

Rare-earth Modified Bismuth Ferrite Ceramics: Composition, Structure and Properties from local to Macroscopic Scales

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Bismuth ferrite (BiFeO₃ or BFO) is a prime candidate lead-free electroceramic with wide sweeping potential as a multiferroic, piezoelectric and nanoelectronic material. As an unmodified perovskite, however, its sensitivity to synthesis conditions render it unsuited to large scale manufacturing, which means that any chance of BFO becoming commercially significant depends on its use in solid solutions. Rare-earth modified bismuth ferrites (RE-BFO) have enhanced magnetic¹ and electrical properties² as well as a simple chemistry, making them an excellent system for mapping the composition-structure-property evolution of a BFO-based solid solution. While there are many studies of the local properties of RE-BFO thin films, and many of the macroscopic behavior of RE-BFO ceramics, very few studies have been able to build a comprehensive behavioral model that captures both local and macroscopic electromechanical properties of the same material. Here, with the advent of a mechanochemically assisted ceramic synthesis method and the expansion of piezoresponse force microscopy (PFM) capabilities, we present a composition-structure-property relationship of RE-BFO ceramics from the local to the macroscopic scale. The antiferroelectric *Pbam* phase discovered by Karimi et al.,³ appears as the composition approaches the polar-to-non-polar phase transition. For example, in the system with samarium (Sm) as the RE component the amount of *Pbam* phase increases from 0 to ~99 wt% in nominal compositions 8–15.5 mol% Sm. The *Pbam* phase is distributed throughout the *R3c* matrix, disrupting the ferroelectric domain structure. This reduces the average domain size and creates complex domain morphologies that include features such as charged domain wall configurations and vortex core-like structures. Unlike some other antiferroelectric compositions, such as those based on NaNbO₃, the *Pbam* phase in RE-BFO exhibits no domain structure distinguishable by either PFM or transmission electron microscopy (TEM). Thus, when *Pbam* phase constitutes close to ~100 wt% of the ceramic, no domain structure is observed. Macroscopic studies reveal that the *Pbam* phase is involved in an electric-field-induced phase transition to the *R3c* phase, this creates the opportunity for a locally inducible phase transition with domain contrast that is stable and visible with PFM. While the phase transition appears to have slow kinetics when observed macroscopically through strain-field measurements (with peak-to-peak strains of ~0.3%), the local domain wall mobility in the *R3c* phase appears to be high. This interesting contrast explains the macroscopic strain-field behavior and is discussed in terms of the possible influence of three dimensional strain profiles within the ceramics on the phase transition due to the large strain of 0.8% in the (111)_{pc} direction associated with the transition. PFM supports this discussion by showing that some regions of *Pbam* phase switch readily to *R3c* while others are unable to switch under the applied voltages of up to 40 V.

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