Magnetoelectric effect in lead-free BNKLBT ceramic/terfenol-D continue fiber composite laminates

C. Y. Lo,[a] S. H. Choy, S. W. Or, and H. L. W. Chan
Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hunghom, Hong Kong, China

(Received 5 February 2010; accepted 13 March 2010; published online 6 May 2010)

A magnetostrictive-piezoelectric laminated composite has been developed by sandwiching a lead-free BNKLBT ceramic plate polarized in the thickness direction between two terfenol-D continuous fiber composite plates. This lead-free magnetoelectric (ME) laminated composite has a large ME voltage sensitivity of 2.5 V/Oe at the resonance frequency of 130.9 kHz under a low magnetic bias field (H_{Bias}) of 0.6 kOe. This work shows the potential of BNKLBT lead-free ceramics in ME sensing application. [doi:10.1063/1.3385413]

I. INTRODUCTION

Magnetoelectric (ME) composites have received an increased interest due to its many potential applications in magnetic field measurement, position sensing, and digital compass electronics.[1–4] Besides single phase ME materials, magnetostrictive-piezoelectric laminated composites with different orientations and scales in the magnetic and electric phases have aroused extra attentions and many studies have been reported in the past years.[5–7] Magnetostrictive-piezoelectric laminated composites consist of magnetostrictive and piezoelectric materials, which generate relatively strong electrical response by external alternating magnetic field especially at its resonance.[8]

In previous studies, the piezoelectric phase in ME composites is dominated by lead zirconate titanate (PZT) or other lead-based material due to their superior piezoelectric properties. However, lead may cause a range of health hazards, from behavioral problems and learning disabilities, to seizures and death. In order to produce an environmental friendly sensor element, it is desirable to use lead-free piezoelectric ceramics to replace lead-based piezoelectric ceramics. Hence, increased attentions have been drawn to the investigation of lead-free piezoelectric ceramic sensors and devices.[9–13]

In this study, we aim to fabricate an environmental friendly, lead-free magnetostrictive-piezoelectric laminated composite with good ME voltage sensitivity. Lead-free BNKLBT ceramic, with a chemical formula of $0.885(Bi_{0.5}Na_{0.5})TiO_3-0.05(Bi_{0.5}K_{0.5})TiO_3-0.015(Bi_{0.5}Li_{0.5})TiO_3-0.05BaTiO_3$, has been selected to be the piezoelectric phase to replace lead-based ceramics as it has relatively good piezoelectric properties. The magnetostrictive phase was made of terfenol-D continuous fiber composite. As shown in Fig. 1, this magnetostrictive-piezoelectric laminated composite consist of two outer terfenol-D continuous fiber composite plates magnetized in the longitudinal direction and a lead-free BNKLBT ceramic plate placed along the longitudinal direction and polarized in the thickness direction. In order to enhance the ME sensitivity, the magnetostrictive phase is made of terfenol-D continuous fiber composite, thus increasing the magnetoelastic response in the high frequency regime. The tailorable magnetostrictive phase can facilitate a higher ME voltage sensitive at both low and high frequency and at its resonance due to reduction in eddy-current loss.

II. EXPERIMENTAL SETUP

The continuous fibers with a square cross section were cut along the length of a [112]-textured monolithic terfenol-D plate (Fig. 2) using an electrical discharge machine. The length and width of the fibers are 45 mm and 1 mm, respectively. Araldite GY251/HY956 (10:2) epoxy was used as the matrix material in the magnetostrictive composite with terfenol-D as the continuous fiber material. The terfenol-D fibers were cleaned to remove the surface oxide by ethanol and aligned along the longitudinal direction with designated volume percent, then the epoxy matrix were homogenously mixed, degassed, and molded using a vacuum resin transfer molding process. After curing at room temperature for solidification, the composite plate was demolded and postcured at 80 °C for 8 h. The conventional mixed oxide technique was used to prepare BNKLBT-1.5 ceramics.[9] The ceramic samples were poled under 4 kV/mm electric field after polished and applied with fired-on silver electrodes.

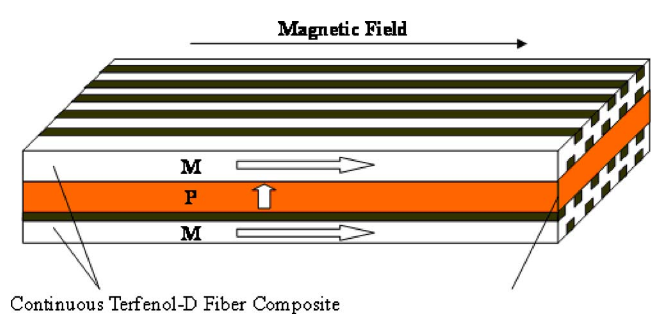

FIG. 1. (Color online) Schematic diagram of the ME laminated composite with terfenol-D continuous fiber composite and lead-free BNKLBT ceramic. The arrows M and P indicate the [112] direction of terfenol-D and polarization direction, respectively.

[a]Electronic mail: apshchoy@polyu.edu.hk.

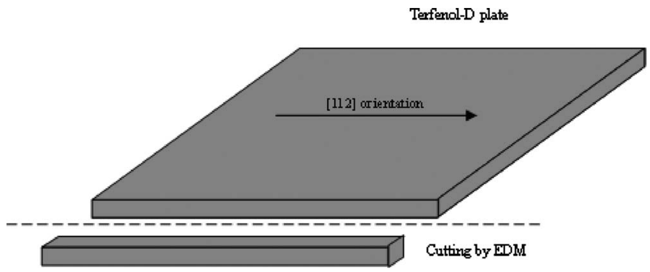

FIG. 2. Terfenol-D continuous fiber is cut along the [112] direction from a terfenol-D plate.

The magnetostrictive composite and the BNKLBT ceramic plates were cut into the dimensions of $12\times6\times1\ \text{mm}^3$. The ME composite laminate shown in Fig. 1 is sensing with the longitudinal-transverse (L-T) mode. The interfaces of the plates were bonded by E-solder® 3022 conductive adhesives (Von Roll Isola, USA) under a vertical pressure of 5 MPa at room temperature for 24 h to provide a good mechanical adhesion between the laminates.

The ME effect of the ME composite laminate was measured by a sinusoidal magnetic drive field (H_{ac}) of 1 Oe with a frequency range of 1–200 kHz and then the voltages (V) generated from the ME composite laminate under various magnetic bias fields (H_{Bias}) of 0–2.0 kOe. Displacement of the terfenol-D and its composite in the thickness direction was measured by a laser vibrometer (OFV 3001 with OFV 303). H_{ac} along the length direction was provided by a Helmholtz coil driven by a signal generator via a high speed power amplifier (AE Techron 7572). H_{Bias} was applied by a variable gap permanent magnet (Pasco EM-8641). H_{ac} and H_{Bias} were measured by a pick-up coil and a Gaussmeter (F.W. Bell 7030), respectively. All quantities were sampled and recorded by a digital oscilloscope (LeCory WaveRunner 44MXi) and stored in a computer. Impedance and phase were measured using an impedance analyzer (Agilent 4294A). Sensitivity of the ME composite at different frequencies under different H_{Bias} was calculated using

$$ME_v = \frac{V(V)}{H(Oe)}. \tag{1}$$

The frequency dependence of dynamic strain coefficient $d_{33,m}$ of the magnetostrictive phase, namely, monolithic terfenol-D and terfenol-D continuous fiber composite, were measured for various H_{Bias} within a frequency range of 1–200 kHz and the $d_{33,m}$ was obtained from

$$d_{33,m} = \frac{s_3}{h_3}, \tag{2}$$

where s_3 is the displacement of the sample in the length direction parallel to the applied ac magnetic field $h_3(=H_{ac})$.

III. RESULTS AND DISCUSSION

The $d_{33,m}$ of both monolithic terfenol-D and terfenol-D continuous fiber composite are shown in Figs. 3(a) and 3(b), respectively. It can be seen in Fig. 3(a) that the resonance of monolithic terfenol-D shifts to higher frequencies when H_{Bias} increases. It is noted that under different H_{Bias}, composite with continuous fiber has similar $d_{33,m}$ in the lower frequency region (<20 kHz). Due to reduction in eddy-current loss, $d_{33,m}$ in the fundamental shape resonance frequency greatly increases to 140 nm/A which is much higher than the $d_{33,m}$ of monolithic terfenol-D (40 nm/A) and the sharp peak of the resonance of the continuous fiber composite indicated the insignificant eddy-current loss. Also, due to reduction in eddy-current loss, $d_{33,m}$ of terfenol-D continuous fiber composite in the higher frequency region (>50 kHz) are obviously higher than that of monolithic terfenol-D. This significant feature greatly increases the ME sensitivity in the high frequency region and at the fundamental shape resonance frequency.

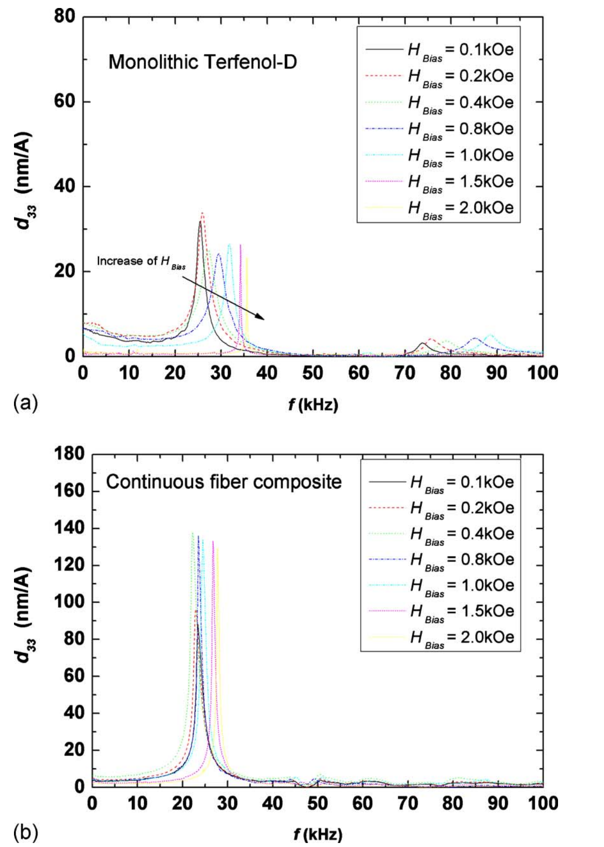

FIG. 3. (Color online) (a) d_{33} vs f at different H_{Bias} for monolithic terfenol-D and (b) d_{33} vs f at different H_{Bias} for the continuous fiber composite.

Figure 4 shows the electrical impedance and phase spectra of the laminated composite. The observed resonance peak (132.3 kHz) is in agreement with the results of ME frequency response shown in Figs. 5(a) and 5(b). At resonance, uniform expansion and contraction occurs in the longitudinal direction of the piezoelectric layer. A clear sharp peak in the electrical impedance spectrum of the composite shows good coupling between the piezoelectric and magnetostrictive layer and also within the epoxy bonded magnetostrictive layer.

The ME_v versus frequency curves at different H_{Bias} are shown in Fig. 5(a). Dependence of H_{Bias} is observed for all curves and also there are variations associated with the fundamental resonance around 132 kHz. This observation agree with Fig. 3(b) that the existence of a small eddy-current ef-

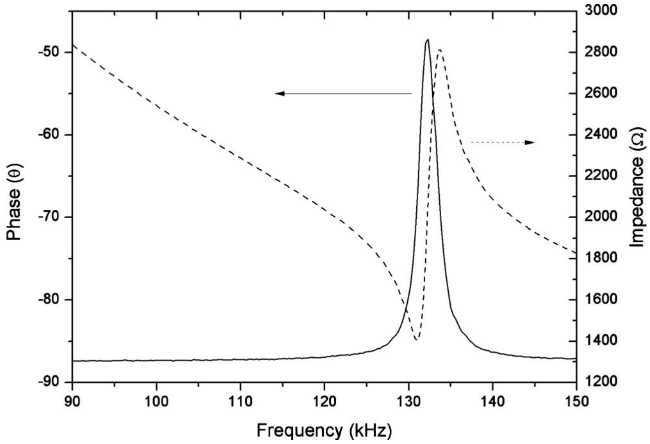

FIG. 4. Electrical impedance and phase vs frequency spectra for a ME laminated composite.

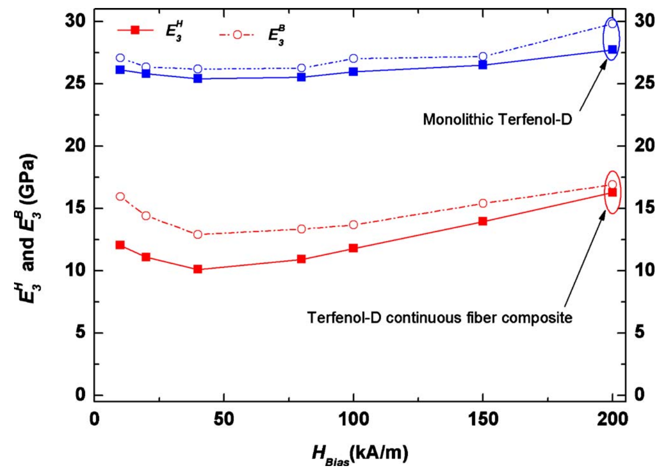

FIG. 6. (Color online) Dependence of Young's modulus E_3^H and E_3^B on H_{Bias} for continuous fiber composite and monolithic terfenol-D.

fect in the terfenol-D continuous fiber composite and thus improved the ME sensitivity of the laminated composite at high frequency. The largest ME effect is observed at $H_{\mathrm{Bias}}=0.6$ kOe for the whole frequency range. In particular, the largest ME_v located at the resonance of 130.9 kHz under this optimal H_{Bias} is as high as 2.5 V/Oe. This is 16 times larger than its off-resonance ME_v of 0.15 V/Oe at 100 kHz. Figure 5(b) illustrates the ME_v versus frequency at different H_{Bias} in the resonance region. ME_v increases initially upto 2.5 V/Oe at $H_{\mathrm{Bias}}=0.6$ kOe and then decreases with increasing H_{Bias}. In the meantime, the resonance frequency decreases with increasing H_{Bias}, reaching 130.9 kHz at 0.6 kOe and then increases with increasing H_{Bias}. The ME of the zero H_{Bias} and optimal H_{bias} (0.4 kOe) are vary from 0.31 to 0.44 at 140 kHz, which is about 42% increase which shown a significant increment on the appearance of H_{bias}.

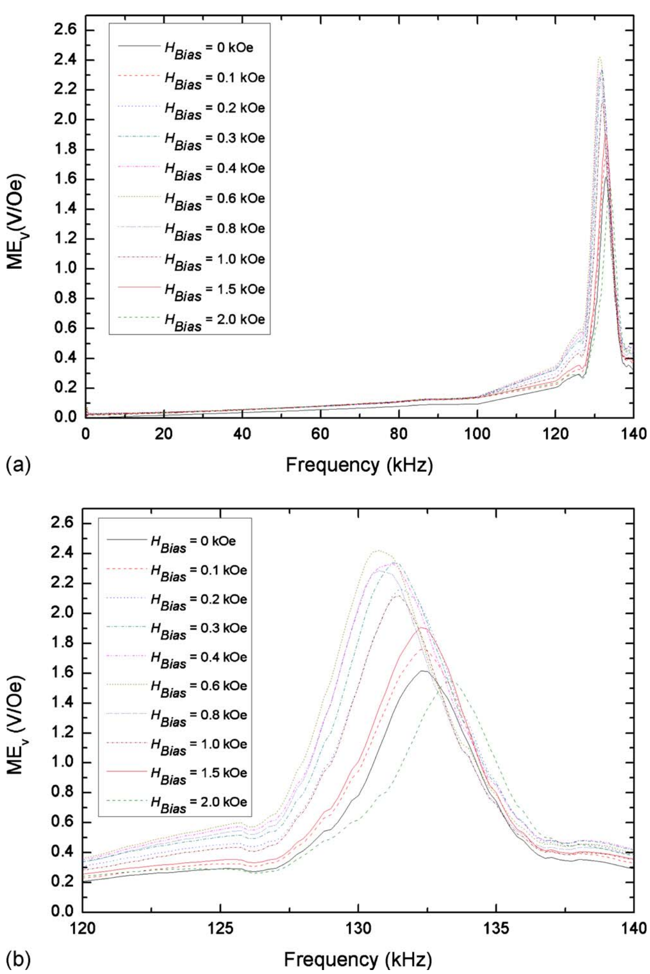

FIG. 5. (Color online) (a) ME_v vs f at different H_{Bias} for the continuous fiber composite (0–140 kHz) and (b) ME_v vs f at different H_{Bias} for the continuous fiber composite (120–140 kHz).

Considering that the non-180° domain wall motion changes both the Young's modulus and the $d_{33,m}$ of terfenol-D continuous fiber composite,[14] therefore, the initial decrease in modulus with increasing H_{Bias} is mainly attributed to the non-180° domain wall motion which agrees with the variation in E_3^H and E_3^B shown in Fig. 6, E_3^H and E_3^B are defined as Young's modulus at constant H field and Young's modulus at constant B field, respectively. They are measured as a function of dc magnetic field H_{Bias} using resonance technique. As H_{Bias} is increased to 0.6 kOe where maximum negative change in E_3^H and E_3^B occurs, the compliance related to increased deformation contribution from this non-180° domain wall motion reaches its maximum, resulting in a minimal stiffness. Above 0.6 kOe, the modulus increases again with H_{Bias} because the limited amount of non-180° domain wall motion in higher H_{Bias} tends to stiffen the composites. Therefore, the change of the resonance frequency and increase of ME_v is contributed by the variation in Young's modulus in response to the increase in H_{Bias}.

In the BNKLBT/terfenol-D continuous fiber composite laminate, which is consider as a L-T composite, the ME voltage coefficient $V_{\mathrm{ME}}^{\mathrm{LT}}$ for L-T laminates is given by[15]

$$V_{\mathrm{ME}}^{\mathrm{LT}} = \frac{|dE_1|}{|dH_3|} = \frac{n d_{33,m} d_{31,p}}{n \varepsilon_{33}^S \varepsilon_{11}^S + (1-n) s_{33}^H (\varepsilon_{33}^S + d_{31,p}^2 / s_{11}^E)}, \quad (3)$$

where n is the magnetic phase thickness ratio. s_{11}^E and s_{33}^H are the elastic compliances of the piezoelectric and magnetostrictive layers, respectively. ε_{33}^S is the dielectric constant of the piezoelectric material at constant strain, and $d_{33,m}$ and $d_{31,p}$ are the longitudinal magnetostriction and transverse piezoelectric coefficients, respectively.

TABLE I. Materials properties of BNKLBT-1.5 ceramics (Ref. 9).

Sample	BNKLBT-1.5
Density (kg m^{-3})	5780
Relative permittivity ε_r	766
tan δ loss (%)	1.61
k_t	0.53
k_p	0.33
k_{31}	0.19
d_{33}(pC/N)	163
d_{31}(pC/N)	−43
Poisson ratio σ	0.278

Although the $d_{31,p}$ of BNKLBT is only −43 pC/N (Table I), which is smaller than the lead-base ceramics, however, the lower dielectric constant of BNKLBT and the superior property of the terfenol-D continuous fiber composite at high frequency and at resonance frequency compensate for the reduction in $d_{31,p}$, therefore the sensitivity gradually increase in the high frequency region.

IV. CONCLUSIONS

We have fabricated a ME laminated composite based on plate-shaped lead-free BNKLBT ceramic/terfenol-D continuous fiber composite and characterized its dynamic ME properties. A large ME_v of 2.5 V/Oe at the resonance frequency of 130.9 kHz with reduced eddy-current loss has been observed at a low H_{Bias} of 0.6 kOe. The lead-free ceramic in the ME conversion device shows good properties coupling with a terfenol-D continuous fiber, this unveils the potential of the lead-free ceramics in ME sensing applications.

ACKNOWLEDGMENTS

Financial support from the NSFC/RGC Project (N-PolyU 501/08) and the Centre for Smart Material of the Hong Kong Polytechnic University are acknowledged.

[1]E. Hristoforou and A. Ktena, J. Magn. Magn. Mater. **316**, 372 (2007).
[2]S. Priya, R. Islam, S. Dong, and D. Viehland, J. Electroceram. **19**, 149 (2007).
[3]E. Quandt, S. Stein, and M. Wuttig, IEEE Trans. Magn. **41**, 967 (2005).
[4]T. Ueno and T. Higuchi, IEEE Trans. Magn. **41**, 3670 (2005).
[5]J. Zhai, Z. Xing, S. Dong, J. Li, and D. Viehland, J. Am. Ceram. Soc. **91**, 351 (2008).
[6]V. Castel and C. Brosseau, Appl. Phys. Lett. **92**, 233110 (2008).
[7]V. Castel, C. Brosseau, and J. B. Youssef, J. Appl. Phys. **106**, 064312 (2009).
[8]M. I. Bichurin, D. A. Filippov, V. M. Petrov, V. M. Laletsin, N. Paddubnaya, and G. Srinivasan, Phys. Rev. B **68**, 132408 (2003).
[9]S. H. Choy, X. X. Wang, H. L. W. Chan, and C. L. Choy, Appl. Phys. A: Mater. Sci. Process. **89**, 775 (2007).
[10]H. L. W. Chan, S. H. Choy, C. P. Chong, H. K. Li, and P. C. K. Liu, Ceram. Int. **34**, 773 (2008).
[11]G. C. Edwards, S. H. Choy, H. L. W. Chan, D. A. Scott, and A. Batten, Appl. Phys. A: Mater. Sci. Process. **88**, 209 (2007).
[12]S. H. Choy, H. K. Li, K. H. Lam, H. L. W. Chan, and C. L. Choy, Ferroelectrics **358**, 85 (2007).
[13]S. H. Choy, X. X. Wang, H. L. W. Chan, and C. L. Choy, Appl. Phys. A: Mater. Sci. Process. **82**, 715 (2006).
[14]G. P. Mcknight, PhD Thesis, University of California, 2002.
[15]J. Zhai, S. Dong, Z. Xing, J. Li, and D. Viehland, Appl. Phys. Lett. **89**, 083507 (2006).