Bismuth Ferrite Single Crystals Studied by Aberration-Corrected Transmission Electron Microscopy

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Bismuth ferrite ($BiFeO_3$, BFO) is an intrinsic multiferroic that simultaneously shows antiferromagnetic and ferroelectric properties at room temperature [1]. This makes it a prototypic example of a candidate material for devices functioning on the basis of an electric control of magnetic order.

In recent years, in particular after it was demonstrated [2] that thin epitactic films of BFO display extraordinary high values of spontaneous electric polarization, the work on electric and magnetic properties and their coupling concentrated on epitactic thin film systems. Also the structure of polarization-domain walls in these films was studied by transmission electron microscopy [e.g. 3-6]. In our work we followed an entirely different approach. It is generally accepted that in order to study the basic, intrinsic physical properties of a material single crystals are required. In fact, compared to thin films there is comparatively little work done on BFO single crystals. And in spite of more than thirty years of BFO research, until recently [7] there was not a single study on single crystals by electron microscopy. Here we give a brief account of first results obtained on single crystals by aberration-corrected TEM. Our study is typical for the high potential of aberration-corrected high-resolution TEM in the field of modern materials science where structures of atomic- to nanoscale may be decisive for physical properties but are not always noticed by non-local techniques.

The growth of BFO single crystals is difficult since, on account of the volatility of Bi_2O_3 and the instability of BFO at high temperatures, thermodynamic and kinetic aspects play a role. We have grown BFO single crystals employing the established flux-growth technique from a $Bi_2O_3/Fe_2O_3/B_2O_3$ flux, at a mol ratio of 4/1/0.8 [8]. The resulting [001]-oriented crystals had a diameter of some millimeters and a thickness of about 300 μm. Samples for TEM with normals parallel to two orthogonal directions, $[\bar{1}\bar{1}0]$ and $[1\bar{1}0]$ were cut by FEI Helios FIB milling followed by a finish by means of a Fischione 1040 NanoMill. Electron microscopy was carried out at 300 keV in a FEI Titan 80-300 TEM equipped with a spherical-aberration corrector. The NCSI technique [9,10] was used throughout. In contrast to conventional imaging modes it gives strong (bright on a dark background) contrast for all atoms, including oxygen. To see and measure oxygen is a prerequisite for exploring the magnetic moments in addition to the electric polarization. Prior to electron microscopy the single crystals where investigated carrying out the usual measurements by piezoresponse force microscopy in order to demonstrate ferroelectric hysteresis and the Curie temperature and SQUID magnetometry to demonstrate the antiferromagnetic ordering and the appertaining Neél temperature.

This proved that the single crystals studied show the established set of physical properties [1] and are typical for BFO single crystals.

Figure 1(a) shows the first important feature characterizing the BFO single crystals. Between a (horizontal) electric polarization stripe domain boundary pattern we see a contiguous vertex pattern filling the entire crystal. This pattern is the projection of a tetrahedral arrangement of nanodomain walls. On the basis of an atomic resolution

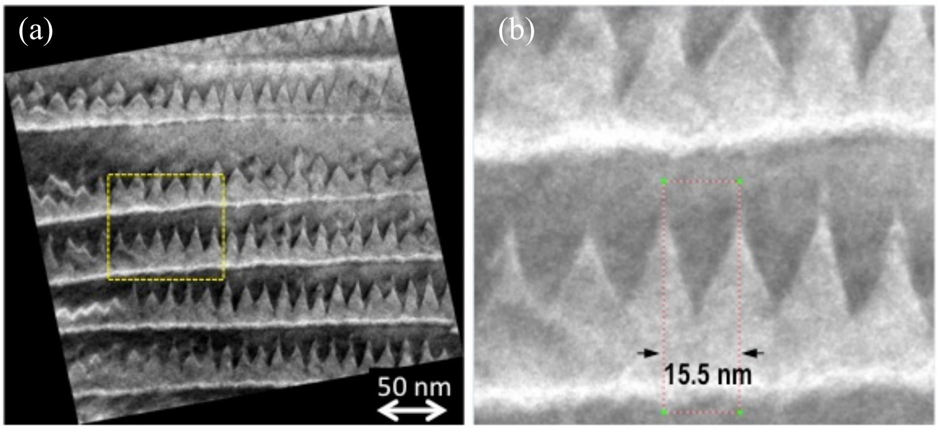

Fig. 1

study these walls could be identified as 180° walls. These nanodomains give rise to satellites at {1/2,1/2,1/2} type reflections in electron diffraction patterns corresponding to a characteristic length of 15.5 nm (Fig. 1b; framed part of Fig. 1a). This challenges the established interpretation of the {1/2,1/2,1/2} type reflections observed in neutron scattering experiments in terms of a long-range cycloidal spin ordering.

The second characteristic feature revealed by our atomic-resolution TEM study is the existence of atomic- to nanoscale disorder in form of random oxygen-octahedron tilts out of the ideal crystallographic [111] directions typical for the rhombohedral structure with R3c space group. These tilts can be related to magnetic (dis)order [11]. Since this disorder does not allow to form the long-range cycloidal spin ordering, also this observation challenges the generally accepted view that the weak ferromagnetism observed in BFO single crystals is related to the cycloidal spin ordering. We note that the magnetic disorder observed in our study averages out to zero over larger areas so that both the vertex domain structure and the disorder revealed by TEM could not be detected by the more integral or low-resolution techniques applied in BFO research before.

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