Available online at www.sciencedirect.com

ScienceDirect

Trans. Nonferrous Met. Soc. China 21(2011) 2438−2442

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Frequency-dependent magnetoelectricity of $CoFe_2O_4$−$BaTiO_3$ particulate composites

Atchara KHAMKONGKAEO[1], Pongsakorn JANTARATANA [2], Chitnarong SIRISATHITKUL[3],
Teerapon YAMWONG[4], Santi MAENSIRI[5]

1. Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand;
2. Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand;
3. Magnet Laboratory, School of Science, Walailak University, Nakhon Si Thammarat 80161, Thailand;
4. National Metals and Materials Technology Center (MTEC), Thailand Science Park, Pathumthani 12120, Thailand;
5. School of Physics, Institute of Science, Suranaree University of Technology,
Nakhon Ratchasima 30000, Thailand

Received 6 January 2011; accepted 13 June 2011

Abstract: $CoFe_2O_4$−$BaTiO_3$ particulate composites were prepared by wet ball milling method, their magnetoelectric (ME) effect was studied as a function of their constituents and modulation frequency. The results show that the ME coefficient increases as a function of modulation frequency from 400 to 1000 Hz and the ME characteristics of ME curves are also modified because the electrical conductivity of the $CoFe_2O_4$ phase is sensitive to the increase in frequency between 400 and 1 000 Hz. The third phase $Ba_2Fe_2O_5$ formed during the sintering tends to reduce the ME effect.

Key words: ferrite; ferroelectric; $CoFe_2O_4$−$BaTiO_3$; magnetoelectric effect; modulation frequency

1 Introduction

Combination of both ferroelectric and magnetic orders in a single material leads to magnetoelectric (ME) effect which is activated by the mechanical coupling between magnetization and polarization [1−2]. Mechanical deformations induced by a magnetic field in a magnetostriction process give rise to an electric field by piezoelectric effect. Conversely, an application of electric field to ME materials can result in a magnetic field. ME materials are classified into single phase materials and multiphase composites. Their potential applications are in data storage, transducers and switching devices [1, 3]. Since the ME effect in single phase materials such as Cr_2O_3 and garnet films is too weak for applications, recent attentions have been turned to 2-phase ferrite-ferroelectric composites. In addition to composites with multilayered structures, a variety of particulate composites have been synthesized and characterized. Examples are combinations of various spinel ferrites (e.g. $CoFe_2O_4$, $NiFe_2O_4$, $Ni_{0.2}Co_{0.8}Fe_2O_4$ and $Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$) and piezoelectric materials (e.g. $BaTiO_3$, $Ba_{0.8}Sr_{0.2}TiO_3$, $BaZr_{0.08}Ti_{0.92}O_3$ and $PbZr_{0.5}Ti_{0.5}O_3$) [4−12].

The objective of this work is $CoFe_2O_4$−$BaTiO_3$ composites which have been investigated since 1974 [13]. The research on this ME composite is still active in recent experiments on particulate composites [10−12], superlattice films [14] and core-shell structures [15−16]. The ME coupling in self-assembled $CoFe_2O_4$−$BaTiO_3$ nanostructures has also been observed and analyzed [17−18]. According to Ref. [1], structural and electromagnetic properties of both magnetic and ferroelectric phases as well as their coupling at interfaces regulate the voltage response to the magnetic field. In addition to the applied static field, the modulation magnetic field is also required to generate ME response [19]. Resonance occurs when the modulation frequency coincides with magnetic, electric or mechanical eigen mode of the ME materials [1]. There have been theoretical suggestions that the modulation frequency has only moderate effect on the ME when it is lower than the electromechanical resonance frequency [20−21]. Hence,

---

Corresponding author: Chitnarong SIRISATHITKUL; Tel: +66-75-673230; Fax: +66-75-672004; E-mail: schitnar@wu.ac.th

DOI: 10.1016/S1003-6326(11)61033-9

the frequency-dependent magnetoelectricity in a low frequency regime has received little attention. However, FETISOV et al [22] observed the maximum ME coupling between 400 and 1 000 Hz from measurements of $Ni_{0.2}Co_{0.8}Fe_2O_4$−$PbZr_{0.5}Ti_{0.5}O_3$ laminate composites up to 100 kHz. Since both theoretical and experimental works on the effect of modulation frequency are based on multilayered structures, this work is proposed to investigate a variation of ME in a low frequency regime in particulate composites with varying constituent phases of $CoFe_2O_4$ and $BaTiO_3$.

2 Experimental

Ferrite−ferroelectric composites $(1-x)CoFe_2O_4$−$xBaTiO_3$ in which volume fraction x varies as 0.3, 0.4, 0.5 and 0.6 were prepared by wet ball milling using $CoFe_2O_4$ (35−55 nm in diameter, 98% purity) and $BaTiO_3$ (85−128 nm in diameter, 99.6% purity) commercial nanopowders (Nanostructured & Amorphous Materials, Inc) as starting materials. The powders were mixed in ethanol and zircronia grinding media for 24 h. Then, the slurry was continuously stirred at 80 °C until dried powders were obtained. The composite powders were compressed using uniaxial pressing in a d16 mm die with an applied pressure of 200 MPa and then sintered at 1 200 °C for 24 h in air. The composite powders and ceramics were characterized for crystal phase identification by X-ray diffractometry (XRD) using Cu K_α radiation with λ=0.154 nm (PW3040 mpd control). Room temperature magnetic hysteresis loops were obtained by using a vibrating sample magnetometer (VSM) (Lake Shore VSM 7403) and ferroelectric hysteresis was examined by the Sawyer-Tower method. The ME effect was measured with a variation of magnetic field up to 366.07 kA/m and superimposed by a modulation magnetic field of 0.80 kA/m. These magnetic fields were supplied by an electromagnet (Walker Scientific HV−4H) with a modulated Helmholz coil and the voltage was detected by a lock-in amplifier (Stanford SR850). The ME coefficient was calculated as a variation of the electric field in response to the applied magnetic field. The effect of the modulation frequency was studied by making ME measurements at 7 different frequencies from 400 to 1 000 Hz.

3 Results and discussion

In Fig. 1, XRD patterns of milled $CoFe_2O_4$−$BaTiO_3$ powders with varying volume fractions are shown with references to $CoFe_2O_4$ and $BaTiO_3$ peaks. The peaks are indexed as cubic spinel ferrite and tetragonal perovskite ferroelectric phases. The intensity of either ferrite or ferroelectric peaks predictably increases with their fractions in the composites. The absence of other unidentified peaks in Fig. 1 means that no chemical reaction occurs between these phases during milling. After sintering, the XRD patterns of all ceramics in Fig. 2 still display both $CoFe_2O_4$ and $BaTiO_3$ phases, and $Ba_2Fe_2O_5$ peaks are also observed in the case of x=0.3 or 0.4. The third phase of $Ba_2Fe_2O_5$ is likely formed by the replacement of $Fe^{2+}\longleftrightarrow Fe^{3+}$ in Ti^{3+}, which is of a minor fraction during the prolonged sintering. In the case of x=0.5 or 0.6, the replacement is suppressed because $Fe^{2+}\longleftrightarrow Fe^{3+}$ is no longer excessive. Only one weak $Ba_2Fe_2O_5$ peak appears in the case of x=0.6 and no third phase is observed at all when the amounts of constituents are in balance.

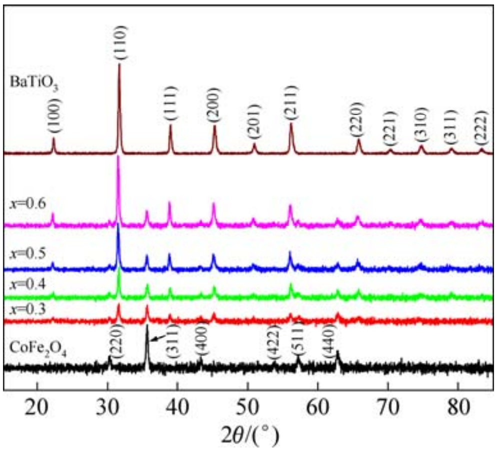

Fig. 1 XRD patterns of $(1-x)CoFe_2O_4$−$xBaTiO_3$ powders

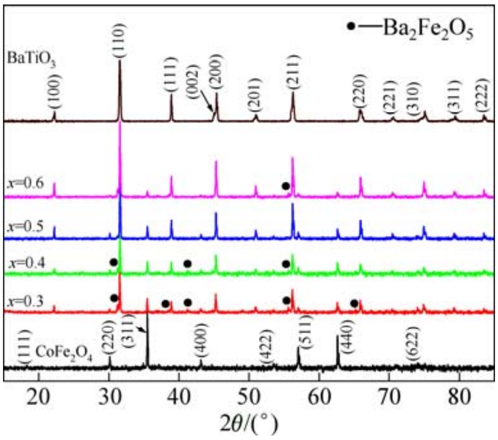

Fig. 2 XRD patterns of $(1-x)CoFe_2O_4$−$xBaTiO_3$ ceramics after sintering at 1 200 °C in air for 24 h

From hysteresis loops of $CoFe_2O_4$-$BaTiO_3$ ceramics at room temperature in Fig. 3, the ferrimagnetism exists in all composites with the saturation magnetization under magnetic field of 795.80 kA/m. According to the appearance of hysteresis loops, the investigated composites can be divided into 2 groups, i.e., the high magnetic fractions (x=0.3 and 0.4) and the low magnetic fractions (x=0.5 and 0.6). The dependence of saturation magnetization (M_s) and coercivity (H_c) on x is shown in Fig. 4. The highest saturation magnetization of about 4.7×10^{-2} A·m^2 is predictably observed in the case of x=0.3. With increasing the $BaTiO_3$ fraction, the magnetization is decreased because each $BaTiO_3$ grain acting like a void for the magnetic phase reduces the magnetic moment per unit volume [6, 9, 16, 23]. The composites with x=0.5 or 0.6 have significantly lower saturation magnetization compared with with those x=0.3 or 0.4, resulting in a variation in magnetization, which does not follow a straight line predicted by Bruggeman's effective medium theory [6, 9, 16, 23]. On the other hand, the increase in the coercivity with increasing x is not abrupt. This can be understood by considering the origins of enhanced coercivity, which are the reduction in interactions between $CoFe_2O_4$ grains and the domain wall pinned by surrounding phases [12]. In this case, the pinning arises from the combination of antiferromagnetic $Ba_2Fe_2O_5$ and ferroelectric $BaTiO_3$ phases which are gradually increased. It follows that the coercivity of the composite with x=0.5 is lower than the extrapolation by a straight line due to the absence of pinning by $Ba_2Fe_2O_5$.

With an exception of x=0.5, voltage up to 10 kV leads to a electrical breakdown in the composites. The internal discharge in ferrite-ferroelectric composites is attributed to the more conductive ferrite phase. It is fitting that ferroelectric loops of $CoFe_2O_4$−$BaTiO_3$ composites of equal fractions shown in Fig. 5 are elliptical in shape. This indicates the lossy characteristics which tend to change with the driving frequency.

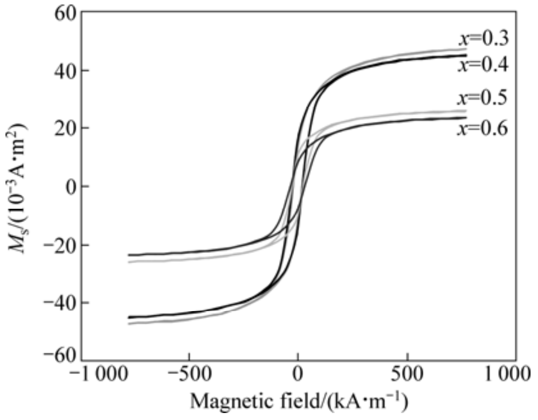

Fig. 3 Magnetic hysteresis loops of $(1-x)CoFe_2O_4$–$xBaTiO_3$ ceramics

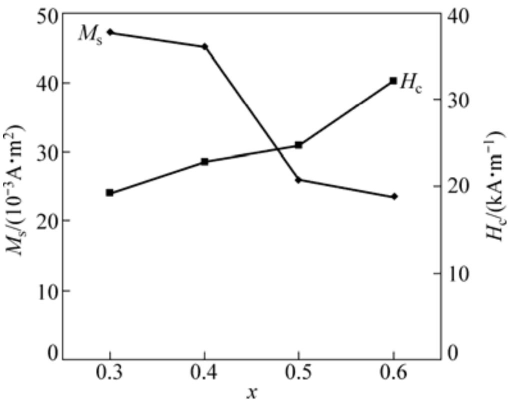

Fig. 4 Saturation magnetization and coercivity of $(1-x)CoFe_2O_4$–$xBaTiO_3$ ceramics

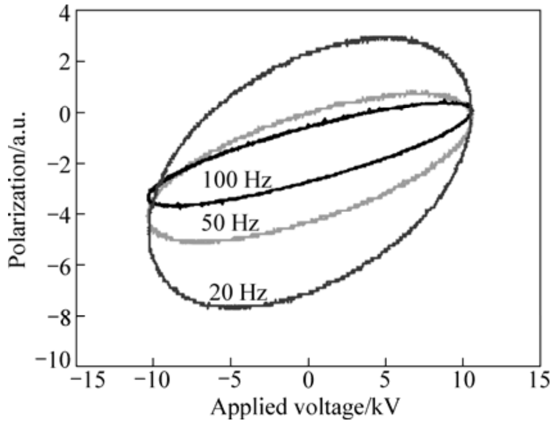

Fig. 5 Ferroelectric hysteresis loops of $(1-x)CoFe_2O_4$–$xBaTiO_3$ ceramics at varying frequency when x=0.5

The ME coefficient as a function of an applied magnetic field is dependent on the $BaTiO_3$ fraction (x). In Fig. 6, all ME curves at 400 Hz exhibit a similar trend with a high sensitivity to changing magnetic field of less than 7.96 kA/m. Beyond this low field regime, the increase in the applied magnetic field gradually raises the ME coefficient until reaching the maximum of around 47.75 kA/m. This peak corresponds to the saturation in magnetostriction of the ferrite phase [9]. With further increasing magnetic field up to 366.07 kA/m, the ME is monotonically decreased because the mechanical stress in $CoFe_2O_4$ can no longer be enhanced. The composites with higher $BaTiO_3$ fractions tend to exhibit lower ME effect which is in contrast to a previous report in $CoFe_2O_4$−$BaTiO_3$ particulate composites [10]. It is commonly known that the increase in a more conductive ferrite phase results in a substantial leakage current in the composites and tends to limit the effect of the poling. However, the larger grains of ferrite can promote favorable interface coupling for the ME. This interface effect may outweigh the reduction in resistivity, giving rise to the increased ME in more conductive composites [12]. Interestingly, the composite without $Ba_2Fe_2O_5$ (x=0.5) shows an unusually high ME coefficient, indicating that the third phase is not only responsible for the magnetic properties but also detrimental to the ME effect. Due to its antiferromagnetic nature, the ME effect is not induced in the $Ba_2Fe_2O_5$ phase and the transfer of mechanical stress between $CoFe_2O_4$ and $BaTiO_3$ is disrupted by its existence.

The effect of modulation frequency on the ME response is exemplified in Fig. 7. In the case of x=0.3, the ME curves at 500−1 000 Hz share some characteristics with that measured at 400 Hz. The low field sensitivity is reduced from 500 to 700 Hz but becomes more pronounced at frequencies higher than 700 Hz. Moreover, the ME curves at 800 and 900 Hz exhibit anomalous fluctuations with another sharp response at a field larger than 79.58 kA/m. Their origin is not clear and deserves further investigations because of its existence in every composition. At every frequency, the peaks around 47.75 kA/m can still be observed. The ME coefficients from such peaks are plotted in Fig. 8 to compare the effect of the frequency and the $BaTiO_3$ fraction (x). The ME coefficients are approximately 2−7 mV/A. In all composites, the ME coefficients exhibit roughly linear variations with the frequency from 400 to 700 Hz. The linearity does not continue into 800 Hz at which the ME characteristics anomalously change. Since the increase in ME coefficient in Fig. 8 resembles that of laminate composites [22], this frequency-dependent ME can also be explained in terms of the variations of the electrical conductivity of the ferrite phase in the low frequency regime.

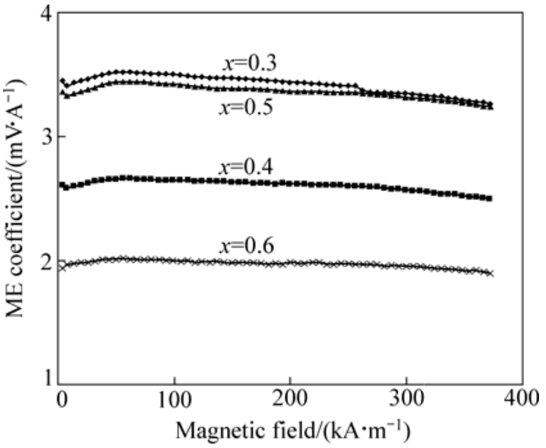

Fig. 6 Comparison of ME coefficients as function of magnetic field modulated at 400 Hz

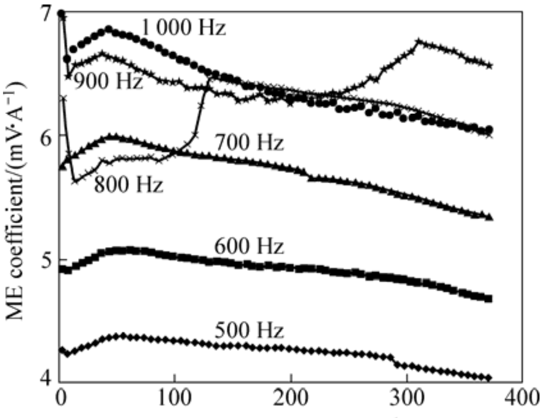

Fig.7 Comparison of ME coefficients as function of magnetic field when x=0.3

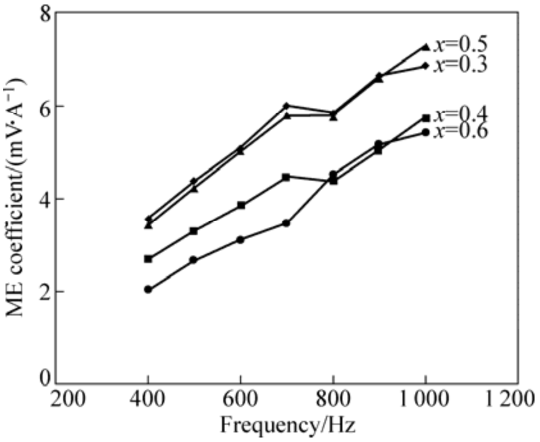

Fig.8 Variations of ME coefficient at peak around 600 Oe in Fig. 7 with different modulation frequencies and x values

4 Conclusions

1) The ME composites $(1-x)CoFe_2O_4-xBaTiO_3$ are successfully prepared by wet ball milling. In addition to cubic spinel $CoFe_2O_4$ and tetragonal $BaTiO_3$, $Ba_2Fe_2O_5$ is clearly observed in XRD patterns of ceramics, the x value of which is 0.3 or 0.4 due to the replacement of $Fe^{2+}\longleftrightarrow Fe^{3+}$ in Ti^{3+} after sintering at 1 200 °C in air for 24 h. This third phase affects the magnetic and ME properties of the composites.

2) The saturation magnetization is decreased whereas the coercivity is increased with the increase in $BaTiO_3$ fraction in the ME composites because this nonmagnetic phase reduces the magnetic moment per unit volume and the interaction between $CoFe_2O_4$ grains.

3) The ME coefficient, ranging between 2 and 7 mV/A, increases with increasing modulation frequency from 400 to 1 000 Hz. The low field response is also sensitive to the change in frequency. This frequency-dependent magnetoelectricity is related to the variation of electrical conductivity of the $CoFe_2O_4$ phase.

Acknowledgements

This collaboration was supported by the Industry/University Cooperative Research Center (I/UCRC) in HDD Component, the Faculty of Engineering, Khon Kaen University and National Electronics and Computer Technology Center (NECTEC), National Science and Technology Development Agency (NSTDA). The TGIST scholarship (TG-33-12-51-048D) is granted to the first author by the National Metal and Materials Technology Center (MTEC) of NSTDA. The authors would like to thank the Ubon Ratchathani University and Department of Chemistry, Khon Kaen University for providing XRD and VSM facilities.

References

[1] FIEBIG M. Revival of the magnetoelectric effect [J]. J Phys D: Appl Phys, 2005, 38(3): R123−R152.

[2] WAN You-ping, ZHONG Zheng, QIU Jin-hao. Magnetoelectric voltage coefficients of magnetoelectric composites [J]. Transactions of Nonferrous Metals Society of China, 2006, 16(S1): s20−s24.

[3] GROESSINGER R, DUONG G V, BUENO-BAQUES D. Magnetoelectric materials—New materials for applications [J]. Int J Appl Electromag Mech, 2007, 25(1): 3−11.

[4] KULKARNI S R, DEVAN R S, CHOUGULE B K. Electrical and magnetoelectric properties of $Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$+$PbZr_{0.5}Ti_{0.5}O_3$ composites [J]. J Alloy Compd, 2008, 455(1−2): 336−339.

[5] PATIL D R, CHOUGULE B K. Effect of resistivity on magnetoelectric effect in $x$$NiFe_2O_4$−(1−$x$)$Ba_{0.9}Sr_{0.1}TiO_3$ ME composites [J]. J Alloy Compd, 2009, 470(1−2): 531−535.

[6] BABU S N, SURYANARAYANA S V, BHIMASANKARAM T. Magnetic and magnetoelectric characterization of $Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_4$ and PZT composites [J]. J Alloy Compd, 2009, 473(1−2): 418−422.

[7] BAMMANNAVAR B K, NAIK L R, PUJAR R B, CHOUGULE B K. Resistivity dependent magnetoelectric characterization of $Ni_{0.2}Co_{0.8}Fe_2O_4$+$Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ composites [J]. J Alloy Compd, 2009, 477(1−2): L4−L7.

[8] KANAMADI C M, KIM J S, YANG H K, MOON B K, CHOI B C, JEONG J H. Magnetoelectric effect and complex impedance analysis of $x$$CoFe_2O_4$+(1−$x$)$Ba_{0.8}Sr_{0.2}TiO_3$ multiferroics [J]. J Alloy Compd, 2009, 481(1−2): 781−785.

[9] KAMBLE R C, SHAIKH P A, BHOSALE C H, RAJPURE K Y, KOLEKAR Y D. Studies on magnetic, dielectric and magnetoelectric behavior of (x)$NiFe_{1.9}Mn_{0.1}O_4$ and (1−x)$BaZr_{0.08}Ti_{0.92}O_3$ magnetoelectric composites [J]. J Alloy Compd, 2010, 489(1): 310−315.

[10] MAHAJAN R P, PATANKAR K K, KOTHALE M B, CHAUDHARI S C, MATHE V L, PATIL S A. Magnetoelectric effect in cobalt ferrite-barium titanate composites and their electrical properties [J]. Pramana J Phys, 2002, 58(5−6): 1115−1124.

[11] REN S Q, WENG L Q, SONG S H, LI F, WAN J G, SENG M. $BaTiO_3$/$CoFe_2O_4$ particulate composites with large high frequency magnetoelectric response [J]. J Mater Sci, 2005, 40(16): 4375−4378.

[12] NIE Jun-wu, XU Guo-yue, QI Xian-jin. Effect of interface recombination on magnetoelectric coupling in $CoFe_2O_4$-$BaTiO_3$ composites [J]. Transactions Nonferrous Metals Society of China, 2009, 19(6): 1593−1598.

[13] van de BOOMGAARD J, TERRELL D R, BORN R A J. An in situ grown eutectic magnetoelectric composite material [J]. J Mater Sci, 1974, 9(10): 1705−1708.

[14] ZHANG J X, DAI J Y, LU W, CHAN H L W. Room temperature magnetic exchange coupling in multiferroic $BaTiO_3$/$CoFe_2O_4$ magnetoelectric superlattice [J]. J Mater Sci, 2009, 44(19): 5143−5148.

[15] DUONG G V, TURTELLI R S, GROESSINGER R. Magnetoelectric properties of $CoFe_2O_4$-$BaTiO_3$ core-shell structure composite studied by a magnetic pulse method [J]. J Magn Magn Mater, 2010, 322(9−12): 1581−1584.

[16] CORRAL-FLORES V, BUENO-BAQUES D, ZIOLO R F. Synthesis and characterization of novel $CoFe_2O_4$-$BaTiO_3$ multiferroic core-shell-type nanostructures [J]. Acta Mater, 2010, 58(3): 764−769.

[17] DENG Y, ZHOU J X, WU D, DU Y L, ZHANG M S, WANG D H, YU H Q, TANG S L, DU Y W. Three-dimensional phases-connectivity and strong magnetoelectric response of self-assembled feather-like $CoFe_2O_4$-$BaTiO_3$ nanostructures [J]. Chem Phys Lett, 2010, 496(4−6): 301−305.

[18] ZHENG H, WANG J, LOFLAND S E, MA Z, MOHADDES-ARDABILI L, ZHAO T, SALAMANCA-RIBA L, SHINDE S R, OGALE S B, BAI F, VIEHLAND D, JIA Y, SCHLOM D G, WUTTIG M, ROYTBURD A, RAMESH R. Multiferroic $CoFe_2O_4$-$BaTiO_3$ nanostructures [J]. Science, 2004, 303(5668): 661−663.

[19] DUONG G V, GROESSINGER R, SCHOENHART M, BUENO-BAQUES D. The lock-in technique for studying magnetoelectric effect [J]. J Magn Magn Mater, 2007, 316(2): 390−393.

[20] FILIPPOV D A. Theory of the magnetoelectric effect in ferromagnetic-piezoelectric heterostructures [J]. Phys Solid State, 2005, 47(6): 2064−2066.

[21] VOPSAROIU M, BLACKBURN J, CAIN M G. A new magnetic recording read head technology based on themagneto-electric effect [J]. J Phys D: Appl Phys, 2007, 40(17): 5027−5033.

[22] FETISOV Y K, KAMENTSEV K E, OSTASHCHENKO A Y. Magnetoelectric effect in multilayer ferrite-piesoelectric structures [J]. J Magn Magn Mater, 2004, 272–276(S1): s2064−s2066.

[23] GRIDNEV S A, GORSHKOV A G, KOROLEVSKAYA O N. Magnetic, ferroelectric, elastic and inelastic properties of $x$$Ni_{0.4}Zn_{0.6}Fe_2O_4$-(1−$x$)$Pb_{0.95}Sr_{0.05}Zr_{0.53}Ti_{0.47}O_3$ composites [J]. Phys Solid State, 2009, 51(8): 1553−1556.

$CoFe_2O_4$−$BaTiO_3$颗粒复合材料的频率相关电磁性能

Atchara KHAMKONGKAEO[1], Pongsakorn JANTARATANA [2], Chitnarong SIRISATHITKUL[3],
Teerapon YAMWONG[4], Santi MAENSIRI[5]

1. Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand;
2. Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand;
3. Magnet Laboratory, School of Science, Walailak University, Nakhon Si Thammarat 80161, Thailand;
4. National Metals and Materials Technology Center (MTEC), Thailand Science Park, Pathumthani 12120, Thailand;
5. School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

摘 要：通过湿法球磨制备 $CoFe_2O_4$−$BaTiO_3$ 颗粒复合材料，研究材料成分和调制频率与电磁效应的关系。结果表明：电磁效应系数随着调制频率由 400 Hz 增加到 1 000 Hz 而增加。由于 $CoFe_2O_4$ 的电导率在 400−1 000 Hz 范围内对频率敏感，电磁效应的曲线特性而发生改变。在烧结过程中形成第三相 $Ba_2Fe_2O_5$，从而导致电磁效应的下降。

关键词：铁氧体；铁电体；$CoFe_2O_4$−$BaTiO_3$；磁电效应；调制频率

(Edited by FANG Jing-hua)