac{\theta^2}{2\mu_r^2}}, \tag{13}$$

which can be used to approximate a wide range of textures by varying μ_r. For example, the random orientation distribution of particles, where $W_r(\theta,\psi,\phi) = 1$, can be obtained by letting $\mu_r \to \infty$, while the aligned distribution of particles, where $W_r(\theta,\psi,\phi) = \delta(\theta)$, can be obtained by letting $\mu_r \to 0$. Thus μ_r can be adjusted for different ODFs and will be called the texture coefficient here. In addition, the orientational averaging is difficult to evaluate analytically in general, and we adopt Gaussian quadrature method for numerical integration, in which the integration is approximated by the sum of the value of its integrand at a set of points called abscissa, multiplied by weighting coefficient w_{ijk},

$$\langle H_r(\theta,\psi,\phi)\rangle = \sum_{i=1}^{I}\sum_{j=1}^{J}\sum_{k=1}^{K} \sin\theta_i H_r(\theta_i,\psi_j,\phi_k) W_r(\theta_i,\psi_j,\phi_k) w_{ijk}. \tag{14}$$

Similar techniques have been applied to study the effective pyroelectric coefficients of ferroelectric ceramics and electrostrictive coefficients of polymeric composites [28,29].

3.2. The effective magnetoelectroelastic moduli and self-consistent approach

With such an averaging technique in mind, we propose that the behavior of the multiferroic composites with macroscopic homogeneity is governed by the effective constitutive equation

$$\bar{\mathbf{\Sigma}} = \mathbf{L}^*\bar{\mathbf{Z}}, \tag{15}$$

where $\mathbf{L}^*$ is the effective magnetoelectroelastic moduli of the composite. Due to the linearity, we have

$$\mathbf{Z}_r(\theta,\psi,\phi) = \mathbf{A}_r(\theta,\psi,\phi)\bar{\mathbf{Z}}, \tag{16}$$

where $\mathbf{A}_r(\theta,\psi,\phi)$ is the concentration factor of particle of phase r at orientation (θ,ψ,ϕ), satisfying

$$\bar{\mathbf{A}} = \mathbf{I}, \tag{17}$$

where $\mathbf{I}$ is a 12×12 unit matrix. As a result, we have

$$\mathbf{L}^* = \sum_{r=1}^{N} f_r\langle \mathbf{L}_r(\theta,\psi,\phi)\mathbf{A}_r(\theta,\psi,\phi)\rangle, \tag{18}$$

from which the effective moduli can be determined for a N-phase composite, if the concentration factor is known. For a two-phase composite, it is simplified as

$$\mathbf{L}^* = f_1\langle \mathbf{L}_1(\theta,\psi,\phi)\mathbf{A}_1(\theta,\psi,\phi)\rangle + f_2\langle \mathbf{L}_2(\theta,\psi,\phi)\mathbf{A}_2(\theta,\psi,\phi)\rangle. \tag{19}$$

In order to determine the effective magnetoelectroelastic moduli of multiferroic composite, approximation must be made regarding the distribution of magnetoelectroelastic field in the composite. We turn to a micromechanical model for this purpose. For elastic or piezoelectric polycrystalline materials, the self-consistent approach is very successful in predicting the effective elastic, piezoelectric, and dielectric moduli of polycrystals [30,31]. However, such a model has only been developed for single phase polycrystalline materials. We intend to address this by extending the effective medium approximation in the self-consistent approach to multiphase polycrystalline multiferroic composites. In particular, we assume that the average field in a particle of phase r at orientation (θ,ψ,ϕ) is equivalent to a single particle embedded in an effective medium with yet unknown magnetoelectroelastic moduli $\mathbf{L}^*$, subjected to yet unknown average field $\mathbf{Z}^0$. Such an inclusion problem in magnetoelectroelastic media has been solved by Li and Dunn [32], with

$$\mathbf{Z}_r(\theta,\psi,\phi) = \mathbf{A}^{\text{dil}}(\theta,\psi,\phi)\mathbf{Z}^0, \tag{20}$$

where the dilute concentration factor is given by

$$\mathbf{A}_r^{\text{dil}}(\theta,\psi,\phi) = \{\mathbf{I} + \mathbf{S}_r(\theta,\psi,\phi)\mathbf{L}^{*-1}[\mathbf{L}_r(\theta,\psi,\phi) - \mathbf{L}^*]\}^{-1}, \tag{21}$$

where $\mathbf{S}_r$ is the magnetoelectroelastic Eshelby tensor for phase r [32,33], which is a function of the yet unknown magnetoelectroelastic moduli of the effective media, and the shape and orientation of phase r, and superscript -1 is used to denote the matrix inverse. It is well known that when the particle shape is ellipsoidal, the field within the single particle is uniform, which can be evaluated using Eshelby tensor. For fibrous or penny shape particles, the closed form expressions for magnetoelectroelastic Eshelby tensor were derived by Li and Dunn [32]. For more general shapes, a numerical algorithm for the evaluation of Eshelby tensor was given by Li [34]. Since the average field is $\bar{\mathbf{Z}}$, the unknown field $\mathbf{Z}^0$ can be determined as

$$\mathbf{Z}^0 = \left[\sum_{i=1}^{N} f_i\langle \mathbf{A}_i^{\text{dil}}(\theta,\psi,\phi)\rangle\right]^{-1}\bar{\mathbf{Z}}, \tag{22}$$

resulting in the following concentration factor for particle of phase r at orientation (θ,ψ,ϕ),

$$\mathbf{A}_r(\theta,\psi,\phi) = \mathbf{A}_r^{\text{dil}}(\theta,\psi,\phi)\left[\sum_{i=1}^{N} f_i\langle \mathbf{A}_i^{\text{dil}}(\theta,\psi,\phi)\rangle\right]^{-1}. \tag{23}$$

Combining Eqs. (23) and (19), we then have an equation for the effective moduli of the composite. However, it is noted that the Eshelby tensor $\mathbf{S}_r$ that is required for the evaluation of $\mathbf{A}_r$ depends on the yet unknown effective moduli **L***, and thus in general Eq. (19) has to be solved numerically by iteration. We also emphasize that this effective medium approximation does not assume the existence of a matrix, and thus is ideal for multi-phase polycrystalline composites.

It is also worthwhile to comment on Eq. (20), where an unknown field $\mathbf{Z}^0$ rather than the average field $\bar{\mathbf{Z}}$ is used. This corresponds to the normalization given in Eq. (22), which is necessary to ensure that the field averaging over particles at all orientations equals the average field $\bar{\mathbf{Z}}$ in the composite.

4. Numerical results and discussions

We have implemented the self-consistent model in a FORTRAN code, which has been validated by comparing with previously published results under several special conditions. The code was applied to calculate the effective magnetoelectroelastic moduli of a multiferroic composite consisting of piezoelectric PZT-5H and piezomagnetic $CoFe_2O_4$ with different volume fractions, texture coefficients, and shapes of both phases. In particular, we assume the particles to be spheroidal, with $\alpha = \frac{A_1}{A_3} = \frac{A_2}{A_3}$, where A_i are the dimensions of the spheroids. The constitutive moduli of both phases are listed in Table 1, which were obtained from Huang and Kuo [35,36], with the exception that the magnetic permeability μ_{11} of $CoFe_2O_4$ is taken to be the same as μ_{33}.

We first consider that particles of both phases are spherical with three different texture coefficients: $\mu = 0.01$ where particles are approximately aligned, $\mu = 10$ where particles are nearly randomly oriented, and $\mu = 1$ where particles are neither aligned nor randomly oriented. The ME coefficients a_{11} and a_{33} as a function of volume fraction of PZT-5H are shown in Fig. 1, and the ME coupling factors k_{11} and k_{33} are shown in Fig. 2. It is observed that the highest ME coefficients and coupling factors occur around volume fraction of 50%, as we mentioned earlier. At this volume fraction, Mori–Tanaka mean field approach might not be applicable, since there may not be a matrix phase. In such a case, the self-consistent effective medium approach is ideal. In addition, for aligned particles, a_{11} is negative while a_{33} is positive, with the magnitude of a_{11} much larger. This is because the piezoelectric coefficients e_{31} and e_{33} of PZT-5H have opposite signs and the piezomagnetic coefficients q_{31} and q_{33} of $CoFe_2O_4$ have the same sign, and thus lead to offset in interaction when

Table 1
Constitutive moduli of PZT-5H and $CoFe_2O_4$ [35,36]

	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)
PZT-5H	126	55	53	117	35.3
$CoFe_2O_4$	286	173	170	269.5	45.3
	e_{15} (C/m^2)	e_{31} (C/m^2)	e_{33} (C/m^2)	κ_{11} ($C^2/N\,m^2$)	κ_{33} ($C^2/N\,m^2$)
PZT-5H	17.0	−6.5	23.3	15.1×10^{-9}	13.0×10^{-9}
$CoFe_2O_4$	0	0	0	0.08×10^{-9}	0.093×10^{-9}
	q_{15} (m/A)	q_{31} (m/A)	q_{33} (m/A)	μ_{11} ($N\,s^2/C^2$)	μ_{33} ($N\,s^2/C^2$)
PZT-5H	0	0	0	5×10^{-6}	5×10^{-6}
$CoFe_2O_4$	550	580.3	699.7	157×10^{-6}	157×10^{-6}

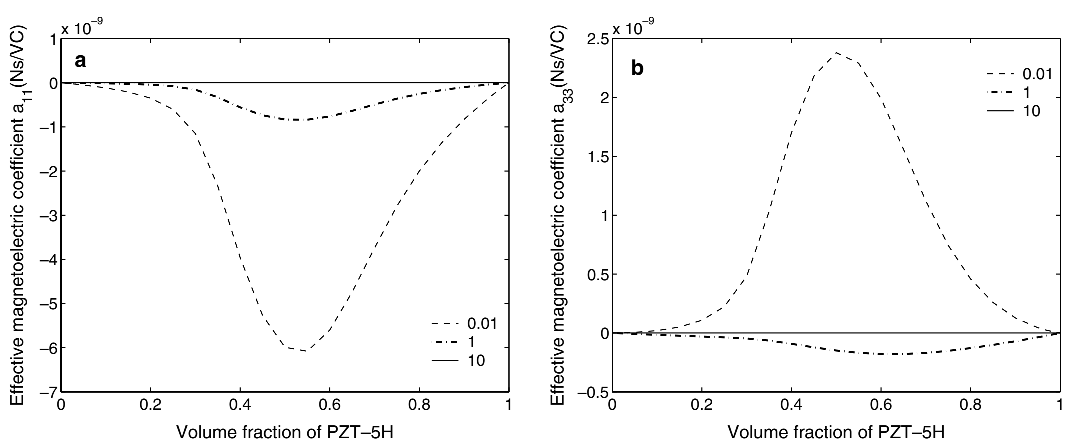

Fig. 1. The effective magnetoelectric coefficients as a function of volume fraction of spherical PZT-5H particles at different texture coefficients: (a) a_{11} and (b) a_{33}.

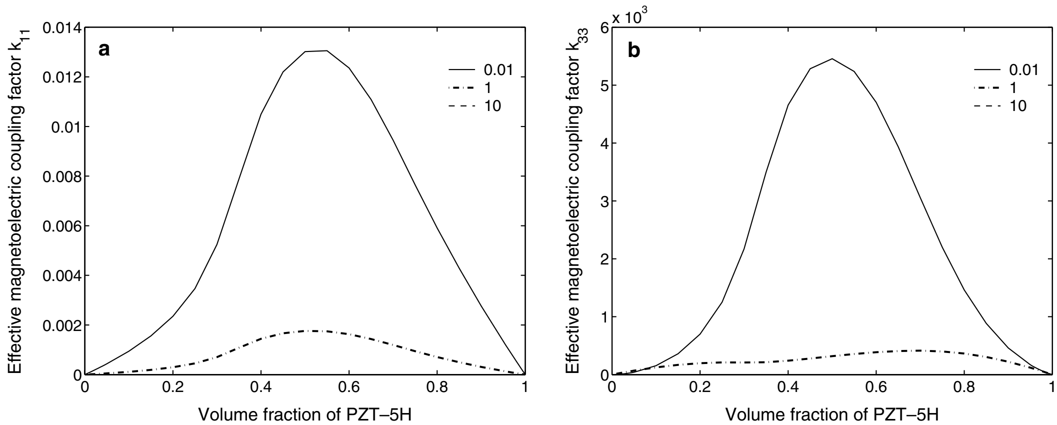

Fig. 2. The effective magnetoelectric coupling factors as a function of volume fraction of spherical PZT-5H particles at different texture coefficients: (a) k_{11} and (b) k_{33}.

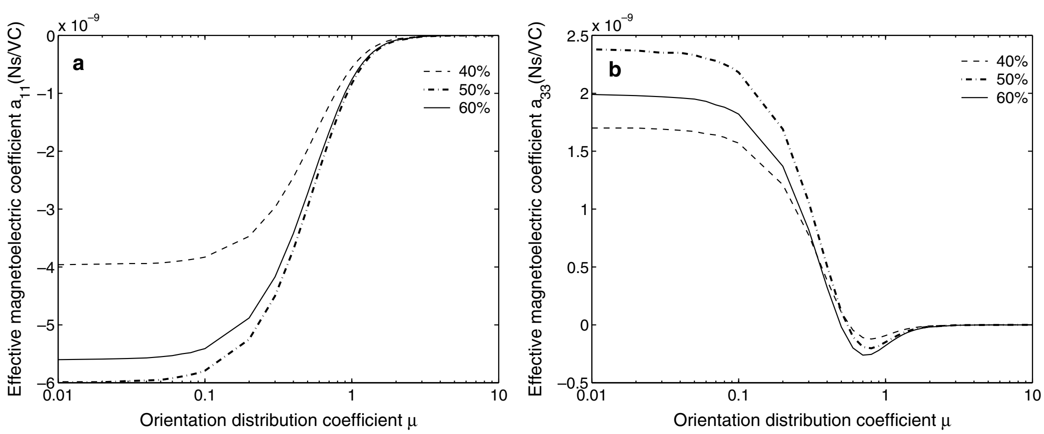

Fig. 3. The effective magnetoelectric coefficients as a function of texture coefficient of spherical particles at different volume fractions: (a) a_{11} and (b) a_{33}.

electric field E_3 or magnetic field H_3 is applied to composite. When particles are not aligned, a_{11} and a_{33} are more or less averaged, resulting in negative a_{33} as shown in Fig. 1(b).

We also notice that the aligned particles produce highest ME coefficients and coupling factors, while composites with randomly oriented particles show virtually no ME coupling. To demonstrate this, we calculated the ME coefficients as a function of texture coefficient μ at three different volume fraction close to 50%, shown in Fig. 3. Clearly, both a_{11} and a_{33} are highest when the particles are aligned, and are essentially zero when they are randomly oriented. We point out that although **a** is an even rank tensor, it is still zero when the composite is central symmetric, since it is induced by the interactions between piezoelectric and piezomagnetic effects; both are odd rank tensorial properties and thus require the lack of central symmetry. We also notice that there is a well for a_{33} near $\mu = 1$, which is consistent with the peak in e_{33} and well in e_{31} in single phase piezoelectric ceramics [31].

From these calculations, it is clear that the orientation distributions of particles play a very important role in the ME coefficients of the composite. This may explain the large discrepancy between experimental measurement and previous theoretical calculations for

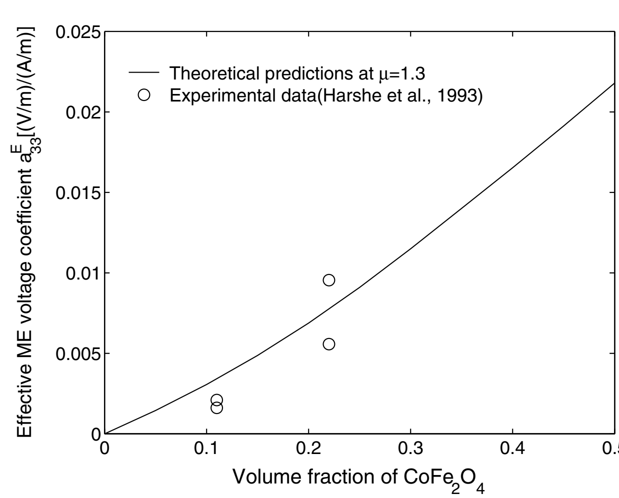

Fig. 4. The effective magnetoelectric voltage coefficient of particulate composites as a function of volume fraction of $CoFe_2O_4$; the experimental data are obtained from [10].

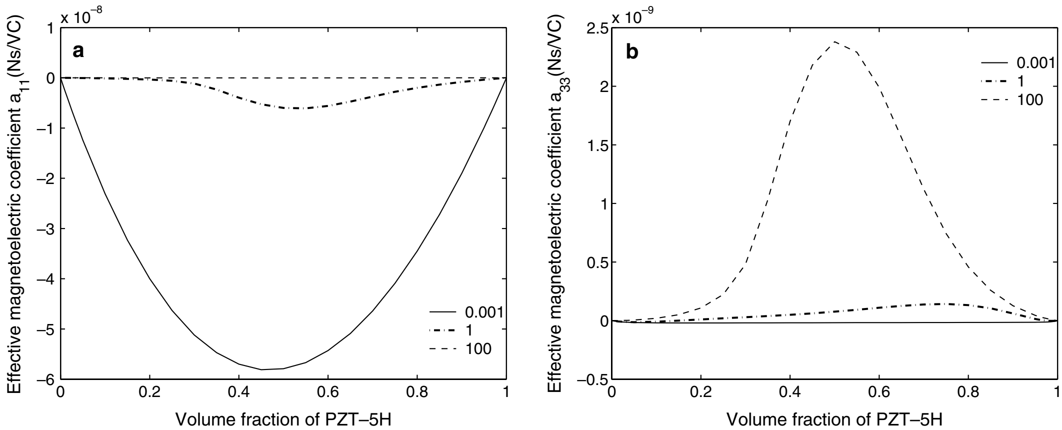

Fig. 5. The effective magnetoelectric coefficients as a function of volume fraction of aligned PZT-5H particles at different shapes: (a) a_{11} and (b) a_{33}.

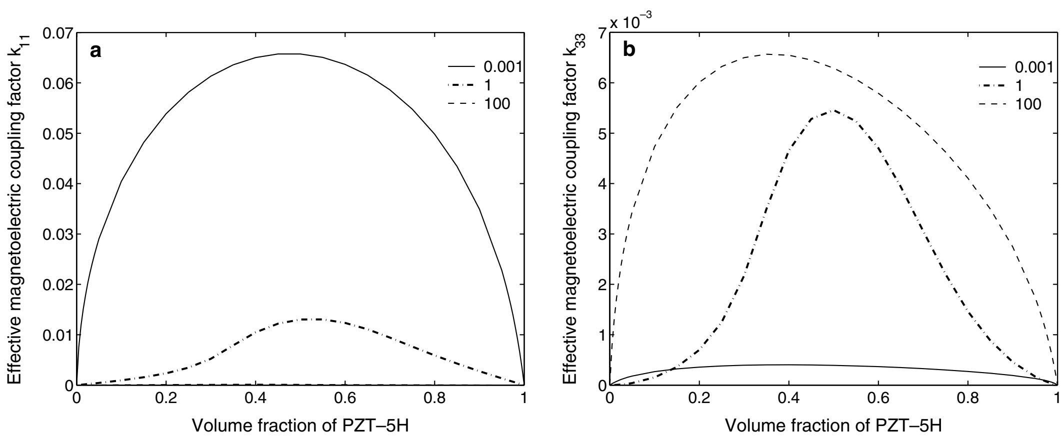

Fig. 6. The effective magnetoelectric coupling factors as a function of volume fraction of aligned PZT-5H particles having different aspect ratios: (a) k_{11} and (b) k_{33}.

particulate composites, where particles were assumed to be aligned in the calculations, which is not very realistic. To demonstrate this, we calculated the ME voltage coefficient [10] $a_{33}^E = -\frac{a_{33}}{\kappa_{33}}$ as a function of volume fraction of $CoFe_2O_4$ for a particulate composite consisting of $CoFe_2O_4$ and $BaTiO_3$; the texture coefficient μ is set to be 1.3. Good agreement with experimental data has been observed as shown in Fig. 4.

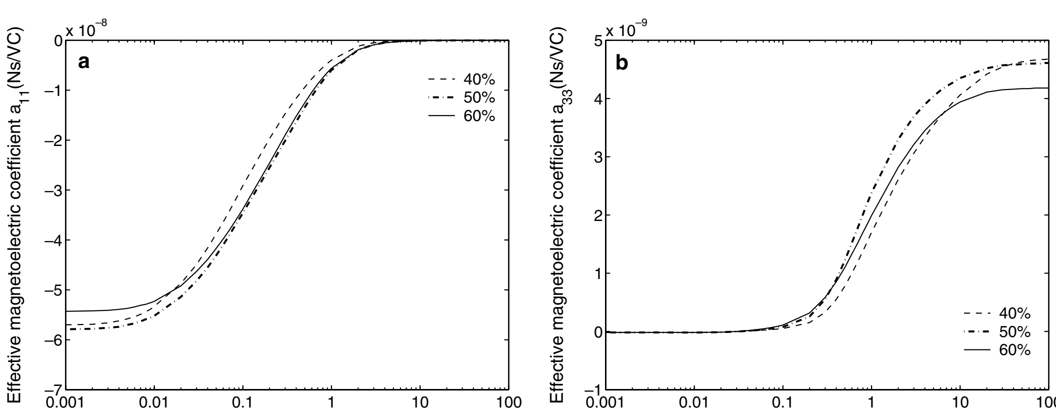

Fig. 7. The effective magnetoelectric coefficients as a function of aspect ratio of aligned PZT-5H particles at different volume fractions: (a) a_{11} and (b) a_{33}.

We then focus on composites with aligned particles since they produce the highest ME coefficients and coupling factors. The ME coefficients and coupling factors as a function of volume fraction of PZT-5H are shown in Figs. 5 and 6 for composites with aligned particles of three different aspect ratios, $\alpha = 0.001$ that is lamellar, $\alpha = 1$ that is spherical, and $\alpha = 100$ that is fibrous. Again, both ME coefficients and coupling factors are highest around a volume fraction of 50%. In addition, lamellar particles lead to highest a_{11} since they maximize the interactions along the x_1 and x_2 directions, while fibrous particles lead to highest a_{33} since they maximize interactions along the x_3 directions. To demonstrate the effect of particle shapes, we calculate the ME coefficients as function of particle aspect ratio α for composites with aligned particles, shown in Fig. 7, and it is observed that a_{11} decreases with the increment of aspect ratio of particles, while a_{33} increases with it.

In summary, we developed a self-consistent approach for multiferroic composites that is particularly suitable for polycrystalline type of microstructure where there is no matrix phase existing. The effects of shape, orientation distribution, and volume fraction of both phases are considered, and good agreement with experimental data is observed.

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