Structural characterization of nanogranular $BaTiO_3$-$NiFe_2O_4$ thin films deposited by laser ablation on Si/Pt substrates

J.R. Gonçalves, J. Barbosa,P. Sá, J.A. Mendes, A.G. Rolo, B.G. Almeida
Dep. Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
bernardo@fisica.uminho.pt

Multiferroic thin films constructed by mixing magnetostrictive and piezoelectric materials have attracted recently much scientific and technological interest [1]. In addition to possessing ferroelectricity and magnetism in each individual phase, they are shown to exhibit a stress mediated coupling between their magnetic and electric properties, the so called magnetoelectric effect [1]. Thus, 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. Here, nanogranular thin films composed by $BaTiO_3$ (piezoelectric) and $NiFe_2O_4$ (magnetostrictive) have been prepared, and their structural properties were characterized. The $BaTiO_3$-$NiFe_2O_4$ thin films were deposited by laser ablation, on platinum covered Si(001) substrates. The depositions were done with a KrF excimer laser (wavelength λ = 248 nm), at a fluence of 2 mJ/cm^2. The oxygen pressure was 1 mbar and the substrate temperature was 650ºC. The ablation targets were obtained by sintering $NiFe_2O_4$ and $BaTiO_3$ powders with different concentrations. Structural studies were performed by X-ray diffraction (XRD), using a Philips PW-1710 diffractometer with CuKα 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 30% - 50%. For comparison, the end members $BaTiO_3$ and $NiFe_2O_4$ are also shown. The films are polycrystalline and composed by a mixture of tetragonal-$BaTiO_3$ and $NiFe_2O_4$ with cubic inverse spinel structure. As the concentration of the nickel ferrite increases the relative intensity of the (311) $NiFe_2O_4$ peak increases, indicating the progressive more oriented growth of this phase. The grain sizes, obtained from the fitted X-ray diffraction peak widths for both phases, were determined by using the Scherrer equation. They are in the range 20 - 71 nm for the barium titanate phase and 15 - 22 nm for the $NiFe_2O_4$ one.

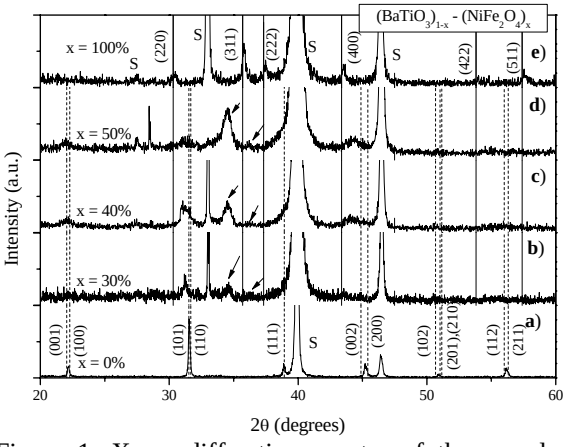

Figure 1: X-ray diffraction spectra of the samples deposited with nickel ferrite concentrations x = 0%-50% and 100%. The peaks marked with an S are from the substrate.

The lattice parameters *a* and *c* of the tetragonal $BaTiO_3$ phase were obtained from the (200) and (002) peak positions. For the pure barium titanate film, *a* is slightly expanded and *c* is slightly contracted relative to the bulk, giving a lower tetragonal distortion of the $BaTiO_3$ structure. However, on the nanocomposites studied, the *a* and *c* lattice parameters of the $BaTiO_3$ phase are always above the bulk ones (but with c/a near the bulk one), indicating an overall expansion of the unit cell due to the presence of $NiFe_2O_4$. On the other hand, the lattice parameter of the $NiFe_2O_4$ phase, obtained from the (311) peak position, is always above the bulk value (a_{bulk} = 4.339Å) and varies from 8.606 Å on the sample with lower cobalt ferrite concentration (x=30%), to 8.624 Å on the sample with higher $NiFe_2O_4$ content (x=50%). Comparing with the bulk $NiFe_2O_4$, in the films the nickel ferrite unit cell has an expansion strain that increases as its concentration increases, up to x=50%.

Figure 2 shows the Raman spectra of the thin film samples deposited with cobalt ferrite concentrations in the range 30%-50%. Also shown are the individual $BaTiO_3$ and $NiFe_2O_4$ bulk reference powders, for comparison. In the $BaTiO_3$ case, the peak at 716 cm^{-1}, corresponds to the longitudinal optical (LO) vibration of the E phonon mode [2] and the decrease of its intensity with increasing nickel ferrite concentration reflects the corresponding decrease of the barium titanate content in the films.

The inverse spinel structure of AFe_2O_4 consists of AO_6 and FeO_4 octahedra and FeO_6 tetrahedra. The modes arising from the octahedra and tetrahedra can be easily distinguished in the Raman spectrum of ferrites. Raman peaks over the region 660-720 cm^{-1} represent the modes of tetrahedra and those in 460-660 cm^{-1} region correspond to modes of octahedra [3]. The nickel ferrite modes appearing at 570 cm^{-1} and 700 cm^{-1} can then be assigned to octahedral site (O-site) sublattice and tetrahedral site (T-site) sublattice vibration modes, respectively [3].

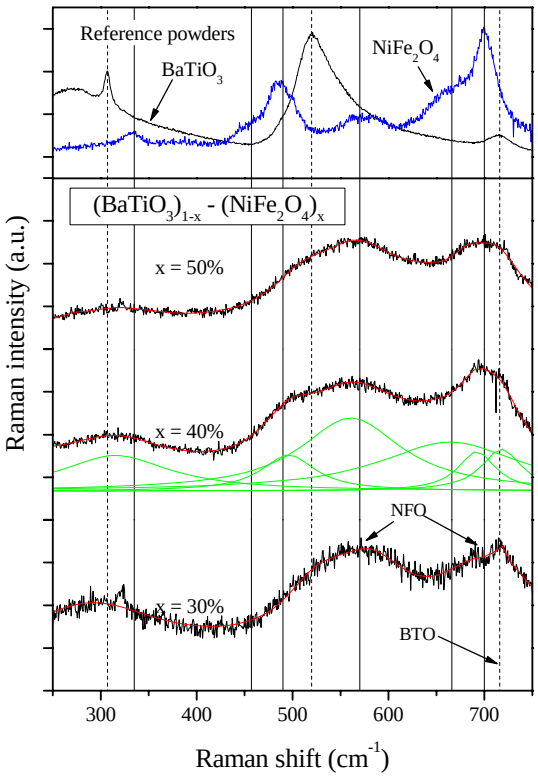

Figure 2: Raman spectra of the samples deposited with $NiFe_2O_4$ concentrations in the range 30%-50%, along with the corresponding fitting curves. Also shown are the $BaTiO_3$ and $NiFe_2O_4$ reference powders, and the Lorentzians obtained from the fit to the spectrum of the sample with x = 40%.

Based on the peaks observed on the powders, the nanocomposite films spectra were deconvoluted by using Lorentzian line-shape functions to least-squares fit the Raman peaks (fig. 2). Figure 3 shows the vibrational modes wavenumbers for the O-site and T-site Raman peaks of the $NiFe_2O_4$ phase as well as of the $BaTiO_3$ phase E peak near 716 cm^{-1}. As the nickel ferrite concentration increases, the barium titanate E peak of figure 3 is near and somewhat oscillates around the bulk value. On the other hand, the $NiFe_2O_4$ T-site mode has a redshift on the nanocomposites, with its wavenumber being systematically below the bulk value. A similar trend is observed for the O-site mode, for the films with 40% and 50% $NiFe_2O_4$ concentration. This redshift of the $NiFe_2O_4$ modes results from the expansion of the lattice parameter of the nickel ferrite, as was similarly observed from the X-ray diffraction results (fig. 1).

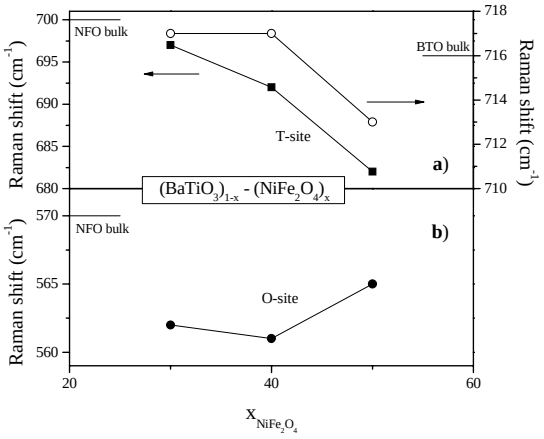

Figure 3: Raman shift as a function of the $NiFe_2O_4$ concentration, for the a) left: O-site and b) T-site modes. In the right axis of a) is the E mode of $BaTiO_3$ which appears at 716 cm^{-1} in the bulk.

References:

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