Giant magnetoelectric effect in Ni–lead zirconium titanate cylindrical structure

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The magnetoelectric (ME) coupling of a bilayered Ni–lead zirconate titanate composite structure synthesized by electrodeposition was studied in this paper. The ME voltage coefficient was measured in the range of 1–120 kHz as the bias field is parallel to the axial. The results indicate that an electromechanical resonance appears at 59.9 kHz. The bilayered cylindrical ME composite exhibits a special field dependence of ME coefficient. Either for the resonant state or the nonresonant state, above 1 kOe, the ME voltage coefficient increased linearly with the strengthening of bias field, up to 30 V/cm Oe at 8 kOe. © *2008 American Institute of Physics*.
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Multiferroic materials have recently drawn increased attention due to their multifunctionality, which provides significant potential for applications in the next generation multifunctional devices.[1] In the multiferroic materials, the coupling interaction between multiferroic orders could produce magnetoelectric (ME) or magnetodielectric effects.[2] The ME response, characterized by the appearance of an electric polarization upon applying magnetic field and/or magnetization due to applied electric field, has been observed in some single phase materials.[3,4] Alternatively, multiferroic composites made of ferromagnetics and ferroelectrics were recently found to exhibit large room-temperature extrinsic ME effects.[5–8] This is a product property,[9] i.e., a new property of such composites that neither one of the individual component phases exhibit. This ME effect can be defined as coupling of magnetic, mechanical, and dielectric behaviors. That is, when a magnetic field is applied to these composites, the ferromagnetic phase changes the shape magnetostrictivity, and then the strain is passed to the piezoelectric phase, resulting in an electric polarization.[10]

To achieve better magnetoelectric properties, giant magnetostrictive material $Tb_{1-x}Dy_xFe_{2-y}$ (Terfenol-D) was used combined with piezoelectric materials, such as lead zirconium titanate (PZT) and polyvinylidene fluoride, in a laminate structure.[11–18] The reported ME voltage coefficient, α_E of bulk laminate samples was around 5 V/cm Oe. Later, much higher ME coefficients at the electromechanical resonance frequency have been achieved, ranging from 30.8 to 238 V/cm Oe for different multilayer structures.[19–23] For these bonded plate or disk samples, ME effect only appeared under low applied magnetic field.[11–19] The disadvantages of bonding layers with an adhesive are nonrigid contact, adhesive fatigue, and aging effects. Electrodeposition can be used to make layered magnetoelectric composites, eliminating the need for the interfacial binder. In this work, the giant ME effect under high applied magnetic field in bilayered Ni-PZT cylindrical composite was studied.

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A $Pb(Zr_{0.52}Ti_{0.48})O_3$ cylinder with a height of 3 mm, inner diameter of 18 mm, and outer diameter of 20 mm was polarized at 425 K in an electric field of 50 kV/cm along the radial direction after electroplating Ni electrode on its outer surface. After the cylinder inner wall was protected by silicone rubber, it was bathed in nickel aminosulfonate plating solution to electrodeposit Ni on the outer cylinder side. After 20 h of electrodeposition, the thickness of Ni layer reached 1 mm, as illustrated in Fig. 1. The composition of the plating solution and processing parameters are listed in Table I. Nickel aminosulfonate plating solution was used because of its high chemical stability, high plating rate, and small resulting residual stresses.

By applying both constant (H_{dc}) and oscillating (δH) magnetic fields with a frequency ranging from 1 to 120 kHz along the cylinder axis, the ME voltage coefficient, $\alpha_{E,A}$ was obtained. The voltage δV across the wall of the cylinder was applied with a power supply, amplified, and measured by an oscilloscope. The ME voltage coefficient was calculated based on $\alpha_E = \delta V / t_{PZT} \delta H$, where t_{PZT} is the PZT thickness and δH is the oscillating magnetic field amplitude generated by Helmholtz coils. In this experiment, $\delta H = 22$ Oe as the ac current amplitude through the coils was kept at 1 A.

The ME voltage coefficient dependence on the applied magnetic field, H_{dc} at $f = 1$ kHz is shown in Fig. 2. It reached a maximum value of 0.012 V/cm Oe at $H_m = 0.6$ kOe, decreased rapidly, and then went through a second smaller peak of 0.0025 V/cm Oe at 2.5 kOe. Past these two peaks, the

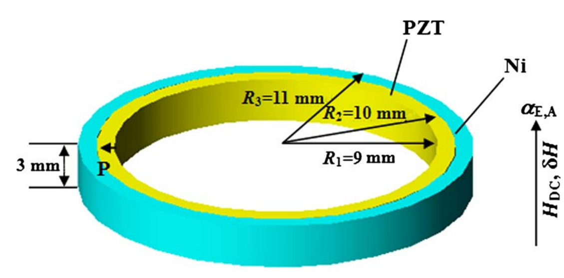

FIG. 1. (Color online) Schematic of the Ni-PZT bilayered cylindrical composite structure.

TABLE I. Composition and process parameters for nickel electrodeposition.

Nickel aminosulfonate concentration (g/l)	600
Nickel chloride concentration (g/l)	20
Boric acid concentration (g/l)	20
Sodium lauryl sulfate concentration (g/l)	0.1
*p*H	4
Temperature (°C)	60
Cathodic current density (A/dm^2)	5

ME voltage coefficient continued to increase linearly with applied magnetic field past 3 kOe.

The frequency dependence of $\alpha_{E,A}$ was measured at the field $H_{dc}=H_m=0.6$ kOe and $H_{dc}=6$ kOe, respectively, as shown in Fig. 3. For both cases, there are sharp peaks at $f_r=59.9$ kHz. Figure 3 shows that giant ME coupling exists not only under low bias field of 0.6 kOe but also under high bias field of 6 kOe as well. The electromechanical resonance peak $\alpha_{E,A(6\text{ kOe})}=21$ V/cm Oe under high field $H_{dc}=6$ kOe is much larger than that under the low field of $H_m=0.6$ kOe.

The bias field dependence of $\alpha_{E,A}$ at resonance frequency $f_r=59.9$ kHz is shown in Fig. 4. The ME voltage coefficient increases linearly with applied magnetic field, up to 30 V/cm Oe at $H_{dc}=8$ kOe.

For ferromagnetic materials, such as Ni, line magnetostriction, $\lambda=\Delta l/l$, increases with bias magnetic field H_{dc}, then reaches a saturation value λ_s at H_s. When $H_{dc}<H_s$, the volume changes, while volume magnetostriction $\omega=\Delta V/V$ is too small to be measured. When $H_{dc}>H_s$, however, volume magnetostriction increases with applied magnetic field, H_{dc}.[24] Under low magnetic field, i.e., $H_{dc}<H_s$, the magnetic field dependence of the ME voltage coefficient α_E is determined by the variation of the piezomagnetic coupling q with the magnetic field H_{dc},[25] and α_E is proportional to q, i.e., $\delta\lambda/\delta H$, where $\delta\lambda$ is the differential magnetostriction. When $H_{dc}=H_s$, $\lambda=\lambda_s$, and then $\delta\lambda/\delta H=0$, therefore, the $\alpha_{E(\lambda)}$ caused by the line magnetostriction is equal to 0 under high applied magnetic field. The volume magnetostriction of ferromagnetic Ni phase under high bias magnetic field $H_{dc}>H_s$ can also generate stress in the piezoelectric PZT phase, resulting in voltage increase of δV across the PZT. According to the field dependence of ME voltage coefficient at resonant state and nonresonant state in our experiment results, the line magnetostriction is saturated below a bias field of 1 kOe, so it will contribute little to the ME effect under a higher magnetic field. The strong ME coefficient under high magnetic field may be induced by the volume

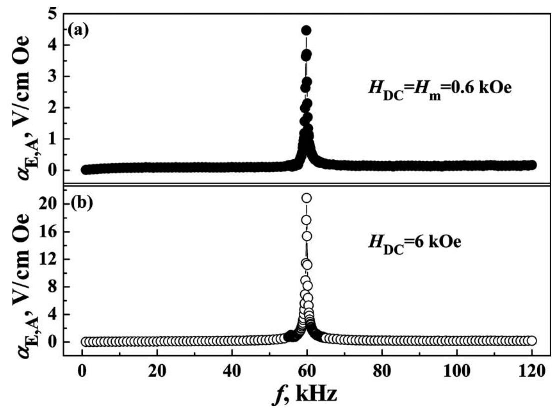

FIG. 3. Frequency dependence of $\alpha_{E,A}$ at (a) $H_m=0.6$ kOe and (b) $H_{dc}=6$ kOe for the Ni-PZT bilayered cylindrical composite.

magnetostriction. The total ME effect is the sum of $\alpha_{E(\lambda)}$ caused by line magnetostriction under low fields and $\alpha_{E(\omega)}$ induced by volume magnetostriction under high fields, i.e., $\alpha_E=\alpha_{E(\lambda)}+\alpha_{E(\omega)}$. For a freestanding unconstrained plate or disk trilayered composite with free boundary conditions, there is no mechanical constraint on the boundary of the ferromagnetic phase; thus, no change in $\alpha_{E(\omega)}$ appears under high field, i.e., $\alpha_E=\alpha_{E(\lambda)}$. However, the stress condition in a cylindrical ME composite is much more complex. When the magnetostrictive Ni ring expands in the magnetic fields, not only its circumference increases but also the diameter rises at the same time due to the self-bound circle effect. So, for the bilayered cylindrical composite, $\alpha_{E(\omega)}$ appears obviously under high bias magnetic field.

Ishio and Takahashi[26] systematically studied the volume magnetostriction in disk fcc Fe–Ni alloys. The volume magnetostriction $(\delta\omega/\delta H)$ was evaluated at about 1×10^{-8} Oe^{-1}, about two orders of magnitude smaller than the line magnetostriction, and was a constant with the strengthening field. However, ME voltage coefficient under high magnetic field is high and increase linearly with the strengthening field. That is related with the complex shape, stress, and boundary conditions of a bilayered cylindrical structure. Further analysis is necessary to quantify and model the stresses and strains and their effect on the ME in the cylindrical composite structure.

There are many ways to sense magnetic fields, most of them are based on the relation between magnetic and electric fields; thus, there are several kinds of magnetic sensors. The

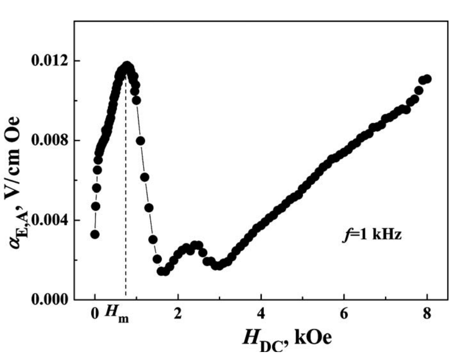

FIG. 2. Magnetoelectric voltage coefficient $(\alpha_{E,A})$ dependence on the bias magnetic field (H_{dc}) at $f=1$ kHz for the Ni-PZT bilayered cylindrical composite.

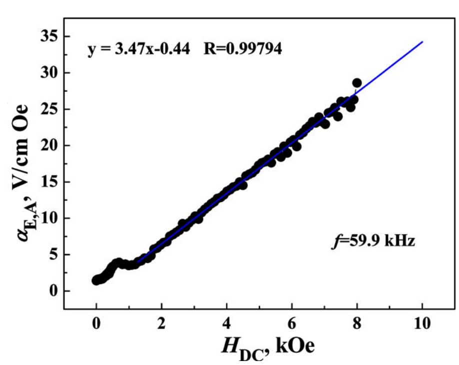

FIG. 4. (Color online) Magnetoelectric voltage coefficient $(\alpha_{E,A})$ dependence on the bias field (H_{dc}) at the resonance frequency of $f_r=59.9$ kHz for the Ni-PZT bilayered cylindrical composite.

most popular sensor technology is based on the Hall effect. The sensor linearity decreases significantly when the external magnetic fields are larger than 1 kOe for most conventional high-field magnetic sensors.[27] As shown in Fig. 4, α_E is linear with the bias magnetic field ($R=0.99794$) for the cylindrical structure, in the 1–8 kOe range. This remarkable linearity at high magnetic field can be utilized for sensor applications.

In summary, the ME voltage coefficient of the Ni-PZT bilayered cylindrical composite may be the sum of $\alpha_{E(\lambda)}$ caused by line magnetostriction, dominating under low magnetic field, and $\alpha_{E(\omega)}$ induced by volume magnetostriction, dominating at higher magnetic field, i.e., $\alpha_E=\alpha_{E(\lambda)}+\alpha_{E(\omega)}$. At the resonance frequency, $\alpha_{E,A(\omega)}$ increases linearly with H_{dc} up to 30 V/cm Oe at $H_{dc}=8$ kOe and is much larger than $\alpha_{E,A(\lambda)}$ at $H_m=0.6$ kOe. The linear relationship between $\alpha_{E,A(\omega)}$ and H_{dc} above 1 kOe could be utilized in using ME Ni-PZT cylindrical composites for the high magnetic field sensor applications.

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