Magnetoelectric effect of $Ni_{0.8}Zn_{0.2}Fe_2O_4/Sr_{0.5}Ba_{0.5}Nb_2O_6$ composites

Y.J. Li, X.M. Chen [*], Y.Q. Lin, Y.H. Tang

Department of Materials Science and Engineering, Zhejiang University, HangZhou 310027, China

Received 16 March 2005; received in revised form 30 May 2005; accepted 10 June 2005
Available online 10 August 2005

Abstract

Novel magnetoelectric composites were prepared by incorporating the dispersed $Ni_{0.8}Zn_{0.2}Fe_2O_4$ ferromagnetic particles into $Sr_{0.5}Ba_{0.5}Nb_2O_6$ relaxor ferroelectric matrix. Dense composite ceramics were obtained with the co-presence of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$, and they could be electrically and magnetically poled to exhibit a significant magnetoelectric effect. A maximum magnetoelectric voltage coefficient of 26.6 mV/cm/Oe was observed from the composites with 70 mol% $Sr_{0.5}Ba_{0.5}Nb_2O_6$, which was much greater than that of magnetoelectric compounds and solid solutions. It is convenient to use the Pb-free $(Sr,Ba)Nb_2O_6$ relaxor as the matrix for ferromagnetic/ferroelectric composites in the future development of magnetoelectric materials.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Composites; Dielectric properties; Electrical properties; Magnetoelectric effect; Sintering; $(Ni,Zn)Fe_2O_4$; $(Sr,Ba)Nb_2O_6$

1. Introduction

The magnetoelectric (ME) effect is defined as the dielectric polarization of a material in an applied magnetic field or an induced magnetization in an external electric field.[1,2] This effect would make the conversion between electric energy and magnetic energy possible, which provides opportunities for potential applications as ME memories, waveguides, transducers, actuators, and sensors.[3–5]

Early in 1894, Curie pointed out the possibility of the polarization of the asymmetric molecular body under an external magnetic field. Subsequently, in 1957, Landau and Lifshitz argued that the ME effect could principally exist in some magnetically ordered crystals. The ME effect was first experimentally observed by Astrov in 1960 in Cr_2O_3,[6,7] and lots of monophase materials had been widely investigated during past few decades.[8–10] Due to the low Neel or Curie temperature and weak ME effects, it was hard to apply the monophase materials to any practical ME devices. Alternatively, bulk or laminate composites[11–19] of piezoelectric and magnetostrictive phases were prepared based on the concept of product properties, which was proposed by Van Suchtelen in 1972.[2] That is, when a magnetic field is applied to the composite, the magnetostrictive phase changes its shape firstly, and the induced strain is passed to the piezoelectric phase, resulting in an electric polarization. The ME voltage coefficient in these multiphase composites, especially in laminate structures,[14–19] has been found two or three orders in magnitude stronger than that in single phase ones, which could be better applied to commercial devices. Leaving alone the intrinsic limitation in the feature size and miniaturizing difficulties of the layered structure, it is still hard, however, to prepare the Terfenol-D/PZT composite,[15,19] which possesses the highest ME voltage coefficient among laminate composites, by a conventional sintering method because of the brittleness. Yet it practically and economically needs some new ME composites in the future.

Relaxor ferroelectrics are also known to have very large electrostrictive responses. Most relaxors, however, contain Pb, and their lack of remnant polarization makes them unsuitable for piezoelectric applications. An exception is the $(Sr,Ba)Nb_2O_6$ family which can sustain a remnant polarization after poling. On the other hand, most studies in the past focused on $CoFe_2O_4$[11–14] which was applied as one of the constituents for its large magnetostriction, but the ME voltage

* Corresponding author. Tel.: +86 571 8795 2112; fax: +86 571 8795 2112.
E-mail address: xmchen@cmsce.zju.edu.cn (X.M. Chen).

coefficient was far smaller than the predicted value due to the poor ME coupling between the two phases. It is known that low anisotropy favors the magnetization mechanism in the crystal, such as domain wall movement and domain rotation which are the key factors for magnetomechanical coupling that gives rise to the ME effect. Hence, soft ferrite $NiFe_2O_4$ with low anisotropy and high initial permeability is a promising candidate. Furthermore, a larger net magnetic moment caused by the ion rearrangement, which favors the ME effect, can be obtained by putting some additional amounts of zinc oxide as one of the bivalent components into nickel ferrite.[20]

In this paper, a new magnetoelectric composite consisting of ferromagnetic $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and relaxor ferroelectric $Sr_{0.5}Ba_{0.5}Nb_2O_6$ as end members has been prepared through a solid-state reaction approach. The ME effect and the dielectric characteristic are investigated together with the microstructures.

2. Experimental

Adequate amounts of high purity NiO (99%), ZnO (99%) and Fe_2O_3 (99%) were used to prepare $Ni_{0.8}Zn_{0.2}Fe_2O_4$. These raw powders were ball-milled in distilled water for 24 h, and then the mixed slurry was dried and calcined at 1000 °C in the air for 3 h. On the other hand, the mixture of $SrCO_3$ (99.95%), $BaCO_3$ (99.93%) and Nb_2O_5 (99.99%) was calcined at 1200 °C in the air for 3 h to synthesize $Sr_{0.5}Ba_{0.5}Nb_2O_6$. The mixtures of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ with $x = 0.5$, 0.6, 0.7, 0.8, 0.9 and 1.0 were pressed into discs with dimensions of 12.5 mm in diameter and 2 mm in height after adding 8 wt.% PVA. Final sintering was carried out from 1200 to 1275 °C in air for 3 h. After sintering, the discs were annealed in oxygen atmosphere at 1000 °C for 4 h, with the flux of 1 L/min. The crystalline phases of the sintered samples were identified by the X-ray powder diffraction using Cu Kα radiation, and the microstructures were characterized by scanning electron microscopy (SEM) on the polished and thermal-etched surfaces. The dielectric constant and the dielectric loss were evaluated by an LCR meter (HP4284A). The ME coefficient was evaluated under a bias magnetic field of 0–3 kOe at 20 °C up to 100 kHz with silver paste as electrode, and was given by the output voltage which was divided by the thickness of samples and the ac magnetic field (i.e., dE/dH). Prior to this measurement, the samples were poled both electrically and magnetically. The electrical poling was conducted by cooling from 200 °C in silicon oil under 2 kV/mm, and the magnetic poling was performed under 5 kOe for 30 min at 25 °C.

3. Results and discussion

As shown in Fig. 1, the coexistence of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $Sr_{0.5}Ba_{0.5}Nb_2O_6$ is confirmed by the XRD patterns, and
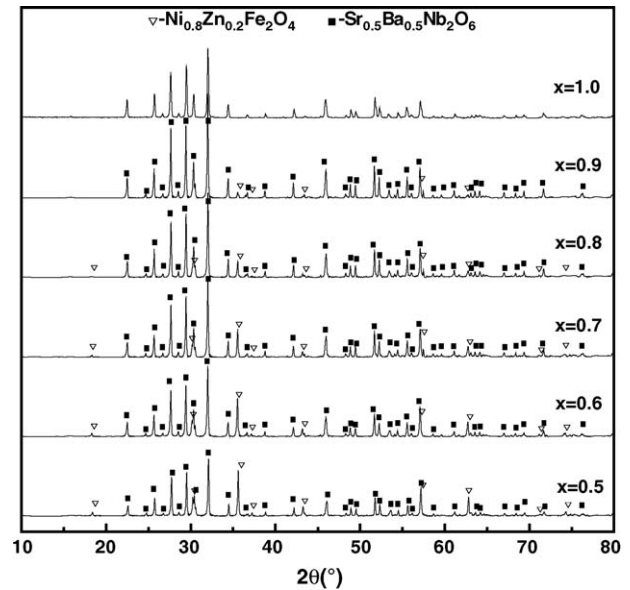
Fig. 1. XRD patterns of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites sintered at 1250 °C for 3 h.

no mutual solubility between the two phases is observed, i.e., the two phases are compatible with each other. The intensity of their diffraction peaks depends on the amount of the corresponding phase. Fig. 2 shows the backscattered electron images of the composites with various compositions sintered at 1250 °C in air for 3 h. Two major phases are observed in these images. The larger white regions are the relaxor ferroelectric matrix grains, which uniformly disperse the smaller dark ferrite phase particles in all directions. Meanwhile, we can see a small numbers of gray regions marked by "2" in Fig. 2(c) are partly surrounded by some ferroelectirc grains. Table 1 shows the EDS analysis results of these three different regions (1, 2 and 3). The above-mentioned gray areas contain both elements of the two end members, which are caused by the interdiffusion between them. On the other hand, in order to investigate the microstructural dependence of ME coefficient of the composites, we sintered the samples of $x = 0.7$ at different temperatures and acquired the secondary electron images of the composites correspondingly (Fig. 3). The grains of both phases grow significantly at a temperature increasing from 1200 to 1225 °C and almost maintain the same shape and distribution until 1250 °C. As shown in Fig. 3(d), the particles of two phases become coarse and uneven, and the ferrite grains partly dissolve into the matrix ones. The grain sizes of two phases in Fig. 3 are characterized by a regular digital image processing (NIH Image J program[1]) and the data are shown in Table 2. The average grain size of the ferroelectric particles is almost three times larger than that of the ferrite particles, which can effectively reduce the leakage current induced by the connection of ferrite particles. The density of

---

[1] NIH Image J public domain program is conducted by Wayne Rasband from the National Institutes of Health (http://rsb.info.nih.gov/ij).
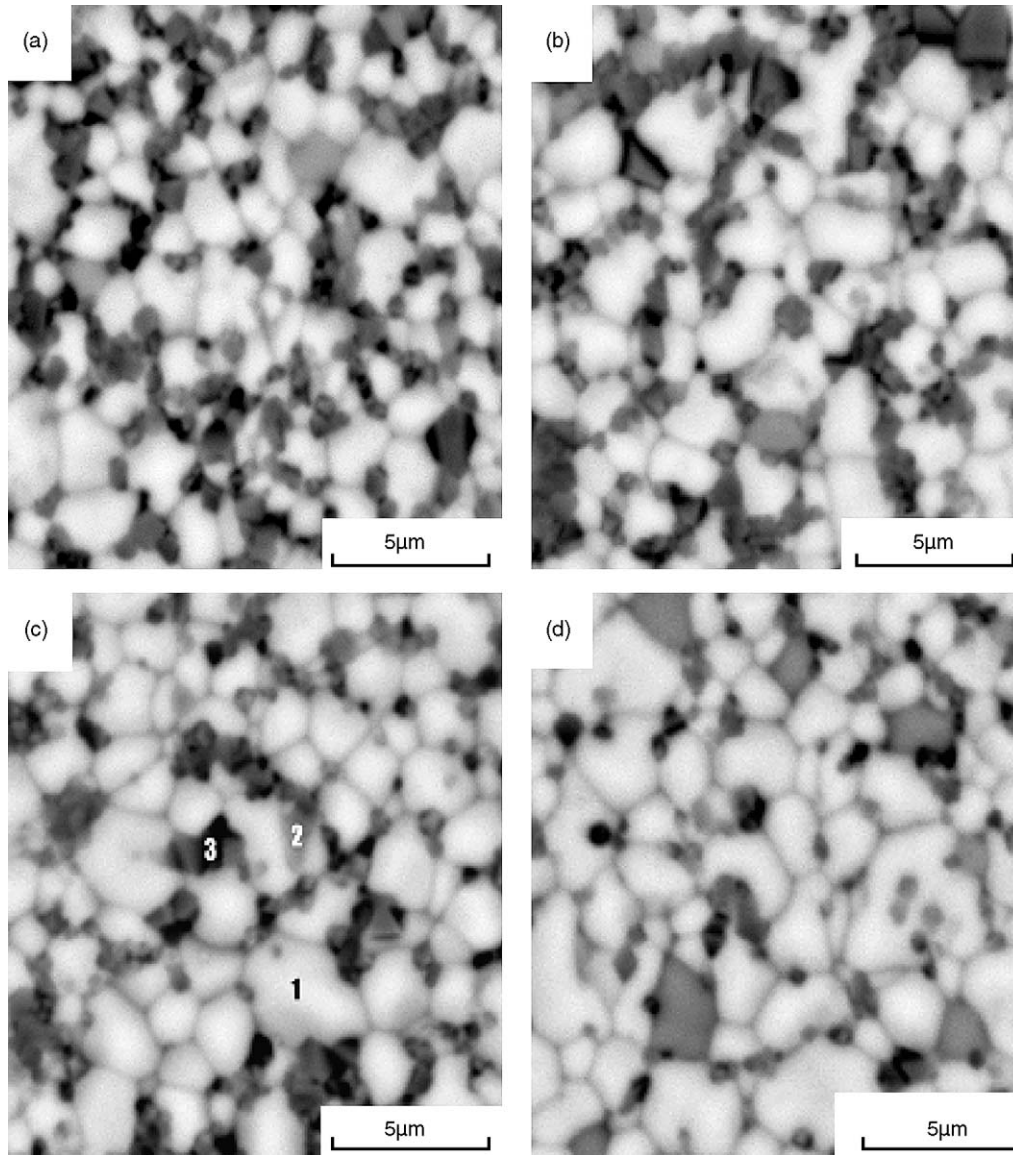
Fig. 2. Backscattered electron images of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites with (a) $x=0.5$ (b) $x=0.6$ (c) $x=0.7$ (d) $x=0.8$ sintered at 1250 °C for 3 h.

Table 1
EDS analysis of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites $(x=0.7)$ with different regions (see Fig. 3(c))

Element	Spectrum 1		Spectrum 2		Spectrum 3	
	wt.%	at.%	wt.%	at.%	wt.%	at.%
C	0.00	0.00	4.03	10.11	4.12	12.00
O	27.29	68.57	35.97	67.80	25.00	54.69
Fe	4.95	3.56	11.63	6.28	21.24	13.31
Ni	1.92	1.32	4.90	2.52	8.91	5.31
Zn	0.00	0.00	0.99	0.46	2.05	1.10
Sr	9.97	4.57	6.72	2.31	6.31	2.52
Nb	40.11	17.36	25.37	8.23	23.09	8.70
Ba	15.76	4.61	10.40	2.28	9.29	2.37

the $x=0.7$ exhibits small change in the measuring temperature range and achieves its maximum value at 1250 °C.

Fig. 4 shows that the frequency dependence of dielectric properties of the composites ranges from 1 kHz to 1 MHz at room temperature. ε decreases rapidly with a very high value on lower frequencies and remains constant on higher frequencies. We can attribute the dielectric dispersion to the interfacial polarization. Because the two mediums have different permittivities and conductivities, when an electrical field is applied to the composite, space charges provided by the $Ni_{0.8}Zn_{0.2}Fe_2O_4$ phase accumulate at the interfaces of the two phases. The high permittivities observed in the lower frequency are not usually intrinsic but are rather associated with a heterogeneous conduction in the multiphase structure of the composites.[21,22] With the increase of $Sr_{0.5}Ba_{0.5}Nb_2O_6$

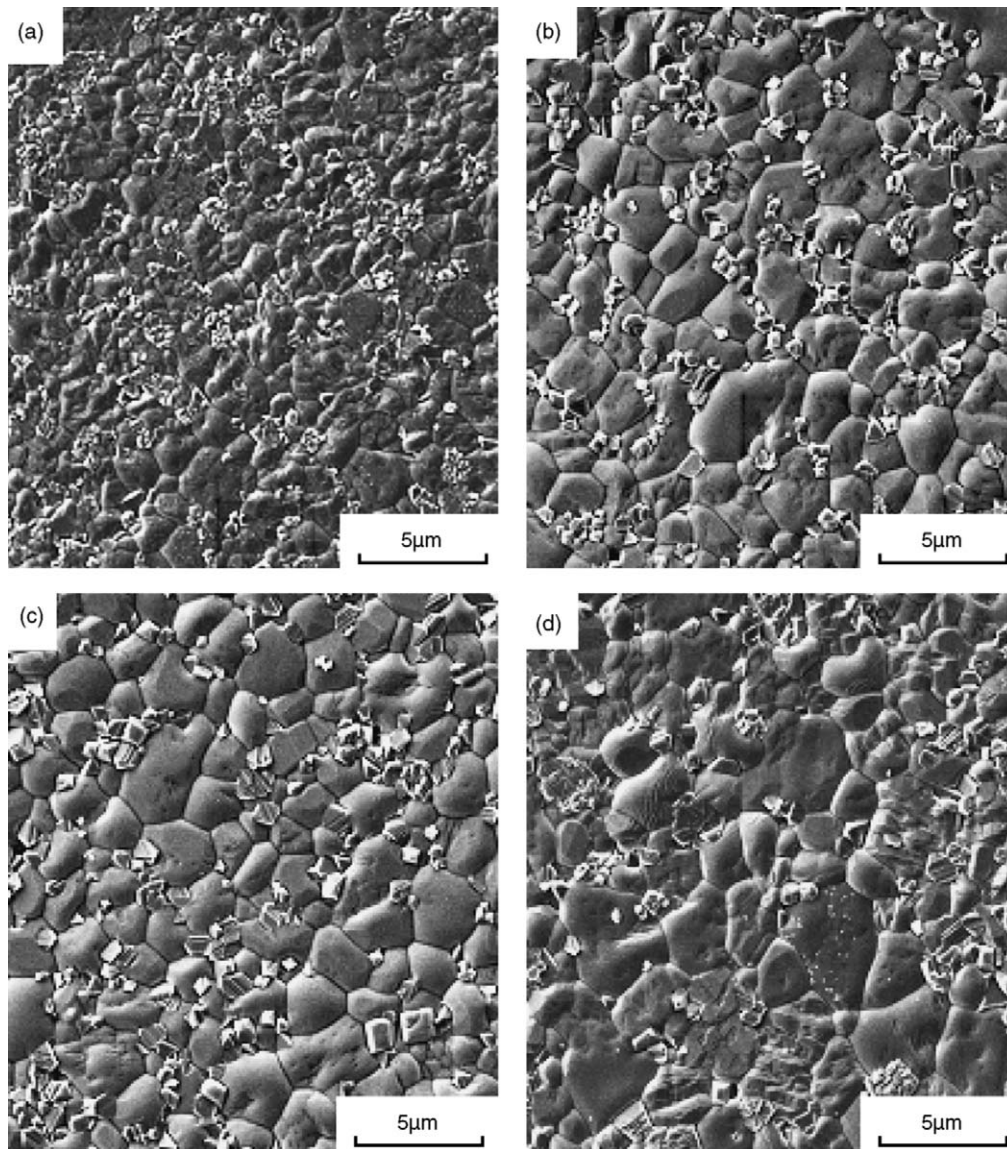Fig. 3. Secondary electron images of $0.3Ni_{0.8}Zn_{0.2}Fe_2O_4/0.7Sr_{0.5}Ba_{0.5}Nb_2O_6$ composites sintered at (a) 1200 °C, (b) 1225 °C, (c) 1250 °C, (d) 1275 °C for 3 h.

concentration, the number of space charges decreases and the related apparent ε of the composites decrease dramatically. In the samples of $x = 0.8$ and $x = 0.9$, the ε of the composites are mainly determined by that of the ferroelectric phase. Since the response time $\tau = 1/\omega_{max}$ of the interfacial polarization compared with other mechanisms is relatively long, we can only observe the dielectric relaxation at lower frequencies. Larger interfacial polarization effect is observed at a lower frequency. It is in accordance with the fact that the dielectric loss peak of the composites shifts to low frequencies with the increase of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ concentration (Fig. 4(b)). Because hardly can the less accumulated space charges affect the apparent ε of the composites unless the frequency reduces.

Table 2
Influence of sintering temperature on the particle size and density of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites $(x = 0.7)$

Sintering temperature (°C)	Maximum size (μm)		Minimum size (μm)		Average size (μm)		Density (g/cm^3)
	NZFO	SBN50	NZFO	SBN50	NZFO	SBN50	
1200	0.41	2.15	0.13	0.41	0.27	0.89	5.377
1225	0.87	4.15	0.31	0.92	0.61	2.07	5.367
1250	1.09	3.99	0.31	1.14	0.64	2.13	5.406
1275	1.51	5.23	0.33	1.58	0.89	2.81	5.302
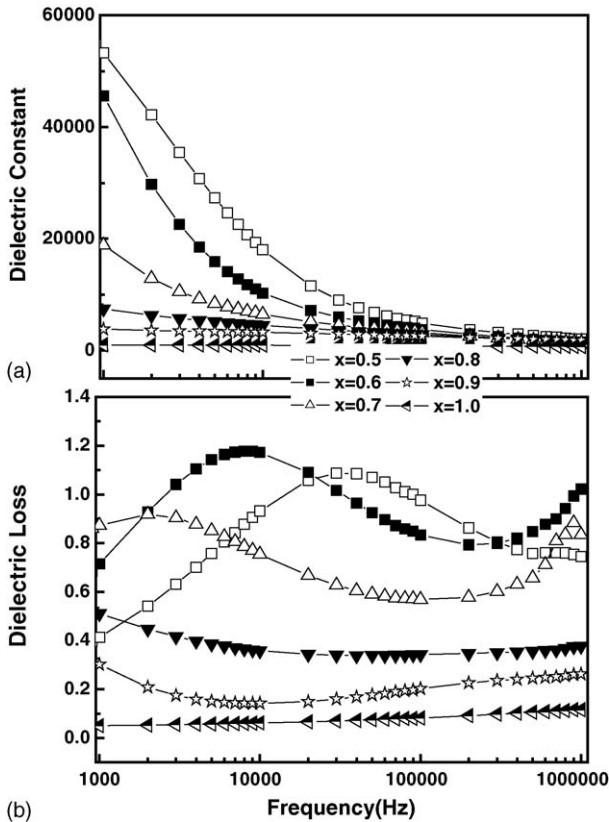
Fig. 4. Dielectric properties of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites sintered at 1250 °C for 3 h as a function of frequency. (a) Dielectric constant and (b) dielectric loss.

Fig. 5 shows the dielectric constant of the composites at 10 kHz with different $Sr_{0.5}Ba_{0.5}Nb_2O_6$ concentrations as a function of temperature. The Curie temperature of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ decreases from 110 to 21.5 °C when 10 mol% ferrite phase is incorporated into the matrix phase. It proves that Ni ions can lead to a strong decrease of the phase transition temperatu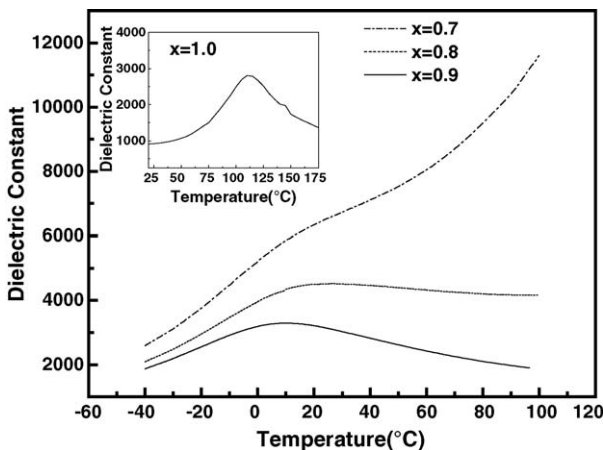re and smearing of the phase transition of $Sr_{0.5}Ba_{0.5}Nb_2O_6$. Volk et al. have reported the similar phenomenon in Ni doped $Sr_{0.61}Ba_{0.39}Nb_2O_6$ crystals.[23] With the increase of ferrite phase concentration, the conduction contribution of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ phase to ε' becomes more and more significant. For the sample with $x=0.7$, the diffuse peak can hardly be observed at 10 kHz, and the apparent ε' increases monotonically with increasing temperature and reaches to ~12,000 at 100 °C.

Since the T_c of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ shifts towards the room temperature, the piezoelectric properties decrease correspondingly. This can partly but crucially explains why the dE/dH peaks are observed for the compositions with low ferrite contents (Fig. 6). Another reason is that the leakage is currently induced by the connection between ferrite grains, which not only reduces the resistance of the samples but also prevents them from poling thoroughly. The composite added with 70 mol% amount of ferroelectric phase indicates the maximum ME voltage coefficient of 26.6 mV/cm/Oe, which is comparable to the best values of reported bulk composites, such as ferrite/piezoelectric ceramics (e.g., $CoFe_2O_4/BaTiO_3$ (16.2 mV/cm/Oe), $CoFe_2O_4$/PZT (30.2 mV/cm/Oe) composites[11,13]) and Tb–Dy–Fe alloys (Terfenol-D)/PZT/poly (vinylidene fluoride–trifluorethylene) copolymer (PVDF) (42 mV/cm/Oe).[18] Lead free is another advantage for the present composite system, even if the dE/dH is lower than that of Ni-ferrite/PZT (115 mV/cm/Oe) composites.[5] Fig. 7 shows the maximum magnetoelectric coefficient of the composites with $x=0.7$ as a function of sintering temperature. The increased dE/dH value is attributed to the uniform distribution and proper grain sizes of two phases. The highest ME voltage coefficient is obtained for the samples sintered at 1250 °C where the nearly full densification is attained for the composition of $x=0.7$. This might be originated from the stronger bonding between two phases. The obvious dropping of dE/dH for the composite sintered at 1275 °C is mainly due to the agglomeration of the ferrite grains and interdiffusion between two phases (Fig. 3(d)).
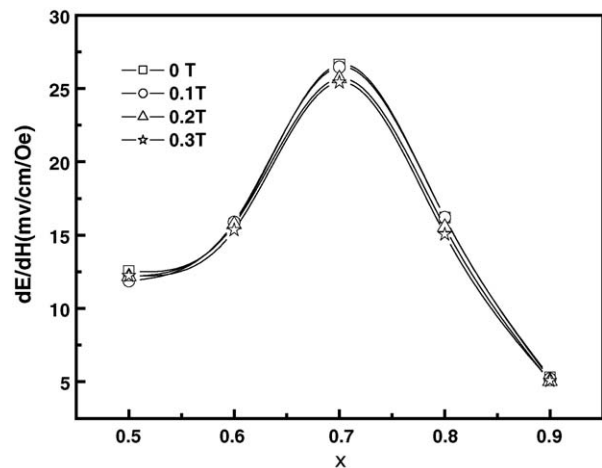

Fig. 5. Dielectric constant of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites with $x=0.7$, $x=0.8$, $x=0.9$ and $x=1.0$ (the inset) as a function of temperature (10 kHz).

Fig. 6. Magnetoelectric effect of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites with various x under different bias fields (100 kHz).
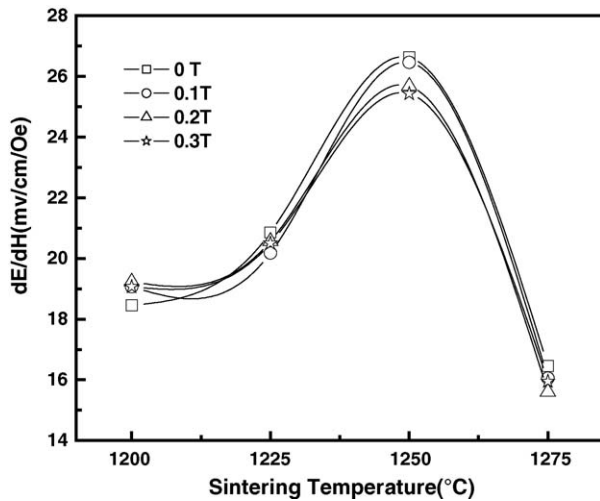
Fig. 7. Maximum magnetoelectric coefficient of $(1-x)Ni_{0.8}Zn_{0.2}Fe_2O_4/xSr_{0.5}Ba_{0.5}Nb_2O_6$ composites as a function of sintering temperature ($x = 0.7$).

The uneven ferrite particles not only reduce the mechanical coupling between the two phases but also cause a significant current loss of the samples.

4. Conclusion

In conclusion, we have developed a new ME composite system with Pb-free $Sr_{0.5}Ba_{0.5}Nb_2O_6$ relaxor ferroelectric and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ ferrite. The present composites can be electrically and magnetically poled to exhibit a significant magnetoelectric effect. A dE/dH value up to 26.6 mV/cm/Oe is observed. This can be applied to other compositions in $(Sr,Ba)Nb_2O_6$-spinel ferrite binary and helps to find out other good ME composites in this system. Moreover, the ME coefficient of the present composites varies significantly with sintering temperature, and therefore the enhanced dE/dH is expected through processing and microstructure controlling.

Acknowledgements

References

1. Smolenski, G. A. and Chupis, I. E., Ferroelectromagnets. *Sov. Phy. Usp.*, 1982, **25**, 475.

2. Suchtelen, J. V., Product properties: a new application of composite materials. *Philips Res. Repts.*, 1972, **27**, 28.

3. Nan, C. W. and Clarke, D. R., Effective properties of ferroelectric and/or ferromagnetic composites: a unified approach and its application. *J. Am. Ceram. Soc.*, 1997, **80**, 1333.

4. Shin, K. H., Inoue, M. and Arai, K. I., Elastically coupled magneto-electric elements with highly magnetostrictive amorphous films and PZT substrates. *Smart Mater. Struct.*, 2000, **9**, 357.

5. Ryu, J., Priya, S., Uchino, K. and Kim, H. E., Magnetoelectric effect in composites of magnetostrictive and piezoelectric materials. *J. Electroceram.*, 2002, **8**, 107.

6. Astrov, D. N., Magnetoelectric effect in antiferromagnetics. *Sov. Phys. -JETP*, 1960, **11**, 708.

7. Astrov, D. N., Magnetoelectric effect in chromium oxide. *Sov. Phys. -JETP*, 1961, **13**, 729.

8. Clin, M., Rivera, J. P. and Schmid, H., Linear and quadratic magnetoelectric effect in boracite $Co_3B_7O_{13}Br$. *Ferroelectrics*, 1988, **79**, 173.

9. Singh, R. S., Bhimasankaram, T., Kumar, G. S. and Suryanarayana, S. V., Dielectric and magnetoelectric properties of $Bi_5FeTi_3O_{15}$. *Solid State Commun.*, 1994, **91**, 567.

10. Kornev, I., Bichurin, M., Rivera, J. P., Gentil, S., Schmid, H., Jansen, A. G. M. *et al.*, Magnetoelectric properties of $LiCoPO_4$ and $LiNiPO_4$. *Phys. Rev. B*, 2000, **62**, 12247.

11. Boomgaard, J. V. D. and Born, R. A. J., A sintered magnetoelectric composite material $BaTiO_3–Ni(Co,Mn)Fe_2O_4$. *J. Mater. Sci.*, 1978, **13**, 1538.

12. Mahajan, R. P., Patankar, K. K., Kothale, M. B., Chaudhari, S. C., Mathe, V. L. and Patil, S. A., Magnetoelectric effect in cobalt ferrite-barium titanate composites and their electrical properties. *Pramana-J. Phys.*, 2002, **58**, 1115.

13. Zhai, J. Y., Cai, N., Liu, L., Lin, Y. H. and Nan, C. W., Dielectric behavior and magnetoelectric properties of lead zirconate titanate/Co-ferrite particulate composites. *Mater. Sci. Eng. B*, 2003, **99**, 329.

14. Harshe, G., Dougherty, J. P. and Newnham, R. E., Magnetoelectric effect in composite materials. *Math. Smart Struct.*, 1993, **1919**, 224.

15. Ryu, J., Carazo, A. V., Uchino, K. and Kim, H. E., Magnetoelectric properties in piezoelectric and magnetostrictive laminate composites. *Jpn. J. Appl. Phys.*, 2001, **40**, 4948.

16. Srinivasan, G., Rasmussen, E. T., Gallegos, J., Srinivasan, R., Bokhan, Y. I. and Laletin, V. M., Magnetoelectric bilayer and multiplayer structures of magnetostrictive and piezoelectric oxides. *Phys. Rev. B*, 2001, **64**, 214408.

17. Srinivasan, G., Rasmussen, E. T. and Hayes, R., Magnetoelectric effects in ferrite-lead zirconate titanate layered composites: the influence of zinc substitution in ferrites. *Phys. Rev. B*, 2003, **67**, 014418.

18. Nan, C. W., Liu, L., Cai, N., Zhai, J., Ye, Y. and Lin, Y. H., A three-phase magnetoelectric composite of piezoelectric ceramics, rare-earth iron alloys, and polymer. *Appl. Phys. Lett.*, 2002, **81**, 3831.

19. Wan, J. G., Liu, J. M., Chand, H. L. W., Choy, C. L., Wang, G. H. and Nan, C. W., Giant magnetoelectric effect of a hybrid of magnetostrictive and piezoelectric composites. *J. Appl. Phys.*, 2003, **93**, 9916.

20. Schoenberg, E. A., Ferrites. *J. Am. Ceram. Soc.*, 1958, **41**, 484.

21. Zhi, Y. and Chen, A., Maxwell-Wagner polarization in ceramic composites $BaTiO_3–(Ni_{0.3}Zn_{0.7})Fe_{2.1}O_4$. *J. Appl. Phys.*, 2002, **91**, 794.

22. Lin, Y. H., Wang, J. F., Jiang, L., Chen, Y. and Nan, C. W., High permittivity Li and Al doped NiO ceramics. *Appl. Phys. Lett.*, 2004, **85**, 5664.

23. Volk, T., Isakov, D., Salobutin, V., Ivleva, L., Lykov, P., Ramzaev, V. *et al.*, Effects of Ni doping on properties of strontium–barium–niobate crystals. *Solid State Commun.*, 2004, **130**, 223.