Magnetoelectric effect of Pb(Zr, Ti)O₃ rod arrays in a (Tb, Dy)Fe₂/epoxy medium

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We report a kind of multiferroic and multifunctional composite with Pb(Zr, Ti)O₃ rod arrays embedded in a ferromagnetic medium of (Tb, Dy)Fe₂/epoxy. The composite structure is similar to that of 1–3-type piezoelectric composites with Pb(Zr, Ti)O₃ rod arrays embedded in an inert epoxy for already commercial applications as transducers. The large magnetoelectric effect, especially at high frequency at which the electromechanical resonance appears, is observed for such multiferroic composites due to coupling elastic interaction between Pb(Zr, Ti)O₃ rods and the ferromagnetic medium, which suggests avenues for designing novel multiferroic materials for practical applications. © 2005 American Institute of Physics. [DOI: 10.1063/1.1991983]

Multiferroic materials with multifunctionality have drawn ever increasing interest, since they provide 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. This magnetoelectric 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., most recently in R MnO₃ ((R=rare earth). In these manganites, however, ME effects can be observed only at very low temperature and high magnetic field. Alternatives that are being pursued are multiferroic composites made by a combination of ferromagnetic and ferroelectric ceramics such as piezoelectric ceramics [e.g., BaTiO₃ and Pb(Zr, Ti)O₃ (PZT)] and ferrites, in which a room-temperature extrinsic ME effect has been found. 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.

Of particular interest, a large ME effect at room temperature has been recently found theoretically and experimentally in the multiferroic composites containing rare-earth-iron alloy (Tb, Dy)Fe₂ (Terfenol-D), especially in laminated Terfenol-D/PZT composites prepared by gluing Terfenol-D and PZT disks with a binder, which is strongly dependent on interface binding between Terfenol-D and PZT disks. However, the laminated Terfenol-D/PZT composites are very brittle. Furthermore, above ~1 kHz, there is a high eddy current loss in Terfenol-D disk. The search for the multiferroic materials with strong room-temperature magnetoelastic coupling has been of significant interest. In this letter, we present a kind of multiferroic material made up of PZT rod arrays embedded in a Terfenol-D/epoxy mixture. The structure of such a novel multiferroic composite is similar to that for well-known 1–3-type piezoelectric composites with PZT rod arrays embedded in an epoxy matrix, originally proposed by Newham and co-workers. Such 1–3-type piezoelectric composites have been technologically important and already commercialized piezoelectric materials for transducers due to their enhanced piezoelectric performance. Instead of using an inert epoxy for the matrix, we use a ferromagnetic Terfenol-D/epoxy (TDE) mixture as the matrix, and introduce this ferromagnetic medium in the PZT rod arrays. By designing the PZT rod arrays, we observe a very large ME response. This potentially makes such multiferroic materials particularly attractive for technological applications, and suggests an avenue for designing novel multiferroic materials with multifunctionality.

The PZT rod arrays in the TDE medium was produced by the dice-and-fill method. Two sets of closely spaced, parallel cuts were made in a poled PZT ceramic samples, the two sets being perpendicular to each other [Fig. 1(a)]. Then the diced ceramic samples [see Fig. 1(a)] were filled with an epoxy resin solution containing Terfenol-D particles. After hardening at room temperature, the samples were polished to get 1–3-type composites with PZT rod (square rods with width of 0.5 mm) arrays embedded in the TDE medium, as shown in Fig. 1. The samples with 2.5 mm in thickness and 10 mm in width were electroded on the top and bottom surfaces by silver paint. The volume fraction f of the PZT rods in the TDE medium is controlled by changing the periodicity of the square PZT rod array. All electrical measurements were performed at room temperature. Dielectric properties were measured by using a HP4194A impedance analyzer. The piezoelectric constant was measured by a standard piece d₃₃ meter. Magnetostriiction was measured by the standard strain-gauge technique. The ME response, i.e., magnetic-field-induced output voltage, dE/dH (ME sensitivity), was measured by using the dynamic method with a small ac magnetic signal superimposed on the dc magnetic field as before.

The relative dielectric and piezoelectric constants measured for the PZT ceramics used are, respectively, e₄₄ = 1100 (at 1 kHz) and d₃₃ = 370 pC/N. The volume fraction of Terfenol-D in the TDE medium is fixed as about 0.23, and the measured resistivity of the TDE medium is above 5 × 10¹⁰ Ω cm, which indicates that the Terfenol-D particles

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are well separated and coated by the epoxy and do not percolate across the samples. As shown in Fig. 2(a), the dielectric constant measured for the TDE medium (i.e., \( f = 0 \)) slightly decrease with increasing frequency. In the frequency range from 100 Hz to 300 kHz, the dielectric constants [Fig. 2(a)] measured for the PZT rod arrays in the TDE medium are nearly independent of the frequency below 80 kHz (their dielectric loss being about 0.02), and at about 100 kHz a resonance peak appears, which is associated with the electromechanical resonance.12 With increasing \( f \) of the PZT rods, the electromechanical resonance becomes stronger and stronger. Figure 2(b) clearly illustrates that the dielectric constants (at 1 kHz) of the composites are linearly dependent on \( f \), which can be given by the simple mixture rule, i.e., \( \varepsilon_{33}^P = \varepsilon_{33}^{PZT} + (1 - f)\varepsilon_{33}^{TDE} \) with \( \varepsilon_{33}^{TDE} = 16 \) [see Fig. 2(a)]. Also shown in Fig. 2(b) is the effective piezoelectric constant \( d_{33}^P \) measured for the PZT rod arrays in the TDE medium. For the 1-3-type piezoelectric composites, \( d_{33}^P \) of the PZT rod arrays in the TDE medium can be described by the simple volume averaging, i.e., \( d_{33}^P = \frac{\varepsilon_{33}^{PZT} d_{33}^{PZT}}{\varepsilon_{33}^{TDE}} = \left( \frac{1 - f}{\varepsilon_{33}^{TDE}} \right) \frac{s_{33}^{PZT}}{s_{33}^{TDE}} (1 - f) s_{33}^{TDE} \), where \( s_{33} \) is the elastic compliance, and \( s_{33}^{PZT} = 7.44 \times 10^{-11} \) and \( s_{33}^{TDE} = 1.87 \times 10^{-11} \) m²/N. As shown in Fig. 2(b), the measured \( d_{33}^P \) values are in good agreement with the calculated.

When a magnetic field is applied to the composites, the magnetostrictive strain in the TDE medium is passed along to the PZT rods, resulting in an electric output. Figure 3 shows a giant electric output induced by the applied magnetic field in the PZT rod arrays. With increasing the magnetic field \( H \), the ME sensitivity \( dE_3/dH \) nonmonotonically depends on the magnetic field with a peak at about 2 kOe [Fig. 3(a)]. The dependence of the ME sensitivity \( dE_3/dH \) of the composites on the magnetic bias field is dominated by the field-dependent magnetostriction of the TDE medium.13 At high magnetic fields, the magnetostriction gets saturated producing a nearly constant electric field in the PZT, thereby decreasing \( dE_3/dH \) with increasing magnetic field.

As clearly shown in Fig. 3(b), the ME sensitivity of the PZT rod arrays is strongly dependent on \( f \). The maximum ME sensitivity for the PZT rod arrays in the TDE medium appears around \( f = 0.1 \). At low volume fraction \( f \), e.g., \( f < 0.05 \), the low piezoelectricity of the samples leads to a low ME response. As \( f > 0.1 \), the ME sensitivity also declines with the increase in \( f \). This decrease in \( dE_3/dH \) is attributed mainly to the decrease in the concentration of the magnetostrictive TDE medium, which leads to low magnetostrictively induced strain of the composites. The \( dE_3/dH \) value of 280 mV/cm Oe at 2 kOe for \( f = 0.12 \) is even higher than

![FIG. 1. (a) A diced PZT ceramic sample; (b) schematic illustration; and (c) a typical micrograph of the PZT rod arrays in the TDE medium.](image1)

![FIG. 2. (a) Frequency dependence of the dielectric constants of the PZT rod arrays in the TDE medium, showing an electromechanical resonance at about 100 kHz as marked by the arrow. (b) The effective dielectric constant \( \varepsilon_{33} \) (at 1 kHz) and piezoelectric constant \( d_{33}^P \) of the PZT rod arrays as a function of the volume fraction \( f \) of the PZT rods, in which the dots are measured data and the lines are calculated.](image2)

![FIG. 3. ME sensitivity \( dE_3/dH \) as a function of (a) the bias magnetic field \( H \) and (b) \( f \), measured at 1 kHz for the PZT rod arrays in the TDE medium.](image3)
FIG. 4. Frequency dependence of the ME sensitivity $dE_3/dH_3$ for the PZT rod arrays in the TDE medium.

those for brittle PZT/ferrite ceramic particulate composites and about 4–8 times higher than that for three-phase polymer-based composites reported so far.

Shown in Fig. 4 is the frequency-dependent ME sensitivity measured for the PZT rod arrays. With increasing the frequency below about 70 kHz, the ME sensitivity slightly increases. However, of interest to note is that the ME sensitivity of the PZT rod arrays demonstrate a peak at about 93–100 kHz at which the electromechanical resonance [see Fig. 2(a)] appears. The resonance frequency slightly increases from 93 to 100 kHz with increasing $f$ from 0.02 to 0.24. The peak ME response between 80 and 110 kHz (see the inset of Fig. 4) is attributed to enhanced coupling elastic interaction between the PZT rods and TDE medium at the electromechanical resonance. In particular, the maximum ME sensitivity in the range of resonance frequencies can reach up to as high as 6000 mV/cm Oe. Such a large ME effect is comparable to those observed recently in the brittle laminated Terfenol-D/PZT cerments made by the sticking method.

In summary, multiferroic and multifunctional composites with the PZT rod arrays embedded in the TDE medium have been prepared via a dice-and-fill technique successfully developed for the 1–3-type piezoelectric composites. As demonstrated by the experimental results, the coupling interaction between the PZT rods and TDE medium can produce the giant magnetoelectric effect, especially at high frequency at which the electromechanical resonance appears, which potentially makes such multiferroic materials particularly attractive for practical applications in magnetic-electric devices. As for technologically important 1–3-type piezoelectric composites, the performance of the PZT rod arrays in the TDE medium can be optimized further by designing geometries. The results presented here suggest routes to materials with large ME effect and multifunctionality.

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