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Large magnetoelectric response in multiferroic polymer-based composites

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A type of multiferroic polymer-based composite is presented which exhibits a giant magnetoelectric sensitivity. Such a multiferroic composite prepared via a simple low-temperature hot-molding technique for common polymer-based composites has a laminate structure with one lead-zirconate-titanate (PZT)/polyvinylidene-fluoride (PVDF) composite layer sandwiched between two Tb—Dy—Fe alloy (Terfenol-D)/PVDF composite layers. The PZT/PVDF layer in the middle dominates the dielectric and piezoelectric behavior of the polymer based composites. The coupling elastic interaction between two outer Terfenol-D/PVDF layers and the middle PZT/PVDF layer in such polymer-based composites produces the giant magnetoelectric response as demonstrated by the experimental results, especially at high frequency at which the electromechanical resonance appears. The maximum magnetoelectric sensitivity of the composites can reach up to as high as about 300 mV/cm Oe at frequency below 50 kHz and about 6000 mV/cm Oe at the resonance frequency of around 80 kHz.

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I. INTRODUCTION

Multiferroic materials have drawn increasing interest due to their multi-functionality,[1] which provides significant potentials for applications as the next-generation multifunctional devices. In these multiferroic materials, the coupling interaction between multiferroic orders could produce some new effects, such as magnetoelectric (ME) or magnetodielectric effect.[2] This ME response, characterized by the appearance of an electric polarization upon applying a magnetic field and/or the appearance of magnetization upon applying an electric field, has been observed as an intrinsic effect in some natural material systems (e.g., in $TbMnO_3$ at low temperature and high magnetic field).[2] Alternatively, multiferroic composites made by a combination of ferromagnetic and ferroelectric substances such as combinations of piezoelectric ceramics [e.g., $BaTiO_3$ and lead-zirconate-titanate (PZT)] and ferrites have been recently found to exhibit a large room-temperature extrinsic ME effect,[3] which has known as a product property,[4] i.e., a new property of such composites that either individual component phase does not exhibit. This ME effect can be defined as a coupling magnetic-mechanical-dielectric behavior. That is, when a magnetic field is applied to the composites, the ferromagnetic phase changes the shape magnetostrictively, and then the strain is passed along to the piezoelectric phase, resulting in an electric polarization.[5]

Most recently, a giant ME (GME) response has been found theoretically[6] and subsequently experimentally[7,8] in the multiferroic composites such as laminated composites of rare-earth-iron alloy $Tb_xDy_{1-x}Fe_2$ (Terfenol-D) and piezoelectric ceramic lead-zirconate-titanate (PZT), and Terfenol-D and polyvinylidene fluoride (PVDF)-based piezoelectric polymers. However, the laminated Terfenol-D/PZT cermets[7] prepared by gluing Terfenol-D and PZT disks together is very brittle. Furthermore, above ~1 kHz, there is a high eddy current loss in Terfenol-D disk sticking. In order to overcome the difficulties, three-phase polymer-based composites of Terfenol-D/PZT/polymer have been recently developed because of their low eddy current loss in the high-frequency range, good toughness, and easy processing.[9–11] In the three-phase Terfenol-D/PZT/polymer particulate composites with magnetostrictive Terfenol-D particles embedded in the piezoelectric ceramic and polymer matrix,[9] the ME effect was greatly limited by a rather low volume fraction of Terfenol-D particles permitted in the matrix, e.g., less than 0.08, due to the percolation effect of conductive Terfenol-D particles. In order to eliminate this limitation on the low volume fraction of Terfenol-D, a 2-2 type laminated composite with a Terfenol-D-based layer sandwiched between two PZT-based layers (denoted as P-T-P composites) has been reported,[10] and its ME sensitivity is about two times higher than those for three-phase particulate composites. However, the ME sensitivity of such P-T-P composites is still low, especially in comparison to that for those brittle laminated Terfenol-D/PZT cermets. In order to greatly enhance the ME sensitivity of the three-phase polymer-based composites, here we present a laminated composite which is an inverse structure of the P-T-P composites, i.e., one PZT/polymer composite layer sandwiched between two Terfenol-D/polymer composite layers (abbreviated as the T-P-T composites below). Such T-P-T multiferroic composites demonstrate GME response, and their ME sensitivity is much larger than that for other three-phase composites reported so far.

II. EXPERIMENT

PZT powder with average particle size of about 150 μm was obtained by crushing the sintered PZT pellets prepared by a conventional solid-state procedure. PZT powder and Terfenol-D powder with average particle size of about 50 μm (from Beijing Institute of Non-Ferrous Metals, China) were first mixed with polymer PVDF powder to get PZT/fPVDF and Terfenol-F/fPVDF mixtures (with $f=0.3$), respectively, where f denotes the volume fraction of the PVDF. These mixed powders were then set in a mould by

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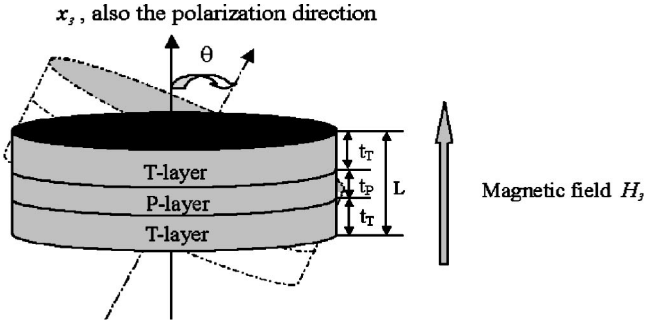

FIG. 1. Schematic illustration of the laminated T-P-T polymer-based composites. The ratio of the thicknesses of the P-layer to the sample is denoted by t_p/L.

turns of Terfenol-D/fPVDF (denoted as T-layer), PZT/fPVDF (denoted as P-layer) and Terfenol-D/fPVDF (T-layer). These three laminated layers were hot-pressed at 180 °C and 10 MPa for 30 min to get the T-P-T laminated composite samples. As shown in Fig. 1, the diameter and thickness of the samples are about 15 and 2.5 mm, respectively, and the thickness ratio t_p/L varies from 1/7 to 1.

All electrical measurements were performed at room temperature by the same procedure and technique as before.[10] In order to perform the electrical measurements, the samples were polished, and electroded by silver paint. And 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. 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 0.5 T (5 kOe). The ac magnetic field of about 2 Oe was applied superimposed on the dc magnetic field. A signal generator was used to drive the Helmotz coils and generate the ac magnetic field with frequency varying from 100 Hz to 200 kHz. The measured voltage represents the electric charge from the piezoelectric layers under an open-circuit condition. The output electric field divided by the ac magnetic field gave the ME sensitivity of the composites. We kept dc and ac magnetic fields in the same direction, but changed the magnetic direction relative to the polarization direction (the sample symmetric axis) by rotating the samples as shown in Fig. 1. When the polarization was parallel to the magnetic field, i.e., $\theta=0$, the longitudinal ME sensitivity α_{E33} $(=dE_3/dH_3)$ was measured; and when the polarization was perpendicular to the magnetic field, i.e., $\theta=90°$, the transverse ME sensitivity α_{E31} $(=dE_3/dH_1)$ was obtained.

III. RESULTS AND DISCUSSIONS

The laminated T-P-T polymer-based composite has a sandwich structure of T-layer/P-layer/T-layer as shown in Fig. 1. The T-layer (or P-layer) is a mixture of Terfenol-D (or PZT) particles and polymer PVDF, and both T-layer and P-layer contain the same volume fraction f of PVDF. Presented in Fig. 2 is a typical micrograph of the fractured surface of the T-P-T composite with $f=0.3$, which was examined by scanning electron microscopy (model HITACHI S-450). Figure 2(a) shows a good three-layer structure of the composite. As shown in Fig. 2(b), the big particles of about 150 μm in the P-layer are polycrystalline PZT containing many microcrystallites, and small Terfenol-D particles of about 50 μm and their clusters are surrounded by the PVDF matrix. PZT and Terfenol-D particles are bonded with the PVDF polymer. Figure 2(b) also shows a good interface bonding between the P-layer and T-layer. The polymer is homogeneously distributed through the P-layer and T-layer across the composite sample, and bonds PZT and Terfenol-D particles together. The volume fraction of the polymer PVDF, just as a matrix binder, is an important parameter, as shown before[9,10] in such three-phase composites. High concentration of the polymer (e.g., $f>0.5$) would lead to weak piezoelectricity and magnetostriction, thereby weak ME response, since a high concentration of the polymer leads to lower concentrations of PZT and Terfenol-D in composites. On the other hand, a low volume fraction of the polymer (e.g., $f<0.3$) would produce weak bonding in the composites, also resulting in weak ME response of the composites. There is an intermediate f range where the performance of the composites can be optimized. The previous experiments demonstrated such an optimized range around $f=0.3$.[9,10] Thus the laminated T-P-T polymer-based composite with $f=0.3$ is presented next.

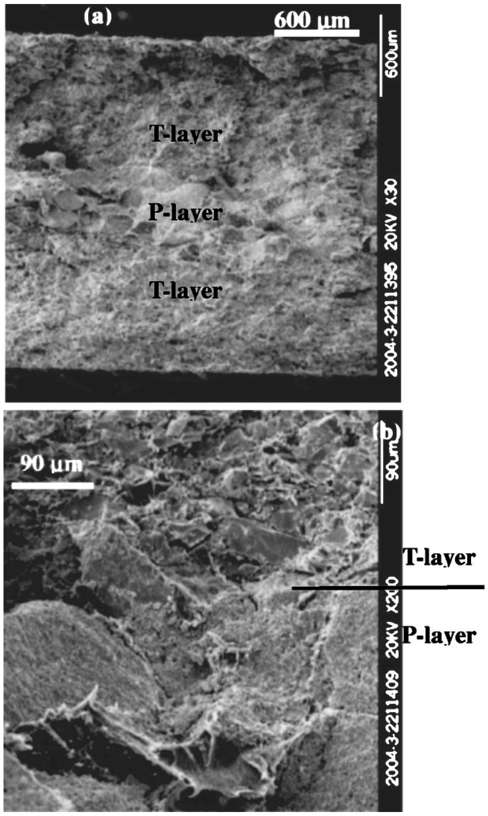

FIG. 2. Typical micrograph of the fractured surface of the T-P-T composite with $f=0.3$: (a) a sandwiched T-layer/P-layer/T-layer structure and (b) interface between two layers.

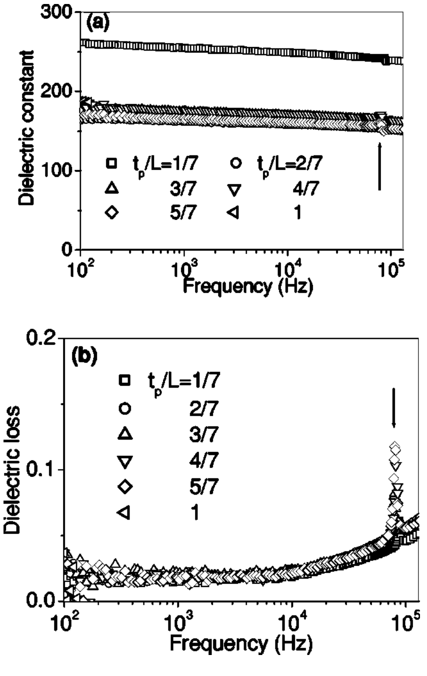

FIG. 3. Frequency dependence of (a) the dielectric constant and (b) loss measured for the T-P-T composites, showing an electromechanical resonance at about 80 kHz as marked by the arrow.

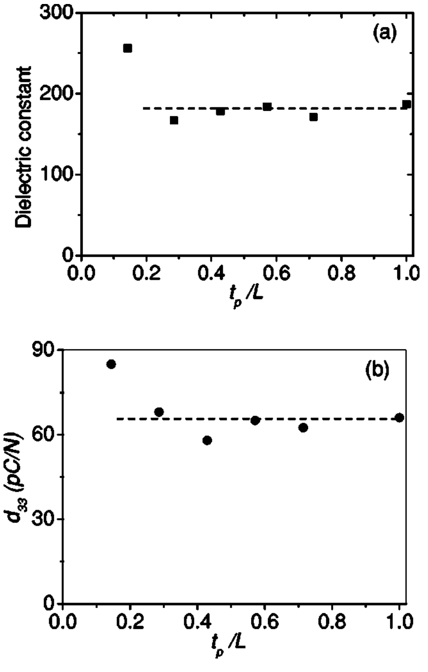

FIG. 4. (a) Dielectric constant and (b) piezoelectric constant d_{33} as a function of the thickness ratio t_p/L measured for the T-P-T composites. The dash lines are guides for the eye.

In the laminated T-P-T polymer-based composite, two outer T-layers with high concentration of conductive Terfenol-D particles are electrically active and thus can also serve as electrodes. Therefore, the dielectric behavior of the T-P-T composite is dominated by that of the P-layer in the middle. As shown in Fig. 3, the dielectric behavior measured for the laminated T-P-T composites with different relative P-layer thickness ratio t_p/L is the same as that for the P-layer with $t_p/L=1$, i.e., the PZT/polymer composite with $f=0.3$. The same as for the PZT/polymer composite (the P-layer with $t_p/L=1$), the dielectric constant [Fig. 3(a)] and loss [Fig. 3(b)] of these laminated composites are nearly independent of the frequency below 60 kHz, and at about 80 kHz there is a resonance peak which is associated with the electromechanical resonance[12] in the thin disk-shaped piezoelectric layer, as observed before.[10]

Figure 4(a) clearly illustrates that the dielectric constants of the composites are quite insensitive to the thickness ratio t_p/L. Similarly, the effective piezoelectric constants [Fig. 4(b)] of the T-P-T polymer-based composites are also dominated by the P-layer and quite insensitive to the thickness ratio t_p/L. It is worth noting that the composite sample with a thin P-layer sandwiched, e.g., $t_p/L=1/7$, shows higher dielectric and piezoelectric constants than the others and the P-layer with $t_p/L=1$. This is attributed to a small thickness of the middle P-layer, i.e., $t_p=L/7\sim 300$ μm, which is comparable to the average PZT particle size (about 150 μm). In this case, some large PZT particles in the thin P-layer could form continuous paths with direct connection of PZT particles cross this P-layer, and as a result, they lead to higher dielectric and piezoelectric constants of this composite sample with a thin P-layer sandwiched than the PZT/polymer composite (i.e., the P-layer with $t_p/L=1$) and the other composite samples with a thick P-layer sandwiched.

Figure 5 shows the field dependence of the longitudinal ME sensitivity α_{E33} and transverse ME sensitivity α_{E31} of the T-P-T polymer-based composites, respectively, measured under the conditions that the polarization is parallel (i.e., $\theta=0$) and perpendicular (i.e., $\theta=90°$) to the applied magnetic field H_{dc} (see Fig. 1). The dependence of the ME response of the

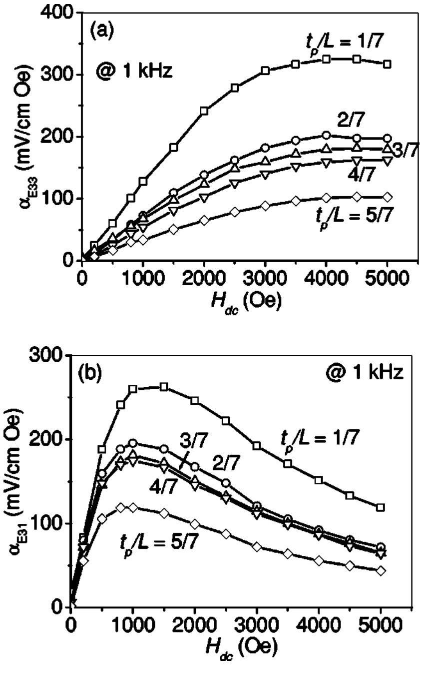

FIG. 5. (a) Longitudinal ME sensitivity α_{E33} and (b) transverse ME sensitivity α_{E31} as a function of the bias magnetic field H_{dc} measured at 1 kHz for the T-P-T composites.

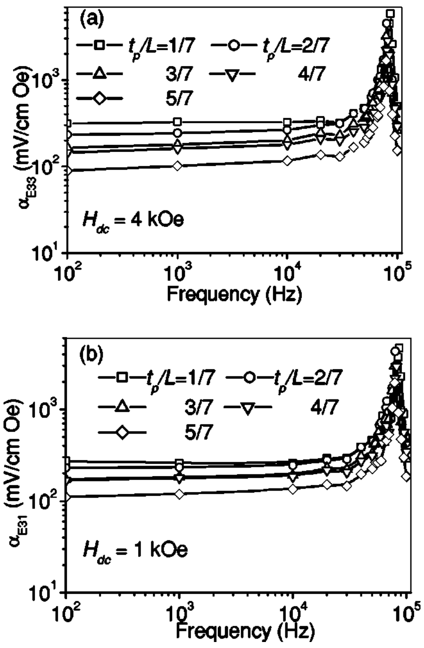

FIG. 6. Frequency dependence of (a) the longitudinal ME sensitivity α_{E33} measured at $H_{dc}=1$ kOe and (b) transverse ME sensitivity α_{E31} measured at $H_{dc}=4$ kOe for the T-P-T composites.

composites on the magnetic bias field is dominated by the field-dependent magnetostriction of the T-layer (i.e., Terfenol-D/polymer composite layer).[10] With increasing the magnetic field H_{dc}, α_{E33} increases linearly with H_{dc} as $H_{dc} < 2$ kOe and then nonlinearly increases to reach its saturation at about 4 kOe. In the high field range where the magnetostriction approaches its saturation, α_{E33} is expected to slightly change with the magnetic field. In comparison, α_{E31} shows different field-dependent behavior from α_{E33}, and it non-monotonically depends on the magnetic field with a peak at about 1 kOe. The difference between α_{E33} and α_{E31} is due to different magnetostrictions arising from the out-of-plane bias and in-plane bias in such anisotropic laminated composite samples. At high magnetic fields the magnetostriction gets saturated faster under the in-plane bias than the out-of-plane bias producing a nearly constant electric field in the PZT, thereby decreasing α_{E31} with increasing magnetic field.

Shown in Figure 6 is the frequency-dependent ME sensitivity measured for the laminated T-P-T composites. With increasing the frequency below about 50 kHz, the ME sensitivity of the laminated composites very slightly increases as for the dielectric constant shown in Fig. 3(a). However, of interest to note is that both α_{E33} and α_{E31} of the composites demonstrate a peak at about 80 kHz at which the electromechanical resonance (see Fig. 3) appears. The peak ME response is attributed to enhanced coupling elastic interaction between PZT/PVDF and Terfenol-D/PVDF composite layers at the electromechanical resonance.[10] In particular, the maximum ME sensitivity below 50 kHz for the T-P-T composites is around 300 mV/cm Oe, which is even higher than those for brittle PZT/ferrite ceramic particulate composites[3] and about four to eight times higher than that for other three-phase polymer-based composites reported so far.[9,10] Furthermore, the maximum ME sensitivity at high resonance frequency can reach up to as high as about 6000 mV/cm Oe. Such a GME effect is comparable to those observed recently in the brittle laminated Terfenol-D/PZT cermets made by the sticking method.

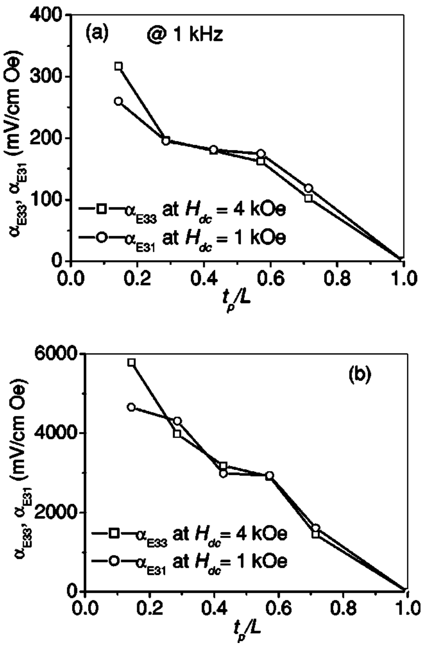

FIG. 7. ME sensitivity at (a) low frequency (1 kHz) and (b) at the resonance frequency as a function of the thickness ratio t_p/L measured for the T-P-T composites.

As shown in Figs. 5 and 6, the ME sensitivity of the T-P-T polymer-based composites is strongly dependent on the

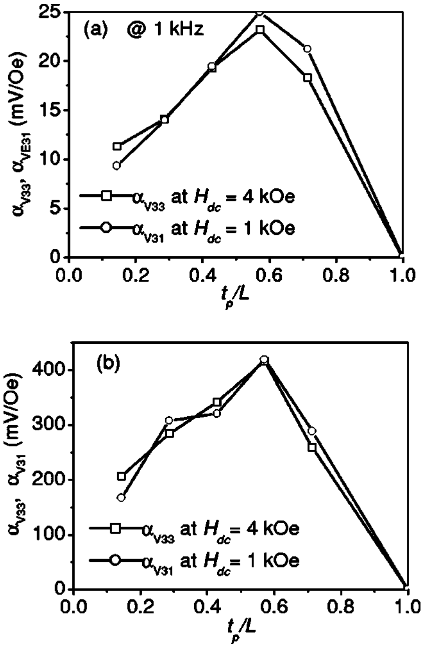

FIG. 8. ME induced voltage (V_3) coefficients α_{V33} ($=dV_3/dH_3$) and α_{V31} ($=dV_3/dH_1$) at (a) low frequency (1 kHz) and (b) at the resonance frequency as a function of the thickness ratio t_p/L measured for the T-P-T composites.

thickness ratio t_p/L. Figure 7 more clearly illustrates such a dependence of the ME sensitivity on t_p/L. Both α_{E33} and α_{E31} of the composites nearly linearly decrease with increasing t_p/L. This behavior is similar to that calculated for the laminated Terfenol-D/PZT/Terfenol-D cermet where two outer Terfenol-D disks are surely served as electrodes and its ME sensitivity linearly decreases with increasing thickness ratio of the middle PZT disk.[13] The dielectric and piezoelectric constants of the T-P-T polymer-based composites are similar to those for the P-layer and insensitive to t_p/L (see Fig. 4), while the effective magnetostriction of the T-P-T composites would decrease with increasing t_p/L due to decreasing concentration of Terfenol-D in the samples, thereby leading to the decrease in α_{E33} and α_{E31} of the composites with increasing t_p/L. Figure 8 shows the dependence of the ME induced voltage (V_3) coefficients α_{V33} $(=dV_3/dH_3)$ and α_{V31} $(=dV_3/dH_1)$ on t_p/L, which are also important parameters used to assess the performance of such a ME material for a magnetic sensor. The maximum ME induced voltages for the P-T-P composites appear in the intermediate t_p/L range around $t_p/L \sim 0.5$. Thus the T-P-T polymer-based composites with a P-layer sandwiched between two T-layers can produce GME.

IV. CONCLUSIONS

The multiferroic three-phase polymer-based composites with a PZT/PVDF composite layer sandwiched between two conductive Terfenol-D/PVDF composite layers have been prepared via a simple hot-molding technique. Such a simple polymer-based composite hot-molding procedure leads to a good bonding between Terfenol-D and PZT, thus ensuring coupling interaction between magnetostriction and piezoelectricity. The PZT/PVDF layer dominates the dielectric and piezoelectric behavior of the T-P-T polymer-based composites, since two outer conductive Terfenol-D/PVDF layers serve just like electrodes. The ME response of the T-P-T polymer-based composites is dependent on frequency, magnitude and direction of the applied magnetic bias, and thickness ratio t_p/L. In particular, the three-phase polymer-based laminated composites exhibit much larger ME response than other three-phase polymer-based composites reported so far, and show the GME effecte specially at high frequency at which the piezoelectric resonance appears. The maximum ME sensitivity of the three-phase laminated composites can reach up to as high as about 300 mV/cm Oe at frequency below 50 kHz and 6000 mV/cm Oe at the resonance frequency of around 80 kHz. The three-phase polymer-based composite would be an important smart multiferroic material for magnetic-electric devices.

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