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Giant magnetoelectric effect in multiferroic laminated composites

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Multiferroic laminated composites consisting of Terfenol-*D*/polyvinylidene-fluoride (PVDF) and lead-zirconate titanate (PZT)/PVDF particulate composite layers were prepared by a simple hot-molding technique. Magnetoelectric coefficients are characterized for the different measuring angles between the directions of polarization and applied magnetic field and at various frequencies. The results indicate that the three-phase laminated composites exhibit remarkable magnetoelectric effect especially at the resonance frequency at which the electromechanical resonance appears. The maximum magnetoelectric sensitivity of such composites is about 6 V/cm Oe at about 90 kHz.

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I. INTRODUCTION

The magnetoelectric (ME) effect is defined as an induced electric polarization under an external magnetic field or an induced magnetization under an external electric field in a material, and can be used in various applications such as transducers, actuators, and sensors.[1] The ME effect was predicted by Pierre Curie in 1894, and observed by Astrov in Cr_2O_3 in 1961.[2] Up to now, a number of studies concerning the ME effect in piezoelectric/magnetostrictive laminate composites have been reported. The multiferroic composites of ferrite and piezoelectric ceramics [e.g., $CoFe_2O_4/BaTiO_3$ and ferrite/lead-zirconate-titanate (PZT)] can exhibit extrinsic larger ME effect, which is ascribed to the coupling interaction between the ferrite and piezoelectric ceramic phases.[3] The theoretical investigation on the ME effect has been supported by a few approaches, e.g., the simplified approximation and the rigorous method, to calculate the effective ME properties of such ferrite/piezoelectric ceramic composites.[4–6] In 1972, Philips[7] developed a magnetoelectric composites of $CoFe_2O_4/BaTiO_3$, and observed a magnetoelectric coefficient of about 130 mV/cm Oe. Due to the high processing temperature, the third phase (e.g., Co_2TiO_4) was formed during sintering. Recently, the laminated Terfenol-*D*/PZT composites made by stacking and bonding together the PZT and Terfenol-*D* disks with conductive epoxy have been found to exhibit a giant magnetoelectric (GME) effect,[8] and a maximum magnetoelectric voltage coefficient of about 5000 mV/cm Oe has been observed. In theory, we calculated and predicated the GME properties of the novel composites containing Terfenol-*D* and a piezoelectric polymer or a piezoelectric ceramic (e.g., PZT).[9] The results indicate that the magnetostrictive-piezoelectric laminate composites have much higher ME coefficients than that of single-phase materials or particulate composites.

However, the laminated Terfenol-*D*/PZT composites are very brittle and their ME response strongly depends on the interfacial bonding between two layers,[10] and on the other hand, there is a high eddy current loss in conductive Terfenol-*D* disk above 1 kHz. In this report, we designed and prepared a laminate PZT/PVDF composite layer sandwiched between two Terfenol-*D*/PVDF composite layers (abbreviated as *TPT* structure) by a simple hot-molding technique, and the PVDF was employed as the binder matrix. The effect of the measuring angles between the polarization direction and applied magnetic direction on the GME properties have been investigated systematically. The maximum magnetoelectric sensitivity of the laminated composites is as high as 6000 mV/cm Oe at the measuring angle of 90° and at the resonance frequency f_r at which the electromechanical resonance appears, which is much higher than that of our previously processed the three-phase Terfenol-*D*/PZT/polymer composites.[11] Such resonance enhancement of the ME effect have recently also been observed in other ME materials.[12–15]

II. EXPERIMENT

The Terfenol-*D* powder was mixed with PVDF powder (employed as a binder) and pressed into a 50 vol % Terfenol-*D*/PVDF composite layer (*T* layer) in a mould. Then the PZT and PVDF powder mixture was also pressed into a 50 vol % PZT/PVDF composite layer (*P* layer). The diameter and thickness of samples can be adjusted as required by a hot-molding technique at 180 °C and 10 MPa for 30 min. The laminated composite can be processed as a sandwich structure of *T*-layer/*P*-layer/*T*-layer (*TPT*). Finally, the samples were polished and electroded by silver paint, and electrically polarized along the thickness direction in silicon oil at about 3 kV/mm and 70 °C. The fractured cross section of the samples was observed by scanning electron microscopy (SEM). The ME response was measured by applying an ac bias superimposed on a dc magnetic field on the sample, and then measuring the output charge signal by a dynamic measurement method. An electromagnet was used to provide a dc magnetic bias field up to 0.5 T (5 kOe). The voltage generated from the laminated sample was measured under an open circuit condition by using a differential amplifier and a digital oscilloscope. The sample holder can be rotated to change the measuring angle θ between the directions of the polarization (also the measurement direction) and the applied

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TABLE I. The ratio t_p/L for various *TPT* composite samples.

Sample No.	t_p/L ($L \approx 2.5$ mm)
TPT-1	1/7
TPT-2	2/7
TPT-3	3/7
TPT-4	4/7
TPT-5	5/7

magnetic field. When the polarization is parallel to the applied magnetic field $\theta=0$ and when the polarization is perpendicular to the applied magnetic field $\theta=90°$. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

The *TPT* composite samples with various t_p/L (*TPT*-1, -2, -3, -4, and -5) as shown in Table I have been successfully processed by the hot-molding technique. Figure 1 is a typical SEM micrograph of the fractured surface of the *TPT*-2 composite, which indicates that the Terfenol-*D* and PZT particles can be dispersed homogeneously and randomly bonded with the PVDF polymer in each layer.

The frequency dependence of the dielectric behavior of the laminated composites is shown in Fig. 2. The dielectric properties of the composites are not very sensitive to t_p/L, and are determined by the PZT/PVDF layer, since the top and bottom *T* layers with high concentration of Terfenol-*D* could be regarded as the electrodes. The dielectric constants of all samples are nearly independent of the frequency below ~70 kHz, and at about 90 kHz a resonance peak appears, which is associated with the electromechanical resonance of the laminated composites. Normally, the thickness resonance frequency is larger than that of radial resonance in the thin disk-shaped piezoelectric samples. Thus this resonance (~90 kHz) is associated with the radial electromechanical resonance in the thin disk-shaped piezoelectric layer of the laminated composites.

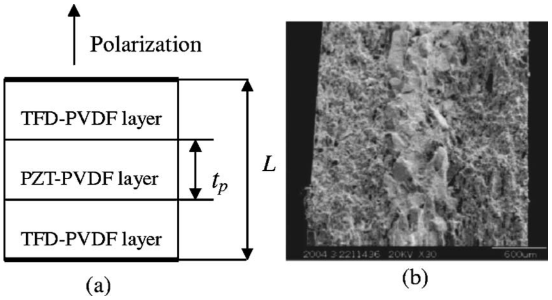

FIG. 1. (a) Schematic illustration and (b) a typical micrograph of the fractured surface of the laminated *TPT* composites. TFD denotes Terfenol-*D*.

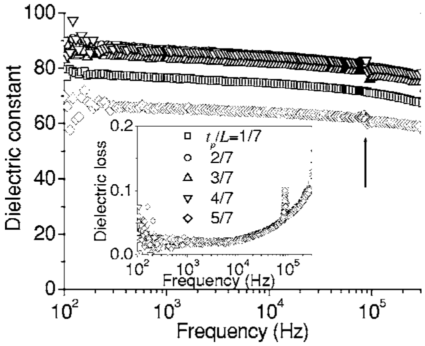

FIG. 2. Frequency dependence of the dielectric constants of the laminated composites, showing an electromechanical resonance at about 90 kHz. The inset is the dielectric loss.

We define α_E (=dE/dH) as the ME sensitivity. Figure 3 shows the frequency dependence of the ME sensitivity of the laminated *TPT* composites. which is similar to the frequency dependence of their dielectric properties (Fig. 2). In the frequency range below 70 kHz, α_E almost remains a constant of about 400 mV/cm Oe at 1 kOe. Moreover, a peak α_E value of the composites can be observed at $f_r \approx 90$ kHz, which is associated with the radial electromechanical resonance. Therefore, the peak ME response is attributed to enhanced coupling elastic interaction between PZT/PVDF and Terfenol-*D*/PVDF composite layers at the resonance frequency. The maximum value of the ME sensitivity can be as high as 6000 mV/cm Oe, which is much higher than those for the PZT/ferrite ceramic composites[3] and three-phase particulate composites.[11] This GME effect is comparable to those observed recently in the laminated Terfenol-*D*/PZT made by the sticking method.[8] The α_E values of the composites also nonmonotonically depend on t_p/L with a maximum ME sensitivity for the *TPT*-2 sample ($t_p/L \sim 2/7$), as shown in the inset of Fig. 3. The α_E values of the composites first increase with t_p/L, which could be attributed to the increase in the effective piezoelectric effect. However, with further increasing t_p/L, the ME sensitivity declines after a maximum value, which is due to the reduction in magnetostrictively induced strain of the laminated composites with increasing t_p/L.

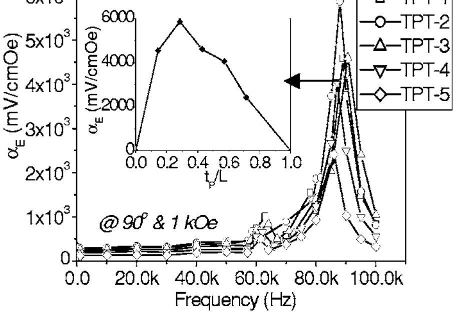

FIG. 3. Frequency dependence of the ME sensitivity α_E values (absolute values) of the laminated composites. The inset shows the variation in α_E with t_p/L at f_r.

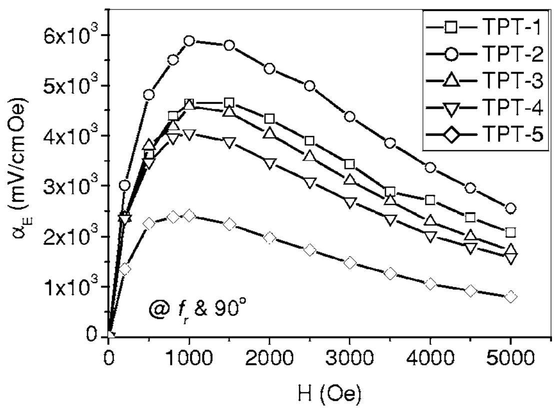

FIG. 4. The ME sensitivity α_E values (absolute values) measured at f_r for the laminated composites as a function of the bias magnetic field at the measuring angle $\theta=90°$.

The ME sensitivity of the laminated *TPT* composites illustrates strong dependence on the bias field, as shown in Fig. 4. It increases first rapidly with increasing the bias field, and then slowly changes with the magnetic field in the high bias field range where the effective magnetostriction becomes to approach its saturation. According to the recent theoretical calculations,[9] the nonlinear ME response of the composites is closely related to the magnetostrictive behavior of the Terfenol-*D*. At high magnetic fields, the magnetostriction gets saturated producing a nearly constant electric field in the PZT, thereby decreasing α_E with further increasing the magnetic field.

The ME sensitivity of the composite is not only dependent on the intensity of the bias magnetic field but also the measuring angle θ. Figure 5 shows a typical ME sensitivity for the *TPT*-2 composites measured as a function of the measuring angle θ. It shows that the absolute values of α_E decreases firstly with increasing θ to a minimum value, and then increases to reach the maximum at $\theta=90°$ (i.e., the polarization direction being perpendicular to the applied magnetic field).

As we define the measuring angle θ between the polarization direction and the magnetic field direction, the ME sensitivity α_E can be expressed as[16]

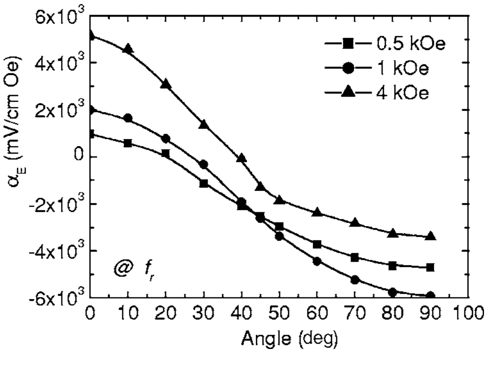

FIG. 5. The ME sensitivity for the *TPT*-2 composites measured as a function of the bias magnetic field and the measuring angle θ.

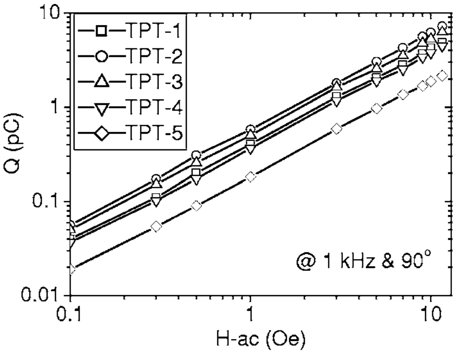

FIG. 6. Induced ME charges as a function of ac magnetic bias measured for the *TPT* composites.

$$\alpha_E=-\frac{(\cos^2\theta+1)q_{31}^N+\sin^2\theta q_{33}^N}{(s_{11}^N+s_{12}^N)\varepsilon_{33}^p t^p+(s_{11}^p+s_{12}^p)\varepsilon_{33}^p t^N-2(d_{31}^p)^2 t^N} d_{31}^p t^N t^p. \tag{1}$$

Therefore, as for the *TPT* composites, Eq. (1) can be further simplified as

$$\alpha_E=-A[(\cos^2\theta+1)q_{31}^N+\sin^2\theta q_{33}^N], \tag{2}$$

where q_{ij}^N are the piezomagnetic coefficients of the magnetostrictive phase, d_{ij}^p is the piezoelectric constants of the piezoelectric phase, ε_{33}^p is the dielectric constant of the piezoelectric phase, t^N and t^p are the volume fractions of magnetostrictive and piezoelectric phases, respectively, and s_{ij}^N and s_{ij}^P are the compliance coefficients of the magnetostrictive and piezoelectric phases, respectively. As seen from Eq. (2), the values of q_{31}^N and q_{33}^N do not remain positive or negative simultaneously and are different from each other, i.e., $q_{31}^N<0$, $q_{33}^N>0$, and $|q_{31}^N|<q_{33}^N$, therefore the sign of the ME sensitivity α_E changes at $\theta=\arcsin\sqrt{2q_{31}^N/(q_{31}^N-q_{33}^N)}$, and the ME sensitivity α_E shows maximum and a minimum value for such *TPT* composites while changing the measuring angle θ. A similar behavior was observed in the PZT/NiFe$_2$O$_4$ system.[17]

It is of interest to note that, in the low magnetic field, the composites have a good linear variation in the ME response (e.g., the magnetically induced charge Q) with a low ac magnetic field (see Fig. 6). This behavior is quite similar to those for the ME devices made from the PZT and Ni,[18] but the *TPT* composites have much higher low-field ME sensitivity than those Ni/PZT devices, which potentially makes such simple *TPT* composites attractive for technological applications for the ME devices.

IV. CONCLUSIONS

The laminated *TPT* composite samples have been prepared by the hot-molding technique. All samples have large magnetoelectric properties especially for the *TPT*-2 samples, which can be as high as 6000 mV/cm Oe at the resonance frequency. The bias magnetic field and the measuring angle θ have a significant influence on the ME sensitivity of the laminated composites. The ME sensitivity has a maximum value in the high bias field range due to the magnetostrictive saturation of the Terfenol-*D* phase. All of the *TPT* composites show a good linear variation in the ME response with the low ac magnetic field, which can be attractive for technological applications for the ME devices.

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