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RESEARCH ARTICLE

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Crystal structure and magnetic properties of $Bi_{1-x}Sm_xFeO_3$ ceramics across the phase boundary: effect of high pressure

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ABSTRACT

The solid solutions $Bi_{1-x}Sm_xFeO_3$ with chemical composition across the morphotropic phase boundary region specific for rhombohedral - orthorhombic structural transition were investigated by X-ray diffraction, electron microscopy and magnetometry. Structural measurements showed a concentration driven transition from the single phase rhombohedral structure to the single phase nonpolar orthorhombic structure through the formation of antipolar orthorhombic phase which coexists with the rhombohedral phase in the compounds with $x < 0.15$ followed by a coexistence with nonpolar orthorhombic phase in the compounds with $x <= 0.18$. Application external pressure provides a stabilization of the orthorhombic phase, viz. the polar rhombohedral phase diminishes and transforms to the anti-polar orthorhombic phase, while the anti-polar orthorhombic phase transforms to the non-polar orthorhombic phase. Magnetic properties of the compounds subjected to external pressure demonstrate an increase in the magnetization of the compounds having dominant rhombohedral phase, wherein coercivity significantly increases, while the spontaneous magnetization remains nearly constant.

1. INTRODUCTION

Recently, the scientific community has seen widespread research focused on bismuth ferrite based materials [1,2,3]. Multiferroics based on $BiFeO_3$ are widely studied due to the great variability of chemical substitution methods that allow controlling chemical and physical properties in a wide range [4, 5]. Compounds with chemical composition near the structural phase transitions are of particular interest as such materials can be extremely sensitive to external influences as pressure, magnetic field, etc. while chemical composition can be easily adjusted by chemical doping [6]. Multiferroics based on $BiFeO_3$ showing single phase or coexistent antipolar orthorhombic phase are of the specific interest due to their reduced structural stability in the phase boundary region controlled by chemical doping with rare earth elements [7].

Chemical substitution of bismuth ions by samarium ions leads to the formation of a single-phase antipolar orthorhombic phase in a narrow concentration range, up to 1% in the $Bi_{1-x}Sm_xFeO_3$ ceramics prepared by solid state reaction method [8], which attracts special attention, since the concentration range described for the structural stability of the antipolar orthorhombic phase becomes extremely dependent on the conditions of preparation and processing of samples after synthesis [7, 9]. When using rare earth elements with an ionic radius smaller than that characteristic for samarium, a direct structural transition occurs from the rhombohedral to the nonpolar orthorhombic phase [10, 11].

This study shows a relationship between the type of structural distortions, the morphology of crystallites, and the appearance of remanent magnetization for Sm-doped $BiFeO_3$ compounds obtained by the sol-gel method as prepared and subjected to high pressure (5GPa). The results obtained show the difference in concentration-controlled phase transition observed for sol-gel powders having nanoscale crystallites, compared to the compounds having the same chemical composition after application of high pressure.

2. EXPERIMENTAL

Samples of $Bi_{1-x}Sm_xFeO_3$ compounds (x = 0.08, 0.12, 0.16, 0.18, 0.20) were obtained by the sol-gel method from components $Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, Sm_2O_3, and ethylene glycol. Initially, Sm_2O_3 was dissolved in 50 ml of H_2O, in which 2 ml of concentrated HNO_3 were previously dissolved. The solution was heated to 80 ° C, the remaining compounds were added with constant stirring, after their dissolution, the solution was stirred for another 1 hour. After that, $C_2H_6O_2$ was added in a 2: 1 ratio to metal ions, after which it was stirred for another 1 hour. The resulting solution was evaporated at 200 °C. The resulting gel was dried for 12 hours at a temperature of 150 °C. The resulting xerogel was ground in an agate mortar and then heated in an oven for 1.5 hours at a temperature of 800 °C. Part of the compound $Bi_{1-x}Sm_xFeO_3$ was left as a powder, other part was pressed into tablets at high pressure (HP) of 5 GPa. X-ray diffraction patterns were recorded in the 2 thetta range of 20 - 60º with a step of 0.02º using Bruker D8 Advance diffractometer with

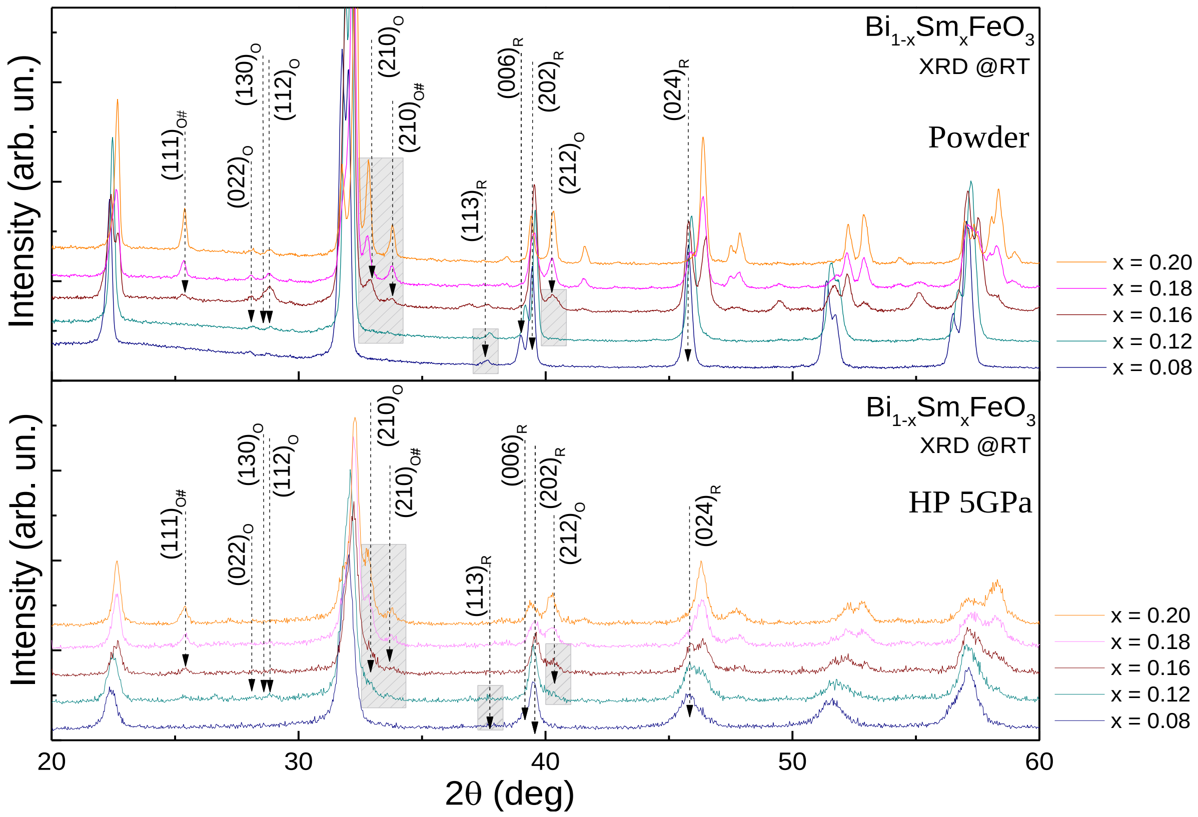

Figure 1. Room-temperature XRD patterns obtained for the compounds $Bi_{1-x}Sm_xFeO_3$ (x = 0.08, 0.12, 0.16, 0.18 and 0.20) as prepared (upper image) and after application of high pressure.

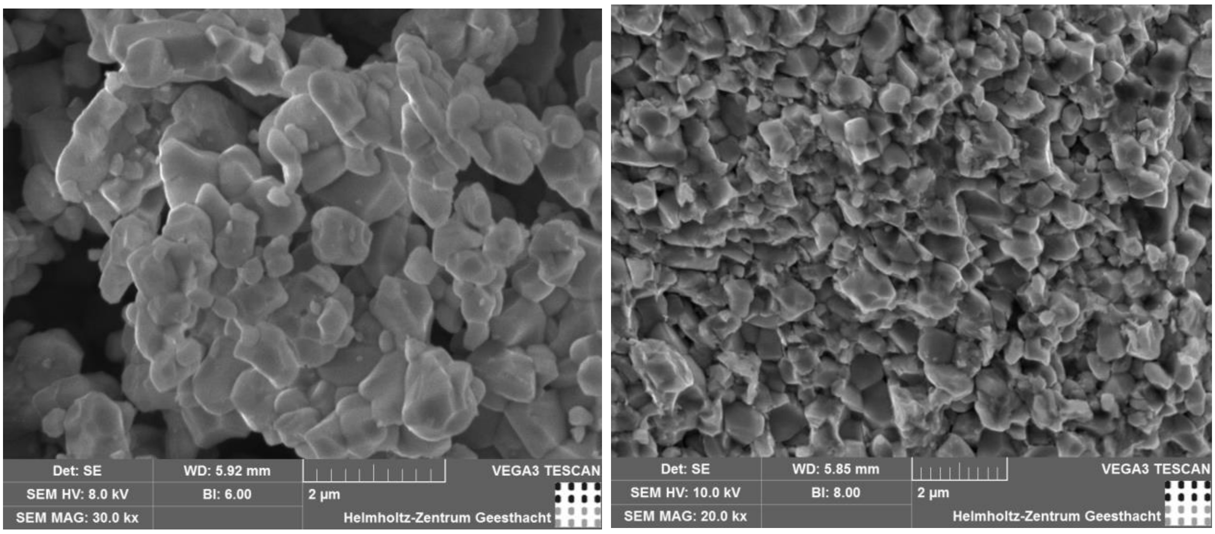

Figure 2. SEM images of the $Bi_{0.92}Sm_{0.08}FeO_3$ before (left) and after application of high pressure of ~5 GPa.

Cu-Kα radiation. Magnetic measurements were performed at T = 300 K and magnetic fields up to ±14 T using Physical Properties Measurement Systems from Cryogenic Ltd.

3. RESULTS AND DISCUSSION

The XRD data obtained for powder samples of the $Bi_{1-x}Sm_xFeO_3$ system (x = 0.08, 0.12, 0.16, 0.18, 0.20) showed that that at low concentration of Sm ions (x < 0.12) the compounds have a single-phase crystal structure with rhombohedral distortion of the unit cell similar to initial compound $BiFeO_3$ (Fig. 1).

The subsequent increase in the concentration of Sm ions (x = 0.12) results in the structural transition into the two-phase state characterized by a coexistence of orthorhombic and rhombohedral phases wherein there is a dominance of the rhombohedral phase with a small contribution of the antipolar orthorhombic phase. The XRD of the

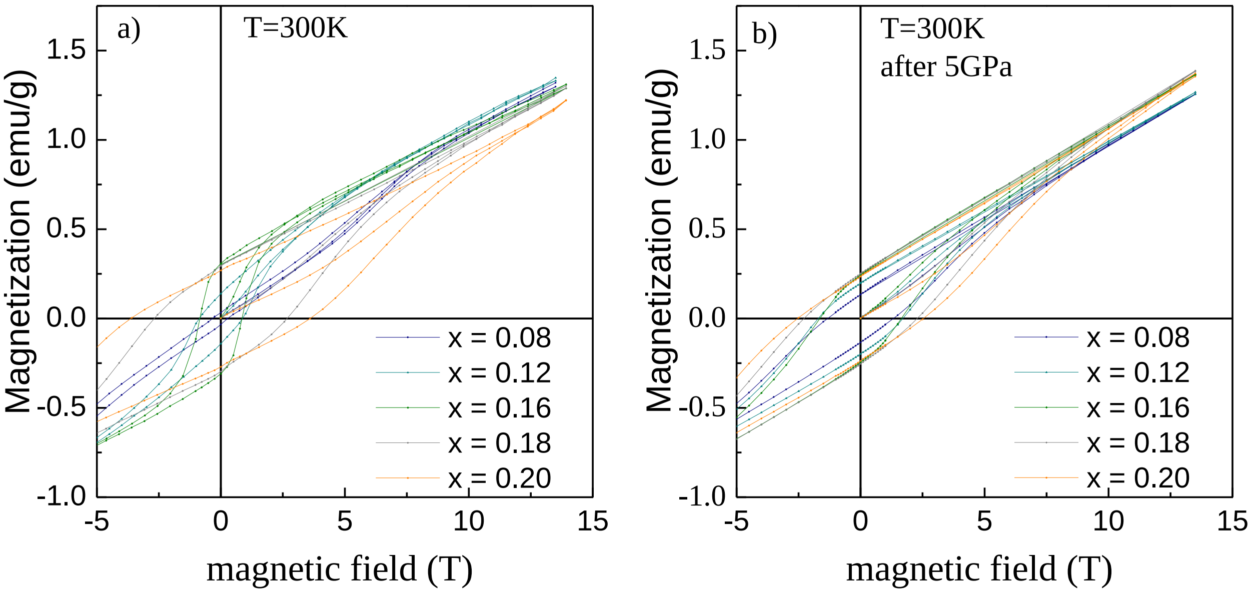

Figure 3. Magnetic field dependencies obtained for the compounds $Bi_{1-x}Sm_xFeO_3$ at temperature 300 K. a) as prepared compounds, b) compounds subjected to high pressure (~5 GPa).

compound with Sm content x = 0.16 also shows the two-phase structural state – a coexistence of the antipolar orthorhombic and the nonpolar orthorhombic phases with nearly equal phases content. The compound with Sm concentration x = 0.18 shows a two-phase crystal structure with a predominance of the non-polar orthorhombic distortions of the unit cell (Fig. 1).

The data obtained for the same compounds $Bi_{1-x}Sm_xFeO_3$ (x = 0.08, 0.12, 0.16, 0.18, 0.20) after application of a high pressure of 5 GPa showed the modification in the structural state of the compounds and crystallite morphology as confirmed by SEM measurements (Fig. 2). In the compound $Bi_{1-x}Sm_xFeO_3$ with x = 0.12, the amount of the antipolar orthorhombic phase is notably increased which is attested by the appearance of specific XRD reflections as $(210)_O$, $(212)_O$ and a decrease in the intensity of the $(113)_R$ peak. For compounds x = 0.16, 0.18, 0.20 a change in the phase ratio is also notable, which shows the diffusion of the reflections $(210)_O$, $(210)_{O\#}$ and $(212)_O$.

The study of the magnetization made it possible to determine the differences in the evolution of the magnetic properties of the $Bi_{1-x}Sm_xFeO_3$ compounds depending on the different concentration of the dopant ions and thus various structural states in the phase boundary region obtained in the form of a powder and after application of high pressure. In the compound $Bi_{0.92}Sm_{0.08}FeO_3$, the presence of the doping ions causes a reduction of the modulated magnetic structure characteristic of the $BiFeO_3$ compound; this modification occurs in magnetic field of 5T. The compound $Bi_{0.88}Sm_{0.12}FeO_3$ is characterized by a remanent magnetization of about = 0.15 emu/g. The compound with x = 0.16 has the antipolar structure and spontaneous magnetization of about 0.34 emu/g. In the compounds with x ≥ 0.18, the magnetic structure is stabilized, the coercive force of the compounds increases notably, which is associated with a sharp decrease in the grain size and associated increase in magnetic anisotropy of the compounds (Fig. 3a). In spite of drastic modification of the structural state of the compounds from the rhombohedral phase to the nonpolar orthorhombic phase the evolution of the magnetic structure occurs monotonically.

For compounds $Bi_{1-x}Sm_xFeO_3$ (x = 0.08, 0,12, 0.16, 0.18, 0.20) subjected to high pressure, the coercivity corresponds to the powdered compounds with x~0.18. This effect is associated with a decrease in the average crystallite size of the compounds (Fig. 2) which leads to increase in the magnetic anisotropy associated with orthorhombic structural phase observed in heavily doped compounds (Fig. 3b).

4. CONCLUSION

Based on the obtained results we conclude that in the powder compounds $Bi_{1-x}Sm_xFeO_3$ a release of the remanent magnetization is associated with a type of structural distortion, viz. the rhombohedral phase is characterized by nearly zero remanent magnetization while the orthorhombic phase with non-collinear orientation of the magnetic moments leading to non-zero remanent magnetization. An application external high pressure leads to a decrease in the average grain size of the compounds and thus to a release of remanent magnetization. A release of remanence is associated with uncompensated average magnetic moments ascribed to non-collinear orientation of the magnetic moments in the orthorhombic phases as well as an appearance of non-zero magentization due to reduced grain size lower than a modulation period of the spatially modulated spin structure ascribed to initial $BiFeO_3$.

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