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 (BiFeO3; 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 \( \{1 \overline{1} 0\} \)-type positions along \( (1 \overline{1} 0) \) 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 BiFeO3 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

1. Introduction

BiFeO3 (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 \( \alpha \) 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, \( (1 \overline{1} 1) \), in the pseudocubic

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This was a major problem for the growth of single-crystal BFO. The early structure and 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 Bi₂O₃–Fe₂O₃ flux demonstrated that the volatility of Bi₂O₃ 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 stoichiometry, also a Bi-rich phase Bi₂FeO₅₉ or an Fe-rich Bi₂Fe₂O₅ phase is formed [9,13–17]. The studies of the Bi₂O₃–Fe₂O₃ phase diagram and the phase evolution during cooling yielded a complex picture, including an irreversible decomposition of BiFeO₃ 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 kinematic factors, in particular the cooling and evaporation rates.

In two pioneering studies on single-crystal growth a 3.3:1 mol ratio Bi₂O₃–Fe₂O₃ flux was employed first [20]. The obtained strongly twinned crystals with ferroelastic and 180° ferroelectric domains indicated that crystal growth had started in the paraelectric 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 ~1110 K, i.e. within the α phase region, Bi₂O₃ was added and a 4:1:1 Bi₂O₃/Fe₂O₃/Bi₂O₃ 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 Bi₂O₃/Fe₂O₃ 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 B₂O₃-modified flux technique was used, the composition of the melt was not given [22–25]. Also in Ref. [26] a Bi₂O₃–Fe₂O₃–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 K ≤ T ≤ 700 K. These measurements demonstrate that our crystals show the same electric and magnetic behavior reported by other groups for Bi₂O₃–Fe₂O₃–Bi₂O₃ 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 subsurface of the single crystals by medium-resolution TEM. Thereby we not only corroborate the preliminary results reported in Ref. [27] but also derive
the type of habit plane of the domain walls forming in projection the vertex domain structure, thereby correcting an incorrect result reported in Ref. [27]. Furthermore, employing high-resolution selected-area electron diffraction we demonstrate that the vertex subdomain structure gives rise to satellite reflections at $\{1 \, \frac{1}{2} \, \frac{1}{2} \}$-type positions along $\langle 1 \, 1 \, 0 \rangle$ directions corresponding to a structural modulation with a characteristic length of 15.5 nm. This is one fourth of the characteristic length of 62 nm derived from neutron-scattering experiments in which likewise satellite reflections at $\{1 \, \frac{1}{2} \, \frac{1}{2} \}$-type positions along $\langle 1 \, 1 \, 0 \rangle$ directions are observed, at lower scattering angle though, which are commonly attributed to long-range cycloidal spin ordering [12,16,28]. Subsequently, in the third part, we employ state-of-the-art aberration-corrected TEM to image all the atoms in these crystals, including oxygen. Using picoimeter electron microscopy, we measure the shift of the iron atoms with respect to the neighboring oxygen atoms. This allows us to derive the electrical dipole moment on the unit-cell level. Also we measure, for the same unit cells, the rotation angle of the oxygen octahedra. Employing recent energetic expressions based on the Dzyaloshinsky–Moriya interaction [5,29], our spatial map of atomically resolved oxygen octahedra tilting angles is converted into a map of magnetic moment. The result is that, in addition to the aforementioned vertex nanodomain structure, the BFO single crystals also exhibit pronounced disorder in the electrical dipole moment and the magnetic moment on a scale ranging from atomic dimensions to some nanometers. Finally, in the fourth part we report results of Monte Carlo simulations on the basis of a state-of-the-art effective Hamiltonian. This study reveals a very sluggish phase evolution which, together with earlier results obtained by first-principles methods on low-energy phases in the BFO system [30], allows to attribute the observed atomic to nanoscale disorder to fundamental difficulties to arrive at an equilibrium structure during the crystal-growth procedure.

2. Experimental

The single crystals were grown following the method in Refs. [21,27] from a flux prepared on the basis of $\text{Bi}_2\text{O}_3$, $\text{Bi}_2\text{O}_3$ (99.999% pure) and (to improve homogeneity) stoichiometric $\text{BiFeO}_3$ corresponding to a net 4/1/0.8 $\text{Bi}_2\text{O}_3$/Fe$_2$O$_3$/B$_2$O$_3$ mole ratio [21]. The milled starting mixture was homogenized in a platinum crucible for 12 h at 1170 K and subsequently cooled at a very slow rate of 0.01 K min$^{-1}$ through the liquidus temperature of 893 K [21] to 875 K followed by cooling to ambient temperature at a rate of 0.1 K min$^{-1}$. The (001)-oriented crystals had a diameter of some millimeters and a thickness between 100 and 300 μm. They were harvested after leaching with diluted HNO$_3$ exploiting the well-documented fact that traces of the aforementioned Fe- or Bi-rich parasitic phases (in contrast to pure BiFeO$_3$) dissolve easily in HNO$_3$ (e.g. [15,16]).

Specimens for TEM were prepared by focused ion beam (FIB) milling. Lamellae with normals parallel to two orthogonal directions $\langle 1 \, 1 \, 0 \rangle$ and $\langle 1 \, 1 \, 0 \rangle$ were cut. Post-processing at low ion energies was carried out in a Fischione 1040 NanoMill to remove the damage layer at sample surfaces introduced in the FIB cutting procedure. The investigations were performed at an electron energy of 300 keV in a FEI Titan 80–300 transmission electron microscope equipped with a spherical-aberration corrected objective lens providing a Rayleigh resolution of 80 pm. The images were recorded employing a 2 k × 2 k GATAN UltraScan 1000 CCD camera. Unfiltered original images were used throughout. We point out that for better readability other experimental details are compiled in the Appendices A and B.

3. Results

3.1. Electrical and magnetic properties

The measured specific dc resistance of $\sim$10$^{12}$ Ω cm is by one to two orders of magnitude higher than the best values reported in the literature [1,8,31], proving the high purity and homogeneity of our single crystals. Their ferroelectric properties were demonstrated by PFM (for methods see Appendix A). Domains were visualized by out-of-plane and in-plane phase and amplitude imaging, and switching of micron-size areas was achieved. The typical hysteretic cycle (Fig. 2 a), $d_{33}$ vs. applied voltage, confirms the ferroelectric behavior. Fig. 2 b shows the temperature dependence of the spontaneous magnetization $M$. At 300 K, prior to the temperature sweep, a 7 T magnetic field was applied. $M$ decreases with increasing temperature and vanishes at 622 K, in good agreement with earlier measurements of $T_N$ in BFO [1,4]. The high purity of the crystals is again demonstrated by the fact that in the sample with a mass of 4 mg we measured only 10$^{-6}$ emu persisting above the transition. The inset in Fig. 1b shows magnetization loops measured at 300 K and 660 K. Above $T_N$ the magnetization increases linearly with magnetic field, as expected in the paramagnetic regime. Below $T_N$ an additional weak ferromagnetic component appears consistent with a canted antiferromagnet [5]. Our data indicate a stable and switchable magnetic moment at 300 K, and confirm that our single crystals reproduce the physical properties already known from the work of other groups [1,16].

3.2. TEM

Our observations by TEM and by selected-area electron diffraction reveal phase-pure BFO single crystals free of lattice defects (dislocations or extended faults). In the following, we report on the TEM investigations in two separate sections. The first section, dealing with observations at relatively low magnification, represents the background for the atomic resolution studies reported in the second section (for atomic resolution TEM see Appendix A, Section A.3). We note for clarity that the terms “low” and “high” magnification refer to TEM standards, i.e. our resolutions are two to more than three orders of magnitude higher than that of the PFM results reported, for example, in Refs. [16,23,27]. It goes without saying that TEM probes the volume of a sample while PFM (like SEM) is a pure surface technique.

According to Refs. [20,21] a new platinum crucible was used since $\text{Bi}_2\text{O}_3$ attacks Pt. We note that in Ref. [16] an alumina crucible was used. Either type of crucible material, due to reactions with the flux, should best be used only once [15,16].
3.2.1. Stripe domain and vertex domain structure

Low-magnification micrographs taken with the (110) Laue orientation exactly aligned (by means of selected area diffraction) with the viewing direction reveal a stripe-domain pattern (Fig. 3a). The projected vertical width of the individual stripe domains is \( \sim 55 \) nm. Our geometrical analysis on the basis of many different samples cut parallel to two orthogonal planes yields the result that the stripe-domain wall habit plane is approximately parallel to the \{113\} plane which, in the sample orientation of Fig. 3a, is inclined to the viewing direction explaining the relatively broad contrast. In Fig. 3b, the stripe-domain walls are essentially seen edge-on and the contrast is sharp. Straight parts are separated by “kinks” (e.g. at the small white arrows). Throughout the samples the stripe domains are “filled” with sub-domains forming a triangular sawtooth-like or vertex pattern. The geometrical analysis shows that these vertex structures are projections of tetrahedron-shaped domain wall arrangements. These are so regular and well defined that they give rise to distinct satellite reflections at \( \{1\frac{1}{2}\frac{1}{2}\frac{1}{2}\} \) type positions along (110) directions in the electron diffraction pattern (Fig. 3c). The shift vector \( k = \{\delta \delta 0\} \) with \( \delta = 0.018 \) yields a modulus of the corresponding modulation vector in real space of 15.5 nm. This agrees with measurements of the vertex tip-to-tip distance along (110) in (110)-oriented samples yielding the same average value (standard deviation \( \sigma = 1 \) nm). We note for clarity that the electron diffraction satellites originate from (along the viewing direction overlapping) very regular domain regions. Therefore the satellite reflections are very sharp, although the domain walls, as discussed in the following section, may be atomically irregular. The type of domain walls can be deduced from the atomic resolution results presented in the next section.

3.2.2. Atomic-resolution studies

Fig. 4a shows an atomic-resolution image of a stripe domain and its internal subdomain structure imaged along the (110) direction. A straight stripe-domain wall (white dotted line) consisting of two parts, “W1” separating domain I and domain II, and “W2” separating domain I and domain III, can be seen. In addition there is a third wall, “W3”, separating domain II and III (yellow dotted line). We note that for a given specimen orientation there are eight possible domain orientations corresponding to different (111) shift vectors and respective rhombohedral orientations. This explains the fact that the stripe-domain wall W1/W2 makes a different angle with the pseudocubic directions although it is of the same type as the stripe-domain walls shown in (110)-orientated samples (Fig. 3b). Furthermore, in a projection along the (110) direction, only the (001) component (vertical arrows in Fig. 4a) of the (111) polarization vector can be measured.

The domains can be distinguished by observing the individual iron and oxygen atom positions inside the individual unit cells and by measuring the direction of the (001) component (arrows), which can be determined for each unit cell by measuring the off-center displacement of Fe with respect to the neighboring O ions. Domains I and III exhibit the same projected structure. In the magnified images (Fig. 4b-d), the structure (one projected unit cell) is outlined. The negative spherical aberration imaging (NCSI)
technique was employed to obtain the atomic images [32,33]. Under these conditions (see Appendix A, Section A.3), the atoms appear bright on a dark background. In the 30 nm thick sample, a strong contrast is observed for the Fe (red) and the O atom (blue) positions, while that of Bi (yellow) is weaker. This is in agreement with quantum–mechanical and optical image calculations. We find (Fig. 4 b–d) that the projected O positions in the images are shifted “upward” and “downward”, corresponding to the alternating sense of the octahedron rotation in the BFO crystal structure. The off-center displacement of Fe with respect to the middle point of the line connecting two neighboring (left and right) O atom positions is clearly visible. This displacement is “upward” in domains I and III (Fig. 4b) and “downward” in domain II (Fig. 4c). As a result of the octahedron rotation and the Fe displacement, the chain –O–Fe–O–Fe–O– forms an “arc” inside the projected unit cell. The arc curvature is mathematically negative for I and III (Fig. 4b) and positive for II (Fig. 4c). In the wall area W3 (Fig. 4d), the –O–Fe–O–Fe–O– atom positions follow a zigzag line, forming a “roof”-type figure, which preserves the rotation of the octahedra while Fe displacements are not seen.

On an atom-by-atom basis (Fig. 4a), it is quite easy to outline the wall areas W1 and W2 with respect to domains I and II, and I and III, respectively. Nevertheless, inspection at higher magnification reveals irregularities and distortions of the atomic contrast inside W1 and W2. This indicates that the stripe-domain wall segments are inclined to the viewing direction and that the image arises from overlapping atom lattices belonging to the two adjoining domains and seen in projection. We note that although
Fig. 4. Atomic resolution images of domains and domain walls. The viewing direction is parallel to the \(\langle 110\rangle\) direction. In the image acquired employing the NCSI technique (see Appendix A, Section A.3) atom positions appear bright on a dark background. The individual atom species, Bi, Fe and O, can be identified by quantitative quantum-mechanical and optical image contrast calculations. (a) A stripe-domain wall (outlined by white dotted lines) can be seen consisting of two sections, W1 separating domain I from domain II and W2 separating domain I from domain III. The wall is inclined to the viewing direction and therefore its image is laterally extended in projection. An additional domain wall W3 (yellow dotted lines) separates domains II and III. Vertical arrows denote the direction of the \(\langle 001\rangle\) component of the \(\langle 111\rangle\) type polarization vector. (b) Magnified image of the atom arrangement in domain I. The tilt of the oxygen octahedra (oxygen: cyan; position of Bi atoms: yellow) and the displacement of the iron atoms (red) are directly visible. (c) Magnification for domain II. (d) Magnified image of domain wall area W3. The sharp dot contrast corresponding to the BiO atom columns (one is marked by an arrow) indicates that in region W3 an overlap of domains II and III along the viewing direction can be excluded. This wall extends parallel to the viewing direction and is broadened since it is electrically charged (see text). In (b)–(d) and from left to right the projected O positions are shifted alternating “upward” and “downward”, corresponding to the alternating sense of the octahedron rotation in the BFO crystal structure. The off-center displacement of Fe with respect to the middle point of the line connecting two neighboring (left and right) O atom positions is clearly visible. This displacement is “upward” in domains I and III (b) and “downward” in domain II (c). As a result of the octahedron rotation and the Fe displacement, the chain \(-O-Fe-O-Fe-O-\) forms an “arc” inside the projected unit cell. The arc curvature is mathematically negative for domains I and III (b) and positive for II (c). In the wall area W3 (d), the \(-O-Fe-O-Fe-O-\) atom positions follow a zigzag line, forming a “roof”-type atom arrangement preserving the rotation of the octahedra while Fe displacements are not seen.
the component of the polarization vector in domains I and III is parallel to the same (001) direction, the (110) components (along the viewing direction) are along opposite directions. The detailed geometrical analysis shows that W2 represents a 109° domain wall.

W3 is a part of a vertex domain wall. We see that for these walls, although they appear rather straight at low magnification, the cut through the wall may be irregular on the atomic scale. It is rather difficult to outline the area of W3 against domains II and III by separating the arc-type atom arrangement (Fig. 4b, c) from the roof-type arrangement (Fig. 4d). However, inside the wall area, a pronounced regular atom contrast can be seen. All atomic positions are sharp, including those of Bi (Fig. 4d). From this it can be concluded that the wall habit plane is parallel to the viewing direction and that the two adjacent lattices are well matched. However, the wall is laterally (in the plane of the image) extended. Geometrical considerations based on these observations (Appendix B) allow us to unambiguously identify W1 as a 71° and W3 as a 180° wall on the atomic scale. This configuration is confirmed by an analysis of the polarization vector components in samples oriented parallel to the (110) direction. This also allows us to identify the kinks in the stripe-domain walls (arrows in Fig. 3b) as 71° wall segments in between 109° segments. Across W3, the polarization vectors in the two adjoining domains II and III are in a tail-to-tail configuration. Across W1 the polarization vectors of domains I and II are head-to-head. This means that both walls are nominally electrically charged.

The off-center displacement vectors (direction and modulus) of the Fe atoms and the rotation angles of the O octahedra were studied quantitatively for W3 and for the adjoining domains II and III. Before going into details we point out that such measurements in atomic dimensions are far from being trivial (the extensive literature on this subject is summarized e.g. in Ref. [34]). Of course the high-precision determination of the individual atom positions starts with a measurement of the positions of the atom intensity maxima by a least-squares fit of the intensity distribution in the image recorded by a CCD camera by two-dimensional Gaussian profiles. However, in order to exploit the full measurement precision in the order of a few picometers attainable by our aberration-corrected electron optics (Appendix A, Section A.3), it has to be taken into account that this primary set of atomic-position data in the electron microscopic image is, in general, not a direct representation of the real crystallographic atom positions in the sample. The reason for this is that the positions of the intensity maxima are affected by residual electron lens aberrations and by small residual tilts of the direction of the incident electron beam with respect to the crystal axis, which are unavoidable in practice in atomic dimensions [34]. However, the technique of numerical absolute contrast matching (ACM) (see Appendix A, Section A.3), based on a quantitative quantum-mechanical and optical treatment of the electron scattering and imaging problem in the computer, allows the residual aberrations as well as the tilting angle to be accurately determined and the corresponding artifacts to be eliminated. The result is a set of corrected atom intensity and position data providing the basis for the high-precision measurements [35] whose results are reported in the following.

Fig. 5a shows a map of the real Fe-atom displacement vectors projected into the (110) plane. Arrows centered at the Fe positions indicate the magnitude and the direction of the displacements obtained from the quantitative evaluation, atom position by atom position, of Fig. 4a. Inside domains II and III, the mean value of the displacement component is ~17 pm (standard deviation σ = 6 pm). This value is in good agreement with the value of 18 pm derived from the crystallographic model of BFO [36]. At the “border line” between the domains and the domain-wall area W3 (red arrows), the displacement changes over a distance of about one single unit cell to the low but finite value of 6 pm (σ = 4 pm).

A striking feature in Fig. 5a is the high degree of disorder on the atomic scale. Both the magnitude and the direction of the projected Fe-displacement vector exhibit substantial random deviations from the exact vertical (001) direction (onto which the (111) direction is projected in the image of Fig. 4a). In some areas nanometer-scale regions with essentially identical directions of dipole vectors can be recognized (e.g. in the areas marked by red ellipses) showing large deviations of up to ~35° from (001). This is significantly larger than our measurement precision, which is related to the precision of the atomic position measurements and, on this basis, is better than 15°.

Fig. 5b shows (for the same area) the magnitude of the O-octahedron rotation angle in color-coded form. The angle was measured in the (110) projection and subsequently converted in an angle around (111). Again a high degree of disorder is evident: we find that the disorder in the form of fluctuations of the rotation angle extends over the whole image, i.e. both the domain area and the domain-wall area are affected. Averaging over an area of 4 × 4 nm², we obtain a mean value of 13° in the blue-dominated areas, in good agreement with X-ray scattering data, i.e. 10.6–13.8° [2,36–39]. However, in the yellow–red-dominated areas the mean value of the angle is found to be 16° (σ < 0.8°). These observations were confirmed taking random samples also in other specimen areas with and without domain walls. Based on the precision of the atomic position measurements and of the (larger) spacing between two oxygen columns the precision for the measurement of the octahedron rotation angle is with 0.8° much higher than in the case of measurement of the dipole-vector deviation. The observation that W3 (white dotted lines) lies within the yellow–red-dominated area, which itself is much larger, was confirmed by measurements in two other samples with the similar domain/domain-wall configuration.

Recently, an energetic expression containing four different macroscopic terms was proposed to describe coupled magnetic orders in terms of the tilting of O octahedra in magnetic and multiferroic perovskites [29]. This expression has its roots in the Dzyaloshinsk–Moriya interaction, and a comparison with data available in the literature and with first-principles calculations confirmed its validity. On this basis of the linear relation given in Ref. [29] between the tilting angles of oxygen octahedra and the magnetization, our map of octahedra tilting angles can be converted into a map of magnetization on the unit-cell scale, as shown in Fig. 5b (right-hand scale).

3.3. Monte Carlo simulation study

In order to find a possible origin of the disorder in the single crystals observed in the present work, we refer to the earlier result of a first-principles study by Diéguez et al. [30]. Searching for potentially stable phases in BFO,
the authors found many distinct low-energy phases. The energy difference of these phases is so small that in nature different low-energy structures may coexist, forming nano-regions of different phases with dipole moments deviating from those in R3c. In order to study this possibility (that has also been investigated in a previous work [40]), we performed Monte Carlo (MC) simulations using a 20 × 20 × 20 supercell employing the effective Hamiltonian described in Ref. [41]. In the simulation, we designed an initial configuration of the system, half of which is perfect R3c, while the other half is perfect Pnma. Interestingly, this structure survived in a slow and long MC relaxation process at 10 K carried out in order to allow sufficient time for the system to evolve in the direction of, and eventually reach, a lowest-energy state. The resulting configuration shows the following features: (i) the relaxed Pnma region possesses electric dipole moments of smaller magnitude compared to the relaxed R3c region (as consistent, for example, with the difference in Fe atom displacements between domain III and the extended wall W3 in Fig. 5a); (ii) the relaxed Pnma region also exhibits larger oxygen octahedral tiltings than those of the relaxed R3c region (as consistent with the inhomogeneity of tilting depicted in Fig. 5b); (iii) in addition to a rather homogeneous G-type antiferromagnetic vector, a weak ferromagnetic vector was also found (leading to a spin-canted structure) with this vector changing magnitude and direction between the relaxed Pnma and R3c regions (this is also consistent with the inhomogeneity of magnetization indicated in Fig. 5b). In addition, we obtained the energy of
the resulting multidomain \textit{Pnma/R3c} structure, finding its value to lie between those of the pure \textit{R3c} and \textit{Pnma} states (while the initial, unrelaxed multidomain structure has a much higher energy).

The MC results thus demonstrate the possibility of a sluggish phase development and, on this basis, the coexistence of two different phases forming a metastable state consisting of nanometer-sized regions. It is likely that our experimental observations reveal such metastable states in the samples at room temperature. The behavior of the unit cell dipoles shown in the blue arrow region of Fig. 5a can be understood as the result of averaging over two or more phase regions over the sample thickness (along the viewing direction).

4. Discussion

4.1. General and low-resolution results

In this study single crystals were grown following the established mole ratio of \([8,21,27]\) with respect to the composition of the \(\text{Bi}_2\text{O}_3/\text{Fe}_2\text{O}_3/\text{B}_2\text{O}_3\) flux. The high quality and purity of the crystals is proven by an extraordinarily high specific dc resistance. The results of our physical property measurements, ferroelectric hysteresis, cycle, the temperature dependence of the spontaneous magnetization from 300 to 660 K and the Néel temperature, are in good agreement with results for single crystals published earlier by other groups. This means that our results are obtained on typical state-of-the-art flux-grown BFO single crystals. In this context we have to repeat that the greater part of the single-crystal results reported in the literature were obtained on crystals where the composition of the flux and other essential details of the crystal growth procedure critical for the quality of the final crystalline product were not communicated.

Starting the discussion with the lower-resolution electron microscopy results, we emphasize the fact that the high quality of our single crystals is further demonstrated by the fact that, as proven by TEM and electron diffraction, the crystals were single-phase throughout and free of extended defects. We could corroborate the principal result of Ref. [27] that the crystals exhibit a dense ferroelectric stripe-domain structure (Fig. 5a, b). Inside these stripe domains, an additional contiguous vortex domain structure occurs. Our atomic-resolution images allowed us to determine the character of the domain walls unambiguously. The stripe-domain walls are of the \(110\) (electric dipoles in head-to-head configuration) and \(109\) type. The vertex domain walls are identified as \(180\) domains (dipoles in tail-to-tail configuration). This result differs from that communicated in Ref. [27] where, due to the limited optical qualities of the electron microscope, atomic-resolution information could not be obtained. Instead, plausibility arguments were employed based on the a priori assumption that the walls should be uncharged.

The vertex-domain structure gives rise to satellite reflections at \(\{111\}\)-type positions along \(\{110\}\) directions in the electron diffraction patterns. The location indicates a structural modulation corresponding to a real-space characteristic distance of 15.5 nm. Satellite reflections in BFO at \(\{111\}\)-type positions along \(\{110\}\) directions, with \(\delta = 0.0045\), are since long known from neutron-scattering experiments on powder samples [12] and on \(\text{Bi}_2\text{O}_3/\text{Fe}_2\text{O}_3\) [16,22,28] and \(\text{Bi}_2\text{O}_3/\text{Fe}_2\text{O}/\text{B}_2\text{O}_3\) [23] flux-grown single crystals. In this case the satellite position corresponds to a modulation with a modulus of the propagation vector of \(\lambda = 62\ nm\), i.e. a value four times larger than the value measured in our case. From the beginning [12] the neutron diffraction result has been interpreted in terms of evidence for cycloidal spin ordering. This long coherence length requires an extraordinarily high crystal perfection over extended distances of which it is unknown whether it was given in the powder samples [12]. Nevertheless, on account of the more recent single-crystal neutron diffraction results [23,28] the explanation of the diffraction satellites at \(\{111\}\)-type positions in terms of the 62 nm cycloidal spin ordering is generally accepted.

Whether there is possibly a correlation between 15.5 nm electron diffraction results and the 62 nm magnetic neutron scattering results has at present to be considered an open question. Whether the vertex domain structure giving rise to electron diffraction satellites at positions \(k = (\delta \delta 0)\) with \(\delta = 0.018\) would also be able to account for diffraction intensity at \(\delta = 0.0045\) can as yet not be elucidated since, due to the finite width of the diffraction-spot intensity distribution in the electron microscope, this very low-angle diffraction range is not accessible. On the other hand, to the best of our knowledge, neutron diffraction data permitting conclusions on possible short-range Fourier components of the modulation are not available.

Recent first-principles studies demonstrate that the magnetoelectric coupling, which is also responsible for the cycloidal spin ordering, depends on a subtle competition between various energy terms, which are largely dependent on likewise rather subtle atomic structural details [1]. This automatically makes very high demands on the structural perfection of the atomic lattices which are the more stringent the higher the physical correlation length defined by a particular ordered structure is. Therefore it appears unlikely that the domain structure evidenced and scrutinized for the first time in this electron-microscopy study and that of Ref. [27] allows the high electric and magnetic coherence required as a prerequisite for the formation of an ordered structure extending both longitudinally and laterally over such a long distance as multiples of the cycloidal wavelength \(\lambda\). The same holds for the atom-to-nanometer-scale disorder discussed below. This challenges the commonly accepted interpretation of reciprocal-space observations in BFO as long as the implicitly implied long-range structural perfection of the investigated crystals has not been proven by electron microscopy in real space.

4.2. High-resolution results

Our work is the first in which domain walls in BFO single crystals were investigated by high-resolution electron microscopy. On the other hand there are numerous electron microscopy studies on domains and domain walls in epitaxial thin films deposited on suitable substrates [42–44]. In particular, after the discovery that domain walls in BFO thin films show substantial electric conductivity [45,46], the properties of domain walls in these films were studied extensively. As already mentioned in Section 1, not only the structure of BFO in thin films but also the physical properties found in these differ substantially from those known for BFO single crystals [1]. As a prominent example
we mention here the fact that in thin epitaxial films the cycloidal spin ordering does not occur [47,48]. This is attributed to epitaxial constraints. More recent neutron scattering and Mössbauer and Raman spectroscopy experiments indicate that with increasing film thickness and increasing degree of strain relaxation there is a transition from a state where cycloidal spin ordering is absent (due to high mechanical strain in very thin films) to a state where the films show a magnetic behavior approaching that of the bulk material [49,50].

Although, as we will see in the following, it is difficult to compare our results on single crystals with those reported in the literature for thin films, we consider it adequate to place them into a joint context, even if this is only serving for a demonstration of the differences. In some cases, the films were characterized by scanning TEM (STEM) employing the high-angle annular dark field (HAADF) technique [51], which cannot supply direct information on oxygen [43,44], and also by TEM [45]. In the latter case, since conventional imaging techniques were employed, oxygen is hardly visible impeding quantitative studies. In contrast in our case the NCSI technique (only available in aberration-corrected TEM) was used. It enables high-contrast imaging of oxygen atoms, allowing localization of these with picometer precision, a prerequisite for electric-dipole studies in perovskites on the unit-cell level [32,33].

In a first principles density-functional study, the configuration of 180° domain walls in thin films was calculated [52]. The wall habit plane chosen for these calculations was the plane parallel to the antiparallel polarization vectors in the two adjoining domains. This automatically yields a head-to-tail configuration of the polarization dipoles, and as a consequence of this, a nominally uncharged domain wall. The width was found to be only about a single unit cell. In a recent study on the same subject, this work was challenged with respect to the wall energies calculated [53]. Nevertheless, the width of the head-to-tail 180° wall was calculated to be in the same order. We point out that there is general disagreement between the values of the domain wall widths measured in Refs. [42,43] and the much smaller values measured by HAADF/STEM in Ref. [53]. In our case, for BFO single crystals, the habit plane (extending along the (110) viewing direction in Fig. 4a) of the 180° wall W3 in general makes a larger angle with the direction of the polarization dipoles in domains II and III. Therefore this wall should be nominally charged. This can also explain the observed extended width ranging from a few up to as many as six unit cell diameters. This confirms earlier atomic-resolution measurements in PbZrTiO3 by aberration-corrected TEM, in which a width of ~1 unit cell was measured for uncharged 180° domain walls and of eight unit cells for charged ones [54].

Our atomic resolution measurements of the bond angle of the –O–Fe–O– chains indicate that in the 180° domain wall W3 the angle is smaller compared to the bulk, in contrast to the result reported in Ref. [52] where, for the head-to-tail wall in thin films, a higher angle was found.

We now turn to our observation in the single crystals of substantial disorder with respect to the off-center Fe atom displacements and the O-octahedron rotation. This disorder occurs on a scale of unit cells up to areas of some nanometers in diameter, in which the displacements and rotations are directed away from the ideal (111) direction by up to a few tens of degrees. Adding up the deviation vectors over larger areas, we find that they essentially sum up to zero. This means that this disorder cannot be detected by lower-resolution or non-local techniques. We recall that by employing the NCSI/ACM technique in aberration-corrected TEM, a lateral measurement precision for the atom positions in the order of a few picometers can be realized [35]. This holds for the position of all atoms including oxygen atoms. This technique is therefore superior to the HAADF technique in STEM, where oxygen, due to its low nuclear charge, cannot be seen but is concluded indirectly, e.g. on the basis of an involved principle-component analysis based on the cation positions only [42]. This makes NCSI/ACM the technique of choice for analyses in which the relative positions of the cations and the oxygen octahedron are the subject of the investigations. Due to the high signal-to-noise ratio and the high contrast of the atomic maxima, the NCSI technique allows a precision of the angle measurements high enough to make the values measured (Fig. 5) statistically significant.

4.3. MC calculation results

We also numerically investigated the formation of dipole patterns in samples where the annealing of the sample was left incomplete (by, e.g. preparing “by hand” an initial configuration made of domains of R3c alternating with domains of Pnma, and then relaxing this initial configuration via MC simulations performed at a given temperature – rather than slowly cooling down in MC simulations this initial structure from very high temperature to that given temperature). Many different metastable states were found at low temperatures, all of which are characterized by complicated dipolar patterns with a dramatic variation of the dipole moment from one unit cell to the next. Moreover, a correlation between large dipole moments and small oxygen octahedral tiltings (and vice versa) has been clearly observed. The simulation result therefore implies that the single crystal preparation conditions can sensitively influence the final state of the measured BFO samples.

5. Conclusions

Following state-of-the-art rules and established procedures, we grew high-purity BFO single crystals. These were thoroughly characterized with respect to their electrical, ferroelectric polarization and magnetization behavior. The results proved that the crystals reproduce the properties of BFO single crystals reported in the literature and – on this basis – can be considered typical for state-of-the-art grown BFO single crystals.

Subsequently, these crystals were investigated by state-of-the-art medium-resolution and atomic-resolution TEM. This revealed three types of structural features, which were studied by quantitative measurements on the atomic scale: (i) a stripe-domain structure with a typical lateral stripe distance of 55 nm; (ii) a contiguous and very regular vertex-domain substructure – based on arrangements of nominally charged 180° domain walls – characterized by satellite reflections at \( \{11\bar{1}\} \)-type positions along (110) directions \( k = \{\delta\delta0\} \) with \( \delta = 0.018 \) corresponding to a modulus of a modulation vector in real space of 15.5 nm; (iii) substantial disorder in the Fe-ion displacement and O-octahedron rotation with disorder regions extending from a few unit cell distances up to some tens of nanometers.

Our MC simulations on the basis of an effective
Hamiltonian indicate that the complex disordered structure on an atomic to nanometer scale may be the result of a particularly sluggish phase evolution during crystal growth and cooling to room temperature.

The classical model of cycloidal spin ordering in bulk bismuth ferrite works on the implicit assumption of an absolutely perfect, defect-free crystal structure guaranteed over dimensions much larger than the cycloidal wavelength \( \lambda \). This assumption has, prior to our study, never been experimentally scrutinized. On the other hand, our observations made by TEM in the size range from that crucial for development of cycloidal spin ordering down to the atomic level reveal substantial disorder incompatible with the aforementioned assumption. Furthermore, our observation of a modulation with a wavelength of \( \lambda/4 \) but otherwise identical reciprocal-space characteristics as those known from neutron diffraction and attributed to cycloidal spin ordering raises intriguing questions concerning a possible relation between the two phenomena. In view of these results, it appears of great interest to carry out further experiments on structure and properties of single crystalline material that has been rigorously pre-characterized by electron microscopy down to the atomic level.

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Appendix A. Methods

A.1. PFM

For PFM investigations, the crystals were polished parallel to the \{001\} surface. Polishing was performed with 0.25 \( \mu \)m diamond paste, followed by chemical mechanical polishing using a SiO\(_2\) colloidal solution (Syton) diluted with water in a 1:1 ratio. PFM investigations were performed using an atomic force microscope (CP-Research, Veeco) equipped with conductive tips (PtIr\(_5\) conductive coatings, ATEC-EFM, Nanosensors) with a nominal elastic constant of 2 N m\(^{-1}\). The measurements were carried out by detecting the vibration of the sample surface under an ac voltage applied through the tip working in contact mode [55]. A fixed frequency of 14.37 kHz and an AC excitation voltage of 2.5 V were used. PFM hysteresis loops were measured applying a DC voltage at the bottom electrode of the BFO crystal.

A.2. Magnetic measurements

Magnetic measurements were carried out in a quantum design (QD) SQUID. Prior to the magnetic measurements, the samples were etched using nitric acid solution. The QD SQUID oven option was employed for scanning in the temperature range 300–800 K. The sample was placed in a geometry described in Ref. [56]. A 7 T magnetic field was applied perpendicular to the polished sample surface. Magnetization loops (collected in no-overshoot mode) and temperature sweeps (3 K min\(^{-1}\)) were collected with a 4 cm long reciprocating sample option. The temperature dependence of the remnant moment was measured upon heating the sample, after cooling in the magnetic field from above \( T_N \sim 622 \) K down to 300 K. The spontaneously formed magnetic moment was measured while cooling the sample in zero field from above \( T_N \), and demagnetizing the coils.

A.3. High-resolution TEM (HRTEM)

The basis for the ultra-high-precision measurements of atomic positions was images recorded employing the negative-spherical-aberration imaging (NCSI) technique, a technique only available in aberration-corrected HRTEM [32,33,57]. As proven by quantum–mechanical and optical image calculations the atom positions appear bright on a dark background. The advantage of this technique is that, on account of the fact that phase and amplitude contrast are of the same sign, compared to conventional contrast techniques a much higher contrast and a substantially improved signal-to-noise ratio is achieved. For picometer precision measurements the recorded images are evaluated in terms of the coordinates and intensities of the atom positions. Subsequently the corresponding data set is corrected for details of electron propagation (extinction), for residual specimen tilt with respect to the precise direction of incident electron beam and for residual optical aberrations of the electron lens. This requires quantum–mechanical and optical image calculations which by iterative solutions of the relativistically corrected Schrödinger equation on a computer allow one to correct for the electron propagation effects and to compensate for the effect of specimen tilt and residual lens aberrations (for the extensive literature on this subject we refer to Refs. [34,58,59] and references therein). For these calculations the MacTempas software package [60] was employed. In TEM it is today state of the art that by the technique of ACM the image contrast can (by the numerical calculations) be matched on an absolute scale, allowing us not only to identify the individual atom species but also to measure the local stoichiometry [35]. On the basis of this quantitative work a measurement precision of a few picometers is reached. The error margin is defined by the standard deviation from the mean defined by the band containing 68.3% of the individual measurement values.

A.4. MC simulations

The effective Hamiltonian, \( H_{\text{eff}} \), developed in Refs. [5,41,61] was used. The total energy is written as a sum of three main terms: (i) representing the energy associated with local modes, elastic interactions and the coupling between local modes and strains [61]; (ii) gathering the energies involving the magnetic degrees of freedom and their interactions with local modes, antiferrodistortive distortions and strains [9,61] and (iii) characterizing the antiferrodistortive interactions and their couplings with local modes and strains [61,62]. The respective parameters were obtained via ab initio computations. Using \( H_{\text{eff}} \), MC simulations were performed on a \( 20 \times 20 \times 20 \) supercell at 10 K.
This allowed us to study the configuration of electric dipoles and the configuration of oxygen octahedra tiltings (magnetic moments) over the supercell.

Appendix B. Identification of domain walls

Fig. 6 shows a schematic of two possible domain configurations for identification of the domain wall angle between domains II and III on the atomic level. The viewing direction is parallel to (110). The viewing direction, (110), in Fig. 4a is now tilted by 90° and is from left to right (thick arrows). The rhombohedral distortion (deviation from a rectangular pattern) is exaggerated. Along the horizontal two adjoining parallelograms make up one projected unit cell. The (111) direction in each domain is indicated by a thin arrow. For details see text (Appendix B).

Fig. 6. Schematic of possible domain configurations for identification of the domain wall angle between domains II and III on the atomic level. The viewing direction is parallel to (110). The viewing direction, (110), in Fig. 4a is now tilted by 90° and is from left to right (thick arrows). The rhombohedral distortion (deviation from a rectangular pattern) is exaggerated. Along the horizontal two adjoining parallelograms make up one projected unit cell. The (111) direction in each domain is indicated by a thin arrow. For details see text (Appendix B).

References