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Magnetic properties of ferrite-titanate nanostructured composites synthesized by the polyol method and consolidated by spark plasma sintering

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Multiferroic systems formed by a mixing of a ferroelectric phase and a ferrimagnetic phase are receiving significant attention because of their wide possibilities for tailoring properties. In this work, the magnetic properties of the cobalt ferrite-barium titanate system were investigated on samples prepared by an original combination of synthesis methods. Cobalt ferrite and barium titanate nanoparticles were synthesized separately by hydrolysis of the metal acetates in a polyol method. Both materials were mixed in a 1:1 ratio and consolidated by spark plasma sintering at 500 °C for 5 min. A high density nanostructured ceramic was obtained with grains smaller than 100 nm and a density about 80% of the theoretical value. Magnetic hysteresis loops showed a hard magnet behavior, with a coercive field larger than cobalt ferrite alone prepared under the same conditions. δM reversible magnetization plots exhibited dipolar interactions with a maximum at the coercive field. These results are interpreted in terms of an efficient mixing of the components, which strongly decreases the magnetic percolation in the composite by separating ferrite grains by titanate grains. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798604]

I. INTRODUCTION

The investigation of composite multiferroic materials has received intense attention in the last few years because of their potentially technological impact on many multifunctional applications such as thermistors, multilayer capacitors, piezoelectric transducers, electrooptical devices, among others.[1,2] Special interest has been placed on ferroelectric-ferrimagnetic systems, and due to their chemical stability and outstanding electrical and magnetic properties on the barium titanate ($BaTiO_3$)-cobalt ferrite ($CoFe_2O_4$) system.[3–5] Several mixing methods of the separately synthesized phases have generally been used with various results.[6,7] These phases can be synthesized by methods such as wet chemical reaction,[8] sol-gel,[9,10] and from commercial nanocrystalline reagents followed by spark plasma sintering (SPS).[4] A common problem has been atomic interdiffusion between the two phases, which deteriorates the expected electrical and/or magnetic properties of the composite.[2,11]

In this paper, we present an investigation of the magnetic properties of $BaTiO_3$-$CoFe_2O_4$ nanostructured composites. The initial precursors were synthesized by the forced hydrolysis in a polyol method,[12,13] which typically provides nanoparticles (NPs) in the 10 nm range. It was followed by SPS,[14,15] which allows phase consolidation to high density at low temperatures and very fast sintering rates, thereby keeping grain size within the nanometric range. Hysteresis loops and δM plots showed an effective mixing and no evidence of phase interdiffusion.

II. EXPERIMENTAL TECHNIQUES

Cobalt ferrite (CF) NPs were synthesized by the forced hydrolysis in a polyol method from the corresponding acetates, as detailed elsewhere.[12,13] This method has been carried out successfully for many spinel ferrites. For barium titanate (BT) synthesis, a solution of barium acetate [$Ba(C_2H_3O_2)$] in titanium isopropoxide $Ti\{OCH(CH_3)_2\}_4$ was first prepared. The solution was dropped in diethylenglycol, and heated to 145 °C to promote the dissolution of the acetate. A small quantity of sodium hydroxide (NaOH) was added as hydrolyzing agent prior to heating to the boiling point of the mixture (~230 °C) under mechanical stirring. After a 3 h reflux, it was cooled down to room temperature. The solid obtained was recuperated by centrifugation, cleaned with ethanol, and dried in air at 50 °C. To improve crystallinity, an annealing at 650 °C for 2 h was carried out. To the best of our knowledge, nanostructured BT has not been prepared by this method before.

The obtained NPs of both compositions were mechanically mixed in a 1:1 molar ratio, and then subjected to a consolidation process by means of SPS[14,15] in a DR Sinter-Lab-SPS 515S system. A pressure of 100 MPa was applied and temperature was slowly increased to 280 °C and maintained by 10 min at this point, to promote an outgassing of any organic remains in the sample. Temperature was then increased to 500 °C and kept at this temperature for 5 min,

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before cooling down. Vacuum was maintained during the whole process. X-ray diffraction patterns were obtained in a Panalytical XperPro diffractometer equipped with a multichannel detector (X'celerator) using cobalt radiation. High resolution transmission electron microscopy (HRTEM) was performed by means of a JEOL 100-CX operating at 100 kV. A JEM-9320 focused ion beam (FIB) facility was used to prepare samples for scanning electron microscopy (SEM). Magnetic hysteresis loops and δM plots were obtained with a LDJ 9200 vibrating sample magnetometer (VSM) at 300 and 79 K, under a maximum applied field of 16 kOe.

III. EXPERIMENTAL RESULTS AND DISCUSSION

As expected, the polyol method produced well crystallized ferrite NPs in the 6–8 nm range, Fig. 1(a). In the case of barium titanate, in contrast, the polyol method led to an amorphous phase, Fig. 1(b). In order to improve the BT crystallinity, an annealing at 650 °C for 2 h was performed. After the SPS process, X-ray diffraction pattern exhibited a combination of the diffraction peaks of both phases, in very good agreement with the corresponding X-ray cards, Fig. 2. A small concentration of metallic cobalt was observed, as often produced in this technique, due to the reducing conditions (graphite mould under vacuum).

An observation of the ion-milled surface by SEM at low amplification revealed a good mixing of the phases, as shown in Fig. 3(a). The vertical direction is the axis of pressing during SPS, which produced some horizontal pattern in the phases. The light phase can be associated with BT, as Ba is a heavier element than Co and Fe. An SEM micrograph with higher amplification is shown in Fig. 3(b), where grains appear smaller than 50 nm.

Hysteresis loops of the CF-BT composite at room temperature are shown in Fig. 4. For comparison, the hysteresis loops of pure cobalt ferrite prepared by the same methods and same conditions (polyol + SPS) appear on the same plot. BT is a diamagnetic compound, so it was not considered for these comparisons. The ferrite sample, Fig. 4(a), showed a saturation magnetization close to 75 emu/g, which agrees well with the value for cobalt ferrite NPs at room temperature.[16]

A decrease in magnetization of composite is observed (close to 50%) at room temperature when compared with the ferrite single phase; this is simply due to the dilution of the ferrimagnetic part of the sample by the BT diamagnetic grains. At 79 K, Fig. 4(b), the difference in coercive field is more evident. This can be attributed to the fact that as

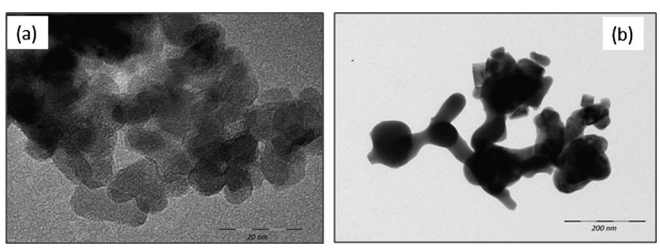

FIG. 1. HRTEM of nanoparticles as obtained from the polyol method: (a) ferrite and (b) titanate.

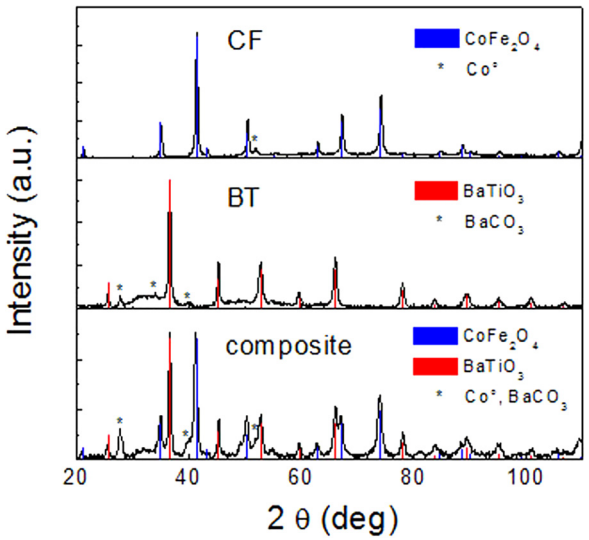

FIG. 2. XRD of the ferrite (high), the titanate (middle), and composite (bottom) after sintering in SPS at 500 °C for 5 min.

temperature decreases, the magnetocrystalline anisotropy for both samples increases; however, the composite sample possesses a higher anisotropy field, and therefore its state of magnetization is lower than the one of the ferrites at the same applied field. In other words, a 16 kOe applied magnetic field represents a lower fraction of anisotropy field for the composite than for the ferrite.

δM plots[17] (a variation of Henkel plots) were obtained for both the consolidated ferrite and the composite, and are shown in Fig. 5 for the two temperatures. In these experiments, the sample is subjected to increasing states of magnetization (by using the same field steps) up to the maximum applied field, and then the same process is carried out for the demagnetization quadrants of the loop. The remanent values for each step are compared, leading to a zero value when the sample approaches the idealized model of Stoner-Wohlfarth (SW). This occurs when the sample approaches the SW model assumptions: single domain particles with no interaction, uniaxial anisotropy, homogeneous inversion of magnetization, and no effects of thermal agitation. The deviations from $\delta M = 0$ point to interacting particles; negative values indicate dipolar interactions (remanent magnetization decreases as compared with the idealized value of SW model), while positive values occur for exchange interactions among particles.

Figure 5 shows values in the negative half of the plot, associated with dipolar interactions between particles, for the two samples at both temperatures. A critical point is

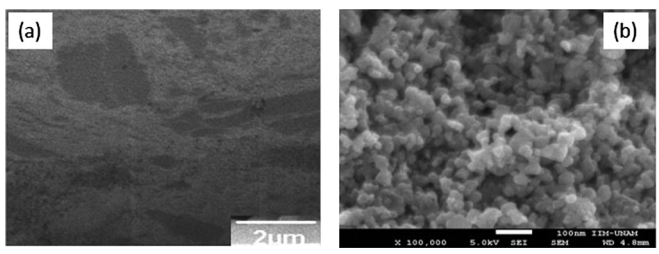

FIG. 3. (a) SEM micrograph of the ion-milled surface of the sample. The light areas are associated with BT (heavier elements); (b) TEM micrograph of the composite, showing the grain size.

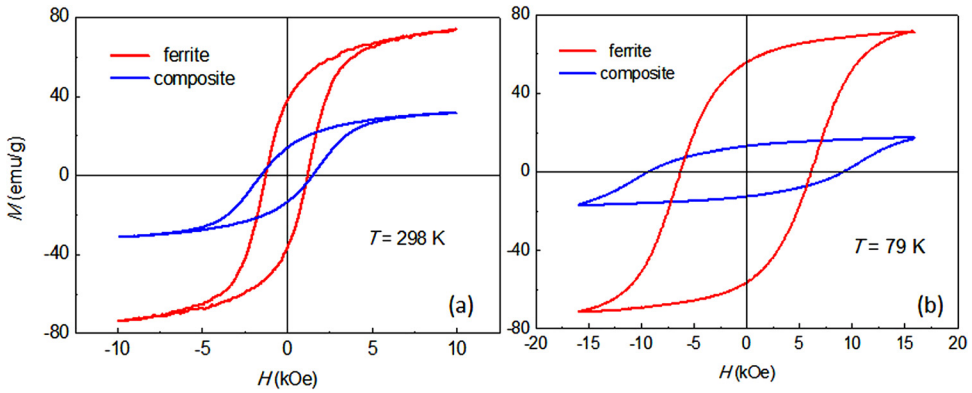

FIG. 4. Hysteresis loops of samples (a) at room temperature and (b) at 79 K.

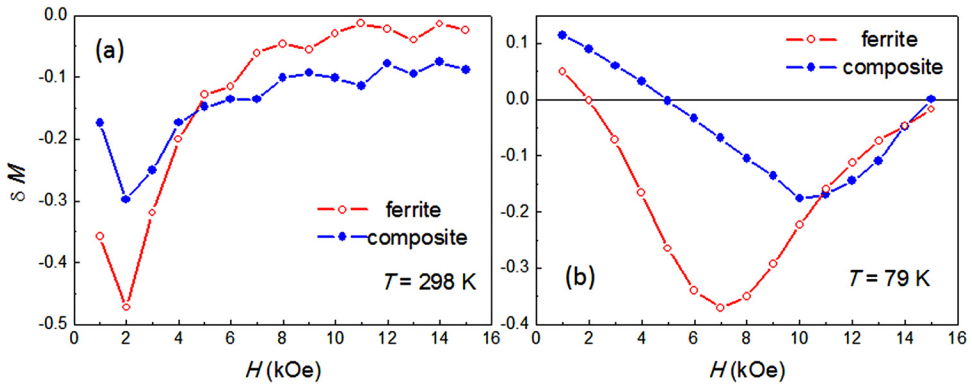

FIG. 5. δM plots for (a) room temperature, and (b) 79 K for the composite and the consolidated ferrite.

observed which is related with the coercive field. This maximum in dipolar deviation can be easily understood by considering that the coercive field corresponds to zero magnetization. At this point, the magnetization of all the grains exactly compensates each other (net magnetization is zero). This configuration leads to the highest dipolar interaction, since there is exactly the same amount of grains oriented in all possible directions. As applied field overcomes this point, grains become progressively oriented in the field direction, thereby decreasing the dipolar interactions.

On the whole field range, composite exhibits values closer to zero as compared with the ferrite, which can be associated with a decrease in the dipolar interaction as ferrite grains are separated by diamagnetic titanate grains. The dipolar interactions between ferrite NPs decrease and at the same time the coercive field of the composite increases because the mixing with a diamagnetic phase leads to a state closer to isolated ferrite NPs.

IV. CONCLUSIONS

$BaTiO_3$-$CoFe_2O_4$ nanostructured composites with grain size below 100 nm and no evidence of phase interdiffusion were successfully synthesized by a combination of forced hydrolysis and SPS methods. The hysteresis loops and the δM plots of these composites showed a higher coercive field when compared with the ferrite alone phase, synthesized under the same conditions, which can be interpreted in terms of an efficient mixing of the ferrimagnetic-diamagnetic phases. The combination of polyol and subsequent SPS treatment of obtained nanoparticles appears, therefore, as a very convenient technique to prepare nanostructured composites of a very wide variety of compositions.

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