Synthesis and magnetoelectric characterization of cobalt ferrite—barium titanate composites using a new pulsed magnetic field method

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Abstract

$BaTiO_3$-$CoFe_2O_4$ composites synthesized by the ceramic method showed a magnetoelectric effect. The $CoFe_2O_4$ powders were synthesized by coprecipitation and mixed with Aldrich reactive quality $BaTiO_3$ powders with particle size <2 μm. The coupling of the magnetostrictive and the piezoelectric phases via elastic deformations of the properly polarized composites produced a magnetoelectric effect. The starting powders and the composites were characterized by thermal analysis, x-ray diffraction with Reitveld refinements, scanning electron microscopy and particle size distribution using light scattering. The magnetoelectric coefficient, α = dE/dH, was measured using the dynamic method, and a new pulsed magnetic field method developed in our laboratory.

Keywords: Cobalt Derrite, barium titanate, magnetoelectric, magnetostrictive, composite, magnetoelectric properties, magnetic pulsed fields.

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 a piezoelectric phase and a magnetoestrictive phase exhibit magnetoelectric effect due to the mechanical coupling between both phases [1, 2]. Curie in 1894 predicted the possibility

to polarize directionally an asymmetric molecular body under the influence of a magnetic field. 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 Cr_2O_3 [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 [8]. A combination of a piezomagnetic phase and a piezoelectric phase, or a combination of a magnetostrictive phase and a piezoelectric phase can yield the desirable property. 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 characterization of magnetoelectric composites. Also a comparison of the magnetoelectric coefficients measured using the dynamic method and also a new pulsed magnetic field method developed in our laboratory is presented.

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 polyvinylic alcohol, then were pressed into circular discs applying a pressure of 5 ton/cm^2 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 for 12 hours. The composites were poled while heating, up to 150◦C to overcome the Curie temperature, and cooling down to 100◦C and applying an electric field of 7 kV/cm for 30 minutes. Afterwards, the composites were cooled down to room temperature under an 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 cobalt ferrite, barium titanate and the three different composite compositions. The intensities and positions of the diffraction peaks in each phase correspond to the $BaTiO_3$ and $CoFe_2O_4$ pure compounds and there are not extra diffraction peaks associated with the formation of any other phase during the processing.

The Rietveld refinement of the diffraction patterns using the Fullprof program [10] allowed the determination of the phase composition as showed in Fig. 2 for the composite with nominal composition of 75 wt.% of barium titanate. In this case the Rietveld refinement reports an actual composition of 75.7±0.5 wt.% of barium titanate.

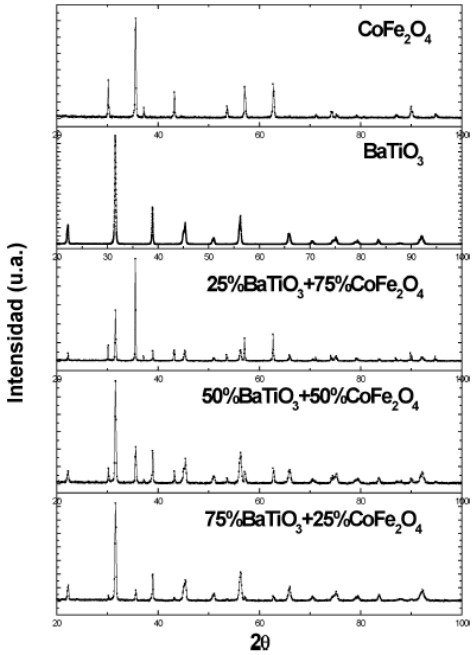

Figure 1. XRD patterns for $CoFe_2O_4$, $BaTiO_3$ and the three composites.

Using X-ray diffraction for cubic spinel cobalt ferrite we obtained a lattice parameter of 8.370 °A and no crystal size broadening of the peaks was observed. The average particle size of cobalt ferrite determined by light scattering was about 3.8 μm, with 80% of the particle in the size range from 1.3 μm to 7.8 μm. For the pure tetragonal barium titanate, we obtained lattice parameters a=b=3.996 Å and c= 4.027 Å. Bariumtitanate 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.

Figure 3 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 a certain amount of porosity during the sintering process.

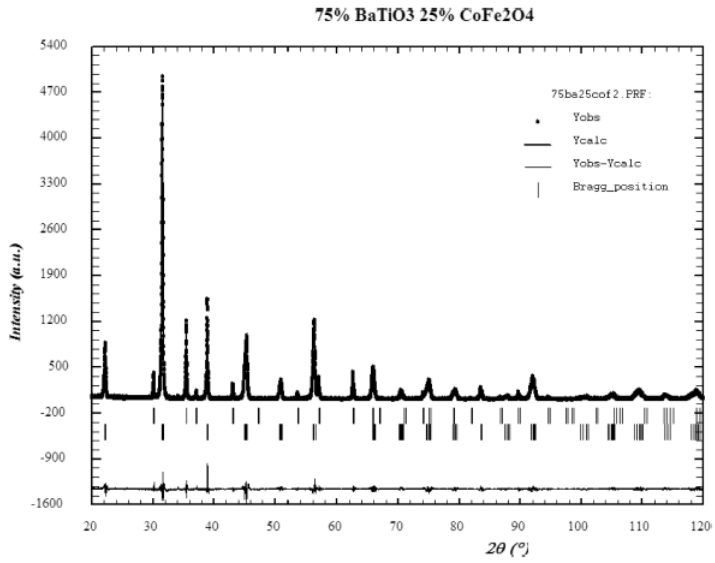

Figure 2. Rietveld refinement of the x-ray diffraction patterns for the 75 wt.% barium titanate composite.

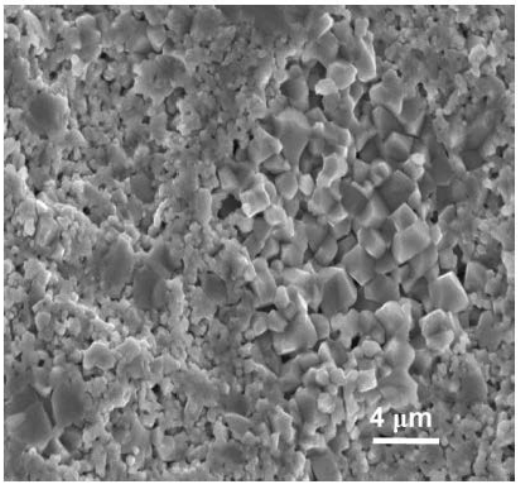

Figure 3. Scanning electron micrograph for the 50 wt.% barium titanate composite.

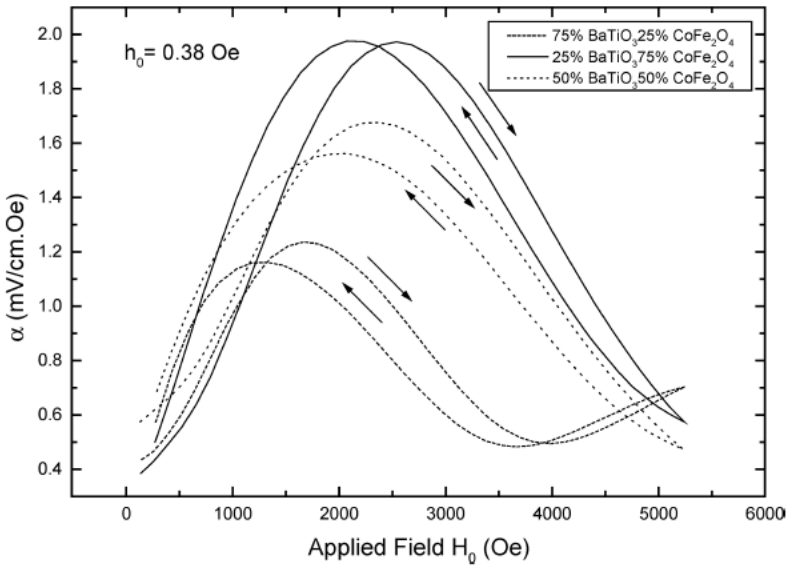

Figure 4. Magnetoelectric coefficient as function of the DC applied magnetic field by the dynamic method.

Figure 4 shows the magnetoelectric measurements for the different composite compositions obtained by the dynamic method. In this technique a small AC magnetic field with amplitude h_o = 0.38 Oe was used in addition to the applied DC magnetic field. All samples show hysteresis and were measured while increasing the applied DC magnetic field from zero up to 5300 Oe and then decreasing the field back to zero. The highest magnetoelectric coefficient, $\alpha = \frac{dE}{dH}$, 1.97 mV/cm · Oe corresponds to the composite with 75 wt. % of cobalt ferrite, the composites with 50 and 25 wt.%of cobalt ferrites have values of 1.67 and 1.23 mV/cm · Oe respectively.

Figure 5 shows the block diagram of the new pulsed magnetic field system for magnetoelectric measurements developed in our laboratory. This system is built on top of a 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.

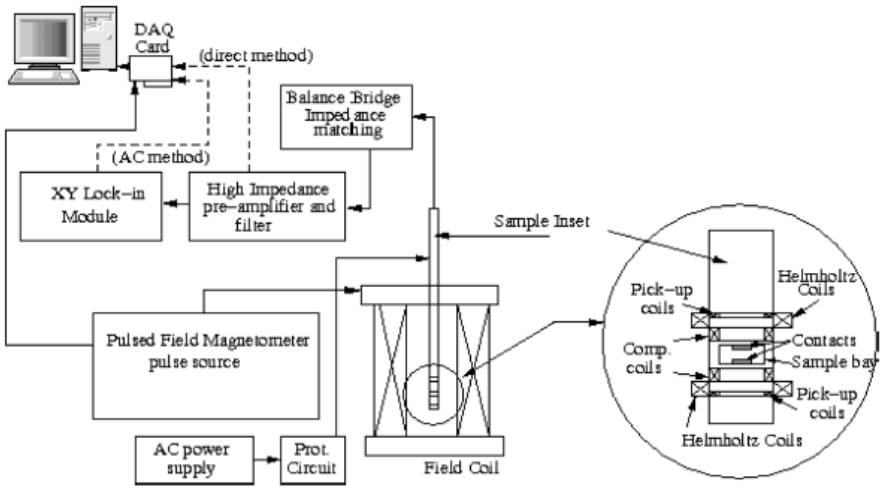

Figure 5. Block diagram of the pulsed field magnetoelectric setup.

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 guarantee the reproducibility of the measurements a zero signal is always taken and then subtracted from 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 the sample is much bigger than the impedance of the matching circuit, the charge can be obtained from Equation (1):

$$Q = \frac{1}{Z_{in}} \int V_{out} dt, \qquad (1)$$

where Z_{in} is the input impedance of the electronic circuitry, and Vout is the voltage measured on the sample. Considering the sample as a parallel plate capacitor with an Area, A, the electric field will be:

$$E = \frac{1}{(Z_{in}\varepsilon_0\varepsilon_r A)} \int V_{out} dt, \qquad (2)$$

where ε_r 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 Equation (2) and the magnetic field H(t), taking the time as a parameter, according to the relation:

$$\alpha_E = \frac{d}{dH}\left[\frac{1}{(Z_{in}\varepsilon_0\varepsilon_r A)} \int V_{out} dt\right]_t, \qquad (3)$$

The above derivative should be done numerically using the data obtained from the sample and from the field pick-up coils. Fast, highly accurate, and sensitive electronics are used in order to obtain smooth experimental data to minimize the numerical noise generated in the mathematical procedure. The magnetoelectric coefficients are determined by the pulsed field method without the help of lock-in amplification.

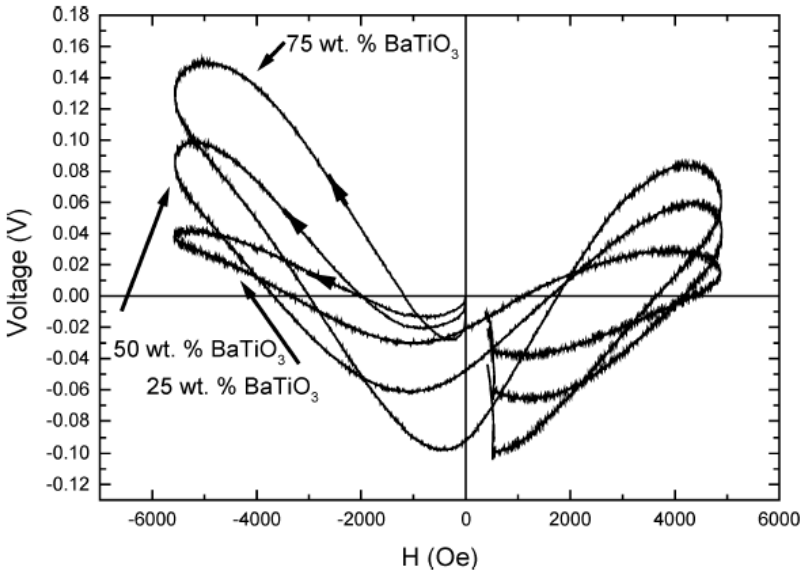

Figure 6. Magnetoelectric response voltage as function of the magnetic field by the pulsed magnetic field method.

Figure 6 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 portions 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
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

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 proportions of barium titanate and cobalt ferrite powders. The magnetoelectric coefficient α measured by a new technique based on pulsed magnetic fields is congruent with that measured by the dynamic method. The largest magnetoelectric coefficient was obtained for the composite with 25% wt. Barium titanate.

Acknowledgments

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