

Magnetoelectric coupling in lead-free composites by Ni-ferrite and $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ -based ferroelectric

YUN ZHOU, SHENGHUA ZHOU^a, YOUXIANG YE^a, LI ZHANG

College of science, China Jiliang University, Hangzhou 310018, China

^aCollege of optical and electronic technology, China Jiliang University, Hangzhou, 310018, China

Nontoxic lead-free magnetoelectric composites $\text{NiFe}_2\text{O}_4/0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-0.052\text{LiSbO}_3$ (NFO/KNN) with different NFO content were successfully prepared by a solid-state reaction method. The dependence of ferroelectric, ferromagnetic properties and magnetoelectric coupling on NFO phase content was studied. The results show that the NFO content significantly affects the ferroelectric, ferromagnetic properties and ME effects. The ME behaviors are strongly dependent on the dc bias magnetic field. The ME voltage coefficients increase initially with the increase in dc magnetic fields and then decrease with further increase in the fields. A maximum magnetoelectric voltage coefficient of $5.59 \text{ mV}\cdot\text{cm}^{-1}\cdot\text{Oe}^{-1}$ is observed from the composite with 15 mol% NFO at the frequency of 1 kHz.

(Received January 19, 2012; accepted April 11, 2012)

Keywords: Magnetic property, Dielectric property, Magnetoelectric effect

1. Introduction

In the past few years, multiferroic materials have attracted a great deal of interest due to their potential applications on transducers, sensors, and actuators [1-2]. In general, Multiferroic materials can be divided into two types: single phase and composite form [3-4]. Due to the reason that single-phase multiferroic materials are rare and their ME coupling responses are weak [2], some magnetoelectric (ME) composites by incorporating both ferroelectric and ferromagnetic phases are being extensively studied. The ME composite is expected to show ME coupling that is mediated by mechanical stress [5]. That is, under applied magnetic field, the mechanical deformation induced by magnetostriction is mediated by mechanical stress and results in electric fields being induced by piezoelectric effect [6]. The ME coupling effects are always characterized by ME voltage coefficient $\alpha_E = \partial E / \partial H$, where ∂E is the electric field produced by an applied ac magnetic field ∂H [7-8].

To get high ME voltage coefficient, both the magnetostriction coefficient of the ferrite phase and piezoelectric coefficient of the ferroelectric phase should be high in the ME composite [9]. In addition, resistivity of the ferrite phase also should be high to avoid the leakage of the charges [9]. $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) is the most suitable ferroelectric material for use in ME composite because of its high piezoelectric coefficient and high resistivity. However, environmental issues may ultimately require the replacement of these lead based materials [10]. Previous studies show that $0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-0.052\text{LiSbO}_3$ (KNN-LS) lead-free composite is a promising candidate for PZT [4, 11-12]. It is well known that soft nickel ferrite NiFe_2O_4 (NFO) exhibit high resistivity and

magnetostriction coefficient [13]. In this article, new lead-free particulate composites of $x\text{NiFe}_2\text{O}_4-(1-x)0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-0.052\text{LiSbO}_3$ ($x\text{NFO}-(1-x)\text{KNN}$) (when $x=0.15, 0.3, 0.5, 0.65$) are fabricated, the ferroelectric, magnetic and ME characteristics are investigated. We expect to find out a proper proportion between ferroelectric phase and ferrite phase in the composites and get the maximum ME voltage coefficient. It is also expected that this research would bring more understanding and give useful information on this kind of composite system.

2. Experimental procedure

NFO and KNN were adopted as the ferromagnetic and ferroelectric phases, respectively. The details of KNN preparation can be found in Ref. [14]. Conventional ceramic processing was used to prepare the NFO materials, with NiO (>99.9 %) and Fe_2O_3 (>99.5%) as starting materials. The powders were milled and calcined at 950°C for 2.5 h. Then we ground them and pressed into pellets. The pellets were sintered at 1200°C for 4 h in air. After that, the pellets of NFO were crushed and ground into powder again. The particulate composites $x\text{NFO}-(1-x)\text{KNN}$ were prepared by mixing 15, 30, 50 and 65 mol% of NFO phase with 85, 70, 50 and 35 mol% of KNN phase, respectively. The composite mixtures were pressed into pellets (thickness 1–2 mm and 10 mm diameter) using a hydraulic press and sintered at 1050°C for 4 h to yield the final products. For the P - E loops characterization, the pellets were cut into the form of thin plates with thickness of 1 mm and silver electrodes were deposited on both sides of the samples.

The particulate composites were characterized by using X-ray diffractometer (XRD, Rigaku 18kW D/max-2500 diffractometer). Ferroelectric loop

measurements were done using a Radiant ferroelectric test system with the fast mode (20 ms). The magnetic properties of the composites $x\text{NFO}-(1-x)\text{KNN}$ were characterized with vibrating sample magnetometer (VSM option on PPMS-9T). The composites were poled electrically and magnetically before measuring the ME voltage coefficient (α_E). The samples were poled in silicone oil under a poling field of 2–20 kV/cm and at a poling temperature of 405K to room temperature. The ME effect α_E measurement was performed as introduced in Ref. [15]. An electromagnet was used to generate the dc bias magnetic field (H_{Bias}) up to 5 kOe. A signal generator was used to drive the Helmutz coils and generate the ac magnetic field δH (0.1 Oe–2 Oe) with frequency of 1 kHz. The dc and ac magnetic fields were in the same direction and both were parallel to the longitudinal direction (polarization direction) of the samples. When a magnetic field was applied to the composites, the magnetostrictive strain in the NFO phase was passed along to the KNN phase, resulting in an electric output. The induced voltage δV between the two sides of the sample was measured by Lock-In Amplifier (Stanford research systems, model SR830 DSP). The ME voltage coefficient α_E was obtained by $\alpha_E = \partial V / (\partial H \cdot t)$, t is the thickness of the sample. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for NFO, KNN and $x\text{NFO}-(1-x)\text{KNN}$ composites. Both the KNN and NFO phases are obviously observed in $x\text{NFO}-(1-x)\text{KNN}$ composites and all the peaks can be identified. There are no impurity phases or intermediate phases are detected within the resolution limit of the XRD. It is also found that the intensity of the KNN phase and NFO phase diffraction peaks depend on the amount of the corresponding phase. NFO retains its spinel cubic structure in the $x\text{NFO}-(1-x)\text{KNN}$ composite and the KNN-LS shows mixed phases [12, 14].

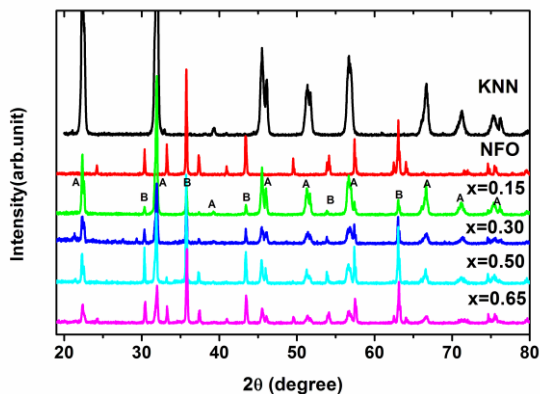


Fig. 1. (Color online) X-ray diffraction pattern of KNN, NFO and $x\text{NFO}-(1-x)\text{KNN}$ composites at room temperature. Here A denotes the KNN phase and B denotes the NFO phase.

The room temperature polarization–electric field (P - E) hysteresis loops of the composites of $x\text{NFO}-(1-x)\text{KNN}$ are shown in Fig. 2. The P - E loop of 0.15NFO–0.85KNN indicates ferroelectric behavior in the composites. The remnant polarization (P_r) of 0.15NFO–0.85KNN is found to be $37.0 \mu\text{C}/\text{cm}^2$ with a coercive field (E_C) of 17.5 kV/cm at room temperature. With the increase in NFO content x , the P - E loops exhibit strong conductive feature. The resistance of the composites drops with an increase in NFO content. It is difficult for the composite to be poled for the high leakage current of the composite. Therefore, choosing high resistivity ferrite phase is necessary to decrease the electric conductivity so as to improve the ferroelectric properties of this kind of ME composite system.

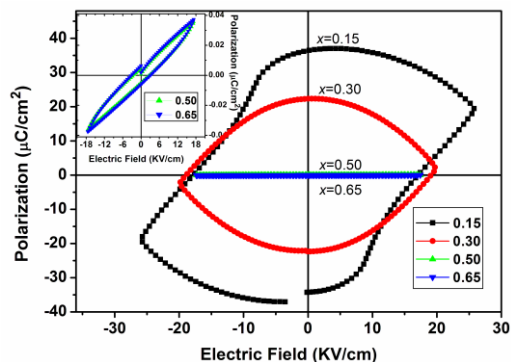


Fig. 2. (Color online) Ferroelectric hysteresis loops of $x\text{NFO}-(1-x)\text{KNN}$ composites at room temperature.

Fig. 3 shows the magnetic hysteresis loops for the NFO and $x\text{NFO}-(1-x)\text{KNN}$ composites. Both the NFO and $x\text{NFO}-(1-x)\text{KNN}$ composites show good soft magnetic properties. The coercive fields (H_c) of the composites are almost the same and the value is 65.9 Oe. The hysteresis obtained in $x\text{NFO}-(1-x)\text{KNN}$ composites is due to the ferrite phase as the ferroelectric phase is nonmagnetic. The calculated saturation magnetic moment (M_s) and remanent magnetization (M_r) are shown in the inset of Fig. 3. The M_s and M_r values increase almost linearly with the increase in NFO content x .

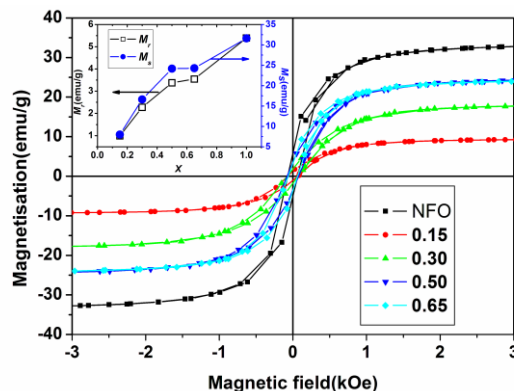


Fig. 3. (Color online) Magnetic hysteresis loops of NFO and $x\text{NFO}-(1-x)\text{KNN}$ composites at room temperature. The inset of Fig. 3: x -dependent variation of saturation magnetizations (M_s) and remanent magnetization (M_r). Lines are guides for the eyes.

The coexistence of the ferroelectric and ferromagnetic features in the particulate composites could generate ME effects. The generation of ME effect yield in the composites is based on the product effect which is available in neither of the two components: a magnetic field is applied to the system, the magnetostrictive component is strained, which is transferred via the two-phase interface to the neighboring piezoelectric component [16]. The electric field generated in piezoelectric component is ascribed to the piezoelectric effect [16]. The variation of ME voltage coefficients (α_E) with dc bias magnetic field (H_{Bias}) at low frequency of 1 kHz are shown in Fig. 4. With an increase in H_{Bias} from zero, all the ME voltage coefficients increase rapidly before reaching their maximum values. With further increase in H_{Bias} , the ME voltage coefficients drop slowly to a minimum values. The peak behavior of α_E indicates that the magnetostriction reaches its saturation at a certain value of the magnetic field. Beyond saturation, the magnetostriction gets saturated, producing a nearly constant electric field in the two sides of the sample, thereby decreasing $\alpha_E (= \partial E / \partial H)$ with increasing magnetic field [11]. The inset of Fig. 4 shows the maximum values of α_E (α_E^{max}) with different contents of NFO (x). The α_E^{max} value decreases with increase in x . Fig. 4 clearly shows that the NFO content x significantly affects the ME output of this composite system. At the frequency of 1 kHz, the maximum value of α_E observed to be $5.59 \text{ mV} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$ at the magnetic bias field of about 800 Oe for the composite with $x=0.15$. This is a high value in the nontoxic lead-free particulate ME composite system for the potential use on actuators and sensors, etc.

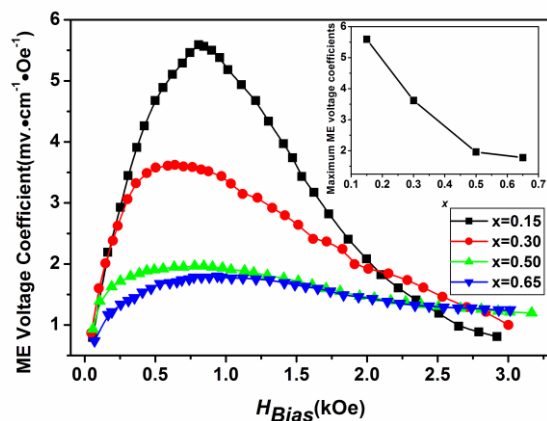


Fig. 4. (Color online) The dependence of ME voltage coefficient on H_{Bias} for the composites at the frequency of 1 kHz. Inset: x -dependent variation of α_E^{max} for $x\text{NFO}-(1-x)\text{KNN}$ composites. Lines are guides for the eyes.

4. Conclusions

A new ME composite system with nontoxic lead-free KNN ferroelectric and NFO ferrite with different NFO

content were successfully prepared. The room temperature ME coupling, P-E loops and magnetic hysteresis loops were investigated in this composite system. The result proves that ME voltage coefficient is strongly dependent on the dc bias magnetic field H_{Bias} . The maximum value of α_E observed to be $5.59 \text{ mV} \cdot \text{cm}^{-1} \cdot \text{Oe}^{-1}$ from the composite with 15 mol% NFO at 1 kHz.

Acknowledgements

The work was supported by National Science Foundation of Zhejiang Province in PRC, Contract No. Y6090564.

References

- [1] Nicola A. Spaldin, Manfred Fiebig, Science, **309**, 391 (2005).
- [2] J. X. Zhang, J. Y. Dai, W. Lu, H. L. W. Chan, J. Mater. Sci. **44**, 5143 (2009).
- [3] S. Y. Tan, S. R. Shannigrahi, S. H. Tan, F. E. H. Tay, J. Appl. Phys. **103**, 094105 (2008).
- [4] Y. Zhou, J. C. Zhang, Z. J. Feng, B. Z. Li, L. Li, Y. L. Su, C. Jing, S. X. Cao, J. Mater. Sci. **46**, 2649 (2010).
- [5] G. Srinivasan C. P. De Vreugd, V. M. Laletin, N. Paddubnaya, M. I. Bichurin, V. M. Petrov, D. A. Filippov, Phys. Rev. B. **71**, 184423 (2005).
- [6] M. Zeng, J. G. Wan, Y. Wang, H. Yu, J.-M. Liu, X. P. Jing, C. W. Nan, J. Appl. Phys. **95**, 8069 (2004).
- [7] Chee-Sung Park, Joe Evans, Shashank Priya, Smart Mater. Struct. **20**, 082001 (2011).
- [8] G. Srinivasan, C. P. DeVreugd, C. S. Flattery, V. M. Laletsin, N. Paddubnay, Appl. Phys. Lett. **85**, 2550 (2004).
- [9] S. A. Lokare, R. S. Devan, D. R. Patil, B. K. Chougule, S. A. Lokare, R. S. Devan, D. R. Patil, B. K. Chougule, J. Mater. Sci.; **18**, 1211 (2007).
- [10] T. Takenaka, H. Nagata, J. Eur. Ceram. Soc. **25**, 2693 (2005).
- [11] Y. Zhou, M.-G. Cheng, Z.-J. Feng, X.-Y. Wang, Y.-J. Cui, J.-C. Zhang, Chin. Phys. Lett. **28**, 107503 (2011).
- [12] Y. Zhou, J. C. Zhang, L. Li, Y. L. Su, J. R. Cheng, S. X. Cao, J. Alloy. Compd. **484**, 535 (2009).
- [13] D. R. Patil, S. A. Lokare, R. S. Devan, S. S. Chougule, Y. D. Kolekar, B. K. Chougule, J. Phys. Chem. Solid. **68**, 1522 (2007).
- [14] S. Zhang, R. Xia, T. R. Shrout, J. Appl. Phys. **100**, 104108 (2006).
- [15] N. Cai, J. Zhai, C. -W. Nan, Y. Lin, Z. Shi, Phys. Rev. B **68**, 224103 (2003).
- [16] Y. X. Liu, M. Zeng, Y. Wang, J. G. Wan, X. P. Jiang, J.-M. Liu, Ceram. Int. **30**, 1999 (2004).

*Corresponding author: zhy7612@shu.edu.cn