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Nanodomains and nanometer-scale disorder in multiferroic bismuth ferrite single crystals

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Abstract—We report on an investigation of state-of-the-art flux-grown multiferroic bismuth ferrite ($BiFeO_3$; BFO) single crystals by transmission electron microscopy and electron diffraction. The crystals were pre-characterized by piezoresponse force microscopy, electrical resistance and superconducting quantum interference device magnetization measurements. The structurally highly perfect crystals show a ferroelectric stripe domain structure characterized by a domain width of 55 nm. Inside these domains an additional contiguous nanodomain substructure occurs, consisting of 180° related domains, giving rise to satellite reflections at $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$-type positions along $\langle 110\rangle$ directions in the electron diffraction pattern corresponding to a characteristic length in real space of 15.5 nm. Furthermore, we present the first atomic-resolution study on the short-range order by aberration-corrected transmission electron microscopy in which all atoms including oxygen are imaged directly. By measuring the –Fe–O–Fe– atom topology, bond angles and atomic distances we derive the electrical dipole moment as well as the magnitude of the magnetic moment on the unit-cell level. The results evidence substantial atomic- to nano-scale disorder. Both the nanodomain substructure as well as the disorder should affect the subtle magnetoelectric interactions in this material and thereby impede the formation of long-range cycloidal spin ordering which up to now was considered an intrinsic feature of the magnetic properties of $BiFeO_3$ single crystals. By Monte Carlo simulation on the basis of a state-of-the-art effective Hamiltonian we scrutinize certain aspects of the phase formation behavior in the BFO system forming the background of single-crystal growth. This study reveals a very sluggish phase evolution behavior, which should make it invariably difficult to obtain structurally fully equilibrated single crystals.

Keywords: Bismuth ferrite; Crystal growth; High-resolution electron microscopy; Atomic structure; First-principles calculations

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1. Introduction

$BiFeO_3$ (BFO) is a room-temperature multiferroic material simultaneously displaying ferroelectric and antiferromagnetic properties. This makes it a candidate for the attractive concept of electric control of magnetic order in a single-phase material. For this reason, BFO has been extensively studied in recent years in order to better understand its ferroelectric and magnetic properties and the nature of their particular coupling [1]. With respect to the morphology of the systems studied, a differentiation can be made between bulk single crystals and epitaxial thin-film systems, for which experimental investigations have revealed varying physical properties [1]. The present paper focuses on the structure of flux-grown single crystals.

The room-temperature α phase of BFO has a rhombohedral structure with $R3c$ space group [2]. As schematically shown in Fig. 1, the rhombohedral structure can be derived from the perovskite cubic structure by applying a tensile distortion along the direction of a body diagonal, which thus becomes the three-fold axis, $\langle 111\rangle$, in the pseudocubic

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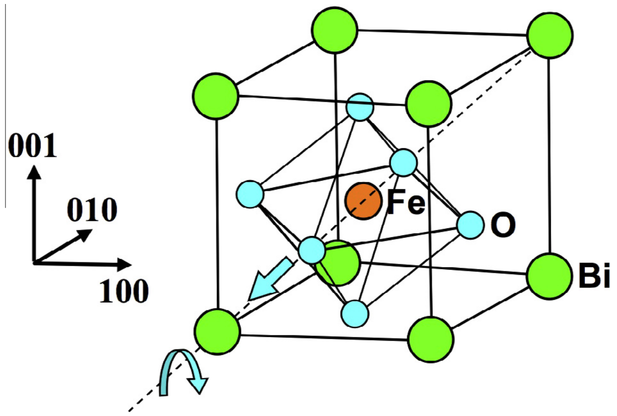

Fig. 1. Schematic of a pseudocubic unit cell of room temperature BFO. A tensile distortion is carried out along the direction of the [1 1 1] body diagonal and the oxygen octahedron rotates around this diagonal axis and is shifted (blue arrow). The sense of the rotation alternates in successive unit cells along [1 1 1]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

notation used here throughout.[1] Adjoining oxygen octahedra rotate around this axis in an alternating sense. The cations and oxygen anions are displaced from their centrosymmetric positions along $\langle 1\,1\,1\rangle$, inducing spontaneous ferroelectric polarization (Curie temperature $T_C \approx 1100$ K) [3]. As a result of electrostrictive effects inducing lattice distortions along $\langle 1\,1\,1\rangle$, there are eight possible ferroelectric variants. BFO exhibits G-type antiferromagnetic ordering (Néel temperature $T_N \approx 640$ K) [4]. A coupling between magnetic moments and tiltings of oxygen octahedra induces a canting of the spins via a Dzyaloshinskii–Moriya-type interaction, resulting in weak ferromagnetism [5,6]. A transition from the α phase to the paraelectric orthorhombic β phase occurs at (1098 ± 10) K [7,8]. This is followed by a transition to a cubic γ phase at 1198 K [8,9].

The early structure and physical property investigations were carried out by employing polycrystalline compacted powder material [3,4,10–12]. Already the first attempts to grow single crystals from a Bi_2O_3–Fe_2O_3 flux demonstrated that the volatility of Bi_2O_3 represents a major problem for preparing phase-pure material and for single-crystal growth. At the 1:1 mol ratio composition phase-pure material cannot be obtained and, depending on the local stoichiometry, also a Bi-rich phase $Bi_{25}FeO_{39}$ or an Fe-rich $Bi_2Fe_4O_9$ phase is formed [9,13–17]. The studies of the Bi_2O_3–Fe_2O_3 phase diagram and the phase evolution during cooling yielded a complex picture, including an irreversible decomposition of $BiFeO_3$ above 1073 K [18,19]. This was confirmed in a more recent study in which the phase diagram was revised [8]. It is evident that BFO crystal growth is dependent not only on thermodynamic variables but also on kinetic factors, in particular the cooling and evaporation rates.

In two pioneering studies on single-crystal growth a 3.3:1 mol ratio Bi_2O_3–Fe_2O_3 flux was employed first [20]. The obtained strongly twinned crystals with ferroelastic and 180° ferroelectric domains indicated that crystal growth had started in the parelectric β phase and that the particular microstructure had formed during the β to α transition. This is in agreement with the phase diagram of Ref. [8]. In order to reduce the liquidus temperature allowing crystal growth below $\sim$1110 K, i.e. within the α phase region, B_2O_3 was added and a 4:1:1 $Bi_2O_3/Fe_2O_3/B_2O_3$ mole ratio was used in Ref. [2] and a 4:1:0.8 ratio in Ref. [21], permitting crystal growth at 893 K. Nevertheless, in Ref. [16] a pure Bi_2O_3/Fe_2O_3 flux with a mole ratio of 3.5:1 was employed. According to Ref. [8] the corresponding liquidus temperature is 1103 K, allowing crystal growth within the α phase region without the addition of boron oxide. In view of the complex phase formation, on the one hand, and the sensitivity of the physical properties to the material composition and structure, on the other hand, it is unfortunate that in the literature on the electric and magnetic properties of bulk BFO the crystal growth conditions have, with few exceptions, not been adequately characterized. In a number of papers in which a B_2O_3-modified flux technique was used, the composition of the melt was not given [22–25]. Also in Ref. [26] a Bi_2O_3–Fe_2O_3–NaCl flux was employed without any details being supplied.

Furthermore, until recently there has not been a single investigation of BFO single-crystalline product by transmission electron microscopy (TEM). Apart from neutron and X-ray diffraction studies, structural characterization of single crystals was, without exception, restricted to low-resolution atomic force microscopy (AFM) topography, to piezoresponse force microscopy (PFM) and to classical metallography assisted by low-resolution scanning electron microscopy (SEM) [8,16,21,23]. That the resolution of these techniques was inadequate and that as a result an important structural feature of BFO single crystals was missed has recently been demonstrated by the first ever TEM study of BFO single crystals [27]. This work revealed a dense ferroelectric vertex domain structure filling the entire single crystal. The characteristic length scale was found to be of the order of some 10 nm, which explains that the corresponding features were out of reach, i.e. far too small in scale to be discernible by the aforementioned low-resolution techniques.

The aim of the present paper is to complement the results reported in Ref. [27] by work that can be grouped in four parts. In the first part we present, for single crystals grown as reported in Ref. [27], ferroelectric hysteresis measurements by PFM and superconducting quantum interference device (SQUID) measurements of magnetization in the temperature range $300\text{ K} \leqslant T \leqslant 700$ K. These measurements demonstrate that our crystals show the same electric and magnetic behavior reported by other groups for Bi_2O_3–Fe_2O_3–B_2O_3 flux-grown single crystals [2,21]. They can therefore be considered typical of the products obtained by this crystal growth technique. In the second part we present the results of a comprehensive investigation of the vertex domain substructure of the single crystals by medium-resolution TEM. Thereby we not only corroborate the preliminary results reported in Ref. [27] but also derive

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[1] We point out that employing pseudocubic indices leads to ambiguity in discussions in which the rhombohedral distortion of the lattice plays a role, e.g. for the relative orientation of different domains. In the following a compromise is made: indices are given in "$\langle i,j,k\rangle$" notation, in order to remind the reader that in neighboring domains the particular axis notation is different. However, in the figures, a consistent set of indices is used for a given domain, allowing orientation relations within the same domain to be expressed.