Ni–PZT–Ni trilayered magnetoelectric composites synthesized by 
electro-deposition

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Abstract

We reported the high strength of magnetoelectric (ME) coupling of trilayered composites 
prepared by electro-deposition. The ME coupling of Ni–lead zirconate titanate–Ni trilayered 
structure was measured in the range of 1–120 kHz. The trilayered composites exhibit high ME 
voltage coefficient because of good interfacial bonding between piezoelectric and 
magnetostrictive layers. The peak value of the ME voltage coefficient can be up to 
33 V cm\(^{-1}\) Oe\(^{-1}\) at the electromechanical resonance frequency. This magnetoelectric effect 
shows promise for application in transducers for magnetoelectric energy conversion.

1. Introduction

Multiferroic materials have drawn increasing interest due to 
their multifunctionality, which provides significant potential 
for applications in the next-generation multifunctional de-
vices [1]. In the multiferroic materials, the coupling inter-
action between multiferroic orders could produce many ab-
sorbing effects, such as the magnetoelectric (ME) effect and 
the magnetodielectric effect [2]. The ME response, charac-
terized by the appearance of an electric polarization upon ap-
plying a magnetic field and/or the appearance of magnetiza-
tion upon applying an electric field, has been observed as an 
intrinsic effect in some single-phase materials (e.g. HoMnO\(_3\) 
at low temperature and in high magnetic field) [3]. Alterna-
tively, multiferroic composites made by combination of fer-
roelectric and ferromagnetic substances, such as piezoelectric 
ceramics (e.g. BaTiO\(_3\) and lead zirconate titanate (PZT)) and 
ferrites, were found to exhibit large room temperature extrinsic 
ME effects [4–9]. This ME effect can be defined as a cou-
pling of magnetic–mechanical–dielectric behaviors. That is, 
when a magnetic field is applied to the composites, the magne-
tostrictive phase changes the shape, the strain is passed along to 
the piezoelectric phase, and then an electric polarization hap-
pens [10].

In the last few years, a variety of layered ME composites 
were investigated. Laletin et al reported the ME interactions in 
layered transition metal/PZT samples synthesized by bonding 
slices of PZT and Fe, Co or Ni [11]. To achieve better ME 
properties, giant magnetostrictive material Tb\(_{1-x}\)Dy\(_x\)Fe\(_{2-y}\) (Terfenol-D) was used to combine with piezoelectric materials, 
such as PZT and polyvinylidene fluoride (PVDF), in a laminate 
structure [12–18]. The ME voltage coefficient was around 
5 V cm\(^{-1}\) Oe\(^{-1}\). Latterly, much higher ME coefficients at 
the frequency of electromechanical resonance (EMR) have 
been achieved (from 30.8 to 238 V cm\(^{-1}\) Oe\(^{-1}\) for different 
multilayer structures) [19–23]. But the bonding plastic has the 
disadvantage of fatigue.

Electro-deposition has been widely used in preparing 
composite functional materials, composed of metal and alloys 
with good adhesion [24–26]. Electro-deposition has many 
other outstanding merits; for example it enables us to make 
materials with complex structure, to control the thickness of 
the plating, and to avoid the bonding plastic.

2. Experimental details

PZT slabs were first sliced as 10 mm \(\times\) 20 mm \(\times\) 0.25 mm, 
materialized using sinter sliver paint, and joined to an electrode 
on both sides. PZT slabs were polarized at 425 K in an 
electric field of 30–50 kV cm\(^{-1}\) perpendicular to the sample 
plane. Then PZT slabs were bathed in nickel aminosulfonate 
plating solution, and 0.05 A cm\(^{-2}\) cathodic current density was
applied to electroplate Ni on both sides of PZT slabs. The components of the plating solution and processing parameters are listed in table 1. Nickel aminosulfonate plating solution was used because of its advantages of solution stability, rapid plating speed and small internal stress. Nickel chloride could help the dissolution of the anode. Boric acid acted as a buffer to stabilize the pH of the plating solution. The pH value was adjusted to about 4 by using sulfamic acid and sodium hydroxide. The surfactant sodium lauryl sulfate was used to prevent pinholes on the surfaces of final products. The volume percentage of the total solution was about 1 l. The plating’s thickness could be controlled by the plating time. The thickness of the Ni layer was 0.1 mm for one hour’s plating, and 0.4 mm for four hours’ plating. Before the ME voltage coefficient was measured, the trilayered composites were dried for six days at 100 °C in an oven.

During measuring the ME voltage coefficient, the samples were put in a bias magnetic field \( H \) and an AC field \( \delta H \) (20 Hz–100 kHz). Since the AC magnetic field \( \delta H \) was generated by a Helmholtz coil, the amplitude of the AC magnetic field \( \delta H \) equals 22 Oe when the amplitude of the AC current is 1 A through the coil. The generated voltage \( 8V \) was amplified and measured using an oscilloscope. The ME voltage coefficient was calculated according to \( \alpha_E = 8V/(t_{PZT} \cdot \delta H) \), where \( t_{PZT} \) is the thickness of PZT. They were measured in two different field orientations. The transverse coefficient \( \alpha_{E,31} \) was measured, with \( H \) and \( \delta H \) parallel to the length of the samples (direction 1) and perpendicular to \( \delta E \) (direction 3). The longitudinal coefficient \( \alpha_{E,33} \) was measured with all the fields perpendicular to the sample plane (direction 3).

Table 1. Components and process parameters of the nickel electro-deposition.

| Component                        | Concentration (g l\(^{-1}\)) |
|----------------------------------|------------------------------|
| Nickel aminosulfonate            | 600                          |
| Nickel chloride                  | 20                           |
| Boric acid                       | 20                           |
| Sodium lauryl sulfate            | 0.1                          |
| pH value                         | 4                            |
| Temperature (°C)                 | 60                           |
| Cathodic current density (A dm\(^{-2}\)) | 5                            |

First, the dependence of \( \alpha_E \) on \( H \) was measured at the frequency of the AC magnetic field \( \delta H \) of 1 kHz in transverse (in-plane) and longitudinal (out-of-plane) magnetic fields respectively (figure 1). With the rise of \( H \), there is a sharp peak in the field dependence of \( \alpha_{E,31} \) at \( H_m = 0.16 \) kOe, while a flat peak at \( H_m = 4.5 \) kOe appears in the field dependence of \( \alpha_{E,33} \). The magnitude and field dependences of \( \alpha_E \) are related to many factors, such as the large magnetoelectric susceptibility of the composites and the variation of the demagnetization field [27]. The ME coefficients are directly proportional to the magnetostrictive coefficient \( q \) of the ferromagnetic layer, which will approach zero at saturation magnetization. So both \( \alpha_{E,31} \) and \( \alpha_{E,33} \) will tend to zero in high field. On account of the shape demagnetization effect, \( H_m \) of \( \alpha_{E,31} \) is much lower than that of \( \alpha_{E,33} \). The trend of \( \alpha_{E,31} \) to zero in high field can be observed in the experimental scope of intensity of the magnetic field, while that is not obvious for \( \alpha_{E,33} \).

Second, \( \alpha_E \) was measured in the bias field of \( H_m \) when the frequency of the AC magnetic field \( f \) varied from 1 kHz to 120 kHz (figure 2). A typical \( \alpha_E \) versus \( f \) profile for transverse fields is shown in figure 2(a). For both \( \alpha_{E,31} \) and \( \alpha_{E,33} \), there is a sharp peak at about 88 kHz. However, the peak value of \( \alpha_{E,33} \), about 1.08 V cm\(^{-1}\) Oe\(^{-1}\), is an order of magnitude smaller than that of \( \alpha_{E,31} \). The resonance peak at about 89.9 kHz which
is associated with the electromechanical resonance [28, 29]. The consistency of the resonant frequencies of the dielectric constant and $\alpha_E$ indicates that the high ME effect is associated with the EMR.

Figure 2 inset shows the frequency dependence of $\alpha_{E,31}$ for the samples with different thicknesses of the Ni layer around the frequency of EMR. The frequency of the EMR shifts towards high frequency when Ni layers get thicker, because it is directly proportional to the thickness of the piezoelectric and piezomagnetic layers [30]. Figure 3 inset also shows the frequency dependence of the dielectric constant for the samples with different Ni layer thicknesses, which is consistent with the frequency dependence of the ME coefficient. The resonant frequency of the ME voltage coefficient corresponds to that of dielectric constant for the sample with the same Ni thickness.

Figure 4 plots the dependence of the ME voltage coefficient on $t_{Ni}/(t_{Ni} + t_{PZT})$ for trilayered Ni–PZT–Ni samples at the frequency of EMR. When $t_{Ni}/(t_{Ni} + t_{PZT})$ rises from 0.2 to 0.65, both $\alpha_{E,31}$ and $\alpha_{E,33}$ increase monotonically. When the total thickness of Ni is about 0.4 mm, $\alpha_{E,31}$ is as high as 33 V cm$^{-1}$ Oe$^{-1}$, and $\alpha_{E,33}$ is 1.08 V cm$^{-1}$ Oe$^{-1}$. According to Bichurin’s theoretical model on resonance magnetoelectric effects, the peak values of the ME coefficient are determined by the effective piezomagnetic $(q_{33})$ and piezoelectric $(d_{31})$ coefficients, compliances and permittivity [29]. The experimental result is qualitatively in agreement with the theoretical prediction.

In summary, this paper presents the first report on ME interaction of Ni–PZT–Ni trilayered composites synthesized by electro-deposition. At the frequency of the EMR, the coefficient $\alpha_E$ has a peak value $\alpha_{E,31}$ up to 33 V cm$^{-1}$ Oe$^{-1}$ when the thickness of Ni is about 0.4 mm. Tight bonding between PZT and Ni layers makes these samples exhibit large ME voltage coefficients among bulk magnetoelectric composites. Electro-deposition provides an effective method for remarkably enhancing the ME coefficient of ME composites. In addition, the electro-deposition method makes easy the preparation of ME composites with complex structure, and can control the structural parameters effectively. It will promote a rapid development of magnetoelectric composites’ applications, such as in various magnetoelectric coupling devices.

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