HAL
open science

Substitution-driven structural and magnetic phase transitions in Bi0.86(La, Sm)0.14FeO3 system

V A Khomchenko, L C J Pereira, J A Paixão

To cite this version:

V A Khomchenko, L C J Pereira, J A Paixão. Substitution-driven structural and magnetic phase transitions in Bi0.86(La, Sm)0.14FeO3 system. Journal of Physics D: Applied Physics, 2011, 44 (18), pp.185406. 10.1088/0022-3727/44/18/185406 . hal-00614342

HAL Id: hal-00614342

https://hal.science/hal-00614342v1

Submitted on 11 Aug 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Substitution- driven structural and magnetic phase transitions in $Bi_{0.86}(La, Sm)_{0.14}FeO_3$ 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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ ($0 \leq x \leq 0.14$) 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 ABO_3 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 $Bi_{0.86}(La, Sm)_{0.14}FeO_3$ compounds were analyzed.

PACS: 64.70.K-; 75.30.-m; 75.85.+t

*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 (ABO_3) 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, $BiFeO_3$ is the only material which is both magnetic and a strong ferroelectric (~100 μC/cm^2) 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, $BiFeO_3$ shows a long- range incommensurate cycloid- type antiferromagnetic structure with a period of ~620 Å along $[110]_h$ direction [8]. The spatial modulation prevents the observation of any net magnetization and the linear magnetoelectric effect. If the modulated magnetic structure in $BiFeO_3$ 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 $Bi_{1-x}Ln_xFeO_3$ (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 $Bi_{1-x}Ln_xFeO_3$ (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 morphotropic phase boundary. In case of Ln= Sm, the phase boundary corresponds to the x= 0.14 composition [13]. In $Bi_{1-x}La_xFeO_3$ 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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ ($0\leq x\leq 0.14$) 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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ ($0\leq x\leq 0.14$) were prepared by a conventional solid- state reaction method using the oxides Bi_2O_3, La_2O_3, Sm_2O_3, and Fe_2O_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 K_α radiation. XRD patterns were collected over an angular range $20° \leq 2\theta \leq 100°$ 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 $[110/\bar{1}\bar{1}0]_C$ directions of the parent cubic perovskite cell [16]. However, it was also proven that this $NaNbO_3$- 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 $a^-a^-c^0$ octahedral tilting with antipolar displacements of *A*- site cations along $[110/\bar{1}\bar{1}0]_C$ axis– the structure is characteristic of $PbZrO_3$ perovskite [19]) can be used in practice [16, 20]. A minor rhombohedral phase (Fig. 1) retains the structural motif characteristic of parent $BiFeO_3$ [24]. With respect to ideal $Pm\bar{3}m$ 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 contains ~64 % and ~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 ~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 $Bi_{1-x}Sm_xFeO_3$ 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 $Bi_{1-x}Ln_xFeO_3$ [13-18] and $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ 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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ ($0.08 \leq x \leq 0.14$) 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~ 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 ~0.25 emu/g [2]. The induced magnetization coincides with the spontaneous one characteristic of weak ferromagnetic state of the orthorhombic antiferroelectric $Bi_{1-x}Ln_xFeO_3$ 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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ 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~ 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 $Bi_{1-x}Ln_xFeO_3$ 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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ 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~ 5 K [25], so magnetic properties of $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ samples at room temperature must be completely determined by iron sublattice. In the $Bi_{1-x}Ln_xFeO_3$ 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 $\mathbf{D}\cdot(\mathbf{S_1}\times\mathbf{S_2})$, 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- inactive 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 magnetoelectric interaction [2]) and determining magnetic properties of the rhombohedral compounds. The assumption is consistent with behavior of the concentrational dependencies of the magnetization reported for the low-doped $Bi_{1-x}Ln_xFeO_3$ 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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ ($0 \leq x \leq 0.14$) 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.

V. A. K. is grateful to the Foundation for Science and Technology of Portugal (FCT) for financial support through the “Ciência 2008” program.

References

1. D. Lebeugle, D. Colson, A. Forget, and M. Viret, Appl. Phys. Lett. **91**, 022907 (2007).
2. A. M. Kadomtseva, Yu. F. Popov, A. P. Pyatakov, G. P. Vorob'ev, A. K. Zvezdin, and D. Viehland, Phase Transitions **79**, 1019 (2006).
3. A. Palewicz, R. Przenioslo, I. Sosnowska, and A. W. Hewat, Acta Cryst. B **63**, 537 (2007).
4. A. Palewicz, I. Sosnowska, R. Przenioslo, and A. W. Hewat, Acta Phys. Pol. A **117**, 296 (2010).
5. R. Haumont, I. A. Kornev, S. Lisenkov, L. Bellaiche, J. Kreisel, and B. Dkhil, Phys. Rev. B **78**, 134108 (2008).
6. S. M. Selbach, T. Tybell, M.-A. Einarsrud, and T. Grande, Adv. Mater. **20**, 3692 (2008).
7. D. C. Arnold, K. S. Knight, F. D. Morrison, and P. Lightfoot, Phys. Rev. Lett. **102**, 027602 (2009).
8. I. Sosnowska, T. Peterlin-Neumaier, and E. Steichele, J. Phys. C **15**, 4835 (1982).
9. C. Ederer and N. A. Spaldin, Phys. Rev. B **71**, 060401 (2005).
10. V. A. Khomchenko, V. V. Shvartsman, P. Borisov, W. Kleemann, D. A. Kiselev, I. K. Bdikin, J. M. Vieira, and A. L. Kholkin, Acta Mater. **57**, 5137 (2009).
11. I. O. Troyanchuk, M. V. Bushinsky, D. V. Karpinsky, O. S. Mantytskaya, V. V. Fedotova, and O. I. Prochnenko, Phys. Status Solidi B **246**, 1901 (2009).
12. V. A. Khomchenko, D. V. Karpinsky, A. L. Kholkin, N. A. Sobolev, G. N. Kakazei, J. P. Araujo, I. O. Troyanchuk, B. F. O. Costa, and J. A. Paixão, J. Appl. Phys. **108**, 074109 (2010).

13. S. Fujino, M. Murakami, V. Anbusathaiah, S.-H. Lim, V. Nagarajan, C. J. Fennie, M. Wuttig, L. Salamanca-Riba, and I. Takeuchi, Appl. Phys. Lett. **92**, 202904 (2008).

14. C.-J. Cheng, D. Kan, S.-H. Lim, W. R. McKenzie, P. R. Munroe, L. G. Salamanca-Riba, R. L. Withers, I. Takeuchi, and V. Nagarajan, Phys. Rev. B **80**, 014109 (2009).

15. S. B. Emery, C.-J. Cheng, D. Kan, F. J. Rueckert, S. P. Alpay, V. Nagarajan, I. Takeuchi, and B. O. Wells, Appl. Phys. Lett. **97**, 152902 (2010).

16. S. Karimi, I. M. Reaney, I. Levin, and I. Sterianou, Appl. Phys. Lett. **94**, 112903 (2009).

17. S. Karimi, I. M. Reaney, Y. Han, J. Pokorny, and I. Sterianou, J. Mater. Sci. **44**, 5102 (2009).

18. I. O. Troyanchuk, D. V. Karpinsky, M. V. Bushinsky, V. A. Khomchenko, G. N. Kakazei, J. P. Araujo, M. Tovar, V. Sikolenko, V. Efimov, and A. L. Kholkin, Phys. Rev. B **83**, 054109 (2011).

19. A. M. Glazer, K. Roleder, and J. Dec, Acta Cryst. B **49**, 846 (1993).

20. I. Levin, S. Karimi, V. Provenzano, C. L. Dennis, H. Wu, T. P. Comyn, T. J. Stevenson, R. I. Smith, and I. M. Reaney, Phys. Rev. B **81**, 020103 (2010).

21. G. Le Bras, D. Colson, A. Forget, N. Genand-Riondet, R. Tourbot, and P. Bonville, Phys. Rev. B **80**, 134417 (2009).

22. J. Rodríguez-Carvajal, Physica B **192**, 55 (1993).

23. A. M. Glazer, Acta Cryst. A **31**, 756 (1975).

24. F. Kubel and H. Schmid, Acta Cryst. B **46**, 698 (1990).

25. R. L. White, J. Appl. Phys. **40**, 1061 (1968).

26. D. Kothari, V. R. Reddy, A. Gupta, C. Meneghini, and G. Aquilanti, J. Phys.: Condens. Matter **22**, 356001 (2010).

27. J. B. Goodenough, Phys. Rev. **100**, 564 (1955).

28. J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959).

29. I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958).

30. T. Moriya, Phys. Rev. **120**, 91 (1960).

31. G. L. Yuan, S. W. Or, and H. L. W. Chan, J. Phys. D: Appl. Phys. **40**, 1196 (2007).

32. T. Shibata, B. Bunker, J. F. Mitchel, and P. Schiffer, Phys. Rev. Lett. **88**, 207205 (2002).

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 $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ system (black squares and red circles are used for rhombohedral and orthorhombic phases, respectively).
3. Field dependencies of the magnetization obtained for the $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ compounds at room temperature. Inset shows residual magnetization and structural phase composition for samples of the $Bi_{0.86}La_{0.14-x}Sm_xFeO_3$ series as a function of Sm content.

Figure 1

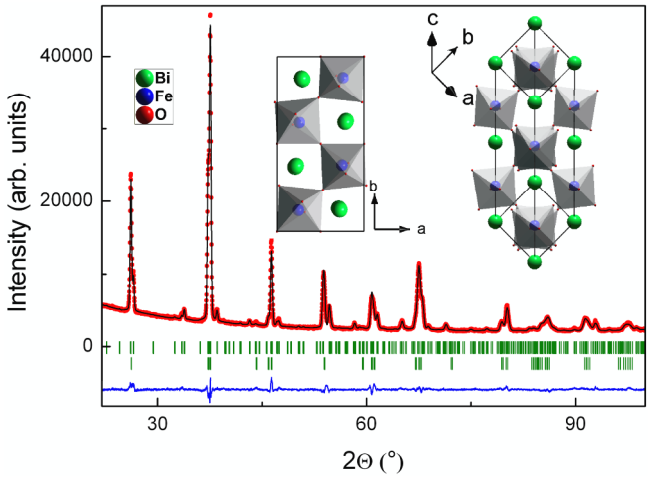


Figure 2

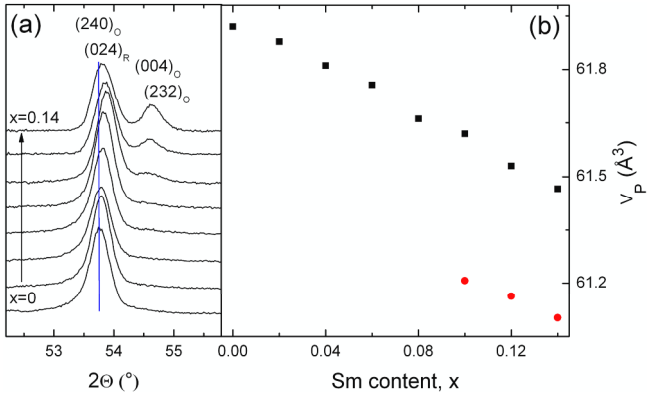
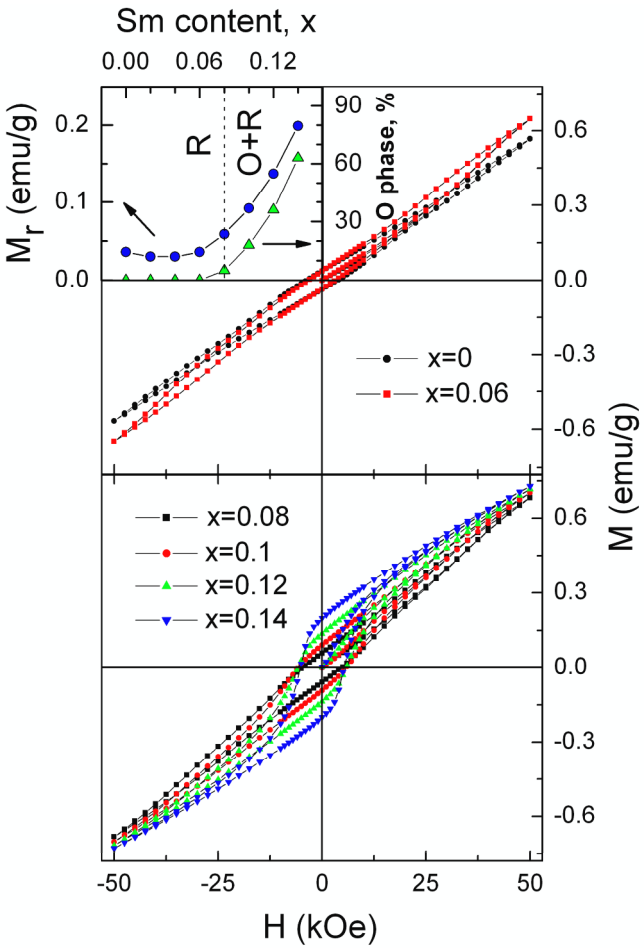

(a)
(240)O
(024)R
(004)O
(232)O
x=0.14
x=0
53
54
55
2Θ (°)
(b)
0.00
0.04
0.08
0.12
Sm content, x
61.8
61.5
61.2
vP (Å3)

Figure 3


Sm content, x
0.00
0.06
0.12
M_r (emu/g)
0.2
0.1
0.0
R
O+R
90
60
30
O phase, %
0.6
0.3
0.0
-0.3
-0.6
x=0
x=0.06
x=0.08
x=0.1
x=0.12
x=0.14
M (emu/g)
-50
-25
0
25
50
H (kOe)