Influence of structural transitions of BaTiO$_3$ on the magnetic properties of Fe nanoparticles

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Abstract. Ferroelectric BaTiO$_3$ single crystals with (001) orientation were implanted with Fe at room temperature with an energy of 100 keV and a fluence of $1 \times 10^{17}$ cm$^{-2}$. For the implanted crystals, the analysis of the magnetic properties shows that Fe nanoparticles are formed and display characteristic superparamagnetic behaviour. The thermal dependence of the nanoparticles magnetisation shows the signature of the structural phase transitions of BaTiO$_3$ with changes in the magnetisations values and thermal hysteresis observed at related temperatures.

1. Introduction

The magnetic control of ferroelectricity or the electric control of ferromagnetism (magnetoelectric coupling) could open the way to new device concepts and the doping of ferroelectric materials with magnetic ions is actively studied as a route to obtain such coupling. Fe doped BaTiO$_3$ single crystals display ferromagnetic behaviour but the ferroelectricity is suppressed for doping concentrations above 1\% [1]. Magnetoelectric coupling has been explored in heterostructures combining a ferroelectric and a ferromagnetic material whose order parameters interact via strain coupling. The effect has been shown in multilayers of BaTiO$_3$/La$_{0.7}$Sr$_{0.3}$MO$_3$ [2] and reversible control via interfacial strain of magnetisation was observed in a Fe film deposited on a BaTiO$_3$ substrate [3]. Another type of heterostructure can be achieved using ion implantation to produce ferromagnetic nanoparticles embedded in a ferroelectric single crystal [4]. Previous reports on Mn and Co implantation of BaTiO$_3$ claimed the dilution of the transition metal ions in the BaTiO$_3$ matrix and room temperature ferromagnetism [5]. In this work we use ion implantation to produce Fe nanoparticles in single

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crystalline BaTiO$_3$ and study the influence of the structural phase transitions of the ferroelectric matrix on the magnetic properties of the system.

2. Results and discussion

Single crystals of BaTiO$_3$ were implanted with Fe ions using a fluence of $1 \times 10^{17}$ cm$^{-2}$. Structural characterization was carried out by Rutherford Backscattering Spectroscopy (RBS) combined with the channeling effect (RBS-C) and X-ray diffraction (XRD) in the $\theta$-2$\theta$ geometry. Magnetisation was measured using a SQUID magnetometer.

The results for RBS-C are shown in figure 1. The spectra recorded for the full alignment of crystal c-axis with the impinging beam show a highly damaged surface layer extending to a depth of 125 nm. The edge for Fe is clearly visible in both spectra - aligned and non-channelling - confirming the presence of the implanted Fe in the matrix. Calculations show that the Fe ions sit at the expected implantation depths with a maximum at 46 nm and a retained fluence of $1 \times 10^{17}$ cm$^{-2}$ confined within 125 nm from the surface, in agreement with theoretical simulations by the MC code SRIM-2008 [6]. The entire Fe ion distribution lies in the implantation damaged region. The isolated Fe contribution to RBS is shown as open circles (in green colour) and the simulated spectrum, based on the experimentally found parameters is shown as a full green line superimposed on the non channelling spectrum. Although the implanted region is highly damaged as seen by RBS-C in figure 1 it is not amorphous. Channelling depends on the steering action of the lattice periodic potential on the motion of ions over lengths of several hundreds of nm. For a locally disordered crystalline structure the loss of this sort of “long-range” order leads to a loss of channelling and to an abrupt increase of the RBS yield that does not necessarily imply true amorphisation.

XRD shows the BaTiO$_3$ (002) diffraction peak and a bump corresponding to a low intensity and large width diffraction peak (figure 2). By fitting the data with a Gaussian shaped peak in the iron position and using the FWHM and the Scherrer formula an estimate of 2 nm is obtained for the particle size. The Gaussian peak is centred at $2\theta = 43.45$ which is close to the (110) peak for bcc Fe ($2\theta = 44.67$ for bulk material), the small shift to lower angles indicating that the Fe particles are under a tensile strain.

The temperature dependence of magnetisation for the implanted sample is characteristic of a magnetic nanoparticle system. After a zero field cooling procedure the magnetisation shows a
maximum at low temperature and a Curie-type behaviour is obtained above this temperature (blocking temperature-T_B) both in the zero field cooled (ZFC) and field cooled (FC) measurements, indicating a superparamagnetic (SP) behaviour (figure 3). This behaviour is confirmed by the measurement of magnetisation as a function of applied field for temperatures above the blocking temperature. A plot of the reduced magnetic moment (m/m_s) as a function of H/T obtained for temperatures between 100 and 300K collapse in a single curve (figure 4). The solid red line in figure 4 is the result of a theoretical fit using the Langevin function to describe the field dependence of each aggregate and a log-normal distribution of magnetic aggregates [7]. From the obtained value of average magnetic moment (1760 μ_B) we can estimate a particle diameter of 2.6 nm.

For a SP system, equating K_effV to the thermal energy available on the time scale of the measurement (30k_BT_B) allows estimating the effective anisotropy of the particles (that includes contributions from magnetocrystalline, stress induced, surface and shape anisotropies). Considering T_B = 15 K and assuming spherical particles of diameter 2.6 nm we obtain a value K_eff = 7.6×10^5 J/m^3. The low temperature value of the magnetocrystalline anisotropy for bulk Fe is K_MC = 5.6×10^4 J/m^3, suggesting a very significant contribution from the other anisotropy terms.

Small discontinuities in magnetisation values were observed in magnetisation versus temperature measurements in the temperature regions 180-200 K and 280-290K. Figure 5 shows the thermal dependence of the magnetisation obtained in these two regions measured upon cooling and heating between room temperature and 170 K under an applied field of 50 mT. In both cases, changes in the magnetic moment are observed at temperatures that depend on the way temperature is varied, showing a thermal hysteresis that extends over a range of 10-15 K.

BaTiO_3 is a perovskite centrosymmetric cubic structure at high temperatures (T ≥ 400 K) that, as temperature is lowered, goes through successive phase transitions to different ferroelectric phases, each involving distortions from the cubic symmetry (respectively tetrahedral, orthorhombic and rhomboedral). The marked increase in microscopic strain observed in BaTiO_3 as the transitions are approached and the significant asymmetric premonitory effects in the lattice parameters near the transitions explain the hysteretic behaviour of the phase transitions. The implanted region is highly damaged (figure 1) but it is not amorphous and if as predicted the critical size for ferroelectric instability in BaTiO_3 is 1 - 2 nm [8], it is likely that the implanted region still displays ferroelectricity.

The temperature regions where changes in magnetisation and thermal hysteresis are detected are close to the reported temperatures where tetragonal to orthorhombic (278 K) and orthorhombic to rhombohedral (183 K) transitions occur in BaTiO_3 showing that the magnetic properties of the particles are sensitive to these transitions. The change in magnetisation of the Fe nanoparticles could be induced by magnetoelastic coupling related to a modification of the stress induced anisotropy. The
volume of the BaTiO$_3$ unit cell increases at the tetragonal-orthorhombic transition and decreases at the orthorhombic-rhombohedral transition [9]. Assuming a corresponding change in the stress induced anisotropy of the particles we can consider that the magnetisation will vary in opposite ways at the two structural transitions. Changes in the polarization direction of BaTiO$_3$ at these transitions could also affect the electronic structure of the interfaces leading to a variation of the magnetocristalline anisotropy of the Fe particles [10]. The overall variation on the effective anisotropy at the transitions would lead to a change in the height of the potential barrier that separates the two magnetization states defined by the direction of the applied field and eventually favour one orientation over the other [11].

In conclusion, BaTiO$_3$ single crystals implanted with a high fluence of Fe ions showed formation of Fe aggregates. Hysteresis observed in the temperature dependence of magnetisation is attributed to coupling between the Fe aggregates and the ferroelectric matrix. Further measurements are under progress in order to clarify the relation between the observed results and the characteristics of the ferroelectric phases of BaTiO$_3$.

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