Peculiar Magnetoelectric Coupling in BaTiO$_3$:Fe$_{113}$ ppm Nanoscopic Segregations


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ABSTRACT: We report polycrystalline BaTiO$_3$ with cooperative magnetization behavior associated with the scarce presence of about 113 atomic ppm of Fe ions, clearly displaying magnetoelectric coupling with significant changes in magnetization (up to $\Delta M/M \approx 32\%$) at the ferroelectric transitions. We find that Fe ions are segregated mostly at the interfaces between grain boundaries and an Fe-rich phase, forming a self-composite with high magnetoelectric coupling above room temperature. We compare our results with ab initio calculations and other experimental results found in the literature, proposing mechanisms that could be behind the magnetoelectric coupling within the ferroelectric matrix. These findings open the way for further strategies to optimize interfacial magnetoelectric couplings.

KEYWORDS: multiferroic, magnetoelectric, BaTiO$_3$:Fe, magnetism, interfaces, autocomposite, nanoscopic segregations

1. INTRODUCTION

Multiferroic materials is one of the most prominent areas of Materials Physics research nowadays. Because of the outstanding applications that arise from magnetoelectric (ME) materials, the different types of electronic devices and sensors associated with ME materials are, in fact, desirable. However, the present knowledge about this subject is still insufficient to synthesize a device with a high enough ME coupling to be considered a breakthrough.$^{1-3}$

Intrinsic ME materials are quite rare because the usual requirements for the existence of ferromagnetism, such as the electrons of the semioccupied d orbitals, tend to be unpropitious to the off-center cations usually required by ferroelectricity.$^4$ For this reason, more and more studies are being made toward the construction of ME composites and heterostructures with both ferroelectric and magnetic materials.$^{2,4}$

This article shows noteworthy results regarding the properties of polycrystalline BaTiO$_3$ (unintentionally) doped with an overall Fe atomic concentration of about 113 ppm, derived from the reagents. Despite the tiny concentration of Fe ions in BaTiO$_3$, unequivocal cooperative magnetic behaviors are visible in the magnetization dependence on the temperature and magnetic field. This last outcome is especially counterintuitive because, for such concentrations of Fe, we would expect a dilute paramagnetic feature. However, the really remarkable result has to do with the changes found in this ordered magnetic behavior with the ferroelectric transitions of the BaTiO$_3$ matrix.

Using Raman spectroscopy, we could confirm a ME coupling between the magnetic properties and the ferroelectric phase transitions of BaTiO$_3$, which was never seen in other works where BaTiO$_3$ was doped/mixed with Fe, even in higher concentrations. This suggests that the Fe present in the matrix must be arranged in very special ways/regions.

We will discuss our experimental results and interpret them using density functional theory (DFT) simulations and experimental work found in the literature to gain insight on possible mechanisms for this ME effect.

2. EXPERIMENTAL DETAILS

The BaTiO$_3$ compound studied was prepared by a solid-state sintering method from 99.9% grade reagents TiO$_2$ and BaCO$_3$ from Merck. The heterogeneously mixed reagents had two stages of calcination (one at 700 °C and the other at 900 °C), and the resultant power was sintered at 1100 and 900 °C for about 40 and 20 h, respectively.

X-ray diffraction (XRD) was made using a Panalytical XPert Pro equipped with an X'Celerator detector and a secondary monochromator for $\lambda$ (Cu K$_\alpha$) = 1.5405(98) Å at room temperature, and Raman spectroscopy was made using a Jobin Yvon 64000 Raman
spectrometer and a 532 nm laser as incident radiation from 77 to 465 K. Magnetic measurements were made using Quantum Design MPMS-5S SQUID and MPMS3 SQUID-VSM instruments from 5 to 410 K. The scanning electron microscopy/energy-dispersive spectrometry (SEM/EDS) map was done by a Hitachi SU-70 high-resolution field-emission scanning electron micrometer equipped with a Bruker QUANTAX 400 instrument for EDS analysis. The scanning transmission electron microscopy (STEM)/EDS study was carried out by an energy-filtered 200 kV JEOL 2200FS transmission electron microscope [HR-(EF)TEM] equipped with an Oxford INCA 250 energy transmission electron microscope for elemental analysis operated at 200 kV.

3. RESULTS AND DISCUSSION

3.1. XRD. XRD was made to check the quality of growth and the phase purity of barium titanate.

Rietveld analysis of room temperature XRD data was done using the software Powder Cell 2.4 to quantify the phases present (Figure 1). The results are summarized in Table 1.

Table 1. Summary of the Rietveld Analysis of Room Temperature XRD Data

<table>
<thead>
<tr>
<th>phase</th>
<th>crystallographic system</th>
<th>symmetry group</th>
<th>lattice parameter (Å)</th>
<th>fraction (%)</th>
<th>crystallite size (nm)</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO₃</td>
<td>tetragonal</td>
<td>99</td>
<td>a: 3.9993 b: 3.9993 c: 4.0241</td>
<td>83</td>
<td>108</td>
<td>4.97</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>orthorhombic</td>
<td>38</td>
<td>a: 3.9947 b: 5.6768 c: 5.6722</td>
<td>10</td>
<td>234</td>
<td>4.97</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>orthorhombic</td>
<td>62</td>
<td>a: 6.5340 b: 5.2458 c: 8.9371</td>
<td>7</td>
<td>37</td>
<td>4.97</td>
</tr>
</tbody>
</table>

Two different phases of barium titanate, 83% of tetragonal BaTiO₃ and 10% of orthorhombic BaTiO₃, were detected, both with a crystallite size of >100 nm. This phase mixing emerges from the shifting in the temperature of the phase transitions in certain grains. All impurity peaks belong to BaCO₃ in a 7% fraction. However, its presence does not interfere with the BaTiO₃ ferroelectric properties.

3.2. Magnetic Studies. Figure 2 shows the temperature-dependent magnetization plot of BaTiO₃. One would expect a purely diamagnetic behavior, while we instead observe two magnetic anomalies at high temperatures and paramagnetic behavior at low temperatures.

Both anomalies occur above room temperature, around 325 K (the major one) and around 373 K (the minor one), signaling the existence of two different cooperative behavior changes in this temperature range, where two ferroelectric phase transitions of BaTiO₃ are known to occur.

At about 55 K, we observe a local maximum, which is attributed to the paramagnetic ↔ antiferromagnetic transition of O₂ due to an air leak in the SQUID sample chamber (as reported by the manufacturer). Chemical analysis was performed, resorting to PIXE spectroscopy. The results are presented in Table 2, showing 113 ppm of Fe content, which can justify the peculiarities of the magnetic curve of Figure 2. The Fe presence can be justified by a possible 60 ppm Fe concentration in the reagents, as indicated in the specifications.

As a further examination of the low-temperature magnetization of Figure 2, we separated the observed paramagnetic behavior in the field-cooled curve, fitting a Curie curve according to eq 1 in the interval T ∈ [5, 300] K, where the second term accounts for the curvature of the temperature dependence of the ordered part (as spin waves). We also excluded the points of the O₂ peak and neighboring points to have an adequate Curie fit.

\[ M = \frac{C}{T} + AT^{3/2} + B \]

Figure 3 shows the paramagnetic contribution to the magnetization, obtained using eq 1 and the remaining contribution due to cooperative phenomena.

From the Curie constant, we can obtain the product NJ(J + 1), which can be written as NS(S + 1), assuming the orbital quenching of Fe ions. Taking these considerations into account, we find that if the Fe ions are in the Fe³⁺ valence (J = S = 5/2),
we have about 39 ppm of diluted paramagnetic ions, or if they are in the Fe$^{2+}$ valence ($S = 2$), we have about 56 ppm of dilute paramagnetic ions, leaving 74 or 57 ppm respectively in ordered magnetic phase(s). Using spontaneous magnetization models, representing the magnetization of Figure 3 as $[M - M_S]^2$ versus $T$ (inset) enables us to determine the $T_C$ values of the magnetic transitions. For the lower-temperature transition, using $M_S \approx M(350 \text{ K})$ and fitting the linear part of the data of the inset of Figure 3, we can obtain $T_C \approx 328 \text{ K}$. Analogously, using a $M_S \approx M(400 \text{ K})$, we obtain $T_C \approx 373 \text{ K}$ for the higher-temperature transition.

Figure 4 presents the low-field detail of the magnetic field dependence measured at temperatures from 10 to 400 K, between $\pm 50 \text{ kOe}$ (5 T) (only in the decreasing field branch). The values are normalized to the Fe weight after subtracting the diamagnetic component of its host matrix (obtained at $T = 400 \text{ K}$).

The saturation value of the magnetization (measured at $T = 5 \text{ K}$ and $B = 5 \text{ T}$) agrees with the Fe concentration obtained by PIXE spectroscopy.

Figure 4 shows that there are temperature-dependent remanent magnetizations and coercive fields (that can reach about 170 Oe at 10 K). The dependence of the remanent magnetization with the temperature is displayed in the inset of Figure 4.

We can observe that the transitions seen in Figure 3 are indeed related to spontaneous/remanent magnetization changes and not single susceptibility changes. Spontaneous magnetization changes are quite significant, reaching $\Delta M / M \approx 14\%$ for the high-temperature magnetic transition and $\Delta M / M \approx 32\%$ for the lower-temperature transition.

3.3. Raman Spectroscopy Study. The two magnetic anomalies detected around 325 and 373 K are suspiciously near of the BaTiO$_3$ ferroelectric phase transitions (273 and 393 K). To analyze the correlation of the magnetization anomalies with the BaTiO$_3$ ferroelectric properties, Raman spectroscopy measurements were performed in the range 250$–$760 cm$^{-1}$ (shown in Figure 5).

Figure 5 shows the temperature dependence of two Raman-active vibrational modes, 520 cm$^{-1}$ [E(TO) + A$_1$(TO)] and 487 cm$^{-1}$ [E(LO) + A$_1$(TO) + E(TO)]. These are the most adequate vibrational modes to identify the ferroelectric phase transitions of BaTiO$_3$. In particular, the 487 cm$^{-1}$ mode is known to vanish in the orthorhombic $\rightarrow$ tetragonal transition. This was confirmed by the observation of a reference sample, a BaTiO$_3$ single crystal purchased from MaTeck and whose 487 cm$^{-1}$ mode disappears around the typical orthorhombic $\rightarrow$ tetragonal transition temperature (Figure 5).

We first analyze this 487 cm$^{-1}$ mode, which is seen to vanish around 320 K, allowing us to determine when BaTiO$_3$ is exclusively in its tetragonal phase. For this reason, we relate the magnetic anomaly seen around 325 K (Figure 2) with the BaTiO$_3$ orthorhombic $\leftrightarrow$ tetragonal transition.

It is also perceptible that around the temperature where this mode disappears in the single crystal there is an accentuated decrease in the intensity of the polycrystalline sample. This suggests that a portion of the sample has already changed its phase to the tetragonal structure, in good agreement with room temperature XRD, which shows the coexistence of both BaTiO$_3$ phases.

As we can see from analysis of the 520 cm$^{-1}$ mode, its energy decreases gradually as the temperature increases, with abrupt changes at some temperatures, which can be more easily

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Figure 3. $M(T)$ of BaTiO$_3$ with 113 ppm of Fe showing the ordered and paramagnetic behaviors as two separate components. Inset: $[M - M_S]^2$ versus $T$ around the 325 K magnetic anomaly.

Figure 4. Magnetic field dependence of the BaTiO$_3$:Fe magnetization for several temperatures (the diamagnetism of BaTiO$_3$ was subtracted). Inset: remanent magnetization dependence with temperature.

Figure 5. Temperature dependence of the Raman-active modes near 520 and 487 cm$^{-1}$ of polycrystalline BaTiO$_3$ and a BaTiO$_3$ single-crystal reference.
detected in the $\partial E/\partial T$ plot. The most evident is indubitably the one around 380 K, which we can associate with the magnetic anomaly seen around 373 K and suspect is due to the tetragonal $\Leftrightarrow$ cubic transition.

The intensity of the 487 cm$^{-1}$ vibrational mode (area plot of Figure 5) shows that around 192 K the intensity starts to decrease, which is a characteristic of the rhombohedral $\Leftrightarrow$ orthorhombic transition (which matches with anomalies in the $S20$ cm$^{-1}$ mode around the same temperature). The faint (and broad) anomaly in the magnetization $M(T)$ curve near 190 K may be related to this.

Combining all of the magnetic measurements with Raman spectroscopy, we can therefore conclude that we are before an above room temperature ME multiferroic compound. Using the same methodology as Duan et al., relating the magnetization above room temperature ME multiferroic compound. Using the spectroscopy, we can therefore conclude that we are before an may be related to this.

Because we observe a magnetically ordered behavior, we can inquire whether the existing Fe is not homogeneously distributed but instead prefers to locate partially segregated in regions that favor cooperative magnetic interactions, instead of remaining dispersed in the BaTiO$_3$ matrix.

To infer this conjecture, a detailed SEM/EDS mapping was performed. Because of the lower limit of detection of the EDS technique being well above the 113 ppm obtained in PIXE, we performed. Because of the lower limit of detection of the EDS technique being well above the 113 ppm obtained in PIXE, we would detect Fe using EDS only if the Fe was actually in a heterogeneous arrangement.

We measured 103 regions, each with an area of about 1150 $\mu$m$^2$, finding an expected value of the Fe concentration of $\bar{x} \approx 0.068\%$ and $\bar{\sigma} \approx 0.022\%$. The 20 areas represented by pink dots in Figure 6 signal the regions where Fe was detected with a $3\sigma$ confidence, where these ions tend to congregate.

Figure 6 presents the observed Fe concentration distribution. Comparing the statistical display of the results obtained in the EDS map with an analogous random distribution, we can confirm that the Fe ions are not distributed randomly, favoring certain locations to coalesce in higher concentrations.

The statistical distribution of the Fe concentration obtained experimentally suggests a superposition of two distributions, one leading to a Poisson distribution with $\lambda = 0.39\%$, associated with the homogeneous paramagnetic ions and the precision of the measurement, and an inhomogeneous distribution of Fe. We should stress that the probability of finding both the 8% and 9% concentrations in such a random distribution is about 1 in $3 \times 10^{17}$.

Quantitative analysis of the excess values of the real Fe distribution, compared with the Poisson distribution, shows that about 82% of Fe belongs to the inhomogeneous cooperative distribution and 12% belongs to the random paramagnetic arrangement. This result corroborates the estimate made from the paramagnetic behavior of higher Fe concentration in the ordered phase, closer to the $S = \frac{5}{2}$ scenario.

There are several studies demonstrating the tendency for the Fe ions to diffuse into specific places. Figueiredo et al. showed that in CaTiO$_3$, a perovskite similar to BaTiO$_3$, Fe ions tend to diffuse to the grain boundaries, resulting in core–shell-structured grains in which the core is constituted of practically pure CaTiO$_3$ and the shell is an Fe-rich phase of CaTi$_{1-x}$O$_x$Fe$_x$.

This kind of evidence is also observed in La$_{0.95}$Sr$_{0.05}$Ga$_{0.90}$Mg$_{0.10}$O$_3$ (LSGM) ceramics, where once again, we can perceive that Fe ions tend to accumulate in the grain boundaries ($\leq 1\%$), whereas the interior of the grains maintain an approximately Fe-free LSGM composition. Such an effect behaves differently depending on parameters such as the grain size and thermal treatments; it is perceptible that for a high enough thermal treatment the Fe dilutes homogeneously all over the sample. We have confirmed this behavior through thermal treatments to our polycrystalline BaTiO$_3$, observing that above 1300 $^\circ$C heat treatment the Fe dilutes throughout the sample, showing a paramagnetic-like magnetization curve.

Ion implantation of 1% Fe was made in a region of 1.5 $\times 10^{-3}$ mm$^3$ (5 mm $\times$ 3 mm $\times$ 100 nm) of a BaTiO$_3$ single crystal to ascertain the importance of the grain boundaries in the ME effect that we report. Despite the higher concentration of Fe ions, the $M$–$T$ curve was paramagnetic-like and did not show any sensibility to the barium titanate phase transitions. On the other hand, Borges et al. have implanted 4% Fe concentration in BaTiO$_3$ (in a region identical with the one implanted by us), but even so, no substantial ME coupling was reported apart from a small thermal hysteresis perceptible around the ferroelectric phase transitions ($\Delta M/M \leq 2.8\%$). A similar study was performed using Co-implantation into a BaTiO$_3$ single crystal and showed the coexistence of magnetic Co nanoclusters and ferroelectric properties, although the effect of the ferroelectric transitions on the magnetic properties was not studied.

Such results suggest a preponderant role of the grain boundaries on Fe segregation.

To validate that some interfaces between grain boundaries play a meaningful role in the reported ME coupling, a thorough STEM/EDS study was performed to analyze the element distribution in more confined scales.

Figure 7a shows an STEM image of a BaTiO$_3$ grain and the grain boundaries with its neighbors. EDS analysis was performed along a line of points across the grain boundary, labeled from 1 to 9, each one separated by about 13 nm.
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In Figure 7b, the EDS results for Fe, Ba, and Ti are presented. One can clearly observe a sudden variation of the Fe concentration from about 0% to about 0.09%. This increase happens exactly at the grain interface, as can be seen in points 5–7 of Figure 7a.

Fluctuations in the concentration are observed, resulting from σ ≈ 0.037% of each individual analysis’ fit. It is clear that the increase of the Fe concentration at the interface is well beyond statistical uncertainties.

On the other hand, the relative variation of the Ti and Ba concentrations fluctuates around the average, hence indicating that BaTiO3 is homogeneous.

We are therefore led to infer that Fe is not homogeneously distributed but partially present at the interfaces between grains. These are large enough to support cooperative magnetic behavior, in close contact with the BaTiO3 matrix, supporting the observed ME coupling.

3.5. Comparison with Literature’s DFT Calculations and Experimental Results. Our results show that we are before a quite peculiar type of BaTiO3:Fe with a close entanglement between the magnetic and ferroelectric properties. However, the observed mechanism behind the ME coupling is still unclear.

Because Fe is strongly correlated with the BaTiO3 matrix, it is quite improbable that this ferromagnetic element is in its metallic form, being instead in an oxidized Fe,Ti,Ba configuration.

As a matter of fact, much experimental and ab initio evidence demonstrates that an electric displacement (D) creates a buffer oxide between a Fe/BaTiO3 interface.

The creation of the oxide can be nonhomogeneous, where different D can lead to different oxide configurations (either magnetic, nonmagnetic or a mixture of both).

Experimental results show that the percentage of magnetic oxides tends to disappear for high values of D, an effect that is reversible if D is not too high, resulting in variation of the coercive magnetic field (Hc) with D.

Such effects can occur because of the inherent polarization (P) of the BaTiO3 ferroelectric domains, and therefore different oxide configurations would be present for different ferroelectric phase transitions.

Considering the hypothesis where the Fe ions are concentrated in/between grain boundaries, we could interpret this arrangement as a composite of an Fe-rich phase interface with the BaTiO3 matrix. Such composite configurations have been widely studied since Duan et al. made DFT calculations of Fe/BaTiO3 multilayers, in which the authors show a ME coupling due to the different character of the chemical bonds between the interface atoms for each possible polarization of the tetragonal BaTiO3 (P̂x and P̂z).

These multilayer DFT studies, as well as experimental ones, were also carried out by other groups, which not only studied the Fe/BaTiO3 layout but also iron oxide interfaces like the Fe3O4/BaTiO3 composite, which also exhibits ME coupling.

In these composites, polarization of the different ferroelectric phases of barium titanate induces different charge/electron densities near the interface, which leads to different kinds of hybridization between the Fe ions and BaTiO3.

For magnetite, an insulator iron oxide, the polarization effects do not suffer from screening effects, being able to enhance its influence in the local bonds of this composite. The diversity of the results suggests that a BaTiO3/Fe3O4/BaTiO3 interface may present a rich variety of relationships between the magnetic and ferroelectric properties.

Hybridization between the interface atoms usually plays a crucial role in the ME effect, and although an alteration in polarization might not modify the magnetic moments of the Fe ions themselves, the moments of the Ti and O atoms can change considerably, by either direct or indirect hybridization with the Fe atoms. For Fe3O4, in particular, the occurrence of oxygen vacancies favors the magnitude of the ME coupling, given the resulting valences and wave function distributions that arise from these vacancies.

Radaelli et al. demonstrated that the chemical bonds between barium titanate and iron oxide, namely, the Fe−O−Fe angle, will dictate the nature of the magnetic cooperative behavior in this interface. When the polarization is pointing toward iron oxide (P̂z), there will be ferromagnetic behavior, while for P̂x, the ordered phase is antiferromagnetic, which leads to one of the biggest ME couplings reported in the literature.

Figure 7. (a) Image obtained by STEM and the numbered points show the specific location where a EDS analysis was made. (b) Fe nominal concentration and Ti and Ba relative concentrations obtained from STEM/EDS analysis of the points indicated in part a. σ ≈ 0.037%
In addition to what we discuss above, we cannot exclude the contribution from strain effects that arise from the magnetostriiction caused by the piezoelectric effect native of the BaTiO$_3$ matrix inherent in the ferroelectric phase transitions or solely due to the structural changes themselves. These effects are reported experimentally to both the Fe/BaTiO$_3$ interface and the Fe$_3$O$_4$/BaTiO$_3$ interface and can be seen in the M–T curves of the interfaces, where abrupt changes in the magnetization occur. These interfaces have different misfits and distortions in the interface atoms and consequently different magnetic anisotropies.

The different polarization directions can change the chemical bonds, and therefore the magnetocrystalline anisotropy is affected. Ultimately, these alterations in the anisotropy energy between the different BaTiO$_3$ ferroelectric phases culminate in changes of the coercive fields and remanent magnetization.

According to these strains effects, one should expect a greater ME effect from the R ↔ O transition (ΔM/M ≈ 25% for the Fe/BaTiO$_3$ interface and ΔM/M ≈ 2.2% for the Fe$_3$O$_4$/BaTiO$_3$ interface).

However, in the Fe$_3$O$_4$/BaTiO$_3$ interface, Vaz et al. (Sahoo et al. for the Fe/BaTiO$_3$ interface) report that for different magnetic field variations of magnetization can be either positive or negative. This means that, for the particular situation where these interfaces would appear to be nonarbitrarily oriented, the summation could result in an insignificant change of magnetization for the R ↔ O transition, whereas in the O ↔ T transition, the result could be sizable. These observations may explain why the change in magnetization at the R ↔ O transition is mild.

4. CONCLUSIONS

In summary, we were able to relate the magnetic transitions of the polycrystalline Fe-doped (ppm range) BaTiO$_3$ with its ferroelectric phase transitions, at temperatures confirmed by analysis of the S20 and 487 cm$^{-1}$ Raman vibration modes. This unexpected ME coupling turns out to be related to heterogeneously distributed Fe-rich agglomerations that are interfacial with the BaTiO$_3$ grain boundaries.

We also discuss the mechanisms to justify the ME coupling reported, which are related to interface effects, by either strain and/or hybridization, and/or to electric displacement-mediated oxidation states of the Fe-rich phase.

BaTiO$_3$:Fe$_{113}$ ppm is a high-temperature extrinsic ME multiferroic, with very large relative magnetization changes up to ΔM/M ≈ 32% and therefore corresponding to a ME coupling of α ≈ 10$^{-2}$ G·cm/V.

This work paves the way for a new kind of extrinsic ME multiferroic that could be applied in devices/industry when mass production of optimized BaTiO$_3$:Fe nanoparticles with the same characteristics as the ones presented in this work is achieved. Their applications would be a breakthrough because this multiferroic operates well above room temperature.

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Notes

The authors declare no competing financial interest.

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