Cobalt Ferrite/Barium Titanate Core/Shell Nanoparticles

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To cite this article: M. Etier, Y. Gao, V. V. Shvartsman, A. Elsukova, J. Landers, H. Wende & D. C. Lupascu (2012): Cobalt Ferrite/Barium Titanate Core/Shell Nanoparticles, Ferroelectrics, 438:1, 115-122

To link to this article: http://dx.doi.org/10.1080/00150193.2012.743773

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Cobalt Ferrite/Barium Titanate Core/Shell Nanoparticles

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Cobalt ferrite/barium titanate nanoparticles with a core/shell structure were synthesized by combining co-precipitation and organosol methods. The average particle size was about 110 nm with an average shell thickness of about 40 nm. Dielectric and magnetic properties of the particles were studied using impedance and Mössbauer spectroscopy, respectively. The particles are promising for fabrication of multiferroic ceramics with the core-shell structure.

Keywords Multiferroic; composite; core-shell

I. Introduction

Multiferroics are materials that possess two or more ferroic orders, e.g. ferromagnetism and ferroelectricity. They have attracted an immense interest due to their fascinating physics and many possibilities of application [1–3]. Of particular interest is the magnetoelectric (ME) effect, which consists of the control of the polarization or magnetization by a magnetic or electric field, respectively [4]. Single phase multiferroics exhibit relatively low values of ME coupling and nearly all of them at low temperatures only. However, a large ME effect can be achieved in the vicinity of room temperature in composite multiferroics commonly consisting of a piezoelectric and magnetostrictive components [2–4]. An external electric field applied to the composite generates a mechanical strain in the piezoelectric constituent. This strain is transferred via common interface to the magnetostrictive component, where a change of magnetization is induced. Analogously, an applied magnetic field results in a change of polarization in the piezoelectric constituent. The type of connectivity and the properties of the phase interfaces strongly influence the value of the coupling. Core-shell type structures are of particular interest, because an enhanced ME effect is expected due to the large well defined interface area [5]. The core shell structure was synthesized by different methods, such as combined hydrothermal and annealing processes [6], the sol-gel method [7–9], and wet chemical methods [10]. In this paper we report on a new procedure to form CoFe2O4/BaTiO3 core/shell nanoparticles based on the organosol route. Combination of barium titanate with cobalt ferrite in multiferroic composites is interesting due to the large piezoelectric and magnetostrictive coefficients of the constituents, as well
as the spinodal decomposition of the CoFe$_2$O$_4$-BaTiO$_3$ system assuring nearly phase pure constituents of the composite [2]. The particles were characterized by x-ray diffraction, transmission and scanning electron microscopy, dielectric impedance spectroscopy, and Mössbauer spectroscopy.

II. Experimental Details

CoFe$_2$O$_4$/BaTiO$_3$ (CFO/BTO) core/shell nanoparticles were synthesized combining co-precipitation and the organosol method. The first step was to synthesize cobalt ferrite nanoparticles with size around 40 nm using the co-precipitation method described in details elsewhere [11]. Coating of the CoFe$_2$O$_4$ nanoparticles with a BaTiO$_3$ shell was achieved using a two-step process. In the first step the hydrophobic CoFe$_2$O$_4$ nanoparticles with oleic acid and oleylamine shell were prepared, which formed a stable ferrofluid in toluene. Carboxylic acid groups were bound to the surface of CoFe$_2$O$_4$ nanoparticles to suspend the particles in a fine state of dispersion. Oleic acid and oleylamine are commonly used as dispersing agents to stabilize dispersions in toluene and other nonpolar solvents [12]. In the second step, the CoFe$_2$O$_4$ ferrofluid in toluene was added to the BaTiO$_3$ organosol to create a multi-phase precursor. The scheme of the process is shown in Fig. 1.

The synthesized CoFe$_2$O$_4$ nanopowder was added to toluene. The obtained mixture was heated up to 80°C under gentle stirring to form a stable ferrofluid/toluene suspension, whereupon 30 wt.% of oleic acid (technical grade 90%, Sigma–Aldrich) and oleylamine (technical grade 70%, Sigma–Aldrich) were added to the suspension. The suspension was premixed and mechanically stirred for about 30 minutes and then moved to rotation milling.

![Figure 1. Schematic illustration of the organosol route to fabricate CoFe$_2$O$_4$/BaTiO$_3$ core/shell nanoparticles.](image-url)
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for 12 hours. This treatment causes the media to repeatedly impact on the coarse and agglomerated particles of cobalt ferrite producing de-agglomerated fine particles coated by the surfactant. The ferrofluid was then separated by centrifugation at about 7000 rpm, washed several times with toluene, ethanol, and water to remove the surfactant and the non-modified particles, and then suspended in toluene again to ultimately obtain a stable ferrofluid.

For synthesizing the core shell structures an organosol technique was used [13]. Ba(C₂H₃O₂)₂ (Sigma-Aldrich) was mixed with titanium (IV) n-isopropoxide (reagent grade 97%, Sigma-Aldrich), oleic acid and toluene to form a yellowish “organosol.” An adequate amount of the ferrofluid was added to the obtained sol to a content of 50 wt.% BaTiO₃ and 50 wt.% of CoFe₂O₄ in the final nanopowders. To promote gelation anhydrous tetramethylammonium hydroxide (TMAH, Sigma-Aldrich) was added at 90°C. The obtained gel was dried for 12 hours at 80°C and then calcined at 800°C for 8 min. One additional sample without ferrofluid was prepared as a reference (sample BTO). All samples were washed with a 0.2 mol acetic acid solution to dissolve impurities, such as barium carbonate. We have noted that when addition of the toluene and TMAH was omitted from the composite preparation, the resulting material did not form a core/shell structure, but consisted of a simple mixture of individual cobalt ferrite and barium titanate nanoparticles.

The phase content of the obtained powders was studied by x-ray diffraction (XRD), using a Siemens D-5000 diffractomete (Cu Kα radiation). Morphology and composition of the powders were analyzed using scanning electron microscopy (SEM, Quanta 400 FEG) and high resolution transmission electron microscopy (HR-TEM, Tecnai F20). The powder was pressed in pellets, which were ground gently, painted by a conductive silver paste, and fired in a vacuum oven at 120°C for 8 h. These disks were then filled with epoxy resin. The dielectric measurements were performed using a Solartron 1260 impedance analyzer with dielectric interface 1296 [13]. Mössbauer spectroscopy measurements were carried out in a custom-built setup at temperature 4.2 K and applied magnetic field 5 T.

III. Results and Discussions

Figure 2 shows x-ray diffraction patterns for both the pure cobalt ferrite powder and the composite powder. A well crystallized single phase of cobalt ferrite with cubic spinel structure (PDF data 22–1086) was detected. The broadening of the diffraction peaks reflects the nanometer size of the particles. For the composite powders both barium titanate and

![Figure 2. X-ray diffraction pattern for: (a) pure cobalt ferrite nanoparticles prepared by co-precipitation method and calcined at 750°C for 15 minutes; (b) CFO/BTO core/shell nanoparticles synthesized by organosol method and calcined at 750°C for 15 minutes.](image-url)
cobalt ferrite phases were detected without any impurity phase (Fig. 2b)—barium titanate in its cubic perovskite structure (PDF 05–0626).

SEM images for both pure CFO powder and CFO/BTO composite powders are shown in Fig. 3. For the CFO powder (Fig. 3a) particles are spherical in shape and show a small degree of agglomeration. The powder exhibits a monodisperse particle size distribution with a mean particle size \( \sim 30-40 \) nm (Fig. 3c). For the composite powder (Fig. 3b) particles are larger and are distributed in a relative narrow size range (Fig. 3d). The mean particle size is \( \sim 110 \) nm. Energy dispersive spectroscopy of these particles revealed the presence of both CFO and BTO phases. The inset in Fig. 3b shows a higher magnification of a composite particle. One can distinguish between a darker core and brighter shell.

More insight into the structure of the composite nanoparticles is given by TEM analysis. Figures 4a and 4b show TEM images for pure \( \text{CoFe}_2\text{O}_4 \) and composite nanoparticles, respectively. Due to the difference of transmission intensities for \( \text{CoFe}_2\text{O}_4 \) and \( \text{BaTiO}_3 \), the interface between these two phases is clearly seen in the TEM images (Fig. 4b) and in the high angular annular dark field (HAADF-STEM) image (Fig. 4c). In the last case the contrast in this figure is proportional to the atomic number of the element. Using the HRTEM it was found that for the core the spacing between [200] and [111] planes was \( d = 0.430 \pm 0.005 \) nm and \( 0.481 \pm 0.005 \) nm, respectively, while for the shell the spacing between [001] and [011] planes was \( d = 0.401 \pm 0.005 \) nm and \( 0.286 \pm 0.005 \) nm, respectively. These values are in good agreement with interplanar spacing estimated from XRD data, when the core is assigned to \( \text{CoFe}_2\text{O}_4 \) and the shell to \( \text{BaTiO}_3 \). Moreover, energy dispersive spectroscopy (EDS) analysis of the element distribution across the particles (Fig. 4d) showed that the concentration of Co and Fe had a maximum in the middle of the particle and decreased towards the edges, while Ba and Ti showed the opposite trend. The average shell thickness can be estimated as \( \sim 40-50 \) nm.
Figure 4. TEM images of: (a) cobalt ferrite single particle synthesized by co-precipitation method and calcinated at 750°C for 15 minutes; (b) CFO/BTO core/shell structure nanoparticles calcinated at 750°C for 15 minutes; (c) HAADF-STEM image of a single CFO/BTO core/shell particle, line shows a cross-section along which the EDS analysis was done; (d) distribution of Ba, Co, Fe elements across the single CFO/BTO particle measured using EDS (Figure available in color online).

The temperature dependences of dielectric characteristics of the composite powder samples measured at 100 kHz are shown in Fig. 5. Both the dielectric permittivity and dielectric loss increase at higher temperatures. We attribute this to an enhanced contribution from the Maxwell-Wagner relaxation of charges accumulated at the CoFe$_2$O$_4$-BaTiO$_3$ interfaces. It has to be mentioned that dielectric spectroscopy has not revealed any anomaly, which may be attributed to a ferroelectric phase transition, at least in the studied temperature range. This may point out that the BaTiO$_3$ phase is rather in the paraelectric than in the ferroelectric state.

Figure 6 shows the Mössbauer spectrum of the CFO/BTO nanoparticles measured at 4.2 K in an applied magnetic field of 5 T. The spectrum consists of two sub-spectra, a sextet

Figure 5. Temperature dependences of the dielectric permittivity (solid symbols) and tangent of dielectric loss (open symbols) measured for CFO/BTO core/shell powder on cooling at $f = 100$ kHz.
Figure 6. Mössbauer spectrum of the CoFe₂O₄/BaTiO₃ core/shell powder at 4.2 K in the presence of an applied magnetic field of 5 T along the propagations of the γ-rays. Subspectra correspond to Fe³⁺ in tetrahedral (dotted sextet) and octahedral surroundings (dashed curve).

representing Fe³⁺ on tetrahedral A-sites (line A) and a distribution of hyperfine magnetic fields for Fe³⁺ on octahedral B-sites (Line B). From the ratio of relative spectral areas of A- and B-sites, \( R_{AB} = A_{A}/A_{B} \), an inversion parameter, \( s \), can be calculated:

\[
s = \frac{2 \cdot R_{AB}}{1 + R_{AB}}
\]

For the ideal inverse spinel structure of CoFe₂O₄ \( s = 1 \). The best fit of the measured spectrum, however, yields the inversion parameter \( s = 0.70 \pm 0.02 \), which corresponds to the following stoichiometry \([\text{Co}^{2+}_{0.30}\text{Fe}^{3+}_{0.70}]_{A}[\text{Co}^{2+}_{0.70}\text{Fe}^{3+}_{1.30}]_{B}\text{O}_4\) and it is in a good agreement to the report on pure cobalt ferrite particles synthesized by a different method [14]. A misplacement of Co²⁺ could be a result of the high-temperature sample treatment during the annealing step. Misplaced Co²⁺ ions produce an ensemble of B-sites with various numbers of next iron neighbors leading to diminished hyperfine magnetic fields.

The spin canting angle, \( \theta \), which gives the average angle between the applied magnetic field and the magnetic moment of the particles, was calculated from the ratio of the spectral areas of the second and the third lines of both sextet subspectra. We obtained \( \theta \) values of about 20° for the A-site and 31° for the B-site that are lower than the literature value for pure cobalt iron oxide mentioned in Ref. [15] and exactly the same values as found in Ref. [16]. It is a well-known feature of nanoparticle spinel systems that the spin canting is more pronounced on the octahedral B-sites. Approximated values of the hyperfine magnetic fields \( B_{hf} \) were estimated from the canting angles \( \theta \) and the observed effective hyperfine fields \( B_{eff} \) using Eq. (2), where the positive and the negative signs refer to the octahedral and tetrahedral sites, respectively:

\[
B_{hf} \approx B_{eff} \pm B_{appl} \cos \theta
\]

The obtained Mössbauer parameters like isomer shift \( \delta \) and averaged hyperfine magnetic field \( B_{hf} \) are gathered in Table 1. They are in good agreement with data for pure CoFe₂O₄ nanoparticles [11].
Mössbauer parameters: isomer shift $\delta$ relative to $\alpha$-Fe at room temperature, quadrupole splitting $\Delta$, relative spectral area $A$, calculated hyperfine magnetic field $B_{hf}$, and spin canting angle $\theta$, for the composite CFO/BTO nanopowder measured at 4.2 K with $B = 5$ T.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$, mm/s</th>
<th>$\Delta$, mm/s</th>
<th>$A$, %</th>
<th>$B_{hf}$, T</th>
<th>$\theta$, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-site</td>
<td>0.36(1)</td>
<td>0.01(1)</td>
<td>35(1)</td>
<td>50.52(5)</td>
<td>20(1)</td>
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<tr>
<td>B-site</td>
<td>0.48(1)</td>
<td>0.00(1)</td>
<td>65(2)</td>
<td>52.94(6)</td>
<td>31(1)</td>
</tr>
</tbody>
</table>

IV. Conclusions

Combining organosol and co-precipitation methods, we have successfully fabricated composite CoFe$_2$O$_4$/BaTiO$_3$ nanoparticles with the desired core-shell nanostructure. The mean size of the obtained particles is about 110 nm with the shell thickness $\sim$ 40–50 nm. Mössbauer spectroscopy studies indicate that the magnetic properties of the composite powder are similar to those of pure CoFe$_2$O$_4$. At the same time the ferroelectricity of BaTiO$_3$ phase has to be proven yet. The obtained nanopowders can be used to prepare ceramic composite samples with nanoscale core-shell structure.

Acknowledgments

Morad Etier acknowledges financial support by Deutscher Akademischer Austauschdienst (DAAD). This work was partly supported by the DAAD-GRISEC program (Grant 50750877) and DFG Forschergruppe 1509.

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