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Magnetoelectric coupling on multiferroic cobalt ferrite–barium titanate ceramic composites with different connectivity schemes

Morad Etier,[a,*] Carolin Schmitz-Antoniak,[b] Soma Salamon,[c] Harsh Trivedi,[a] Yanling Gao,[a] Ahmadshah Nazrabi,[a] Joachim Landers,[c] Devendraprakash Gautam,[d] Markus Winterer,[d] Detlef Schmitz,[e] Heiko Wende,[c] Vladimir V. Shvartsman[a] and Doru C. Lupascu[a]

[a]*Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Universitätsstraße 15, 45141 Essen, Germany*

[b]*Peter Grünberg Institute (PGI-6), Jülich Research Centre, 52425 Jülich, Germany*

[c]*Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Lotharstraße 1, 47057 Duisburg, Germany*

[d]*Nanoparticle Process Technology, Faculty of Engineering and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Lotharstraße 1, 47057 Duisburg, Germany*

[e]*Helmholtz-Zentrum für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany*

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Abstract—In this article we report on the synthesis and multiferroic properties of cobalt ferrite ($CoFe_2O_4$)–barium titanate ($BaTiO_3$) biphasic composites. The initial composite nanopowder was synthesized by a combination of co-precipitation and organosol methods. A ceramic sample with (3–0) connectivity, i.e. $BaTiO_3$ grains in a $CoFe_2O_4$ matrix was obtained by a combination of spark plasma sintering and annealing. In order to understand the correlations between morphology, electric properties, and magnetization, we present a detailed study at different preparation steps and compare it to the properties of a conventionally sintered sample with the traditional (0–3) connectivity, i.e. $CoFe_2O_4$ grains in a $BaTiO_3$ matrix. We observe that the (3–0) sample shows improved magnetic properties in comparison to the conventionally sintered composite of the same composition. In spite of relatively large leakage current for the (3–0) sample compared to the traditional (0–3) one, it exhibits a converse magnetoelectric effect that follows the H_{dc} dependence of the piezomagnetic coefficient. The magnetic field-dependence of electric polarization at the surface was investigated utilizing X-ray absorption spectroscopy and its associated linear and circular dichroisms.

Keywords: Multiferroics; Converse magnetoelectric effect; Composite; Spark plasma sintering

1. Introduction

Magnetoelectric (ME) materials can be electrically polarized by a magnetic field or magnetized by an electric field. They can be used in different technological applications such as magnetic sensors, microelectromechanical systems (MEMS), and energy harvesters [1–3]. Composite multiferroic materials, which consist of ferroelectric and ferromagnetic phases, show a much larger magnetoelectric effect compared to single-phase materials. In the composites, the magnetoelectric effect is typically generated through a mechanical strain arising under an applied magnetic or electric field at interfaces between the two constituents. Of particular interest are nanoscale-structured materials, where a high density of interfaces may enhance the magnetoelectric coupling.

Nano-composites, which exhibit multiferroic, as well as magnetoelectric properties, have been prepared by various methods including solid state reaction, sol–gel, and hydrothermal synthesis [4–6]. Barium titanate, $BaTiO_3$, is often used as the ferroelectric constituent due to its excellent piezoelectric properties and lead free chemical composition. Cobalt ferrite, $CoFe_2O_4$, is a widespread magnetic component due to its strong magnetostriction. An important advantage of $CoFe_2O_4$–$BaTiO_3$ composites is the spinodal decomposition of this binary system, which prevents reaction between the constituents during high-temperature processing. It is well documented that ferroelectric properties of $BaTiO_3$ and ferromagnetic properties of $CoFe_2O_4$ depend on particle size [7,8]. Correspondingly, one should expect a size effect on the magnetoelectric coupling in the composites.

To obtain dense ceramics with nanometer grain size the spark plasma sintering (SPS) technique can be used. This technique is based on applying a pressure simultaneously

* Corresponding author.

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with an electric pulse through the material causing high heating rates. SPS decreases the densification time from hours to minutes, suppresses grain growth, and reduces the diffusion at grain boundaries. The SPS method has been used e.g. for barium titanate densification [9,10]. Ghosh et al. reported on the synthesis of multiferroic nano-composites $CoFe_2O_4$–$BaTiO_3$ at weight ratios 10/90 and 20/80 via the SPS technique [11]. They found a reduction of dielectric permittivity with increasing $CoFe_2O_4$ content and related this to Fe diffusion into the $BaTiO_3$ phase.

The properties of biphasic ferromagnetic/ferroelectric composites, in particular the magnetoelectric (ME) coupling, depend on the type of connectivity between the two constituent phases. In this sense, the connectivity means the number of dimensions through which the material is continuous. For bulk materials, the (0–3) connectivity scheme [12] is typically used, in which ferromagnetic regions are distributed in a ferroelectric dielectric matrix and are well separated from each other, i.e. the ferromagnetic phase has connectivity 0 and the dielectric matrix has connectivity 3. Such a scheme provides sufficient electric resistivity of the composites and facilitates the electric poling process which is necessary to achieve a large ME response. Due to larger conductivity, the multiferroic composites with the (3–0) connectivity (ferroelectric inclusions in a ferromagnetic matrix) are less studied. Nevertheless, they can find applications in devices using switching or modulation of electrical polarization by a magnetic field, materials with magnetically tunable dielectric permittivity, or microwave absorbing materials [13,14]. Furthermore, measurements of the ME effect in (3–0) composites provides a different approach for understanding the strain mediated ME effect via interfaces for different connectivity schemes in modeling.

The aim of the present paper is to investigate the multiferroic properties and the ME effect of a $CoFe_2O_4$–$BaTiO_3$ (3–0) ceramic composite synthesized by the SPS method and compare it to the (0–3) one.

2. Experimental techniques

The procedures for the synthesis of the composite nanopowders are described in detail elsewhere [15]. Shortly, the co-precipitation method is utilized to synthesize 40-nm $CoFe_2O_4$ nanoparticles. After that, a colloidal suspension of $CoFe_2O_4$ nanoparticles is prepared using oleic acid and oleylamine [16,17]. The obtained ferrofluid is added to the $BaTiO_3$ precursor. The weight percentage of $CoFe_2O_4$ and $BaTiO_3$ components is nominally 50% each. The two-phase precursor is mixed and then calcined at 750 °C in a conventional chamber furnace for 15 min in order to form a powder (sample S1). Agglomerates are destroyed using ball milling.

The resulting powder was then introduced to a SPS instrument (FCT HP D5, FCT Systeme GmbH, Raunstein, Germany). The powder mixture was loaded into a graphite die with an inner diameter of 20 mm, an outer diameter of 45 mm, and a height of 50 mm. A boron nitride coated graphite foil was used to avoid contact between the powder and the inner surface of the die. This is to ascertain that the current flows through the sample during sintering and not through the die. To minimize radial temperature distribution and radiation heat losses the graphite die was covered by graphite wool. The sample was heated by a pulsed electric current from room temperature to 1000 °C with a heating rate of 100 °C/min. The sample was held at 1000 °C for 5 min and then cooled down to 500 °C with a rate of 100 °C/min, and further to room temperature by natural cooling. An uniaxial pressure of 35 MPa was applied on the sample over the complete heating–cooling cycle. The pressure on the sample was released during natural cooling. The complete sintering process was performed in vacuum at about 1 Mbar. Temperature measurements were carried out with an optical pyrometer focused on the surface of the upper graphite push–punch. The as-sintered ceramics were polished to remove the graphite foil from the surface of the sintered pellet (sample S2). One of the SPS sintered ceramics was annealed at 900 °C for 2 h in a normal chamber furnace (Nabertherm GmbH) (sample S3). For comparison, another sample was prepared by sintering nanoparticle powder normally at 1200 °C for 2 h without SPS (sample S4).

The phase content and crystal structure of the composites were analyzed by X-ray diffraction (XRD) (Siemens D5000) while sample morphology was studied by scanning electron microscopy (SEM) (Quanta 400 FEG). Before SEM measurements, the samples were well polished and thermally etched. The program AnalySIS (Soft Imaging Systems) was used for analyzing SEM micrographs and particle/grain sizes determination. The ferroelectric properties were studied locally using piezoresponse force microscopy (PFM) (MFP-3D, Asylum Research) and macroscopically using a self-built Sawyer–Tower circuit. Dielectric characteristics were measured using a Solartron 1260 impedance analyzer with the dielectric interface 1296. For electrical measurements, silver electrodes were painted onto the sample faces. The magnetic measurements were performed by SQUID magnetometry (MPMS-5S, Quantum Design).

Usually the magnetoelectric coupling in composites is characterized by measurements of the direct ME effect (polarization or voltage produced by an applied magnetic field), e.g. by using the dynamic lock-in technique [18]. However, for samples which are poor insulators it is difficult to detect the direct ME effect, because the leakage current will partly short-circuit the sample and reduce the measured ME voltage coefficient. This complication can be circumvented by measuring the converse ME effect (-magnetization produced by an electric field). In this case, the electric power supply can compensate the ohmic losses and still provide sufficient electric fields to generate the magnetic signal. Attention must be paid to Joule heating, though. In this study, we performed measurements of the converse ME effect using a custom-built setup based on the AC susceptometer of a SQUID magnetometer [19]. An AC electric field induces an alternating magnetic moment. Its first harmonic is detected using an internal lock-in amplifier. We addressed the longitudinal magnetoelectric effect, where the applied magnetic field, applied electric field, and the measured magnetization were parallel to each other and perpendicular to the sample surface. Before the ME measurements the ceramic samples S3 and S4 were poled in silicon oil under an electric field of 12-kV/cm applied perpendicular to the sample surface at a temperature of 415 K. The electric field was kept as the samples were cooled to room temperature.

X-ray absorption spectroscopy in the soft X-ray regime was performed at the high-field end station at the helical undulator beamline UE46-PGM1, HZB-BESSYII syn-