

Structural and Magnetic Properties of Nanogranular BaTiO₃-CoFe₂O₄ Thin Films Deposited by Laser Ablation on Si/Pt Substrates

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Abstract. Thin film nanocomposites of cobalt ferrite (CoFe₂O₄) dispersed in barium titanate (BaTiO₃) matrix, have been deposited with different cobalt ferrite concentrations (from 20% to 70% CoFe₂O₄), as well as pure barium titanate and cobalt ferrite thin films (end members). The films were prepared by pulsed laser ablation on platinum covered Si(001) substrates. The films structure was studied by X-ray diffraction and their surface was examined by scanning electron microscopy (SEM). The magnetic properties were measured in a SQUID magnetometer. The results show that the deposited films are polycrystalline with a slight (111) barium titanate phase orientation and (311) CoFe₂O₄ phase orientation. The grain sizes measured from the X-ray diffraction peak widths, for both phases, are in the range 40nm to 100nm. However, as the concentration of the cobalt ferrite increases, the grain size of the BaTiO₃ phase decreases, from 100nm to 30nm, up to 40% CoFe₂O₄ concentration beyond which the BaTiO₃ grain size has an approximately constant value near 30nm. On the other hand the cobalt ferrite grain size does not show a clear trend with increasing cobalt ferrite concentration, fluctuating in the range 20nm to 30nm. The magnetic measurements show an increase of the magnetic moment from the low concentration region where the magnetic grains are more isolated and their magnetic interaction is small, towards the bulk value at higher CoFe₂O₄ concentrations. Also, a strong reduction of the magnetization with increasing temperature was observed, due to the corresponding decrease of the magnetocrystalline anisotropy of the cobalt ferrite.

Introduction

Nanocomposite multiferroic thin films formed by combining a piezoelectric ceramic and a magnetostrictive material, such as in the BaTiO₃-CoFe₂O₄ system, have been attracting much scientific and technological interest [1]. In these systems, the elastic interactions between the phases provides the coupling mechanism inducing a magnetoelectric behavior [1,2]. 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 thin films of cobalt ferrite (CoFe₂O₄) dispersed in a barium titanate (BaTiO₃) matrix were deposited with different cobalt ferrite concentrations, as well as pure barium titanate and cobalt ferrite films (end members). CoFe₂O₄ has a cubic inverse spinel structure [3] and 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 [5], which has a cubic structure at high temperatures. Below ~395 K BaTiO₃ transforms from a

cubic to a tetragonal structure, that remains at ambient temperature. The high temperature cubic phase is paraelectric and the ambient temperature tetragonal phase is ferroelectric.

Experimental

The nanogranular BaTiO_3 - CoFe_2O_4 thin films were prepared by pulsed laser ablation, on platinum covered $\text{Si}(001)$ 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 $p\text{O}_2 = 1$ 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. The end members targets, barium titanate and cobalt ferrite, were also prepared in this way. The 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. The films surface was examined using a Leica Cambridge S360 scanning electron microscope (SEM), with 10 kV operating voltage. Energy dispersive X-ray analysis (EDX) was used in order to perform chemical studies. The magnetic properties were measured with a Quantum Design MPMS SQUID magnetometer. 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.

Discussion

Figure 1a) shows the X-ray diffraction spectra measured on the nanocomposite thin films with cobalt ferrite concentrations in the range 20% - 100%. Figure 1b) shows a SEM micrograph obtained on the sample deposited with 40% cobalt ferrite concentration. The films are polycrystalline and composed by a mixture of tetragonal- BaTiO_3 and CoFe_2O_4 with the cubic inverse spinel structure. They present a granular surface, as observed by SEM, with a broad range of grain sizes. The bigger grains observed in the micrograph of figure 1b) have an average size of 647nm. The concentration of the elements composing the films, obtained from EDX measurements on different regions (and grains) of the micrographs, is uniform over the analyzed area. Inherent to the laser ablation technique is the appearance of droplets on the films surface, with sizes $\sim 2 - 5 \mu\text{m}$. In our samples, the surface shows a low density of these droplets.

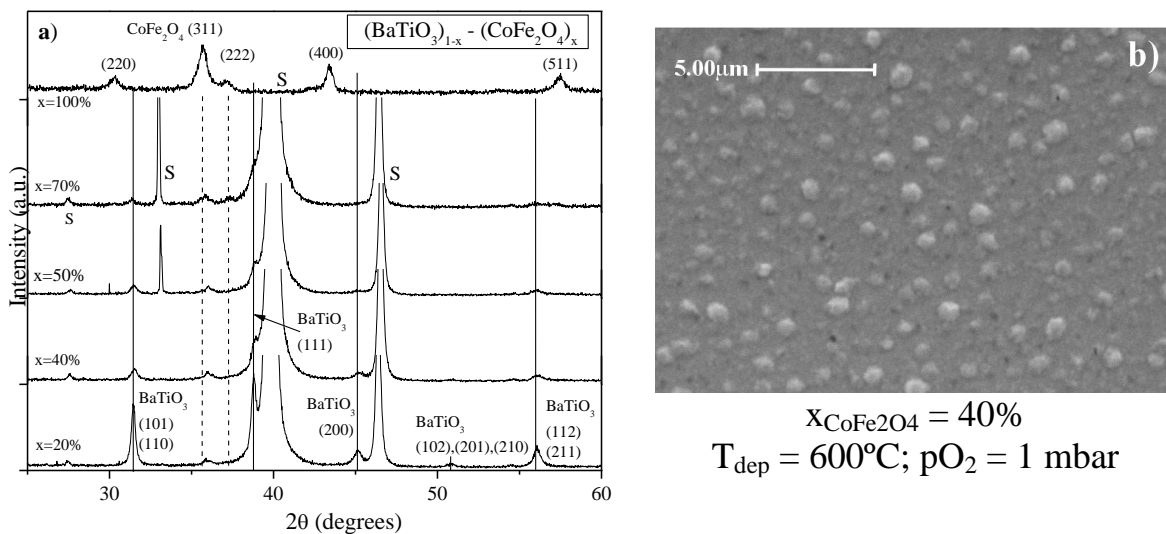


Figure 1: X-ray diffraction spectra of the samples deposited with CoFe_2O_4 concentrations in the range 20%-100% (a), and SEM micrograph obtained on the film with $x = 40\%$ (b). The vertical lines mark the peak position of the bulk CoFe_2O_4 cubic spinel phase (---), and the tetragonal- BaTiO_3 phase (—). The peaks marked with an S are from the substrate.

The grain sizes as measured from the X-ray diffraction peak widths for both phases ((112) for BaTiO₃ and (311) for CoFe₂O₄), were determined by using the Scherrer equation [6]. They are shown in figure 2a) for the different nanocomposite films. The grain sizes are in the range 20nm to 100nm. However, as the concentration of the cobalt ferrite increases, the grain size of the BaTiO₃ phase decreases, from 91.5 nm to 30nm, up to 50% CoFe₂O₄ concentration beyond which the BaTiO₃ grain size fluctuates in the interval 25-35nm. On the other hand the cobalt ferrite grain size

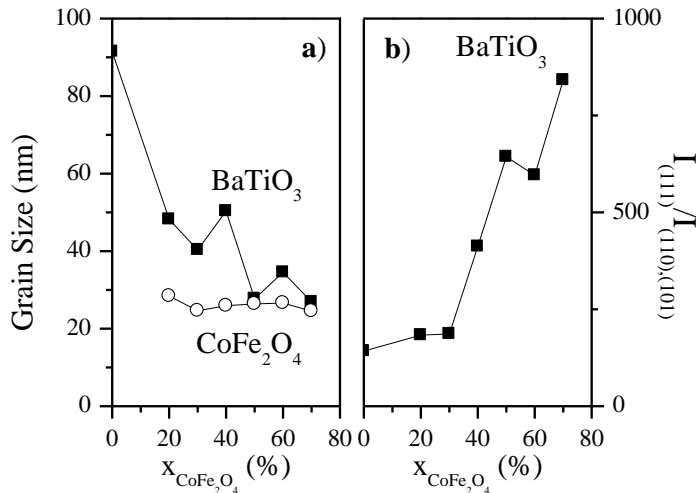


Figure 2: Grain sizes of the BaTiO₃ and CoFe₂O₄ phases (a) and relative intensity of the (111) peak (b), for different CoFe₂O₄ concentrations.

does not show a clear trend with increasing cobalt ferrite concentration, fluctuating in the range 25nm to 30nm. Since the average grain sizes of the phases composing the films are below 100nm and the SEM micrographs show the existence of a significant number of grains up to ~650 nm, this again indicates the presence of a broad distribution of grain sizes in the films.

Figure 2b) shows the relative intensity between the (111) peak and the (110),(101) peaks of the BaTiO₃ phase in the films, for different CoFe₂O₄ concentration. The (110),(101) peaks are the most intense ones in bulk tetragonal BaTiO₃. As the concentration

of the cobalt ferrite increases, the relative intensity of the (111) BaTiO₃ peak increases, indicating a more oriented growth of this phase. The opposite occurs with the (311) peak from the CoFe₂O₄ phase. From figure 1a), as *x* increases the (222) peak starts to appear, while the intensity of the (311) peak only slightly changes, indicating a progressive increase of the polycrystallinity of the CoFe₂O₄ phase in the films.

The lattice parameter of the cobalt ferrite phase was determined from the X-ray diffraction spectra measured on the nanocomposites. For CoFe₂O₄ it was obtained from the (311) peak position and varied from 8.26Å in the sample deposited with cobalt ferrite concentration *x* = 20%, to 8.35Å in the sample deposited with *x* = 70%. Comparing with the bulk CoFe₂O₄ lattice parameter (*a* = 8.3919Å), in the films the cobalt ferrite is under compressive stress that relaxes as its concentration progressively increases.

Figure 3 shows the magnetic moment hysteresis loops measured on the nanocomposite films at the temperatures *T* = 10 K and *T* = 300 K. The loops were measured on the films plane and corrected by subtracting the diamagnetic contribution from the substrate. Taking the value of the magnetic moment at the higher applied magnetic field (60kOe) and dividing by the volume of the films, the saturation magnetization (*M_s*) was obtained. Figure 4 shows *M_s* for the nanocomposite thin films, at the temperatures *T* = 10 K and *T* = 300 K. The magnetization increases with increasing cobalt ferrite concentration, so that the

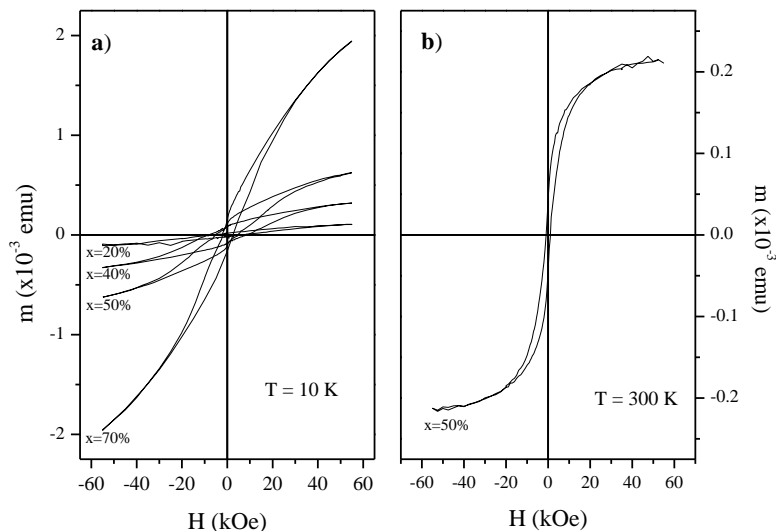


Figure 3: Magnetic hysteresis cycles of the nanocomposite (BaTiO₃)_{1-x}-(CoFe₂O₄)_x films, measured at a) T=10 K and b) T=300K.

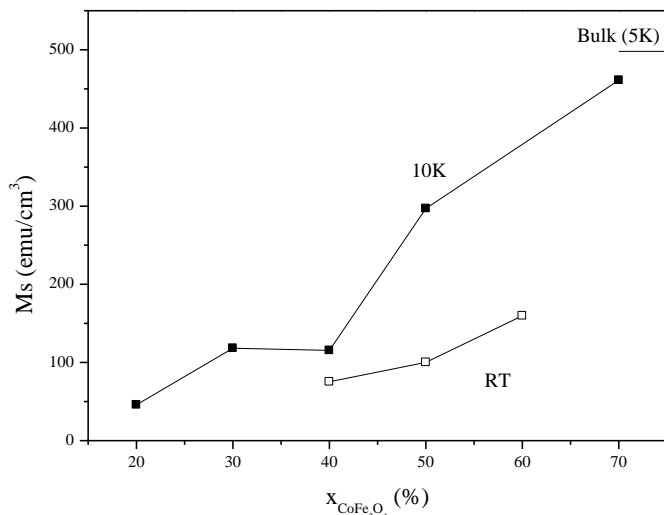


Figure 4: Saturation magnetization obtained from the hysteresis cycles, at $T=10\text{K}$ and $T=300\text{K}$. The horizontal line mark the bulk value reported at 5K [9].

interactions between them. Thus, the magnetic moment of these isolated grains is more difficult to align along the applied magnetic field, particularly for the smaller grains ($<40\text{nm}$) which are monodomain. As the cobalt ferrite concentration increases, the nanograins start to form larger clusters of less isolated nanoparticles, the magnetic interparticle interaction increases, and the saturation magnetization progressively increases towards the bulk CoFe_2O_4 value. Also, the magnetization strongly decreases, from 10K to 300K (fig. 4), due to the decrease of the magnetocrystalline anisotropy of CoFe_2O_4 [3,7]. Consequently, the loops measured at 10K are not fully saturated and a higher applied magnetic fields would be needed in order to attain the true M_s . However, at 300K , the hysteresis loops saturate for applied fields below 60kOe , due to the decrease of the magnetocrystalline anisotropy, as shown in figure 3b) for the sample with $x = 50\%$.

Conclusions

Nanogranular composites of cobalt ferrite dispersed in a barium titanate matrix were deposited with different CoFe_2O_4 concentrations. Detailed structural and magnetic measurements were performed on the films. The barium titanate phase presented a tetragonal structure, while the cobalt ferrite had the cubic spinel structure, and a broad distribution of grain sizes was present in the films. An increase of the magnetization with increasing CoFe_2O_4 concentration was observed, due to a higher magnetic inter-particle interaction with increasing cobalt ferrite content. The decrease of the magnetocrystalline anisotropy of the cobalt ferrite with increasing temperature induced a corresponding decrease of the magnetization, and a less difficult saturation of the hysteresis loops of the films.

Acknowledgments

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References

- [1] W. Eerenstein, N.D. Mathur and J.F. Scott: Nature Vol. 442 (2006), p. 759
- [2] H. Zheng, J. Wang, S.E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S.R. Shinde, S.B. Ogale, F. Bai, D. Viehland, Y. Jia, D.G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, Science: Vol. 303 (2004), p. 661

saturation magnetization, at 10K , becomes near from the bulk value at higher CoFe_2O_4 concentrations.

During deposition of the thin films, the cobalt ferrite phase nanograins are formed with a broad range of sizes, with average grain size between 25nm and 30nm as referred earlier. Due to the magnetocrystalline anisotropy, the Co-ferrite particles are monodomain for sizes smaller than 40nm [7,8], while the bigger particles (larger than 40nm) divide into domains. Magnetization vector rotation is considered to be the mechanism responsible for the hysteresis [3] of small particles. For low concentrations, the CoFe_2O_4 grains are more isolated weakening ferromagnetic

- [3] S. Chikazumi, *Physics of Ferromagnetism*, Oxford University Press, New York, (1997)
- [4] M. Grigorova, H.J. Blythe, V. Blaskov, V. Rusanov, V. Petkov, V. Masheva, D. Nihtianova, L.M. Martinez, J.S. Muñoz, M. Mihov, *J. Magn. Magn. Mat.:* Vol. **183** (1998), p. 163
- [5] Seung-Eek Park, S. Wada, L.E. Cross, and T.R. ShROUT, *J. Appl. Phys.:* Vol. **86** (1999), p. 2746
- [6] B.D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley, Reading MA, (1978)
- [7] C. N. Chinnasamy, B. Jeyadevan, K. Shinoda, K. Tohji, D. J. Djayaprawira M. Takahashi, R. Justin Joseyphus and A. Narayanasamy, *Appl. Phys. Lett.:* Vol. **83** (2003), p. 2862
- [8] J.S. Jung, J.H. Lim, K.H. Choi, S.L. Oh, Y.R. Kim, and S.-H. Lee, D.A. Smith, K.L. Stokes, L. Malkinski, and C.J. O'Connor, *J. Appl. Phys.:* Vol. **97** (2005), p. 10F306
- [9] L. D. Tung, V. Kolesnichenko, D. Caruntu, N. H. Chou, C. J. O'Connor, and L. Spinu, *J. Appl. Phys.:* Vol. **93** (2003), p. 7486