Enhanced piezomagnetic coefficient of cobalt ferrite ceramics by Ga and Mn doping for magnetoelectric applications

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The magnetic, magnetostrictive and electrical properties of Ga- and Mn-doped cobalt ferrite, are reported as a function of composition. Materials with improved functionality for magnetoelectric composites are obtained. Magnetic characterizations reveal the effectiveness of the dopants to reduce the typically high magnetocrystalline anisotropy of cobalt ferrite and significantly enhance piezomagnetic coefficients. $CoGa_{0.15}Fe_{1.85}O_4$ ceramic shows large effective piezomagnetic coefficient q_{11} , $3.9 \times 10^{-6} \text{ kA}^{-1}\text{m}$, which is among the highest values reported for cobalt ferrite-based ceramics. Additionally, a two order of magnitude increase of resistivity is found after doping, which makes this material specially suitable for particulate composites. On the contrary, $CoMn_{0.25}Fe_{1.75}O_4$ ceramic has the highest value of $q_{11} + q_{21}$ ($\sim 1.9 \times 10^{-6} \text{ kA}^{-1}\text{m}$), which is the relevant parameter for laminated composites. Analytical calculations of the transverse magnetoelectric coefficient α_{31}^E , for bilayers containing these optimized magnetostrictive phases are also reported, and they demonstrate their high potential for developing new magnetoelectric composites.

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I. INTRODUCTION

Magnetoelectric (ME) materials might enable a range of novel electronic and magnetic devices. Examples are several types of sensors, energy harvesters, random access memories, phase shifters, resonators, inductors and biomedical applications, to name but a few.¹⁻³ New ME materials are continuously being developed.² However, the highest ME responses have been found for composites formed by magnetostrictive and piezoelectric phases. Magnetic metallic alloys or spinel oxides are used for the former component, while ferroelectric polymers or perovskite phases are preferred for the latter one.^{2,4-8} Interest in cofired ceramic composites has grown due to their low cost, easy manufacturing, possibility of co-sintering the magnetostrictive and piezoelectric oxide phases, and high electrical resistivity when compared to metallic alloys as Metglas or Terfenol-D.⁹⁻¹⁴ Among magnetostrictive phases, $CoFe_2O_4$ (CFO) stands out because of its very high magnetostriction (λ).¹⁵ However, studies in ME composites formed by CFO-based compositions mostly resulted in ME coefficients lower than those using $NiFe_2O_4$ -based magnetostrictive phases.^{9,13,16-18} This is so because the magnetoelectric coupling in composites results from changes of polarization in the piezoelectric phase caused by the dynamical mechanical deformation of the magnetostrictive one under a varying magnetic field. Thus, the relevant characteristic to obtain high ME coupling is a large strain sensitivity $\frac{d\lambda}{dH}$ (or effective piezomagnetic coefficient), and CFO shows low piezomagnetic coefficient because its high magneto-crystalline anisotropy and coercive field.

The spinel crystalline structure of CFO allows modification of the magnetostrictive properties by cation substitution. Therefore, efforts are concentrated in reducing the magneto-crystalline anisotropy and hence, in increasing piezomagnetic coefficient. Several cation substitutions have been studied, such as trivalent Al^{3+} ,¹⁹ Mn^{3+} ,^{20,21} Cr^{3+} ,^{20,22} Ga^{3+} ,²³ or divalent Zn^{2+} ,²⁴ Cu^{2+} ,²⁵ and Mg^{2+} ,²⁶ substituting Fe^{3+} and/or Co^{2+} , and tetravalent Ge^{4+} ,²⁷ Ti^{4+} ,^{28,29} Zr^{4+} ,³⁰ co-substituting with Co^{2+} for two Fe^{3+} . These substitutions modify the overall distribution of the cations in tetrahedral or octahedral sites of the spinel structure, which affects their exchange interactions and, consequently, modify the magneto-crystalline anisotropy.³¹

In particular, Ga- and Mn-doped CFO have shown substantially increased piezomagnetic coefficient with respect to pure CFO. Indeed, Song, Lee et al.^{22,23}, reported enhancements of the effective piezomagnetic coefficients as high as 300 and 213 %, for $CoGa_{0.2}Fe_{1.8}O_4$ and

$CoMn_{0.2}Fe_{1.8}O_4$ compositions, respectively. However, in those studies, authors increased the dopant content by steps of 20 mol%, so that the studied compositions were $CoZ_xFe_{2-x}O_4$ with Z being Ga or Mn, and $x = 0.0, 0.2, 0.4, 0.6$ and 0.8 . There is then a possibility that doping levels of 0.2 are not the optimum ones, and that even higher strain sensitivities can be achieved for different compositions in the $0 < x < 0.4$ range. Besides, the effect of the substitution on the electrical properties, which greatly determines the poling level of the piezoelectric component in a ceramic composite, was not addressed.

Considering the aforementioned points, this work reports the magnetic, magnetostrictive and electrical properties of Ga- and Mn-doped cobalt ferrite ceramic materials with optimized microstructure, as a function of composition. In addition, their use as magnetostrictive phase of ME composites is assessed. Analytical calculations of the expected transverse ME coefficient α_{31}^E , when combined with most topical state-of-the-art ferroelectric materials are provided. This may be used as a starting point for developing new ME composites.

II. EXPERIMENT

Specific CFO-based compositions were chosen after the results obtained by Song, Lee et al.,^{22,23} so that doping levels around $x=0.2$, not studied before, were prepared and characterized. These were $CoZ_xFe_{2-x}O_4$ ($Z = \text{Ga or Mn}$) with $x = 0.10, 0.15, 0.20, 0.25$, which were labeled as CF(first letter of Z)100x. For instance, CFG15 stands for the composition $CoGa_{0.15}Fe_{1.85}O_4$.

Powders were synthesized by solid state reaction of stoichiometric mixtures of Co_3O_4 ($> 99.9\%$ pure), Fe_2O_3 ($> 99.5\%$ pure), Ga_2O_3 ($> 99.999\%$ pure) and MnO_2 ($> 99.9\%$ pure). A two-step calcination process, involving thermal treatments at 900°C for 12 h and 1000°C for 12 h, both in air, was used.³² Intermediate hand milling was accomplished between calcinations to increase chemical homogeneity. X-ray diffraction (XRD) of the resulting material only showed peaks that belonged to the cubic spinel structure for all CFG and CFM compositions. This evidences the absence of any additional spurious phase at this stage (see patterns in Fig. S1 of the Supplemental Material) Finally, powders were ball milled for 24 h in isopropyl alcohol with Y_2O_3 -stabilized zirconia grinding media to reduce particle size. Unimodal distributions, with average size of 550 nm and 200 nm, were obtained for the CFG and CFM compositions, respectively, as determined by scanning electron microscopy

(SEM) (micrographs available in Fig. S2 of the Supplemental Material).

Conventional sintering was used. Green pellets were obtained by uniaxial and subsequently isostatic pressing and sintered at 1350 °C for 24 h in air, with heating and cooling rates of 5 °C/min. Samples of 15 mm in diameter and 8 mm in thickness were prepared for all the studied compositions. Formation of secondary phases or modification of the crystalline structure during sintering was controlled by XRD. All ceramics showed single spinel structure (patterns available in Fig. S3 of the Supplemental Material). A diffractometer LabX XRD-6000 of Shimadzu with $\text{CuK}\alpha$ radiation was employed for all XRD characterizations.

Density was measured by the Archimedes' method, and densification levels were obtained with the crystallographic density determined from cell parameters, derived from XRD data of the studied ceramics. The calculated crystallographic densities were 5.29 gcm^{-3} , 5.32 gcm^{-3} , 5.36 gcm^{-3} and 5.39 gcm^{-3} for the CFG10, CFG15, CFG20 and CFG25 ceramics, respectively, and 5.26 gcm^{-3} , 5.25 gcm^{-3} , 5.24 gcm^{-3} and 5.23 gcm^{-3} for the CFM10, CFM15, CFM20 and CFM25 ceramics, respectively. Relative densities higher than 96 % were consistently obtained for all CFG and CFM ceramics.

Ceramic microstructure was characterized by SEM with a Jeol JSM-5800 LV microscope (Peabody, MA, USA) on polished and thermally etched and quenched ceramic surfaces. Dense and homogeneous coarse grained microstructures with average grain sizes as large as 60 μm were obtained (micrographs available in Fig. S4 of the Supplemental Material). Large grain size is known to be advantageous for enhanced magnetoelastic properties.³³

Magnetic field dependences of magnetization were collected with a PPMS Quantum Design, model 7100; and magnetostriction measurements were carried out by the strain gauge method using PA-06-060BG-350-LEN strain gauges from Excel Sensors. Strain gauge resistance was measured by a high-speed Wheatstone bridge of National Instruments, model NI 9237. Magnetic field was applied either parallel or perpendicular to the gauge with an EM4-HVA Lakeshore electromagnet, which provided the longitudinal λ_{11} and transversal λ_{21} magnetostrictive strains, respectively.

Additionally, the electrical response was characterized, for which Ag electrodes were painted on ceramic samples. Impedance spectroscopy analysis was accomplished to obtain electrical conductivity. Measurements were carried out in static conditions, from 25 to 400 °C, at 20 °C intervals, in the 20 Hz - 1 MHz range with the HP4284A precision LCR meter. The Z-view2 commercial software was used for the analysis.

III. RESULTS AND DISCUSSION

A. Magnetic and magnetostrictive characterizations

Fig. 1 shows the magnetic field dependence of magnetization (M-H loops) for CFG (a) and CFM (b) ceramics, at room temperature (~ 300 K). For CFG materials, saturation magnetization (M_S) initially increases with the Ga concentration (from CFG10 to CFG15), and subsequently decreases for higher doping levels (CFG20 and CFG25), while coercivity (H_C) shows a minimum for CFG15 (see inset in Fig. 1a). A different behaviour is found for CFM materials, so that M_S increases monotonically while H_C decreases with increasing Mn content (see inset in Fig. 1b).

FIG. 1. Magnetic field dependence of magnetization for (a) CFGx and (b) CFMx ceramics at 300 K. Insets show coercivity (H_C) as a function of doping level for each material system. Dashed lines represent the reference values of saturation magnetization (M_S) and H_C for $x=0$ (CoFe_2O_4), extracted from Ref. 34.

The combination of high M_S and low H_C indicates magnetic soft behaviour that is the key to enhanced piezomagnetic coefficient. It is necessary then to build up an understand-

ing of the physics behind the observed trends of M_S and H_C with Ga and Mn additions, in order to rationalize the magnetostrictive properties of these materials. Cobalt ferrite tends to crystallize with the inverse spinel structure³⁵ that can be represented by the formula $(Fe^{3+})[Co^{2+}Fe^{3+}]O_4$, where cations inside the round and square brackets occupy the tetrahedral (A) and octahedral (B) sites, respectively. Doping not only modify lattice parameters but also cation distribution in the spinel-type structure, with a direct effect on exchange interactions and hence, on magnetic and magnetoelastic properties.³⁵ For magnetic spinel oxides, an antiparallel arrangement of magnetic moments at A (m_A) and B (m_B) sites takes place, so that a net moment $n = m_B - m_A$ results. For the cobalt ferrite ideal inverse spinel, this is equal to the magnetic moment of Co^{2+} in the B site, since Fe^{3+} evenly distributes between the A- and B-sites.³⁶ Relating the doping effects, Mn^{3+} has been reported to replace Fe^{3+} at the B-site. This causes a concomitant decrease of the degree of inversion by some Co^{2+} entering the A site.³⁷ In relation to Ga^{3+} doping, this species substitutes for Fe^{3+} preferentially in the A site, at least for low Ga concentrations.³⁸

Dependences of the lattice parameter a of the cubic spinel oxide with doping level for the CFGx and CFMx ceramics are given in Fig. 2. Trends are discussed with the ionic radii of the different species present in both tetrahedral and octahedral sites, listed in Table I. The lattice parameter a decreases with increasing Ga content, which is expected since the ionic radius of Ga^{3+} both in four-fold and six-fold coordinations is smaller than those of Fe^{3+} . Note the abrupt drop that occurs between compositions CFG15 and CFG20 that might indicate the onset of Ga entering B-sites. Indeed, the initial increase of M_S for small amounts of nonmagnetic Ga (see Fig. 1a) is the well-known tendency for spinel ferrites when nonmagnetic ions substitute for iron in the tetrahedral site.^{36,39} This rise of M_S results from the exclusive entrance of the nonmagnetic ion into the A site, which decompensates the number of magnetic Fe^{3+} in A and B sites, so that the total magnetic moment n increases. In this scenario, the subsequent decrease of M_S for larger Ga contents would indicate the nonmagnetic ion entering the B site,³⁶ in agreement with the evolution of the lattice parameter.

In spinel oxides, coercivity H_C is closely related to the strength of exchange interactions between cations in A and B sites,³⁶ so that a decrease is expected when nonmagnetic Ga^{3+} substitutes for Fe^{3+} . This justifies the initial decrease of H_C with increasing x up to $x = 15$ for the CFGx ceramics (see inset in Fig. 1a). The subsequent increase of H_C for $x = 20$

FIG. 2. Lattice parameter a of the cubic spinel structure as a function of Ga and Mn contents x for CFGx and CFMx ceramics at 300 K.

TABLE I. Ionic radii for cations Fe^{3+} , Co^{2+} , Ga^{3+} and Mn^{3+} with coordination numbers 4 (IR_4) and 6 (IR_6). Data extracted from Ref. 40.

	Fe^{3+}	Co^{2+}	Ga^{3+}	Mn^{3+}
$\text{IR}_4(\text{pm})$	49.0	58.0	47.0	-
$\text{IR}_6(\text{pm})$	64.5	74.5	62.0	64.5

might be associated with the sharp contraction of the crystal lattice for this composition as shown in Fig. 2, since the strength of exchange interactions rise rapidly with the decreasing distance between ions.³⁶

A different trend was found for CFMx materials. Lattice parameter a in this case monotonically increases with Mn concentration, as shown in Fig. 2. Although the ionic radius of Mn^{3+} in octahedral coordination is very similar to that of Fe^{3+} (see Table I), the displacement of Co^{2+} to the tetrahedral sites causes the observed expansion of the crystal cell. Note that the ionic radius of Co^{2+} in tetrahedral coordination is larger than that of Fe^{3+} (see Table I). Accordingly, a progressive decompensation of the number of Fe^{3+} in A and B sites takes place. As a consequence, M_S increases, as observed with increasing Mn content (see Fig. 1b). Nevertheless, note that this behavior is expected to hold only for small amounts of Mn, and a decrease of M_S would be anticipated for high Mn concentrations.²¹ In addition, exchange interactions between irons in A and B sites (Fe^{3+})-[Fe^{3+}] are much stronger than

those between cobalt in A site and iron in B site (Co^{2+})- $[\text{Fe}^{3+}]$.⁴¹ As a result, a decrease of exchange interactions and then, of coercivity is expected from the displacement of Co^{2+} to A sites with Mn doping, as observed (see inset of Fig. 1b).

Fig. 3 shows the magnetic field dependence of magnetostriction (λ_{11}) and its derivative (q_{11}) for CFG and CFM ceramics, measured in the direction of the applied magnetic field at room temperature. All magnetostriction curves show an initial contraction until a minimum is reached, above which a limited partial recovery (expansion) takes place before a stationary situation is reached. This behaviour is typical of cobalt-based ferrites in ceramic form, and has been associated with the crystal anisotropy. Namely, magnetostriction is negative along the magnetization easy axis that dominates response in the low field regime (negative coefficient), while it is positive along the hard axis that gives an opposite contribution that only becomes apparent above a certain field (positive coefficient).^{25,42} Overall, magnetostriction is larger along the easy axis and thus, a final contraction result. Maximum magnetostriction and its corresponding magnetic field both decreased with doping, either Ga or Mn, which is in accordance with previously reported results.^{21,23} Effective piezomagnetic coefficients, however, show a distinctive maximum for specific compositions, so that CFG15 and CFM25 ceramics present the largest piezomagnetic coefficients among CFG and CFM materials, being $3.9 \times 10^{-6} \text{ kA}^{-1}\text{m}$ and $2.7 \times 10^{-6} \text{ kA}^{-1}\text{m}$, respectively. In particular, the effective piezomagnetic coefficient of $3.9 \times 10^{-6} \text{ kA}^{-1}\text{m}$ for CFG15 is approximately 390 % higher than that observed for CFO ($0.8 \times 10^{-6} \text{ kA}^{-1}\text{m}$),^{25,28} and being to our best knowledge, among the highest values reported for cobalt ferrite-based ceramics.²⁰⁻³⁰

Note that while q_{11} is the relevant magnetostrictive parameter when particulate and fibre-type ME composites are concerned (0-3 and 1-3 connectivities), q_{21} has also to be considered in the case of laminate composites (2-2 connectivity). In this case, the transverse ME coefficient α_{31}^E directly depends on the sum of the longitudinal (q_{11}) and transversal (q_{21}) effective piezomagnetic coefficients of the magnetostrictive phase. This is illustrated by Eq. (1), which was deduced for a bilayer composite formed by two piezoelectric and magnetostrictive layers.⁴³

$$\alpha_{31}^E = \frac{E_3}{H_1} = \frac{-k\nu(1-\nu)(q_{11} + q_{21})d_{31}^p}{\varepsilon_{33}^p(s_{12}^m + s_{11}^m)k\nu + \varepsilon_{33}^p(s_{12}^p + s_{11}^p)(1-\nu) - 2kd_{31}^p{}^2(1-\nu)} \quad (1)$$

In Eq. (1), E is the electric field, H - the magnetic field, k - an interface coupling pa-

FIG. 3. Magnetic field dependence of magnetostriction (λ_{11}) and effective piezomagnetic coefficient (q_{11}) for CFGx (a,b) and CFMx (c,d) ceramics at 300 K. Dashed lines represent the reference maximum values of λ_{11} and q_{11} for $x=0$ ($CoFe_2O_4$), extracted from Ref. 28

parameter being 1 for an ideal interface and 0 for the case with no friction, ν - the volumetric fraction of the piezoelectric phase, d - the piezoelectric coefficient, ε - the dielectric permittivity and s - compliance. Superscripts p and m refer to piezoelectric and magnetostrictive phase, respectively. Note that q_{11} and q_{21} have opposite signs and thus, large q_{11} values do not guarantee composites with high ME response in this configuration. Magnetic field dependences of the modulus of q_{11} and q_{21} and of the sum $q_{11} + q_{21}$ for the CFG15 and CFM25 ceramics were calculated from magnetostriction measurements, and are given in Fig. 4. CFG15 ceramic shows q_{11} values higher than the CFM25 one. However, the sum $q_{11} + q_{21}$ was larger for CFM25 than for CFG15 sample, with maximum values of $\sim 1.9 \times 10^{-6} \text{ kA}^{-1}\text{m}$ and $1.1 \times 10^{-6} \text{ kA}^{-1}\text{m}$, respectively. Also, an important parameter, the bias magnetic field for maximum $q_{11} + q_{21}$ was 0.13 kOe for the CFG15 ceramic, and 0.21 kOe for the CFM25 one. Low bias magnetic field for maximum response can be also advantageous for applications.

FIG. 4. Magnetic field dependences of the modulus of the longitudinal (q_{11}) and transversal (q_{21}) effective piezomagnetic coefficients and of the sum $q_{11} + q_{21}$ for the (a) CFG15 and (b) CFM25 ceramics at 300 K.

B. Electrical characterization

Arrhenius plots for the total conductivity of CFG15 and CFM25 materials are compared in Fig. 5a with that for a $CoFe_2O_4$ ceramic material with similar microstructure. In the case of Ga substitution, a distinctive decrease of conductivity takes place with no change of activation energy. This then reflects a decrease of the concentration of charge carriers that are likely holes. Electrical conduction in CFO is known to occur by a Verwey's hopping mechanism between Fe^{2+}/Fe^{3+} at the octahedral B-sites of the inverse spinel, with activation energies ranging from 0.55 and 0.66.^{44,45} Bulk and grain boundary contributions were obtained, and both decreased with Ga substitution (see Fig. 5b). It is remarkable that room temperature conductivity decreases two order of magnitude as a result of the Ga substitution. This is very advantageous for particulate composites, for which the finite conductivity of the magnetostrictive component greatly hinders the electrical poling of the piezoelectric matrix.

In the case of CFM25, a more complex scenario appears. Two differentiated regimes are

FIG. 5. Arrhenius plots for (a) the total conductivity of CFG15, CFM25 and CoFe_2O_4 (CFO) ceramic materials and (b) the bulk and grain boundary (GB) contributions for CFG15 and CFM25.

found. At high temperature, and analogously to that discussed for CFG15, conductivity decreases with Mn substitution with no change of activation energy. However, at low temperature, a new mechanism with lower activation energy is apparent. As a consequence, and differently to the case of CFG15, room temperature conductivity is similar to that of CFO. Unlike Ga, Mn has a strong tendency to be in multivalent states. For instance Mn^{4+} has been found in multiferroic BiMnO_3 -based perovskite solid solutions resulting in high conductivity.⁴⁶ However, partial oxidation of Mn^{3+} into Mn^{4+} in that case was driven by cation vacancies resulting from Bi_2O_3 volatilization, whose formation in the current case is not clear. Bulk and grain boundary contributions were also obtained, and the new mechanism was found to be a grain boundary effect (see Fig. 5b). Grain boundaries are known to be a place for accumulation of defects, so it is feasible that cation vacancies exist at the boundaries as a result of grain growth processes.

C. Potential for ME composites: analytical calculations

Magnetic field dependence of $q_{11} + q_{21}$ enable us to make a series of analytical calculations of the transverse ME coefficient α_{31}^E as a function of the magnetic field for bilayer composite structures constituted by either CFG15 or CFM25 and different piezoelectric phases, among the most topical ones. Three ferroelectric materials were considered: state-of-the-art lead zirconate titanate (PZT)⁴³ as a reference, and $(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}Nb_{0.8}Ta_{0.2}O_3$ (LKNNT)^{47,48} and $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$ (BCZT)⁴⁹ as examples of the two families of lead-free ferroelectrics that currently concentrate most attention.

Caution must be taken when using effective piezomagnetic coefficients obtained from quasistatic magnetostriction measurements. It has been recently shown the strain derivative calculated from strain-field curves so obtained is not the appropriate parameter to describe dynamic deformation under alternate driving for semi-hard materials such as cobalt ferrite.⁵⁰ Instead, effective piezomagnetic coefficients directly obtained from dynamic magnetostriction measurements, which are consistently lower than quasistatic ones, must be used to calculate ME coefficients, as shown in Ref. 50. Dynamic piezomagnetic coefficients can reach up to 70 % of the quasistatic ones under optimized ac and bias magnetic fields.⁵⁰ Therefore, transverse ME coefficients α_{31}^E in this work were calculated using 70 % of the $q_{11} + q_{21}$ data in Fig. 4.

Fig. 6 shows these calculations for bilayer composites formed by a piezoelectric phase: PZT⁴³, LKNNT^{47,48} or BCZT⁴⁹, and a magnetostrictive phase: CFG15 or CFM25. Eq. (1) and $0.7 \times (q_{11} + q_{21})$ data were used for the calculation. Also, a perfect interface coupling ($k=1$) and $\nu=0.5$ were considered. Compliances for CFG15 and CFM25 were taken as that for cobalt ferrite, $s_{11} = 6.5 \times 10^{-12} m^2/N$, $s_{12} = -2.4 \times 10^{-12} m^2/N$.⁵¹ All the simulated composites with lead-free piezoelectric phases show maximum α_{31}^E values larger than 0.3 $Vcm^{-1}Oe^{-1}$. Indeed, LKNNT- and PZT-based composites have similar ME response, in spite of a difference of 45 % between their piezoelectric coefficients (d_{31}). This is due to the lower dielectric permittivity and elastic constants of LKNNT when compared with PZT, which compensates the drop in piezoelectric response. Regarding BCZT-based composites, they present the highest ME coefficients, being 0.52 and 0.82 $Vcm^{-1}Oe^{-1}$ with CFG15 and CFM25 phases, respectively. These values are significantly larger than those of PZT-based composites (0.35 and 0.56 $Vcm^{-1}Oe^{-1}$ with CFG15 and CFM25 phases, respectively),

FIG. 6. Transverse magnetoelectric coefficient α_{31}^E , calculated from Eq. (1) at 300 K, as a function of bias magnetic field (H) for bilayer composites formed by a piezoelectric phase: lead zirconate titanate (PZT),⁴³ $(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}Nb_{0.8}Ta_{0.2}O_3$ (LKNNT),^{47,48} or $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$ (BCZT)⁴⁹ and a magnetostrictive phase: (a) CFG15 or (b) CFM25.

which demonstrates the potential of this combination of magnetostrictive and piezoelectric materials to be used for the design of lead-free ME composites with high performance. Specifically, CFM25-based composites show maximum α_{31}^E coefficients higher than those including the CFG15 phase.

Fig. 7a provides a comparison among the transverse ME coefficients α_{31}^E , calculated from Eq. (1) ($k=1$), of bilayer composites formed by piezoelectric BCZT⁴⁹ and different magnetostrictive phases including CFG15, CFM25 and $(Ni_{0.8}Zn_{0.2})Fe_2O_4$ (NZFO),¹⁵ as a function of the piezoelectric volumetric fraction ν . The latter magnetic oxide was considered as a good alternative to be used in lead free ME composites because its high magnetoelastic coupling.^{15,16} Both composites containing the optimized magnetostrictive phases of this work (BCZT/CFG15 and BCZT/CFM25) showed a higher response than the BCZT/NZFO one. This result evidences the effectiveness of the Ga and Mn doping in CFO for decreas-

FIG. 7. Transverse ME coefficient α_{31}^E , calculated from Eq. (1) ($k=1$) at 300 K, as a function of the volumetric fraction of the piezoelectric phase (ν) for (a) bilayer composites formed by piezoelectric $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (BCZT)⁴⁹ and the magnetostrictive phases CFG15, CFM25, and $(\text{Ni}_{0.8}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$ (NZFO) and (b) a bilayer composite CFM25/BCZT with different interface coupling parameter k .

ing the magnetic anisotropy and, consequently, enhancing piezomagnetic response. It must be remarked, as mentioned previously, that composites incorporating cobalt-based ferrites generally show ME coefficients lower than those using nickel-based ones.

Finally, Fig. 7b shows the dependence of the transverse ME coefficient, calculated from Eq. (1), for the bilayer composite CFM25/BCZT with different interfacial couplings. This is important because obtaining good interface coupling in real composites is generally very difficult. Maximum α_{31}^E value decreases when k decreases, as expected. Nevertheless, a relatively high value of $0.2 \text{ Vcm}^{-1}\text{Oe}^{-1}$ remains, even for couplings as low as 0.2. Note that the piezoelectric fraction for maximum response shifts towards higher values when k is decreased. Indeed, this might be behind the relatively low α_{31}^E value of $10.7 \text{ mVcm}^{-1}\text{Oe}^{-1}$ reported for a bonded BCZT/CFO bilayer composite with $\nu=0.5$ in off-resonance condition.⁵² Results in this work might guide researchers to tailor the composition of the magnetostrictive phase (CFM25 or CGF15 instead of CFO) and geometry (piezoelectric volume fraction) with respect to those used in Ref. 52, which should result in a considerably larger ME response.

Note that analytical calculations in this work refer to bilayer composites, and it is well

known that multilayer configurations (three layers or more) show larger ME responses.^{14,52} Besides, ME coupling in 1-3 composite structures is considerably stronger than in laminated ones because response arises from d_{33} and q_{11} instead of d_{31} and $q_{11} + q_{21}$,¹⁵ and, d_{33} and q_{11} are known to be greater compared than d_{31} and $q_{11} + q_{21}$, respectively. In fact, the large q_{11} value showed by the CFG15 composition suggest it to be an excellent candidate for magnetostrictive phase in 1-3 ME composites.

Furthermore, 0-3 ME composites are also extensively being investigated, for they have advantages such as simplicity of the sintering process and easy tuning of ME properties by modifying starting particles and processing parameters. Issue here is poling, because the current leakage due to the low resistivity in the magnetostrictive phase makes the electric poling quite difficult. In this way, the highly decreased conductivity of CFG15 is very appealing, while α_{33}^E is relevant again.

IV. SUMMARY AND CONCLUSIONS

Highly dense Ga- and Mn-doped ceramics with large grain size and uniform microstructure have been obtained, and their functionality as magnetostrictive phase of ME composites has been assessed. Both magnetic and electrical characterizations have been carried out. $CoMn_{0.25}Fe_{1.75}O_4$ and $CoGa_{0.15}Fe_{1.85}O_4$ ceramics showed the largest effective piezomagnetic coefficient q_{11} , with maximum values of $2.7 \times 10^{-6} \text{ kA}^{-1}\text{m}$ and $3.9 \times 10^{-6} \text{ kA}^{-1}\text{m}$, respectively. The last number entails an enhancement of 390 % with respect to pure cobalt ferrite and it is among the highest values reported for cobalt ferrite-based ceramics. This characteristic may be particularly important to develop 1-3 and 0-3 composites with high ME coupling. Indeed, CFG15 might be especially suitable for 0-3 materials, because it also shows a strongly reduced conductivity as compared with CFO. On the contrary, CFM25 is more suited for 2-2 composites, for which the parameter $q_{11} + q_{21}$ rather than q_{11} is relevant. Besides the layered configuration highly facilitates poling. Analytical calculations of the transverse ME coefficient α_{31}^E for bilayers including these magnetostrictive phases with enhanced response and selected lead-free ferroelectrics demonstrate their high potential for their use in the design of new lead-free ME composites with high performance. Specifically, laminated composites formed by piezoelectric BCZT and magnetostrictive CFM25 phases could reach α_{31}^E values as high as $0.8 \text{ Vcm}^{-1}\text{Oe}^{-1}$, obtained by analytical calculation from

the magnetostrictive material parameters here obtained and piezoelectric coefficients from literature.

SUPPLEMENTARY MATERIAL

See supplementary material for XRD patterns and SEM micrographs of CFG and CFM compositions.

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