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Effects of the chemical composition of the magnetostrictive phase on the dielectric and magnetoelectric properties of cobalt ferrite–barium titanate composites

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ABSTRACT

Magnetostrictive–piezoelectric composites of $CoFe_2O_4$–$BaTiO_3$ and $CoMn_{0.2}Fe_{1.8}O_4$–$BaTiO_3$ were obtained with standard solid-state ceramic processing. X-ray diffraction (XRD) analysis revealed the presence of the spinel and perovskite phase without the appearance of the residual phase. The influence of the phase content on the dielectric constant, loss tangent, magnetization, magnetostriction and magnetoelectric signal was studied, and the results were correlated with the microstructure and the amount of ferrite. The magnetoelectric response of the composite indicated that the substitution of iron ions for manganese ions decreased the dielectric loss and improved the magnetoelectric signal of the composite samples.

1. Introduction

The development of magnetoelectric materials with high magnetostriction and piezoelectric coefficients has received much attention in recent years due to their possible application as sensors, memories, transducers and actuators [1]. In magnetoelectric materials, an electric polarization (or a magnetization) is induced when a magnetic (or an electric) field is applied. One of the important classes of magnetoelectric materials includes ferrite-piezoelectric composites. In these systems, the magnetoelectric effect is a product property that depends on the piezoelectric and piezomagnetic coefficients, volume fraction of composite components, elastic properties, magnetic and dielectric properties of composite components. Studies performed on these systems have revealed that the increase of ferrite content decreases the magnetoelectric signal due to the leakage currents that appear because of the low resistivity of the ferrite phase [2,3]. Although the ferrite lowers the magnetoelectric signal, it is still added in appreciable amounts because earlier studies have shown that the increase of the ferrite content improves the elastic interactions [4].

Among ferrites, cobalt ferrite has the highest magnetostriction coefficient, which is essential for magnetoelectric composites. The magnetic, electric, and mechanical properties can be varied by modifying the stoichiometry and fabrication parameters [5,6]. Studies performed on the influence of sintering conditions on the microstructure and magnetostriction of cobalt ferrites have shown that the presence of small and uniform grains with a less porous structure in the sintered material leads to an increase of the magnetostrictive coefficient [7]. A good mechanical coupling between the ferrite and ferroelectric grains in the composites is required to achieve a high magnetoelectric signal. The mechanical coupling between grains in magnetoelectric composites could be increased by increasing the sintering temperature [8], but the high sintering temperature would lead to another problem. It is well known that at high temperatures Fe^{2+} ions form in ferrite ceramics and chemical reactions take place between grains [9,10]. The presence of Fe^{2+} ions in ferrites decreases their electric resistivity. In magnetoelectric composites, high resistivity is important for achieving a high magnetoelectric signal [11]. The substitution of one of the metallic ions with another or with a combination that ensures electrical neutrality drastically influences the electric, magnetic and magnetostrictive properties of cobalt ferrites [12,13]. The substitution of Fe with Mn or Cr, increases the stress sensitivity and decreases the saturation magnetostriction constant relative to stoichiometric cobalt ferrite [14]. Recently published papers on magnetoelectric composites that contain substituted cobalt ferrites as the magnetostrictive phase show that they possess a useful magnitude of the dynamic magnetoelectric coefficient [15–18]. To the best of our knowledge, relatively few reports discuss the magnetostrictive properties of magnetoelectric composites [17].

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Table 1
Sample details, densities ρ and contractions C of the disks after sintering.

Sample	ρ [g/cm^3]	C [%]
CT1 20%$CoFe_2O_4$ 80% $BaTiO_3$	3.94	2.56
CT2 40%$CoFe_2O_4$ 60% $BaTiO_3$	3.85	3.22
CMT1 20%$CoMn_{0.2}Fe_{1.8}O_4$ 80% $BaTiO_3$	3.72	2.56
CMT2 40%$CoMn_{0.2}Fe_{1.8}O_4$ 60% $BaTiO_3$	3.61	2.56

In this paper, the magnetic, magnetostrictive, dielectric and magnetoelectric properties of magnetostrictive–piezoelectric composites that contain manganese-substituted cobalt ferrite ($CoMn_{0.2}Fe_{1.8}O_4$) as the magnetostrictive phase and $BaTiO_3$ as the piezoelectric phase are investigated. The results are compared with those obtained for composites that contain stoichiometric cobalt ferrite ($CoFe_2O_4$). The sintering temperature was chosen to be below 1200 °C to avoid the formation of a large amount of Fe^{2+} ions.

2. Experimental details

The standard ceramic method was used to prepare $CoFe_2O_4$–$BaTiO_3$ and $CoMn_{0.2}Fe_{1.8}O_4$–$BaTiO_3$ composites in which the ferrite content varies as 20% and 40%. The individual ferrites $CoFe_2O_4$ and $CoMn_{0.2}Fe_{1.8}O_4$ were prepared separately by the standard ceramic method and mixed with commercial $BaTiO_3$. The $CoFe_2O_4$ and the $CoMn_{0.2}Fe_{1.8}O_4$ ferrite powders were calcined for 5 h in air at 900 °C and 950 °C, respectively. The powders were mixed in suitable proportions in a ball mill for 8 h. The powders were pressed into disk shapes and sintered in air for 1 h at 1150 °C. Table 1 shows the values of the densities and contractions of the composite samples after the sintering process.

The contraction C of the samples was calculated with the following formula:

$$C = \left(1 - \frac{D_T}{D_o}\right) 100\%$$

where D_o and D_T are the diameter of the disk before and after sintering process, respectively. These data were compared with those obtained for $CoFe_2O_4$ (CFO) and $CoMn_{0.2}Fe_{1.8}O_4$ (CFMO) prepared in the same conditions as composite samples. The density measured for CFO is 3.6 g/cm^3 and that for CFMO is 4.07 g/cm^3. After sintering at 1150 °C, the disks were 5 mm high and 15 mm diameter.

The structural analysis of the samples was performed with a Bruker D8 X-ray diffractometer (Cu Kα radiation). The magnetic properties were measured with an AGM/VSM 2009 Princeton Magnetometer. The dielectric properties of the samples were investigated by applying a small ac voltage with a variable frequency up to 2 MHz superimposed on a dc voltage of 1 V with a E4980A Precision LCR Meter. The magnetostriction coefficients were measured with the strain gauge technique by means of a P3 Strain Indicator and Recorder. The magnetoelectric coefficient was determined by the induced electric field E at a small ac magnetic field. Before measurement, the samples were heated to 140 °C and cooled in the presence of an electric field of about 2500 V/cm. The ac magnetic field was superimposed onto a dc magnetic bias H_{dc}, both of which were parallel to the thickness direction of the pellets. The amplitude of the ac magnetic field was 10 Oe and the frequency was 10 kHz. The induced electric field E was measured with a lock-in amplifier (Model SR830 DSP Lock-In Amplifier). All measurements were performed at room temperature.

3. Results and discussion

3.1. XRD results

For all samples, the analysis of the XRD patterns shows the existence only of the ferrite and ferroelectric phase without phase percolation. For all samples, the increase of the sintering temperature leads to the increase of the average crystallite size of the ferrite phase, while the average crystallite size for ferroelectric phase decreases. The XRD patterns for samples sintered at 1150 °C are shown in Fig. 1. In Table 2, the results of the XRD analysis for the composite samples before and after sintering at 1150 °C are summarized.

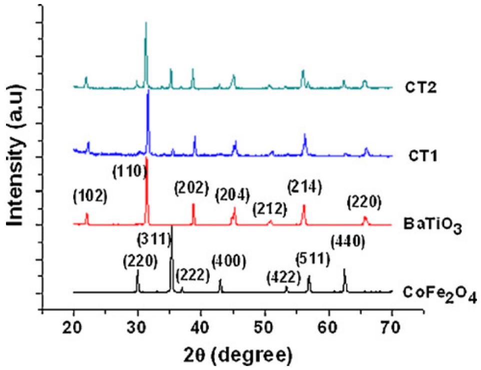

Fig. 1. XRD patterns for composite samples and for the starting materials.

The lattice parameter a_o of the ferrite phase increases when a small amount of the iron ions are replaced by manganese. This distortion of the lattice is due to the manganese ion, which is a Jahn–Teller ion. For composites that contain stoichiometric cobalt ferrite, a small decrease of a_o is observed. In the form of the mechanical mixture, the values of the average crystallite sizes for the CMT samples are lower than those obtained for CT series. During sintering the average crystallite size of the ferrite phase increases, while that for the ferroelectric phase decreases. The average crystallite of the $BaTiO_3$ commercial powder is 76 nm.

3.2. Magnetic measurements

The results of the magnetic measurements for the samples sintered at 1150 °C are summarized in Table 3, where H_C is the coercive field and M_{max} and M_R are the maximum and remanent magnetization, respectively. When the iron ions are substituted with manganese ions, the coercive field decreases and maximum magnetization show a small increase from 78 emu/g for CFO to 81 emu/g for CFMO. The results are similar to those obtained by other authors [19,20]. The small increase of the maximum magnetization can be explained taking into consideration the oxidation state of the manganese ions. From spectroscopic measurements, it was determined that Mn^{3+} ions have strong site preference for octahedral sites, while Mn^{2+} have no particular preference for either coordination. If the amount of Mn^{2+} ions from octahedral sites exceeds that of Mn^{3+}, a large increase in the magnetization is expected, whereas if the amount of Mn^{3+} ions is larger, the increase in the magnetic moment will be smaller.

The manganese substitution for iron ions decreases the coercive field. This decrease of H_C has been observed by other authors who have studied $CoMn_xFe_{2-x}O_4$ systems. Mossbauer studies performed on these systems [21] have shown that the substitution of iron with manganese ions causes the displacement of cobalt ions from octahedral sites. Because the large anisotropy in cobalt ferrite is due to the presence of cobalt ions in the octahedral sites, their displacement decreases the anisotropy and, consequently, the value of H_C.

For all composite samples, the value of the coercive field decreases, especially for those that contain manganese-substituted ferrite, with the CMT1 sample having the lowest coercive field. The lowest values of the coercive field for the CMT series could be due to their larger average crystallite size relative to that of the samples that contain stoichiometric cobalt ferrite. For the same sintering temperature, the H_C values do not vary significantly when the amount of ferrite increases, which suggests the presence of ferrite particle agglomeration in the composites. For a constant amount of

Table 2
Analysis of the XRD results.

Composite	Magnetostrictive Phase		Piezoelectric Phase	
	Phases/latice parameters (Å)	Crystallite size (nm)	Phases/latice parameters (Å)	Crystallite size (nm)
CT1	Spinel/ $a_o = 8.3812$	∼82	Tetragonal/ $a = 3.99$ $c = 4.02$	∼71
CT1 (mechanical mixture)	Spinel/ $a_o = 8.3751$	∼41	Tetragonal/ $a = 3.9910$ $c = 4.0225$	∼98
CT2	Spinel/ $a_o = 8.3742$	∼83	Tetragonal/ $a = 3.9919$ $c = 4.0184$	∼88
CT2 (mechanical mixture)	Spinel/ $a_o = 8.3779$	∼85	Tetragonal/ $a = 3.9933$ $c = 4.0249$	∼90
CMT1	Spinel/ $a_o = 8.3867$	∼108	Tetragonal/ $a = 3.9935$ $c = 4.0212$	∼77
CMT1 (mechanical mixture)	Spinel/ $a_o = 8.3818$	∼64	Tetragonal/ $a = 3.9912$ $c = 4.0223$	∼98
CMT2	Spinel/ $a_o = 8.3840$	∼86	Tetragonal/ $a = 3.9918$ $c = 4.0193$	∼82
CMT2 (mechanical mixture)	Spinel/ $a_o = 8.3886$	∼63	Tetragonal/ $a = 3.9940$ $c = 4.0253$	∼89

magnetic material, small decreases of the maximum magnetization are observed when the composites contain substituted cobalt ferrite. The M_{max} values for the composites increase when the amounts of ferrite increases and are lower than those of the ferrites. The net magnetization of the composite is the vector sum of the individual contributions from the ferrite grains, which act as centers of magnetization. When the amount of ferrite increases, the magnetic contacts between the grains also increases, which leads to a higher value of composite magnetization.

3.3. Electrical properties

In Figs. 2(a) and (b) and 3 the variation of the real part of the permittivity ε' and loss tangent $tg\delta$ versus frequency are presented. For all samples, ε' decreases in the low frequency range, and it attains a constant value independent of the frequency thereafter, which is characteristic of a Maxwell–Wagner type of interfacial polarization.

The high values of ε' observed at low frequencies can be attributed to the dipoles that result from changes in the valence states of the cations and the space charge polarization due to the inhomogeneous microstructure. In polycrystalline samples, the inhomogenities are impurities, pores, grains and grain boundaries. When the frequency increases, only the electronic polarization contributes to the total polarization due to the fact that the electric dipoles that appeared due to the inhomogeneous microstructure have low mobility and cannot follow the fast variation of the electric field. Although the $BaTiO_3$ is a good dielectric material and its dielectric permittivity is larger than that of cobalt ferrite, composites that contain cobalt ferrites have lower ε' values than $BaTiO_3$. This could be due to the lower electrical resistivity of the ferrite phase relative to that of the ferroelectric phase. The dielectric behavior of the ferrite-ferroelectric composites could be also explained by taking the results obtained in Ref. [22] into consideration, which showed that beyond the phase percolation limit, the dielectric properties could also be explained on the basis of

Table 3
Magnetic properties of the composite and ferrite samples.

Sample	$M_{\max}$ (emu/g)	M_R (emu/g)	H_C (Oe)
CFO	78	100	987
CT1	16	21	590
CT2	30	43	619
CFMO	81	98	514
CMT1	15	18	453
CMT2	31	40	498

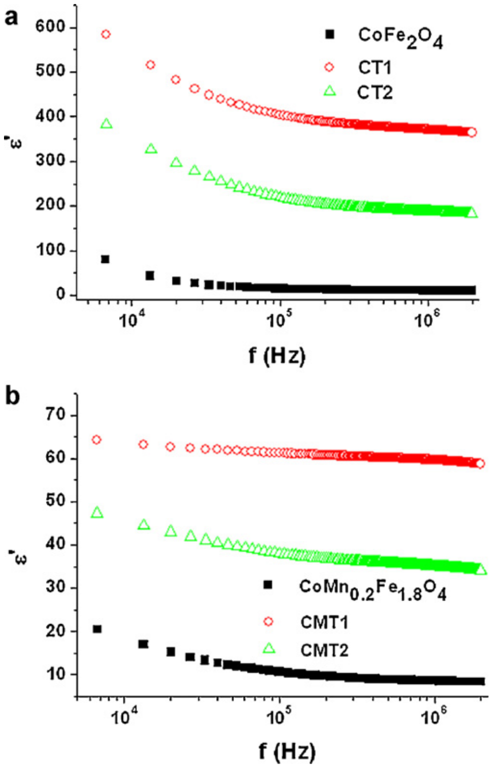

Fig. 2. (a) Variation of the real part of the dielectric permittivity versus the frequency f of the applied electric field for $CoFe_2O_4$, CT1 and CT2. (b) Variation of the real part of the dielectric permittivity versus the frequency f of the applied electric field for $CoMn_{0.2}Fe_{1.8}O_4$, CT1 and CT2.

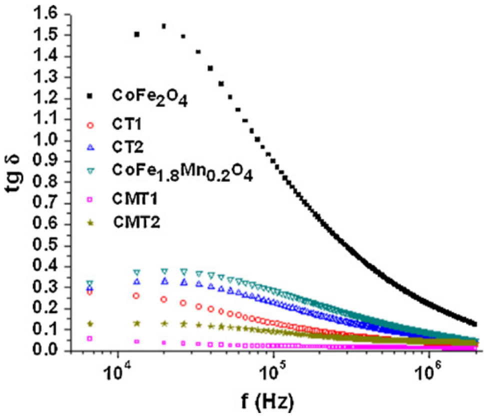

Fig. 3. Variation of the dielectric loss tangent with the frequency of the applied electric field.

a polarization mechanism in the ferrite, which is similar to the conduction process. In the ferrites studied in this paper, the presence of Co^{2+}/Co^{3+} and Mn^{2+}/Mn^{3+} ions gives rise to p-type carriers, while the presence of Fe^{2+} and Fe^{3+} ions from octahedral sites gives rise to n-type carriers. Due to the low mobility of the p-type carriers, their contribution to the polarization decreases rapidly when the frequency increases [18].

Composites that contain stoichiometric ferrite show the highest values of ε'. The substitution of iron by manganese ions decreases the maximum value of ε' in the low frequency range. The lower values of ε' for the CMT series could be attributed to a smaller number of Fe^{2+} ions and to lower density values. The substitution of iron ions with manganese reduces the number of Fe^{2+} ions, and close pores will reduce ε' because of the dielectric constant of the air filling the pores.

For composites, ε' increases with the amount of $BaTiO_3$. The value of ε' is higher for stoichiometric cobalt ferrite than for CFMO. This could be attributed to the presence of a higher number of Fe^{2+} ions in the CFO sample.

In the low frequency range (up to 1 kHz), the $tg\delta$ values obtained for composites that contain manganese-substituted cobalt ferrite are lower than those obtained for samples that contain stoichiometric cobalt ferrite. This could be due to the low values of density and contraction, which indicate micro-structural defects, such as pores.

For the low frequency range, the CFO sample has the highest value of the loss tangent. The substitution of iron ions for manganese decreases the loss tangent. The composites that contain manganese-substituted cobalt ferrites have lower values of $tg\delta$ than the composites that contain stoichiometric cobalt ferrite. When the frequency increases above 10 kHz, the values of $tg\delta$ for the CMT series decrease to almost 50% of their initial value, whereas $tg\delta$ does not vary too much for the CT series. The substitution of iron ions by manganese ions decreases the number of Fe^{2+}–Fe^{3+} pairs and, consequently, the conductivity. The dielectric losses increase with the increase of ferrite material for all composites. At higher frequencies, the species that contribute to electrical polarization cannot follow the alternating electric field, so the values of $tg\delta$ are smaller than those obtained at lower frequencies.

3.4. Magnetostriction measurements

Fig. 4(a) and (b) shows the magnetostriction curves for composites sintered at 1150 °C and for the CFO and CFMO. Although the substituted ferrites in magnetoelectric composites increase the electrical resistivity, the magnetoelectric signal decreases because the magnetostrictive properties of the ferrite phase are altered [23]. A high magnetostriction coefficient is desirable to achieve a high magnetoelectric signal. From the data shown in Fig. 4(a), it is observed that the substitution of a small amount of iron with manganese ions does not significantly alter the magnetostrictive properties of the composites.

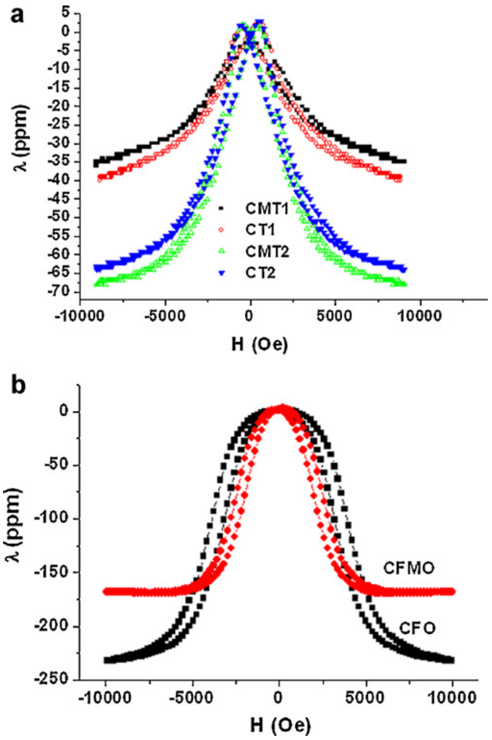

Fig. 4. (a) Magnetostriction curves for composite samples. (b) Magnetostriction curves for CFO and CFMO.

The relative deformation was measured in a direction that is parallel to the direction in which the magnetic field of intensity H is applied. The shape of the magnetostriction curves for the CFO and CFMO samples are similar to those obtained by other authors [19,20]. For composite materials, the magnetostriction coefficient λ decreases considerably. For the 20% ferrite concentration, the maximum magnetostriction coefficient λ_{max} for the CT1 sample is −40 ppm, while for the CMT1, the value is −35 ppm. When the amount of ferrite increases, λ_{max} increases from −63 ppm for CT2 to −68 ppm for CMT2. To explain the influence of ferroelectric phase on the magnetostriction of composites, it must be taken into consideration the fact that in a magnetic body consisting of many magnetostrictively distorted domains, the overall dimensions change when the magnetization within a domain rotates by an external field and when the domains that have the magnetization close to magnetic field direction grow at the expense of those with magnetization further away from the magnetic field [24]. The presence of the ferroelectric grains hampers the movement of the domains, and consequently, the overall dimensions of the composite will change less when the amount of $BaTiO_3$ is high. The values of the maximum magnetostriction coefficient obtained for the CT samples are smaller than those expected for the 20% and 40% CFO samples, which could be a hint that the strain produced by the ferrite phase may be partly absorbed by the ferroelectric phase. For CMT samples, the λ_{max} values are in good agreement with those expected for the 20% and 40% CFMO samples. This could be explained taking into consideration the fact the density values for the CMT series are lower than those of the CT series, so the mechanical coupling with ferroelectric phase is weaker, and the strain produced is less absorbed.

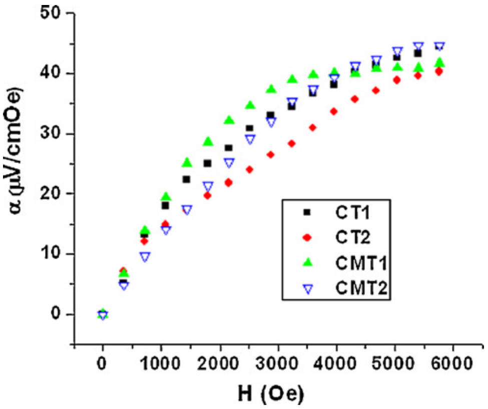

Fig. 5. The magnetoelectric coefficient versus dc magnetic field.

3.5. Magnetoelectric effect

The values of the magnetoelectric coefficient α_E versus the applied magnetic field H_{dc} are presented in Fig. 5. The α_E values shown in Fig. 5 are obtained after subtraction of the α_E value at $H = 0$. The magnetoelectric coefficient is calculated with the following formula [25]:

$$a_E = \frac{V}{H_{ac} \cdot d}$$

where V is the voltage generated due to the magnetoelectric effect, H_{ac} is the amplitude of the sinusoidal magnetic field and d is the thickness of the sample. The increase of the amount of ferrite increases the values of magnetoelectric coefficient.

The increase of the magnetoelectric signal with magnetic field could be attributed to the increase of the mechanical deformation in the magnetoestrictive phase. The shapes of the curves represented in Fig. 5 are similar to those shown in Fig. 4 for magnetostriction, which indicates a strong dependence on the piezomagnetic coupling strength, as reported in [26]. Although the values of the magnetostriction coefficients depend strongly on the amount of ferrite, there are small decreases of the magnetoelectric signal when the ferrite amount increases. This could be attributed to the higher values of the dielectric loss of the composites that contain 40% ferrite. Comparing the CT2 and CMT2 samples, a small increase of the magnetoelectric signal is observed for dc field values higher than 2000 Oe. This could be due to the lower dielectric loss of the composite that contains 40% manganese-substituted cobalt ferrite.

4. Conclusions

In this study, the influence of a low level of manganese substitution in cobalt ferrite-based magnetoelectric composites on the dielectric, magnetic, magnetostrictive and magnetoelectric properties was analyzed. Two series of composites of $CoFe_2O_4$–$BaTiO_3$ and $CoMn_{0.2}Fe_{1.8}O_4$–$BaTiO_3$, in which the amount of ferrite was 20% and 40%, were characterized. The results obtained for $tg\delta$ beyond 10 kHz show that the low level of substitution of iron ions with manganese ions could present another method of decreasing the dielectric loss in cobalt ferrite–barium titanate composites. Although the low level of substitution significantly decreased the magnetostriction coefficients of the raw ferrites, the magnetostrictive properties of the ferrite-based composite were less influenced by the chemical composition of magnetostrictive phase. The magnetoelectric measurements indicate that using manganese-substituted cobalt ferrite as a magnetostrictive phase could lead to a small increase of the magnetoelectric signal.

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