

Dielectric, ferroelectric, magnetic, and magnetoelectric properties of multiferroic laminated composites

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Multiferroic laminated composites consisting of lead-zirconate titanate (PZT)/polyvinylidene-fluoride (PVDF) particulate composite layers and Tb-Dy-Fe alloy (Terfenol-D)/PVDF particulate composite layers, prepared by a simple hot-molding technique, were reported. In the laminated composites, the polymer PVDF is inert and used just as a binder. The measured dielectric, ferroelectric, magnetic, and magnetoelectric properties demonstrate strong dependence on volume fraction f of the PVDF in the laminated composites. As f is low (e.g., $f < 0.3$), a low concentration of binder leads to low quality of the composites and thus low performance. Better performance of the composites appears in the intermediate f range. As f further increases, high concentration of the inert PVDF results in weak dielectric, magnetostrictive, piezo- and magnetoelectric responses of the laminated composites. Our results illustrate that the three-phase laminated composites exhibit remarkable magnetoelectric effect especially at high frequency at which the electromechanical resonance appears.

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I. INTRODUCTION

Multiferroic materials made by combining ferroelectric and ferromagnetic substances together have drawn significant interest in recent years due to their multifunctionality, in which the coupling interaction between ferroelectric and ferromagnetic substances could produce an interesting effect.¹ These multiferroic materials provide opportunities for potential applications as transducers, actuators, and sensors. The first kinds of such multiferroic composites are ferrite/piezoelectric ceramic composites, such as $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ 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) on 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 That is, when a magnetic field is applied to the composites, the ferrite particles change their shape magnetostrictively, and the strain is passed along to the piezoelectric phase, resulting in an electric polarization. What is more important is that the ME_H response of these multiferroic ceramic composites is larger than that observed in ME crystal families³ currently available (e.g., antiferromagnetic Cr_2O_3 ,⁴ yttrium iron garnets, boracites, rare-earth ferrites, and phosphates).²

Recently, we have calculated the ME properties of the composites containing a giant magnetostrictive rare-earth-iron alloy [e.g., SmFe_2 , TbFe_2 , or $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$ (Terfenol-D) which is the most widely used magnetostrictive alloy⁵] by developing the Green's-function technique,⁶⁻⁸ and predicted that both particulate composites with Terfenol-D embedded in a piezoelectric polymer matrix such as poly(vi-

nylidene fluoride-trifluoroethylene) copolymer [P(VDF-TrFE)] or piezoelectric ceramic matrix such as PZT and the laminated composites of Terfenol-D/P(VDF-TrFE) or Terfenol-D/PZT can exhibit a giant magnetoelectric (GME) effect which is markedly larger than that in the best known 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 together the PZT and Terfenol-D disks with silver epoxy¹⁰ and laminated Terfenol-D/PVDF composite made by gluing the polarized PVDF film on Terfenol-D disks with conductive epoxy¹¹ have been most recently found to exhibit such a GME sensitivity as predicted, which potentially makes such multiferroic composites particularly attractive for technological applications. The ME response of the laminated composites is strongly dependent on the interfacial bonding between two layers by gluing together. Among the multiferroic composites found so far, Terfenol-D/PZT and Terfenol-D/P(VDF-TrFE) (or PVDF) possess the highest ME sensitivity. However, the Terfenol-D/PZT cermet is very brittle and it is hard to prepare the Terfenol-D/PZT composite by a conventional sintering method. On the other hand, for the Terfenol-D/P(VDF-TrFE) composite, P(VDF-TrFE) is expensive and it is hard to polarize the Terfenol-D/P(VDF-TrFE) composite. Furthermore, there is a high eddy current loss in conductive Terfenol-D disk stucked above ~ 1 kHz. To overcome these difficulties, we develop three-phase composites of Terfenol-D/PZT/PVDF because of their low eddy current loss in the high-frequency range and toughness.¹²

In the three-phase Terfenol-D/PZT/PVDF particulate composites recently developed,¹² the volume fraction of Terfenol-D particles allowed in the composites is quite low, e.g., less than 0.08, due to the percolation effect, which greatly limits ME response of the composites. To eliminate this limitation, in the present work, we report a different class of multiferroic, laminated composites of Terfenol-D/PVDF and PZT/PVDF, which is simply a combination of

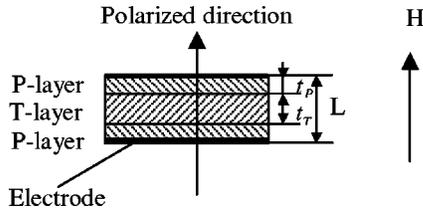


FIG. 1. Schematic illustration of the laminated P-T-P composites with $t_p/t_r/t_p = 1/1.5/1$.

Terfenol-D and PZT particles embedded in a PVDF matrix by laminating the Terfenol-D/PVDF and the PZT/PVDF particulate composite layers and then simply hot pressing these layers together. The motivation is to investigate the overall dielectric-magnetic properties of such a laminated composite prepared via a simple, common hot-pressing procedure which ensures a good interfacial bonding between composite layers. In the laminated composites, the PVDF polymer is used just as a matrix binder and thus can be replaced by other polymers. The coupling interaction between magnetostriction of the Terfenol-D/PVDF composite layer and piezoelectricity of the PZT/PVDF composite layer can also result in an extrinsic ME effect.

II. EXPERIMENT

As for magnetostrictive material in our multiferroic composites, high magnetostriction under a low magnetic-field bias is preferred. Thus Terfenol-D alloy was employed as the

magnetostrictive phase for the composites, since Terfenol-D is the currently best known and most widely used magnetostrictive alloy.⁵ The Terfenol-D powder with particle size of about 50 μm was obtained by crushing bulk $\text{Tb}_{0.28}\text{Dy}_{0.72}\text{Fe}_2$ single crystal in an argon atmosphere. As for the piezoelectric phase, PZT synthesized by a conventional solid-state procedure was chosen due to its high piezoelectricity. The mean particle size of PZT powder is about 6 μm . PVDF was employed as a binder to bind these two components.

PZT or Terfenol-D powders were first mixed with PVDF to get PZT/*f*PVDF or Terfenol-D/*f*PVDF mixtures, respectively, where *f* denotes the volume fraction of the PVDF. These mixed powders were then set in a mold by turns of PZT/*f*PVDF (denoted as P layer), Terfenol-D/*f*PVDF (denoted as T layer) and PZT/*f*PVDF (P layer). The sample pallets with 15 mm in diameter and about 2 mm in thickness as shown in Fig. 1 were obtained by hot pressing the three laminated layers of mixtures at 180 °C and 10 MPa for 30 min. The laminated composite has a sandwich structure of P-layer/T-layer/P-layer (abbreviated as the P-T-P composite below). Figure 2 shows a typical micrograph of the fractured surface of the P-T-P composite with $f = 0.4$, which was examined by scanning electron microscopy. There are no obvious interfaces between these three layers [Fig. 2(a)], and a good interface bonding [Fig. 2(b)] between the P layer and the T layer forms by this hot pressing procedure. In the P layer [Fig. 2(c)], small PZT particles and their clusters are surrounded by the PVDF matrix and are bonded with the PVDF. In the T layer [Fig. 2(d)], large and irregular

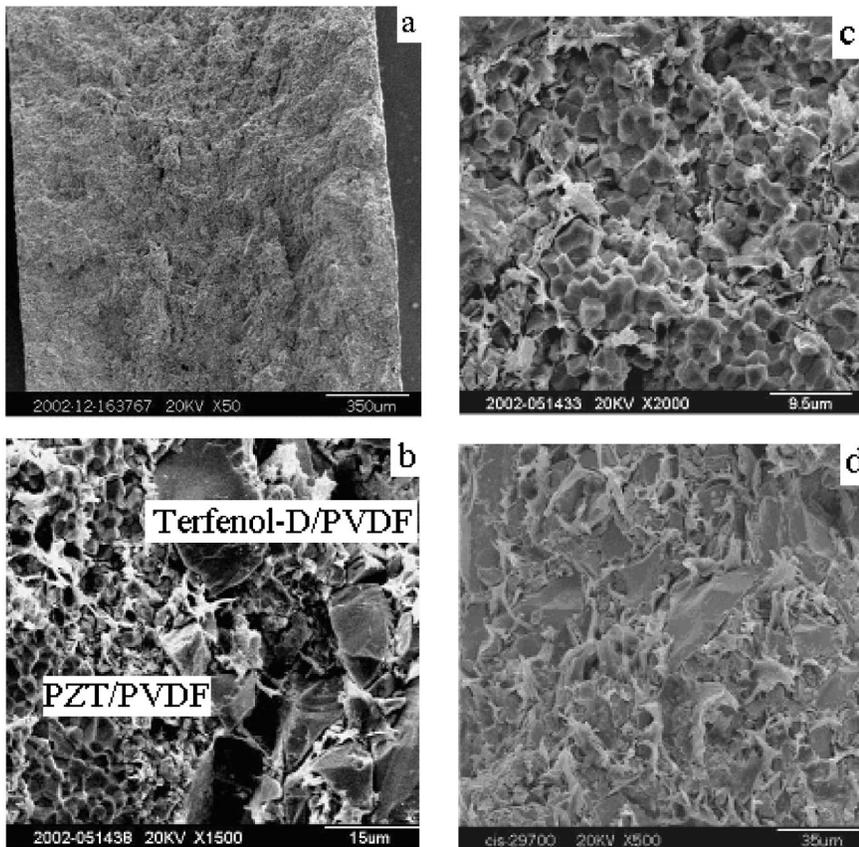


FIG. 2. A typical micrograph of the fractured surface of the P-T-P composite with $f = 0.4$: (a) sandwiched P-T-P structure, (b) interface between two layers, (c) the P layer, and (d) the T layer.

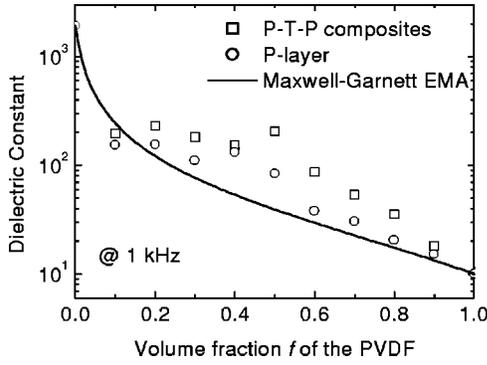


FIG. 3. Dielectric constants of the laminated P-T-P composites and PZT/*f*PVDF particulate composites (i.e., the P-layer) as a function of the volume fraction *f* of the PVDF. The solid line is the calculated dielectric constant of the PZT/*f*PVDF composites by using Maxwell-Garnett EMA.

Terfenol-D particles are also randomly bonded with the PVDF.

In order to perform the electrical measurements, the samples were polished, and electroded by silver paint (Fig. 1). Then the samples were electrically polarized in silicon oil under a poling field of about 3 kV/mm and at poling temperature of 70 °C. Dielectric properties were measured by using a HP4194A impedance analyzer. The piezoelectric constant was measured by a standard piezo d_{33} meter. Polarization hysteresis loops were measured by Radiant RT 6000 (American Radiant Co.). Magnetic hysteresis was measured by VSM-7307 (American Lakeshore Co.). Magnetostriction measures were performed by the standard strain-gauge technique. Metal strain gauges with a maximum measurement up to 5% and the highly elastic epoxy resin were utilized to ensure measurement reliability and avoid gauge debonding.

The ME response was measured in terms of the variation of the ME coefficient as a function of dc magnetic field. An electromagnet was used for generating the dc magnetic field up to 0.4 T (4 kOe). The ac magnetic field of about 2 Oe was applied superimposed on the dc magnetic field, both parallel to the sample thickness axis. A signal generator was used to drive the Helmholtz coils and generate the ac magnetic field with frequency varying from 100 to 2×10^5 Hz. The measured voltage represents the electric charge from the piezoelectric layers under a short-circuit condition. The output voltage was obtained from the charge Q and the capacitance C of the composite by using $V = Q/C$. The output voltage divided by the sample thickness and the ac magnetic field gave the ME response, $\alpha_{E33} = dE_3/dH_3$ (i.e., the ME_H sensitivity), of the composites. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSIONS

A. Dielectric properties

Figure 3 illustrates the dielectric constant of the laminated P-T-P composites. For such a laminated composite, the impedance Z can be expressed by using the series-mixture rule as

$$Z = 2Z_P + Z_T, \quad (1)$$

where Z_P and Z_T are the impedances of the P layer and the T layer, respectively. Because Z_T of the T layer with conducting Terfenol-D particles is quite small in comparison with Z_P , the dielectric constant of the P-T-P composite can be simply expressed as

$$\epsilon_{eff} \approx \epsilon_p \frac{L}{2t_p}, \quad (2)$$

where ϵ_p is the dielectric constant of the P layer (PZT/PVDF composites), and $t_p/L = 2/7$ (see Fig. 1). For comparison, the measured dielectric constants for the PZT/*f*PVDF composites, i.e., the P layer, are also shown in Fig. 3. It is clear that both measured dielectric constants exhibit quite similar behavior, as described by Eq. (2). The dielectric constants decrease with increasing *f*, as expected.

For such a two-phase composite as the PZT/*f*PVDF composite, the effective dielectric constant can be well described by effective-medium approach (EMA).¹³ For illustration, the calculations are performed by using a simple Maxwell-Garnett EMA, i.e.,

$$\epsilon_p = \epsilon_m \frac{\epsilon_{PZT} + 2\epsilon_m + 2(1-f)(\epsilon_{PZT} - \epsilon_m)}{\epsilon_{PZT} + 2\epsilon_m - (1-f)(\epsilon_{PZT} - \epsilon_m)}, \quad (3)$$

with $\epsilon_{PZT} = 1900$ for the PZT and $\epsilon_m = 10$ for the PVDF matrix, respectively. The dielectric constant increases with the decrease in *f*, as shown in Fig. 3. In high *f* range, i.e., at low concentration of PZT, the measured dielectric constant of the PVDF matrix composites is in good agreement with Maxwell-Garnett model. In the intermediate *f* range, the dielectric constant measured is higher than the calculated, since high concentration of PZT particles become aggregated to form large clusters. But in the low *f* range, the dielectric constant of the composites does not further increase. This is because the high concentration of the PZT particles at low *f* makes it difficult to fabricate dense composite samples.

Figure 4 shows the frequency dependence of the dielectric constant and loss of the P-T-P composites. The dielectric constants are independent of frequency in the range of $10^2 - 10^6$ Hz. The dielectric loss has no big difference for different *f*. Above 10^6 Hz, there is a dielectric relaxation which is associated with the dielectric relaxation in the PZT.

B. Piezoelectric behavior

The polarization-field hysteresis loops of the P-T-P composites with various fractions of the PVDF are shown in Fig. 5. The loops show quite small remanence and saturation polarization in comparison with that for the PZT ceramic (see the inset in Fig. 5), which is due to the dilution effect of the inert PVDF matrix and the T layer.

Figure 6 shows the effective piezoelectric constant measured for the P-T-P composites. In the composites, the polymer PVDF is used just as a matrix binder. High concentration of the inert PVDF would lead to weak piezoelectric properties (see Fig. 6) because the higher concentration of PVDF must lead to lower concentration of PZT, and, on the

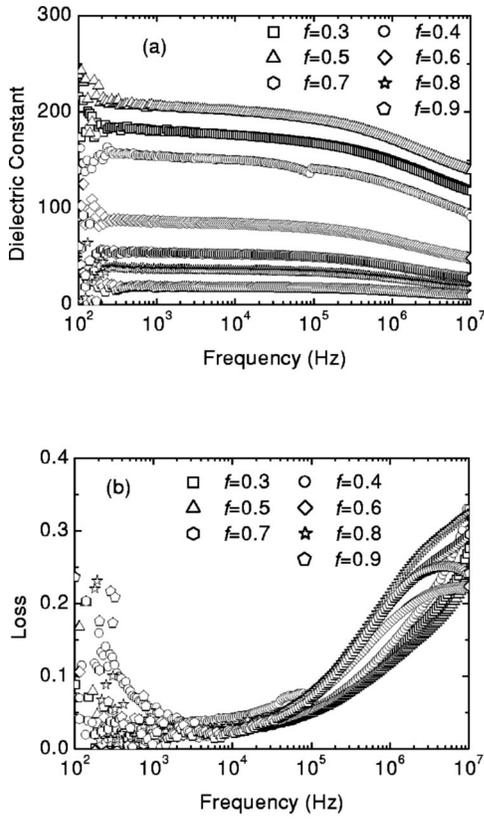


FIG. 4. Frequency dependence of (a) the dielectric constant and (b) dielectric loss for the laminated P-T-P composites at various fraction of the PVDF.

other hand, low volume fraction of PVDF would produce weak bonding in the composites. Thus there must be a intermediate f range where piezoelectric properties can be optimized. The measured piezoelectric constant in Fig. 6 illustrates such an optimized range around $f=0.5$.

C. Magnetic properties

Figure 7(a) shows the $M-H$ hysteresis loops measured for the Terfenol-D/ f PVDF particulate composites which

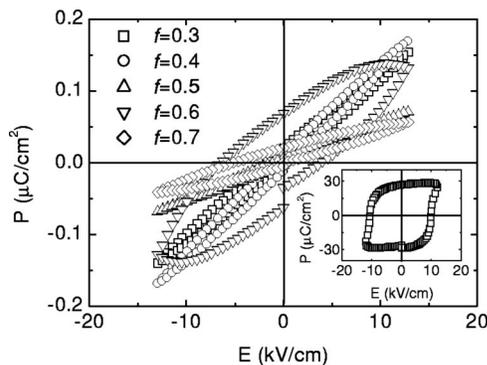


FIG. 5. Polarization-electrical field hysteresis of the laminated P-T-P composites. Shown in the inset is the hysteresis loop for the pure PZT ceramic.

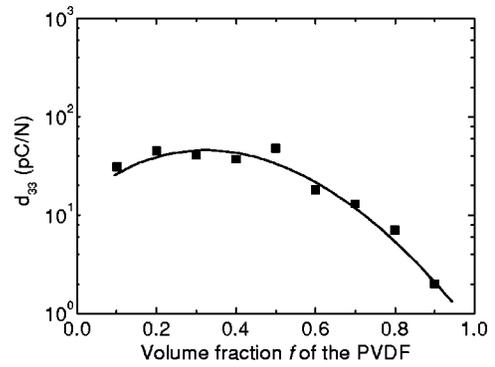


FIG. 6. The volume fraction dependence of the piezoelectric constant for the laminated P-T-P composites. The solid line is guide for the eye.

were used as the T layer in the P-T-P composites. Their loops are symmetrical and display small coercivity and remanence. From the initial magnetization slopes in Fig. 7(a), the initial permeability of the Terfenol-D/ f PVDF composites are obtained, as shown in Fig. 7(b). Also shown in Fig. 7(b) is the saturation magnetization. With decreasing f , i.e., increasing the concentration of the Terfenol-D, the saturation magnetization of the composites increases linearly. The initial permeability μ_i of the composites also increases about linearly with the increase in the volume fraction of the Terfenol-D.

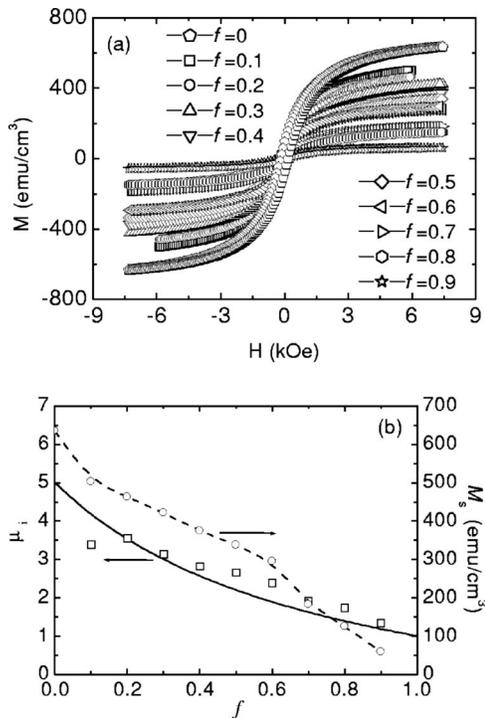


FIG. 7. (a) Magnetic hysteresis loops and (b) initial permeability μ_i and saturation magnetization M_s of the Terfenol-D/ f PVDF composites (i.e., T layer) with various fraction f of the PVDF. The data for $f=0$ were obtained by measuring the pure Terfenol-D powder. The dash line is guide for the eye. The solid line is the calculated μ_i from Eq. (4).

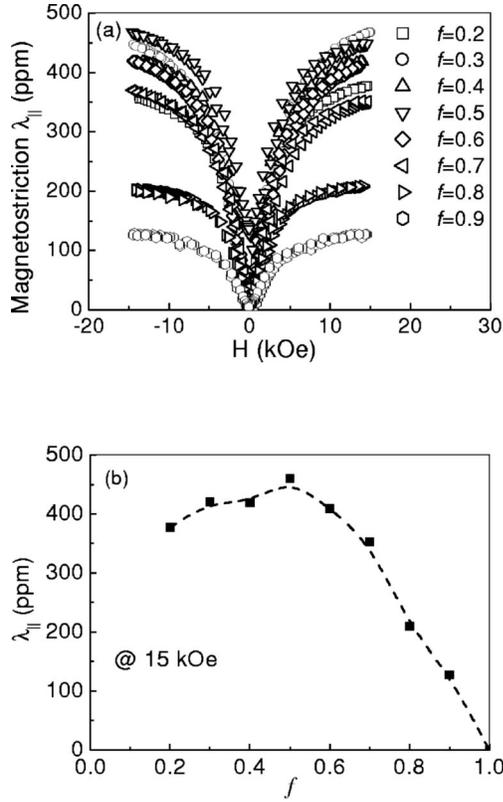


FIG. 8. The longitudinal magnetostriction $\lambda_{||}$ measured for the Terfenol-D/PVDF (T layer) composites as a function of (a) the applied magnetic field and (b) the volume fraction of the PVDF. The dash line is guide for the eye.

Similarly to the dielectric constant shown in Fig. 3, this dependence of μ_i on f can also be described by using a simple EMA similar to Eq. (3),¹³ i.e.,

$$\mu_i = \frac{\mu_o + 2 + 2(1-f)(\mu_o - 1)}{\mu_o + 2 - (1-f)(\mu_o - 1)}, \quad (4)$$

where $\mu_o = 5$ is the initial permeability of the Terfenol-D, and the initial permeability of the PVDF is taken as 1. The calculations [the solid line in Fig. 7(b)] from this simple EMA equation reasonably match the experimental μ_i data.

Figure 8 shows the longitudinal magnetostriction $\lambda_{||}$ measured for the Terfenol-D/ f PVDF composites. As expected, with the increase in the applied field, the magnetostriction increases sharply in low-field range of < 5 kOe. At high magnetic field range of > 5 kOe, $\lambda_{||}$ goes up steadily to approach its saturation, especially for $f = 0.8$ and 0.9 . The longitudinal maximum magnetostriction value of the composites is about 470 ppm at 15 kOe. Due to the dilution effect of the nonmagnetic phase PVDF, the magnetostriction of the composites is smaller than that of the Terfenol-D crystal under use. The magnetostriction of the composites is strongly dependent on the volume fraction of the PVDF binder in the composites [Fig. 8(b)]. Similarly to the variation of the pi-

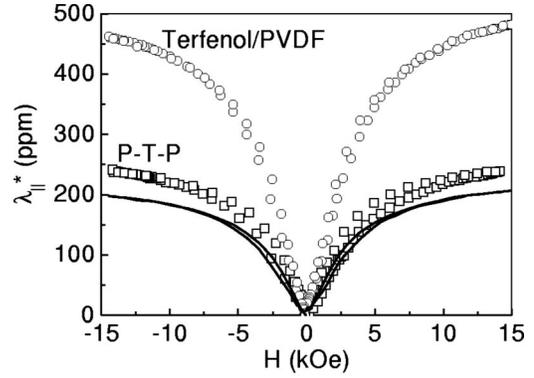


FIG. 9. Comparison between $\lambda_{||}$ for the Terfenol-D/0.5PVDF composite and the effective longitudinal magnetostriction $\lambda_{||}^*$ measured for the laminated P-T-P composite with $f = 0.5$. The solid line is the calculated $\lambda_{||}^*$ from Eq. (5).

ezoelectric constant shown in Fig. 6, there is an optimal range around $f = 0.5$ where the magnetostriction of the composites is maximum.

The effective magnetostriction of the P-T-P composites is further lower than that for the Terfenol-D/PVDF composites, since those two P layers are not magnetostrictive. Figure 9 shows such a comparison between $\lambda_{||}$ for the Terfenol-D/0.5PVDF composite and the effective longitudinal magnetostriction $\lambda_{||}^*$ measured for the P-T-P composite with $f = 0.5$. Because both the P layer and the T layer exhibit similar elastic properties, to the first-order approximation, $\lambda_{||}^*$ of the P-T-P composite can be simply expressed as⁸

$$\lambda_{||}^* \approx \lambda_{||} \frac{t_T}{L}, \quad (5)$$

where $t_T/L = 3/7$ (see Fig. 1). As can be seen in Fig. 9, the calculated $\lambda_{||}^*$ (the solid line in this figure) is in reasonable agreement with the experimental $\lambda_{||}^*$ values.

D. Magnetoelastic response

Figure 10 shows the ME_H sensitivity α_{E33} of the P-T-P composites. α_{E33} nonlinearly increases with bias field [Fig. 10(a)] due to the nonlinear dependence of the magnetostriction (see Figs. 8 and 9) on the applied magnetic field. In the high bias field range where the effective magnetostriction approaches its saturation, α_{E33} is expected to slightly change with the magnetic field. The behavior of the magnetic-field dependence of α_{E33} is similar to that for the magnetostrictive behavior, and Fig. 10(b) further illustrates $\alpha_{E33} \propto \lambda_{||}^*$, as predicted.⁹

The ME_H sensitivity strongly depends on f , as shown in Fig. 10(c). As $f < 0.3$, the low quality of the samples due to low concentration of the PVDF binder leads to the large loss of stress/strain transfer from the T layer to the P layer and thus low ME_H response. As $f > 0.5$, the ME_H sensitivity also declines with the increase in f . This decrease in α_{E33} is attributed to the decrease in piezoelectric phase and magnetostrictive phase concentrations, which lead to low magneto-

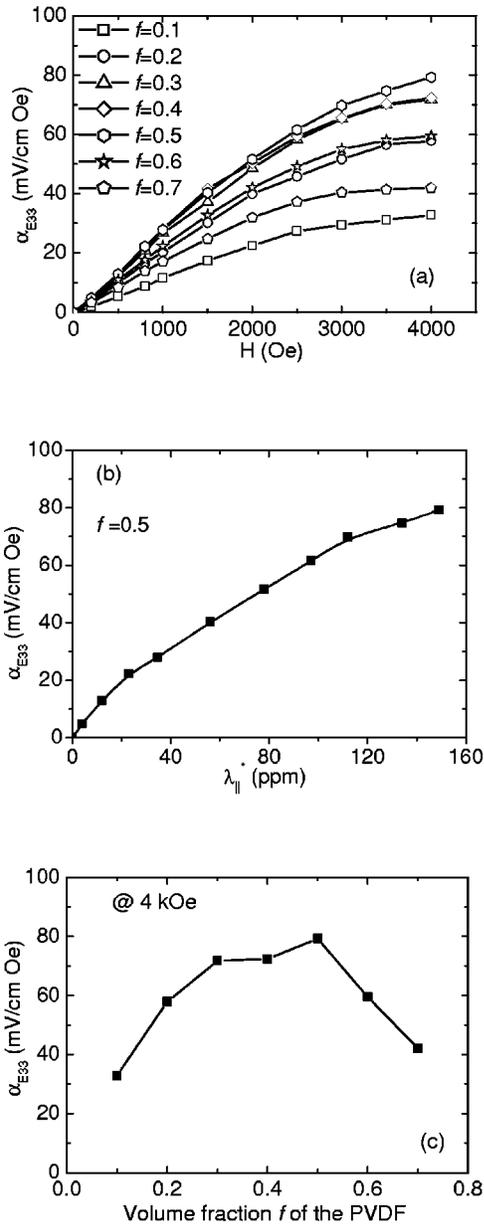


FIG. 10. The ME_H sensitivity α_{E33} measured for the laminated P-T-P composites as a function of (a) the dc bias magnetic field, (b) λ_{\parallel}^* at $f = 0.5$, and (c) the volume fraction f of PVDF, at 1 kHz.

strictively induced strain [Fig. 8(b)] and low piezoelectricity (Fig. 6) of the composites. The maximum α_{E33} value of the P-T-P composites appears in the intermediate volume fraction range of $f = 0.3-0.5$. The α_{E33} value of about 80 mV/cm Oe at 1 kHz and 4 kOe for $f = 0.5$ is comparable to those for the PZT/ferrite ceramic composites,¹ and higher than that for recently reported three-phase Terfenol-D/PZT/PVDF particulate composites¹² due to higher magnetostriction achieved in the P-T-P composites than in the particulate composites. The ME response observed in the P-T-P composites was found to be quite stable, as evidenced by the sequential measurements conducted over six months.

Figure 11 shows a typical frequency dependence of the

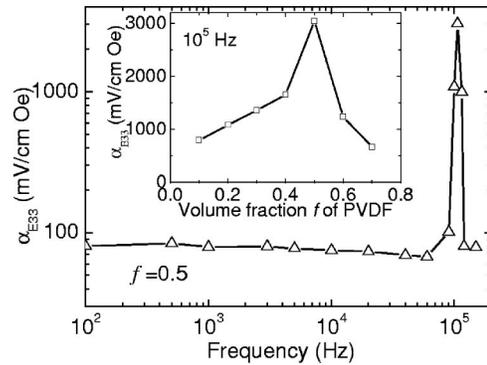


FIG. 11. Frequency dependence of the ME_H sensitivity α_{E33} measured at 4000 Oe for the laminated P-T-P composite with $f = 0.5$. The inset shows α_{E33} at 10^5 Hz of the composites as a function of the volume fraction f of PVDF.

ME_H sensitivity α_{E33} of the laminated P-T-P composite with $f = 0.5$. In the frequency range below about 85 kHz, α_{E33} almost keeps constant. But of interest to note is that α_{E33} of the composites demonstrate a peak at about 10^5 Hz, at which the dielectric measurement of the *polarized* composites demonstrated a resonance (not presented here). This resonance is associated with the electromechanical resonance¹⁴ in the thin disk-shaped piezoelectric layer, since the *polarized* PZT ceramic disk-shaped pellet with the similar sizes also showed such a thickness electromechanical resonance. The peak ME_H response is attributed to enhanced coupling elastic interaction between PZT/PVDF and Terfenol-D/PVDF composite layers at the resonance. The values of the peak ME_H response also depends on f (see the inset of Fig. 11), and the maximum α_{E33} value for the composite with $f = 0.5$ can reach up to as high as over 3000 mV/cm Oe. This GME effect at high frequency demonstrates that the three-phase Terfenol-D/PZT/PVDF composites can be used for high-frequency applications at least up to 200 kHz, since the problem of high eddy current loss for Terfenol-D over the high-frequency range has been overcome in the composites.

IV. CONCLUSIONS

Multiferroic laminated composites by sandwiching Terfenol-D/PVDF particulate composite layer between two PZT/PVDF particulate composite layers have been prepared by a simple hot-molding technique. The dielectric behavior of the P-T-P composites is dominated by the PZT/PVDF layers, since the Terfenol-D/PVDF layer sandwiched is conducting. The inert polymer PVDF used as a binder in the composites has a significant effect on the properties of the composites, e.g., leading to small remanence and coercivity, as well as small remanence and saturation polarization of the laminated composites. The piezoelectric, magnetostrictive, and magnetoelectric properties of the laminated composites are quite sensitive to the concentration of the PVDF binder. A low concentration of the PVDF binder leads to low quality of the laminated composites and thus low performance. On the other hand, high concentration of the inert PVDF results

also in low piezoelectric, magnetostrictive, and magnetoelectric responses of the laminated composites. In particular, the composites exhibit giant magnetoelectric sensitivity at high frequency. Better performance of the laminated composites appears only in the intermediate concentration range. For instance, the maximum magnetoelectric response has been measured in the P-T-P composites with $f=0.5$. Further improvement of the laminated composites lies in ensuring perfect interface contact between phases and/or layers by opti-

mization of composites processing, and in designing geometry of the laminated composites.

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