

X-Ray diffraction and Raman study of nanogranular BaTiO₃-CoFe₂O₄ thin films deposited by laser ablation on Si/Pt substrates

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Received ZZZ, revised ZZZ, accepted ZZZ

Published online ZZZ

PACS 61.46.-w, 77.84.Lf, 85.80.Jm, 81.15.Fg, 61.10.Nz, 78.30.-j

Nanocomposite thin films composed by (BaTiO₃)_{1-x}-(CoFe₂O₄)_x with different cobalt ferrite concentrations (x) have been deposited by pulsed laser ablation on platinum covered Si(001) substrates. The films structure was studied by X-ray diffraction and Raman spectroscopy. It was found that the CoFe₂O₄ phase unit cell was compressed along the growth direction of the films, and it relaxed with increasing x . The opposite behavior was observed in the BaTiO₃ phase where the lattice parameters obtained from the X-ray measurements presented a progressive distortion of its unit cell with increasing x . The presence of the strain in the films induced a blueshift of the Raman peaks of CoFe₂O₄ that decreased with increasing CoFe₂O₄ concentration. Cation disorder in the cobalt ferrite was observed for lower x , where the nanograins are more isolated and subjected to more strain, which was progressively decreased for higher CoFe₂O₄ content in the films.

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1 Introduction

The synthesis of materials that exhibit simultaneous ferromagnetic and ferroelectric characteristics has been attracting much scientific and technological interest. In these multiferroic materials, the coupling between the magnetic and electric degrees of freedom, the so-called magnetoelectric effect, may give rise to new physical phenomena and applications [1,2].

Recently, nanostructured multiferroic composites formed by the combination of a piezoelectric ceramic and a magnetostrictive material have been deposited in a film-on-substrate geometry. In these systems, the elastic interactions between the phases provide the coupling mechanism inducing a magnetoelectric behavior [2]. As a result, the 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

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are surrounded by twelve nearest-neighbor oxygens and each titanium ion has six oxygen ions in octahedral coordination. The barium and oxygen ions together form a face centered cubic lattice, with titanium ions fitting in octahedral interstices. BaTiO_3 is known to undergo several phase transitions as a function of temperature. Starting from the high temperature, at ~ 395 K BaTiO_3 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.

2 Experimental

The nanogranular BaTiO_3 - CoFe_2O_4 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 with cobalt ferrite weight concentrations $x = 20\%$, 30% , 40% , 50% , 60% and 70% . They 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 X-ray diffraction spectra measured on the laser ablation targets showed that they were polycrystalline and composed by mixtures of tetragonal- BaTiO_3 and CoFe_2O_4 with the cubic spinel structure.

3 Results and discussion

Figure 1 shows the X-ray diffraction spectra measured on the nanocomposites 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 cobalt ferrite phase grows with a preferential (311) orientation which is enhanced for samples with lower CoFe_2O_4 concentration. The peaks were fitted using pseudo-Voigt functions in order to determine their angular positions and integral widths. The grain sizes obtained from the fitted 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] and are in the range 25nm to 100nm. When the concentration of the cobalt ferrite increases, the grain size of the BaTiO_3 phase decreases, from 91nm to 28nm, up to 50% CoFe_2O_4 concentration, beyond which the BaTiO_3 grain size has an approximately constant value near 28nm. On the other hand the cobalt ferrite grain size does not show a clear trend with increasing cobalt ferrite concentration, fluctuating in the range 25nm to 30nm.

Figure 2 shows the lattice parameters of the cobalt ferrite

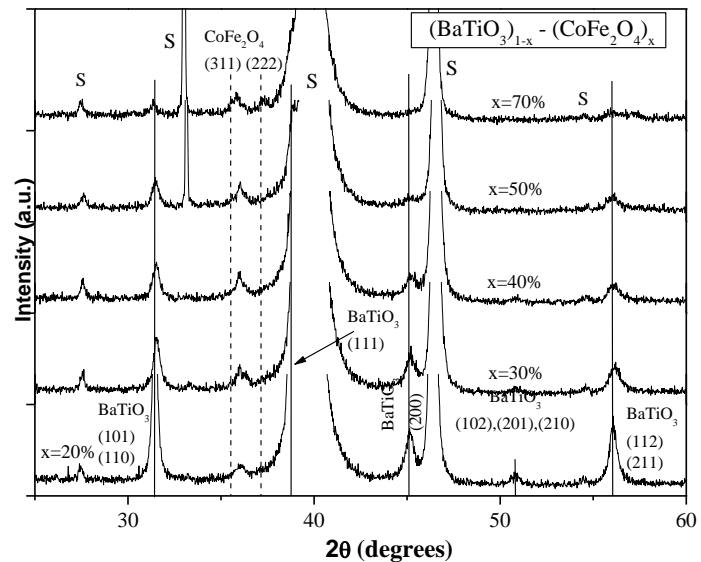


Fig. 1 X-ray diffraction spectra of the samples deposited with cobalt ferrite concentrations in the range 20%-70%. The vertical lines mark the peak positions of the bulk CoFe_2O_4 cubic spinel phase (...), and the tetragonal- BaTiO_3 phase (—). The peaks marked with an S are from the substrate.

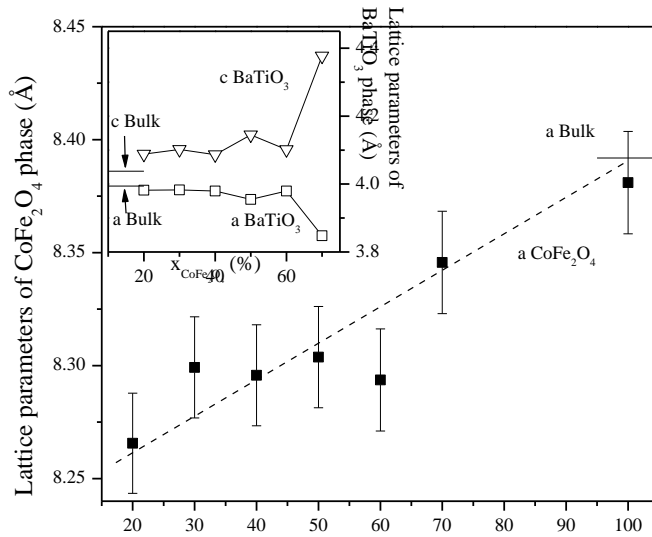


Fig. 2 Lattice parameters of the CoFe_2O_4 and (inset) BaTiO_3 component phases. The values were obtained from the (311) peak position of CoFe_2O_4 , and (111) and (101) peaks positions of BaTiO_3 . The straight dashed line is a guide to the eye.

comparing with the bulk CoFe_2O_4 lattice parameter, it is observed that the cobalt ferrite unit cell is compressed and relaxes as the concentration of CoFe_2O_4 progressively increases. Since the lattice parameter was determined from the (311) peak, which is the preferential growth direction of the CoFe_2O_4 phase, this indicates that the lattice planes are compressed along the growth direction.

The lattice parameters a and c of the BaTiO_3 phase were obtained from the (111) and (101) peaks. The values of the lattice parameter a are always below the bulk one indicating that the tetragonal- BaTiO_3 phase unit cell is contracted along the a axis. Correspondingly the values of the lattice parameter c are always higher than the bulk one indicating an expansion of the BaTiO_3 unit cell along the c axis. Initially, a slowly decreases with increasing CoFe_2O_4 concentration, up to $x = 40\%$, reflecting the fact that in the nanocomposite films the smaller concentration of the cobalt ferrite only slightly distorts the BaTiO_3 matrix structure. A similar behaviour is observed for the c axis lattice parameter. However, as the concentration of the cobalt ferrite increases and the CoFe_2O_4 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. This departure from the bulk is more pronounced for the film with the higher concentration ($x = 70\%$).

Figure 3 shows the Raman spectra of the thin film samples deposited with cobalt ferrite concentrations in the range 20%-70%. The sharp peak appearing near 520 cm^{-1} is due to the characteristic plasma laser line from the Ar laser. In order to understand the contributions of the different phases to the Raman spectra of the nanocomposite films the individual BaTiO_3 and CoFe_2O_4 bulk powders that were used to prepare the ablation targets were also measured. All the significant Raman peaks appearing on the cobalt ferrite reference powder, which has the cubic spinel structure, also appear in the nanocomposite films. In particular, two main peaks are observed in the spectrum of the CoFe_2O_4 powder. They appear at 470 cm^{-1} and 690 cm^{-1} and their positions are represented by dotted lines in figure 3. In the BaTiO_3 powder the main observed peaks appear at 520 cm^{-1} and 716 cm^{-1} , and their positions are represented by solid lines in figure 3. The BaTiO_3 peak position at 307 cm^{-1} coincides with a smaller one from CoFe_2O_4 .

and barium titanate phases that were determined from the X-ray diffraction spectra measured on the thin nanocomposite films (fig. 1). On the left axis of the inset graph, the horizontal lines mark the a and c axis bulk lattice parameters of barium titanate (BaTiO_3) with the tetragonal structure: $a = 3.994\text{ \AA}$, $c = 4.038\text{ \AA}$. Similarly, on the right axis of figure 2, the horizontal line marks the value of the lattice parameter of the bulk cobalt ferrite (CoFe_2O_4) with the cubic inverse spinel structure: $a = 8.3874\text{ \AA}$.

The lattice parameter of the CoFe_2O_4 phase was obtained from the fitted (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 CoFe_2O_4 lattice parameter, it is observed that the cobalt ferrite unit cell is compressed and relaxes as the concentration of CoFe_2O_4 progressively increases. Since the lattice parameter was determined from the (311) peak, which is the preferential growth direction of the CoFe_2O_4 phase, this indicates that the lattice planes are compressed along the growth direction.

CoFe_2O_4 has a cubic inverse spinel structure belonging to the $O_h^7(Fd\bar{3}m)$ space group. The metallic cations can occupy two types of positions: either surrounded by six oxygen ions forming an octahedron or by four oxygen ions forming a tetrahedron. This structure gives rise to 39 normal modes among which 5 are Raman active [7]. The modes appearing at 470 cm^{-1} and 690 cm^{-1} were assigned to octahedral site (O-site) sublattice and tetrahedral site (T-site) sublattice vibration modes, respectively [7]. They reflect the local lattice effects in the tetrahedral and octahedral sublattices.

The tetragonal form of BaTiO_3 belongs to the $C_{4v}^1(P4mmm)$ space group. The corresponding optical modes transform according to the irreducible representations $3(A_1+E)+E+B_1$, where the modes E are doubly degenerate and the modes A_1 and B_1 are nondegenerate [8, 9], giving twelve long wavelength optical modes. All of the A_1 and E modes are both Raman and infrared active and the B_1 mode is only Raman active. In the BaTiO_3 powder the peaks appearing in the Raman spectrum at 520 cm^{-1} and 716 cm^{-1} correspond, respectively, to transverse optical (TO) and longitudinal optical (LO) vibrations of the A_1 and E phonon modes [9].

Based on the peaks observed in the powders, the nanocomposite films spectra were deconvoluted using Lorentzian line-shape functions to least-squares fit the Raman peaks. From the fitted Lorentzians, the resonance wavenumber was determined by the peak position and the damping factor by its full-width-half-maximum (FWHM). Figure 3 shows the fitted Lorentzians for the particular case where the concentration of the cobalt ferrite is $x = 40\%$.

In the nanocomposite thin films, the main observed peaks appear near 470 cm^{-1} and 690 cm^{-1} and correspond to the cubic inverse spinel CoFe_2O_4 O-site and T-site modes referred above. As the cobalt ferrite concentration is increased they become more pronounced indicating a higher contribution of the CoFe_2O_4 phase to the Raman spectra. The peaks from BaTiO_3 are not so visible, but two slight bumps appear near 520 cm^{-1} and 716 cm^{-1} , corresponding to the BaTiO_3 modes

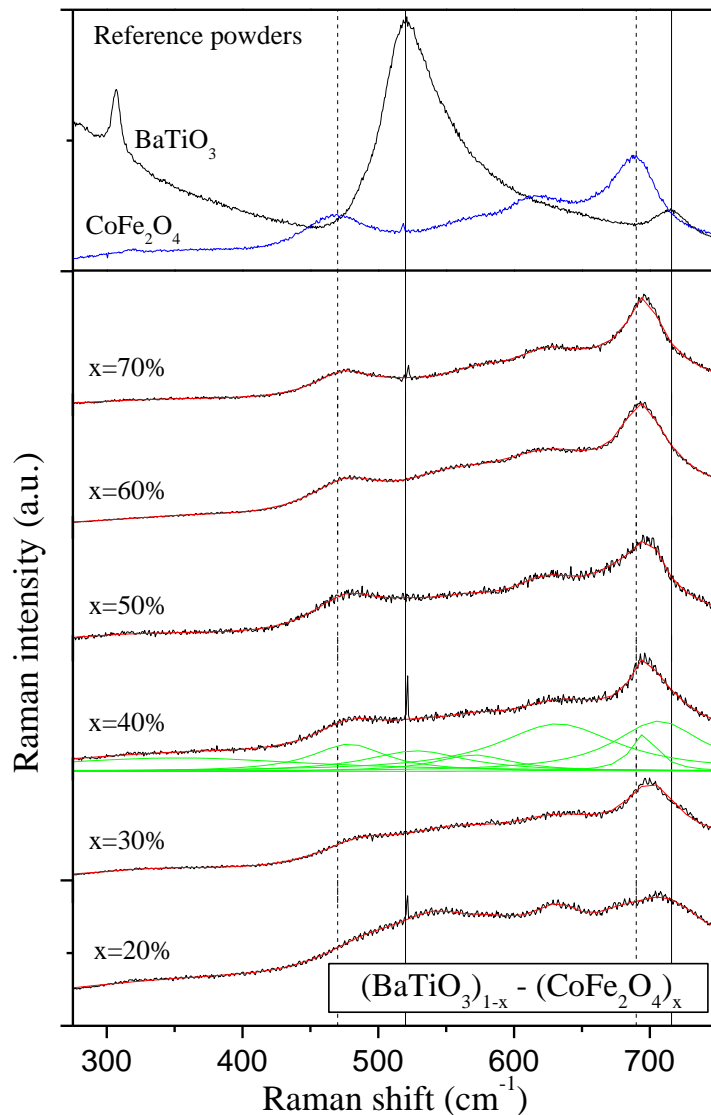


Fig. 3 Raman spectra of the samples deposited with CoFe_2O_4 concentrations in the range 20%-70%, along with the corresponding fitting curves. Also shown are the BaTiO_3 and CoFe_2O_4 reference powders, and the Lorentzians obtained from the fit to the spectrum of the sample with $x = 40\%$.

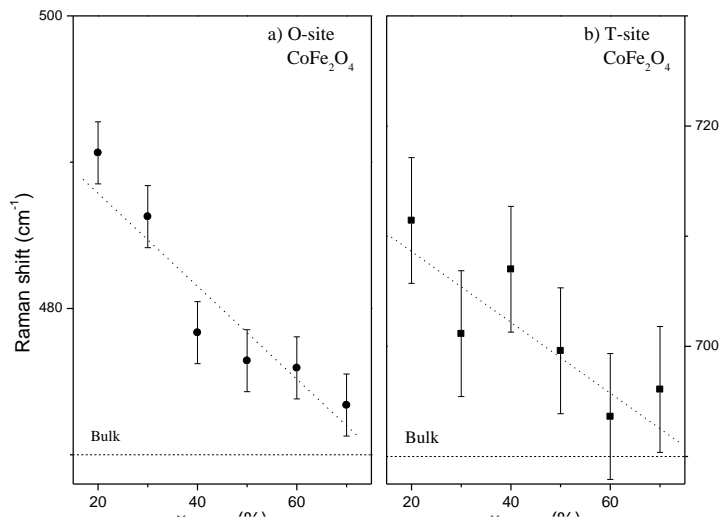


Fig. 4 Raman shift as a function of the CoFe_2O_4 concentration, for the a) O-site and b) T-site modes. The lines are a guide to the eye.

strain as already observed on cobalt ferrite thin films with thicknesses near 50nm [10] and shown by our X-ray diffraction results (figures 1 and 2).

The FWHM for both the T-site and O-site mode peaks of the cobalt ferrite phase are shown in figure 5. Comparing with the bulk reference powder values (46cm^{-1} for the T-site and 48cm^{-1} for the O-site modes) obtained by fitting the corresponding Raman spectra (fig. 3), the damping factors are higher than the bulk ones for low cobalt ferrite concentration, but then decrease towards bulk for higher x . Since from the X-ray diffraction results the nanoparticles of CoFe_2O_4 in the films have similar grain sizes for the different cobalt-ferrite concentrations, the broadening of the Raman peaks is then due to cation disorder [7, 11]. In fact, during the deposition process and formation of the CoFe_2O_4 nanoparticles some of the Co^{2+} ions can occupy tetrahedral sites (instead of octahedral), while extra Fe^{3+} cations can occupy octahedral sites, leading to the break of the long-range cation order. The results shown in figure 5 indicate that this disorder is more prominent in the films with lower cobalt ferrite concentration, where the CoFe_2O_4 nanoparticles are more isolated and subjected to a higher compression. As the CoFe_2O_4 content in the films is increased, more cobalt ferrite nanograins become connected, strain is relaxed and this cation disorder is reduced, so that at higher CoFe_2O_4 concentrations the bulk values of the damping

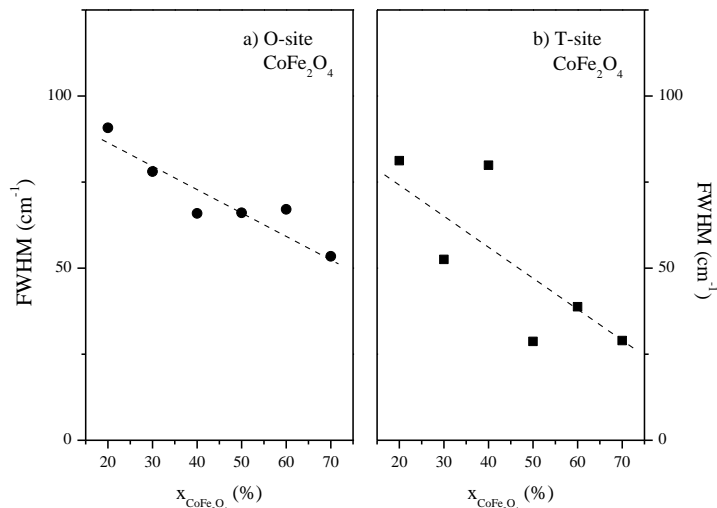


Fig. 5 FWHM of the fitted lorentzians as a function of the CoFe_2O_4 concentration, for the a) O-site and b) T-site modes. The lines are a guide to the eye.

referred above. They present the opposite behavior from the cobalt ferrite phase, decreasing their intensity as the BaTiO_3 concentration decreases in the films. Their fitted positions remain approximately the same, showing no clear trend.

On the other hand, as the CoFe_2O_4 concentration increases, the O-site mode decreases from 491cm^{-1} , for $x = 20\%$, to 473cm^{-1} , for $x = 70\%$, being systematically above the bulk 470cm^{-1} value, as shown in figure 4. A similar trend was observed for the T-site mode. Since the grain size of the films is relatively high to observe confinement effects, this blueshift of the CoFe_2O_4 modes result from the lattice

factor are attained. Indeed, from magnetic measurements, a corresponding progressive decrease of the coercive field with increasing CoFe_2O_4 concentration was observed [12], due to the increased agglomeration of the cobalt ferrite nanograins and to the decrease of the strain in the CoFe_2O_4 phase.

4 Conclusions

Thin film nanocomposites composed by CoFe_2O_4 mixed in a BaTiO_3 matrix were deposited by pulsed laser ablation on platinum covered Si(001) substrates, with different cobalt ferrite concentrations. The films structure presented a mixture of tetragonal- BaTiO_3 and CoFe_2O_4 with the cubic spinel structure. The cobalt ferrite nanograins unit cell was compressed along the growth direction and progressively relaxed as the CoFe_2O_4 concentration was increased. An opposite behaviour was observed on BaTiO_3 phase with a corresponding progressive increase of the distortion of its unit cell. Disorder of the cation distribution in the cobalt ferrite was observed for lower CoFe_2O_4 concentration that was strongly decreased for higher CoFe_2O_4 content in the films.

Acknowledgements This work has been financially supported by the Portuguese Foundation for Science and Technology (FCT), through the project POCI/CTM/60181/2004 and the Bilateral Research Action n°B48-06 between CRUP (Portugal) and British Council (UK).

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