

STRUCTURAL CHARACTERIZATION OF NANOGRANULAR $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ THIN FILMS DEPOSITED BY LASER ABLATION ON SI/PT SUBSTRATES

J. Barbosa, B.G. Almeida, J.A. Mendes, A. Rolo, J.P. Araújo

*Dep. Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
Dep. de Física and IFIMUP, Univ. Porto, Rua Campo Alegre, 687, 4169-007 Porto, Portugal
bernardo@fisica.uminho.pt*

Magnetolectric nanocomposite thin films constructed by mixing magnetostrictive and piezoelectric materials have attracted recently much scientific and technological interest [1]. The stress mediated coupling between the magnetic and the electric component phases engenders a material presenting properties which are not available in the individual materials. 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 BaTiO_3 (piezoelectric) and CoFe_2O_4 (magnetostrictive) 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 mJ/cm^2 . The oxygen pressure during deposition was 1 mbar, and the substrate temperature was 600°C . The ablation targets were prepared by sintering CoFe_2O_4 and BaTiO_3 powders with different concentrations. Structural studies were performed by X-ray diffraction (XRD) and were carried out with a Philips PW-1710 diffractometer using Cu $K\alpha$ radiation. Raman studies were performed using a Jobin-Yvon T64000 spectrometer.

Figure 1 shows the X-ray diffraction spectra measured on the nanocomposites with cobalt ferrite concentrations in the range 20% - 70%. They are polycrystalline and composed by a mixture of tetragonal- BaTiO_3 and CoFe_2O_4 with the cubic inverse spinel structure. The grain sizes 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. They are in the range 30nm to 100nm. The lattice parameter of the CoFe_2O_4 phase was obtained from the (311) peak position, and varied from 8.26\AA for $x=20\%$ to 8.35\AA for $x=70\%$, with an almost linear trend. Comparing with the bulk cubic inverse spinel CoFe_2O_4 lattice parameter ($a=8.3874\text{\AA}$), it is observed that in the films the cobalt ferrite is under compressive stress, that relaxes as its concentration progressively increases. On the other hand the BaTiO_3 lattice parameters (a, c) were obtained using the (111) and (110) peaks. The lattice parameter a is approximately constant as function of concentration ($a\sim 4.04\text{\AA}$) and expanded relative to the bulk phase. However, the lattice parameter c decreases from 4.006\AA for $x=20\%$ to 3.93\AA for $x=70\%$, so that the BaTiO_3 c axes is increasingly compressed as the quantity of the barium titanate phase is reduced in samples. This behavior is the opposite of the observed one in CoFe_2O_4 .

Figure 2 shows the Raman spectra of the thin film samples deposited with cobalt ferrite concentrations in the range 20%-70%. 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. 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 2. 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 2. The BaTiO_3 peak at 307 cm^{-1} coincides with a smaller one from CoFe_2O_4 .

CoFe_2O_4 has a cubic inverse spinel structure with $O_h^7(Fd\bar{3}m)$ 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[2]. The modes appearing

at 470 cm^{-1} and 690 cm^{-1} were assigned to octahedral site (O-site) and tetrahedral site (T-site) modes, respectively [2]. On the other hand, the tetragonal form of BaTiO_3 belongs to the $C_{4v}^1(P4mmm)$ space group, and 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 [3].

Based on the peaks observed in the powders, the nanocomposite films spectra were deconvoluted by using Lorentzian line-shape functions to least-squares fit the Raman peaks as shown in figure 2. In the nanocomposite thin films, the main observed peaks appear near 470 cm^{-1} and 690 cm^{-1} and they correspond to the cubic inverse spinel CoFe_2O_4 O-site and T-site modes referred above. 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 referred above. Their positions remain approximately the same in this concentration range. On the other hand, as the CoFe_2O_4 concentration increases, the O-site mode decreases from 491 cm^{-1} , for $x=20\%$, to 473 cm^{-1} , for $x=70\%$, being systematically above the bulk 470 cm^{-1} value (figure 3). A similar trend was observed for the T-site mode. This blueshift of the CoFe_2O_4 modes results from the lattice strain, as already observed also by X-ray diffraction and shown in figure 1.

References:

- [1] - Zheng H., Wang J., Lofland S.E., Ma Z., Mohaddes-Ardabili L., Zhao T., Salamanca-Riba L., Shinde S.R., Ogale S.B., Bai F., Viehland D., Jia Y., Schlom D.G., Wuttig M., Roytburd A., Ramesh R. *Science*, **303** (2004) 661
 [2] - T. Yu, Z.X. Shen, Y. Shi and J. Ding, *J. Phys.: Condens. Matter*, **14** (2002) L613
 [3] - U.V. Venkateswaran, V.M. Naik and R. Naik, *Phys. Rev. B*, **58** (1999) 14256

Figures:

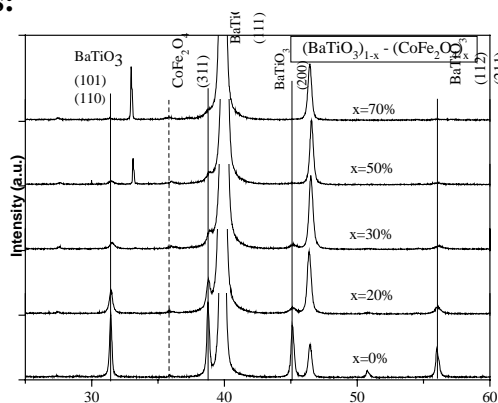


Figure 1: X-ray diffraction spectra of the samples deposited with cobalt ferrite concentrations in the range 20%-70%.

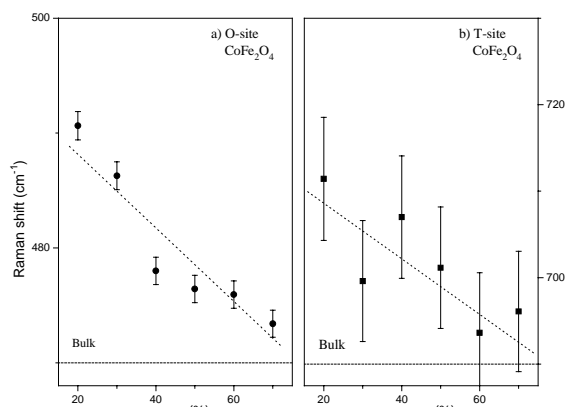


Figure 3: Raman shift as a function of the CoFe_2O_4 concentration, for the a) O-site and b) T-site modes. The lines are a guide to the eye.

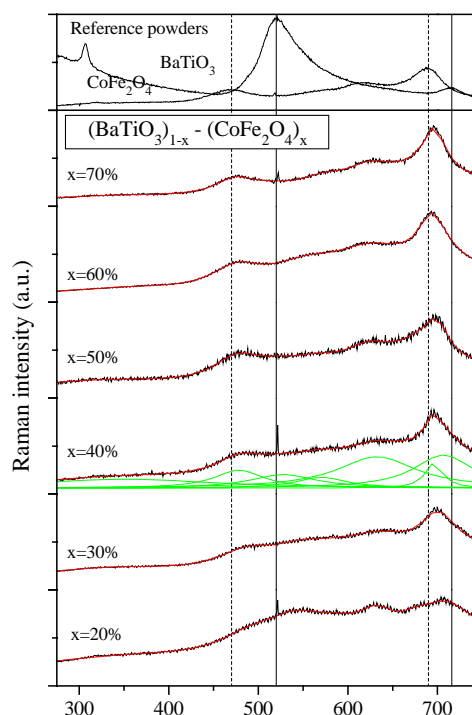


Figure 2: Raman spectra of the samples deposited with CoFe_2O_4 concentrations in the range 20%-70%, along with the corresponding fitting curves. Also shown are the BaTiO_3 and CoFe_2O_4 reference powders, and the Lorentzians obtained from the fit to the spectrum of the sample with $x=40\%$.