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**BaTiO₃–CoFe₂O₄–BaTiO₃ trilayer composite thin films prepared by
chemical solution deposition**

Till Walther^a, Norman Quandt^a, Roberto Köferstein^a, Robert Roth^b, Matthias Steimecke^c,

Michael Bron^c, Kathrin Dörr^b, Stefan G. Ebbinghaus^{a*}

^a *Institute of Chemistry, Inorganic Chemistry, Martin Luther University Halle-Wittenberg, Kurt Mothes Strasse 2, 06120 Halle, Germany.*

^b *Institute of Physics, Martin Luther University Halle-Wittenberg, von Danckelmann Platz 3, 06120 Halle, Germany.*

^c *Institute of Chemistry, Industrial Chemistry, Martin Luther University Halle-Wittenberg, von Danckelmann Platz 4, 06120 Halle, Germany*

Abstract

Multiferroic BaTiO₃–CoFe₂O₄–BaTiO₃ thin films were synthesized by spin coating of Co(NO₃)₂ – Fe(NO₃)₃ and Ba(OAc)₂ – Ti(*i*-OPr)₄ solutions in a solvent mixture of acetic acid and dimethylformamide. Subsequent stepwise thermal treatment at 200, 400 and 800 °C leads to the desired ferroelectric and ferrimagnetic phases. The phase formation process was monitored by thermogravimetric, XRD, IR and Raman measurements. SEM was used to characterize the layered sandwich structure and the thickness of each layer. Two samples with different thicknesses of the perovskite and spinel layers are discussed. Sample **1** consists of a 120 nm layer of CoFe₂O₄ between two 70 nm thick BaTiO₃ layers. For sample **2** the 90 nm

thick top and bottom layers of BaTiO₃ are enclosing a 220 nm CoFe₂O₄ layer. The quality of the samples surfaces was determined by AFM leading to root mean square roughness values of about 4 nm. Magnetic investigations reveal a slightly anisotropic behavior for in-plane and out-of-plane magnetizations and coercivities. Polarization measurements show hysteresis loops (maximum $P_S = 29 \mu\text{C cm}^{-2}$; maximum $P_R = 17 \mu\text{C cm}^{-2}$) with pronounced switching peaks at the corresponding coercive fields of 200 and 360 kV cm⁻¹, respectively.

Keywords: *Multiferroics, Thin films, BaTiO₃, CoFe₂O₄, Spin Coating, Chemical Solution Deposition*

1. Introduction

Multiferroics are compounds that exhibit at least two ferroic order phenomena^[1]. The coupling between ferroic orders, especially the ability to change the electric polarization by an external magnetic field, i.e. the magneto-electric effect (ME), has high potential to be used in new devices and applications^[2,3]. Different possibilities of connections between electric and magnetic phases in multiferroic composites have been suggested and investigated^[4,5]. Whereas magneto-electric effects of particulate composites (0-3) are often significantly lower than theoretically predicted, laminated thick film structures (2-2 composites) of various piezoelectric and magnetostrictive phases have been reported to show high ME voltage coefficients^[6,7]. Over the past years the focus of the development of layer-structured multiferroics shifted from epoxy glued composites to submicron- and finally nano-scaled samples with direct interfaces between magnetostrictive and piezoelectric phase^[8]. Generally two basic principles are used for the preparation of thin layered oxides. The first one is the gas phase deposition, used e.g. in chemical vapor deposition (CVD), pulsed laser deposition (PLD) or molecular beam epitaxy (MBE). The second principle is the deposition from a liquid phase like electrochemical deposition, chemical solution deposition (CSD) and co-

precipitation methods (e.g. sol gel). The latter two methods generally comprise a coating step like dip or spin coating. Although deposition from the gas phase often leads to very thin and epitaxial films of the ferroelectric and magnetic phase as well as high-quality interfaces, the needed machinery is quite expensive and challenging to operate. In contrast, with liquid phase deposition methods the growth control may be limited but the equipment is comparatively inexpensive and easy to handle. Thus, a variety of sample compositions and synthesis conditions can be screened quite fast.

Here, we report on BTO-CFO-BTO layer-structured 2-2 composites consisting of ferroelectric BaTiO_3 and ferrimagnetic CoFe_2O_4 prepared by a chemical solution spin coating approach. Spin coating has been frequently described in literature, e.g. [9–15] but has not yet been investigated systematically for CoFe_2O_4 - BaTiO_3 composites^[16].

The optimum synthesis temperatures for the formation of the perovskite and spinel were investigated via thermogravimetric experiments and the phase evolution and purity of the composites was confirmed by XRD, IR and Raman measurements. SEM and AFM images were used to examine the thickness, morphology and surface quality of the samples. Magnetic and electric measurements show ferroelectric and hard magnetic behavior for the composite thin films.

2. Experimental

2.1 Material Preparation

All chemicals were used without further purification if not stated otherwise. 2×2 cm pieces of Pt-sputtered, 100-oriented Si-wafers (Micromotive GmbH) were chosen as substrates. An alkaline tenside solution (Hellmanex[®] III) was used for cleaning the substrates. For the CoFe_2O_4 layers, stoichiometric amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (both Sigma Aldrich) were dissolved in a mixture of acetic acid and dimethylformamide (DMF) (volume ratio: 1:3) with a concentration of $[\text{Co}^{2+}] = 0.3 \text{ mol l}^{-1}$. For the BaTiO_3 layers, initial

Ba^{2+} and Ti^{4+} solutions were prepared separately. $\text{Ba}(\text{CH}_3\text{COO})_2$ (Sigma Aldrich) was dissolved in acetic acid at 60 °C and then cooled to room temperature. Freshly distilled $\text{Ti}(i\text{-OPr})_4$ (Alfa Aesar) was dissolved in a mixture of acetic acid and DMF (volume ratio: 4:9). Ba^{2+} and Ti^{4+} solutions were combined prior to the coating process resulting in a final solution with $[\text{Ba}^{2+}] = [\text{Ti}^{4+}] = 0.3 \text{ mol l}^{-1}$. The cleaned substrates were covered with the corresponding precursor solution and spin-coated for 1 min at 4000 rpm with a modular spin processor WS-650-23NPP from Laurell Technologies Corporation. After a drying step at 200 °C the samples were calcined at 400 °C for 5 min followed by a phase formation step at 800 °C for 5 min. After cooling down to room temperature, the next layer was coated. This process was repeated until the desired number of layers was accomplished. Finally, the samples were annealed at 800 °C in air for one hour to increase the crystallinity and slowly cooled down to room temperature.

Two samples with different numbers of layers and hence film thicknesses after thermal treatment are discussed in this paper. Sample **1** consists of 3 BaTiO_3 layers, followed by 5 layers CoFe_2O_4 topped with 3 layers BaTiO_3 . **2** is built up from 4 bottom BaTiO_3 layers, 8 middle CoFe_2O_4 and 4 top BaTiO_3 layers. A flowchart of the coating process and schematic sample structures is shown in Fig. 1.

Fig. 1 Flowchart of the spin coating process (left) and schematic structure of sample **1** and **2** (right).

2.2 Characterization

Thermogravimetric measurements in flowing synthetic air (flow rate 20 ml min⁻¹, heating rate 10 K min⁻¹) of the predried (200 °C) solutions were performed using a Netzsch STA 449 system. X-Ray diffraction patterns were recorded in locked uncoupled mode (θ/θ scan with 5° offset between X-ray tube/detector and the normal of the sample surface) on a Bruker AXS D8Advance diffractometer operating with CuK α radiation. Fourier transformed infrared (FT-IR) spectra were collected at room temperature using a Bruker Tensor 27 spectrometer equipped with a diamond ATR unit. A Raman microscope consisting of an InVia Raman spectrometer (Renishaw) with 1800 1×mm⁻¹ grating and a 532 nm laser (Cobolt CWDPSS, 100 mW, Renishaw) was used to obtain spectra in the region of 200 to 800 cm⁻¹. The laser power was fixed at 5% with an exposure time of 60 s. Cross sectional scanning electron microscope images from freshly fractured samples were taken with a Philips ESEM XL30 FEG. Topographical measurements were performed using an atomic force microscope (AFM) MFP3D (Asylum Research Oxford Instruments) equipped with commercial ultra-sharp silicon

tips (type SSS-NCL, Nanosensors) with tapping mode technique. Magnetic measurements were carried out using a Quantum Design PPMS 9. Hysteresis loops were measured at 300 K with cycling of the magnetic field between 90 and -90 kOe. For anisotropic investigations the sample plane was aligned either parallel or perpendicular to the magnetic field. Data sets were corrected for the diamagnetic contributions of the substrate and the sample holder by a linear fit of the ranges ± 50 to ± 90 kOe. Magnetization values are normalized to the CoFe_2O_4 volume fractions. For ferroelectric measurements the Pt layer on the substrate was used as bottom electrode. For top electrodes $80 \times 80 \mu\text{m}^2$ copper films (40 nm) were evaporated on the sample surfaces and covered with gold (20 nm). Ferroelectric polarization and leakage currents were measured as a function of applied voltage with a TF2000 Analyzer from aixACCT Systems GmbH.

3. Results and discussion

3.1 Thermal analysis

Drying of the $\text{Ba}^{2+}/\text{Ti}^{4+}$ solution at 200°C for 1 h in air resulted in a yellowish powder. TG and DTA investigations up to 1000°C in flowing air (heating rate: 10 K min^{-1}) were carried out on this powder (Fig. 2). The endothermic weight loss of roughly 6.5% in the temperature range $50\text{--}250^\circ\text{C}$ is due to the evaporation of remaining water from the sample. A series of exothermic reactions -which can be assigned to the stepwise decomposition of the organic components- starts at 250°C and is finished at 750°C with a total weight loss of 45.6%. No further weight change was detected up to 1000°C . The XRD measurement of the resulting white powder indicated phase-pure BaTiO_3 .

Fig. 2 Simultaneous TG and DTA investigations of predried solution of barium(II) acetate and titanium(IV) isopropoxide in acetic acid and DMF.

Simultaneous TG and DTA investigations of the $\text{Co}^{2+}/\text{Fe}^{3+}$ solution predried for 1 h at 200 °C are shown in Fig. 3. The endothermic signal in the DTA curve below ca. 200 °C with a corresponding weight loss of 8.0% again can be assigned to the release of water. Strong exothermic DTA signals between 200 and roughly 370 °C are accompanied by an additional weight loss of 22.4%. A slight gradual weight change up to 600 °C leads to a total weight loss of 41.1%. The exothermic DTA signal at 600 °C (without significant weight change) most likely stems from the crystallization of the spinal phase. No further change in weight was detected up to 1000 °C and XRD measurements of the resulting dark powder indicated phase-pure CoFe_2O_4 .

Fig. 3 Simultaneous TG and DTA investigations of the predried solution of cobalt(II) and iron(III) nitrate dissolved in acetic acid and DMF.

These thermal investigations show that for the used solutions a calcination temperature of 750 °C is sufficient to ensure the completion of the phase formation of both BaTiO₃ and CoFe₂O₄.

3.2 XRD, IR, Raman

X-Ray diffractograms of **1** and **2** are shown in Fig. 4. All detected diffraction peaks can be assigned to cubic CoFe₂O₄, BaTiO₃ or the substrate^[17]. From the measurements it cannot be differentiated between the cubic and tetragonal modification of BaTiO₃ due to relatively small crystallites and thus broadened reflections^[18]. The XRD measurements show that the coating process leads to phase-pure BaTiO₃ and CoFe₂O₄ layers without any secondary phases, such as BaTi₁₄O₁₉ or BaFe₁₂O₁₉.

Fig. 4 X-Ray diffraction patterns of (a) sample 1, (b) sample 2 and (c) the uncoated, thermally treated substrate. An axis break was inserted at the Pt (111) peak.

Infrared spectra of composites and single component film samples are shown in Fig. 5. Due to the small layer thickness and the diamond ATR set-up no transversal but only longitudinal vibrations were detected, known as Berreman effect^[19]. Longitudinal metal-oxygen bond vibration bands at 460 and 690 cm^{-1} can be assigned to cubic or tetragonal BaTiO_3 ^[20] while the bands at 433 and 668 cm^{-1} belong to cubic CoFe_2O_4 ^[21], respectively. Due to the thicker CoFe_2O_4 layer in sample 2 one additional weak transversal vibration at 550 cm^{-1} was detected^[22].

Fig. 5 FT-IR spectra (ATR-technique) of sample **1** (a) and **2** (b) compared to films of pure BaTiO₃ (c) and CoFe₂O₄ (d).

In Fig. 6 confocal Raman spectra of the composite samples are shown. At the Raman laser wavelength of 532 nm, BaTiO₃ possesses a relatively low absorption (<15 %)^[23], compared to CoFe₂O₄ (>90 %)^[24]. Hence only Raman active modes of CoFe₂O₄ can be seen in the spectra. In the measured range from 200 to 800 cm⁻¹ there are five intensity maxima. All of them are in accordance with literature data for CoFe₂O₄ and BaTiO₃-CoFe₂O₄ thin film composites^[25,26]. Raman active modes in ferrite spinels have A_{1g} , E_g and $3 \times T_{2g}$ symmetry. The maximum at 302 cm⁻¹ can be assigned to the E_g mode, the maxima at 468 and 567 cm⁻¹ to two of the T_{2g} modes and the maximum at 690 cm⁻¹ to the A_{1g} mode. A third T_{2g} mode with a very small intensity should be located close to 210 cm⁻¹ but was not detected in our measurements. On the other hand, due to partial cation distribution between octahedral and tetrahedral sites another Raman active mode with A_{1g} character appears at 616 cm⁻¹, in

accordance with the partial occupation of the tetrahedral sites by Fe^{3+} ions in inverse spinel ferrites^[27–29].

Fig. 6 Confocal Raman spectra of sample **1** and **2**.

3.3 SEM and AFM

Cross-section and surface scanning electron micrographs were taken for both samples (Fig. 7 and Fig. 8). The SEM images of sample **1** show a clearly distinguishable sandwich structure. The thickness of the bottom BaTiO_3 layer is about 70 nm, followed by the 120 nm thick CoFe_2O_4 and the top layer BaTiO_3 of again 70 nm. Since three and five spin coating steps were applied for the BaTiO_3 - and CoFe_2O_4 -layers, respectively, it can be stated that each coating step leads to an individual layer of 25 ± 5 nm thickness independent of type of oxide deposited.

Fig. 7 SEM images of Sample **1**: surface (SE mode) and cross section (Inset; BSE mode).

The sandwich structure of sample **2** is shown in Fig. 8. The CoFe₂O₄ layer (eight spin coating steps) with a thickness of 220 nm is embedded between two 90 nm BaTiO₃ layers (four spin coating steps each). The secondary electron mode SEM images of sample **1** and **2** reveal the uniform and smooth surfaces of both samples.

Fig. 8 SEM images of Sample **2**: surface (SE mode) and cross section (Inset; BSE mode).

Between the top BaTiO₃ and the CoFe₂O₄ layers of both samples uniform interfaces with direct contact of the two phases formed, whereas the interfaces between the bottom BaTiO₃ and the CoFe₂O₄ layers is partially disturbed by voids. Thus, BaTiO₃ is growing much better on CoFe₂O₄ than vice versa.

To further investigate the quality of the sample surfaces, atomic force microscopy (AFM) was applied (Fig. 9). The AFM images of **1** and **2** show similar surfaces consisting of small spherical particles. The root mean square value (rms) of 3.8 nm from **1** is slightly smaller than the 4.6 nm from **2**, probably because of the larger number of coating steps and in turn increased sample thickness of sample **2**. The grain size of the BaTiO₃ particles was estimated to be 50 - 120 nm for **1** and 60 - 160 nm for **2**. These diameters correspond roughly to the determined top-layer thickness (from cross sectional SEM investigations) of 70 nm (**1**) and

90 nm (2) indicating an aspect ratio close to unity for the BTO particles. In general, our AFM investigations reveal good quality surfaces consistent with earlier literature reports on spin-coated BaTiO₃ and respective composite thin films.^[30–32]

Fig. 9 AFM image and line trace (black line) of sample 1 and 2.

3.4 Magnetic and electric properties

Field dependent magnetization curves of sample 1 and 2 are shown in Fig. 10 and Fig. 11. The in-plane and out-of-plane saturation magnetization values (M_S) for sample 1 are both $M_S = 307 \text{ emu cm}^{-3}$. Whereas the M_S values for sample 2 slightly differ, with 319 emu cm^{-3} in-plane and 338 emu cm^{-3} out-of-plane. The difference between the saturation magnetizations of sample 1 and 2 is probably due to the thicker CoFe₂O₄ layer, thus increased grain sizes, for sample 2. Pronounced anisotropies were observed for the remanence magnetizations and coercivities. The remanence magnetization values (M_R) of sample 1 are

$M_R = 122$ (in-plane) and 75 emu cm^{-3} (out-of-plane), while for sample **2** the difference between M_R values is even higher with $M_R = 132$ (in-plane) and $M_R = 81 \text{ emu cm}^{-3}$ (out-of-plane). The in-plane coercivities are $H_C = 900$ for **1** and $H_C = 800 \text{ Oe}$ for **2**. In contrast, the coercivity values for out-of-plane aligned samples are about 400 Oe higher than for in-plane with $H_C = 1300$ for **1** and $H_C = 1200 \text{ Oe}$ for **2**. There are three possible sources for the magnetic anisotropy, namely shape, magnetocrystalline and strain induced anisotropy^[33]. A preferred orientation of the CoFe_2O_4 grains in the films would lead to magnetocrystalline anisotropy, whereas strain induced anisotropy would indicate a strong coupling between CoFe_2O_4 and BaTiO_3 interface, that is crucial for magneto-electric properties^[5]. Therefore the determination of the specifics of the anisotropy will be interesting to investigate in future work.

Fig. 10 Magnetic hysteresis of sample **1**: 70 nm BaTiO_3 | 120 nm CoFe_2O_4 | 70 nm BaTiO_3 .

Fig. 11 Magnetic hysteresis of sample 2: 90 nm BaTiO₃ | 220 nm CoFe₂O₄ | 90 nm BaTiO₃.

Field dependent polarization (P–E) and simultaneous current – voltage (I–V) measurements of sample 1 and 2 are shown in Fig. 12 and Fig. 13. Both P–E curves show a hysteresis with saturation polarizations (determined from the maximum of P) of 1: $P_S = 29$ and 2: $P_S = 24 \mu\text{C cm}^{-2}$, , remanence polarizations $P_R = 17$ and $P_R = 11 \mu\text{C cm}^{-2}$ and coercive electric fields with $E_C = 360$ and $E_C = 200 \text{ kV cm}^{-1}$, respectively. Both samples show ferroelectric behavior^[34]. The peaks in the I–V curves at the corresponding P–E coercive fields E_C are typical for the polarization switching in ferroelectric compounds^[35]. To the best of our knowledge, the observed P_S and P_R values are among the highest reported for CoFe₂O₄-BaTiO₃ composites, with P_S varying from 3.4 to about $30 \mu\text{C cm}^{-2}$ [36–40] with a remarkable exception of $P_S = 64(1) \mu\text{C cm}^{-2}$ reported in [41]. Our measurements can also compete with various PLD films of pure BaTiO₃ (e.g. $P_S = 28 \mu\text{C cm}^{-2}$ [35], $P_R = 12.3 \mu\text{C cm}^{-2}$ [42]). In addition, the saturation polarizations $P_S = 27.3$ and $23 \mu\text{C cm}^{-2}$ found for single crystal^[43] and

bulk^[44] BaTiO₃, respectively, agree well with our results, too. On the other hand, it has to be noted that at high voltages (> 20 V) our films become slightly leaky. This is probably due to the presence of oxygen vacancies, which might be healed by annealing in oxygen.

Fig. 12 Ferroelectric hysteresis and corresponding current loop of sample 1: 70 nm BaTiO₃ | 120 nm CoFe₂O₄ | 70 nm BaTiO₃.

Fig. 13 Ferroelectric hysteresis and corresponding current loop of sample 2: 90 nm BaTiO₃ | 220 nm CoFe₂O₄ | 90 nm BaTiO₃.

Conclusion

Two sandwich-structured BaTiO₃–CoFe₂O₄–BaTiO₃ thin films with different thicknesses of the two oxide phases were prepared by a chemical solution based spin coating process. Thermal investigations of the precursor solutions revealed that a calcination temperature of 750 °C is high enough to ensure a complete phase formation of both the spinel and perovskite. In the infrared spectrum of sample 1 only longitudinal vibrations are detectable due to the Berreman effect, whereas the thicker sample 2 additionally shows one small transversal vibrational band. In Raman measurements only vibrational modes of CoFe₂O₄ were detected for both samples because of the low absorption of BaTiO₃ at the used laser wavelength of 532 nm. The thickness of individual layers and the composite films in whole were derived from cross sectional SEM images. Each coating step leads to a growth of the layers by about

25 nm. Thus, the individual layer thickness of each sample is easily controllable by the number of the spin coating steps. While the interface of CFO on top of BTO showed some voids the reverse interface (BTO on CFO) was almost defect-free on the SEM scale. From atomic force microscopic measurements surface roughness values of $rms = 3.8$ and 4.6 nm were calculated for sample **1** and **2** respectively. The saturation magnetization values of 307 emu cm^{-3} (in and out-of-plane) for **1** with 120 nm CoFe_2O_4 layer are slightly lower than the corresponding values of 319 (in-plane) and 338 emu cm^{-3} (out-of-plane) for sample **2** with a thicker CoFe_2O_4 layer of 220 nm. Both samples exhibit a magnetic anisotropy, that hints to a preferred orientation of the CoFe_2O_4 particles and a strong coupling between BaTiO_3 and CoFe_2O_4 layers with the magnetic easy axis in sample plane. Concerning the ferroelectric properties, the saturation and remnant polarization values $P_S = 29$ and $P_R = 17 \text{ } \mu\text{C cm}^{-2}$ are higher for sample **1** (two 70 nm BaTiO_3 layers) than for sample **2** with $P_S = 24$ and $P_R = 11 \text{ } \mu\text{C cm}^{-2}$ (two 90 nm BaTiO_3 layers). The polarization values of our spin coated films are comparable to the ones reported for PLD films and bulk BTO, indicating a very good film quality.

In summary, the spin coating of Ba/Ti- and Co/Fe-salts dissolved in HOAc/DMF was found to be a fast and versatile solution-based method to obtain high-quality multiferroic thin films exhibiting both ferrimagnetism and ferroelectricity. The thickness of the films can easily and reproducibly be controlled by the number of coating steps.

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