Synthesis and Characterization of Nickel Ferrite-Barium Titanate Ceramic Composites

J. A. Matutes-Aquino, M. E. Botello-Zubiate, V. Corral-Flores,
J. de Frutos, F. Cebollada, E. Menéndez, F. J. Jiménez,
and A. M. Gonzalez

ABSTRACT

Magnetoelectric composites were synthesized from piezoelectric BaTiO3 and ferrimagnetic NiFe2O4. These two phases are mixed, mechanically milled and heat treated. A characterization is made by means of electronic microscopy and x-ray diffraction. The results of the magnetic, electric, ferroelectric and piezoelectrical response of two different compositions are obtained. The composites are superparamagnetic in all the measured temperature range. It was observe a magnetic change induced by a structural transition of the ferroelectric phase. The composites behaves as an acceptable mechanical resonator when the content of the ferroelectric phase is equal or greater than 60 wt.%.

Keywords: composites, ferroelectric properties, magnetic properties, piezoelectric properties, functional applications

INTRODUCTION

Composites and single phase materials with simultaneous ferroelectricity and ferro/ferrimagnetism have brought about much interest in the last few years due to the possibility of having double excitation source sensors and actuators available, or multifunctionals, which opens up an enormous field of applications which exceeds the traditional use of magnetoelectric properties. These applications range from the control of the magnetic phase by means of electric fields [1], to the magnetic control of ferroelectric polarization [2]. Magneto-electricity becomes an objective in the achievement of ferroelectric magnets [3] whilst at the same time trying to explain the causes of ferroelectricity in differ-ent 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 and Ni ferrites, with PZT, BaTiO3 or LiTaO3, with combinations both of ferrites and piezoelectrics. The materials processing varies from multilayer growths [7–10] interspersing both materials to developing a system of manufacture that permits the coexistence of both phases together [10–14]. Magnetoelectricity [10] is one of the most developed applications for this type of material. A material has magnetoelectricity when there are induction of magnetization by an electric field or of polarization by a magnetic field. This effect takes place in mixed or compound materials that have ferro piezoelectric 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, 16]. A suitable combination of the two phases must lead jointly to the coexistence of piezoelectric and piezomagnetic/ magnetostrictive phases. In this work we manufactured two compositions of nickel ferrite/barium titanate ferroelectric–ferromagnetic composite and characterized their structural, electric and magnetic properties.

EXPERIMENTAL

Nickel ferrite was synthesized making use of the coprecipitation method with Fe(NO3)2·6H2O and Ni(NO3)2·6H2O from the firm Baker as main reactants. NaOH was added to precipitate the ferrite at room temperature, followed by a digestion stage at 90◦C for 1 hour. Applying the Scherrer's formula to the

X-ray diffraction peaks, the average size of the particles of the ferrite has been calculated at approximately 6 nm. For the ferroelectric phase, BaTiO3 from the firm Aldrich was used, with a particle size of less than 2 μm. In a first step it went through a mechanical milling action at a high energy (SPEX 8000) for 30 minutes in order to reduce the size of the particle. It was then mixed in a suitable proportion with the Ni ferrite to obtain fractions of 0.2 and 0.4 (20 and 40 weight %) of nickel ferrite with respect to BaTiO3. Each of the mixtures was milled again for 15 minutes with the aim of achieving a homogeneous mixture between both phases. The powder was 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 was then synthesized at 1,200◦C for 12 hours, to reach a final density of 95% of the theoretical density.

The different compositions were characterized by means of X-ray diffrac-tion, scanning microscopy, and its dielectric, piezoelectric and magnetic re-sponses were studied.

The microstructures was rather uniformly distributed and both the X-ray diffraction patterns and the observed microstructure clearly demonstrate the coexistence of the two phases. A small proportion of the Barium that reacts forming barium hexaferrite may be assumed, but the X-ray diffraction patterns do not seems to hint at it.

RESULTS AND DISCUSSION

For this study, the samples were machined into discs of 12 mm in diameter and 1 mm in thickness. They were metallized with silver electrodes, and then electrically polarized by applying a field of 20 kV/cm at 110◦C for 30 minutes and allowed to cool down to room temperature with the field still applied.

The d33 values were measured with a d33 APC model 8000 gauge, and the dielectric measurements and piezoelectric behaviour were carried out with an HP4192 impedance bridge, and making use of the characterization in resonance method.

Magnetoelectric coefficient were calculated from the data obtained from a modified pulse field magnetometer, which allows the charge in the sample to be acquired because of the polarization induced by the action of a magnetic field [17]. ZFC and FC measurements and magnetization measurements were made as function of temperature in a vibrating sample magnetometer. The process of making magnetic field ramps and plates is totally automatic.

Figure 1 shows the room temperature x-ray diffraction patterns for the cobalt ferrite and barium titanate starting phase, as well as for the composites with 20 and 40 wt.% of nickel ferrite. Barium titanate has narrow diffraction peaks corresponding its 2 µm average size, while cobalt ferrite synthesized by chemical coprecipitation has wide peaks due to its nanometric crystal size. On the other hand, the x-ray diffraction patterns of both composite compositions clearly show the peaks of both phase and the peaks wide indicates crystal growing of cobalt ferrite during the high temperature synthesis at 1,200◦Cfor 12 hours.

Table 1 shows the measured values of the piezoelectric, d33, and the magnetoelectric, α33, coefficients for the two analyzed compositions. The piezoelectric response obtained for the 20 wt.% nickel ferrite composite is almost 3 times higher than for 40 wt.% nickel ferrite composite, while the magnetoelectric coefficient is a little higher for the 40 wt.% nickel ferrite composite.

Figure 2 shows the magnetization curves for three different temperatures for a) 20 wt.% nickel ferrite composite and b) 40 wt.% nickel ferrite com-posite, with a superparamagnetic behaviour from temperatures of 4 K. One can observes that the maximum magnetizations are higher for the composite

Table 1
Piezoelectric (d33) and Magnetoelectric (α) values

Coposite composition	d_{33}(pC/N)	α_{33} (mV/cmOe)
20% $BaTiO_3$ + 80% $NiFe_2O_4$	19,9	0.430
40% $BaTiO_3$ + 60% $NiFe_2O_4$	7,2	0.440

with higher content of nickel ferrite, as expected, and in both case the maximum magnetization increases as the measurement temperature diminishes. Notice also that none of the curves saturates completely for the maximum ap-plied fields. Another interesting result comes about from the ZFC-FC curves. Figure 3 shows the field cooling (FC) and zero field cooling (ZFC) curves for a) the 20 wt.% nickel ferrite composite and b) the 40 wt.% nickel ferrite composite. 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 appears at temperatures that correspond to the characteristic phase transition of barium titanate from rhombohedral to orthorhombic at about 200 K. We assume that the structural changes associated with this transition 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. 4, we can see that even in the samples with low content of the ferroelectric phase, they behave as acceptable mechanical resonators, even at high frequencies.

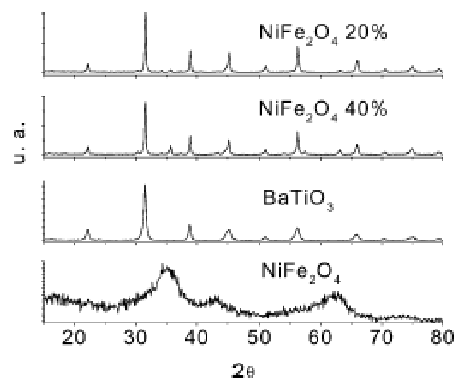

Figure 1. Room temperature x-ray diffraction patterns for the cobalt ferrite and barium titanate starting phase, as well as for the composites with 20 anf 40 wt.% of nickel ferrite.

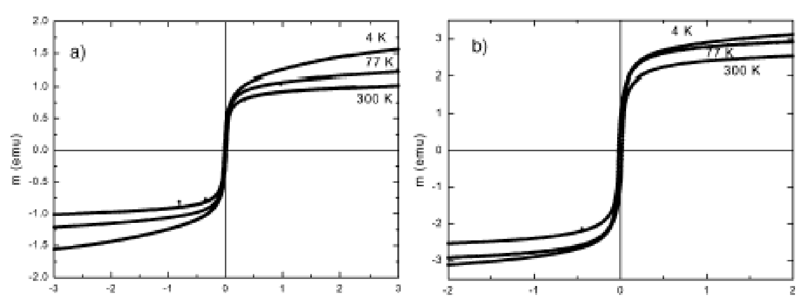

Figure 2. Magnetization curves for three different temperatures for the a) 20 wt.%nickel ferrite composite and for the b) 40 wt.% nickel ferrite composite.

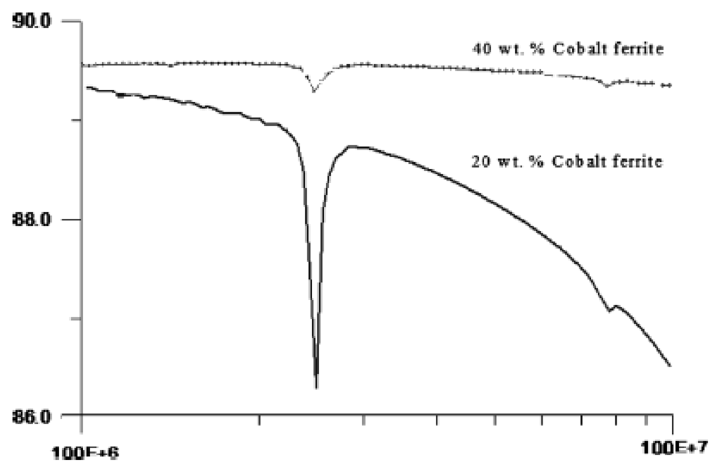

Figure 4. Piezoelectric resonance at thickness mode.

CONCLUSIONS

We have synthesized multiferroic magnetoelectric composites in which ferroelectric and ferromagnetic phases coexist. These samples with nickel ferrite provide piezoelectric as well as magnetoelectric responses. Its magnetic behaviour is superparamagnetic from temperatures of 4 K, and behaves as an acceptable mechanical resonator when the content of the ferroelectric phase is equal or greater than 60 wt.%. A structural transition of the ferroelectric phase induce strong structural changes associated with the transition, that produce microscopically distributed mechanical pressures on the ferromagnetic state inducing phase changes in it. All of the aforementioned brings us to the con-clusion that mixed barium titanate/nickel ferrite systems, with high contents of the ferroelectric phase, are excellent as a candidate for multiferroic materials.

ACKNOWLEDGMENTS

The authors thank to CICYT (Project MAT2004-04843-C02-02) for financial support.

REFERENCES

1. T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature 430, 541 (2004).

2. T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature 426, 55 (2003).

3. C. Ederer and N. A. Spaldin, Nature Materials 3, 849 (2004).

4. B. B. Van Aken, T. T. M. Palstra, A. Filippetti, and N. A. Spaldin, Nature Materials 3, 164 (2004).

5. NA Spaldin and M. Fiebig, Science 15, 391 (2005).

6. M. Fiebig, Journal of Physics D, Applied Physics 38, R123 (2005).

7. G. Srinivasan, E. T. Rasmussen, and R. Hayes, Phys. Rev. B 67, 014418 (2003).

8. M. I. Bichurin, D. A. Fillipov, V. M. Petrov, U. Laletsin, and G. Srinivasan, Phys.Rev.B68, 132408 (2003).

9. G. Srinivasan, M. I. Bichurin, and J. V. Mantese, Integrated Ferroelectrics 71, 45 (2005).

10. L. Mitoseriu, Bol. Soc. Esp. Ceram. Vidrio 44, 177 (2005).

11. J. Matutes-Aquino, M. E. Botello-Zubiate, and V. Corral Flores, J. de Frutos, Ferroelectrics 338,1663 (2006).

12. M. E. Botello-Zubiate, D. Bueno-Baques, J. de Frutos, L. E. Fuentes,

and J. A. Matutes-Aquino, Integrated Ferroelectrics 83, 33 (2006).

13. C. W. Nan, L. Liu, N Cai, J. Zhai, Ye Y., Y. H. Lin, L. J. Dong, and C. X. Xiong., Applied Physics Letters 81, 3831 (2002)

14. J. Ryu, A. Vazquez Carazo, K. Uchino, and H. E. Kim, Journal of Electroceramics 7, 17 (2001)

15. F. Cebollada, J. M. González, J. de Frutos, and A. M. González., Bol. Soc. Esp. Ceram. Vidrio 44, 169 (2005)

16. J. Fontcuberta, Ll. Balcells, J. Navarro, D. Rubí, B. Martínez, C. Frontera,

M. Lacaba, A. M. González, C. Forniés, A. Calleja, and L. L. Aragonés, Bol. Soc. Esp. Ceram. Vidrio 43, 627 (2004)

17. D. Bueno-Baques, R. Grossinger, M. Schonhart, G. V. Doung, R. Sato,

V. Corral-Flores, and J. Matutes-Aquino, Journal of Applied Physics 99, 08D908–1 (2006).