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Substitution-driven structural and magnetic phase transitions in

$\text{Bi}_{0.86}(\text{La, Sm})_{0.14}\text{FeO}_3$ system

V. A. Khomchenko, a, * L. C. J. Pereira, b and J. A. Paixão a

a CEMDRX/Department of Physics, Faculty of Sciences and Technology, University of
Coimbra, P-3004-516 Coimbra, Portugal

b UCQR, Instituto Tecnológico e Nuclear/CFMCUL, P-2686-953, Sacavém, Portugal

Solid state synthesis and investigation of crystal structure and magnetic properties of
$\text{Bi}_{0.86}\text{La}_{0.14-x}\text{Sm}_x\text{FeO}_3$ ($0 \leq x \leq 0.14$) ceramics were performed. It was found that a
rhombohedral to orthorhombic phase transition took place in the series with decreasing
average ionic radius of the substituting elements occupying the A-site of the ABO3
perovskite. Magnetic properties of the compounds were shown to correlate with
evolution of their structural state. Pure rhombohedral samples $0 \leq x \leq 0.06$ were obtained
in a mixed antiferromagnetic/weak ferromagnetic state. A small residual magnetization
characteristic of the compounds was found to weakly depend on change of the chemical
composition. Progressive increase of the residual magnetization was observed upon the
rhombohedral to orthorhombic transition. Reasons of appearance of the weak
ferromagnetism in orthorhombic and rhombohedral phases of the $\text{Bi}_{0.86}(\text{La, Sm})_{0.14}\text{FeO}_3$
compounds were analyzed.

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*Corresponding author: Dr. V. A. Khomchenko
Department of Physics, University of Coimbra, P-3004-516 Coimbra, Portugal
E-mail: uladzimir@fis.uc.pt
Phone: +351 239 410 637
Fax: +351 239 829 158
1. Introduction

Complex transition- metal oxides with the perovskite (ABO₃) structure are materials demonstrating a large variety of attractive physical phenomena such as high-temperature superconductivity or colossal magnetoresistance. Since 2000s, renewal of interest to magnetoelectric effect has given additional impulse to investigation of perovskite- type compounds. Among them, BiFeO₃ is the only material which is both magnetic and a strong ferroelectric (~100 μC/cm²) at room temperature [1]. As a result it is the most extensively studied multiferroic system sometimes called “The Holy Grail” of multiferroicity [2]. In ferroelectric phase (i.e. below the Curie temperature of 1100 K), the compound possesses a rhombohedral R₃c structure [3, 4]. Symmetry of a high- temperature paraelectric phase is still a matter of intensive research [5-7]. Below the Neel point of 640 K, BiFeO₃ shows a long- range incommensurate cycloid- type antiferromagnetic structure with a period of ~620 Å along [110]ₜ direction [8]. The spatial modulation prevents the observation of any net magnetization and the linear magnetoelectric effect. If the modulated magnetic structure in BiFeO₃ would be suppressed, the system would be weak ferromagnetic [9]. It was recognized, that the modulation can be eliminated by strain (either induced by substrate in epitaxial thin films or by doping) or by application of high magnetic field [2]. The spontaneous magnetization is known to arise in the substituted BiₓLn₁₋ₓFeO₃ (Ln= lanthanide) compounds [10-12], however, it is not quite clear how the appearance of the magnetization correlates with the substitution- induced structural changes (in other words, whether the antiferromagnetic- weak ferromagnetic transition coincides with a doping- driven structural/ferroelectric transformation).
It was recently proven that the crystal structure of Bi$_{1-x}$Ln$_x$FeO$_3$ (Ln= Sm, Nd, La) compounds undergoes a ferroelectric- to- antiferroelectric structural phase transition at $x$~ 0.14-0.18 (the concentration boundary of the phase transformation shifts towards smaller $x$ with decreasing ionic radius of substituting element) [13-18]. The antiferroelectric phase has the orthorhombic structure closely related to that characteristic of PbZrO$_3$ perovskite [19] and demonstrates a weak ferromagnetic behavior with a typical spontaneous magnetization of ~0.25 emu/g [18, 20]. To reveal a relationship between the structural chemistry and magnetic properties of BiFeO$_3$- based multiferroics it would be useful to follow evolution of the magnetization behavior near the morphotrophic phase boundary. In case of Ln= Sm, the phase boundary corresponds to the $x$= 0.14 composition [13]. In Bi$_{1-x}$La$_x$FeO$_3$ system, the same concentration is slightly smaller than the highest one for maintaining the initial noncentrosymmetric rhombohedral structure [21]. Taking into account these facts, we carried out the structural and magnetic characterization within co-substituted Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ ($0 \leq x \leq 0.14$) series. Such a substitution gives a compositional sweep allowing to estimate the evolution of the magnetic properties near the rhombohedral- to- orthorhombic phase boundary without varying a total concentration of rare- earth dopants in the host lattice.

2. Experimental

Polycrystalline samples Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ ($0 \leq x \leq 0.14$) were prepared by a conventional solid- state reaction method using the oxides Bi$_2$O$_3$, La$_2$O$_3$, Sm$_2$O$_3$, and Fe$_2$O$_3$ taken in desired cation ratio. The synthesis was carried out in air in closed alumina crucibles at 960 °C for 8 h with heating/cooling rates of 5 °C/min. Phase analysis of the samples and investigation of their crystal structure were performed by X-
Ray diffraction (XRD) technique using automated Philips PW 1050/35 diffractometer with Co Kα radiation. XRD patterns were collected over an angular range 20°≤2θ≤100° with step of 0.02° and exposition intervals of 25 sec/step. The data were analyzed by the Rietveld method using the FullProf program [22]. Magnetic measurements were performed with a superconducting quantum interference device (SQUID) magnetometer (S700X, Cryogenic Ltd).

3. Results and Discussion

Rietveld refinement of XRD spectra obtained for the Bi_{0.86}Sm_{0.14}FeO_3 compound confirmed the expected coexistence [13-15] of the orthorhombic (~63 %) and rhombohedral (~37 %) phases (Fig. 1). Previous electron diffraction characterization of the orthorhombic phase showed that it should have the Pnam structure combining a complex (a⁻a⁺c⁺)/(a⁻a⁺c⁻) octahedral tilting (in Glazer's notation [23]) with antipolar displacements of A-site cations along [110/110]C directions of the parent cubic perovskite cell [16]. However, it was also proven that this NaNbO₃-like tilting is not strong and/or sufficiently ordered to give any superlattice reflections in X-ray or neutron diffraction experiments [16, 20]. Accordingly, the space group Pbam (combines a⁻a⁺c⁰ octahedral tilting with antipolar displacements of A-site cations along [110/110]C axis— the structure is characteristic of PbZrO₃ perovskite [19]) can be used in practice [16, 20]. A minor rhombohedral phase (Fig. 1) retains the structural motif characteristic of parent BiFeO₃ [24]. With respect to ideal Pm̅3m perovskite, the ferroelectric R3c structure is obtained by antiphase a⁻a⁺a⁻ octahedral tilting and off-center ionic displacements along [111]C direction. Sketches of both Pbam and R3c structures are shown in insets of Fig. 1.
Lanthanum substitution in Bi$_{0.86}$$(La, Sm)$_{0.14}$FeO$_3$ series results in a drastic decrease of the orthorhombic phase fraction: the $x=0.12$ and $x=0.1$ compounds contain $\sim$64\% and $\sim$82\% of the rhombohedral phase, respectively. For the $x=0.08$ compound, the orthorhombic phase is almost completely suppressed: corresponding diffraction peaks are present only on a background level (accordingly, content of the phase should not exceed $\sim$5\%). In case of $0\leq x \leq 0.06$ samples, no traces of the orthorhombic phase was reliably detected (Fig. 2 (a)). The results are consistent with the previous electron diffraction and high-resolution synchrotron X-ray diffraction experiments performed for Bi$_{1-x}$Sm$_x$FeO$_3$ films and suggesting that the orthorhombic clusters can exist in the rhombohedral matrix in a broad compositional range down to $x=0.09$-0.1 [14, 15]. Average ionic radius of A-site ions in the threshold composition (and, hence, the Goldschmidt tolerance factor $t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$, where $r_A$, $r_B$ and $r_O$ are the ionic radii of A, B and O ions, respectively, determining the degree of distortion in perovskites) is very close to that estimated for the Bi$_{0.86}$La$_{0.06}$Sm$_{0.08}$FeO$_3$ compound. This fact implies a similarity of nature of the substitution-induced structural evolution in Bi$_{1-x}$Ln$_x$FeO$_3$ [13-18] and Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ systems and confirms that not only a concentration of polar-active Bi$^{3+}$ ions, but also a geometrical factor determines the doping-driven ferroelectric-to-antiferroelectric phase transformation in (Bi, Ln)FeO$_3$.

Unit cell volumes of the rhombohedral and orthorhombic lattices in Bi$_{0.86}$(La, Sm)$_{0.14}$FeO$_3$ increase with decreasing Sm concentration without any pronounced anomalies on corresponding concentrational dependencies. For the two-phase compounds, the primitive cell volume of the orthorhombic lattice is about 0.6\% smaller than that obtained for the rhombohedral one. The step-like character of the primitive cell volume change (Fig. 2 (b)) suggests that the structural transformation takes place as a first-order transition. It is worth noting that increasing the temperature or duration of
the heat treatment does not change the ratio between the rhombohedral and orthorhombic phases in Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ (0.08$\leq x \leq$0.14) samples, but leads to decomposition of the perovskite phases.

Before analyzing magnetic properties of the series under study, let us remind that parent BiFeO$_3$ demonstrates an antiferromagnet- weak ferromagnet phase transition at $H_C \approx 200$ kOe [2]. The transition is associated with a magnetic- field induced removal of the initial spatially- modulated magnetic structure. The field- induced weak ferromagnetic phase possesses a magnetization of $\sim 0.25$ emu/g [2]. The induced magnetization coincides with the spontaneous one characteristic of weak ferromagnetic state of the orthorhombic antiferroelectric Bi$_{1-x}$Ln$_x$FeO$_3$ compounds [18, 20], thus suggesting a similar origin of the weak ferromagnetism in the rhombohedral and orthorhombic phases. A-site chemical substitution reduces the threshold magnetic field $H_C$ for cancelling the magnetic cycloid in the polar rhombohedral phase [11, 21]. Taking into account these facts, the main experimental findings related to magnetic properties of the Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ compounds (Fig. 3) can be summarized as follows:

1. Rhombohedral samples, structurally- homogeneous in approximation of the integrated picture given by powder XRD, demonstrate nonzero residual magnetization ($M_r \sim 0.03-0.035$ emu/g) incompatible with a pure antiferromagnetic state.

2. Comparing the residual magnetization with the value characteristic of spontaneous or field- induced weak ferromagnetic state in BiFeO$_3$- based compounds suggests that the rhombohedral samples contain 12-14% of a weak ferromagnetic phase.

3. The rhombohedral samples demonstrate a metamagnetic behavior similar to that observed in Bi$_{1-x}$Ln$_x$FeO$_3$ compounds upon the field- induced suppression of the magnetic cycloid [11, 18, 21]. Threshold field of the phase transition decreases with
increasing Sm concentration: a clear deviation from linearity expected for antiferromagnets is observed above $H_C \approx 35$ kOe for $x = 0.02$, $H_C \approx 30$ kOe for $x = 0.04$, and $H_C \approx 25$ kOe for $x = 0.06$ (with increasing magnetic field).

4. Within concentrational range of the pure rhombohedral compounds ($0 \leq x \leq 0.06$), the percentage of the weak ferromagnetic phase weakly depends on the chemical composition (the samples have almost the same residual magnetization).

5. Residual magnetization rapidly increases with increasing orthorhombic phase content reaching a value of 0.2 emu/g for $x = 0.14$ sample containing ~ 63 % of orthorhombic phase.

Thus, compositional dependence of the residual magnetization correlates with a structural phase evolution of the Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ compounds. Rhombohedral samples possess the main antiferromagnetic state. Significant increase of the net magnetization driven by change of the average ionic radius of A-site substituting elements follows the increasing of orthorhombic phase content (see inset in Fig. 3).

Let us consider the origin of the spontaneous magnetization in orthorhombic phase of the Bi$_{0.86}$(La, Sm)$_{0.14}$FeO$_3$ compounds. First of all, it is necessary to emphasize that increasing the net magnetization taking place in the system with increasing samarium concentration is not related to magnetic contribution of the magnetically-active Sm$^{3+}$ ions. Indeed, rare-earth (RE) subsystem in REFeO$_3$ ferrites orders magnetically only below $T \sim 5$ K [25], so magnetic properties of Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ samples at room temperature must be completely determined by iron sublattice. In the Bi$_{1-x}$Ln$_x$FeO$_3$ compounds, iron has the valence state Fe$^{3+}$ and the high-spin configuration $t_{2g}^3 e_{g}^2$ [26]. The Goodenough–Kanamori rules predict an antiferromagnetic superexchange interaction Fe$^{3+}$: $t_{2g}^3 e_{g}^2 – O – Fe^{3+}$: $t_{2g}^3 e_{g}^2$ [27, 28], so ordered spins should create a G-type antiferromagnetic structure, in which each Fe$^{3+}$
ion is surrounded by six nearest neighbors with antiparallel magnetic moments. Accordingly, the only reason of appearance of the spontaneous magnetization in orthorhombic phase of Bi$_{0.86}$(La, Sm)$_{0.14}$FeO$_3$ samples is a canting of antiferromagnetic sublattices. In fact, there are two mechanisms giving rise to a canting of the antiferromagnetic alignment of spins: the single ion magnetic anisotropy and the antisymmetric spin- spin interaction of the form $D \cdot (S_1 \times S_2)$, where $D$ is the so-called Dzyaloshinsky vector (the microscopic origin of this term is attributed to the anisotropic superexchange interaction including spin- orbital coupling) [29, 30]. For compounds with a high Neel temperature the latter mechanism is known to be more important (the Dzyaloshinsky- Moriya interaction is proportional to the exchange interaction, while the anisotropy energy of single spin nature, which comes from the spin- orbit coupling under the crystalline electric field, does not depend on the superexchange mechanism) [29, 30].

In case of rhombohedral samples, existing net magnetization must be attributed to the suppression of the initial cycloid- type modulated magnetic structure. Indeed, symmetry of the space group $R3c$ permits the existence of the Dzyaloshinsky- Moriya interaction [9], however the spatial magnetic modulation results in a periodic variation of the canting angle between the magnetic sublattices, so the magnetization averaged over the cycloid period becomes zero. Accordingly, destruction of the spin cycloid is a necessary condition for the appearance of the spontaneous magnetization in the parent structural phase. Taking into account that decreasing the average ionic radius of A- site ions in the rhombohedral Bi$_{0.86}$(La, Sm)$_{0.14}$FeO$_3$ samples effectively influences the major antiferromagnetic phase to reduce the field of the induced magnetic transition, but has no appreciable effect on residual magnetization, one could suggest that geometrical factor cannot be the main one directly responsible for appearance of the spontaneous
magnetization in the rhombohedral phase. Apparently, quantity of the polar-active dopants favoring the suppression of dipole ordering is the more important factor controlling stability of the magnetic structure modulation (cycloidal modulation in bismuth ferrite is a result of magnetoelastic interaction [2]) and determining magnetic properties of the rhombohedral compounds. The assumption is consistent with behavior of the concentrical dependencies of the magnetization reported for the low-doped Bi$_{1-x}$Ln$_x$FeO$_3$ compounds, when the residual magnetization gradually increases with increasing the lanthanide content [31]. Local deviation from a homogeneous distribution of the substituting elements typical of perovskite solid solutions [32] or/and lattice defects might be the driving force of the local suppression of the initial spatial modulation in the rhombohedral phase to induce appearance of the small magnetization [18].

4. Conclusions

In conclusion, investigation of crystal structure and magnetic properties of Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ ($0 \leq x \leq 0.14$) ceramics was carried out with XRD and SQUID-magnetometry techniques. It was shown that $0 \leq x \leq 0.06$ samples retain the rhombohedral structure typical of parent BiFeO$_3$. Further increasing Sm content leads to appearance of the orthorhombic phase possessing the structure closely related to that characteristic of PbZrO$_3$ antiferroelectric. Both structural phases coexist in a broad compositional range up to $x=0.14$. Pure rhombohedral samples were found to possess a small residual magnetization, whose value very weakly depends on change of the average ionic radius of the substituting elements occupying $A$-site of the perovskite. Comparison of the magnetization with that expected for weak ferromagnetic state in BiFeO$_3$-based
compounds suggests that the major magnetic phase (~86-88%) of the rhombohedral samples remains antiferromagnetic. The compounds possessing the main rhombohedral phase demonstrate a metamagnetic behavior; the threshold field of the magnetic transformation decreases with increasing Sm concentration. Progressive increase of the net magnetization correlating with the structural evolution takes place with increasing orthorhombic phase content. Reasons explaining existence of the spontaneous magnetization in orthorhombic and rhombohedral phases of the Bi$_{0.86}$(La, Sm)$_{0.14}$FeO$_3$ compounds were discussed.

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References


Figures

1. Observed (solid circles), calculated (solid line) and difference (solid line at the bottom) XRD patterns for the Bi$_{0.86}$Sm$_{0.14}$FeO$_3$ compound at room temperature ($Pbam + R3c$ model). Bragg reflections are indicated by ticks. Insets show schematic representations of the $Pbam$ and $R3c$ structures (left and right sketches, respectively).

2. (a) Characteristic part of the XRD spectra obtained for the Bi$_{0.86}$(La, Sm)$_{0.14}$FeO$_3$ compounds at room temperature and demonstrating a composition-driven structural evolution. (b) Concentrational dependence of the primitive cell volume for the Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ system (black squares and red circles are used for rhombohedral and orthorhombic phases, respectively).

3. Field dependencies of the magnetization obtained for the Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ compounds at room temperature. Inset shows residual magnetization and structural phase composition for samples of the Bi$_{0.86}$La$_{0.14-x}$Sm$_x$FeO$_3$ series as a function of Sm content.
Figure 1
Figure 2

(a) [Graph showing X-ray diffraction peaks with labels (240), (024), (004), and (232).]

(b) [Graph showing the change in a parameter with Sm content, x.]
Figure 3