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ABSTRACT

It is well known that the performance of magnetoelectric properties in multiferroic materials is dependent on the electric poling conditions. Few reports, however, have investigated electric poled state effects on their magnetic properties. In this paper, M-H hysteresis loops were monitored from 5 K up to room temperature, for both unpoled and poled 0.80{0.675[Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.325PbTiO$_3$]}-0.20[CoFe$_2$O$_4$] particulate composites. The study was performed for samples with average grain size of 0.8 μm and 4.4 μm. Magnetoelectric voltage response was also evaluated for samples poled under 20kV/cm, 30 min., at different temperatures. The results show that the magnetic anisotropy is strengthened by remanent electric polarization, probably due to an enhancement of the strain anisotropy at the biphasic grain boundaries, which depends upon the grain size distribution.

1. Introduction

The magnetoelectric effect is characterized by coupling between electric and magnetic order parameters resulting in the possible control of electric polarization (magnetization) by magnetic field (electric field). The magnetoelectric coupling occurs in a single phase as well as in composite multiferroic materials [1, 2]. In composites, the coupling is mediated by the mechanical strain between a ferroelectric and a magnetostrictive phase. When a magnetoelectric composite is under an external DC and AC magnetic fields, the magnetostrictive effect produces stress on the ferroelectric phase, which induces an AC voltage due to the piezoelectric effect [3–5]. Their high magnetoelectric coupling coefficients at room temperature make such composites potentially fit for applications in several novel multifunctional devices as sensors [6], inductors [7], miniature solid-state power transformers [9], and specially in spintronics [8].

Many reports have shown the possibilities of controlling and switching magnetic properties of magnetoelectric composites with the application of an external electric field. For instance, for multilayer heterostructures Co$_{0.9}$Fe$_{0.1}$/BiFeO$_3$/SrRuO$_3$/SrTiO$_3$, in which a multiferroic exchange coupling between ferromagnetic, ferroelectricity and antiferromagnetic orders has been created, a significant enhancement of the magnetic

coercive field was achieved by applying an electric field, in comparison to that observed for the alloy Co0.9Fe0.1 only [10].

There are many mechanisms that could be used for explaining the effects of the electric field on magnetic properties such as magnetic-anisotropy, magnetic order and magnetic domain wall motion in biphasic composites [11]. Possible control mechanisms of the electric field upon magnetic properties are the magneto-elastic effect, charge modulation effect, and bonding and ionic modulation that depends on the type of composition and material structure. The manipulation of this property is of great interest. For example, magnetization measurements performed in thin films of $SrRuO_3/Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ as a function of applied magnetic field (M-H) under zero and 12 kV/cm revealed differences in saturation magnetization [12]. In magnetization versus electric field (M-E) measurements, when an electric field is applied on PMN-PT, a contraction appears along the in-plane direction which causes a 9.2% magnetization reduction in the upper SRO layer at 20 kV/cm. On the other hand, when the direction of the electric field is reversed, a tensile strain is produced and the magnetization values reach about 6.7% at the coercivity field of 10.8 kV/cm. The manipulation of these properties is associated to the rotation of the RuO_3 oxygen octahedral caused by the electric field-induced strain. Similarly, as reported by Zhou *et al.* [13], the creation of a channel of control exchange bias for $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ through the modulation interfacial exchange interactions due to ionic displacement of Fe^{3+} in $BiFeO_3$ relative to $Mn^{3+/4+}$ in $La_{0.7}Sr_{0.3}MnO_3$ produce bipolar modulation. Many authors refer to this type of effect as quasi-intrinsic magnetoelectric coupling [14], where the magnetoelectric response is originated from interfacial strain-mediated coupling of piezoelectricity and magnetostriction.

This work presents a systematic investigation of the influence of an applied electric field upon magnetic properties in particulate composites of PMN-PT/CFO 80/20 with 0–3 connectivity particulates, where the magnetic behavior by piezomagnetic response and the stress of the environment are considered.

2. Experimental procedures

The compounds $0.675[Pb(Mg_{1/3}Nb_{2/3})O_3]$-$0.325(PbTiO_3)$ (PMN-PT) and $CoFe_2O_4$ (CFO) were prepared by solid-state reaction method. The calcined powders with a molar concentration ratio of 80/20 were mixed in a ball mill, dried, ground and cold pressed into pellets (10 mm in diameter and ∼2 mm in thickness). Conventional sintering of the PMN-PT/CFO compacts was carried out at 1080 °C, under PbO atmosphere, using two different soaking times: 1 h and 10 h (hereafter referred to as S1 and S10 sample groups, respectively). Altering the sintering time of the composite ceramics allows to control the grain size of the phases, particularly of the PMN-PT matrix. The average grain size of the ferroelectric phase in the S1 and S10 samples was 0.8 μm and 4.4 μm, respectively. More details on the composite ceramic processing can be found in a previous report [15]. To determine the coercive electric field, the electric polarization loops of the composites S1 and S10 were monitored at room temperature and at 20 Hz, through a Sawyer-Tower circuit. Considering the results from the ferroelectric hysteresis measurements, a DC electric field of 20 kV/cm was applied during the poling process, which occurred at room
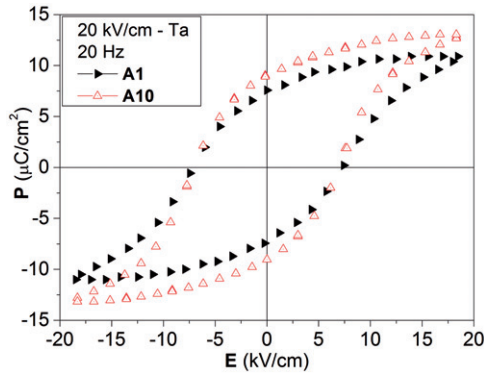
Figure 1. Electric polarization loops at room temperature and at 20 Hz of the PMN-PT/CFO particulate composites. S1 and S2 refer to sintering soaking time of 1 h and 10 h, respectively.

temperature (T_{RT}) and 74 °C (T_P). Magnetization measurements were performed on unpoled and poled S1 and S10 samples using a VSM SQUID Magnetometer by Quantum Design over a temperature range of 5 to 300 K. For the poled ceramic composites, the magnetoelectric induced voltage coefficient ME^{33} was determined at room temperature with a lock-in amplifier and a varying bias magnetic field up to 10 kOe, under a rate of 50 Oe/s, overlapped by an AC magnetic field (peak of 2 Oe), at 1 kHz.

3. Results and discussion

Figure 1 shows the P-E hysteresis at room temperature of the samples S1 and S10, while the ferroelectric characteristics extracted from the polarization loops are summarized in Table 1. It can be seen that the saturation (Ps) and the remanent polarization (Pr) of the S10 sample are ~20% higher when compared to those of S1. As already well discussed in previous reports, grain-size effect is expected for PMN-PT relaxor ferroelectrics [16]. Thus, the higher polarization for S10 can be attributed to the coarsening of the microstructure. In this case, the reduction of the internal stress due to grain size increasing contributes to enhance PMN-PT ferroelectric properties.

Figure 2 shows a complete room temperature cycle of the magnetoelectric coefficient ME^{33} as a function of DC magnetic field in S1 (Figure 2a) and S10 (Figure 2b) composites. In each case, the coefficient curve is compared for two different poling temperatures, T_{RT} (room temperature) and T_P (74 °C). The maximum value of ME^{33} of the samples poled at T_P is slightly higher for both sets of composites, S1 and S10 (4% and 6% higher, respectively). On the other hand, as expected from the polarization results (Figure 1), the magnetoelectric response showed grain-size dependence reflected in the higher maximum coefficient values of the S10 composites, although no remarkable shift of the maximum was detected in any of the analyzed conditions. The reduced internal stress and the more favorable poling condition of the S10-T_P have probably enhanced the piezoelectric coefficient, which consequently reflected as an increase in the magnetoelectric figure of merit ME^{33}.

Figure 3 presents the M-H curves of the unpoled S1 and S10 composites compared to the loops of the samples poled at T_{RT} and T_P temperatures. These hysteresis loops

Table 1. Electric properties (saturation polarization, Ps, remanent polarization, Pr, and coercive electric field, Ec) of the PMN-PT/CFO particulate composites S1 and S10.

Property sample	Ps ($\mu C/cm^2$)	Pr ($\mu C/cm^2$)	Ec (kV/cm)
S1	10.9	7.6	7.2
S10	13.1	9.0	7.2
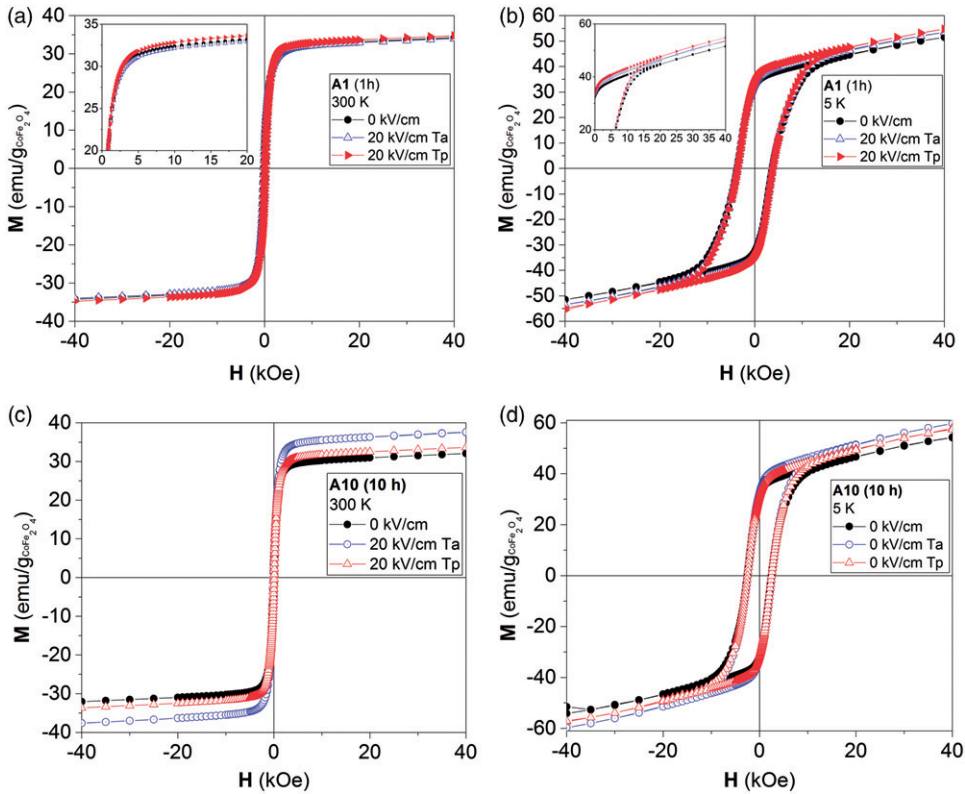
Figure 2. Magnetoelectric coefficient as a function of the DC magnetic field of the PMN-PT/CFO composites S1 (a) and S10 (b), at room temperature, overlapping an AC magnetic field up to 2.0 Oe, at 1 kHz. Samples were poled under 20 kV/cm at room temperature (T_{RT}) and at 74 °C (T_P). The insets zoom the curves around the positive peak range.

are shown for measurements at 5 K (Figure 3a,b) and 300 K (Figure 3c,d). It is noticeable that the magnetization loops show dependence on temperature and poling conditions, particularly for the samples with coarse microstructure (S10).

To better understand the magnetization results, saturated magnetization (Ms), remanent magnetization (Mr), and coercive field (Hc) are plotted in Figure 4 as a function of temperature over the range of 5 K to 300 K. The temperature dependence curves of these magnetic characteristics show a quasi-linear decrease as temperature increases, except for the coercive field, which tends to a constant value over room temperature. When samples are poled, saturated magnetization values at any temperature are higher or at least the same as those observed for the unpoled composites. In fact, Ms-T_P is higher than Ms-T_{RT} for composites sintered for 1 h (S1). Although the saturated magnetization change is more intense for composites sintered for 10 h (S10), in this case
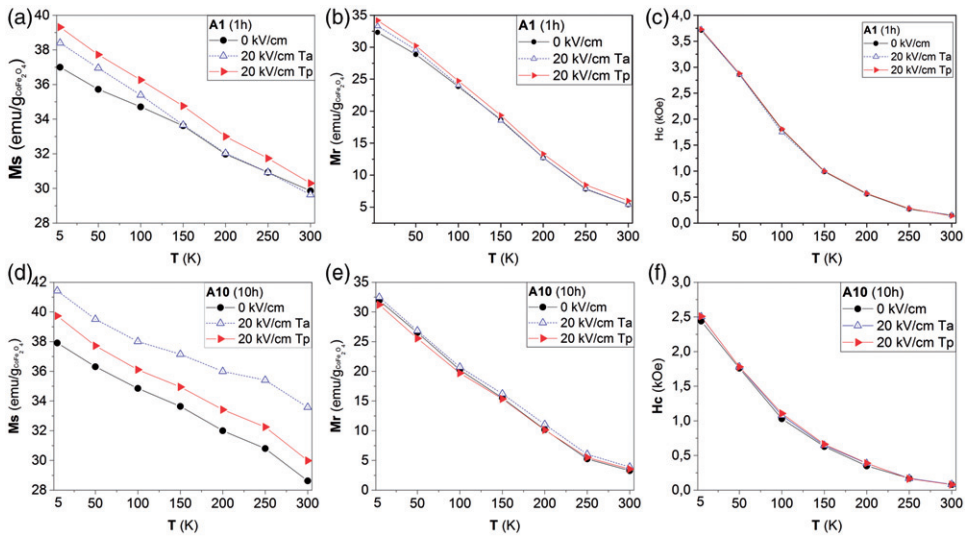
Figure 3. Magnetization (M) as a function of applied DC magnetic field (H) of unpoled and poled PMN-PT/CFO S1 and S10 composites at 5 K (a and b) and 300 K (c and d). The insets show details of saturated magnetization. Samples were poled under 20 kV/cm, for 30 minutes, at room temperature (T_{RT}) and at 74 °C (T_P).
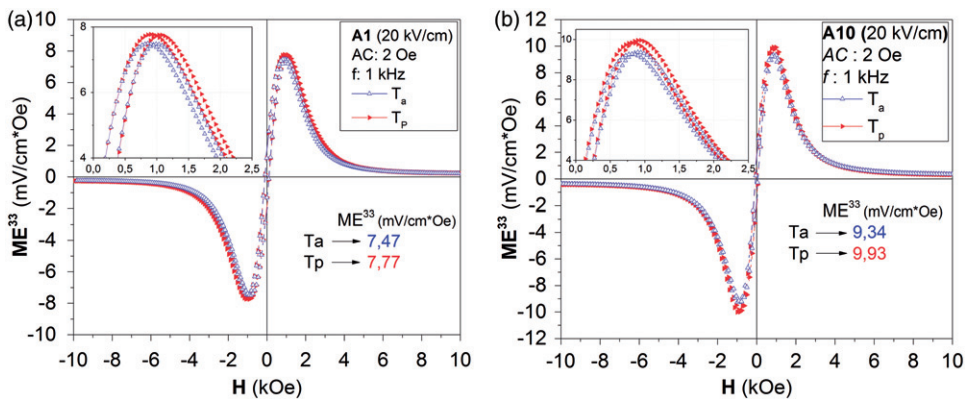

Figure 4. Temperature dependence of saturated magnetization (Ms), remanent magnetization (Mr) and coercive field (Hc) of unpoled and poled PMN-PT/CFO S1 and S10 composites. Samples were poled under 20 kV/cm, for 30 minutes, at room temperature (T_{RT}) and at 74 °C (T_P).

Ms-T_{RT} is higher than Ms-T_P. This inversion on the behavior of Ms as a function of the poling temperature could be attributed to different roles played by the interfacial strain-mediated coupling between piezoelectric and ferromagnetic phases for different grain size distributions. Microcracks or other physical defects, perhaps generated by increases in the poling temperature, and that could be unfavorable to the remanent polarization of the S10-T_{RT} composites, were discarded as a reason for this inversion, since ME^{33} enhances as the poling temperature is raised (Figure 2). On the other hand, Mr and Hc do not present relevant changes as a function of the poling conditions. It is known that the coercive field shows a dependence on magnetocrystalline anisotropy [13, 14]. If the ferromagnetic system is stressed by environment, in our case represented

by the ferroelectric matrix, the coercivity should increase or decrease depending on the material type. However, this result could not be observed from the characterization carried out in this work.

4. Conclusion

In summary, magnetic properties of PMN-PT/CFO particulate composites showed strong temperature dependence, and saturated magnetization presents significant changes under different electric conditions (unpoled and poled states), whose increase or decrease in magnetization would be caused by interfacial strain-mediated coupling of the phases. The maximum magnetoelectric coefficient was higher for composites sintered at 10 h than for those sintered at 1 h, as expected from the grain size distribution dependence of the ferroelectric and ferromagnetic phases.

Funding

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