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Bonded cylindrical Terfenol-D-epoxy/PZT magnetoelectric composites prepared by the one-step compression molding

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Magnetoelectric composites with bonded Terfenol-D-epoxy (TDE) and PZT cylindrical ceramics were prepared by the one-step compression molding at room temperature. The PZT cylindrical ceramics not only provided the piezoelectric phase, but also acted as a mold for TDE. The axial ME voltage coefficient of the cylindrical composites, $\alpha_{E,A}$, was studied. By contrast, the new structure has a larger ME voltage coefficient compared with the effective planar laminated composites due to the self-bound state. This study decreases the ME composite dimensions, making it a promising candidate for the magnetic field sensor applications. [http://dx.doi.org/10.1063/1.4914106]

I. INTRODUCTION

Multiferroic composites made by combining ferroelectric and ferromagnetic materials have been rapidly developing due to the excellent magnetoelectric (ME) effect. The coupling between the ferromagnetic and ferroelectric orders can lead to the ME effect, defined as the induced dielectric polarization under applied magnetic field (H), and vice versa.[1] Due to the weak properties of the single phase multiferroics, composites and multilayer approaches involving strain-coupled piezoelectric (PE) and magnetostrictive components are quite close to practical applications.[2–5] ME composites have many potential applications in multifunctional devices, including transducers, actuators and sensors.[6–9] Therefore, ME composites have become a popular research topic.[10–14]

Giant ME effect of the ME composites is capable to meet practical applications demands. Ma et al.[15] prepared Terfenol-D-epoxy (TDE) medium as a piezomagnetic (PM) phase to solve bulk Terfenol-D problems of brittleness and high eddy current losses at high frequencies by using room temperature curing methods. To ensure the ability of the TDE mixture to fill the mold, about 27 vol% Terfenol-D powder was used. Zuo et al.[16,17] prepared TDE/PZT composites by the two step method. First, TDE with 97 wt% Terfenol-D powder was formed by warm compaction. Then the TDE/PZT plate layered composites were produced by the bonding method, resulting in the excellent voltage coefficient performance. Pan et al.[18,19] prepared Ni/PZT cylindrical composites and discovered that they have larger ME voltage coefficients compared with the plate layered composites due to the fact that cylinder outer and inner faces are constrained in the axial, radial and circumferential directions (the self-bound state). Therefore, these research efforts have demonstrated that better ME properties can be obtained through structural design. These self-bound composites are more efficient in terms of materials and space use. TDE displays better magnetoelastic performance than nickel (Ni).[15]

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TABLE I. Typical characteristics of some representative ME composites.

Representative ME composites	Advantages	Disadvantages	Ref.
Terfenol-D/PZT (2-2-type) laminated composite	(1) Simple and quick fabrication process (2) Large ME voltage coefficient	(1) High eddy current loss at high frequency. (2) Brittleness.	3,16,20
TDE/PZT (1-3-type) composite	(1) Less eddy current loss (2) Stabile mechanical performance	(1) Complex fabrication process (dice-and-fill procedure). (2) Less effective materials (Terfenol-D ~ 27 vol%) in piezomagnetic phase (TDE).	3,11,15
Ni/PZT cylindrical composite prepared by electrodeposition/ electroless-deposition	Preferable structure with larger ME voltage coefficient than 2-2-type laminated composite at same size	(1) Lower magnetoelastic performance of piezoelectric phase (Ni).	21–24

Typical characteristics of some representative ME composites are given in Table I. Comparing the advantages and disadvantages, it is valid to consider that substitute TDE for Ni to make a cylindrical composite can lead to better performance of the composite. The aim of this work is to present TDE/PZT cylindrical composites with a simpler one-step room temperature compression molding method that leads to higher magnetoelectric performance, saves time, energy and expenses associated with fabrication due to a simpler and more rapid manufacturing method. The ME voltage coefficient of these cylindrical composites was investigated.

II. EXPERIMENT

The TDE/PZT cylindrical composites were prepared. The detailed schematic of the composites is shown in Fig. 1. The PZT cylinder with the $\Phi_1 \times \Phi_2 \times h = 15 \times 13 \times 5$ mm^3 dimensions was polarized along the radial direction with Ni electrodes on both inside and outside surfaces. The Terfenol-D particles with ~180 μm size were obtained by crushing bulk Terfenol-D single crystal in argon. A homogeneous mixture consisting of 12 wt% epoxy resin binder and 88 wt% Terfenol-D particles was compacted by uniaxial pressing with randomly oriented particles. Terfenol-D-epoxy needs 24 hours for curing. The TDE with randomly oriented Terfenol-D particles is cured without prestress. The XRD pattern of bonded Terfenol-D particles is highly identical to the standard XRD pattern in detail elsewhere.[16] The ME effect of the TDE/PZT composites was obtained using the ME measurement system (supported by Jun Lu, State Key Laboratory of Magnetism, Institute of Physics,

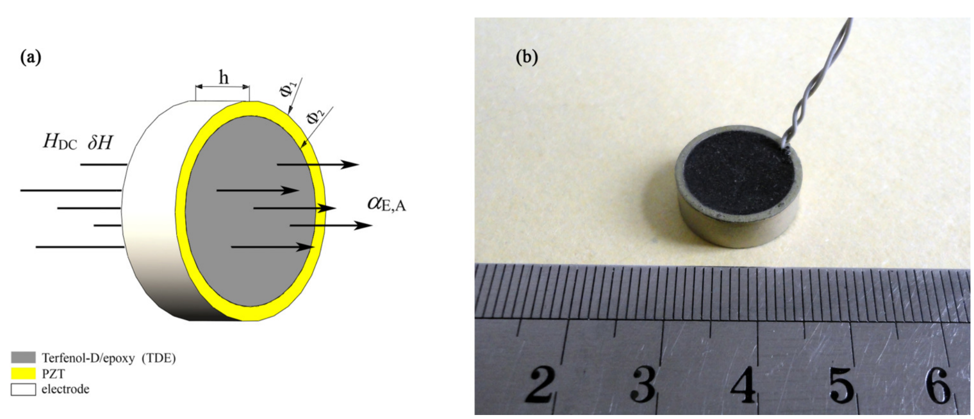

FIG. 1. (a) Schematic illustration of the TDE/PZT cylindrical composites. Vectors identify the direction of the applied magnetic field, and the corresponding ME voltage coefficients; (b) Picture of the actual sample. The scale is in cm.

Chinese Academy of Sciences, Beijing 100190, China) where constant (H_{DC}) and alternating (δH) magnetic fields were applied in the parallel (axial) mode. The ME voltage coefficient was calculated as $\alpha_E = \delta V/(t_{PE} \cdot \delta H)$, where t_{PE} is the PZT layer thickness and δH is the amplitude of the AC magnetic field generated by the Helmholtz coils. The AC current flowing through the coil with the applied magnetic field amplitude of $\delta H = 1.2$ Oe was equal to 1 A. The ME voltage coefficient, $\alpha_{E,A}$, was measured when H_{DC} and δH were applied along the axial direction of the cylinder.[21]

III. RESULTS AND DISCUSSION

Fig. 2 shows typical $\alpha_{E,A}$ and H_{DC} dependence on frequency for the Terfenol-D/PZT composites. As seen in Fig. 2(a), a giant ME coefficient $\alpha_{E,A}$ of 3.37 V/cm · Oe at 64.8 kHz is observed. This giant ME response at high frequency is attributed to the electromechanical resonance,[25] which significantly enhances the elastic coupling interaction between the TDE medium and the PZT cylinder. The ME coefficient $\alpha_{E,A}$ dependence on the magnetic field is seen in Fig. 2(b). In the low field range $\alpha_{E,A}$ increases approximately linearly with the magnetic bias due to the increasing magnetostriction. In the high magnetic field range $\alpha_{E,A}$ increases to a maximum value at the optimal magnetic field, $H_m = 2.6$ kOe, and then, $\alpha_{E,A}$ decreases. The maximum ME voltage coefficient of these composites, $\alpha_{E,A}$ is 3.35 V/cm · Oe.

According to the Pan's model,[24] cylindrical ME composite axial coupling mode can be dealt with as an effective plate bi-layered ME composite in the width direction mode. The dimensions of the simplified plate bi-layered ME composites are $h \times L^{eff} \times t$, where t is the total thickness of the piezoelectric phase, t_{PE}, and the PM phase, t_{PM}, as shown in Fig. 3. To ensure similar conditions of the ME coupling, this study designated $t_{PE} = 1$ mm, $h = 5$ mm (the same as the PZT cylinder) with the effective length of about 41 mm ($L^{eff} = \pi \cdot \Phi_2$). To have the same contact area between the two phases, t_{PM} was set at about 3 mm ($\pi \cdot r^2 = t_{PM} \cdot h$), which guaranteed that there is the same TDE volume. So that $h \times L^{eff} \times t = h \times L^{eff} \times (t_{PE} + t_{PM}) = 5\ \text{mm} \times 41\ \text{mm} \times 4\ \text{mm}$. After simplification, the effective magnetic fields ${H_{DC}}^{eff}$ and δH^{eff} are along the width direction, and their values are the same as the measured and the applied magnetic fields (${H_{DC}}^{eff} = H_{DC}$, $\delta H^{eff} = \delta H$).

The effective plate bi-layered ME composite sample has been prepared. Fig. 4 shows the test result of the effective plate sample. The ME voltage coefficient, $\alpha_{E,A}$ is in a transverse direction of the plate composite, while $\alpha_{E,32}$ is about 2.75 V/cm · Oe at the corresponding 1.7 kOe optimal magnetic field and 31 kHz resonant frequency. Comparing the two composites, the peak value of $\alpha_{E,A}$ is 3.37 V/cm · Oe, about 1.2 times larger than $\alpha_{E,32}$. This demonstrates that the self-bound state of the cylindrical structure can promote the ME effect, compared with the planar laminated structure with more free surfaces.[19,24] There is a slight difference in H_m between the two samples with the same piezomagnetic (PM) phases, suggesting that H_m strongly depends on the geometry of the composites.

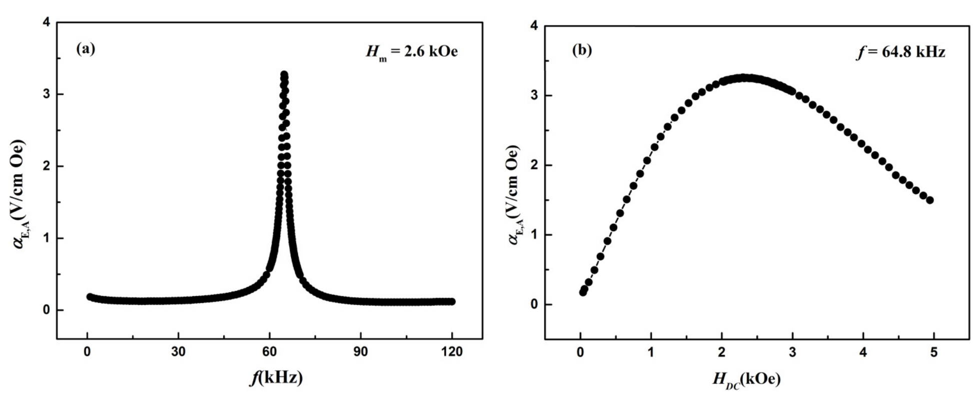

FIG. 2. (a) $\alpha_{E,A}$ dependence on the AC magnetic field frequency (f) at the optimal magnetic field (H_m), corresponding to the maximum ME coupling; (b) $\alpha_{E,A}$ dependence on H_{DC} at the resonant frequency.

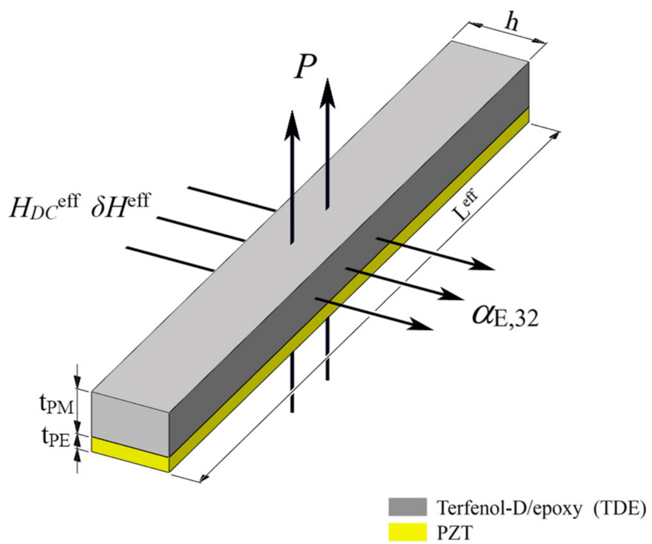

FIG. 3. Schematic illustration of the TDE/PZT planar laminated composites for the differential coefficient calculation.

The complex structure (such as the cylindrical structure) of the ME composites is usually prepared by Ni electrodeposition or electroless deposition.[22,26] In this work, cylindrical ME composites were successfully obtained using Terfenol-D-epoxy instead of Ni, which has much better magnetostrictive performance. The ME effect was compared using the representative axial mode with the 32 direction of the planar laminated sample. The overall $\alpha_{E,A}$ is about 1.2 times larger than $\alpha_{E,32}$. This suggests that the different bonding layered structure of the piezoelectric phase (such as PZT) has a different stress state. The cylindrical PE phase is under higher normal stress and lower shear stress due to the self-bound state. By contrast, the planar PE phase is primarily under shear stress due to the planar laminated structure which allows more free surfaces. Since the cylinder can be simplified as a bi-layer plate, $\alpha_{E,A}$ and $\alpha_{E,32}$ are equivalent for the ME composite with the $5 \times 41 \times 4$ mm^3 dimensions. Using the Pan's model conversion,[24] the dimensions of the ME composites can be decreased further using the TDE/PZT cylindrical composites with the same ME voltage coefficient.

IV. CONCLUSIONS

The TDE/PZT cylindrical ME composites have been prepared using the one-step compression molding, without any additional processes. The fabrication process is much simpler than the previous bonded TDE/PZT composites, which makes it more cost efficient. The experimental results

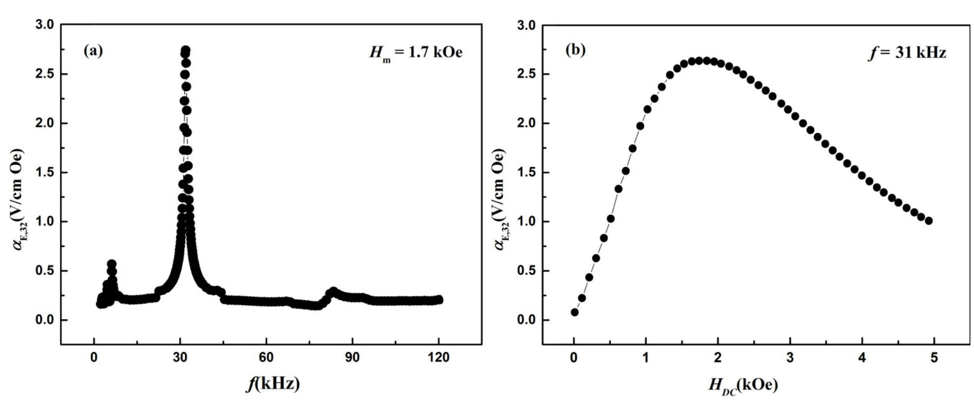

FIG. 4. (a) $\alpha_{E,32}$ dependence on the AC magnetic field frequency (f) at the optimal magnetic field (H_m), corresponding to the maximum ME coupling; (b) $\alpha_{E,32}$ dependence on H_{DC} of at the resonant frequency.

have demonstrated that this composite structure has larger ME voltage coefficient and smaller geometric dimensions compared with the effective planar laminated composites due to the self-bound state. The favorable performance of the TDE/PZT cylindrical composites with a simple and effective manufacturing method can facilitate the ME devices miniaturization and design for practical applications.

ACKNOWLEDGMENTS

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[1] M. Bibes and A. Barthelemy, Nat Mater. **7**, 425 (2008).
[2] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature. **442**, 759 (2006).
[3] C.-W. Nan, M. I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, J. Appl. Phys. **103**, 031101 (2008).
[4] R. Ramesh and N. A. Spaldin, Nat Mater. **6**, 21 (2007).
[5] J. H. Lee, L. Fang, E. Vlahos, X. Ke, Y. W. Jung, L. F. Kourkoutis, J.-W. Kim, P. J. Ryan, T. Heeg, M. Roeckerath, V. Goian, M. Bernhagen, R. Uecker, P. C. Hammel, K. M. Rabe, S. Kamba, J. Schubert, J. W. Freeland, D. A. Muller, C. J. Fennie, P. Schiffer, V. Gopalan, E. Johnston-Halperin, and D. G. Schlom, Nature. **466**, 954 (2010).
[6] M. Vopsaroiu, M. G. Cain, G. Sreenivasulu, G. Srinivasan, and A. M. Balbashov, Mater. Lett. **66**, 282 (2012).
[7] S. Marauska, R. Jahns, C. Kirchhof, M. Claus, E. Quandt, R. Knöchel, and B. Wagner, Sensors and Actuators A: Physical. **189**, 321 (2013).
[8] P. Li, Y. Wen, X. Huang, J. Yang, J. Wen, J. Qiu, Y. Zhu, and M. Yu, Sensors and Actuators A: Physical. **201**, 164 (2013).
[9] M. Li, Y. Wen, P. Li, and J. Yang, Sensors and Actuators A: Physical. **194**, 16 (2013).
[10] F. D. Ma, Y. M. Jin, Y. U. Wang, S. L. Kampe, and S. Dong, Acta Mater. **70**, 45 (2014).
[11] J. Ma, J. Hu, Z. Li, and C.-W. Nan, Adv. Mater. **23**, 1062 (2011).
[12] M. Liu, Z. Zhou, T. Nan, B. M. Howe, G. J. Brown, and N. X. Sun, Adv. Mater. **25**, 1435 (2013).
[13] S. Dasgupta, B. Das, M. Knapp, R. A. Brand, H. Ehrenberg, R. Kruk, and H. Hahn, Adv. Mater. **26**, 4639 (2014).
[14] D. A. Pan, Z. J. Zuo, S. G. Zhang, B. Liu, L. J. Qiao, and A. A. Volinsky, AIP Advances. **4**, 117108 (2014).
[15] J. Ma, Z. Shi, and C. W. Nan, Adv. Mater. **19**, 2571 (2007).
[16] See supplementary material at http://dx.doi.org/10.1063/1.4914106 for XRD pattern of the bonded Terfenol-D particles (TDE) composite.
[17] Z. J. Zuo, D. A. Pan, Y. M. Jia, S. G. Zhang, and L. J. Qiao, AIP Advances. **3**, 122114 (2013).
[18] D. A. Pan, Y. Bai, A. A. Volinsky, W. Y. Chu, and L. J. Qiao, Appl. Phys. Lett. **92**, 052904 (2008).
[19] D. A. Pan, J. J. Tian, S. G. Zhang, J. S. Sun, A. A. Volinsky, and L. J. Qiao, Materials Science and Engineering: B. **163**, 114 (2009).
[20] Z. J. Zuo, D. A. Pan, J. Lu, S. G. Zhang, J. J. Tian, L. J. Qiao, and A. A. Volinsky, Appl. Phys. Lett. **104**, 032906 (2014).
[21] D. a. Pan, J. Wang, Z. Zuo, S. Zhang, B. Liu, A. A. Volinsky, and L. Qiao, Mater. Lett. **133**, 255 (2014).
[22] D. Pan, J. Wang, Z. Zuo, S. Zhang, L. Qiao, and A. Volinsky, Appl. Phys. Lett. **104**, 122903 (2014).
[23] D. A. Pan, S. G. Zhang, A. A. Volinsky, and L. J. Qiao, Journal of Physics D: Applied Physics. **41**, 172003 (2008).
[24] D. A. Pan, S. G. Zhang, A. A. Volinsky, and L. J. Qiao, Journal of Physics D: Applied Physics. **41**, 205008 (2008).
[25] M. Bichurin, D. Filippov, V. Petrov, V. Laletsin, N. Paddubnaya, and G. Srinivasan, Phys. Rev. B. **68** (2003).
[26] D. Xie, Y. G. Wang, and J. H. Cheng, J. Alloy. Compd. **615**, 298 (2014).