

Nanogranular BaTiO₃-CoFe₂O₄ Thin Films Deposited by Pulsed Laser Ablation

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Abstract

Detailed structural and magnetic measurements were performed on nanostructured composite thin films of cobalt ferrite (CoFe_2O_4 - magnetostrictive) dispersed in a barium titanate (BaTiO_3 - piezoelectric) matrix, with different CoFe_2O_4 concentrations (ranging from $x=20\%$ to $x=70\%$). The films were deposited by laser ablation on platinum covered Si(100). Their structure was studied by X-ray diffraction and Raman spectroscopy. The magnetic properties were measured with a SQUID magnetometer. The nanocomposite films were polycrystalline and composed by a mixture of tetragonal- BaTiO_3 and CoFe_2O_4 with the cubic spinel structure. The lattice parameter of the CoFe_2O_4 phase varied from 8.26\AA ($x=20\%$) to 8.35\AA ($x=70\%$), and, comparing with bulk CoFe_2O_4 , it was under compressive stress that relaxed as its concentration progressively increased. In the tetragonal- BaTiO_3 phase, the lattice parameter a was contracted relative to the bulk phase and decreases with x . The lattice parameter c increased from 4.088\AA ($x=20\%$) to 4.376\AA ($x=70\%$), so that the BaTiO_3 c axes was increasingly expanded as the quantity of the barium titanate phase was reduced. This behavior was the opposite of that observed in CoFe_2O_4 . The magnetic measurements showed that the coercive fields decreased from 6.6 kOe ($x=20\%$) to 2.3 kOe ($x=70\%$) which was attributed to the progressive relaxation of the stress in the films as well as to the increase of particle agglomeration in bigger polycrystalline clusters with increasing cobalt ferrite concentration. For higher temperatures $T=300\text{ K}$ the reduction of magnetocrystalline anisotropy induced a strong reduction of the coercive field.

Introduction

Magnetoelectric materials exhibiting a coupling between their electric and magnetic degrees of freedom have been attracting much scientific and technological interest. In nanostructured composites formed by combining piezoelectric and magnetostrictive materials the elastic interactions between the phases provide the coupling mechanism inducing the magnetoelectric response [1,2]. As a result, the magnetic properties and performance of these nanostructures depend critically on the phase morphology and internal stress distribution, which, in turn, are determined by the elastic phase/phase and phase/substrate interactions. In order to address this problem, nanogranular thin films composed by BaTiO₃ (piezoelectric) and CoFe₂O₄ (magnetostrictive), with different relative concentrations, were prepared by pulsed laser ablation on platinum covered Si(001) substrates.

CoFe₂O₄ has a cubic inverse spinel structure [3] in which the octahedral B sites are occupied by eight Co²⁺ and eight Fe³⁺ cations, while the tetrahedral A sites are occupied by the remaining eight Fe³⁺. It presents a high magnetocrystalline anisotropy and magnetostriction [4], making it suitable for application in magnetoelectric composite thin films.

BaTiO₃ is a well studied ferroelectric perovskite and is a good candidate for high-performance lead-free piezoelectric applications [5]. At high temperatures BaTiO₃ is cubic, in which the large barium ions are surrounded by twelve nearest-neighbor oxygens and each titanium ion has six oxygen ions in octahedral coordination. At a temperature ~395 K BaTiO₃ transforms from a cubic to a tetragonal structure, which in turn changes to an orthorhombic phase at ~280 K and finally to a rhombohedral phase at ~193 K. The ambient temperature tetragonal phase is ferroelectric and the high temperature cubic phase is paraelectric.

The nanogranular BaTiO₃ - CoFe₂O₄ thin films were prepared by pulsed laser ablation, on platinum covered Si(001) substrates. The depositions were done with a KrF excimer laser

(wavelength $\lambda = 248$ nm), at a fluence of 1.5 J/cm^2 and 10 Hz repetition rate. The oxygen pressure during deposition was 1 mbar, and the substrate temperature was 600°C . The ablation targets were prepared by mixing CoFe_2O_4 and BaTiO_3 powders that were then compressed and sintered at 1200°C during 1 hour. Structural studies were performed by X-ray diffraction (XRD) and were carried out with a Philips PW-1710 diffractometer using $\text{Cu K}\alpha$ radiation. Raman studies were performed using a Jobin-Yvon T64000 spectrometer with an excitation wavelength at 514.5 nm, from an Ar laser. The magnetic properties were measured with a Quantum Design MPMS SQUID magnetometer.

Results and discussion

Figure 1 shows the X-ray diffraction spectra measured on the nanocomposite thin films with cobalt ferrite concentrations in the range 20% - 70%. The films are polycrystalline and composed by a mixture of tetragonal- BaTiO_3 and CoFe_2O_4 with the cubic inverse spinel structure. The grain sizes as measured from the X-ray diffraction peak widths for both phases ((112) for BaTiO_3 and (311) for CoFe_2O_4), were determined by using the Scherrer equation [6]. They are in the range 25nm to 100nm. In particular, the cobalt ferrite grain size does not show a clear trend with increasing cobalt ferrite concentration, fluctuating in the range 25nm to 30nm.

Figures 2a) and 2b) show the lattice parameters of the cobalt ferrite and barium titanate phases, respectively, that were determined from the X-ray diffraction spectra measured on the thin nanocomposite films (fig. 1). The lattice parameter of the CoFe_2O_4 phase was obtained from the (311) peak position and varied from 8.26\AA in the sample deposited with cobalt ferrite concentration $x = 20\%$, to 8.35\AA in the sample deposited with $x = 70\%$. Comparing with the bulk

CoFe₂O₄ lattice parameter, it is observed that in the films the cobalt ferrite is under compressive stress that relaxes as its concentration progressively increases.

The lattice parameters a and c of BaTiO₃ phase were obtained using the (111) and (101) peaks. The values of the lattice parameter a (c) are always below (above) the bulk one indicating that the tetragonal-BaTiO₃ phase unit cell is contracted (expanded) along the a (c) axis. Initially, a slowly decreases with increasing CoFe₂O₄ concentration, up to $x = 40\%$, reflecting the fact that in the nanocomposite films the smaller concentration of the cobalt ferrite only slightly distorts the BaTiO₃ matrix structure. However, as the concentration of the cobalt ferrite increases and the CoFe₂O₄ starts to be the dominant phase in the films, both the a and c lattice parameters vary faster with x , presenting values that are, on average, further from the bulk ones.

Figures 2c) and 2d) show the Raman spectra measured on individual tetragonal-BaTiO₃ and cubic-spinel-CoFe₂O₄ bulk powders and on the thin film samples. The sharp peak appearing near 520 cm⁻¹ is due to the characteristic plasma laser line from the Ar laser. Two main peaks are observed in the spectrum of the CoFe₂O₄ powder and of the nanocomposite films. They appear at 470 cm⁻¹ and 690 cm⁻¹ and their positions are represented by dotted lines in figures 2c) and 2d). They were assigned to octahedral site (O-site) sublattice and tetrahedral site (T-site) sublattice vibration modes, respectively [7], and reflect the local lattice effects in the tetrahedral and octahedral sublattices. As the cobalt ferrite concentration is increased on the nanocomposite films these peaks become more pronounced indicating the increased contribution of the CoFe₂O₄ phase to the Raman spectra. Also, their peak positions are systematically above the corresponding bulk values. This blueshift of the CoFe₂O₄ modes results from the lattice strain as already observed on cobalt ferrite thin films with thicknesses near 50nm [8] and shown by our X-ray diffraction results (figures 1 and 2a). The peaks from BaTiO₃ are not so visible, but two slight bumps appear

near 520 cm^{-1} and 716 cm^{-1} , corresponding to the BaTiO_3 transverse optical (TO) and longitudinal optical (LO) vibrations of the A_1 and E phonon modes [9].

Figures 3a) and 3b) show hysteresis loops measured on the nanocomposite films at the temperatures $T = 10\text{ K}$ and $T = 300\text{ K}$, respectively. The loops were measured on the films plane and corrected by subtracting the diamagnetic contribution from the substrate. Figure 3c) shows the coercivity (at 10 K and 300 K) for the nanocomposite thin films, taken from the corresponding hysteresis loops.

At low temperatures, the thin films present a high coercivity (H_c) that decreases with increasing cobalt ferrite concentration. During film deposition, the cobalt ferrite phase nanograins of each sample are formed with a broad range of sizes. However, their average grain size does not change much for different Co-ferrite concentrations, as referred earlier. At lower CoFe_2O_4 concentration, the cobalt ferrite nanograins are more isolated. The coercivity of isolated Co-ferrite particles increases with increasing diameter and reaches a maximum for particles with diameters near 40 nm [10,11]. Magnetization vector rotation is considered to be the mechanism responsible for the coercivity of small particles (smaller than 40 nm), where H_c is proportional to the magnetocrystalline anisotropy [3]. Additionally, the bigger particles present in each sample, due to grain size distribution (larger than 40 nm), divide into domains and the mechanism for coercivity depends on the stress in the films [3]. For low concentrations, the CoFe_2O_4 grains are more isolated weakening ferromagnetic interactions between them. Thus, in each film, the increased coercivity of smaller grains as well as the increased coercivity of larger grains due to increased stress, add to a higher global coercive field. As the cobalt ferrite concentration increases, the nanograins start to form larger clusters of less isolated nanoparticles and the stress in the cobalt ferrite grains decreases. These effects combine to reduce the coercivity of the nanocomposite thin films with increasing CoFe_2O_4 concentrations. Also, the coercivity strongly

decreases with increasing temperature, from 10 K to 300 K, due to the corresponding decrease of the magnetocrystalline anisotropy of CoFe_2O_4 [3,10]

In conclusion $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ nanocomposites have been deposited by laser ablation on platinum covered $\text{Si}(001)$ substrates, with different cobalt ferrite concentrations. Their structural and magnetic properties were characterized. A decrease of the coercive field with increased CoFe_2O_4 concentration was observed, due to the relaxation of the stress in the films as well as to the increase of particle agglomeration in bigger polycrystalline clusters with increasing cobalt ferrite concentration.

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Figure captions

Figure 1: X-ray diffraction spectra measured on the nanocomposite thin films deposited with cobalt ferrite concentrations in the range 20%-70%. The peaks marked with an S are due to the substrate. The vertical lines indicate the peak positions of the bulk tetragonal-BaTiO₃ and CoFe₂O₄ cubic spinel ferrite phases.

Figure 2: Lattice parameters of the a) cobalt ferrite and b) barium titanate phases, determined from the (311) peak position of CoFe₂O₄, and (111) and (101) peaks positions of BaTiO₃. The dashed line is a guide to the eye. The horizontal lines mark the lattice parameters of bulk cobalt ferrite with the cubic spinel structure ($a = 8.3874 \text{ \AA}$) and of barium titanate with the tetragonal structure ($a = 3.994 \text{ \AA}$, $c = 4.038 \text{ \AA}$). Also shown are the Raman spectra measured on the c) bulk reference powders and d) nanocomposite films.

Figure 3: Magnetic hysteresis cycles of the nanocomposite (BaTiO₃)_{1-x}(CoFe₂O₄)_x films measured at the temperatures a) 10 K and b) 300 K, for cobalt ferrite concentrations in the range 20%-70%. In c), the coercivity of the loops is also represented.

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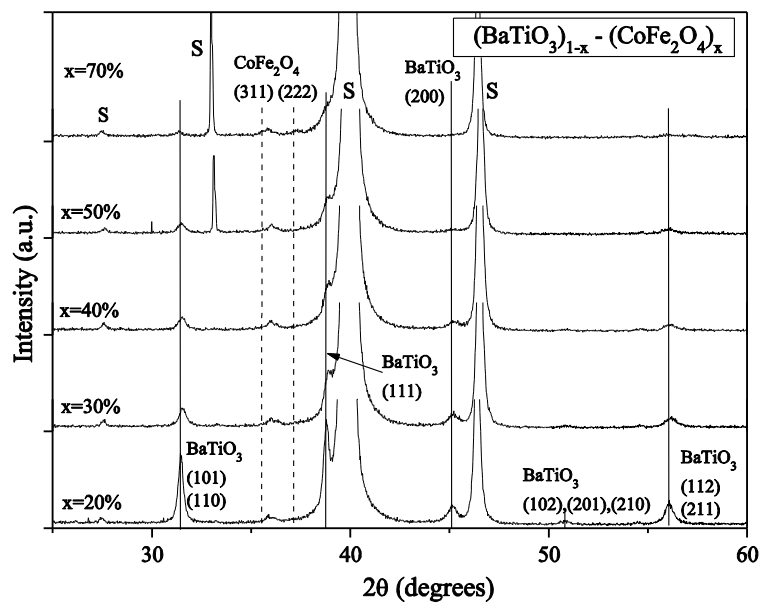


Figure 1

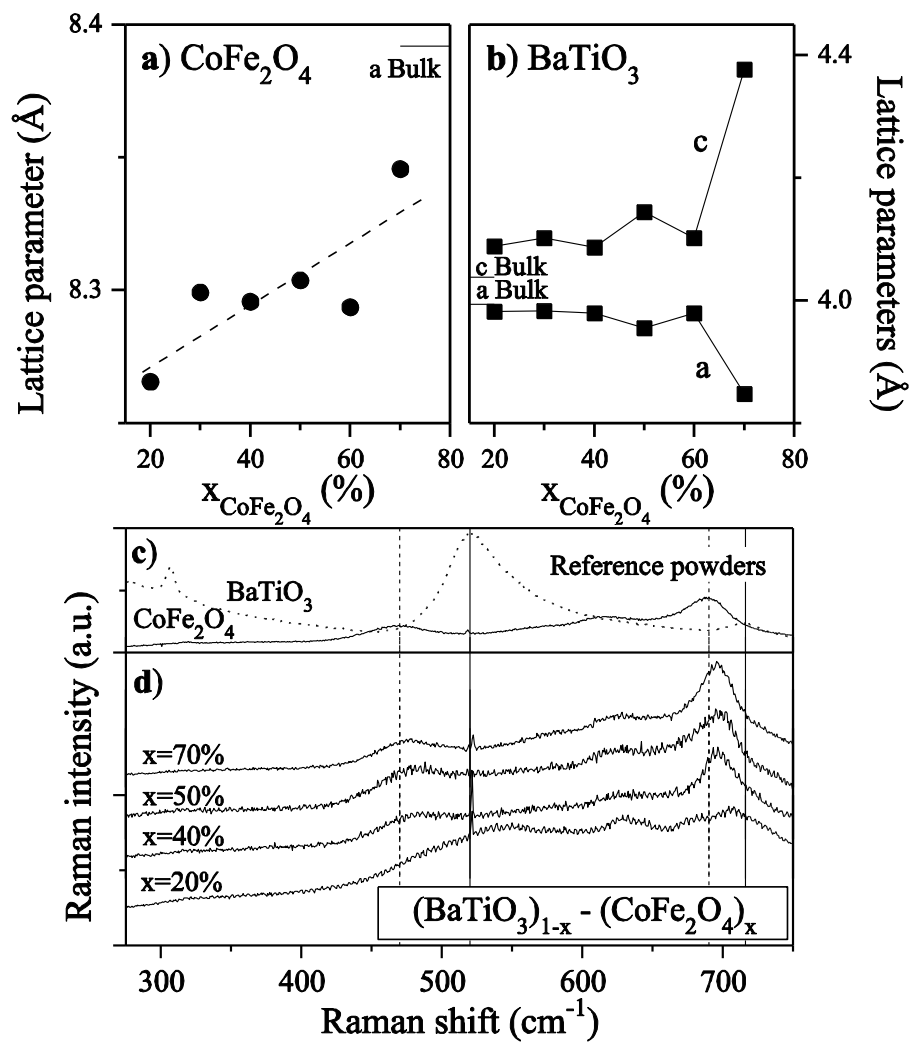


Figure 2

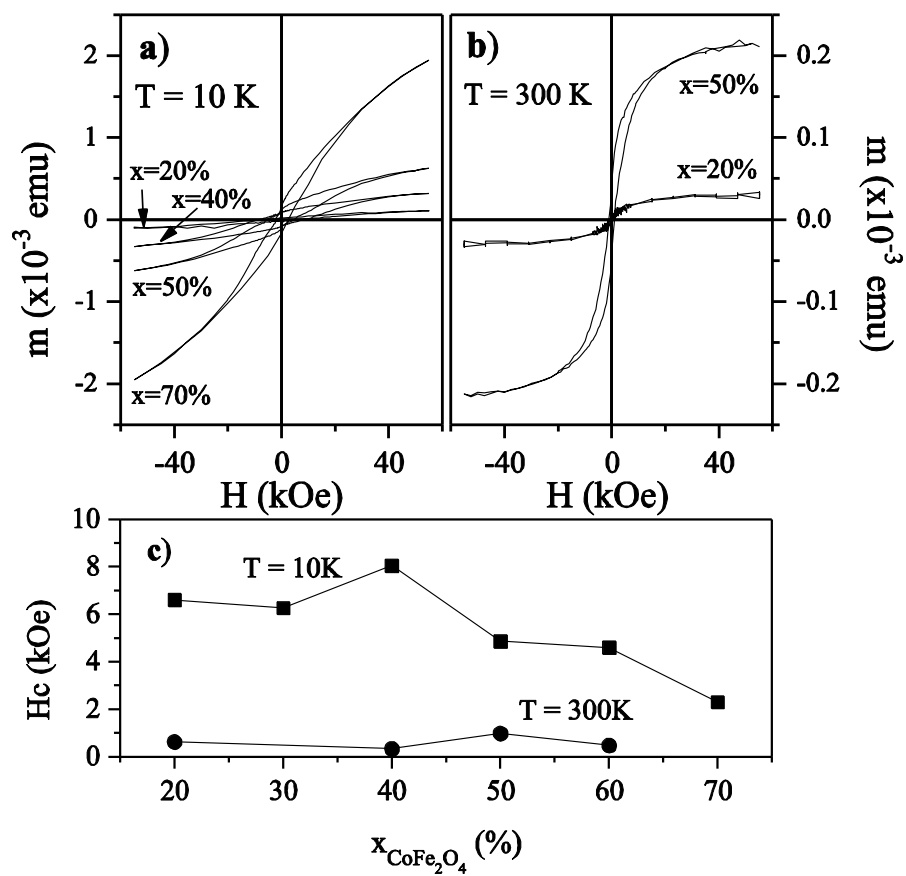


Figure 3