Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 3663–3666

www.elsevier.com/locate/jeurceramsoc

Synthesis and characterization of electroceramics with magnetoelectric properties

J. de Frutos[a,*], J.A. Matutes-Aquino[b], F. Cebollada[a], M.E. Botello-Zubiate[b], E. Menéndez[c], V. Corral-Flores[b], F.J. Jiménez[a], A.M. González[a]

[a] *Grupo POEMMA, E.T.S.I. Telecomunicación, U.P.M. 28040, Madrid, Spain*
[b] *CIMAV, Centro Industrial Chihuahua, CP 31109 Chihuahua, Mexico*
[c] *IETCC-CSIC, C/Serrano Galvache 4, Madrid, Spain*

Abstract

Electroceramics with ferropiezoelectric and ferri-ferromagnetic properties have been studied. These ceramics consist of two phases, a ferroelectric one (commercial $BaTiO_3$) and a ferromagnetic one (MFe_2O_4, with M = Ni, Zn, Co, obtained through co-precipitation methods), which are later mixed using mechanical milling. A characterization of the previous phases is made by means of electronic microscopy and X-ray diffraction. The results of the magnetic, electric, ferroelectric and piezoelectrical response of the different compound compositions are obtained. The coexistence of phases is made clear, with a greater magnetic response in the samples of ferrite with Co and a greater piezoelectric in the samples of ferrite with Ni. These results are analysed, and the potential of the use of different mixtures is discussed.

Keywords: Composites; Ferroelectric properties; Magnetic properties; Piezoelectric properties; Functional applications

1. Introduction

The use of mixed ferropiezoelectric–ferromagnetic systems has brought about much interest in the last few years. The possibility of having double excitation source sensors and actuators available, or multifunctionals, opens up an enormous field of applications which exceeds the traditional use of magnetoelectric properties. From the control of the magnetic phase by means of electric fields,[1] to the magnetic control of ferroelectric polarisation,[2] magnetoelectricity becomes an objective in the achievement of ferroelectric magnets[3] whilst at the same time trying to explain the causes of ferroelectricity in different materials with magnet-electricity[4] or the advent of a new era in materials science with the renaissance of magnet–electric multiferroics.[5,6] The most widely studied systems correspond to Co or Ni ferrites, with PZT, $BaTiO_3$ or $LiTaO_3$, with combinations both of ferrites and piezoelectrics. The procedure for the manufacture of the material varied from multilayer growths[7–10] interspersing both materials or by developing a system of manufacture that permits the coexistence of both phases together.[10–14] One of the most developed applications for this type of material has traditionally been magnetoelectricity.[10] It is said that a material has magnetoelectricity when there are induction of magnetization by an electric field or of polarisation by a magnetic field. This effect takes place in mixed or compound materials that have ferro-piezoelectrical and magnetoestrictive phases and results from the linking of both phases. The magnetoelectric effect in compound materials is analysed from the Van Suchetelene approach, as a result of the properties of each phase.[15] A suitable combination of the two phases must lead jointly to the coexistence of piezoelectric and piezomagnetic phases or a combination of magnetostrictive and piezoelectric phases[16]. In this work, we try to verify the coexistence of phases in ferroelectric–ferromagnetic (ferric) compounds in which the existence of magnetoestrictive effects are clear. With this aim, we will manufacture and characterize compositional, structural, electric, piezoelectric and magnetically mixed ferroics systems of nickel, zinc, and cobalt ferrites combined in different proportions with ferroelectric barium titanate.

2. Experimental

Cobalt, nickel and zinc ferrites have been synthesised making use of the co-precipitation method. That of cobalt ferrite

---

* Corresponding author.
E-mail address: jfrutos@fis.upm.es (J. de Frutos).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.084

$CoFe_2O_4$ is synthesised from $CoCl_2·6H_2O$ and $FeCl_3·6H_2O$ adding NaOH as a precipitant agent. The reaction takes place at 65 °C for 1 min under constant agitation. The particles thus obtained, are alternatively washed and dried at 60 °C.

Using an equivalent procedure, $Ni(NO_3)_2·6H_2O$ and $Zn(NO_3)_2·6H_2O$ has been used to prepare the nickel ($NiFe_2O_4$) and zinc ($ZnFe_2O_4$) ferrites, respectively. Again, NaOH is added to precipitate the ferrites at ambient temperature, followed by a digestion stage at 90 °C for 1 h. Through X-ray diffraction, the size of the particles of the three ferrites has been calculated at approximately 6 nm.

For the ferroelectric phase, $BaTiO_3$, from the firm Aldrich has been used, with a particle size of less than 2 μm. In a first step, it goes through a mechanical milling action at a high energy (SPEX 8000) for 30 min in order to reduce the size of the particle. It is then mixed in a suitable proportion with the Co, Ni and Zn ferrites to obtain fractions of 0.2 and 0.4 (20 and 40% in weight) of the ferrite with respect to $BaTiO_3$. Each of the mixtures is milled again for 15 min with the aim of achieving a homogeneous mixture between both phases. The powder is then pressed into cylindrical pastilles, at a pressure of 280 MPa, to arrive at a density of 60% of the theoretical density of the mixture. It is then synthesised at 1200 °C for 12 h, to reach a final density of 95% of the theoretical density.

The different compositions have been characterized by means of X-ray diffraction, scanning microscopy, and its dielectric, piezoelectric and magnetic response has been studied.

The microstructures are very different for each system, with the presence of large particles surrounded by an interface in the case of cobalt ferrites, a more uniform microstructure with some inclusions in the nickel ferrite, and a more laminar structure, with a greater density of pores in the case of zinc ferrite. Both the diffraction values and the observed microstructures, clearly demonstrate the coexistence of the two phases, and by carrying out a Rietveld refinement analysis, for the case of the ferroelectric cobalt ferrite, with a fraction of the ferrite of 20%, the values determined are 19.3 ± 0.5%. A small proportion of the barium that reacts forming barium hexaferrite may be assumed, but neither X-ray diffraction, not Rietveld refinement seems to hint at it.

3. Dielectric, magnetic, magnetoelectric and piezoelectric characterization

For this study, the samples are machined into discs of 12 mm in diameter and 1 mm in thickness. It is metallised with silver electrodes, and it is then electrically polarised by applying a field of 20 kV/cm at 110 °C for 30 min and allowed to cool down to room temperature with the field still applied.

The value of d_{33} has been measured with a d_{33} APC model 8000 gauge, and the dielectric measurements and piezoelectric behaviour have been carried out with an HP4192 impedance bridge, and making use of the characterization in resonance method. For its part, the ME coefficient has been calculated from the data obtained from the modified pulse field magnetometer, which allows the charge in the sample to be acquired because of the polarisation induced by the action of a magnetic field.

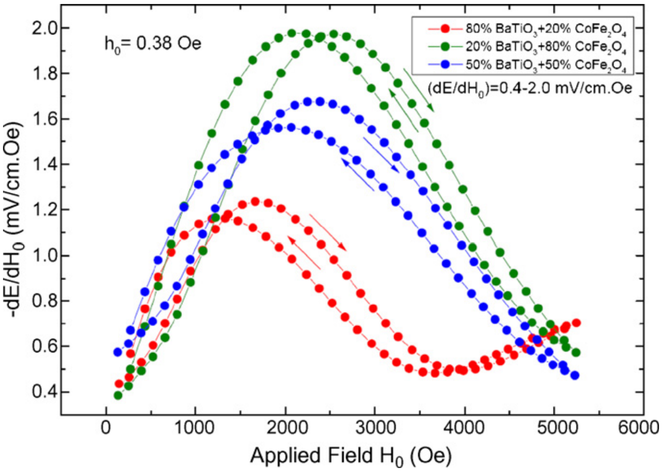


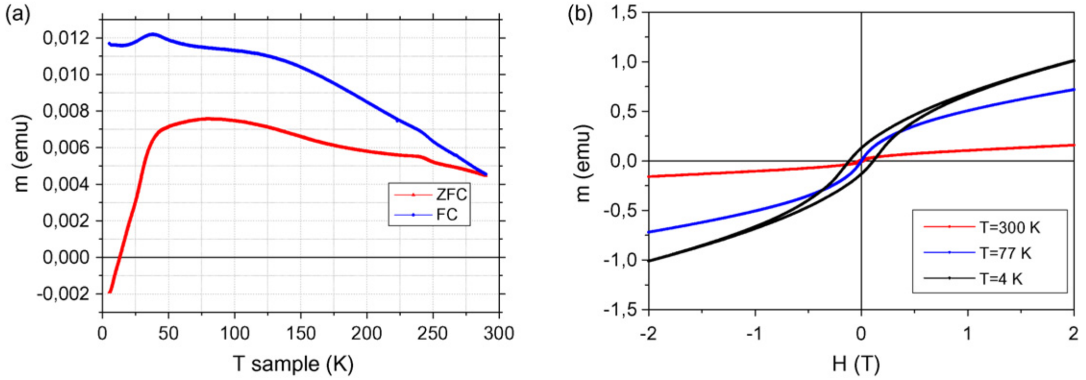
Fig. 1. Magnetoelectric response for the cobalt ferrite samples with barium titanate in different proportions.

The ZFC and FC measurements have been made, as well as the magnetization measurements according to the magnetic field up to nine Teslas, at ambient temperature. The field is generated by a horseshoe electromagnet. The air gap is variable in dimension until being able to close the magnetic circuit. The process of making magnetic field ramps and plates is totally automatic.

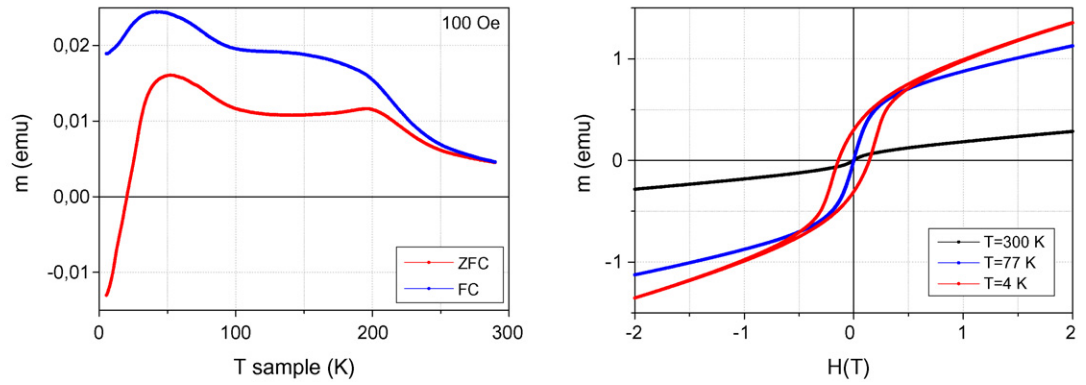
Fig. 1 shows the magnetoelectric response for the cobalt ferrite samples with barium titanate in different proportions. It can be shown that the samples with the greatest magnetoelectric response are those with the highest content of barium titanate. The response for these samples is practically the same rising or lowering the magnetic field applied, and a clear hysteresis can be seen between the two processes. On applying the initial field in one direction, it maintains a strong magnetic remanence, which is not totally inverted when the field is reduced. On the other hand, and as was expected, as the content of the ferroelectric phase increases, piezo-ferroelectric response of the compound increases. We have measured values for both the piezoelectric, d_{33}, and the magnetoelectric, α_{33}, coefficients for the different compositions analysed (Table 1). It can be seen that the composition with the least response, both piezoelectric and magnetoelectric is that made up of Zn ferrites (2,4-0,0 and 0,9-0,0). For its part, the greatest piezoelectric response was obtained from the samples of Ni ferrite (19,9-0,43 and 7,2-0,44), and which were very similar to the magnetoelectric in both these and those of cobalt (5,5-0,9 and 4,2-1,24). It is clear in all cases, that when the ferroelectric phase is greater, the piezoelectric

Table 1
Piezoelectric (d_{33}) and magnetoelectric (α) values

	d_{33} (pC/N)	α_{33} (mV/cm Oe)
20% $BaTiO_3$ + 80% $ZnFe_2O_4$	2.4	0.000
40% $BaTiO_3$ + 60% $ZnFe_2O_4$	0.9	0.000
20% $BaTiO_3$ + 80% $NiFe_2O_4$	19.9	0.430
40% $BaTiO_3$ + 60% $NiFe_2O_4$	7.2	0.440
20% $BaTiO_3$ + 80% $CoFe_2O_4$	5.5	0.900
40% $BaTiO_3$ + 60% $CoFe_2O_4$	4.2	1.240



40% $BaTiO_3$ 60% $ZnFe_2O_4$



20% $BaTiO_3$ 80% $ZnFe_2O_4$

Fig. 2. Magnetic characterization of Zn mixed system. (a) ZFC, FC and (b) hysteresis.

response increases, and when the ferromagnetic phase increases, the magnetoelectric response increases.

It can be demonstrated that in the case of compositions with Zn the worst values are obtained both piezoelectric and magnetoestrictive, and those of Ni provide the best responses both piezoelectric and magnetoestrictive.

These results are in agreement with those obtained from the ZFC–FC curves, which are set out in Fig. 2, and those of the piezoelectric response in Fig. 3. If we complete the results with the analysis of the magnetic hysteresis cycles (Fig. 2), we can see that while the samples with Co and Zn ferrites show a clear ferroelectric behaviour, it is precisely the Ni compositions that provide a more differentiated behaviour. Thus, while the compositions with Co are clearly ferromagnetic until ambient temperature, where they present a super-paramagnetic behaviour, the compositions with Ni ferrite are super-paramagnetic in the whole of the range analysed.

Another interesting result comes about from the ZFC–FC values. In this case, the most interesting response corresponds to the samples with Zn and Ni ferrites. It can be seen, especially, in the samples with a greater ferroelectric phase content, two magnetic phases in the material. This behaviour was not expected at the beginning. A more detailed analysis of the behaviour was able to demonstrate that the second phase appear at temperatures that correspond to characteristic phase transitions of the barium titanate. We assume that the structural changes associated with these transitions bring about sufficiently large internal pressures in the ferromagnetic material as to bring about the transitions that are seen. Finally, if we take a close look at Fig. 3, we can see that in the samples with Ni ferrite, even with low contents in the ferroelectric phase, they behave as acceptable mechanical resonators, even at high frequencies, for the samples with Co ferrite the capacity to resonate is surmised, and those of Zn do not present any evidence of mechanical resonance.

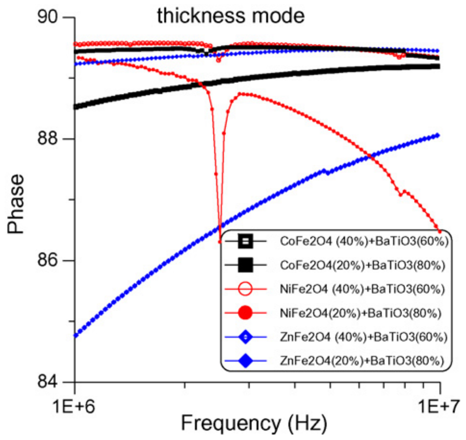


Fig. 3. Piezoelectric resonance at thickness mode.

4. Conclusions

We have demonstrated the capacity to manufacture multiferroic materials, in which ferroelectric and ferromagnetic phases coexist. Each one of the systems provides different responses. From the data obtained, we can conclude that the samples with nickel ferrite provide altogether a better piezoelectric and magnetoestrictive response. Its magnetic behaviour is superparamagnetic from temperatures of −269 °C, and behaves as an acceptable mechanical resonator when the content of the ferroelectric phase is greater than 60%. We conclude that in systems with Ni and Zn ferrites de Ni, the ferroelectric phase transitions induce structural changes associated with the transition, strong microscopically distributed mechanical pressures on the ferromagnetic state inducing phase changes in it.

All of the aforementioned brings us to the conclusion that mixed barium titanate–nickel ferrite systems, with high contents of the ferroelectric phase, are excellent as a candidate for multiferroic materials.

Acknowledgement

We thank CICYT (Project MAT2004-04843-C02-02) for financial support.

References

1. Lottermoser, T., Lonkai, T., Amann, U., Hohlwein, D., Ihringer, J. and Fiebig, M., Magnetic phase control by an electric field. *Nature*, 2004, **430**, 541–544.
2. Kimura, T., Goto, T., Shintani, H., Ishizaka, K., Arima, T. and Tokura, Y., Magnetic control of ferroelectric polarization. *Nature*, 2003, **426**, 55–58.
3. Ederer, C. and Spaldin, N. A., Magnetoelectrics: A new route to magnetic ferroelectrics. *Nature Materials*, 2004, **3**, 849–851.
4. Van Aken, B. B., Palstra, T. T. M., Filippetti, A. and Spaldin, N. A., The origin of ferroelectricity in magnetoelectric YMnO3. *Nature Materials*, 2004, **3**, 164–170.
5. Spaldin, N. A. and Fiebig, M., Materials science. The renaissance of magnetoelectric multiferroics. *Science*, 2005, **15**(309(5733)), 391–392.
6. Fiebig, M., Topical review: revival of the magnetoelectric effect. *Journal of Physics D: Applied Physics*, 2005, **38**(8), R123–R152.
7. Srinivasan, G., Rasmussen, E. T. and Hayes, R., Magnetoelectric effects in ferrite-lead zirconate titanate layered composites: studies on the influence of zinc substitution in ferrites. *Physical Review B*, 2003, **67**, 014418.
8. Bichurin, M. I., Fillipov, D. A., Petrov, V. M., Laletsin, U. and Srinivasan, G., Resonance magnetoelectric effects in layered magnetostrictive-piezoelectric composites. *Physical Review B*, 2003, **68**, 132408.
9. Srinivasan, G., Bichurin, M. I. and Mantese, J. V., Ferromagnetic-ferroelectric layered structures: magnetoelectric interactions and devices. *Integrated Ferroelectrics*, 2005, **71**, 45–57.
10. Mitoseriu, L., Magnetoelectric phenomena in single-phase and composite systems. *Boletin de la Sociedad Espanola de Ceramica y Vidrio*, 2005, **44**(3), 177–184.
11. Matutes-Aquino, J., Botello-Zubiate, M. E., Corral Flores, V. and de Frutos, J., Magnetoelectric ferrite-barium titanate composites: synthesis and comparative characterization. *Ferroelectrics*, 2006, **338**, 1663–1669.
12. Botello-Zubiate, M. E., Bueno-Baques, D., de Frutos, J., Fuentes, L. E. and Matutes-Aquino, J. A., Synthesis and magnetoelectric characterization of cobalt ferrite–barium titanate composites using a new pulsed magnetic field method. *Integrated Ferroelectrics*, 2006, **83**, 33–40.
13. Nan, C. W., Liu, L., Cai, N., Zhai, J., Ye, Y., Lin, Y. H., Dong, L. J. and Xiong, C. X., A three-phase magnetoelectric composite of piezoelectric ceramics, rare-earth iron alloys, and polymer. *Applied Physics Letters*, 2002, **81**(20), 3831–3833.
14. Ryu, J., Vazquez Carazo, A., Uchino, K. and Kim, H. E., Piezoelectric and magnetoelectric properties of lead zirconate titanate/ni-ferrite particulate composites. *Journal of Electroceramics*, 2001, **7**, 17–24.
15. Cebollada, F., González, J. M., de Frutos, J. and González, A. M., Reversal mechanisms and interactions in magnetic systems: coercitivity versus switching field and thermally assisted demagnetization. *Boletin de la Sociedad Espanola de Ceramica y Vidrio*, 2005, **44**(3), 169–176.
16. Fontcuberta, J., Balcells, Ll., Navarro, J., Rubi, D., Martínez, B., Frontera, C., Lacaba, M., González, A. M., Forniés, C., Calleja, A. and Aragonès, L. L., Cerámicas magnetorresistivas. Progresos recientes: desde el entendimiento básico a las aplicaciones. *Boletin de la Sociedad Espanola de Ceramica y Vidrio*, 2004, **43**(3), 627–633.