



Intermediate structural phases in rare-earth substituted BiFeO₃

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ARTICLE INFO

Article history:

Received 30 September 2009

Received in revised form 19 November 2009

Accepted 18 December 2009

Available online 28 December 2009

Keywords:

A. Ceramics

C. Atomic force microscopy

C. X-ray diffraction

D. Crystal structure

D. Ferroelectricity

ABSTRACT

The room-temperature crystal structure and local ferroelectric properties of Bi_{0.85}RE_{0.15}FeO₃ (RE = Sm, Gd, Dy) polycrystalline samples have been investigated by X-ray diffraction (XRD) and piezoresponse force microscopy (PFM) techniques. XRD measurements show that the rare-earth substitution causes the transformation of *R3c* structure typical of BiFeO₃ to yield orthorhombic phases with $\sqrt{2}a \times 2\sqrt{2}a \times 2a$ and $\sqrt{2}a \times 2a \times \sqrt{2}a$ superlattices (*a* is the parameter of the cubic perovskite subcell). Results of PFM investigations imply that both the orthorhombic phases are polar. The models describing crystal structure of the phases are discussed.

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1. Introduction

Despite considerable efforts undertaken in a rapidly developing area of multiferroic research [1,2], the effect of temperature [3,4], high pressure [5,6], and chemical substitution [7,8] on crystal structure and physical properties of bismuth ferrite is still a matter of intensive research. At ambient conditions, the compound has a rhombohedrally distorted structure with a space group *R3c* [9]. *A*-site substitution with lanthanides (Ln) is known to induce a number of structural transitions in BiFeO₃, but symmetry of the intermediate structural forms existed between polar *R3c* and nonpolar *Pnma* phases characteristic of the end members of (BiFeO₃)_{1-x}(LnFeO₃)_x series [9,10] is not unambiguously determined yet. In one of the pioneering work on this topic, the *R3c* → *P1* → *C222* → *C222*₁ → *Pn2₁a* → *Pnma* sequence of the composition-driven transitions (at *x* ≈ 0.06, 0.24, 0.40, 0.55, and 0.7, respectively) was proposed for Bi_{1-x}Ln_xFeO₃ single crystals [11]. With decreasing Ln³⁺ ionic radius, the concentrational boundaries of the structural phases were claimed to shift towards smaller *x* [11]. More recent investigation of Bi_{1-x}Gd_xFeO₃ polycrystalline samples confirmed existence of the intermediate polar structure *Pn2₁a* (0.1 < *x* < 0.2) [8,12]. Study of Bi_{1-x}Ln_xFeO₃ (Ln = Nd, Sm) compounds revealed a substitution-induced transition to antipolar PbZrO₃-like phase at *x* ~ 0.15 [13,14]. A coexistence of *R3c*, *Imma*, and *Pnma* phases was found for Bi_{1-x}Ln_xFeO₃ (Ln = La, Nd) samples

in a broad concentration range [15]. Such a variety of the structural models is probably explained by a strong tendency of the Bi_{1-x}Ln_xFeO₃ multiferroics to phase separation and formation of impurity phases [15], that hampers true crystal structure identification. To reveal the intermediate phases of Bi_{1-x}Ln_xFeO₃ which can be easily stabilized during a conventional solid-state reaction and to define the basic properties, which can help to determine the crystal symmetry of the phases, we performed synthesis of Bi_{0.85}RE_{0.15}FeO₃ (RE = Sm, Gd, Dy) compounds at moderate temperature. Taking into account that formation of the intermediate phases in Bi_{1-x}Ln_xFeO₃ seems to be the result of the cation diffusion between the easily forming phases with BiFeO₃-type (*R3c*) and LnFeO₃-type (*Pnma*) structures [15], the moderate-temperature synthesis is expected to give us a “composition sweep” of the possible structural forms.

2. Experimental

Polycrystalline samples with nominal chemical compositions Bi_{0.85}RE_{0.15}FeO₃ (RE = Sm, Gd, Dy) were prepared by the conventional solid-state reaction method using Bi₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃, and Fe₂O₃ oxides. The synthesis was carried out in air at moderate temperature of 850 °C [12–15] for 6 h with a heating/cooling rate of 5 °C/min. The crystal structure of the samples was studied by X-ray diffraction technique using an automated Philips PW 1050/35 diffractometer with Cu K_α radiation. XRD patterns were collected over the angular range 20 ≤ 2θ ≤ 100° with step of 0.02° and exposition of 25 s/step. Local ferroelectric properties of the samples were investigated with piezoresponse force micros-

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copy using a commercial setup Multimode NanoScope IIIA (Veeco) equipped with a lock-in amplifier (SR-830A, Stanford Research) and a function generator (FG-120, Yokagawa). A commercial tip-cantilever system Arrow™ Silicon SPM Sensor (NanoWorld) was used. Domain visualization was performed under an applied *ac* voltage with the amplitude $V_{ac} = 2.5$ V and frequency $f = 50$ kHz. Local piezoelectric hysteresis loops were measured inside individual grains by applying the consecutive voltage pulses and measuring the piezoelectric response as a function of the voltage.

3. Results and discussion

In spite of the rather complex character of the obtained XRD spectra, suggesting a multiphase structural state of the samples, a careful analysis made using the FullProf software package allowed us to identify all the diffraction peaks and to separate out contributions from different structural forms (Fig. 1). For $\text{Bi}_{0.85}\text{Sm}_{0.15}\text{FeO}_3$ sample, the main contribution is related to an orthorhombic phase O_I with $\sqrt{2}a \times 2\sqrt{2}a \times 2a$ superlattice ($a, \sim 4$ Å, is the parameter of the cubic perovskite subcell). Crystal structure of the phase was recently studied by Karimi et al. [13,14]. Taking into account a close analogy between the X-ray and electron diffraction data obtained for the $\text{Bi}_{1-x}\text{Ln}_x\text{FeO}_3$ ($\text{Ln} = \text{Nd}, \text{Sm}; x \sim 0.15$) and well-known PbZrO_3 [16], the authors identified this phase as having *antiferroelectric* structure [13,14]. It was also shown that the simplest unit cell that fitted the electron diffraction and was consistent with the XRD data was similar to that of PbZrO_3 except that the *c* parameter was quadrupled rather than doubled with respect to the fundamental perovskite lattice (i.e. the unit cell should have a $\sqrt{2}a \times 2\sqrt{2}a \times 4a$ metrics) [13,14]. We, however, did not find any additional XRD peaks suggesting the quadrupling the unit cell along the *c* axis. The same superstructure $\sqrt{2}a \times 2\sqrt{2}a \times 2a$ was found upon the synchrotron X-ray powder diffraction characterization of the structural phase stabilizing in the vicinity of the ferroelectric $R3c$ phase of BiFeO_3 during application of external pressure [6]. The similarity of the structures is unlikely to be accidental: because of the difference in ionic radii between the host and the substituting elements, a chemical substitution could act on interatomic distances in the similar way as an external pressure, thus leading to appearance of the same structures [17]. As expected, two other dominant contributions to the resulting XRD pattern of the Sm-substituted sample were attributed to an orthorhombic phase O_{II} with $\sqrt{2}a \times 2a \times \sqrt{2}a$ superlattice characteristic of LnFeO_3 [10] and a rhombohedral

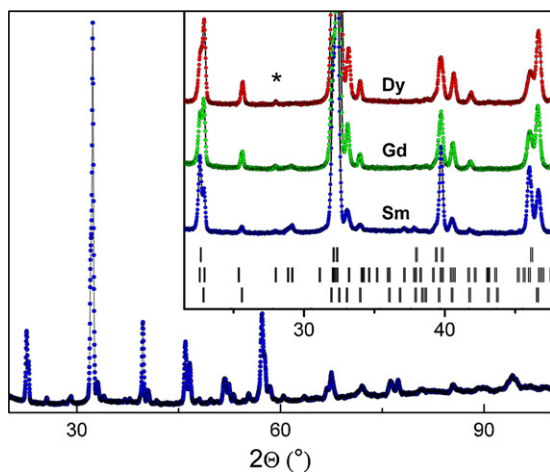


Fig. 1. Experimental XRD pattern for $\text{Bi}_{0.85}\text{Sm}_{0.15}\text{FeO}_3$ sample. Inset shows parts of the spectra obtained for $\text{Bi}_{0.85}\text{RE}_{0.15}\text{FeO}_3$ samples together with the Bragg reflections allowed by the space groups $R3c$, $Pbam/Pba2$, and $Pnma/Pn2_1a$, from top to bottom (see Section 3). *Position of the main peak characteristic of $\text{Bi}_{25}\text{FeO}_{39}$.

phase R typical of BiFeO_3 [9]. Traces of $\text{Bi}_{25}\text{FeO}_{39}$ impurity, which often accompanies the formation of the perovskite-like phase of BiFeO_3 [6,12–15], were also detected. The same main structural forms O_I, O_{II}, R were found for Gd and Dy-substituted compounds, the volume fraction of the phase O_I being reduced with decreasing ionic radius of substituting element.

To shed light on crystal structure of the discovered phases, we undertook investigation of local ferroelectric properties of the samples with piezoelectric force microscopy. Indeed, if the O_I phase is really characterized by *antiferroelectric* PbZrO_3 -like structure, it will be immediately confirmed by observation of the local areas showing no piezoresponse contrast, but demonstrating double piezoelectric hysteresis loops [18]. If the O_{II} phase has $Pnma$ symmetry, neither PFM contrast, no local piezoelectric hysteresis loops will be observed [8]. PFM experiment, however, did not reveal a presence of any extended regions with zero piezoresponse. Typical examples of our PFM investigation are presented in Fig. 2. A piezoelectric contrast corresponding to the antiparallel ferroelectric domains was found in all locations tested (Fig. 2(a–c)). A unipolar piezoelectric response after scanning with a *dc* voltage applied to the tip was also observed. The shape of the PFM hysteresis loops taken on the surface of the samples is typical of ferroelectric materials (Fig. 2(d)). These facts imply that the phases found in the $\text{Bi}_{0.85}\text{RE}_{0.15}\text{FeO}_3$ composites are ferroelectric and their crystal structures must have a polar symmetry. The data are consistent with the results of investigations of piezoelectric, pyroelectric, and ferroelectric properties of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$

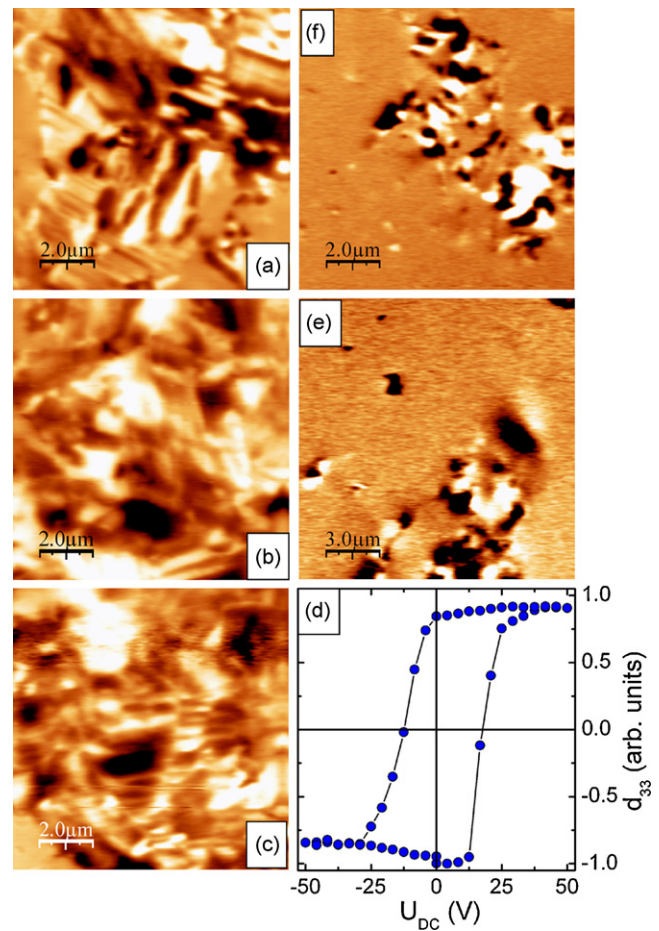


Fig. 2. (a–c) Piezoresponse force microscopy images demonstrating existence of ferroelectric domains in $\text{Bi}_{0.85}\text{RE}_{0.15}\text{FeO}_3$ samples (RE = Sm, Gd, Dy, respectively). (d) Local piezoelectric hysteresis loop obtained for $\text{Bi}_{0.85}\text{Sm}_{0.15}\text{FeO}_3$ sample. (e and f) PFM images for $\text{Bi}_{0.8}\text{RE}_{0.2}\text{FeO}_3$ samples (RE = Sm and Dy, respectively).

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