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Magnetoelectric effect probe through ppm Fe doping in $BaTiO_3$

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ABSTRACT

The nominal $BaTiO_3$ compound often exhibits an assortment of controversial magnetic signals which can be simply explained through minute presence of spurious magnetic elements in the perovskite matrix, even when this compound is synthesized from high grade Ba and Ti precursors. Proton Induced X-Ray Emission (PIXE) technique enable to confirm ~100 ppm of Fe contaminant which masks the utterly $BaTiO_3$ diamagnetism. Nevertheless, besides the expected paramagnetism of highly diluted Fe ions, it is also possible to observe a cooperative magnetic moment signature which exhibits an intricate relation with the phase transitions of the $BaTiO_3$ matrix. Such magneto-electric coupling signature is further corroborated by Raman spectroscopy, dielectric and X-ray diffraction measurements, indicating to a partial segregation of a rich Fe oxide phase, having a local structure clamped to the perovskite crystallites, hence acting as a practical probe sensitive to the local structural transitions of the host material.
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1. Introduction

The characteristic susceptibility response of pristine $BaTiO_3$ (BT) is utterly diamagnetic ($\chi_{DM} = -10^{-7}$), considering the composition based only on pure, Ba^{2+}, Ti^{4+} and O^{2-} species, corresponding to electronic configuration of ions with complete subshells and full spin-paired electrons. Nonetheless, magnetic moment measurements performed in nominal $BaTiO_3$ ceramics, thin films or single crystals, turn to be an effective method to inspect the compound's phase quality and purity. In fact, non-diamagnetic signals are often found in high graded samples and several reports over anomalous magnetic effects in nominal $BaTiO_3$ samples can be found. The origin of these signals is broadly speculated by several authors, along with hypotheses of Ti^{3+} ions or O^{2-} vacancies along grain boundaries [1–3], although these assumptions are not supported by a coherent relation between the grain features and the speculated amount of Ti^{3+}. Relevant studies consider the contingency of undesired Fe, Co, Ni contaminations as most probable source of the peculiar magnetic signals [4,5] On the other hand, the $BaTiO_3$ system has been extensively studied for deliberate magnetic elements doping ≥1%, leading to the general conclusion that these dopants inhibit the grain growth and increase current losses, hence compromising the ferroelectric properties of the perovskite phase [6]. However, unexpected and non-negligible responses can easily appear when in the presence of minimal quantities of spurious elements [7]. In the broader span of materials with multiferroic and magneto-electric effect potential, the $BaTiO_3$ system can easily exhibit more complex magnetic responses once tainted with a marginal presence of an element like Fe, or other ferromagnetic ions; whereas minimal doping (<<1%) underrates chemical deviations from parental stoichiometry [8], hence preserving the original crystalline structure and ferroelectric properties.

2. Experimental

Polycrystalline samples were prepared by conventional solid state route from stoichiometric amounts of >99% grade $BaCO_3$ and TiO_2 (*Merck*). Effective formation of the $BaTiO_3$ ceramic was achieved after two 2 h calcinations at 700 and 900 °C and by 1100 and 1300 °C sintering under air with multiple grinding, sieving, pressing into pellets intermediate steps; final treatment at ~900 °C to

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prevent excessive grain growth followed by room temperature quenching. This first sample was identified as *BT*100-00. Derived samples were prepared with sequential heat treatments at: 800 °C for 24 h, 1000 °C for 12 h, 1200 °C for 6 h, 1300 °C for 4 h, 1400 °C for 3 h; identified respectively as *BT*100-08, *BT*100-10, *BT*100-12, *BT*100-13 and *BT*100-14. The reference sample consist of a $BaTiO_3$ $(100)_T$ single crystal (*MaTeck*) which was cut in 6 pieces of about $5 \times 3 \times 1$ mm^3 in order to perform controlled ion implantation of ^{56}Fe and ^{57}Fe at 100 KeV. The ion implantation was made on 4 pieces with the help of the *TRIM* software, each having different concentrations of 0.05; 0.10; 0.50 and 1.00 at.% of Fe implanted in the top ~100 nm of each sample [9]; the samples were identified as *BT*000-sc (without implantation), *BT*005-sc, *BT*010-sc, *BT*050-sc, *BT*100-sc respectively. X-ray diffraction (XRD) was performed with a *Panalytical X'Pert Pro* equipped with *X'Celerator* monochromator detector for $\lambda(Cu\ K_{\alpha 1}) = 1.5405(98)$ Å. Rietveld refinements [10] were calculated using *PowderCell* and *FullProf* software. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) characterization were performed with a *FEI Quanta 400* with an *EDS/EDAX* detector. Rutherford Back Scattering (RBS) and Proton Induced X-Ray Emission (PIXE) spectrograms were simultaneously accumulated, samples were irradiated with 2 MeV protons focused in 3×4 μm^2 and sweeping thru 1.5×1.5 mm^2. Magnetization measurements in the temperature range of 5–400 K with a magnetic field up to 5 T used a *Quantum Designs MPMS-S* Superconducting Quantum Interference Device (SQUID). Dielectric measurements were performed in a high resolution dielectric analyzer *ALPHA* in a 1 kHz to 1 MHz frequency range, between 143 and 473 K. Raman Spectroscopy measurements in the temperature range 77–450 K used a *Linkan 600* system, the 514.5 nm laser line and a *Jobin-Yvon T6400* spectrometer.

3. Results and discussion

XRD measurements were performed in the series of nominal $BaTiO_3$ bulk compounds with different anneal treatments and in the original BT100-00 sample at distinct temperatures, in order to inspect the structural evolution of the system and enable a comparison to the conventional $BaTiO_3$ phase diagram [11]. Diffractograms indexed to reference data, from *ICDD's* Powder Diffraction Files (PDF), are depicted in Fig. 1. Rietveld refinements simulations considered single and multiple phase coexistence in the samples, encompassing the rhombohedric (*R*) PDF# 04-008-6883, orthorhombic (*O*) PDF# 04-008-6888, tetragonal (*T*) PDF# 04-008-6892 [11] and cubic (*C*) PDF# 04-008-4556 [12] phases of $BaTiO_3$. Presence of 1–8% of $BaCO_3$ PDF# 04-007-6606 [13] and 4–8% of Ba_2TiO_4 PDF# 04-007-4821 [14] was detected on samples exposed to lower temperature heat treatments; these spurious phases tend to disappear after further annealing at higher temperatures. Consistent results obtained from Rietveld refinements estimate lattice parameters and typical crystallite sizes are accounted in Table 1.

The use of a different sample holder necessary to perform XRD measurements apart from room temperature justifies the additional dampening and apparent dissimilarity between the calculated crystallite sizes of sample BT100-00 found at 300 K and found at 84, 250, 350 and 450 K. Relevant grain growth is particularly observed for sample BT100-14.

Representative SEM image and EDS spectrum of sample *BT*100-08 depicted in Fig. 2, exhibit high coarseness and porosity, enabling to recognize the overall presence of smaller grains below 100 nm, while some larger grains can reach 0.5 μm. Chemical analysis confirmed the intended atomic ratio averaging |Ba|/|Ti| ~1.0 ± 1%. Possible presence of contaminants is below the experimental detection limit of standard EDS survey technique. With RBS/PIXE techniques it was possible to detect and quantify the contaminants listed in Table 2. In practical terms, the presence of impurities is within the tolerance values expected from 99% grade precursors. This technique is proven crucial to identify and quantify the elusive magnetic elements overcoming the $BaTiO_3$ diamagnetism. Most of the accounted contaminants exhibit inconsequential diamagnetic responses. However, the magnetic contribution of ~100 ppm of Fe ions can justify alone a biased 10^{-2} emu/g signal and unexpected magnetic behaviors. Although such marginal presence of extrinsic elements could hardly be considered as a composite, the appearance of a ferri/ferromagnetic features is primarily settled through magnetic exchange between spins from neighboring Fe ions, which would imply some nucleation and segregation of Fe-rich nanometric clusters embedded in the $BaTiO_3$ matrix.

Magnetization measurements as function of applied magnetic field, exemplified in Fig. 3, exhibits a superimposition of the intrinsic $BaTiO_3$ diamagnetism with a contribution arising from the Fe ions present in the different samples. For the samples *BT*100-13, −14 and −sc, paramagnetic s are revealed particularly dominant at lower s (5 K). Whereas for samples *BT*100-00, −08 and −12 the magnetic response incorporates a narrow hysteresis at low H fields ($|H| < 0.5$ T) still patent at higher temperatures (300–400 K). By fitting a Brillouin function to $M(H)$ curves at 5 K it is possible to estimate a quantum number J ~1.8 and attest the number of magnetic ions of the order 10^2 ppm. The presence of such hysteresis loops and the obtained values for J points out for a partial segregation of Fe rich phase in cluster like nanosized structures; remarkably, for some studies concerning doped $BaTiO_3$ [6], the diluted ions only show pertinent cooperative behavior in concentrations ranges above 5%.

Magnetic measurements as function of temperature, shown in Fig. 4, reveal overall positive susceptibility of the order of 10^{-3} emu/g/T consistent with the presence of ~100 ppm of Fe. With exception of an anomaly at ~57 K detected in sample *BT*100-08 attributed to condensation of adsorbed O_2; significant variations of magnetization manifest at temperatures analogous to typical structural transitions of $BaTiO_3$. For samples *BT*100-00, −08 and −12 the magnetization observes relevant signal decay with temperature, most pronounced at ~327 K (*O*–*T*) only culminating at ~335 K, with another remarkable steps at ~373 K (*T*–*C*). For sample *BT*100-14, a minor step is observed at ~180 K (*R*–*O*), together with samples *BT*100-13 and -sc exhibit less significant cooperative effects, evidencing a higher dispersion of the magnetic ions. Recurring to the basic analysis of the magnetization behavior by means of fitting the Curie–Weiss model over $M(\mathbf{T})$ curves, below 50 K, the value of $J \sim 5/2$ can be readily found, also confirming the expected presence of paramagnetic Fe^{3+} ions.

The presence of different nano sized particles leads to the coexistence of different phases and respective temperature shift of structural transitions [15]. Temperature dependent Raman spectroscopy measurements were performed in order to understand if there's an actual relation between the observed magnetic variances and the structural changes occurring at the phase transitions of the $BaTiO_3$ matrix.

Fig. 5 shows the temperature dependence of representative Raman active vibrational modes, assigned respectively to transversal (TO) and longitudinal (LO) optical modes: [E(TO) + A1(TO)] at ~487 cm^{-1} and [E(LO) + A1(TO) + E(TO)] at ~520 cm^{-1} [16]. As expected the resonant frequency decreases gradually as the temperature increases, nonetheless there are some abrupt changes at specific temperatures which can be evidently related to the $BaTiO_3$ phase transitions.

The most evident seen around 380 K can be easily associated to the *T*–*C* transition which is suitably close to the magnetic anomalies observed at ~373 K. The mode around 487 cm^{-1} is typically associated with orthorhombic phase [17] and the observation of the

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