Converse magnetoelectric effect in CoFe₂O₄–BaTiO₃ composites with a core–shell structure

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Abstract

Multiferroic composites were prepared by covering CoFe₂O₄ nanoparticles with a shell of BaTiO₃ using a sol–gel technique. Scanning probe microscopy confirmed the formation of a core–shell structure with a magnetic core and a piezoelectric shell. The converse magnetoelectric effect was studied at different temperatures and bias fields. The magnetoelectric coefficient peaks at approximately 270 K and reaches the value $\alpha_H \approx (2.2 \pm 0.1)10^{-11}$ s m^{-1}, which surpasses those reported previously for similar structures. A change of the sign of the magnetoelectric coefficient observed for an increasing magnetic bias field is related to the non-monotonic field dependence of magnetostriction in polycrystalline CoFe₂O₄.

Q.2   (Some figures in this article are in colour only in the electronic version)

1. Introduction

The last decade has seen a growing research interest in materials exhibiting the magnetoelectric (ME) effect [1–3]. It describes the cross-linking dependence of the magnetization, M, and polarization, P, on applied electric, E, and magnetic, H, fields, respectively [4]. The ME effect is expected to be large in multiferroic materials, where two different ferroic states, e.g. ferroelectricity and ferromagnetism, coexist [1]. Single phase multiferroics are quite rare [5] and usually show a reasonably large ME effect only far below room temperature [6]. Therefore, a vast number of research activities have been focused on heterogeneous composite materials, where an artificial ME coupling is engineered between the order parameters of ferroelectric and ferromagnetic components, which separately do not permit the ME effect [3]. The most popular approach is based on a combination of piezoelectric and magnetostrictive compounds [2]. An external electric field applied to the composite will induce a mechanical strain in the piezoelectric constituent transferred at interfaces to the magnetostrictive component, where it induces a change of the magnetization. Analogously, an applied magnetic field results in a change of the polarization in the piezoelectric constituent. The magnitude of the ME effect in composites is substantially larger than in single phase multiferroics [3]. It depends not only on the corresponding mechanical, electric, and magnetic properties of the constituents, but also on the type of connectivity. In particular, a strong ME coupling is expected in systems with relatively large, well-defined interface areas. This is the case, e.g., in composites with a core–shell structure, where a magnetostrictive core is surrounded by a piezoelectric shell. In such a configuration an insulating ferroelectric layer is supposed to prevent an electrical contact between the more conductive magnetic particles. Finite conductivity impedes poling of the composites to reach the maximal ME performance. Up to now, there have only been a few reports on investigations of the direct ME effect, $P(H)$, in core–shell structures, where the core is, e.g., formed by ferrimagnetic CoFe₂O₄ and the shell consists of ferroelectric BaTiO₃ [7–10]. The maximal ME coupling was found for compounds with a
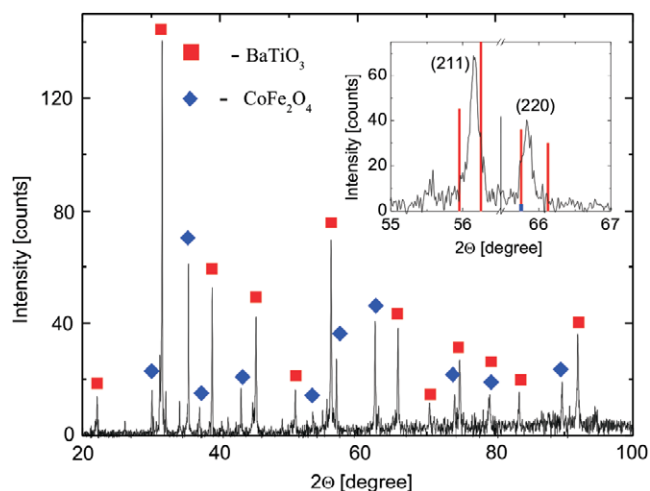
Figure 1. X-ray diffraction pattern of the $CoFe_2O_4$–$BaTiO_3$ (50/50) composite ceramics. The inset shows a magnified view in the vicinity of the (211) and (200) perovskite peaks of $BaTiO_3$.

weight fraction of 50% $CoFe_2O_4$ [7]. The value of the ME coefficient depends on the sintering conditions and is as high as 1.5 mV cm^{-1} Oe^{-1} [7] and 3.5 mV cm^{-1} Oe^{-1} [9] at room temperature.

In the present paper we report on the magnetoelectric characterization of a similar $CoFe_2O_4$–$BaTiO_3$ composite synthesized by a sol–gel route. The core–shell structure of our samples was verified by scanning probe microscopy measurements. The converse ME effect, $M(E)$, has been investigated as a function of temperature and external electric and magnetic fields.

2. Experimental details

The composite ceramic samples were prepared using a sol–gel route. Barium acetate was mixed with titanium (IV) isopropoxide and glacial acetic acid at 90 °C to form a sol. Then $CoFe_2O_4$ powder with nominal particle size of ∼40 nm (Pi-Kem Ltd) was added in an amount to provide a molar ratio of 1:1 between cobalt iron oxide and barium titanate. Ethylene glycol was added to promote gel formation. The obtained gel was dried at 90 °C for 20 h and then calcined at 800 °C for 18 h, the heating rate was 5 °C min^{-1}. After cooling back to room temperature, the material was ground gently and pressed into discs with diameters of 5–7 mm. The ceramics were then sintered at 1200 °C in air for 12 h. For electrical measurements the electrodes were painted onto the top and bottom sides of the specimens using silver paste. The thickness of the samples was 0.4 mm.

The structural characteristics of the samples were studied by x-ray diffraction (XRD), using a Siemens D-5000 diffractometer (Cu Kα radiation). The measurements were scanned at steps of $\delta(2\Theta) = 0.01°$ with a time constant of 1 s. To address the spatial distribution of the ferroelectric and ferrimagnetic phases, piezoresponse (PFM) and magnetic force microscopy (MFM) were used, respectively. These measurements were performed using an Ntegra commercial

atomic force microscopy system (NT-MDT) equipped with an MFMR magnetic coated tip (Nanosensors). Prior to these measurements one face of the sample was polished to optical quality.

The electric field dependence of the polarization was measured at room temperature using a home-built Sawyer–Tower circuit. The dielectric permittivity of the ceramics was measured using a Solartron 1260 impedance analyzer with dielectric interface 1296. The samples were placed in a measuring cell, where the temperature was controlled between 200 and 450 K by a Lake Shore Model 340 temperature controller. Magnetic measurements were performed using a SQUID magnetometer (Quantum Design MPMS-5S) in the temperature interval from 4.5 to 300 K at magnetic fields up to 5 T. Magnetoelectric measurements were performed using a modified SQUID ac susceptometer [11], where the first harmonic of the ac magnetic moment induced by an external ac electric field is measured.

3. Results and discussion

The x-ray diffraction pattern (figure 1) of the sample confirms the presence of both the perovskite and spinel phases corresponding to $BaTiO_3$ and $CoFe_2O_4$, respectively. No traces of other phases have been found. Peaks corresponding to the perovskite phase are not split as they should be for bulk $BaTiO_3$ at room temperature (see the inset in figure 1), which is usually tetragonal at this temperature. This indicates that either the tetragonal distortion of the unit cell is small or the $BaTiO_3$ in the studied composite is in its paraelectric cubic state.

Figure 2 shows typical piezoresponse and magnetic force microscopy images of the studied samples. Images are presented in false color code, where bright and dark colors correspond to regions with positive and negative response, respectively, while an intermediate contrast indicates regions with a negligible response. Bright contrast on the PFM image indicates piezoactive regions attributed to the $BaTiO_3$ phase (figure 2(b)). They appear on the perimeters of the non-piezoactive (brownish) areas. The latter, in turn, show a distinct dark and bright contrast on the MFM image corresponding to the magnetic domains of opposite polarity (figure 2(c)). Therefore, they represent the $CoFe_2O_4$ phase. These magnetic regions have sizes of a few microns indicating strong agglomeration of the initial $CoFe_2O_4$ nanoparticles. These scanning probe microscopy studies confirm a core–shell-like structure of the investigated samples, where the core is formed by agglomerates of ferrimagnetic nanoparticles and the shell consists of a piezoelectric phase. At the same time, the non-zero PFM response proves that the $BaTiO_3$ component of our composite is in the ferroelectric state.

The temperature dependence of the dielectric permittivity, ε, measured at 100 kHz is shown in figure 3(a). The dielectric permittivity exhibits a broad peak around 318 K and then continuously reincreases upon heating starting from $T \sim$ 350 K. At the same time, the dielectric losses also increase on heating (figure 3(b)) reaching tg$\delta \approx 0.8$ at 410 K. We attribute the increase of both ε and tgδ at higher temperature to an enhanced contribution from Maxwell–Wagner relaxation
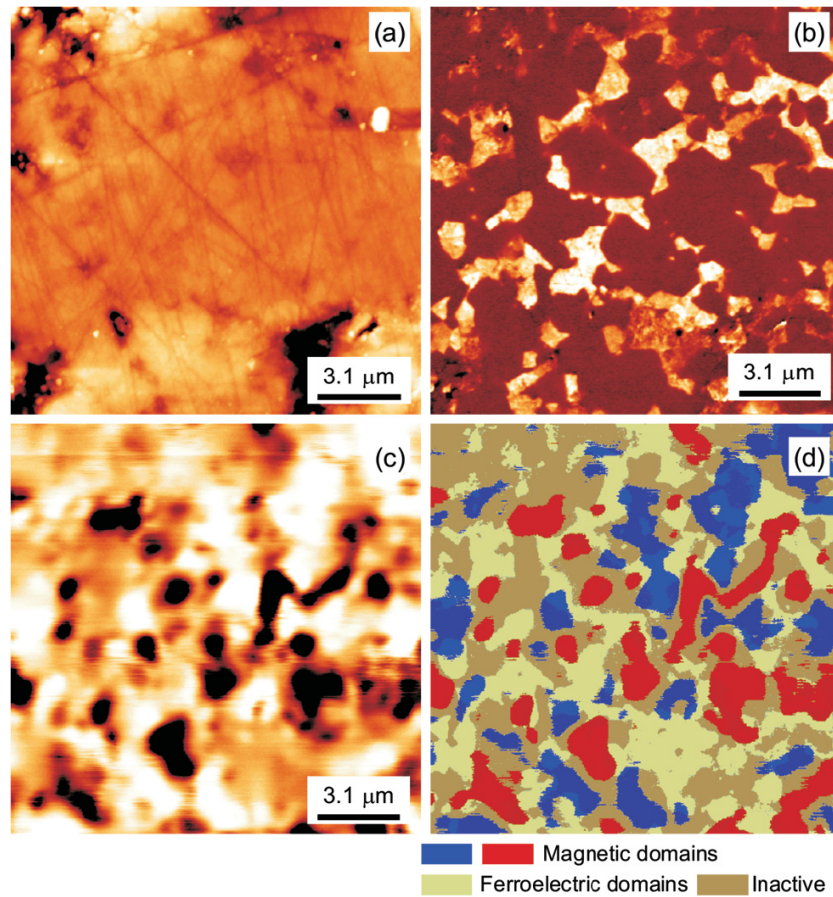
Figure 2. Typical topography (a), piezoresponse (b), and magnetic (c) force microscopy images taken on a surface of the CoFe$_2$O$_4$–BaTiO$_3$ (50/50) composite ceramics; (d) a reconstructed distribution of piezoelectric and magnetic regions.

of charges accumulated at the CoFe$_2$O$_4$–BaTiO$_3$ interfaces. This contribution becomes substantial at lower frequencies providing the growth of the relative dielectric permittivity from 360 at 100 kHz to 9100 at 1 Hz (not shown). The polarization hysteresis loops measured at room temperature are typical for leaky dielectrics (see the inset in figure 3(a)). No saturation of the polarization was reached, the remanent polarization, $P_r \approx 1\ \mu$C cm^{-2}, is rather small in comparison to that of bulk BaTiO$_3$ [12]. It seems that the relatively small resistivity of the studied composites ($\rho_{DC} \sim 1.5 \times 10^7\ \Omega$ m) prevents an effective poling of the samples.

The data witness the formation of a core–shell-type composite with a magnetic core and a ferroelectric shell. An average core diameter of a few micrometers is obtained. It is much larger than would be expected for the starting CoFe$_2$O$_4$ powder with a mesh size of ∼40 nm. Probably, the nanoparticles are partly agglomerated in the starting powder already. Further sintering of the cobalt ferrite nanoparticles to micron-sized entities takes place in the course of sample preparation. One may expect that the relatively large magnetic particles cannot be effectively covered with an insulating BaTiO$_3$ shell to fully prevent percolation between them. Once we have an infinite CoFe$_2$O$_4$ cluster, the total resistance of the composite will be determined by the resistance of the more conductive phase, cobalt ferrite in our case. This

consideration can explain the leaky character of the observed $P(E)$ hysteresis loops and the difficulties in poling the samples.

Figure 4 shows the temperature dependence of the electrically induced magnetization. The measurements were performed on cooling from room temperature at an ac electric field with amplitude $E_{AC} = 250$ V cm^{-1} and a superimposed dc magnetic field $\mu_0 H_{DC} = 0.15$ T. Prior to the measurements, the sample had been kept under a constant electric field of ∼25 kV cm^{-1} for 30 min to ensure at least partial poling. The magnetoelectric response rises at decreasing temperature and reaches a maximum at approximately 270 K. On further cooling the ME signal decreases and finally vanishes at ∼200 K. Figure 5(a) shows the dc electric field dependence of the magnetoelectrically induced magnetization at $T = 280$ K. The measured signal increases approximately ten times when the dc electric field rises from 0 to 2.5 kV cm^{-1}. On the one hand, the superimposed dc electric field can provide a better degree of poling of the sample and thus enhances the ME response. On the other hand, it is possible that a mechanical stress arising due to the dc electric bias on the BaTiO$_3$/CoFe$_2$O$_4$ interface results in an enhancement of the magnetostriction of cobalt ferrite, which in turn leads to an increase of the ME coupling coefficient. A similar effect has been reported for PZT–Terfenol-D laminates [13].
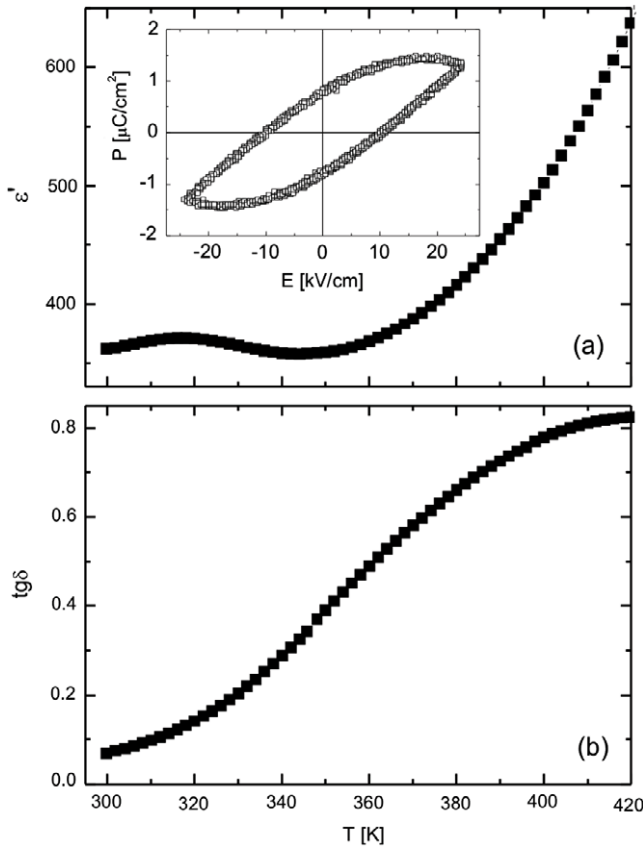
Figure 3. Temperature dependences of the dielectric permittivity (a) and dielectric loss tangent (b) of the $CoFe_2O_4$–$BaTiO_3$ (50/50) composite ceramics measured at a frequency of 100 kHz. The inset shows the electric field dependence of the polarization of the $CoFe_2O_4$–$BaTiO_3$ (50/50) composite ceramics measured at room temperature.
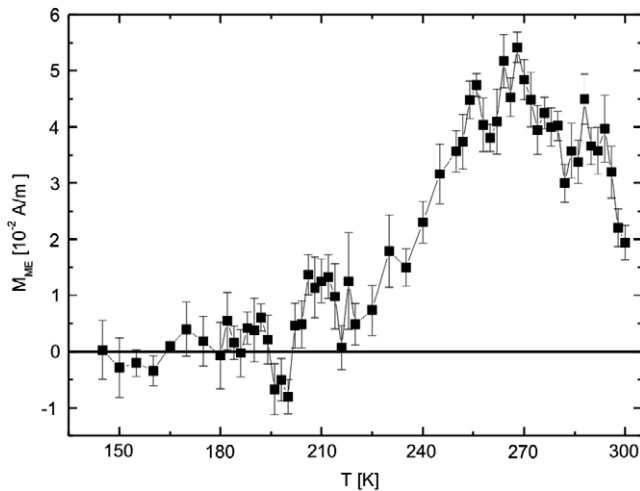

Figure 4. Temperature dependence of the electrically induced magnetic moment of the $CoFe_2O_4$–$BaTiO_3$ (50/50) composite ceramics measured at $E_{AC} = 250$ V cm^{-1}, $f_{AC} = 10$ Hz, $\mu_0 H_{DC} = 0.15$ T.

To estimate the magnetoelectric coefficient we have measured the ac electric field dependence of the induced magnetization (figure 5(b)). The observed ME response is
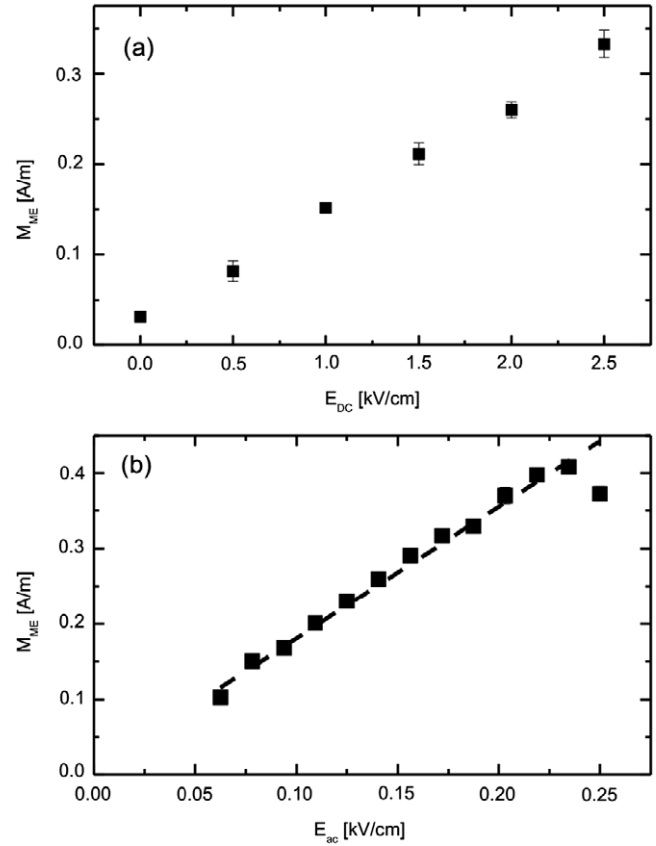

Figure 5. The dc (a) and ac (b) electric field dependences of the electrically induced magnetic moment of the $CoFe_2O_4$–$BaTiO_3$ (50/50) composite ceramics measured at $\mu_0 H_{DC} = 0.15$ T, $T = 280$ K, $f_{AC} = 10$ Hz.

linear and hysteresis free in the studied field range. The best linear fit of $M_{ME}(E_{AC})$ yields a value of the ME coefficient $\alpha_C = (2.2 \pm 0.1) \times 10^{-11}$ s m^{-1} = $(2.2 \pm 0.1) \times 10^{-5}$ G cm V^{-1}. To the best of our knowledge no data have been reported for the converse ME effect in similar composites. To compare our results with those for the direct ME effect we have estimated a link between the direct and converse ME coefficients.

For media without losses and hysteresis (linear theory) one expects to obtain the same values of the magnetoelectric susceptibility, α, for the converse and direct ME effects. Here α links the magnetoelectrically induced polarization and the applied magnetic field, $P = \alpha H$, as well as the magnetoelectrically induced magnetization and the applied electric field, $\mu_0 M = \alpha E$ [14]. In the work of Wu *et al* [15] the equivalence of the direct and converse ME coefficients has been proven also for laminate ME composites. For the direct ME effect in composites the ME voltage coefficient, α_D, is usually reported: $\alpha_D = dE/dH = \alpha/\varepsilon_0\varepsilon$. Correspondingly, for the converse ME effect in composites the coefficient α_C is reported: $\alpha_C = dB/dE = \alpha$. The coefficient for the direct ME effect can thus be estimated as $\alpha_D = \alpha_C/(\varepsilon_0\varepsilon) \approx$ 6.7 mV cm^{-1} Oe^{-1} for an intrinsic value of $\varepsilon = 300$. The value of α_D thus obtained is comparable to those reported earlier for similar core–shell composites [7, 8].
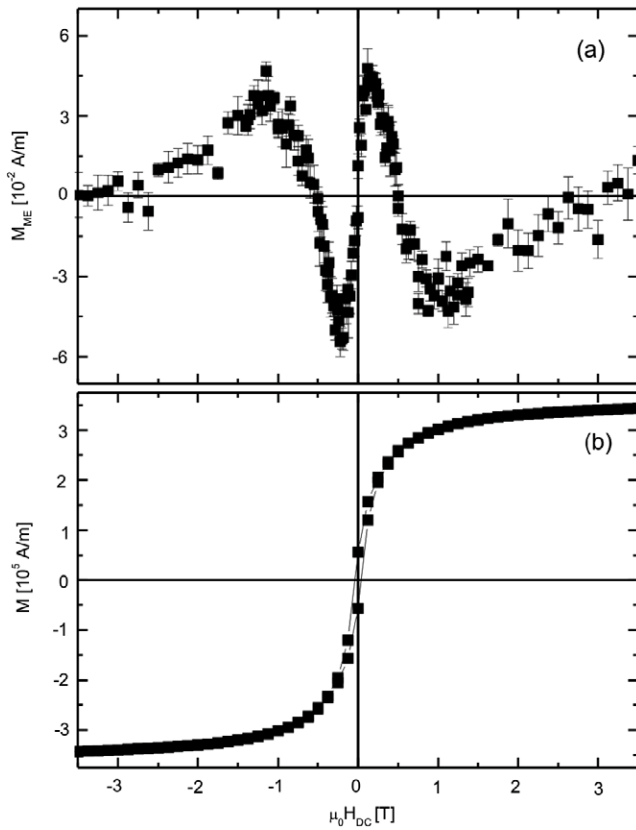
Figure 6. (a) Magnetic field dependence of the electrically induced magnetic moment of the $CoFe_2O_4$–$BaTiO_3$ (50/50) composite ceramics measured at $E_{AC} = 250$ V cm^{-1}, $f_{AC} = 10$ Hz, $T = 280$ K.

Figure 6(a) shows the ME response measured at 280 K as a function of an external dc magnetic field at zero dc electric field. The measured signal is initially growing for an increasing magnetic field in the range $0 < \mu_0 H_{DC} < 0.15$ T, then starts to decrease, changes the sign at $\mu_0 H_{DC} \sim 0.5$ T, reaches the maximal negative value at $\mu_0 H_{DC} \sim 1$ T, and then increases again, approaching zero at $\mu_0 H_{DC} > 3$ T. While a peak of the magnetoelectric response at a moderate magnetic field has been reported for some multiferroic composites, e.g. for laminated systems [16], a change of the sign of the ME signal has rarely been observed. In particular, it was reported for direct magnetoelectric measurements of $CoFe_2O_4$–$BaTiO_3$ core–shell structures [8]. In that case, the magnetoelectric coefficient, $\alpha_C(H)$, peaks at $\mu_0 H_{DC} \sim 0.25$ T and changes sign at $\mu_0 H_{DC} \sim 0.65$ T. This change of the sign of the ME response cannot be directly related to the magnetization switching which occurs at much smaller magnetic field (figure 6(b)).

To explain the shape of the $M_{ME}(H)$ dependence we should take into account that the electrically induced magnetization is $M_{ME} \sim q_l d_l E$ for mechanically coupled composite multiferroics, where E is the applied electric field, d_l is the longitudinal piezoelectric coefficient of the ferroelectric phase, and q_l is a piezomagnetic coefficient of the magnetic phase [15]. Thus, the ME response essentially tracks the H_{DC} dependence of the piezomagnetic coupling coefficient. The latter can be defined as $q_l = \delta\lambda/\delta H$, where λ is the

magnetostrictive strain [17]. For the polycrystalline $CoFe_2O_4$ the magnitude of the longitudinal magnetostriction exhibits a non-monotonic field dependence, reaching a maximal value approximately at 0.3 T for bulk [18, 19]. Chen *et al* [19] related the decrease of magnetostriction above this magnetic field to a rotation of the magnetization of the particles or grains away from easy directions. For polycrystalline materials the magnetostriction can be expressed as $\lambda = (2\lambda_{100} + 3\lambda_{111})/5$ [20]. For $CoFe_2O_4$ the magnetoelectric coefficients λ_{100} and λ_{111} are negative and positive, respectively, and $|\lambda_{100}| \gg |\lambda_{111}|$ [21]. Bozorth *et al* reported on magnetic field dependences of λ_{100} and λ_{111} [21]. In particular, they showed that $\lambda_{100}(H)$ increases strongly at low magnetic fields, but is saturated above 0.4 T. At the same time λ_{111} grows continuously. Thus, for polycrystalline samples a decrease of the magnetostriction coefficient, λ, should be observed at $\mu_0 H > 0.4$ T. For nanosized materials this critical field value might be higher [9]. Correspondingly, q_l changes sign at the field corresponding to maximal magnetostriction, resulting in the reverse of the ME response. Finally, at very large magnetic field magnetostriction is saturated, and therefore the piezomagnetic and the related magnetoelectric couplings tend to zero.

Obviously, in view of this very qualitative picture one should also take into account other factors into account, such as anisotropy, domain structure, interface defects, grain boundaries, all affecting the ME coupling. Model calculations are planned to explain details of the ME coupling under core–shell symmetry. Since the value of the ME coefficient, $\alpha_E = 130$ mV cm^{-1} Oe^{-1}, obtained in the pioneering research of Boomgaard *et al* [22] on $BaTiO_3$/$CoFe_2O_4$ ceramics with preponderant rectangular symmetry remains unrivaled, it is not ruled out that the nanoparticles cannot profit from maximal coupling constants owing to the local spherical symmetry.

In summary, a magnetoelectric $CoFe_2O_4$–$BaTiO_3$ core–shell composite has been successfully prepared using a sol–gel route. The formation of a core–shell structure has been directly confirmed by scanning probe microscopy. The magnetoelectric coefficient reaches $\sim 2.2 \times 10^{-11}$ s m^{-1}, which is comparable to the highest value for analogous core–shell composites reported previously. A further enhancement of the ME response may be achieved by more efficient poling of the samples with lower resistivity. The investigation of the effect of the processing conditions on the resistivity and magnetoelectric performance of the composites is presently underway.

Acknowledgments

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