Stress induced magnetic anisotropy on $BaTiO_3$-$CoFe_2O_4$ nanogranular composite thin films

J. Barbosa[1], B. Almeida[1,*], A.M. Pereira[2], J.P. Araújo[2], I. Gomes[1], J. Mendes[1]
[1]*Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portuga*
[2]*Departamento de Física and IFIMUP, Univiversidade do Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal*

Abstract

The influence of stress on the magnetic properties of $BaTiO_3$-$CoFe_2O_4$ nanocomposites deposited by laser ablation on platinum covered Si(001) substrates, was characterized. The cobalt ferrite phase was under compressive strain in the growth direction that progressively relaxed as its concentration increased. A stress induced perpendicular magnetic anisotropy was observed, that decreased with increasing $CoFe_2O_4$ content, due to the relaxation of stress in the films.

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1. Introduction

Composite thin films formed by mixing a magnetostrictive material in a piezoelectric matrix have recently attracted much interest [1]. In addition to possessing ferroelectricity and magnetism in each individual phase, they are shown to exhibit a coupling between their magnetic and electric degrees of freedom, the so called magnetoelectric effect. In these composites it is the elastic interaction between the piezoelectric and magnetostrictive materials that is providing the coupling mechanism inducing the magnetoelectric response [1]. Thus, their electric and magnetic properties are strongly dependent on phase morphology and internal stress distribution. Here, nanogranular thin films of cobalt ferrite ($CoFe_2O_4$) dispersed in a barium titanate ($BaTiO_3$) matrix were prepared with different cobalt ferrite concentrations, in order to study the influence of stress on the magnetic anisotropy of the films.

Bulk $CoFe_2O_4$ has a cubic inverse spinel structure and presents a high magnetocrystalline anisotropy and magnetostriction [2]. $BaTiO_3$ is a well studied piezoelectric perovskite [3] and has a tetragonal ferroelectric structure at ambient temperature.

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[*] Tel. +321253604063, Fax. +351253678981, e-mail: bernardo@fisica.uminho.pt

The nanogranular $BaTiO_3$ - $CoFe_2O_4$ thin films were prepared by pulsed laser ablation, on platinum covered Si(001) substrates. Details of their deposition conditions are in [4]. The ablation targets were prepared by mixing $CoFe_2O_4$ and $BaTiO_3$ powders with cobalt ferrite concentrations $x = 20\%$, 30%, 40%, 50%, 60%, 70% and 100%. They were then compressed and sintered at 1200ºC during 1 hour. The structural studies were performed by X-ray diffraction (XRD) using a Philips PW-1710 diffractometer with Cu Kα radiation. The magnetic properties were measured with a Quantum Design MPMS SQUID magnetometer.

2. Results and discussion

The X-ray diffraction measurements, scanned along the growth direction, were previously discussed [4] and the main result is summarized on figure 1a). The nanocomposite films are polycrystalline and composed by a mixture of tetragonal-$BaTiO_3$ and $CoFe_2O_4$ with the cubic inverse spinel structure. The lattice parameter of the cobalt ferrite phase (fig. 1a) was obtained from the position of the (311) diffraction peak of $CoFe_2O_4$. Comparing with the bulk $CoFe_2O_4$ lattice parameter, in the films the cobalt ferrite is under compressive strain that progressively relaxes as its concentration increases towards pure cobalt ferrite.

Figure 1b shows the magnetization hysteresis cycles measured at ambient temperature on the nanocomposites with $x = 50\%$ and $x = 70\%$, respectively. The loops were obtained with the magnetic field (H) applied perpendicular and parallel to the films plane. They were corrected by subtracting the diamagnetic contribution from the substrate. For the loops measured with in-plane H the magnetization is harder to saturate, particularly for the films with lower $CoFe_2O_4$ concentrations that have more strained lattice parameters. However, the loops measured with H perpendicular to the plane are squarer, showing a clear saturation. This indicates the presence of an anisotropy favouring the orientation of the magnetization in the direction perpendicular to the films plane. Extrapolating linearly the in-plane magnetization curve towards the saturation values of the perpendicular magnetization loops gives an anisotropy field of $H_A = 47$kOe, $H_A = 42$kOe and $H_A = 12$kOe, for the samples with $x = 40\%$, $x = 50\%$ (fig 1b) and $x = 70\%$ (fig. 1b), respectively.

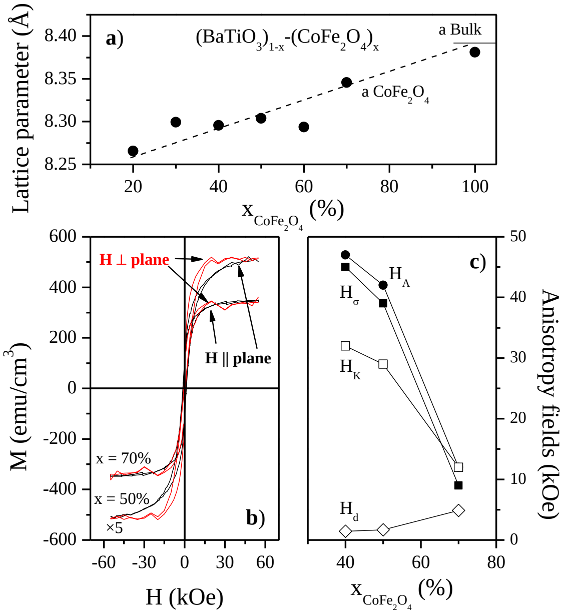

Fig. 1. Lattice parameter of the cobalt ferrite phase a), determined from the X-ray diffraction spectra of the films. The line is a guide to the eye. In b) are the hysteresis cycles measured with the magnetic field applied perpendicular and parallel to the film's plane, for the samples with $x = 50\%$ and $x = 70\%$. The anisotropy fields represented in c) are: H_A – experimental, H_σ - stress induced, H_K- magnetocrystalline and H_d – due to the shape.

Several competing sources of magnetic anisotropy must be taken into account in order to understand the origin of the perpendicular anisotropy of the polycristalline films, namely, the shape anisotropy energy (E_d), the magnetocrystalline anisotropy energy (E_K) and the strain energy (E_σ) due to the magnetostriction of the cobalt ferrite.

To avoid the complex problem of the magnetostatic interactions of the $CoFe_2O_4$ magnetic particles in the nonmagnetic matrix we use a well known approach proposed by Netzelmann [5]. Thus, the effective magnetostatic energy is calculated as a combination of an isolated particle with demagnetization factor N_P and a homogeneous film with demagnetization factor $N_F = 4\pi$ [5]. Considering spherical cobalt ferrite particles with $N_P = 4\pi/3$, saturation magnetization M_S and volume fraction f_P, the shape anisotropy energy becomes:

$$E_d = \frac{2\pi}{3}(1+2f_p)M_s^2 \qquad (1)$$

The maximum saturation value measured on the composite films, normalized by the volume fraction of the ferrite, was 485 emu/cm^3 (x = 70%), giving a shape anisotropy field of $H_d = 2E_d/M_S = 4.88$ kOe. This value is too small to account for the perpendicular magnetic anisotropy of the films as shown in figure 1c).

The magnetocrystalline anisotropy field for a cubic crystal is determined by $H_K = 2K_1/M_S$, where K_1 is the crystal anisotropy constant. For $CoFe_2O_4$ $K_1 = 3\times10^6$ erg/cm^3 [6], giving $H_K = 32$kOe, $H_K = 29$kOe and $H_K = 12$kOe for the samples with x = 40%, x = 50% and x = 70%, respectively. For the higher cobalt ferrite content H_K is similar to the experimentally determined perpendicular anisotropy field (12kOe), but due to the random character of the polycrystalline films it is not expected to be the dominant contribution. On the other hand, for the lower and more strained $CoFe_2O_4$ concentrations H_K is clearly below the ones experimentally determined from the loops (~40kOe, fig. 1c).

Regarding the strain energy, in a cubic crystal, as in $CoFe_2O_4$, when the magnetostriction is not isotropic but has different values at saturation of λ_{100} and λ_{111}, E_σ depends on the direction cosines of the magnetization and stress [2]. However, for a polycrystalline material containing a random distribution of crystallites an averaged saturation magnetostriction coefficient can be determined by $\lambda = (2\lambda_{100}+3\lambda_{111})/5$ [2], so that:

$$E_\sigma = -\frac{3}{2}\lambda_s\sigma \qquad (2)$$

Cobalt ferrite has $\lambda_{100} = -5.9\times10^{-4}$ and $\lambda_{111} = 1.2\times10^{-4}$ [2], giving $\lambda_S = -1.64\times10^{-4}$ for the nanocomposite films. Using the Young's modulus coefficient of the Co-ferrite ($Y = 1.5\times10^{12}$ dyn/cm^2 [6]), the stress is obtained from $\sigma = Y\varepsilon$ where the strain is $\varepsilon = (a_{CoFe2O4,film} - a_{CoFe2O4,bulk})/a_{CoFe2O4,bulk}$. Then, the induced stress anisotropy field $H_\sigma = 2E_\sigma/M_S$ [6] values are $H_\sigma = 45$kOe, $H_\sigma = 39$kOe and $H_\sigma = 9$kOe for the samples with x = 40%, x = 50% and x = 70%, respectively. Thus, the obtained H_σ values (fig. 1c) are similar to the experimental ones for the perpendicular anisotropy fields of these samples ($H_A = 47$kOe, $H_A = 42$kOe and $H_A = 12$kOe, respectively). Since the deposited films have a compressive strain in the growth direction, this indicates the presence of in-plane tensions. Thus, due to the negative effective magnetostriction of the cobalt ferrite in the nanocomposites, these tensions induce a tendency to align the magnetization in a direction perpendicular to them and, thus, perpendicular to the plane of the films. The decrease of this magnetic anisotropy with increasing $CoFe_2O_4$ concentration is then due to the relaxation of the strain with increasing cobalt ferrite content in the films.

In conclusion $BaTiO_3$-$CoFe_2O_4$ nanocomposites have been deposited by laser ablation on platinum covered Si(001) substrates and their structural and magnetic properties were characterized. A stress induced perpendicular magnetic anisotropy was observed in the films. The decrease of this anisotropy with increasing $CoFe_2O_4$ concentration was due to the relaxation of the stress in the nanocomposites.

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References

[1] W. Eerenstein, N.D. Mathur and J.F. Scott, Nature 442 (2006) 759

[2] S. Chikazumi, *Physics of Ferromagnetism*, Oxford University Press, New York (1997)

[3] A.J. Moulson, J.M. Herbert, *Electroceramics. Materials, Properties and Applications*, Chapman and Hall, London, UK (1997)

[4] J. Barbosa, B. Almeida, J.A. Mendes, A.G. Rolo, J.P. Araújo, Phys. Stat. Solidi A 204 (2007) 1731

[5] U. Netzelmann, J. Appl. Phys. 68 (1990) 1800

[6] P.D. Thang, G. Rijnders, D.H.A. Blank, J. Magn. Magn. Mater. 310 (2007) 2621