AIP Journal of Applied Physics

Self-biased magnetoelectric response in three-phase laminates

Su-Chul Yang, Chee-Sung Park, Kyung-Hoon Cho, and Shashank Priya

Citation: Journal of Applied Physics **108**, 093706 (2010); doi: 10.1063/1.3493154
View online: http://dx.doi.org/10.1063/1.3493154
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/108/9?ver=pdfcov
Published by the AIP Publishing

Self-biased magnetoelectric response in three-phase laminates

Su-Chul Yang, Chee-Sung Park, Kyung-Hoon Cho, and Shashank Priya[a]
Department of Materials Science and Engineering, Center for Energy Harvesting Materials and Systems (CEHMS), Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA

(Received 16 June 2010; accepted 25 August 2010; published online 3 November 2010)

This study reports the experimental observation and analysis of self-biased magnetoelectric (ME) effect in three-phase laminates. The 2–2 L-T mode laminates were fabricated by attaching nickel (Ni) plates and ME particulate composite plates having 3–0 connectivity with $0.948Na_{0.5}K_{0.5}NbO_3-0.052LiSbO_3$ (NKNLS) matrix and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) dispersant. The presence of two types of ferromagnetic materials, Ni and NZF, results in built-in magnetic bias due to difference in their magnetic susceptibilities and coercivity. This built-in bias (H_{bias}) provides finite ME effect at zero applied magnetic dc field. The ME response of bending mode trilayer laminate NKNLS-NZF/Ni/NKNLS-NZF in off-resonance and on-resonance conditions was shown to be mathematical combination of the trilayers with configuration NKNLS-NZF/Ni/NKNLS-NZF and NKNLS/Ni/NKNLS representing contributions from magnetic interaction and bending strain. © *2010 American Institute of Physics*. [doi:10.1063/1.3493154]

I. INTRODUCTION

Multiferroic magnetoelectric (ME) materials have coexistence of ferroelectric and ferromagnetic order which makes them attractive for magnetic field sensors, tunable transformers, and memory devices.[1–5] It is well known that ME effect in 3–0 particulate composites is small but 2–2 laminate composites have been shown to provide giant enhancement in the magnitude of ME coefficient by optimizing the properties of individual piezoelectric and magnetostrictive phases.[6,7] ME coefficient is dependent upon the magnetoelastic and elastoelectric interactions and is favored in composites with high elastic compliance. Most of the reported ME composites in literature require magnetic dc bias to invoke piezomagnetic response and only recently, Mandal *et al.* demonstrated self-biased laminate composites where ME response at zero field was correlated with presence of flexural deformation in a compositionally graded structure.[8–10] However, this method of generating self-bias is dependent upon the composition grading and requires special synthesis process. Our research has been focused on finding a methodology where we can achieve self-biasing by just changing the electrical connections with regular laminate composites. In this study, we report the success in demonstrating the self-biased ME effect in three-phase laminates having "sandwich" structure, with Ni embedded between the $0.8[0.948\ Na_{0.5}K_{0.5}NbO_3-0.052\ LiSbO_3]-0.2[Ni_{0.8}Zn_{0.2}Fe_2O_4]$ (NKNLS-NZF) ME particulate composite layers. This three-phase composite consists of lead-free materials which is critical for the applications.[11–14]

II. EXPERIMENTAL

$0.948\ Na_{0.5}K_{0.5}NbO_3-0.052\ LiSbO_3$ (NKNLS) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) ceramics were synthesized by mixed oxide sintering method.[13,15] NKNLS-NZF/Ni bilayer and NKNLS-NZF/Ni/NKNLS-NZF trilayer laminates were fabricated by bonding Ni plates with dimension of $15 \times 15\ mm^2$ with NKLNS-NZF disks of diameter 10 mm, using epoxy with curing temperature of 80 °C. Each layer had a thickness of 0.5 mm and the ME composite operated in L-T mode. Magnetic properties of the laminate were measured by using vibrating sample magnetometer (VSM 7304, Lake Shore Cryotronics). The impedance spectrum of the laminates was measured by an LCR meter (HP4194A, USA). ME voltage constants of the laminates were measured by applying dc bias magnetic field with $H_{ac}=1$ Oe at 1 kHz.[16] The voltage induced on the laminates was monitored by using a lock-in amplifier.

III. RESULTS AND DISCUSSION

Figure 1 shows the M-H curves for NZF particles and Ni plates. NZF particles had saturation magnetization (M_s) of 64.6 emu/g under an applied magnetic field of 3000 Oe. The magnetic susceptibility (χ) was calculated to be 3.3×10^{-2} emu/g Oe in the magnetic field range of (−1000)–1000 Oe, as shown in Fig. 1(a). Nickel plates were found to posses the saturation magnetization (M_s) of 50.2 emu/g at an applied magnetic field of 4000 Oe. The magnetic susceptibility (χ) was calculated to be 1.6×10^{-2} emu/g Oe in the magnetic field range of (−1000)–1000 Oe, as shown in Fig. 1(a). Using Fig. 1(b), the coercive field (H_c) of NZF particles was found to be 5 Oe and the H_c for Ni was found to be 14 Oe. The remnant magnetizations (M_r) for Ni and NZF particles was of the same amplitude, 0.29 emu/g. These results indicate that the composite fabricated by using Ni and NZF phase will have built-in bias field (H_{bias}) which is related to difference in the magnitude of susceptibility and coercivity.

Figure 2 shows the ME voltage coefficient (α_E) for bilayer and trilayer laminates. All the measurements in this figure were conducted at 1 kHz. It can be seen in Fig. 2(a) that NKNLS-NZF/Ni bilayer had maximum α_E of 166 mV/cm Oe at an applied magnetic dc bias of 120 Oe

[a]Electronic mail: spriya@vt.edu.

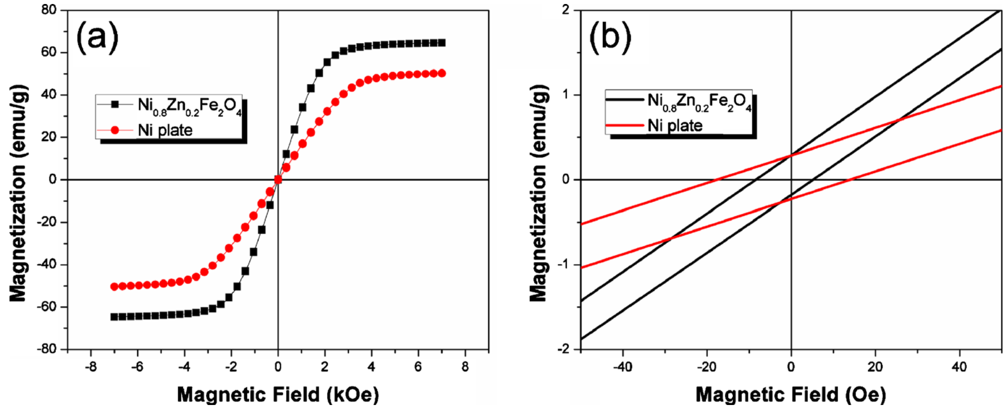

FIG. 1. (Color online) M-H curves for NZF particles and Ni plates, (a) saturated magnetic hysteresis loops under high field and (b) exploded view in the low field region.

and remanant ME coefficient α_{ER} of 30 mV/cm Oe at zero magnetic dc bias. It should be noted here that in these structures, Ni plays three roles, as: (i) it acts as electrode, (ii) it induces bending modes in the composite at low frequencies by lowering the overall stiffness, and (iii) it magnetically couples with the NZF phase. In bilayer, there is structural asymmetry and mismatch of coercive force induced by differences in χ and H_c of two ferromagnetic materials given by H_{bias}. This asymmetry is further enhanced at higher magnetic dc bias owing to mismatch in the magnetostrictive strain of NZF and Ni. Thus, the ME response is summation of three effects, one related to the H_{bias}, second related to the resultant of applied magnetic dc bias field (H_{appl}) and H_{bias} given as $\Sigma\vec{H}_{appl}+\vec{H}_{bias}$ which is frequency dependent term, and third related to structural asymmetry which induces bending modes. The bending strain is also frequency dependent term. The data in Figs. 2(b) and 2(c) further strengthens this argument. Figure 2(b) shows that NKNLS/Ni bilayer exhibited maximum α_E of 120 mV/cm Oe at an applied magnetic dc bias of 150 Oe without any α_{ER}. The low α_E and zero α_{ER} could be related to absence of magnetic interaction between Ni and NZF. A comparison of Figs. 2(a) and 2(b) indicates that hysteresis is related to the magnetic interaction between Ni and NZF. The NZF phase was absent in Fig. 2(b) and the ME behavior was similar to that obtained for conventional laminates with linear response. The magnitude of α_E for NKNLS-NZF/Ni/NKNLS-NZF trilayer exhibited maximum α_E of 385 mV/cm Oe at an applied magnetic dc bias of 96 Oe without any α_{ER} as shown in Fig. 2(c). This configuration in Fig. 2(c) will be referred to as "radial-mode trilayer (RMT)." High α_E of trilayer and zero α_{ER} was related to structural symmetry which reduces in-plane strain and maximizes the out-of-plane strain.[8] The peak position in this curve corresponds with the maximum in gradient of the magnetostriction versus magnetic dc bias curve. Please note the electrical connection in Fig. 2(c) which will generate charge

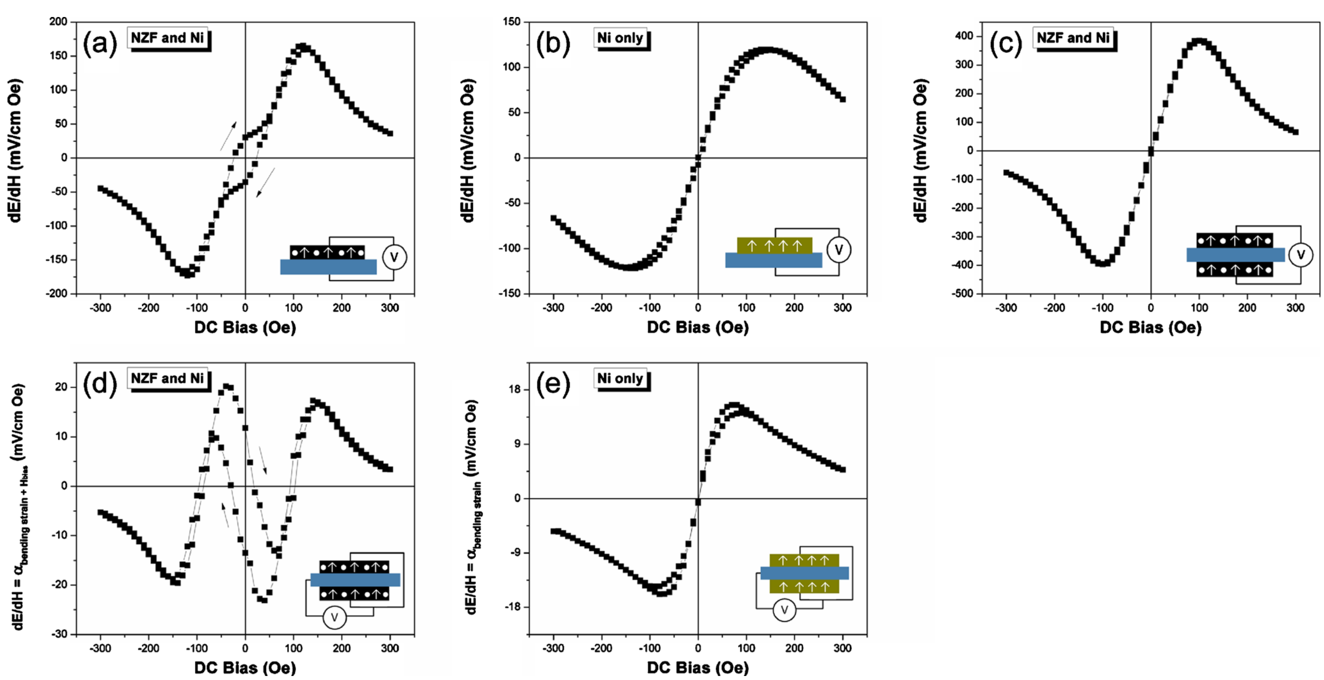

FIG. 2. (Color online) ME voltage coefficients (α_E) for various laminates, (a) NKNLS-NZF/Ni bilayer, (b) NKNLS/Ni bilayer, (c) NKNLS-NZF/Ni/NKNLS-NZF RMT, (d) NKNLS-NZF/Ni/NKNLS-NZF BMT, and (e) NKNLS/Ni/NKNLS trilayer.

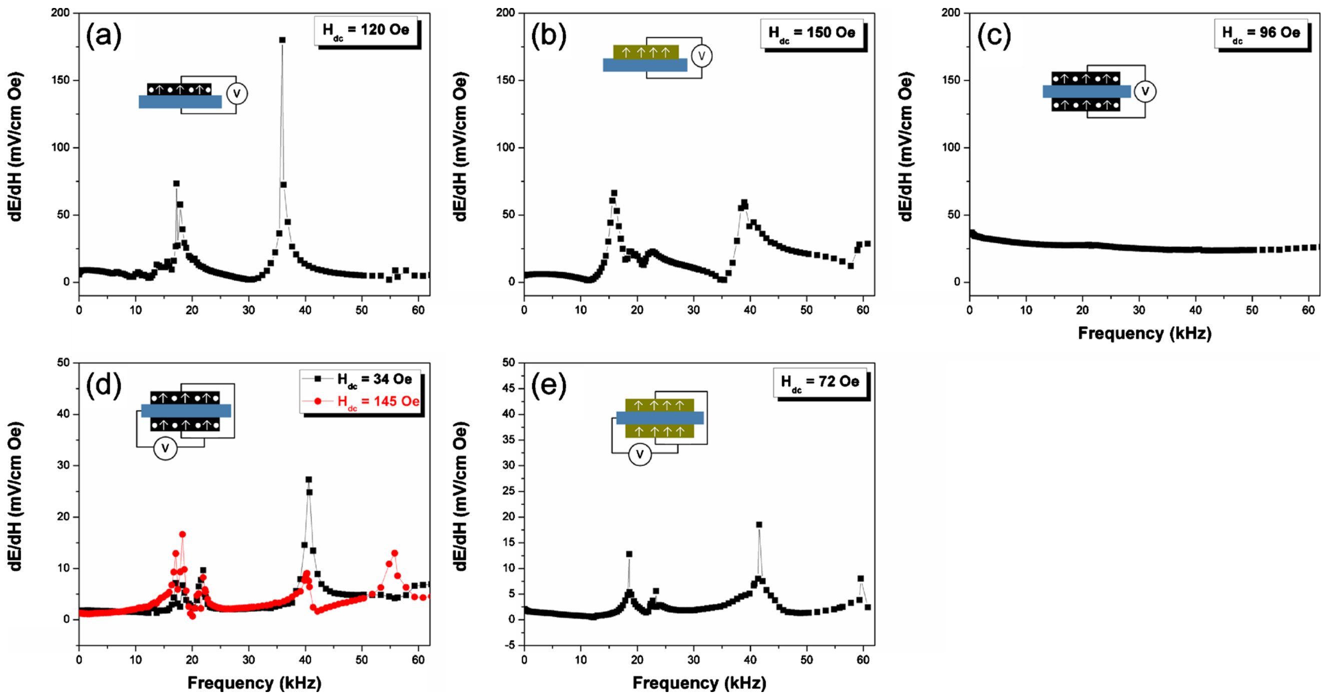

FIG. 3. (Color online) ME voltage coefficients (α_E) for bilayer and trilayer laminates as a function of frequency from 0.1 to 60 kHz, (a) NKNLS-NZF/Ni bilayer, (b) NKNLS/Ni bilayer, (c) NKNLS-NZF/Ni/NKNLS-NZF RMT, (d) NKNLS-NZF/Ni/NKNLS-NZF bending-mode laminate, and (e) NKNLS/Ni/NKNLS trilayer.

on the piezoelectric layer due to symmetric deformation in top and bottom layer. In contrast, Fig. 2(d) shows the ME response of NKNLS-NZF/Ni/NKNLS-NZF trilayer composite with modified electric connections to excite the bending mode, and will be referred as "bending mode trilayer (BMT)." In this case, there was clear hysteresis in the forward and backward sweep of ME response with zero-cross over points. The region defined by $-50 < H_{dc} < 50$ Oe represents the switchable states by changing the applied dc bias. In the forward sweep, the minimum in α_E was found to occur at ~16.6 mV/cm Oe and maxima was found at ~20 mV/cm Oe. In the backward sweep, the maxima was found at 23.1 mV/cm Oe with minimum occurring at ~10 mV/cm Oe. The magnitude of α_{ER} was 11.78 mV/cm Oe at zero dc bias. BMT has clear α_{ER} as well as two zero-cross over points at magnetic dc bias of 17.7 and 92.8 Oe. The behavior was not exactly symmetric in the positive and negative quadrants of applied magnetic field with slight shift toward negative Y-axis. We think that this shift is related to the magnitude of $\Sigma\vec{H}_{appl}+\vec{H}_{bias}$ which may have different magnitude during the forward and backward sweep depending upon the alignment of $\vec{H}_{appl}$ with $\vec{H}_{bias}$.

In order to understand the ME response of Fig. 2(d), we present data on BMT without any NZF phase. Figure 2(e) shows the ME response of NKNLS/Ni/NKNLS trilayer without any NZF. A maximum α_E of 15.5 mV/cm Oe was obtained at magnetic dc bias field of 72 Oe without any α_{ER}. Further, the magnitude of α_E was quite small as compared to ME behavior shown for RMT. This result clearly shows that interaction between NZF and Ni is important to achieve high α_E and finite α_{ER} with zero-cross over points. This also confirms our hypothesis that BMT ME response is governed by $\Sigma\vec{H}_{appl}+\vec{H}_{bias}$. Higher magnitude of α_{ER} in Fig. 2(a) has some contribution from the lower stiffness of the bilayer structure. In order to illustrate the role of radial and bending vibration modes, we show the impedance and phase spectra in Ref. 17 (Fig. S1) for bilayer and trilayer laminates under a small applied ac electric field. It was found that NKNLS-NZF/Ni bilayer exhibited resonance peaks at 17.2, 35.9, and 55.8 kHz which were related to bending modes. NKNLS/Ni bilayer exhibited resonance peaks at 18.9, 38.9, and 60.0 kHz which were related to bending modes due to structural asymmetry. This structure represents the conventional unimorph. However, NKNLS-NZF/Ni/NKNLS-NZF RMT did not exhibit any peaks in the same range. The impedance measurements indicate that RMT composite had dominant radial mode at low frequencies. BMT exhibited low frequency resonance peaks at 18.4, 22.2, 40.9, 55.8, and 58.3 kHz. BMT without any NZF, given by NKNLS/Ni/NKNLS also exhibited resonance peaks at 18.8, 22.5, 41.3, and 58.8 kHz. Thus, both the BMT composites shown in Figs. 2(d) and 2(e), exhibited bending resonance peaks but only the structure shown in Fig. 2(d) had the self-bias magnetic response with zero-cross over points. This result confirms that the self-biased ME effect has prime contribution from the magnetic interaction between the NZF and Ni, or H_{bias}.

Figure 3 shows the variation in α_E for bilayer and trilayer laminates as a function of frequency from 0.1 to 60 kHz. ME response of NKNLS-NZF/Ni bilayer is shown in Fig. 3(a), exhibiting peaks at bending mode frequencies of 17.2, 17.8, and 35.9 kHz under applied magnetic dc bias of $H_{appl}=120$ Oe with an superimposed ac magnetic field of 1 Oe. Figure 3(b) shows that NKNLS/Ni bilayer without any NZF phase exhibited peaks at bending mode frequencies of 16.0 and 38.9 kHz under applied magnetic dc bias of H_{appl}

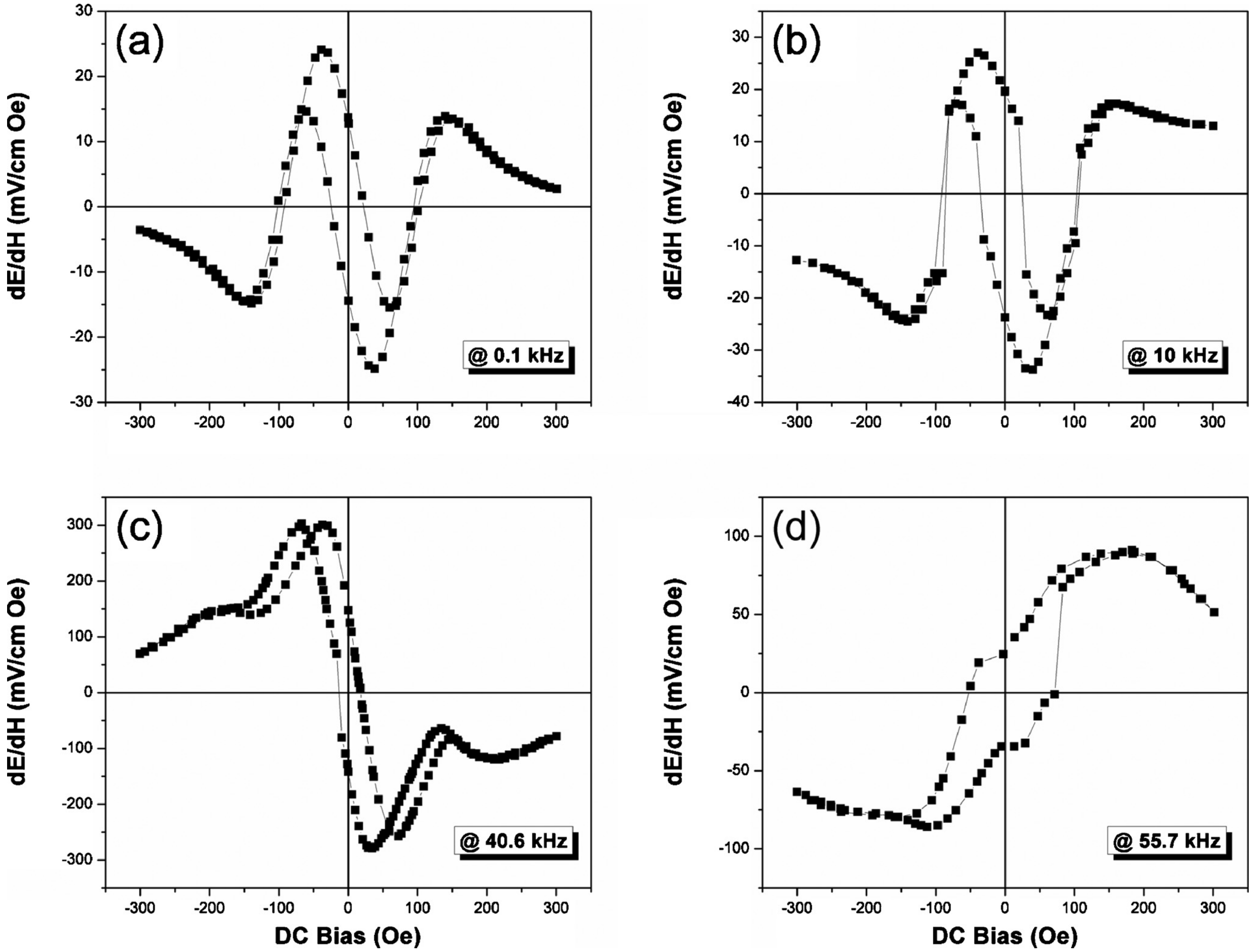

FIG. 4. ME voltage coefficients (α_E) for bending mode NKNLS-NZF/Ni/NKNLS-NZF trilayer as a function of magnetic dc bias field at frequencies of (a) 0.1 kHz, (b) 10 kHz, (c) 40.6 kHz, and (d) 55.7 kHz.

=150 Oe with an superimposed ac magnetic field of 1 Oe. In comparison to Fig. 3(a), the ME peak near 35 kHz was reduced significantly in the absence of NZF. Thus, the ME peak at 35.9 kHz in Fig. 3(a) is related to both magnetic interaction between Ni and NZF, and bending related to structural asymmetry. ME response of the RMT composite remained almost constant over the whole frequency range at magnetic dc bias of $H_{appl}=96$ Oe as shown in Fig. 3(c). The magnitude of applied dc bias was determined from the ME peak obtained in Fig. 2 for the corresponding laminate structures. ME response of BMT exhibited peaks at frequencies of 17.0, 18.2, 21.9, and 40.6 kHz under applied magnetic dc bias of $H_{appl}=34$ Oe, and 17.0, 18.2, 21.9, 40.2, and 55.7 kHz under magnetic dc bias of $H_{appl}=145$ Oe as shown in Fig. 3(d). Near 40.6 kHz, the ME response at magnetic dc bias of $H_{appl}=34$ Oe was higher than that at magnetic dc bias of $H_{appl}=145$ Oe. Further near 55.8 kHz, there is a peak in ME response at magnetic dc bias of $H_{appl}=145$ Oe which was not observed at magnetic dc bias of $H_{appl}=34$ Oe. This result shows that in BMT composite the magnitude of H_{bias} changes with frequency and confirms the hypothesis that the magnitude of summation $\Sigma\vec{H}_{appl}+\vec{H}_{bias}$ determines the magnitude of α_E. The ME response of BMT without any NZF phase exhibited peaks at frequencies of 18.5, 23.3, 41.5, and 59.5 kHz under magnetic dc bias of $H_{appl}=72$ Oe, as shown in Fig. 3(e). These peak ME frequencies are related to bending only, quite similar to that obtained for BMT with NZF phase at $H_{dc}=145$ Oe in Fig. 3(d). Therefore, we can determine that magnetic interaction dominates the ME response in BMT with NZF phase at $H_{dc}=35$ Oe and bending strain dominates the ME response in BMT with NZF phase at $H_{dc}=134$ Oe.

Figure 4 shows the ME voltage coefficient for BMT as a function of magnetic dc bias at frequencies of 0.1, 10, 40.6, and 55.7 kHz under applied ac magnetic field of 1 Oe. At the nonresonance frequencies of 0.1 and 10 kHz, BMT has small remanant α_{ER} and two zero-cross over points of α_E, as shown in Figs. 4(a) and 4(b). Further, at frequency of 10 kHz, BMT has wider hysteresis area than that of BMT at the frequency of 0.1 kHz. At the resonance frequency of 40.6 kHz in Fig. 4(c), BMT has high remanant α_{ER} of 147.3 mV/cm Oe and one zero-cross over point of α_E. This data illustrates that increased ME coefficient at low dc bias magnetic field of 34.5 Oe leads to one zero-cross over point of α_E by reducing relative change in ME coefficient at high dc bias magnetic field of 134.2 Oe. At the resonance frequency of 59.5 kHz, BMT has remanant α_{ER} of 24.4 mV/cm Oe and one zero-cross over point of α_E, as

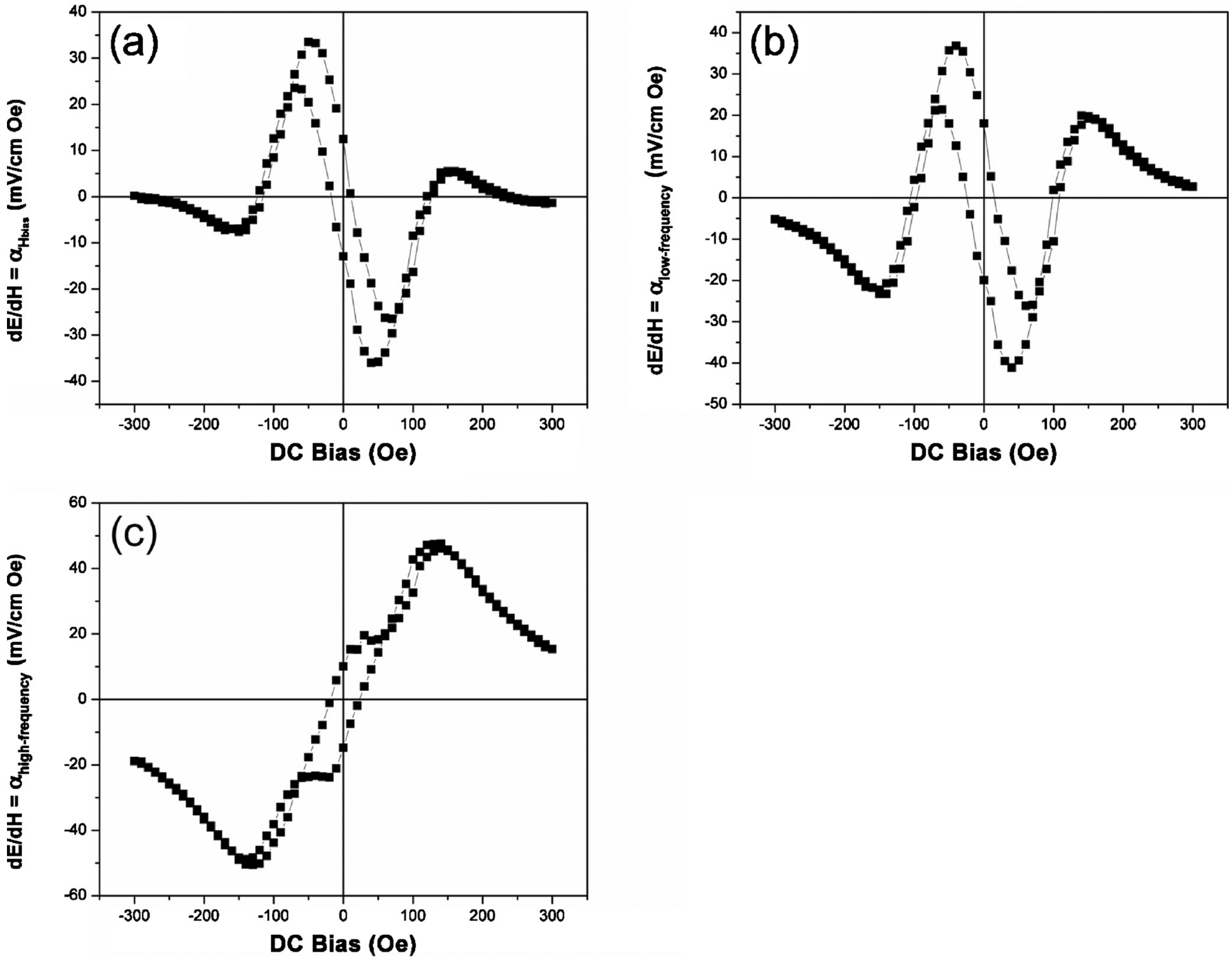

FIG. 5. ME voltage coefficients (α_E) calculated by using measured values of NKNLS-NZF/Ni/NKNLS-NZF ($\alpha_{\text{bending strain+H}_{\text{bias}}}$) and NKNLS/Ni/NKNLS ($\alpha_{\text{bending strain}}$) trilayer, (a) $\alpha(\text{H}_{\text{bias}})$, (b) $\alpha_{\text{low-frequency}}=(\alpha_{\text{bending strain+H}_{\text{bias}}}+0.5\alpha_{\text{H}_{\text{bias}}})$, and (c) $\alpha_{\text{high-frequency}}=(\alpha_{\text{bending strain+H}_{\text{bias}}}+2.5\alpha_{\text{bending strain}})$.

shown in Fig. 4(d). It also illustrates that increased ME coefficient at magnetic dc bias of 169.3 Oe leads to only one zero-cross over point of α_E. This figure clearly shows the promise of this structure in providing the possible electrically tuned memory states, and leads us to the possibility of designing a magnetic field controlled memristor element.

The ME response of BMT as a function of frequency can be explained by using the measured values of α_E for the NKNLS-NZF/Ni/NKNLS-NZF BMT and NKNLS/Ni/NKNLS BMT laminates. Figures 5(a)–5(c) summarizes the role of magnetic interaction and bending strain on the hysteresis in ME voltage coefficients (α_E). Figures 2(d) and 2(e) show the measured values of α_E for NKNLS-NZF/Ni/NKNLS-NZF BMT and NKNLS/Ni/NKNLS trilayer. Please note that the structure in Fig. 2(d) has NZF phase so there is magnetic interaction with Ni, while that in Fig. 2(e) does not have any NZF phase. Besides this difference, the electrical connections and layer dimensions are exactly similar in both the cases. Comparing Figs. 2(d) and 2(e), one can immediately notice that ME hysteretic response requires the presence of magnetic interaction. Subtracting the magnitude of ME coefficient in Fig. 2(e) ($\alpha_{\text{bending strain}}$) from that in Fig. 2(d) ($\alpha_{\text{bending strain+H}_{\text{bias}}}$), we can delineate the contribution arising from the magnetic interaction, or $\alpha(\text{H}_{\text{bias}})$ as shown in Fig. 5(a). Next, we try to understand the role of H_{bias} by increasing its contribution to the overall ME response. Figure 5(b) plots the ME coefficient given as $\alpha_{\text{low-frequency}}=(\alpha_{\text{bending strain+H}_{\text{bias}}}+0.5\alpha_{\text{H}_{\text{bias}}})$, which resembles the data shown in Figs. 4(a) and 4(b) at low frequencies. This indicates that by increasing the contribution related to magnetic interaction in proportion to that from bending strain, high remnant α_{ER} and narrow hysteresis near zero dc bias can be induced. Figure 5(c) plots the ME coefficient given as $\alpha_{\text{high-frequency}}=(\alpha_{\text{bending strain+H}_{\text{bias}}}+2.5\alpha_{\text{bending strain}})$, which resembles the behavior obtained at resonance frequency of 55.7 kHz as shown in Fig. 4(d). These calculations show that a linear relation between the contributions from the magnetic interaction and bending strain leads to emergence of remanant α_{ER} and zero-cross over point of α_E. The increase in contribution from the bending strain leads to increase in the magnitude of α_E and suppresses the peaks at higher magnetic dc bias. As a result, the BMT's hysteresis and remnant α_{ER} with first cross over point of α_E dominantly depend on magnetic interaction. On the other hand, bending strain is important for high magnitude of α_E at higher dc bias with second cross over point.

IV. SUMMARY

In summary, we report self-biased ME effects in lead-free three-phase laminates. The laminates consist of one piezoelectric phase and two ferromagnetic phases which couple with each other through differences in susceptibilities and coercive field. The self-biased ME response of NKNLS-NZ/Ni/NKNLS-NZF trilayer laminates was shown to be combination of ME behavior of NKNLS-NZF/Ni/NKNLS-NZF BMT and NKNLS/Ni/NKNLS trilayer composites.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from National Science Foundation (Award No. 0757502) and Army Research Office (W911NF0910061).

[1]N. A. Hill, J. Phys. Chem. B **104**, 6694 (2000).
[2]S. X. Dong, J. G. Bai, J. Y. Zhai, J. F. Li, G. Q. Lu, D. Viehland, S. J. Zhang, and T. R. Shrout, Appl. Phys. Lett. **86**, 3 (2005).
[3]N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).
[4]Y. H. Chu, L. W. Martin, M. B. Holcomb, M. Gajek, S. J. Han, Q. He, N. Balke, C. H. Yang, D. Lee, W. Hu, Q. Zhan, P. L. Yang, A. Fraile-Rodriguez, A. Scholl, S. X. Wang, and R. Ramesh, Nature Mater. **7**, 478 (2008).
[5]C. W. Nan, M. I. Bichurin, S. X. Dong, D. Viehland, and G. Srinivasan, J. Appl. Phys. **103**, 031101 (2008).
[6]J. Das, J. Gao, Z. Xing, J. F. Li, and D. Viehland, Appl. Phys. Lett. **95**, 092501 (2009).
[7]J. Zhai, Z. Xing, S. Dong, J. Li, and D. Viehland, J. Am. Ceram. Soc. **91**, 351 (2008).
[8]S. K. Mandal, G. Sreenivasulu, V. M. Petrov, and G. Srinivasan, Appl. Phys. Lett. **96**, 192502 (2010).
[9]C. Sudakar, R. Naik, G. Lawes, J. V. Mantese, A. L. Micheli, G. Srinivasan, and S. P. Alpay, Appl. Phys. Lett. **90**, 062502 (2007).
[10]J. V. Mantese, A. L. Micheli, N. W. Schubring, R. W. Hayes, G. Srinivasan, and S. P. Alpay, Appl. Phys. Lett. **87**, 082503 (2005).
[11]S. N. Babu, K. Srinivas, and T. Bhimasankaram, J. Magn. Magn. Mater. **321**, 3764 (2009).
[12]X. L. Zhong, M. Liao, J. B. Wang, S. H. Xie, and Y. C. Zhou, J. Cryst. Growth **310**, 2995 (2008).
[13]S. J. Zhang, R. Xia, T. R. Shrout, G. Z. Zang, and J. F. Wang, J. Appl. Phys. **100**, 6 (2006).
[14]R. A. Islam and S. Priya, Appl. Phys. Lett. **89**, 152908 (2006).
[15]R. A. Islam and S. Priya, J. Mater. Sci. **43**, 3560 (2008).
[16]C. S. Park, C. W. Ahn, S. C. Yang, and S. Priya, J. Appl. Phys. **106**, 5 (2009).
[17]See supplementary material at http://dx.doi.org/10.1063/1.3493154 for impedance and phase spectra for bilayer and trilayer laminates under applied ac electric field, (a) NKNLS-NZF/Ni bilayer, (b) NKNLS/Ni bilayer, (c) NKNLS-NZF/Ni/NKNLS-NZF RMT, (d) NKNLS-NZF/Ni/NKNLS-NZF bending-mode laminate, and (e) NKNLS/Ni/NKNLS trilayer.