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Magnetodielectric and magnetoelectric correlation in (1-x)PMN-PT/xCFO 0–3 particulate composites

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ABSTRACT

In this work, the relationship between dielectric, ferroelectric, piezoelectric properties and the magnetoelectric coupling in (1-x)PMN-PT/xCFO multiferroic particulate composites were investigated. The magnetodielectric response showed strong frequency and CFO concentration dependence, which for composites with CFO concentration higher than 30 M%, it was reported a magnetodielectric response up to 10% around the electromechanical resonance regime for magnetic fields of 15 kOe. Additionally, at low magnetic fields a positive magnetodielectric coefficient (~2%) associated to the magnetoelectric coupling was observed. The MD effects for particulate composites were attributed to the co-contribution of the magnetoelectric polarization, at low magnetic fields, and a compressive stress on ferroelectric phase due to magnetostriction effect, at high magnetic field.

1. Introduction

Over the past years there has been a considerable attention to magnetoelectric (ME) coupling in composite materials consisting of separated piezoelectric and magnetostrictive phases [1–3]. In the case of composites, the ME effect is due to the magnetic-mechanical-electric interaction between the piezoelectric and magnetostrictive phases based on the concept of product properties. It means, when a magnetic field is applied to the composite, the shape of magnetic particles change by magnetostrictive effect. The strain generated by magnetic field is a stress source to the piezoelectric phase, resulting in the electric polarization [4]. Based on this principle, a suitable combination of magnetostrictive and piezoelectric phases can be performed to obtain strong ME response.

The degree of the ME coupling is assessed by measuring the extrinsic ME susceptibility by monitoring an electrical voltage induced on poled sample by an oscillating magnetic field, called “dynamic ME method” [5]. Since the ME coupling affects the dielectric properties of magnetoelectric composites, important information about the ME coupling can be also provided by the magnetodielectric coefficients [6–8]. Such coefficients can be easily evaluated experimentally by measuring the dependence of dielectric permittivity under a magnetic field. Several work report MD response in different types of materials including particulate ceramic composites [9,10] and polymer-ceramic composites [11] or thin films systems [12,13]. Jang, H.M. et al. discuss a model to obtain the ME coupling from MD measurements in case of the thin films [7]. However, the magnetodielectric effect can be affected by magnetoresistive response combined with the Maxwell-Wagner dielectric relaxation [14], which provides a mechanism for magnetodielectric response that is not originated from any magnetoelectric characteristic of the material. In case of BSPT/LSMO thin films, Zhang et at. report a MD coefficient close to 10%, which is related to the co-contribution of the magnetostriction and magnetoresistance properties to the magnetodielectric response of samples [15]. On the other hand, the stress condition of the ferroelectric grains generates changes in the dielectric properties by reduction of domain movement [16,17] resulting in the MD effect without correlation to the ME coupling effect. At the present stage, the MD effect is commonly investigated in laminate composites [18,19], which are reported giant values ($\Delta\varepsilon$>10%) close to electromechanical resonance (EMR). However, a systematic study of the MD effect in particulate composite does not have done, mainly at EMR. Also, the relationship between magnetodielectric and magnetoelectric interaction in ME composites is still discussed. Thus, in this study we purpose a systematic investigation of the magnetodielectric response in ME particulate composites prepared using [Pb $(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$] as ferroelectric phase and $CoFe_2O_4$ as magnetostrictive phase in order to clarify the

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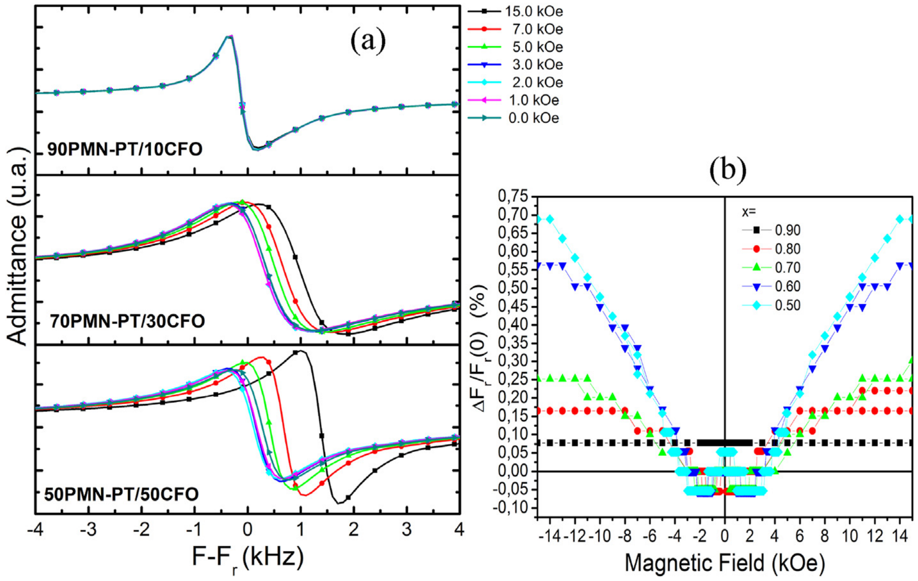

Fig. 1. (a) Room temperature frequency dependence of the admittance at different magnetic field for PMN-PT/CFO composites; and, (b) Resonant frequency values as a function of magnetic field.

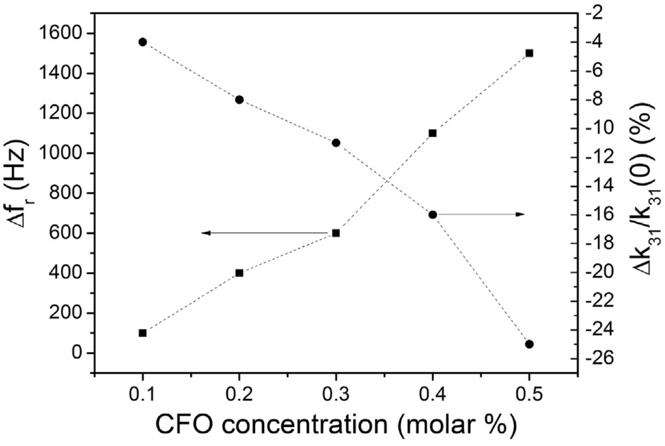

Fig. 2. Dependence of resonance frequency and electromechanic coupling constant k_{31} variation as a function of CFO concentration.

contribution of ME effect on MD effect.

2. Experimental procedure

The magnetoelectric composites of (1-y)[Pb $(Mg_{1/3}Nb_{2/3})O_3$]–y($PbTiO_3$) (y = 0.325), or PMN-PT, and $CoFe_2O_4$, or CFO, were prepared by solid state reaction method. The cobalt ferrite ceramic powder was prepared by using Co_3O_4 and Fe_2O_3 as starting materials. The powders were mixed through ball-milling (in distilled water with ZrO_2 cylinders), calcined at 900 °C, for 4 h, and then, grinded (through ball milling), for 10 h. The 0.675PMN-0.325 PT powder was obtained by columbite method. The columbite precursor, $MgNbO_6$ (MN) was prepared from MgO and Nb_2O_5 mixed powders and calcined at 1100 °C, for 4 h. Following the batching formula, MN precursor was mixed with PbO and TiO_2, calcined at 900 °C, for 4 h, and ball milling grinded for 10 h. The particulate composites (1-x)PMN-PT/xCFO, for $0.10 \leq x \leq 0.50$ M ratio, were prepared by ball-milling. The powders were uniaxial and hydrostatic cold-pressed into pellets (~10 mm diameter and ~2 mm thickness). Thus, the green bodies were densified at 1050 °C, for 3 h,

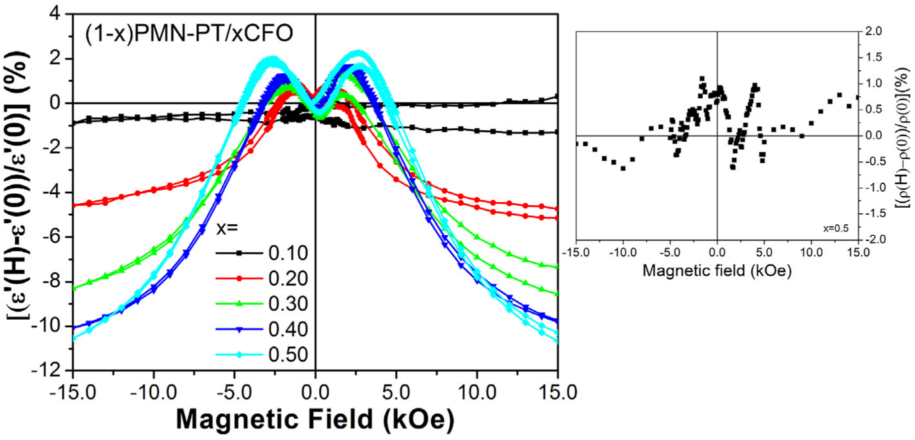

Fig. 3. Magnetic field dependence of MD coefficient at room temperature for (1-x)PMN-PT/xCFO particulate composites.

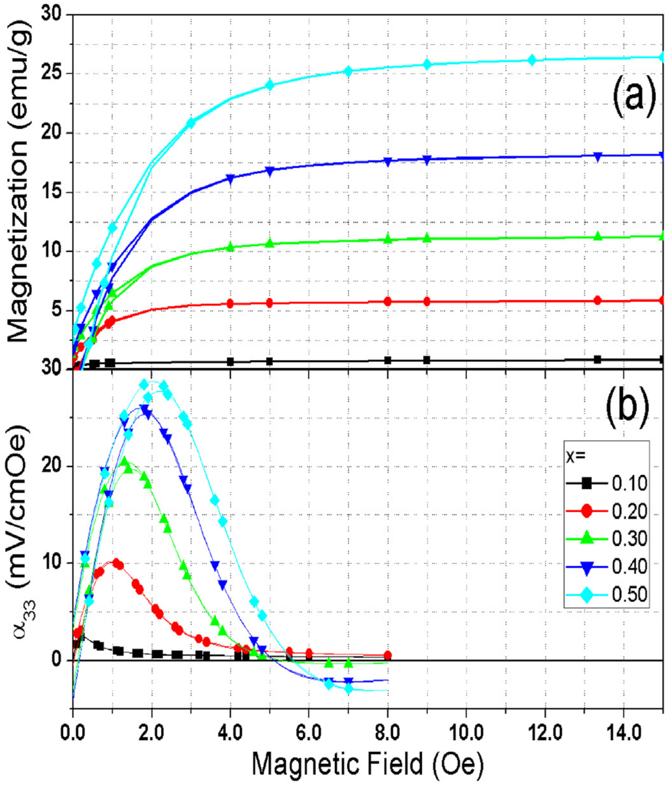

Fig. 4. (a) Half-cycle magnetic hysteresis loops at room temperature, and: (b) magnetoelectric coefficient as a function of magnetic applied field for (1-x) PMN-PT/xCFO sintered at 1050 °C, for 3h.

by conventional sintering method. Details about the structural, microstructural, electric and dielectric properties of samples are reported on reference 20. The samples were poled at 20 kVcm-^{1}, for 30 min, at room temperature. The XRD measurement was carried out at room temperature using a diffractometer Shimadzu (model XRD-6100). The magnetic properties of samples were measured using a Magnetic Property Measurement System (MPMS®3, Quantum Design Company), at room temperature. The magnetodielectric effect (MD) was measured using an IET labs LCR meter in a frequency range between 100 kHz and 800 kHz. The dc magnetic field, from 0 to 15 kOe, was provided by an electromagnet (EM7, Lake Shore Cryo.). The magnetoelectric coefficients (α_{ME}) were determined by dynamic method. In this case, a bias magnetic field between 0 and 8 kOe overlapped by an ac magnetic field (2 Oe at 1 kHz) was applied, and the induced voltage V_{out} was measured using a lock-in amplifier.

3. Results and discussions

The electrical admittance as a function of frequency for (1-x) PMNPT-xCFO composites under different dc magnetic field are shown in Fig. 1. The sharp maximum and minimum corresponding to the electromechanical resonance (EMR) frequency is observed, independently of CFO concentration. It can be reported a tuning effect of admittance values with increment of dc magnetic field (from 0 Oe to 15 kOe) for composites with high concentration of CFO phase followed by a systematic increase of the Δf_r (f_r ^{15kOe}-f_r ^{0Oe}). This fact is evidenced by the analysis of changes in the $\Delta f/f_r$ with applied magnetic field, showed in Fig. 1b. For 50PMN-PT/50CFO composite, it is clear to see an initial decrease of $\Delta f_r/fr$ parameter for magnetic field up to 3 kOe, and then an increase of $\Delta f_r/fr$ parameter between 3 kOe and 15 kOe. As result of the changes in resonance frequency, the electro-mechanical coupling constant k_{31} can be modulated by magnetic field and CFO concentration, as seen in Fig. 2. The increase of the magnetic field decreases the k_{31} reaching a reduction of ~25% for composites with 50% of the CFO phase.

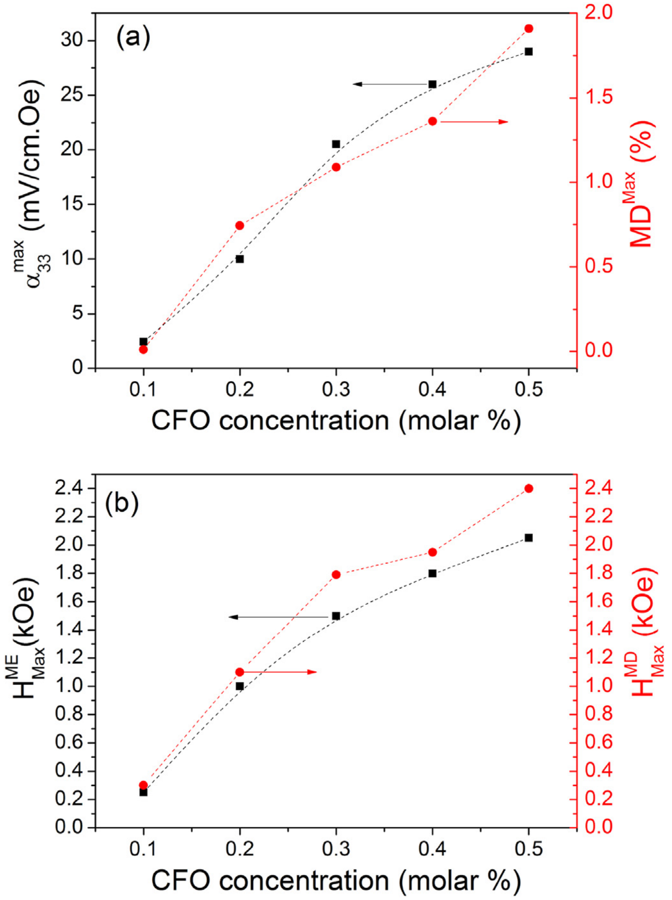

Fig. 5. (a) Magnetoelectric coefficient α_{33} and MD coefficient; and (b) magnetic field for maximum magnetoelectric and magnetodielectric response, as a function of CFO concentration for PMN-PT/CFO particulate composites.

The magnetic field dependence of the magnetodielectric effect (MD), at frequencies close to the EMR, is shown in Fig. 3. The MD coefficient is defined as a relative variation of the real part of the dielectric permittivity [ε'(H)- ε'(0)]/ε'(0)) with magnetic field. It is clear to see the MD coefficient depends of the CFO concentration, which has positive values for magnetic fields up to 3 kOe and then decrease monotonically until 15 kOe. Additionally, the CFO concentration enhances the MD response at high magnetic field, reaching 10% at 15 kOe, for $x > 0.30$. The magnetoresistance response for 0.50PMNPT/0.5CFO is illustrated on panel of Fig. 3. It is clear to see no significant magnetoresistance response. Magnetoresistance properties are a typical effect reported in thin films and/or metal materials [21,22]. Hossain et al. report colossal magnetoresistance effect in Nickel doped $ZnFe_2O_4$ spinel ceramics, however the effect is absent in the $NiFe_2O_4$ due to the increase of the electric resistivity with increment of Ni concentration [23]. On the other hand, the $CoFe_2O_4$ spinel ferrite has been used as magnetic layer in fabrication of giant magnetoresistance (GMR) devices due to present high Curie temperature and high saturation magnetization, good chemical stability and large magnetic anisotropy [21,24]. However, the MR values are dependent of the $CoFe_2O_4$ layer

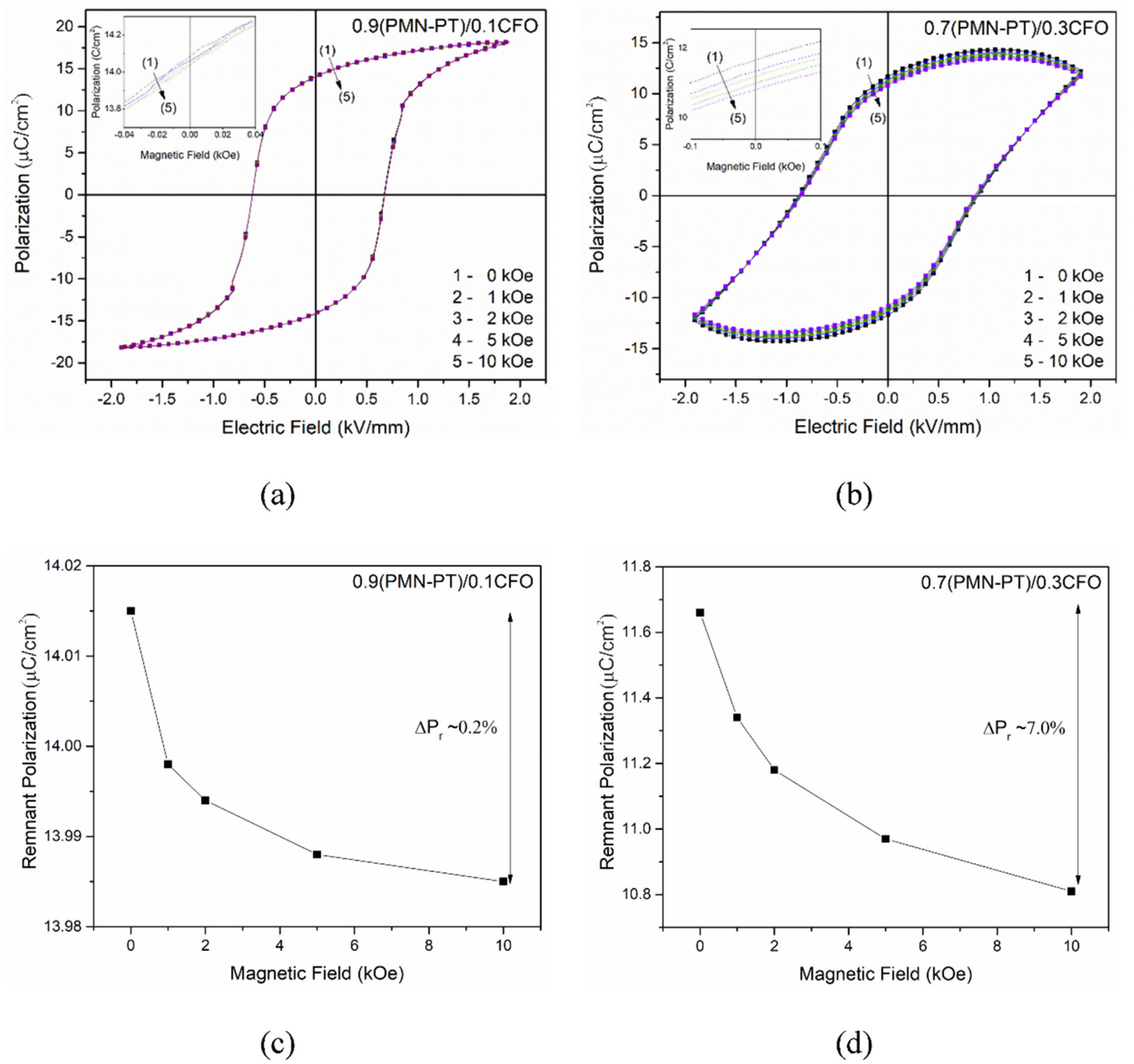

Fig. 6. Magnetic field dependence of ferroelectric properties for (1-x) PMNPT/xCFO composites: a) and c) x = 0.1; b) and d) x = 0.3.

thickness, which for thickness larger than 62 nm the value of the GMR evanesces [25]. The authors explain this fact based on existence of an active and an inactive region in the CoFe$_2$O$_4$ layer, which the active part will give the main contribution to the GMR ratio while inactive part will shunt the current and reduce the GMR ratio. Thus, similarly to NiFe$_2$O$_4$, is not expected appreciable MR effect for CoFe$_2$O$_4$ polycrystalline ceramics. Since the electric resistivity of samples is larger than 2×10^{10} Ω cm (details about the structural, microstructural, electric and dielectric properties of samples are reported on reference 20) and based on absence of the magnetoresistive effect for 0.50PMNPT/0.5CFO samples, the magnetoresistive artifact, as expected by Catalan et al. [14], can be ruled out of the explanation of the MD effect observed on samples.

Fig. 4 shows the magnetic field dependence of the magnetoelectric (ME) coefficient to the (1-x)PMN-PT/xCFO composites, for $0.1<x<0.5$. The ME coefficient values between 3 and 30 mV/cm.Oe was obtained, which is strongly dependent of the CFO concentration. The high values of ME coefficient are consequence of the high resistivity and the 0–3 connectivity maintenance of our composites, as previously reported [20]. Additionally, the magnetic dc bias field in which the maximum ME coefficient occurs (H_{ME}^{Max}) is related with the maximum variation of magnetostriction of magnetic phase that increases from 500 Oe to 2100 Oe for x = 0.10 and 0.50, respectively. A comparison between the H_{ME}^{Max} and the magnetic field where MD response is maximum (H_{MD}^{Max}), and the maximum values for ME and MD coefficients are shown in Fig. 5. Similar trend was observed to the ME and MD coefficients indicating a correlation between the initial increases in the dielectric

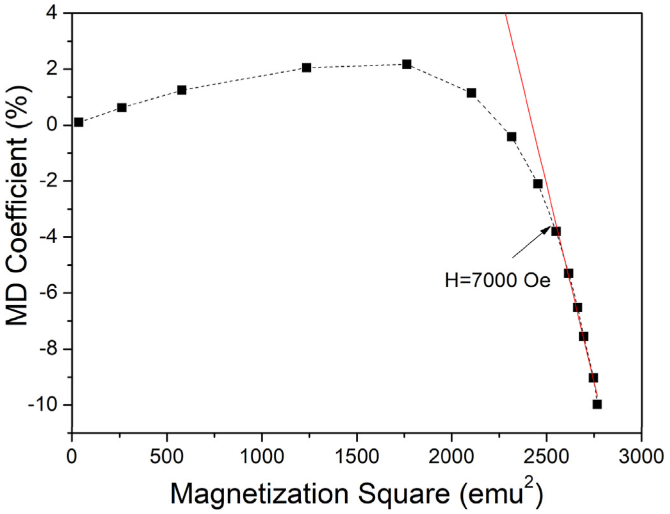

Fig. 7. Magnetodielectric coefficient as a function of magnetization square for (1-x) PMNPT/xCFO composites, x = 0.5.

permittivity, for magnetic field up to 3 kOe and ME coupling in the samples. This fact can be explained in terms of the magnetic field-induced polarization generated by ME effect, which can be evaluated by $\frac{\varepsilon(\acute{H})-\varepsilon(\acute{0})}{\varepsilon(\acute{0})} \propto \alpha_{ME} H_{dc}$ [7]. According to this equation, the influence of the magnetoelectric polarization in the MD coefficient is predominant on magnetic field in which the ME coefficient is maximum and evanesces for magnetic field higher than H_{ME}^{Max}. For all samples characterized in this work, magnetic fields higher than 7 kOe became α_{ME} null, and in consequence, the influence of ME coefficient in MD effect.

Moreover, at high magnetic field the dielectric permittivity values decreases leading MD coefficients larger than 10%, for high CFO concentration. In fact, the MD effect depends on the dielectric permittivity ε, which can be changed by extrinsic factor as internal stress or mechanical strain [16–18]. For PMNPT ferroelectric ceramics, it has been reported that both dissipation energy and polarization decrease as the compressive stress increases without significant changes in the coercive field [16]. Similar behavior is reported for other ferroelectric system [17,18]. In case of the studied composites, increasing the amount of CFO phase increase the stress generated by magnetic field in to ferroelectric grain matrix. Assuming a net deformation of the CFO phase inducing a compressive stress on PMN-PT matrix, it is expected a decrease of the ferroelectric properties, which is related to the reduction of the domains and domains walls movement [16].

Fig. 6a and b illustrate the ferroelectric hysteresis, under different bias magnetic field, for x = 0.1 and 0.3, respectively. A typical hysteresis curve can be observed in both samples, but the increment of CFO concentration increases a conductive contribution on hysteresis behavior, evidenced by rounding the curve at high electric field. Additionally, it can be observed a reduction of remaining polarization (Pr) values as a function of magnetic field close to 0.21% and 7.0%, for x = 0.1 and 0.3, respectively (Fig. 6c and d). The larger reduction of Pr with increment of magnetostrictive CFO phase and magnetic field is an evidence of the existence of compressive stress acting on ferroelectric matrix. This stress on ferroelectric grains create a clamping condition for domain and domain wall motion which reduces the switchable part of domains, reducing the ferroelectric and dielectric properties of PMNPT phase, in corroboration to the MD response of composites.

The strain (S) generated by magnetostriction effect, in a first approximation, is proportional of the square of magnetization, i.e. S α $(M/M_{sat})^2$ $S\ \alpha \left(\frac{M(H)}{M_{sat}}\right)^2$ (where M represents the magnetization and M_{sat} represents the saturation magnetization) [26]. Based on this fact, in Fig. 7 is represented the MD coefficient as a function of M^2 for sample 50PMNPT/50CFO. It is clear to see a linear relationship between MD values and M^2 for high magnetic field ($H > 7$ kOe), indicating a stress related changes in dielectric properties for this magnetic field region, which MD contribution associated to the ME effect can be ruled out of analyses, according to the ME response of composites.

Thus, the stress generated by magnetostriction effect reduces the wall mobility of ferroelectric domains causing a tuning in the relative electric permittivity, ferroelectric properties as well as in the piezoelectric constants k_{31} values (as seen in Fig. 2). In this regime, it was observed a tuning up to 10% in electric permittivity values for sample with 50% of CFO, which is high compared to MD values reported in literature for particulate systems [27–29].

4. Conclusions

In summary, a giant room temperature magnetodielectric effect over 10% is observed in (1-x)PMN-PT/xCFO particulate composites, for x > 0.30, near to EMR region, which is related to the increase of the stress in the ferroelectric phase grain due to strain variation associated with the magnetostriction properties of ferrite phase. Additionally, a positive MD coefficient associated to the ME polarization at low magnetic field and dependent of the CFO concentration was reported. These results show the magnetodielectric response in particulate composites can be associated to the ME properties, at low magnetic field, and the reduced wall mobility of ferroelectric grains due to increase of stress by magnetostriction effect of ferrite phase, at high magnetic fields. These results provide a better knowing about the nature of magnetodielectric properties and its correlation with magnetoeletric properties in particulate composites and a new way to tune the MD effect by changing the CFO concentration for application in magnetic sensor based on magnetoelectric composites at room temperature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

F.L. Zabotto: Writing - original draft, Formal analysis. **F.P. Milton:** Formal analysis. **A.J. Gualdi:** Formal analysis. **A.J.A. de Oliveira:** Formal analysis. **J.A. Eiras:** Formal analysis. **D. Garcia:** Formal analysis.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2020.154517.

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