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The effect of phase assemblages, grain boundaries and domain structure on the local switching behavior of rare-earth modified bismuth ferrite ceramics



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ABSTRACT

Piezoelectric properties and ferroelectric/ferroelastic domain switching behavior of polycrystalline ceramics are strongly influenced by local scale (i.e. <100 nm) phenomena, such as, the phase assemblages, domain structure, and defects. The method of ceramic synthesis strongly effects the local properties and thus plays a critical role in determining the macroscopic ferroelectric and piezoelectric performance. The link between synthesis and local scale properties of ferroelectrics is, however, rarely reported, especially for the emerging lead-free materials systems. In this work, we focus on samarium modified bismuth ferrite ceramics ($\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$, BSFO) prepared by two methods: standard solid state reaction (SSR) and mechanochemically assisted synthesis (MAS). Each ceramic possesses different properties at the local scale and we used the piezoresponse force microscopy (PFM) complemented by transmission electron microscopy (TEM) to evaluate phase distribution, domain structure and polarization switching to show that an increase in the anti-polar phase assemblages within the polar matrix leads to notable changes in the local polarization switching. SSR ceramics exhibit larger internal bias fields relative to the MAS ceramics, and the grain boundaries produce a stronger effect on the local switching response. MAS ceramics were able to nucleate domains at lower electric-fields and grow them at faster rates, reaching larger final domain sizes than the SSR ceramics. Local evidence of the electric-field induced phase transition from the anti-ferroelectric *Pbam* to ferroelectric *R3c* phase was observed together with likely evidence of the existence of head-to-head/tail-to-tail charged domain walls and domain vortex core structures. By comparing the domain structure and local switching behavior of ceramics prepared by two different methods this work brings new insights the synthesis-structure-property relationship in lead-free piezoceramics.

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1. Introduction

Bismuth ferrite (BiFeO_3 or BFO) is part of a rare group of materials known as multiferroics with exciting potential for emerging technologies such as spintronics, microelectromechanical systems (MEMS), magnetoelectric memories and nanoelectronics [1–3]. The development of BFO has strongly relied on the powerful tool of piezoresponse force microscopy (PFM), which is often used to

investigate piezoelectric and ferroelectric phenomena at the micro- and nano- (i.e. local) scales [4–7]. PFM has proven to be indispensable for BFO-based material development; for example, it has been the central technique used for discovering domain-wall conductivity [8,9], deterministic ferromagnetic switching by an electric-field [10] and electromechanical enhancements in BFO modified with rare earths (RE-BFO).

RE-BFO has been identified as having a morphotropic phase boundary (MPB)-like behavior [11,12], that is highly sought after in lead-free piezoelectric systems [13]. PFM investigations of RE-BFO have mostly been carried out on epitaxial thin films [11,12,14–18],

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and solution deposition derived thin films [19–21], while there are only a few studies carried out on polycrystalline ceramics [22–26]. Greater understanding of both the macroscopic and local piezoelectric behavior of polycrystalline ceramics is essential for the development of BFO-based materials, as many piezoelectric devices for sensors, actuators and transducers require the ceramic form [27]. Of specific interest is the effect that different synthesis methods have on the local properties, as they are known to influence the chemical homogeneity, phase composition [24] and macroscopic polarization switching behavior [28]. As a result, the methods used for the synthesis of BFO-based materials are likely responsible for a wide variation of the reported electrical properties of ceramics. The analysis of the local domain structure and polarization switching in ceramics prepared by different synthesis methods is therefore necessary to understand the local structure and properties from which the macroscopic piezoelectric behavior is derived.

Here we focus on the samarium (Sm) modified BFO composition $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ (BSFO) and use PFM to study the phase assemblage, domain structure, and local switching behavior in two ceramics of identical composition but prepared with two different methods: a regular solid state reaction (SSR) and a mechanochemically assisted synthesis (MAS) method [28]. The PFM measurements are complemented by transmission electron microscopy (TEM) revealing fundamental differences in the phase assemblage. We provided a comparison of the resulting domain structures and domain switching behavior demonstrating how the synthesis method fundamentally influences the nanoscale ferroelectric and piezoelectric properties of the RE-BFO ceramics.

2. Experimental

For the synthesis of both ceramics powders were milled individually in a planetary mill with polyethylene containers and yttrium stabilized zirconia (YSZ) milling balls with ethanol and ammonium polyacrylate surfactant, until the mean particle size $< 1 \mu\text{m}$. The powders were then weighed into stoichiometric mixtures of $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$. Full details this procedure are provided elsewhere [28]. After mixing, the SSR ceramics were dried, pressed at 150 MPa and reactively sintered (i.e. directly reacted and sintered in a single heating process, at a temperature of 820 °C for 4 h, with a ramp rate of 10 °C min^{-1}). After mixing the MAS ceramics were dried and then dry milled at high energy for a total of 40 h in a tungsten-cobalt (WC-Co) milling containers with WC-Co 10 mm diameter milling balls and a rotational frequency of 300 min^{-1} . These activated powders were again planetary milled before being dried, milled again in the polyelethe with YSZ to reduce the mean particle size $< 1 \mu\text{m}$, after which pellets were pressed to 150 MPa and reactively sintered 800 °C for 4 h.

The investigated samples were sliced with a wire cutter and polished to 1-mm-thick pellets. PFM investigations were performed with the scanning probe microscopes (SPM) NTEGRA Aura (NT-MDT, Russia) and MFP-3D (Asylum Research, Oxford Instruments, UK). Asylum ASYELEC-01 commercial tips with Ti/Ir coating were used. A typical value of the curvature radius of the coated tips was about 28 nm as specified by the manufacturer. The spring constant and the resonance frequency of the cantilevers used were $\sim 2 \text{ N/m}$ and $\sim 70 \text{ kHz}$, respectively. The sample was attached to a polished metal disc by a conductive silver paint used also as a bottom electrode. The PFM signal was acquired by the application of an AC modulated voltage $U_{mod}(t)$ at low frequency ($\approx 20 \text{ kHz}$) and near the resonance frequency ($\approx 280 \text{ kHz}$) and a 5 V amplitude. The signal from the PFM photodetector was analyzed using a lock-in amplifier SR-845 (Stanford Research Systems, USA) or with the internal electronics of the commercial AFM system. The

piezoresponse signal (Y_{pfm}) directly from the lock-in amplifier was recorded in all cases as a single response combining both phase (θ) and amplitude (R) by the relationship: $Y_{pfm} = R \cdot \sin\theta$. Piezoresponse histograms extracted from the noise image (image measured using AC voltage) were used as reference signals for detecting the areas with zero piezoresponse. Phase assemblages were evaluated by the analysis of twenty $10 \times 10 \mu\text{m}^2$ scans from different regions in ceramics.

Voltage spectroscopy (measurements of the local piezoelectric hysteresis loops) was carried out by the application of a sequence of bipolar switching pulses $U_{sw}(t)$ (U_{sw} denotes the magnitude of the pulse) with a maximum amplitude of 30 V and duration 10 s applied to the SPM tip in contact with the sample surface. In this case the $U_{sw}(t)$ pulse was modulated with an AC voltage $U_{mod}(t)$ to measure the local piezoresponse as a function of U_{sw} . The hysteresis loop data was recorded as the piezoresponse signal Y_{pfm} versus the pulse magnitude U_{sw} . After that, the contribution from the electrostatic signal was minimized by the subtraction of its corresponding linear dependence, in accordance with the approach previously described in the literature [29,30]. Coercive voltages (V_c^+ , V_c^-) and bias voltages $V_b = (V_c^+ + V_c^-)/2$ were determined from the hysteresis loops. Local switching experiments within individual grains were conducted by applying rectangular pulses with amplitude from 5 to 60 V, and duration from 10 ms to 100 s. Only grains with spontaneous polarization perpendicular to the surface were selected for switching experiments; this was done by identifying grains with simultaneous maximum and minimum out-of-plane and in-plane signals, respectively. All polarization reversal experiments were done at ambient conditions with humidity ~ 20 –25%.

The samples for transmission electron microscopy (TEM) analyses were prepared using standard methods; after cutting, the samples were ground, polished down to 100 μm and, after dimpling, thinned down to electron transparency using Gatan PIPS ion-milling system. TEM studies were carried out using a JEOL JEM 2010 operated at 200 kV.

3. Results and discussion

3.1. Domain structure and phase distribution

The SSR and MAS synthesis methods used in this study are known to result in BSFO ceramics with different amounts [28] of coexisting polar rhombohedral $R3c$ [31] and anti-polar orthorhombic $Pbam$ phases [32,33]. In addition, the Sm modified BFO system exhibits a non-polar phase for Sm compositions ≥ 15 –16 mol% [33]. This phase is usually identified as either orthorhombic $Pnma$ [33] or $Pbnm$ [34] and is an intermediate phase that forms during the reaction of SSR ceramics [28]. However, the non-polar $Pbnm$ phase is not expected to remain in the final sintered ceramics with the nominal composition of $\text{Bi}_{0.88}\text{Sm}_{0.88}\text{S}_{0.12}\text{FeO}_3$ as according to the pseudo-binary BiFeO_3 – SmFeO_3 phase diagram, this composition lies in the region of coexisting $R3c$ and $Pbam$ phases. The non-polar phase was not observed in the X-ray diffraction patterns of both SSR and MAS ceramics, presented in Ref. [24].

Both SSR and MAS ceramics exhibit regions that are piezoelectrically active (i.e. with PFM signal above the level of experimental noise) and regions that are piezoelectrically inactive (i.e. with PFM signal below noise level) for both in-plane and out-of-plane PFM images (Fig. 1a,b). In the MAS ceramics, piezoelectrically active regions with domain contrast have previously been identified as $R3c$ phase, by the analysis with TEM and fast-Fourier-transforms (FFTs) [22]. Regions without a piezoelectric signal were identified as belonging to $Pbam$ phase by the same method and this was also

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