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Strong converse magnetoelectric effect in (Ba,Ca)(Zr,Ti)O_3 - $NiFe_2O_4$ multiferroics: A relationship between phase-connectivity and interface coupling

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ABSTRACT

Studying multiferroic magnetoelectrics has been a focus field for the last decade and a half, and the exploration of new materials is one of the several aspects of this quest. Here we report on the synthesis and characterization of $NiFe_2O_4$-based multiferroic composites which employ (Ba,Ca)(Zr,Ti)O_3 as the ferroelectric/piezoelectric component and $NiFe_2O_4$ as the magnetostrictive phase. We find that these composites show excellent magnetoelectric properties. Especially the composite with 30 vol% of $NiFe_2O_4$ has a converse ME coefficient approximately two times larger than the previously reported one for $BaTiO_3$-$CoFe_2O_4$ composites. A relationship between the phase connectivity within these composites and the ME properties was explored by the time of flight secondary ion mass microscopy. We believe that our investigation will be helpful for the design of magnetoelectric materials as components of sensors and memory devices.

1. Introduction

The modification of magnetism with an electric field and the variation of electric polarization with a magnetic field is a phenomenon of high interest these days [1–6], known as magnetoelectricity. Typically, magnetoelectricity exists in materials that contain at least two of the following ferroic orders: ferroelectricity, ferromagnetism, or ferroelasticity. The manipulation of the polarization by a magnetic field (direct ME effect) and the variation of the magnetization in response to an external electric field (converse ME effect) show potential for applications in sensors and memory elements [3]. During the last decade, magnetoelectric composites have been investigated in numerous structures including bulk ceramic composites of ferrites and piezoelectrics, dual phase magnetoelectric composites, laminated composites of magnetic alloys and piezoelectric materials, three phase magnetoelectric composites, magnetoelectric thin films, and heterostructures of ferroelectric and magnetic oxides [7].

The converse magnetoelectric effect has an enormous significance of application in new concepts for high-speed, ultra-low power consumption and non-volatile magnetoelectric memories [8,9]. Control of magnetism with electric fields has been demonstrated in ME composites composed of piezoelectric and magnetostrictive phases, both in bulk and thin films [10–12]. Among the mechanisms for electrically driven magnetism are a strain-induced ME effect across the interface [13], exchange bias [14], charge mediated [15], or co-mediated ME effects [16]. Lead (Pb) based materials are the most widely used ferroelectric component in biphase ferroelectric/magnetic composites because they show superior polarization and piezoelectric properties. However, the toxicity of Pb has raised severe concerns [17], and research on Pb-free materials has increased in the last two decades.

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$0.5Ba(Ti_{0.8}Zr_{0.2})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ (BCZT) is a well-studied piezoelectric material with the piezoelectric coefficient d_{33} having values in the range of 500–600 pC/N and it is a ferroelectrically soft material [18,19]. Several studies have shown that these properties of BCZT can be attributed to its proximity to one of the polymorphic phase boundaries in the phase diagram of the $Ba(Ti_{0.8}Zr_{0.2})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ system, which also make it elastically soft [20]. These properties make BCZT a potential replacement for the ubiquitous $Pb(Zr,Ti)O_3$ at room temperature.

Magnetostriction is a property quantifying the change in the dimensions of a magnetic material when an external magnetic field is applied [21]. Terfenol-D is an alloy of Tb, Dy, and Fe with the composition $Tb_{0.3}Dy_{1.7}Fe_2$ [22] exhibiting magnetostriction up to 2000 ppm at room temperature in a magnetic field of 200 kA/m. It is the most commonly used magnetostrictive material today for various sensor applications. However, this material suffers from certain drawbacks such as the high cost of Tb and Dy, the high cost of single crystal production for applications, and poor mechanical properties. The most suitable alternatives are oxide-based materials such as spinel type ferrimagnetic $NiFe_2O_4$. $NiFe_2O_4$ is a soft magnetic material with a large magnetostriction derivative ($d\lambda/dH$), and high magnetomechanical coupling factor [23].

This article reports on the synthesis of the multiferroic composite (1-*x*)BCZT-*x*NFO with the volume content of the ferrite phase $x = 0.2$–0.5. Crystal structure, magnetic, magnetoelectric, and local multiferroic properties were studied in the context of relative phase distribution. The values of the converse ME coefficient show an enhancement compared with those of $BaTiO_3$-$CoFe_2O_4$ based composites. To the best of our knowledge, the converse magnetoelectric effect has not been studied before in these composites.

2. Experimental

The synthesis of BCZT powder was carried out using the solid-state reaction method using reagent grade carbonates and oxides. The details of the synthesis can be found elsewhere [19]. This composition was chosen keeping in mind the phase diagram of BZT-*x*BCT with a particular focus on the pronounced piezoelectric properties of this composition [24].

$NiFe_2O_4$ (NFO) was also prepared by the solid state synthesis. The oxides Fe_2O_3 (Alfa Aesar GmbH KG, purity > 99%) and NiO (Alfa Aesar GmbH KG, purity > 99%) were mixed in ethanol in proper ratios according to a balanced chemical equation and ball-milled for 10 h at 300 rpm. The mixture was let to dry in air for 24 h and afterward calcined at 1050 °C for 6 h (heating rate of 5 °C/min). The calcined powder was ball-milled again with the previously used parameters. The obtained BCZT and NFO powders were mixed in the ratios according the volume content of the ferrite phase 20%, 30%, 40%, and 50% and wet-milled in ethanol for 6 h at 300 rpm. The final mixtures were dried and pressed into disk-shaped pellets (diameter of 6 mm and thickness of around 1 mm) under a uniaxial pressure of 300 MPa for 2–4 min. All sample pellets were sintered in covered alumina crucibles in air at 1200 °C for 6 h (heating rate of 5 °C/min). The obtained ceramics are designated as BCZTNFO20 (0.8BCZT-0.2NFO), BCZTNFO30 (0.7BCZT-0.3NFO), BCZTNFO40 (0.6BCZT-0.4NFO), and BCZTNFO50 (0.5BCZT-0.5NFO).

X-ray diffraction of the ceramic pellets was performed at room temperature using a Philips X-ray diffractometer (PW1730). Rietveld refinement was performed using GSAS-II software [25]. Local magnetic and ferroelectric properties of the samples were addressed by magnetic force microscopy (MFM) and piezoresponse force microscopy (PFM), respectively. Both MFM and PFM studies were performed using a commercial scanning probe microscope MFP-3D (Asylum Research). For MFM and PFM studies the samples were finely polished with diamond polishing pastes down to 1/4 micron and thermally etched at 1100 °C for 2 h. Magnetic measurements were performed by a SQUID magnetometer MPMS-5S (Quantum Design).

The converse magnetoelectric effect was measured using a modified ac SQUID susceptometer, in which the *ac* magnetic moment (the first harmonic only) induced by an external *ac* electric field is measured [26]. The electrodes were made by applying silver paste to both sides of the sintered pellets which then were fired at 500 °C for an hour. Prior ME measurements, all samples were poled by applying a dc electric field of 1 kV/mm for 20 min at temperatures 80–100 °C and then cooling down to room temperature at the applied field.

To get information about distribution of the BCZT and NFO phases time of flight secondary-ion-mass spectrometry measurements were performed on a TOF.SIMS 5 machine (IONTOF). The primary ion-beam consisted of Bi_1-ions at 30 kV with a spatial resolution of about 200 nm. Depth-profiling was done using 2 kV O_2-ions. The area of analysis with the Bi-beam was 25 μm × 25 μm, while the sputter crater was 200 μm × 200 μm. The crater depth was measured *ex-situ* in a DEKTAK-profilometer. To calculate the sputter rate, it was assumed that the sputter-yield was constant during the entire measurement time and independent of the depth and material in the samples. It was taken care, that the beam currents for both the Bi_1-and O_2-beam were the same at the beginning and end of the measurement.

3. Results

3.1. XRD analysis

Fig. 1(a–d) displays X-ray diffraction profiles for all four samples measured at room temperature. Rietveld refinement has been performed on all samples using a two-phase model, consisting of perovskite tetragonal (*P4/mmm*) and the cubic spinel ($Fd\bar{3}m$) phases employing GSAS-II software [25]. The data for all the samples show excellent fitting to the refinement. Various parameters extracted from the fitting are listed in Table 1. Moreover, it is evident that the tetragonal phase peaks decrease in intensity while those of spinel grow with the increasing NFO content. From the above analysis it is clear that the two phases coexist in these composite ceramics without any inter-reaction, and also without any impurities of significant amount. Moreover, the different values of lattice constants for different tetragonal and spinel phases are an indication of different types of internal stresses.

3.2. TOF-SIMS measurements

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) stands for a technique for surface and depth analysis which concentrates a stream of primary ions onto a surface, which gives rise to secondary ions during a sputtering process. Analysis of these secondary ions yields information about the existence of molecular and elemental species on the surface, both in 2D and 3D on the μm-scale [27]. TOF-SIMS studies are usually conducted in one of two manners:

a. The TOF-SIMS gives us total-ion maps of particular surface areas of the sample. The cumulative ion maps can be used to distinguish between different phases of the sample characterized by certain types of ions, e.g., in our case by analyzing distributions of Ba^{2+} and Fe^{3+} ions we can distinguish between the BCZT and NFO phases. The chosen measurement conditions in this work result in a spatial resolution of roughly 200 nm.
b. By recording 2D-maps in combination with depth-profiling, one can obtain a 3D reconstruction of the sample and thus the