Magnetoelectric Measurements by Two Different Methods of Cobalt Ferrite-Barium Titanate Composites

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Abstract

The magnetoelectric coefficient, α = dE/dH, of different compositions of $BaTiO_3$-$CoFe_2O_4$ composites was measured by using the dynamic method and also a new method developed in our laboratory which is based on pulsed magnetic fields. The values obtained by both methods are congruent, with the largest magnetoelectric coefficient obtained for the composite with 25% wt. Barium titanate. The magnetoelectric composites were synthesized by the ceramic method. The magnetoestrictive cobalt ferrite powders were synthesized by coprecipitation of cobalt and iron sulfates in acetone and a heat treatment at 1100°C. Commercial piezoelectric barium titanate powders were used of reactive quality (Aldrich, size < 2 μ m). The coupling via elastic deformations of these two phases inside the composite properly polarized, produced a magnetoelectric effect. The starting powders and the composites were characterized by thermal analysis, x-ray diffraction, scanning electron microscopy and particle size distribution using light scattering. Rietveld refinements were also made at the starting powders and composites.

Keywords: Magnetoelectric properties, magnetic pulsed fields, composites

Introduction

The magnetoelectric effect is defined as the electric polarization of a material upon application of a magnetic field, or conversely, as the magnetization of a material upon application of an electric field. Composite materials containing piezoelectric (ferroelectric) and magnetoestrictive (ferrite) phases exhibit magnetoelectric effect and this effect is due to the mechanical coupling between both phases [1, 2]. The possibility to polarize directionally an asymmetric molecular body under the influence of a magnetic field was predicted by Curie in 1894 [3]. Later Landau and Lifshitz showed, from symmetry considerations, that a linear magnetoelectric effect can occur in magnetically ordered crystals [4]. Subsequently Dzyaloshinskki predicted, on the basis of theoretical analysis, the existence of the magnetoelectric effect in antiferromagnetic $Cr2O3$ [5]. This was confirmed by Astrov [6] and later by Rado and Folen [7]. The ME effect in composite materials is realized by using the concept of product properties introduced by Van Suchetelene [1]. A suitable combination of two phases can yield the desirable property such as a combination of piezomagnetic and piezoelectric phases or a combination of magnetoestrictive and piezoelectric phases. The magnetoelectric effect in a given composite is usually characterized by measuring the magnetoelectric coefficient, $\alpha = dE/dH$ where E is electric field and H is the magnetic field.

In this paper we describe the preparation procedure and the structural characterization of the studied materials. We also compare the measurements of the magnetoelectric effect using the dynamic method and also a new method developed in our laboratory which is based on pulsed magnetic fields.

Experimental

Cobalt ferrite, prepared by chemical precipitation [9] and commercial barium titanate (Aldrich, size <2 µm) were used as raw materials to prepare the composites. The magnetoelectric composites were prepared by mixing cobalt ferrite and barium titanate powders with addition of polyvinyl alcohol, then were pressed into circular discs applying a pressure of 5 ton/cm2 during 30 seconds. Afterwards, the composites were heated at 2◦C/min up to 300◦C, then at 5◦C/min up to 1200◦C and sintered at 1200◦C during 12 hours. The composites were poled heating up to 150◦Cto overcome the Curie temperature, and cooling down to 100◦C and applying an electric field of 7 kV/cm during 30 minutes. Afterwards, the composites were cooled down to room temperature with the applied electric field. X-ray diffraction patterns identification confirmed the formation of the ferrite phase and the presence of both phases in the composites.

Results and Discussion

Figure 1 shows the x-ray diffraction patterns of the cubic cobalt ferrite (a = 8.370 ˚A), the tetragonal barium titanate (a = b = 3.996 ˚A and c = 4.027 ˚A) and the three different composite compositions. Not extra diffraction peaks associated with the formation of any other phase during the processing were observed. All diffraction pattern were refined by the Rietveld method using the Fullprof program [10].

For cobalt ferrite the average particle size determined by light scattering was about 3.8 µm, with 80% of the particle in the size range from 1.3 µmto7.8 µm. Barium titanate forms particles agglomerates with an average crystal size, determined by the diffraction peaks broadening, of about 0.033 µm and an average particle size of about 0.17 µm determined by light scattering. Fig. 2 shows a scanning electron micrograph corresponding to the composite with 50 wt. % of barium titanate where the smaller particles correspond to barium titanate and they form agglomerates which produced certain porosity during the sintering process.

The Fig. 3 shows the magnetoelectric measurements for the different composite com-positions obtained by the dynamic method. In this technique a small AC magnetic field with amplitude ho = 0.38 Oe was used in addition to the applied DC magnetic field. All samples showed hysteretic behavior and were measured increasing the applied DC magnetic field from zero up to 5300 Oe and then decreasing this field again to zero. The highest magnetoelectric coefficient, α = dE, of 1.97 mV/cm. Oe corresponds to the composite with 75 dH wt. % of cobalt ferrite followed by the composites with 50 and 25 wt.% of cobalt ferrites

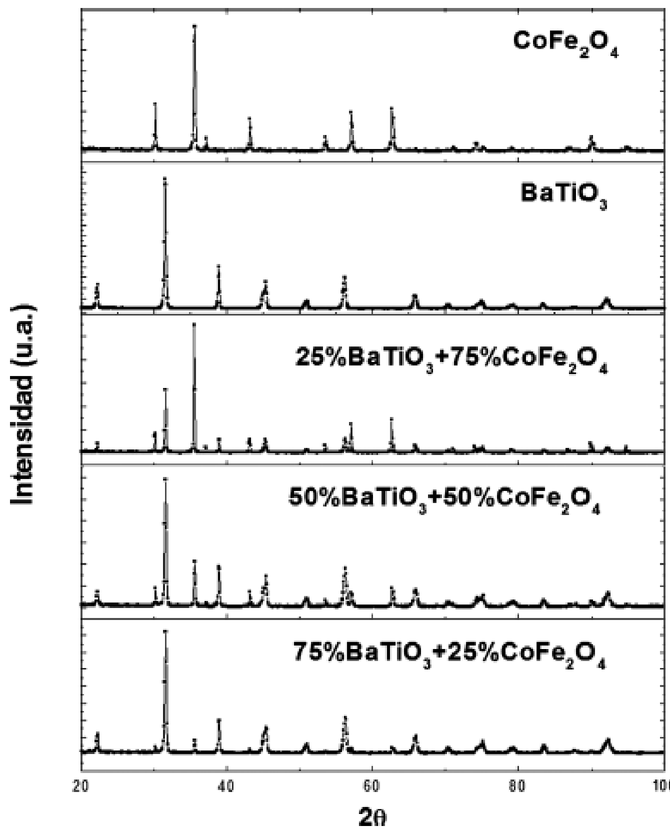

Figure 1. XRD patterns for $CoFe_2O_4$, $BaTiO_3$ and the three composites.

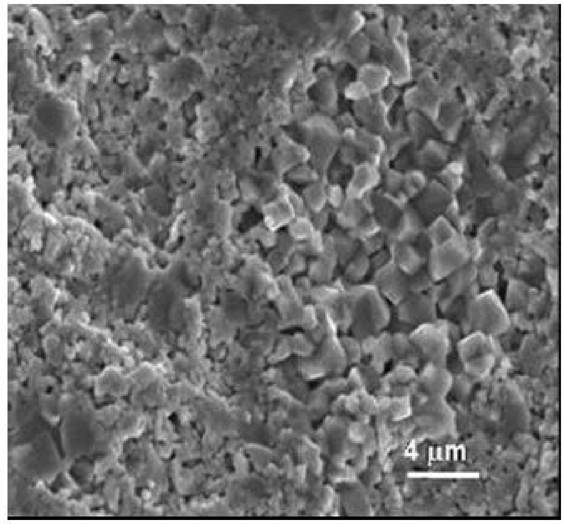

Figure 2. Scanning electron micrograph for the 50 wt.% barium titanate composite.

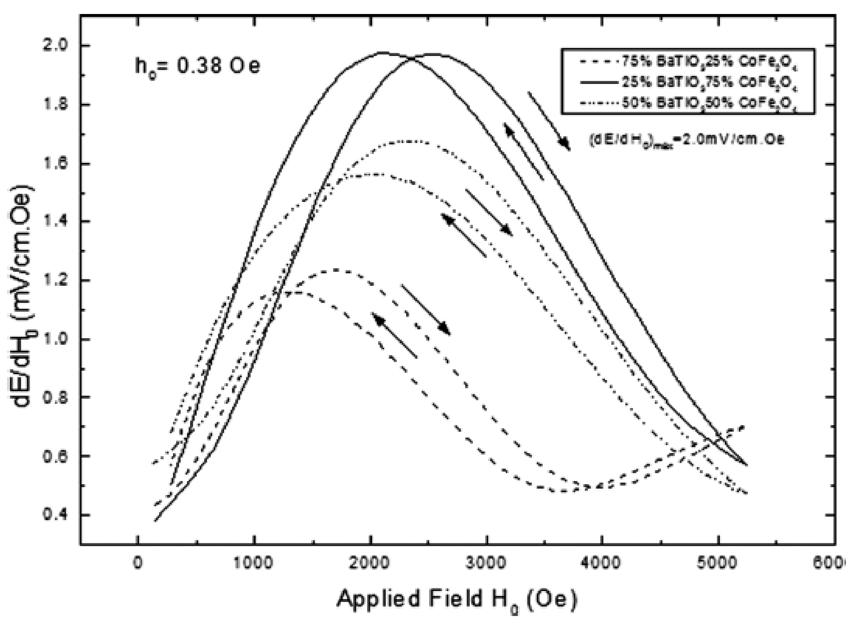

Figure 3. Magnetoelectric coefficient as function of the DC applied magnetic field by the dynamic method.

coefficient are related to the microstructure of the composites which present porosity and inhomogeneity producing lower values than those reported by others authors (1, 8).

The Magnetoelectric Measurement Using a New Pulsed Magnetic Field

Technique

Figure 4 shows the block diagram of the pulsed field magnetoelectric setup. The system for measuring magnetoelectric properties by the new pulsed magnetic field technique is built on top of a tailored pulsed field magnetometer with a pulse duration of 25 ms and a field coil with a 25 mm bore. The main part of the measurement system is a specially designed sample holder, which contains the fixed electric contacts for measuring the voltage across the sample, two special coils (compensation coils) to compensate the induced signal on the contacts wiring during the field pulse, and a pick up coil for sensing the field amplitude. Special care was taken in the design of contacts in order to warranty the reproducibility of the measurements and to avoid an excessive pressure, which could pre-stress the samples. The holder also contains a small furnace and a temperature sensing device for measuring the ME voltage coefficient as a function of the temperature.

The output voltage from the sample is amplified and filtered with a high impedance pre-amplifier, and measured with a DAQ Card (NI PCI-6110E). The measurement is triggered and controlled by the PC computer of the pulsed field magnetometer. To warranty the reproducibility of the measurements a zero signal is always taken and then subtracted to the signal from the sample. The measured voltage is proportional to the current in the circuit which is the first derivative of the charge (dQ/dt) generated by the induced polarization due to the deformation caused by the magnetic field pulse. Considering that the impedance of

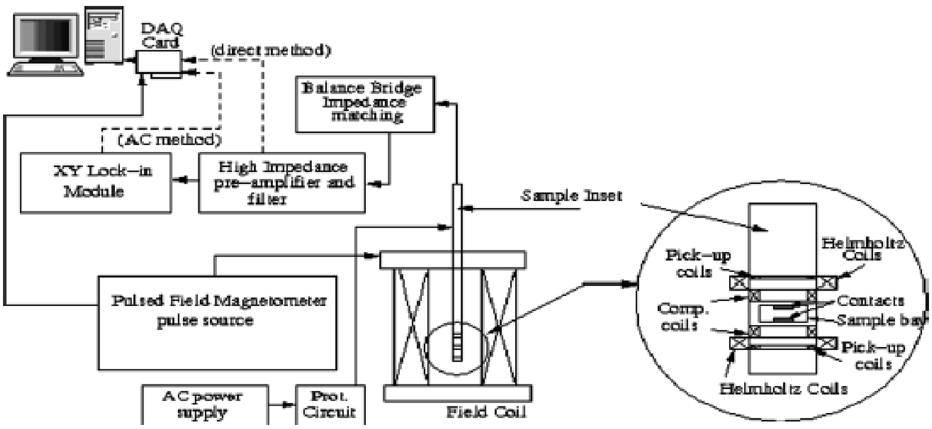

Figure 4. Block diagram of the pulsed field magnetoelectric setup.

the sample is much bigger than the impedance of the matching circuit, the charge can be obtained from eq. 1:

$$Q = \frac{1}{Z_{in}} \int V_{out} dt$$

Where Zin is the input impedance of the electronic circuitry, and Vout is the voltage measured on the sample. Considering the sample as a plane parallel capacitor with an Area A, the

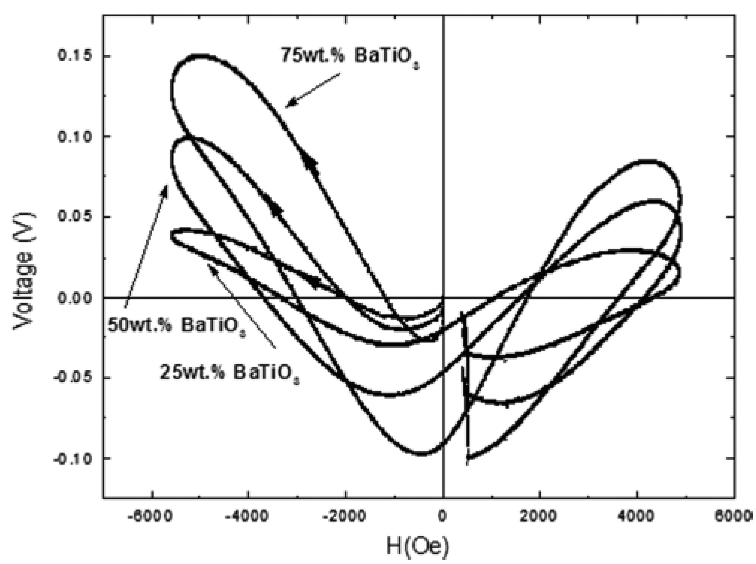

Figure 5. Magnetoelectric response voltage as function of the magnetic field by the pulsed magnetic field method.

Table 1
Magnetoelectric coefficient values

Composite composition	Dynamic method (mV/cm.Oe)	Pulsed magnetic field method (mV/cm.Oe)
25%$BaTiO_3$-75%$CoFe_2O_4$	1.97	1.67
50%$BaTiO_3$-50%$CoFe_2O_4$	1.67	1.45
75%$BaTiO_3$-25%$CoFe_2O_4$	1.23	1.20

Electric field will be:

$$E = \frac{1}{(Z_{in}\varepsilon_0\varepsilon_r A)} \int V_{out}\, dt$$

Where εr is the relative permittivity of the material, and A is the area of the plated surface of the sample. Then the magnetoelectric voltage coefficient can be obtained from eq. 2 and the magnetic field H(t), taking the time as a parameter, according to the relation:

$$\alpha_E = \frac{d}{dH}\left[\frac{1}{(Z_{in}\varepsilon_0\varepsilon_r A)} \int V_{out}\, dt\right]_t$$

The above derivative should be done numerically using the data obtained from the sample and from the field pick-up coils. Here a fast, highly accurate and sensitive electronics is desirable, in order to obtain a smooth experimental data to minimize the numerical noise generated in the mathematical procedure.

The magnetoelectric coefficients are determined by the pulsed field method without lock-in amplification. This method also allows measuring with higher dH/dt values, which is more adapted to the fast writing and reading rates in potential magnetoelectric recording applications.

Figure 5 shows the magnetoelectric response voltage as a function of the applied magnetic field for different composite compositions, obtained by the new pulsed magnetic field method. We can observe a hysteretic behavior in these curves. To make the calculation of the magnetoelectric coefficients we used only the first parts of these curves (from zero applied field up to the maximum value of the lobe in the second quadrant). In this way the calculated magnetoelectric coefficients are comparable with the values obtained by the dynamic method.

Table 1 shows the measured magnetoelectric coefficient values for the dynamic and the pulsed magnetic field methods for the three different composites.

Conclusions

Magnetoelectric composites were prepared by mixing, pressing and sintering different pro-portions of barium titanate and cobalt ferrite powders. The magnetoelectric coefficient α was measured by a new technique based on pulsed magnetic fields and the values are congruent with those measured by the dynamic method. The largest magnetoelectric coefficient was obtained for the composite with 25% wt. Barium titanate.

Acknowledgments

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