

STRUCTURAL AND MAGNETIC PROPERTIES OF NiFe_2O_4 - BaTiO_3 MULTIFERROIC CORE-SHELL TYPE NANOSTRUCTURES

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Introduction

Magnetoelectric composites, as part of multiferroic materials, had gained great attention during last years, since they exhibit a response in excess of two orders of magnitude higher than single phase magnetoelectric materials [1]. The magnetoelectric effect in composite materials, where in general, a magnetostrictive phase is mechanically coupled to a piezoelectric phase, is originated by the elastic interaction among the subsystems via stress mediation [2]. In these materials, the magnetoelectric response depends not only on the intrinsic properties of each phase but also on the mechanical coupling at the interface. Here different connectivities have been proposed, leading particulate [3,4] and multilayers [5,6] composites with enhanced properties.

In this work, we report the preparation, structural and magnetic properties of core-shell like $\text{NiFe}_2\text{O}_4/\text{BaTiO}_3$ nanostructured composites. The main focus was to clarify the correlation between the structure and properties of the composites. The understanding of such relations is imperative in order to tailor the properties of the nanostructured composites.

Experimental

Nickel ferrite – Barium titanate nanocomposites were synthesized by a combination of co-precipitation and sol-gel methods following a two step procedure. Specific details of the preparation procedure were published elsewhere [7].

In a first step, NiFe_2O_4 core particles were synthesized by chemical co-precipitation starting from a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The precipitating agent was a 5 M NaOH solution with 100% molar excess. Oleic acid (reagent grade, Sigma-Aldrich) was added to the suspension at 30 wt.% respects to the nickel ferrite. Octane was added to the mixture to transfer the nanoparticles from the aqueous phase to an organic phase, forming a ferrofluid.

Core-shell nanostructures of NiFe_2O_4 - BaTiO_3 were synthesized in a second step by the sol-gel technique. $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ was mixed with titanium (IV) n-butoxide, stearic acid and glacial acetic acid to form a sol. The previously obtained ferrofluid was added to the sol and 2-Methoxyethanol anhydrous was added to promote the gel formation. The final compositions have a content of 20, 30, 40, 50 and 60 wt.% of nickel ferrite with respect to the barium titanate, namely samples Ni20, Ni30,

Ni40, Ni50 and Ni60, respectively. The obtained gels were dried and sintered at 700°C for 2 hours. A NiFe_2O_4 pure sample was sintered under the same conditions than the nanostructures (sample NFO-s) and an additional sample without ferrofluid was also prepared as a reference (sample BTO).

The properties of the samples were studied by x-ray diffraction (XRD), from a Siemens diffractometer (CuK α radiation, operated at 25 mA, 35 kV). The average crystallite size was determined with the PowderCell 2.4 software. The exact composition of the nanocomposites was determined by chemical analysis of the constituent elements (obtained from Galbraith Laboratories, Inc.). The magnetic properties were measured at room temperature at a Quantum Design PPMS-7 (physical properties measurement system) with VSM option.

Results and discussion

X-ray diffraction patterns of the nanostructures revealed the presence of both the spinel and perovskite phases, corresponding to NiFe_2O_4 and BaTiO_3 respectively. Figure 1 shows the crystallite size values of both phases, obtained from the refinement. As the amount of BaTiO_3 decreased in the nanocomposites, its crystallite size decreased, while the crystallite size of the nickel ferrite increased slightly, being noticeably smaller than that of the sample NFO-s.

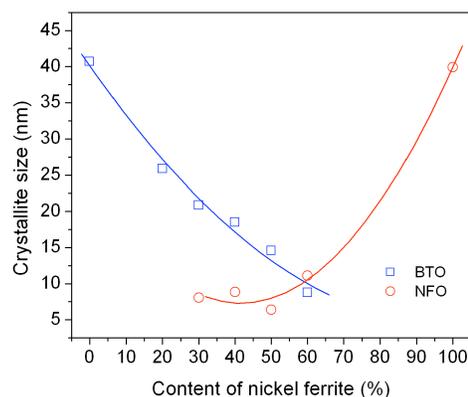


Figure 1. Crystallite size of barium titanate and nickel ferrite.

This could be attributed to the diffusion inhibition between the ferrite nanoparticles during sintering due to the BaTiO_3 shell, which may maintain each ferrite nanoparticle isolated. This result is an indirect evidence of the core-shell nature of the nanostructures. For the barium titanate, the crystallization may occur epitaxially

over the nickel ferrite nanoparticles, promoting the formation of more than one crystallite in each nanostructure. Due to the mass ratio of the phases, it is expected that at higher content of ferrite, the shell will be thinner.

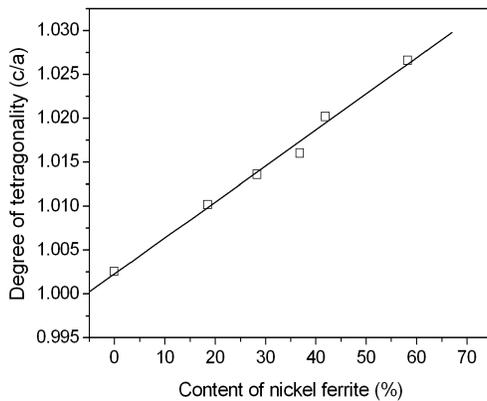


Figure 2. Degree of tetragonality in barium titanate shells.

Figure 2 shows the degree of tetragonality of the barium titanate phase, calculated as the ratio of the lattice parameters c and a , in the nanostructures. The degree of tetragonality increased with the ferrite content. Similar results were obtained for core-shell type nanostructures of Cobalt ferrite and Barium titanate [7]. Based on the fact that the crystallite size of the barium titanate decreased with the content of ferrite, it's possible to conclude that the degree of tetragonality increases as the barium titanate crystallite size decreases. This may be attributed to a possible strain induced in the barium titanate phase when crystallizing over the nickel ferrite core due to the crystallographic mismatch between the phases.

All composite samples showed a superparamagnetic like behavior at room temperature (RT). Figure 3 shows the ZFC-FC magnetization curves for the samples. The NFO-s sample showed a ferromagnetic behavior at RT so the ZFC-FC curves were omitted from the figure. The curves exhibit typical features of an assembly of magnetic particles with a distribution of blocking temperatures. The values of the mean blocking temperature, associated to the maxima of the ZFC curves, reflect the previously presented changes in the particle size.

The curves also reflect a slightly increase in the irreversibility temperature, considered as the point where the ZFC and FC begins to separate. The separation between the blocking temperature and the irreversibility temperature is not observed in the as synthesized ferrite, being a distinct behavior of the nanostructured composites. Furthermore, such behavior could be expected for a system of nanoparticles with random anisotropies and dipole-dipole interactions [8]. In the case of the present nanostructures this could be a

consequence of thinner shells at higher contents of ferrite, which could result in a higher interaction between the magnetic cores.

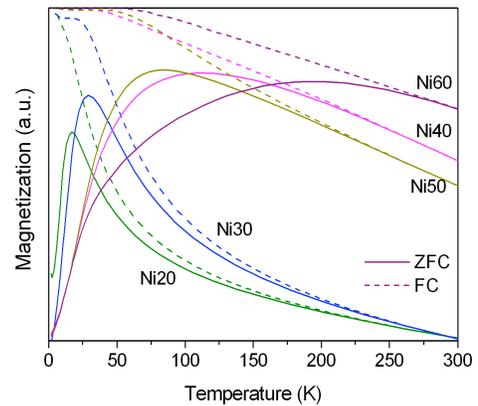


Figure 3. ZFC and FC magnetization curves.

Summary

Multiferroic core-shell type nickel ferrite-barium titanate nanostructures were successfully synthesized by a novel wet chemical procedure. The structural and magnetic data suggest the insulation of the nickel ferrite core inside a BaTiO_3 shell. The increase in the mass ratio of the phases leads to an increase in the degree of tetragonality of the BaTiO_3 shell as the crystallite size decreases. Furthermore, the reduction in the thickness of the shells results in a higher interaction between the magnetic cores.

References

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