Giant magnetoelectric effect of a hybrid of magnetostrictive and piezoelectric composites

J. G. Wan[a] and J.-M. Liu
Department of Physics and National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China and Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Kowloon, Hong Kong, China

H. L. W. Chand and C. L. Choy
Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Kowloon, Hong Kong, China

G. H. Wang
Department of Physics and National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

C. W. Nan
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

(Received 18 December 2002; accepted 2 April 2003)

A magnetoelectric (ME) hybrid structure is constructed by an efficient coupling between magnetostrictive Terfenol-D ($Tb_{0.27\text{-}0.30}Dy_{0.73\text{-}0.70}Fe_{1.90\text{-}1.95}$)/epoxy and piezoelectric lead–zirconate–titanate [$Pb(Zr_{0.52}Ti_{0.48})O_3$]/epoxy composites. Significant ME effect produced by the piezoelectric k_{31} coupling with the longitudinal vibration of the magnetostrictive component over a wide range of frequency is observed. It is revealed that the ME effect can be enhanced by applying an optimized magnetic bias. A magnetoelectric voltage coefficient as high as 8700 mV/cm Oe is recorded at the resonance frequency of 59.2 kHz for the structure with an optimized magnetic bias of 0.7 kOe. Our measurement confirms that the eddy current loss remains negligibly small at an operating frequency as high as ~200 kHz, predicting very promising applications of the present ME structure. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1577404]

I. INTRODUCTION

Magnetoelectric (ME) effect is defined as a variation of dielectric polarization in a system as a response to an applied magnetic field, or an induced magnetization by an external electric field.[1] With this effect, an effective conversion between electric energy and magnetic energy becomes possible. The ME materials thus represent one kind of smart structures which have received continuous attentions as potential sensors for magnetic field measurements and transducers for magnetoelectric conversion.[2,3] Since the ME effect was observed in antiferromagnetic Cr_2O_3 compound,[4] quite a lot of ME materials and structures have been discovered and developed. Unfortunately, for almost all ME compounds ever discovered, the ME effect, characterized by the magnetoelectric voltage coefficient, e.g., $\alpha_E=(\partial E/\partial H)_T$ with E the probed electric field and H the applied magnetic field, and T the temperature, is too small ($\alpha_E\sim 20$ mV/cm Oe) to be utilized for practical purposes.[4–6]

However, a much higher ME effect has been identified in specially designed composites in which the magnetostrictive phase is combined with the piezoelectric one so that an efficient magnetomechanical–piezoelectric coupling between the two phases is achieved.[7] Since then, much effort has been made along this line. For example, Van den Boomgaard *et al.*[8,9] synthesized a bulk composite of CFO (cobalt ferrite) with $BaTiO_3$, but the ME yield was ~50 times lower than that predicted theoretically. The CFO–lead–zirconate–titanate (PZT) multilayered structures prepared by Harshe *et al.*[10] showed an $\alpha_E\sim 75$ mV/cm Oe, which was still much lower than the predicted value. Recently, strong ME effect was demonstrated in a nickel ferrite (NFO)/PZT multilayered structure prepared by Srinivasan *et al.* using the tape casting technique.[11,12] The reported α_E value was ~1500 mV/cm Oe, which was in excellent agreement with the theoretical prediction.

These earlier studies allow us to emphasize the essential role of two issues in fabricating magnetoelectric composites with enhanced ME effect, on one hand, the two phases chosen must have, respectively, large magnetostrictive and piezoelectric effects. On the other hand, an effective coupling between the magnetomechanical transfer and piezoelectric transfer is the key factor for an enhanced ME effect. In 2001, Ryu *et al.* developed a sandwich structure stacked by giant magnetostrictive material Terfenol-D ($Tb_{0.27\text{-}0.30}Dy_{0.73\text{-}0.70}Fe_{1.90\text{-}1.95}$) and PZT disks. The measured largest value of α_E reached 5900 mV/cm Oe.[13,14] However, the wider application of this structure is seriously limited by the presence of high eddy current loss in Terfenol-D above a few keloherz.[15] To overcome this difficulty, Terfenol-D/polymer composite is an excellent alternative because of its lower eddy current loss in the region of high frequency.[16]

[a]Author to whom correspondence should be addressed; electronic mail: wanjg@nju.edu.cn

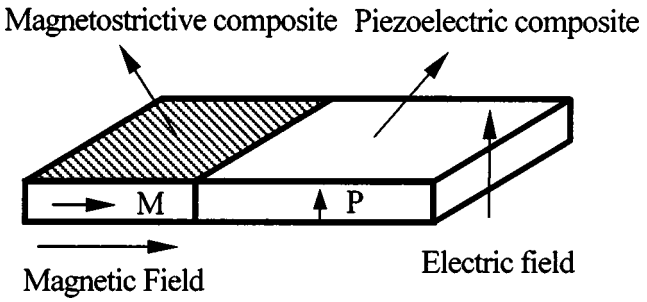

FIG. 1. Schematic of the magnetoelectric composite structure. The arrows *P* and *M* show the poling direction of piezoelectric composite and magnetic domain direction of magnetostrictive composite, respectively.

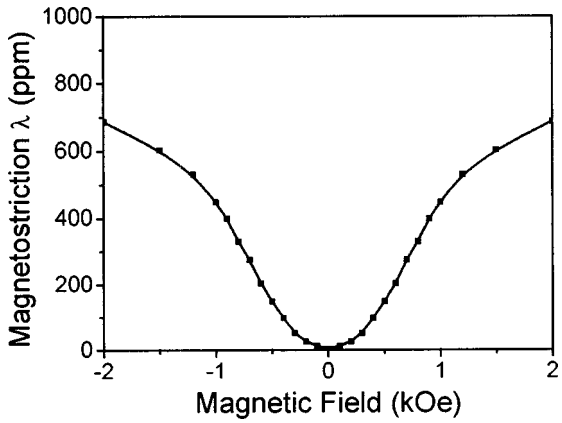

FIG. 2. Mangeostriction response of the Terfenol-D composite as function of applied magnetic field.

Moreover, its tailorable properties enable it to meet the special ME coupling.[16–18]

In this article, we report a ME composite structure based on 0-3 Terfenol-D/Epoxy composite [magnetostrictive component (MSCP)] combined with 0-3 Pb $(Zr_{0.52}Ti_{0.48})O_3$/epoxy composite [piezoelectric component (PECP)]. The structure operates on the longitudinal vibrational mode and a very strong ME yield at the resonance frequency is observed. The PZT/epoxy composite is chosen as the PECP for two reasons. One is that an effective interface matching between MSCP and PECP can be easily achieved by introducing the PZT/epoxy composite. The other is that an efficient ME coupling between the two components is allowed, noting that the acoustic impedance of the two components can be adjusted to optimization by changing the contents of the polymer. Figure 1 is a schematic illustration of the ME composite structure. The arrows *P* and *M* show the poling direction of the PECP and magnetic domain orientation of the MSCP, respectively. Therefore, the MSCP is activated in the longitudinal vibrational mode. When an external ac magnetic field is applied, the mechanical deformation in the MSCP is acoustically transferred to the PECP, thereby resulting in an induced electric field due to the transverse piezoelectric coupling k_{31}.

II. EXPERIMENT

The ME composite structure was prepared by using a compression technique. Terfenol-D powder (from Baotou Rare-earth Institute, China) with an average size of 100 μm and PZT-502 ceramic powder (from PKI, USA) with an average size of 60 μm were separately mixed with epoxy resin (Spurr low-viscosity embedding media. Polyscience Inc.) and precompressed in the rectangular Plexiglass molds to form the Terfenol-D/Epoxy and PZT/epoxy composites with dimensions of 20 mm×20 mm×10 mm (thickness). The volume fractions of Terfenol-D and PZT in the composites are 0.7 and 0.6, respectively. Subsequently, the two precompressed composites were placed into a compaction die with cavity dimensions of 20 mm×20 mm×25 mm (depth) in turn and laminated. The laminated composite was then compacted under a pressure of 50 MPa. In order to align the Terfenol-D powders, compaction was carried out under a static magnetic field of 1.5 kOe, the direction of which is parallel to that of the pressure. After that, the laminated composite was cured at 70 °C for 8 h and then sliced into the samples, as shown in Fig. 1. The dimensions of the Terfenol-D composite and PZT composite in the sample were 6.8 mm (length)×6.2 mm×0.7 mm and 9.1 mm (length)×6.2 mm×0.7 mm, respectively. Finally, the PZT/epoxy component was covered by air-dried silver electrodes and poled in silicone oil at 90 °C and 35 kV/cm for 25 min.

The piezoelectric coefficient of the PZT composite as measured by a piezo d_{33} meter (Model ZJ-3B) is $d_{33}=50$ pm/V. The magnetostriction coefficient λ for the Terfenol-D composite was measured by using a MTI-2000 optical fiber displacement sensor. The ME coefficient $\alpha_E=(\partial E/\partial H)_T$ is determined by the induced electric field generated in the PECP under a small ac magnetic field less than 5 Oe (generated by a solenoid) superposed onto a dc magnetic bias H_{Bias} of up to 2.1 kOe (generated by a pair of permanent NdFeB magnets). Both the ac magnetic field and magnetic bias are parallel to the longitudinal direction of the MSCP. The frequency *f* of the ac magnetic field varies in the range of 0–200 kHz. The solenoid was driven by a signal generator and power amplifier. The induced electric field was measured with a high input impedance circuit and oscilloscope. The ac magnetic field and flux density were, respectively, measured by using a pick-up coil and a search coil connecting with a fluxmeter.

III. RESULTS AND DISCUSSION

Figure 2 shows magnetostriction response of the Terfenol-D composite as function of applied magnetic field. One can observe the changing slope and saturation strain in the butterfly-shaped curve of the double-sided strain versus applied magnetic field. The typical magnetostriction coefficient λ for the Terfenol-D composite at 1.0 kOe is ~450 ppm. Figure 3 presents the flux density of the MSCP in the sample versus magnetic field frequency *f* at various H_{Bias}. The measured response is quite similar to the relative permeability μ_r response reported earlier.[16] Given a magnetic bias H_{Bias}, the fundamental longitudinal resonance appears at *f* ~60 kHz and the peak at ~120 kHz represents the second harmonic resonance.

Figure 4 shows the dependence of α_E on *f*, i.e., disper-

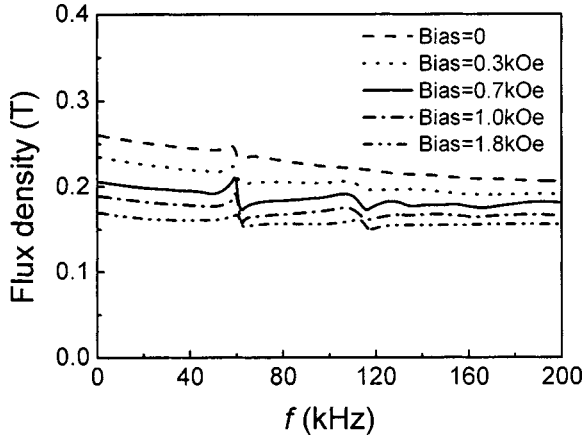

FIG. 3. Flux density of MSCP in the sample as a function of applied magnetic field frequency *f*.

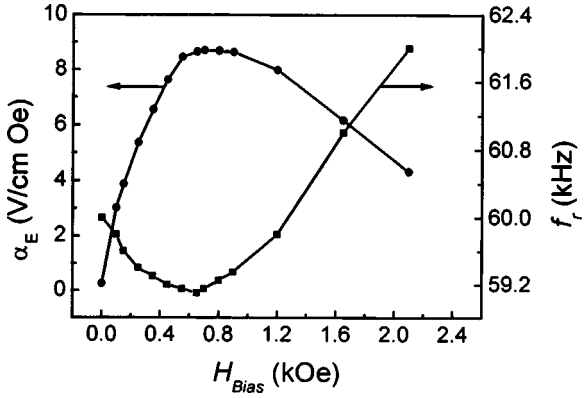

FIG. 5. Magnetoelectric voltage coefficient α_E measured at the resonance and corresponding resonance frequency f_r as functions of magnetic bias H_{Bias}.

sion of the ME effect, under different H_{Bias}. In all cases, no remarkable frequency dispersion is observed except for the resonance ranges, indicating an excellent frequency stability of the ME effect. At $H_{\mathrm{Bias}}=0$, two peaks located at $f=59.8$ and 29.9 kHz, respectively, are observed. The corresponding peak values for α_E are 400 and 180 mV/cm Oe, which are comparable to the values reported.[8–12] The peak at $f=59.8$ kHz is obviously attributed to the fundamental longitudinal vibration of the sample, as confirmed by the measured response of the flux density in Fig. 3, whereas the weaker peak at $f=29.9$ kHz is caused by the double-sided strain response of the Terfenol-D composite versus applied magnetic field. In more detail, the magnetostriction of the Terfenol-D composite is symmetric with magnetization and the double-sided strain versus applied magnetic field or ''butterfly'' results, as shown in Fig. 2. Hence the induced strain of the MSCP shows a doubling of the applied magnetic field frequency *f*, which leads to the piezoelectric vibration of the PECP at 2*f* by the magnetomechanical–electric coupling. When the applied magnetic field frequency *f* is 29.9 kHz, the sample vibrates at a frequency of $2f=59.8$ kHz, which agrees exactly with the fundamental longitudinal resonance of the sample, thus a resonance peak of α_E appears. Once a nonzero magnetic bias H_{Bias} is applied, this so-called frequency doubling of the Terfenol-D composite will be gradually suppressed,[19] and the consequent ME effect will become weaker. In fact, the peak of a_E at $f=29.9$ kHz almost disappears when the applied magnetic bias is above 0.2 kOe in this work.

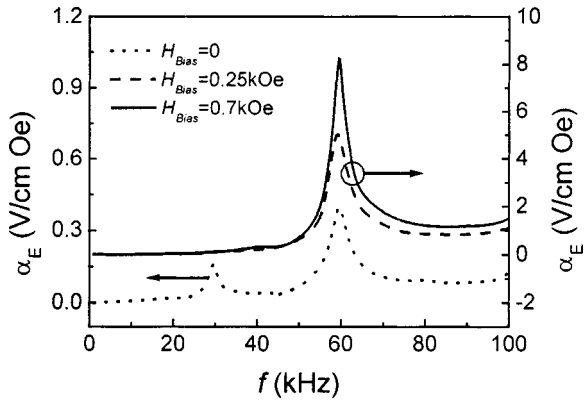

FIG. 4. Freuqency dependence of magnetoelectric voltage coefficient α_E with different magnetic bias H_{Bias}.

Since the magnetostriction slope of the Terfenol-D composite around the zero magnetic bias point is so shallow, vibration of the MSCP under an ac magnetic field is very inefficient, which causes the ME effect to be very weak in this region. By applying a magnetic bias H_{Bias}, however, ac operation of MSCP can be moved to steeper regions of magnetostriction curve, eventually getting into the middle of the burst region, where much larger strains are realized for a given ac magnetic field, hence much stronger ME effects are achieved. As shown in Fig. 4, with H_{Bias} increasing to 0.25 and 0.7 kOe, the peak intensities of α_E at fundamental longitudinal resonance are enhanced by 1 order of magnitude, reaching up to ~5100 and ~8700 mV/cm Oe, respectively. The detailed H_{Bias} dependence of α_E is given in Fig. 5. With increasing H_{Bias} from zero, α_E increase rapidly before reaching a maximum at $H_{\mathrm{Bias}}\sim 0.7$ kOe, and then drops slowly. At the same time, the resonance frequency shifts as a function of H_{Bias}, decreases with increasing H_{Bias} before reaching a minimum at $H_{\mathrm{Bias}}\sim 0.7$ kOe, and then rises slowly. To understand this magnetic bias dependence further, one notes the negative ΔE effect for the MSCP,[18,20] where $\Delta E=(E_{H_{\mathrm{Bias}}}-E_0)/E_0$ with $E_{H_{\mathrm{Bias}}}$ and E_0 the Young's modulus at a given magnetic bias H_{Bias} and zero bias, respectively. At the small ac magnetic field, with increasing H_{Bias} from zero, the mobility of the non-180° domain wall in the MSCP is enhanced and magnetically favored domains grow, which leads to the negative ΔE effect (the elastic moduli at constant magnetic field strength E_H decreases). At the so-called optimized magnetic bias (here it is $H_{\mathrm{Bias}}=0.7$ kOe), the motion of the non-180° domain is maximum and E_H reaches minimum. The MSCP is softened enough that the magnetostrictive coupling factor k_{33} is the highest, leading to the largest strain response. Assuming that the coupling between the MSCP and PECP has nothing to do with the magnetic bias, which seems reasonable, the observed α_E has a maximum at $H_{\mathrm{Bias}}=0.7$ kOe. In fact, k_{33} can be calculated by[17]

$$k_{33}=[1-(f_r^E/f_a^E)^2]^{1/2}, \tag{1}$$

where f_r^E and f_a^E are the resonance frequency and antiresonance frequency, respectively. By taking these characteristic frequency from Fig. 3, the calculated maximum k_{33} at $H_{\text{Bias}}=0.7$ kOe is 0.311, corresponding to a maximum $\alpha_E=8700$ mV/cm Oe at 59.2 kHz, which is much higher than the values of previously reported magnetoelectric materials and structures.[4,10,11,13]

Moreover, the problem of high eddy current loss for Terfenol-D over the high frequency range has been overcome in the Terfenol-D/epoxy composite. The measurement demonstrates that the upper frequency limit for this ME composite structure can be extended up to 100 kHz and higher, as shown in Fig. 4. According to the classical eddy current theory,[21] the critical operating frequency f_c at which serious eddy current loss is expected can be calculated by

$$f_c=\frac{2\rho}{\pi\mu_r\mu_0 t^2}, \tag{2}$$

where ρ is the electric resistivity and t is the effective diameter of the MSCP. Taking $\rho=390\ \mu\Omega\,\text{m}$, $t=7$ mm, and $\mu_r=1.85$ measured at $H_{\text{Bias}}=0.7$ kOe, one has $f_c\sim 2.2$ MHz, which is $\sim$1000 times higher than the critical frequency for bulk Terfenol-D. In fact, apart from the resonance near 60 and 120 kHz, the measured relative permeability μ_r as a function of f is flat enough until $f\sim 200$ kHz. This verifies that the eddy current loss is negligible over a wide range of frequency and the present ME composite structure can be used for high frequency applications at least up to 200 kHz.

IV. CONCLUSION

In conclusion, we have developed a ME composite structure which combined the Terfenol-D/epoxy and PZT/epoxy composites as the MSCP and PECP, respectively. It operates by the longitudinal vibration of the MSCP driving the piezoelectric output of the PECP. Giant magnetoelectric voltage coefficient at the fundamental longitudinal resonance mode of the MSCP with low eddy current loss has been observed, demonstrating a promising application potential for this ME composite structure. The frequency dependence and magnetic bias dependence of the magnetoelectric coefficient suggest that even higher conversion efficiency can be accomplished if the coupling parameters, such as resonance frequency, coupling coefficient, and acoustic impendence etc. are further optimized.

ACKNOWLEDGMENTS

This work was supported by Centre for Smart Materials of the Hong Kong Polytechnic University, the NSFC (Grant No. 10021001), and the National Key Projects for Basic Research of China (Grant No. 2002CB613303) as well as LSSMS of Nanjing University.

[1] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960), p. 119.
[2] T. H. O'Dell, Electron. Power **11**, 266 (1965).
[3] L. P. M. Bracke and R. G. van Vliet, Int. J. Electron. **51**, 255 (1981).
[4] V. J. Folen, G. T. Rado, and E. W. Stalder, Phys. Rev. Lett. **6**, 607 (1961).
[5] S. Foner and M. Hanabusa, J. Appl. Phys. **34**, 1246 (1963).
[6] H. Tsujino and K. Kohn, Solid State Commun. **83**, 639 (1992).
[7] J. van Suchtelen, Philips Res. Rep. **27**, 28 (1972).
[8] J. Van den Boomgaard, D. R. Terrell, and R. A. J. Born, J. Mater. Sci. **9**, 1705 (1974).
[9] J. van den Boomgaard and R. A. J. Born, J. Mater. Sci. **13**, 1538 (1978).
[10] G. Harshe, J. P. Dougherty, and R. E. Newnham, Int. J. Appl. Electromagn. Mater. **4**, 161 (1993).
[11] G. Srinivasan, E. T. Rasmussen, J. Gallegos, R. Srinivasan, Yu. I. Bokhan, and V. M. Laletin, Phys. Rev. B **64**, 214408 (2001).
[12] G. Srinivasan, E. T. Rasmussen, B. J. Levin, and R. Hayer, Phys. Rev. B **65**, 134402 (2002).
[13] J. Ryu, S. Priya, A. V. Carazo, and K. Uchino, J. Am. Ceram. Soc. **84**, 2905 (2001).
[14] J. Ryu, A. V. Carazo, K. Uchino, and H. E. Kim, Jpn. J. Appl. Phys., Part 1 **40**, 4948 (2001).
[15] D. Kendall and A. R. Piercy, J. Appl. Phys. **73**, 6174 (1993).
[16] J. Hudson, S. C. Busbridge, and A. R. Piercy, Sens Actuators **81**, 294 (2000).
[17] J. Hudson, S. C. Busbridge, and A. R. Piercy, J. Appl. Phys. **83**, 7255 (1998).
[18] T. A. Duenas and G. P. Carman, J. Appl. Phys. **87**, 4696 (2000).
[19] F. T. Calkins, M. J. Dapino, and A. B. Flatau, Proc. SPIE **3041**, 293 (1997).
[20] S. W. Or, N. Nersessian, and G. P. Carman, Proc. SPIE **4699**, 451 (2002).
[21] T. F. Hueter and R. H. Bolt, *Sonics* (Wiley, New York, 1955), p. 177.