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Magnetoelectric Properties of Composites of Single Pb(Zr,Ti)O_3 Rods and Terfenol-D/Epoxy with a Single-Period of 1-3-Type Structure**

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Multiferroic composites made by combining ferroelectric and ferromagnetic substances have been rapidly developed for their excellent magnetoelectric (ME) effect above room temperature, which ensures large potential applications in multifunctional devices, transducer, actuators, and sensors.[1–3] The magnetoelectric effect is characterized by the appearance of an electric polarization (ME_H output) on applying a magnetic field or a magnetic polarization (ME_E output) on applying an electric field. It is well known that the ME effect in the composites is a product property deriving form the coupling between a piezoelectric effect in the ferroelectric phase and a magnetostrictive effect in the ferromagnetic phase.[4,5] That is, when a magnetic field is applied to the composites, the ferromagnetic phase changes its shape magnetostrictively, and the strain is passed along to the piezoelectric phase, resulting in a change of electric polarization.

Among bulk multiferroic composites, the composites containing giant magnetostrictive alloy $Tb_{1-x}Dy_xFe_2$ (Terfenol-D) and piezoelectric Pb(Zr,Ti)O_3 (PZT), exhibiting high magneto- and electromechanical energy densities, respectively, are the most attractive due to their giant ME response.[6–8] Using the concept of phase connectivity,[9] we can describe the structures of a two-phase composite by notations like 0-3, 2-2, and 1-3 etc., in which each number denotes the connectivity of the phase. So far, 0-3, 2-2, and 1-3 type structured composites containing Terfenol-D and PZT (especially 0-3 and 2-2 composites) have been widely investigated. For example, a three-phase 0-3 type composite in which Terfenol-D particles (notated as 0) are dispersed in PZT/polymer matrix (notated as 3) has been developed.[10] Similarly, by using polymer as binder and matrix, the pseudo 2-2-type composites have been fabricated by stacking and easily hot-pressing the Terfenol-D/polymer layer and PZT/polymer layer together.[11] The low-frequency ME sensitivity of such 0-3 type and pseudo 2-2 type composites is about 100 mV cm^{-1} Oe order of magnitude. In particular, by directly gluing Terfenol-D and PZT plates together, a much stronger ME effect was observed in such 2-2 Terfenol-D/PZT laminated composites, and the ME coefficient can reach up to several V cm^{-1} Oe,[7,8] which is one order of magnitude larger than the former 0-3 and pseudo 2-2 type composites. But the brittleness and high eddy current loss at high frequency of Terfenol-D plates restrict their applications.

Besides these 0-3 and 2-2 structures, the 1-3 structure, that is, a fiber (or rod) reinforced composite, is another important structure. Recently, such 1-3 structured composites with PZT rod arrays in a Terfenol-D/epoxy (TDE) medium have been reported,[12] and were fabricated via the same dice-and-fill procedure as for the well-known piezoelectric 1-3 composites,[13] to exhibit a high ME coefficient of about 6 V cm^{-1} Oe at resonance frequency. By the dice-and-fill procedure, the preparation of PZT rod arrays becomes more difficult when the aspect ratio of the rods increases. In this Communication, we present a very simple ME composite (Fig. 1) made up of just a single PZT rod embedded in a Terfenol-D/epoxy mixture without complicated dicing processing of the PZT rod arrays. The simple ME composite can be regarded as one single period element of the 1-3 ME composites with PZT rod arrays, and also exhibits larger ME response, which makes it particularly attractive for technological applications and expedites future modeling efforts due to its simple structure.

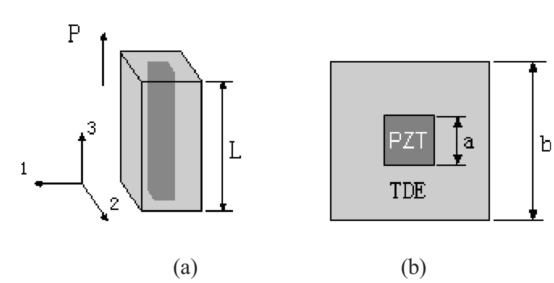

Figure 1. a) Three-dimensional and b) cross-sectional schematic illustration of the single period of 1-3-type structure.

The TDE medium is insulating, where the Terfenol-D particles are well dispersed and coated in the epoxy and no percolation occurs in the medium. The dielectric constant and loss of the TDE medium are about 15 and 0.03, respectively, in the measured frequency range from 1 kHz to 10 MHz. The TDE

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medium exhibits a large magnetostrictive strain of 300 ppm at 6 kOe (Fig. 2a). The longitudinal magnetostriction λ of the single period 1-3 composite with $a/b = 0.25$ is about 215 ppm at 6 kOe due to the dilute effect of the nonmagnetic PZT. The differential magnetostriction $d\lambda/dH$ is also shown in Fig-

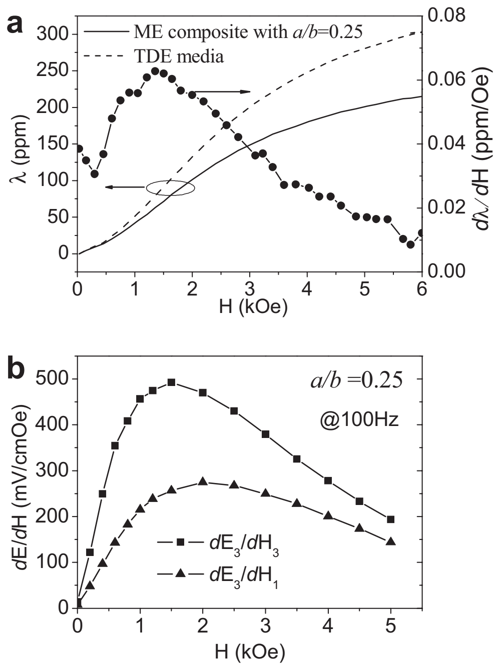

Figure 2. The magnetic-field dependence of a) the longitudinal magnetostrictive strain λ and b) the ME coefficients dE_i/dH_j at 100 Hz in the single period of 1-3-type structure with $a/b = 0.25$.

ure 2a, and shows a peak around 1.5 kOe. Because the ME response is directly proportional to the differential magnetostriction,[6] that is, $dE/dH \propto d\lambda/dH$, the ME response of the single period 1–3 composite presents a similar bias-dependent behavior, as shown in Figure 2b. Both the longitudinal and transverse magnetoelectric coefficients (i.e., dE_3/dH_3 and dE_3/dH_1, respectively) depend on the magnetic field, which is dominated by the bias-dependent magnetostriction. In the low field range, dE_3/dH_3 and dE_3/dH_1 increase approximately linearly with the increasing magnetic bias H_{bias}, due to the increasing magnetostriction. At high magnetic field, the magnetostriction gets saturated producing a nearly constant electric field in PZT rod, thereby decreasing dE_3/dH_3 and dE_3/dH_1. The maximum longitudinal ME coefficient of this composite with $a/b = 0.25$ is about 500 mV cm^{-1} Oe at 1.5 kOe.

We further observed that the ME response is strongly dependent on the relative sizes a/b and a/L of the PZT rod (see Fig. 1), as shown in Figure 3. In the present experiment, $a = 1$ mm remains unchanged. At low a/b, the increasing effective piezoelectric effect of the samples with increasing a/b leads to an increasing ME response. But after reaching a maximum around $a/b = 0.25$, the ME coefficients decline owing to the decrease in the volume fraction of the magnetostrictive

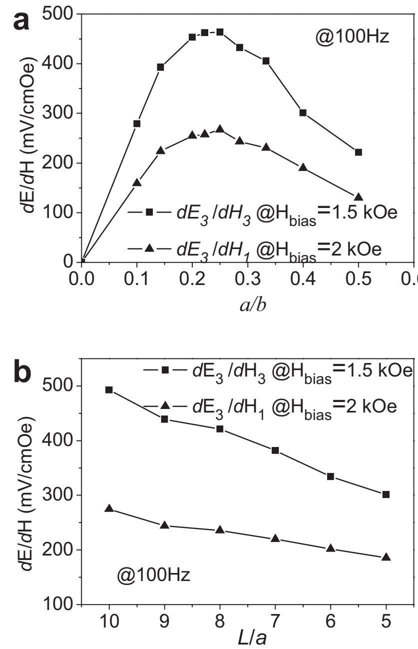

Figure 3. Variation in the ME coefficients of the single period of 1-3-type structure with a) the relative size a/b and b) the aspect ratio L/a of the PZT rod.

TDE medium, resulting in low magnetostrictively-induced strain of the composites. The aspect ratio of the PZT rod also affects the ME coefficient of this single period 1-3-type composites. As shown in Figure 3b, both dE_3/dH_3 and dE_3/dH_1 decrease with the decline in the aspect ratio, which is attributed to the decreasing effective piezoelectric effect of such 1-3 type piezoelectric composites with decreasing the aspect ratio. The size effects shown in Figure 3 imply that much smaller-sized ME rods (e.g., micro-ME rods) with large ME response can be obtained by using a single PZT fiber, which promises micro ME devices.

Figure 4 shows a typical frequency dependence of the ME coefficients of the single period 1–3-type composites. In the low frequency range below about 40 kHz, dE_3/dH_3 and dE_3/dH_1 are almost constant at a high value of about

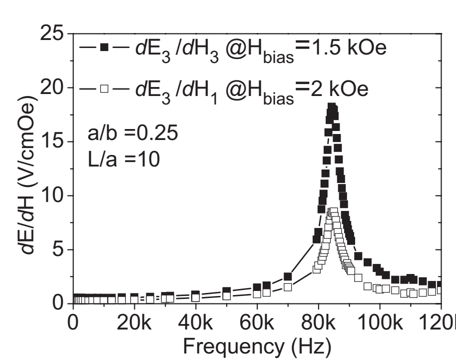

Figure 4. Frequency dependence of the ME coefficients for the single period of 1-3-type structure with $a/b = 0.25$ and $L/a = 10$.

500 mV cm^{-1} Oe and 290 mV cm^{-1} Oe, respectively. A giant ME coefficient dE_3/dH_3 of 18.2 V cm^{-1} Oe at 84 kHz is observed. This giant ME response at high frequency is attributed to the electromechanical resonance enhancement,[5] which significantly enhances the elastic coupling interaction between the TDE medium and PZT rod. In particular, the length of this sample is 10 mm, so a giant sensitivity of 18.2 V Oe^{-1} can be achieved at this resonance frequency. The ME coefficient dE_3/dH_3 is large than dE_3/dH_1 in our test, because of the large anisotropy of the rod reinforced composites.

In summary, a single period of 1-3-type structured ME composite has been prepared, and its fabrication process is much simpler than the PZT rod arrays in a Terfenol-D/epoxy medium. The experimental results have demonstrated that the coupling interaction between the PZT rod and TDE medium can generate much larger ME response than other three-phase composites reported so far. Especially at high frequency where the electromechanical resonance appears, the composite shows a giant ME effect. This single period 1-3-type composite presents a size-dependent ME response, which implies that much smaller-sized ME rods (e.g., micro-ME rods) with large ME response can be obtained by using a single PZT fiber, and promises future micro-ME devices.

Experimental

The PZT ceramic rod used here was prepared via conventional solid-state processing. Its dimensions were 10 mm length and 1×1 mm^2 in cross-section area, and it was polarized along the longitudinal direction under a poling field of 2 kV mm^{-1} in silicon oil of 70 °C. Its dielectric, piezoelectric, and electromechanical coupling coefficients were $\varepsilon_{33} = 1600$, $d_{33} = 383$ pC N^{-1}, and $k_{33} = 0.65$, respectively. For the preparation of the composites, Terfenol-D powder of about 27 vol % was well-mixed with low-viscosity epoxy with a little harder added, and then the Terfenol-D/epoxy (TDE) mixture was slowly poured into a mold where the PZT rod was put at the center of the mold, followed by vacuo-degassing. After epoxy hardening at room temperature, we polished the samples to get the single period of 1-3-type structures with the PZT rod embedded in the TDE medium (see Fig. 1). The samples were fitted with an electrode on the top and bottom surface perpendicular to the X_3 axis by silver paint.

All the measurements were performed at room temperature. The standard field-gauge technique was utilized to measure magnetostriction. To measure the ME coefficients, a small sine disturbing magnetic field H_{ac} superimposed on the H_{dc} was applied on the sample and a charge amplifier measured the induced charge [10–12]. The longitudinal and transverse magnetoelectric coefficients were denoted as dE_3/dH_3 and dE_3/dH_1, which were measured when the magnetic field was parallel and perpendicular to the polarization direction (i.e., the X_3 axis) of the PZT rod, respectively.

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