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# Multiferroic interfaces in bismuth ferrite composite fibers grown by laser floating zone technique

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ABSTRACT

In this work we explore the formation of enhanced multiferroic interfaces in bismuth ferrite crystalline fibers grown by laser floating zone technique. An underlying mechanism of self-segregation during the fibers growth process enables to establish a textured microstructure of a dominant $BiFeO_3$ phase bordered by the presence of $Bi_{25}FeO_{40}$ secondary phase. The crystallites ***c*** axis of the $BiFeO_3$ phase shows a preferential orientation along the longitudinal axis of the fibers, together with grain boundaries that also present a significant alignment with the same direction. These features induce a systematic disturbance of the antiferromagnetic structure of the $BiFeO_3$ phase at the interfaces with the $Bi_{25}FeO_{40}$ diamagnetic phase. The structural anisotropy confirmed by High Resolution X-ray diffraction and scanning electron microscopy images is also manifested in the magnetic properties of the fibers, which reveal an enhanced susceptibility response in comparison to the conventional $BiFeO_3$ phase diagram.



## 1. Introduction

A considerable focus have been given to the metal oxide materials as they manifest a broad range of structural and exciting physical properties [1,2]. Only small subgroups of all magnetically and electrically polarizable materials are either ferromagnetic or ferroelectric and fewer still simultaneously exhibit both order parameters [3]. Among many of the promising functional responses exhibited by a few of these materials is the existence of two or more "ferroic" order parameters simultaneously (ferroelectricity, anti/ferromagnetism, ferroelasticity), whereas the degree of coupling between the magnetic and polarization properties is classified as magnetoelectric effect [4]. Such is the case of single-phase multiferroic $BiFeO_3$ among other like rare earth manganites (e.g. $TbMnO_3$, $HoMnO_3$) or $BaNiF_4$ or even chalcogenides like $ZnCr_2Se_4$. Most of these interesting materials are found to be in a group of pseudo-perovskite structure, characterized by a general chemical formula $ABO_3$ (e.g., $CaTiO_3$, $SrRuO_3$, $BiFeO_3$) comprising corner-sharing six oxygen octahedral with a central B-cation and a A-cation that can coordinate with up to twelve oxygen ions. The particular case of $BiFeO_3$ (BFO) attracted much attention, as it is essentially the only known multiferroic that simultaneously possesses both magnetic and ferroelectric order at and above room temperature [5].

$BiFeO_3$ has a rhombohedral unit cell characterized by two distorted perovskite blocks connected along their body diagonal [1 1 1], where the two oxygen octahedra of the two cells are rotated clockwise and counterclockwise around the [1 1 1] by $\pm 13.8(3)^\circ$ and the Fe-ion is shifted by 13.5 pm along the same axis [6]. $BiFeO_3$ is a robust antiferromagnetic–ferroelectric with a cycloid spin structure having a period of 62 nm [7]. The symmetry also permits a small canting of the moments in the structure resulting in a weak canted ferromagnetic moment of the Dzyaloshinskii–Moriya type [8,9]. Spurred on by a 2003 paper focusing on the growth and properties of $BiFeO_3$ thin films [10], dramatic advances in the study and understanding of this material have occurred. Much work is available on the magnetic, magnetoelectric and magneto transport [11] properties of the $BiFeO_3$ films as a function of the growth parameters [12] and there exist different thermodynamic (e.g. Landau-type) models [13,14] to examine the extent of contribution of domain walls in the enhancement of magnetization in these films. He et al. [11] have also demonstrated that in magneto transport certain types of domain walls (i.e., 109° walls) can exhibit strong temperature- and magnetic field-dependent magneto resistance (as large as 60%) which is thought to be the result of local symmetry breaking at domain walls and the formation of magnetic moments. Not much detailed work on the properties of the bulk BFO ceramics is available because of the difficulty in reducing the secondary phases obtained, during the preparation of crystalline $BiFeO_3$ bulks by several methods such as sol–gel [15], solid state reaction [16], simple precipitation [17], rapid liquid phase sintering [18], chemical solution deposition [19] and high-energy ball milling [20].

The laser floating zone (LFZ) technique is a well-known method to grow large, clean and homogeneous single crystals, particularly considering that a high temperature gradient ahead to the solidification interface can lead to the formation of single crystals with high quality of

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crystallinity [21,22]; while at a higher growth rate it also enables to synthesize textured crystal fibers with enhanced anisotropic physical properties [23,24]. The main parameters that have large influence on the quality of the crystal grown by this technique are the temperature gradient, the growth rate and atmosphere. The LFZ technique allows producing highly textured materials with superior properties when compared to their sintered forms, which produce drawbacks such as disordered grain boundaries and high anisotropy in the charge transport [25–27]. In this study, we used the LFZ technique to produce fibers from initial nominal composition $Bi_{1.2}Fe_{0.8}O_3$, in an attempt to obtain the stoichiometric phase of $BiFeO_3$. The stoichiometry of precursor materials is chosen based on the study by Pradhan et al. [28] in order to compensate the effect of vaporization loss of Bismuth during the high temperature melting in the LFZ. Our study focuses on the effect of the fibers growth rate on phase development, texturing and magnetic properties.

## 2. Experimental procedures

Appropriate amount of $Bi_2O_3$ and $Fe_2O_3$ powders from Aldrich (purity > 99%) to obtain the $Bi_{1.2}Fe_{0.8}O_3$ composition, were mixed with ethanol and ball milled for 40 min at 250 rpm. The obtained homogenous mixture was dried at 100 °C, then added to a 2% polyvinyl alcohol (PVA) binder enabling the precursor to be extruded into rods of 2 mm diameter [29]. These rods are used as feed and seed in the LFZ growth process in normal room atmosphere. The LFZ system used is equipped with a continuous $CO_2$ *Spectron SLC* laser ($\lambda = 10.6$ μm; 200 W) suitable to grow dense fibers. In order to provide better homogeneity of the target fibers, the seed and feed rod precursors rotated respectively at $\omega_s = 0.166\pi$ and $\omega_f = 0.5\pi$ $s^{-1}$ (5 and 15 rpm) in opposite directions,. Three different growth rates were analyzed in detail: 25, 50 and 100 mm/h. X-ray diffraction (XRD) was performed using a *X'Pert MPD Philips* diffractometer (Cu Kα radiation, $\lambda = 0.154056$ nm) at 40 kV and 30 mA, based in a Bragg–Brentano para-focusing optics configuration. Rietveld refinement analysis [30] of diffractograms enables to estimate phase's proportion and crystallographic structure. Surface morphology of the fibers was observed using a *Hitachi S4100-1* scanning electron microscopy (SEM), and phase's composition analyzed using energy dispersion spectroscopy (EDS) mode (25 kV, 10 mA). The magnetic susceptibility measurements were performed using a *Cryogenics* vibrating sample magnetometer (VSM). The magnetic properties as a function of temperature were acquired in field cooling (FC) and zero field cooling (ZFC) modes, applying a magnetic field of 0.5 Tesla, and magnetization versus magnetic field at constant temperatures of 5 and 300 K. The magnetic measurements were made in two different geometries, by placing the samples in a parallel and perpendicular position relative to the direction of the applied magnetic field [31].

## 3. Results and analysis

Fig. 1 shows the X-ray powder diffraction pattern obtained for fiber grown at 25 mm/h by LFZ. According to the respective Rietveld analysis the majority phase matches the $BiFeO_3$ pseudo-perovskite, in agreement to the results obtained by Pradhan [28], indexed to the SG *R3c h* (161) [32]; in parallel, a considerable amount (~40%) of secondary phase can be indexed to the $Bi_{25}FeO_{40}$ *I23* (197) cubic phase [33]. Fig. 1 also compares the XRD diffractograms taking in consideration the fiber cross sections. For the measurement performed in a transversal section, planes like (0 0 6), (0 1 8) and (1 0 10) of $BiFeO_3$ phase are highly enhanced when compared to the measurement obtained from the longitudinal cut geometry, which exhibits as main peaks planes (1 1 0) and (2 1 1) indicative of a preferred orientation of ***c*** axis parallel to the fiber growth direction (***z***). In its turn, $Bi_{25}FeO_{40}$ phase profiles are much similar in both diffractograms as inherent from a cubic symmetry.

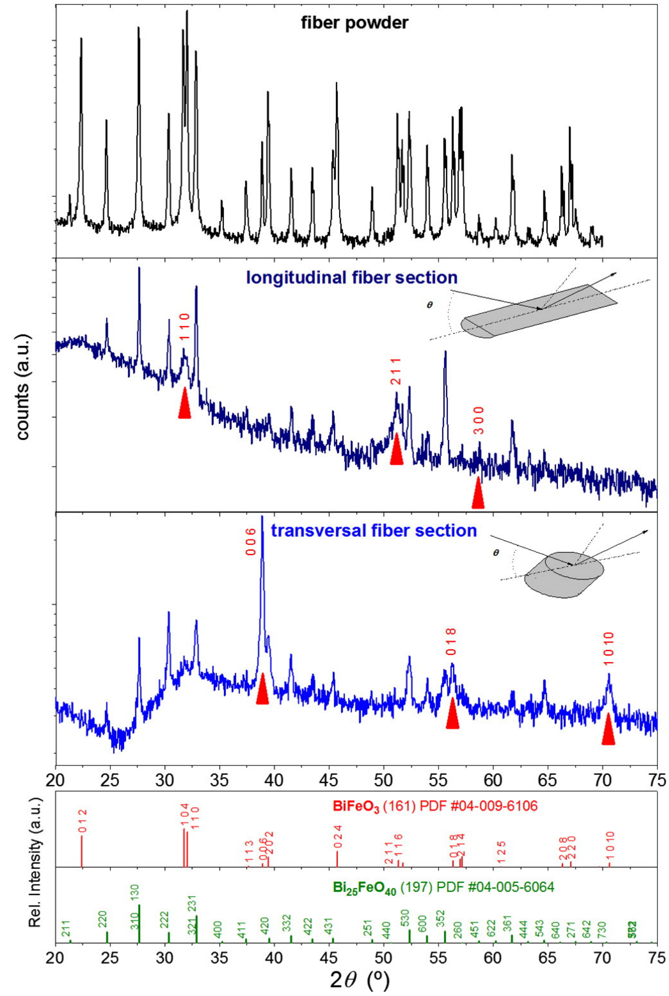


**Fig. 1.** Comparison of X-ray diffractograms obtained from the fiber grown by LFZ at 25 mm/h, for the powder, longitudinal and transversal sections, respectively indexed to $BiFeO_3$ and $Bi_{25}FeO_{40}$ phases.

Table 1 compares the structural results calculated from the diffractograms obtained from the 25, 50 and 100 mm/h fibers growth speed. A perceptible increase (up to ~5%) of the secondary $Bi_{25}FeO_{40}$ phase can be associated with the fibers processing rising speed.

Further confirmation and scrutiny of the structure can be obtained from pole figures; the preferable orientation of the (0 0 6) planes of crystallites is visible from padding of peaks at $2\theta = 39.0°$ within $\Delta\psi < 30°$ dispersion as shown in Fig. 2a. In Fig. 2b the reflections of (1 1 0) planes at $2\theta = 32.0°$ display a consistent distribution $\Delta\psi < 30°$ along the fiber main direction ($\varphi \sim 0°$) exhibiting the expected set of reflections at $\psi \sim 60°$ from the symmetric group of planes.

Fig. 3 a), b) and c) shows the morphology of the polished surface in the longitudinal direction of the fibers grown by LFZ at 25, 50 and

**Table 1**
Structural parameters obtained from Rietveld analysis of LFZ fiber grown at 25, 50 and 100 mm/h.

| Growth speed | % vol. $BiFeO_3$ | $a = b$ | $c$ | % vol. $Bi_{25}FeO_{40}$ | $a$ | $R_p$ | $R_{wp}$ |
|---|---|---|---|---|---|---|---|
| (mm/h) | *R3c h* | (nm) | (nm) | *I23* | (nm) | | |
| 25 | 63 | 0.5576 | 1.387 | 37 | 1.0176 | 10.6 | 15.5 |
| 50 | 62 | 0.5578 | 1.387 | 38 | 1.0176 | 8.8 | 11.5 |
| 100 | 58 | 0.5579 | 1.388 | 42 | 1.0176 | 9.7 | 12.6 |