

Evolution of magnetization of $\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ ceramics at the morphotropic phase boundary attested by multistep magnetization measurements, time aging and electric field

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Abstract

$\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ ceramics with compositions at the rhombohedral- orthorhombic morphotropic phase boundary ($y = 0.1, 0.12, 0 \leq x \leq 0.1$) were prepared by solid state reaction method. Analysis of the crystal structure of the compounds based on the results of laboratory and synchrotron X-ray diffraction measurements as well as Raman spectroscopy experiments revealed a coexistence of the rhombohedral phase (SG $R3c$) and the anti-polar orthorhombic phase (SG $Pbam$) in the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with $0 \leq x \leq 0.1$; the compounds $\text{Bi}_{0.9}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ are characterized by the mixed structural state for the concentration range $0 \leq x \leq 0.06$ and by the single phase rhombohedral state within $0.06 < x \leq 0.1$. Room temperature magnetization measurements demonstrate a gradual increase of remanent magnetization with Ti content in the compounds of both systems up to the maximal value of $M_R \sim 0.28$ emu/g for compounds with $x = 0.06$ which is followed by a decrease in magnetization with further titanium doping. Temperature decrease leads to a reduction of remanent

magnetization which is mainly caused by a partial recovery of spatially modulated spin structure occurred in the compounds of both systems. Time aging of the compounds for about ~ 1 year leads to a drastic increase of M_R , which is caused by a change in the structural phase ratio, homogeneity of the structural state and a contribution of unbounded spins demonstrated by low field measurements. Subjecting of the annealed compounds to external electric field of $E \sim 40\text{kV/cm}$ leads to a decrease of magnetization associated with backward structural transformations and redistribution of the local structural defects in the compounds.

1. Introduction

A number of the phase transitions occurred in ferrites and in particular multiferroic BiFeO_3 -based compounds under external stimuli and via chemical doping attract particular attention of researchers over the last decades [1-6]. It is known that chemical substitution of the Bi and/or Fe ions in BiFeO_3 can significantly change the structural state of the compounds as well as to control their physico-chemical parameters and properties [7-9]. Thus, BiFeO_3 -based compounds are characterized by a complex interplay between the crystal structure, electrical and magnetic subsystems which results in a rich phase diagrams [10-13]. A significant improvement in the physico-chemical parameters of BiFeO_3 -based solid solutions based on near structural phase transitions was theoretically predicted and experimentally confirmed [2, 4, 14-17], whereas a formation of the compounds with chemical compositions close to the morphotropic phases notably complicates the phase diagrams adding the new degree of freedom. The most plausible model to explain an improvement of the piezoelectric and dielectric properties of the compounds assumes a contribution of the components associated with domain wall movements and a formation of the multiphase structural state phenomena [18-20]. Increase of magnetization in the compounds near the morphotropic phase boundaries (MPB) is mainly associated with a stabilization of weak ferromagnetic state with non-collinear orientation of the spin magnetic moments [21-23].

Chemical substitution of Bi ions by rare-earth elements (RE) leads to structural transformation from the polar rhombohedral (*R*) phase to the anti-polar orthorhombic (*O*) phase in the case of $\text{RE} = \text{La} - \text{Sm}$ and to the non-polar orthorhombic phase if $\text{RE} = \text{Gd}, \text{Tb}, \text{Dy}$ [12, 24]. It should be noted that $\text{Bi}_{1-y}\text{Sm}_y\text{FeO}_3$ system attracts particular attention due to a very narrow concentration range ascribed to the single phase anti-polar orthorhombic among others

RE doped BFO systems. Low structural stability of the Sm doped compounds near the *R-O* morphotropic phase boundary opens up new possibilities for practical applications of the BiFeO₃-based multiferroic materials [25, 26]. In contrast to RE doping scheme a co-doping in A- and B- perovskite positions can stabilize the initial rhombohedral phase [27] or even more symmetrical tetragonal and cubic phases [28-30] and thus can be used as an effective tool to control structural state and functional properties of the compounds [31-33].

In the compounds having mixed structural state each structural phase can be associated with specific magnetic phase while in the BiFeO₃-based compounds the magnetic phases remain antiferromagnetic ordering regardless the symmetry of the respective structural phases. The differences in the magnetic phases are mainly caused by small alterations in the geometry of the chemical bond lengths Fe – O and respective angles Fe – O – Fe which leads to a remnant magnetization value about $\sim 0.1 - 0.5$ emu/g in the case of a disruption of the spatially modulated spin structure [34, 35]. Nonlinear evolution of the remnant magnetization observed in the compounds across the morphotropic phase boundary can be explained by additional components of magnetization associated with the unbounded spins located in the phase boundary regions thus the maximal value of remnant magnetization is observed in the compounds with equal volume fractions of the coexistent structural phases [22, 36, 37].

Recent studies of the doped Bi_{1-y}Sm_yFeO₃ system have clarified that remnant magnetization reaches its maximal value in the compounds having nearly single phase rhombohedral structural state. Whereas an evolution of the structural state of compounds Bi_{1-y}Sm_yFe_{1-x}Ti_xO₃ changes in non-trivial way with the dopants increase. The compounds Bi_{1-y}Sm_yFeO₃ with $y \sim 0.12$ are characterized by a coexistence of the dominant polar rhombohedral phase and a minor amount of the anti-polar orthorhombic phase, while a complementary doping with Ti leads to stabilization of the parent *R*-phase in spite of the smaller ionic radii of the Ti ions as compared to those of the Fe ions [38]. In the present paper we have focused our studies on the evolution of the crystal structure and magnetic properties of Bi_{1-y}Sm_yFe_{1-x}Ti_xO₃ ceramics ($y = 0.1, 0.12; 0 \leq x \leq 0.1$) which are characterized by a dominance of the rhombohedral phase with a minor amount of the anti-polar orthorhombic phase which disappears with Ti doping. Moreover a time aging (~ 1 year) of the compounds leads to a drastic increase of M_R , which cannot be explained just by a concomitant change in the structural phase ratio while subjecting of the compounds to external electric field causes a decrease of

magnetization to nearly initial values of the remanent magnetization. The origin of non-trivial evolution of the magnetization and structural state of the compounds occurred under external stimuli as well as via chemical doping are discussed in the paper.

2. Experimental

The ceramic compounds of $\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with $y = 0.1, 0.12$; $0 \leq x \leq 0.1$ were prepared by a conventional solid-state reaction using high-purity oxides Bi_2O_3 , Sm_2O_3 , Fe_2O_3 , TiO_2 ($\geq 99.0\%$, Alfa Aesar). The mixed oxides were thoroughly mixed using a planetary ball mill RETSCH PM-200 in alcohol medium for $\sim 3\text{h}$. The obtained slurry was dried ($T \sim 120^\circ\text{C}$) and then pressed into pellets and annealed in air at $T \sim 900^\circ\text{C}$ for $\sim 20\text{h}$. After annealing the samples were reground, pressed into pellets (10 mm in diameter, 1 mm - thickness) and sintered in air at $\sim 960^\circ\text{C}$ for 12 h. The crystal structure of the compounds were analyzed using X-ray diffraction data obtained with a PanAlytical X'pert Pro diffractometer and Bruker D2 Phaser with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) as well as synchrotron powder diffraction (SPD) data obtained at the BL02B2 beamline (SPring-8, $\lambda = 0.42019 \text{ \AA}$). The diffraction data were analyzed by the Rietveld method using FullProf software [39]. Raman scattering (RS) spectra were recorded using an XploRa-Plus micro-Raman spectrometer (excitation wavelength $\lambda = 532 \text{ nm}$). Scanning electron microscopy images were obtained using Hitachi S - 4800 setup; ImageJ software was used to analyze the SEM images. Magnetization measurements were performed on a Physical Properties Measurement System (Cryogenic Ltd.) in magnetic fields up to 14 Tesla in the temperature range 5 – 300 K.

3. Results and discussion

X-ray diffraction measurements

It is known that chemical substitution of Bi ions by Sm ions leads to structural transformation from the rhombohedral phase specific for initial BiFeO_3 to the anti-polar orthorhombic phase and then to the non-polar orthorhombic phase [40, 41]. The mentioned phases having different structural symmetries can be easily distinguished by analyzing the XRD patterns, the notable difference in the metrics specific for the anti-polar orthorhombic (s.g. $Pbam$, $\sqrt{2}a_p \times 2\sqrt{2}a_p \times 2a_p$, a_p is a parameter of pseudocubic unit cell) and the non-polar orthorhombic phases (s.g. $Pnma$, $\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$) also can be definitely determined as declared in the works [42, 43].

The concentration range specific for single phase anti-polar orthorhombic state in $\text{Bi}_{1-y}\text{Sm}_y\text{FeO}_3$ is declared for $0.12 < y < 0.14$ [41] and it is the most narrow range among others RE doped BFO systems [12]. The rhombohedral and the anti-polar orthorhombic phases are coexistent in the concentration range $0.10 < y \leq 0.12$. A complementary chemical substitution of Fe ions by Ti ions in the mentioned compounds leads to a stabilization of the rhombohedral phase. **Figure 1** shows the refined diffraction pattern of the solid solution $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ recorded using synchrotron radiation. The XRD patterns of the compounds $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ and $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with $0 \leq x \leq 0.10$ are presented in the **Figure S1**. The XRD data confirm high phase purity of the compounds, the compounds $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ are considered to be single phasic with rhombohedral structure (space group $R3c$) in the studied concentration range of $0 \leq x \leq 0.10$, whereas the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ possess a mixed structural state with a dominance of the rhombohedral phase and a minor amount of the antipolar orthorhombic phase (space group $Pbam$). The volume fraction of the orthorhombic phase gradually decreases from $\sim 50\%$ in the compound $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ down to $\sim 10\%$ in the compound $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{0.94}\text{Ti}_{0.06}\text{O}_3$, in the compounds with larger Ti content the orthorhombic phase becomes undetectable by the conventional X-ray diffraction measurements as well as the synchrotron diffraction experiments.

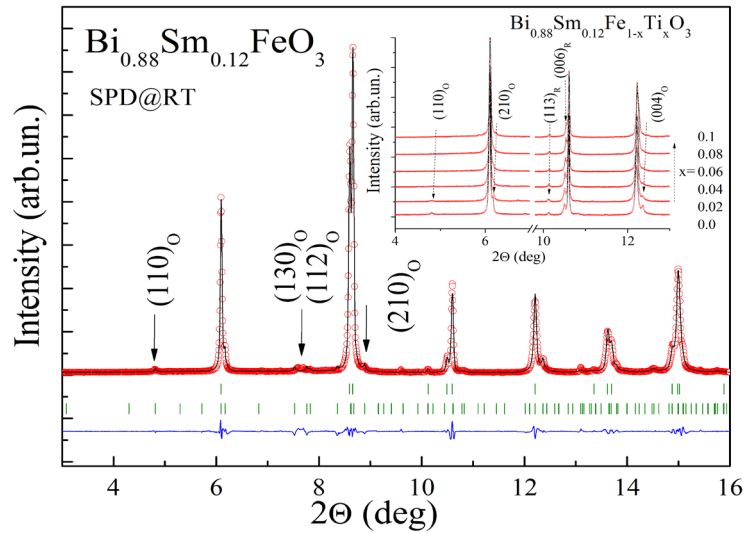


Figure 1. Synchrotron (SPring-8) diffraction pattern of compound $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ refined using the two-phase model (upper ticks row denotes $R3c$ (R) phase, second row ticks - $Pbam$ (O) phase). The inset shows the concentration-driven changes of the reflections specific for the rhombohedral and the antipolar orthorhombic phases of the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$.

It should be noted that Ti doping causes a reduction of the unit cell parameters, thus the unit cell volume estimated for the rhombohedral phase decreases from $V_R = 61.67 \text{ \AA}^3$ in the compound $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ down to $V_R = 61.15 \text{ \AA}^3$ in the compound $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ (Figure 2). The chemical doping with Ti ions also leads to a gradual decrease in the magnitude of the rhombohedral distortion as confirmed by a decrease in the c/a ratio. The unit cell volume calculated for the anti-polar orthorhombic phase also reduces with the Ti content, while these changes are not so prominent as compared to the alterations observed for the rhombohedral phase (Figure 2). The unit cell parameters calculated for the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ indicate notably smaller shrinkage of the lattice, viz. from $V_R = 61.24 \text{ \AA}^3$ in the compound $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ down to the $V_R = 61.17 \text{ \AA}^3$ in the compound $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$.

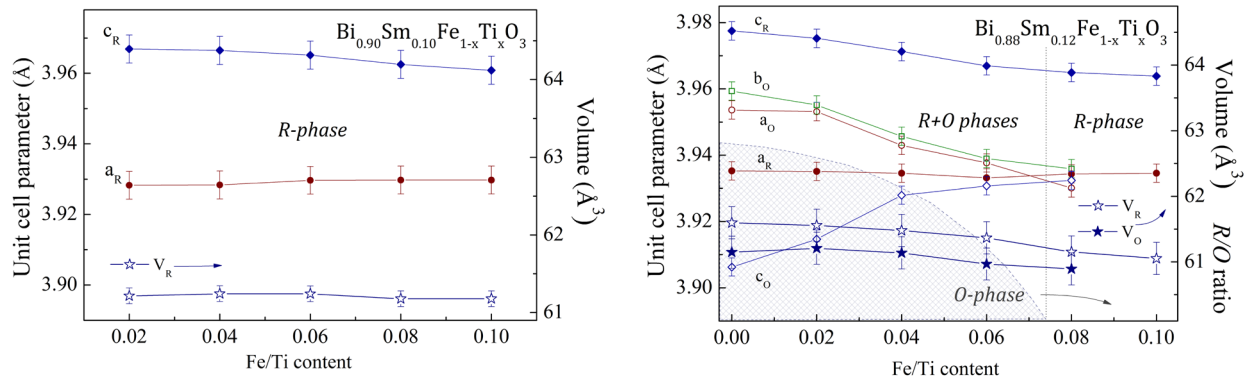


Figure 2. The unit cell parameters calculated for the *R*- and *O*- phases of compounds $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ and $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ for different Ti content; the estimated volume ratio of the *R/O* phases calculated for compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ is denoted by the dashed area.

The structural changes occurred in the compounds $\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ under chemical doping with Ti ions denote a stabilization of the rhombohedral phase albeit it is not conventional scenario of the phase evolution of the BiFeO_3 -based compounds [37, 44]. In BiFeO_3 -based systems a chemical substitution of Fe ions by the ions with smaller ionic radii usually leads to shrinkage of the unit cell and a stabilization of the phases having lower symmetry. In the case of $\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ compounds the chemical doping leads to a monotonous decrease of the unit cell parameters while the symmetry changes in a particular way. Moreover in the case of the system $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ the diffraction patterns of the compounds with $x \geq 0.08$ denote a

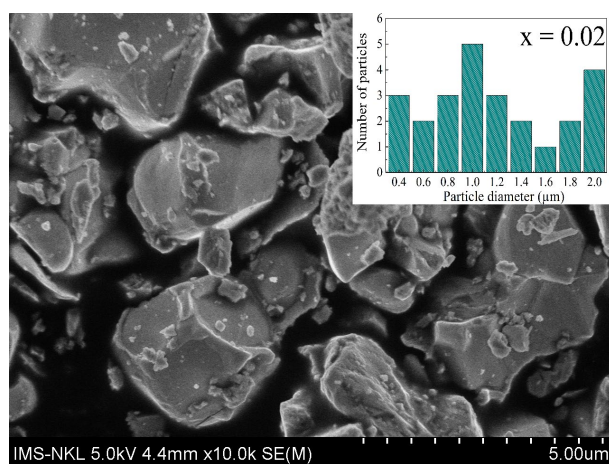
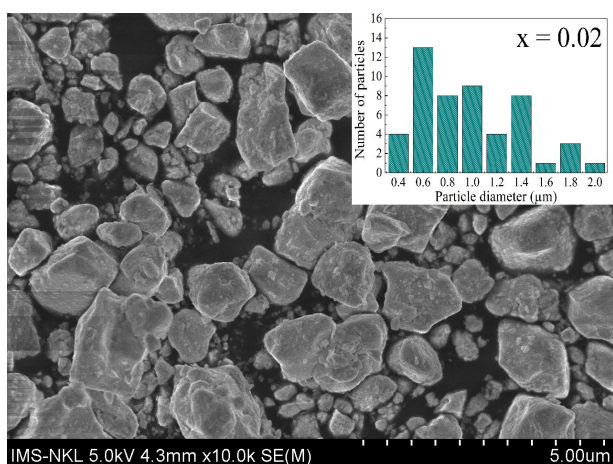
broadening ($x = 0.08$) and further splitting ($x = 0.1$) of the reflection located at $2\theta \sim 12.2^\circ$ and indexed as $(024)_R$ and $(240)_O$. It should be noted that the R - and O - phases do not assume a splitting of the mentioned reflection while it is split in the case of tetragonal symmetry [45] and this phenomenon is planned for further investigations. The available diffraction data do not allow a precise clarification of the structural state of the compounds, while it is evident that the compounds possess complex structure with coexistent long-range phases and local inhomogeneities associated with cation vacancies formed to compensate a residing of Ti^{4+} ions in the lattices; the mentioned factors can significantly affect the structural stability and functional properties of the solid solutions.

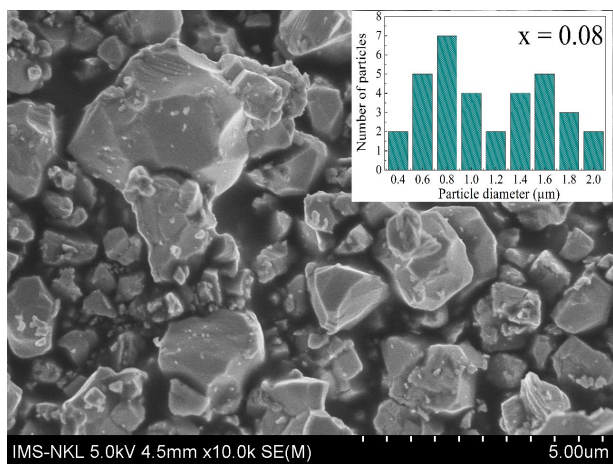
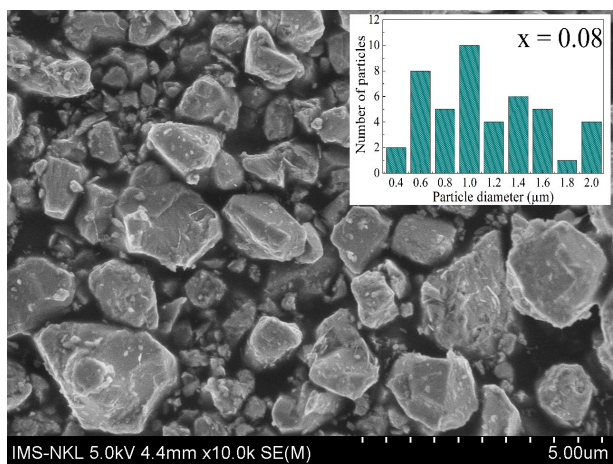
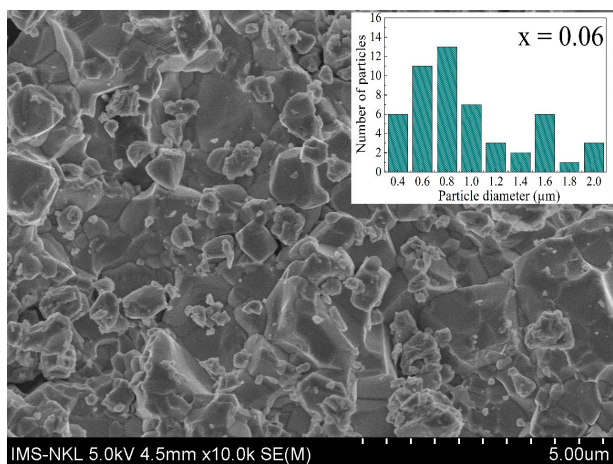
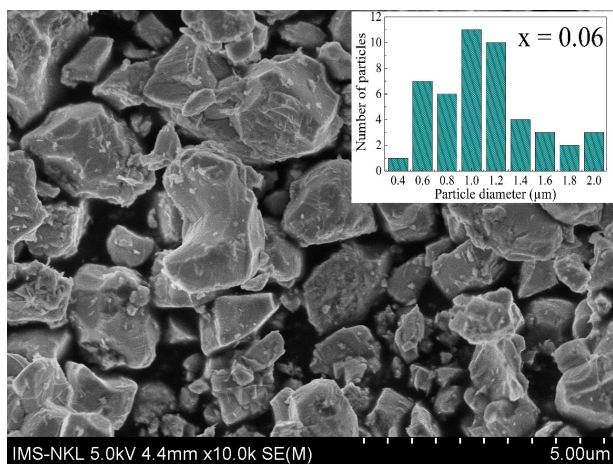
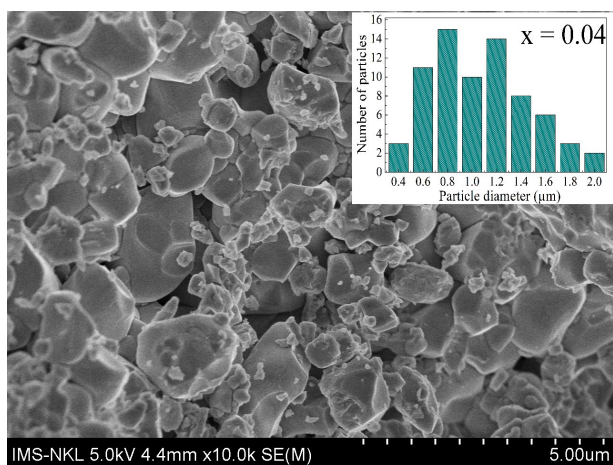
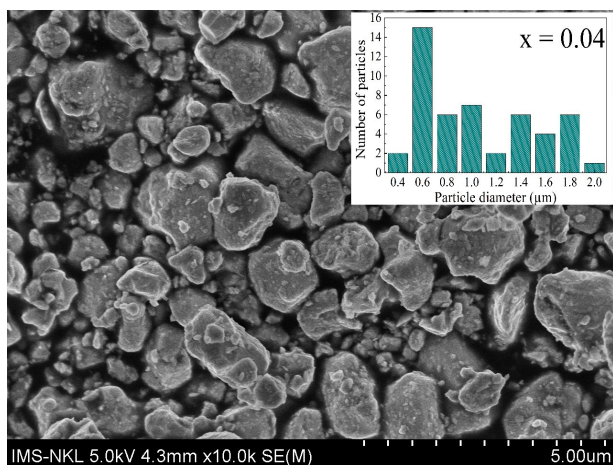
SEM measurements

It is known that particle sizes, their morphology, and porosity of ceramic compounds can significantly affect their structural state and properties, for the compounds with chemical compositions near the morphotropic phase boundaries this correlation becomes greatly pronounced [41, 46]. Synthesis conditions can define dielectric and piezoelectric properties of the compounds via modification of crystallinity of the compounds and their porosity, modification of the grain size can notably change magnetic properties of the compounds via formation of phase boundary spins or a disruption on long range magnetic structure and a formation of uncompensated resulting magnetic moment [22, 37]. A modification of the grains size and the morphology of the compounds $\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ was estimated based on the SEM data. As the compounds of both systems were prepared using similar synthesis conditions, the chemical composition is the only factor which affects morphology of the ceramics.

The compounds $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ are characterized by a distribution of the grains size in the range $\sim 0.4 - 2 \mu\text{m}$, quite narrow ($\sim 1.5 \mu\text{m}$) distribution range denotes high chemical homogeneity of the compounds (Figure 3). The average value of the grains size of $\sim 0.6 - 0.7 \mu\text{m}$ gradually changes with Ti concentration (Figure 3, insets). The grains have mainly rounded shape which is specific for the ceramic compounds with rhombohedral symmetry [47]. The compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ are characterized by a bit different morphology, viz. a distribution of the grains size is in the range $\sim 0.4 - 3.0 \mu\text{m}$, the average grain size is $\sim 0.8 - 1.2 \mu\text{m}$ and this value gradually reduces with Ti content. The grains in the $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ have

more rectangular shape with quite sharp edges which is more specific for the compounds with orthorhombic structure [37]. Analysis of the grains shape testifies their diffuse character which does not allow ascribing some specific grains to either rhombohedral or orthorhombic phase. Nearly micron size of the grains observed for the compounds of both systems is characteristic for ceramics prepared by solid-state reaction method. The grains size assumes presence of a number of crystallites of the coexisting structural phases which was experimentally confirmed for the $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ compounds by the diffraction data. Growth and formation during the synthesis process the grains consisting of the crystallites of different structural phases point at high chemical homogeneity of the solid solutions, the distribution of the ions specific for two coexisting phases of $\sim 1\%$ is close to the accuracy of the EDS method, used to attest the chemical compositions of the compounds. It should also be noted that EDS data confirm close to stoichiometric values of oxygen content along with small (1-2%) deficit in the Bi and Fe ions occupation which can balance an electroneutrality of the compounds and thus compensate a formation of Ti^{4+} ions. The larger average size of the grains of $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ system and the wider grain size distribution range are caused by a higher chemical reactivity of Sm ions as compared to that of Bi ions as well as easier diffusion of the ions in the compounds with mixed structural state. Analysis of the SEM images performed for the compounds of both solid solutions systems indicates quite slight differences in the average gains size, distribution and shape thus denoting negligible effect of the grains morphology on the magnetic properties of the compounds.





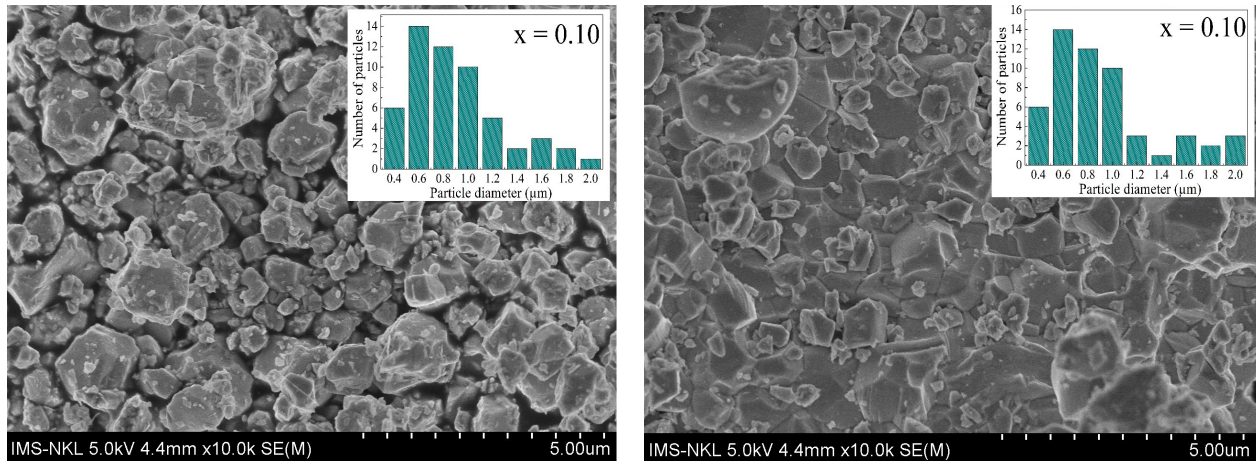
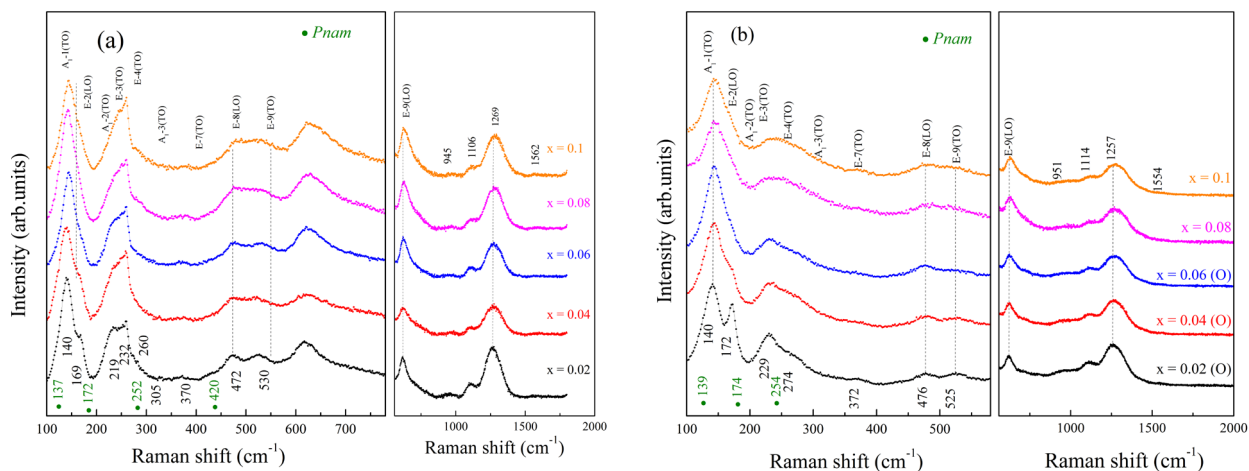


Figure 3. SEM images of compounds $\text{Bi}_{0.9}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ (left panels) and $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-y}\text{Ti}_y\text{O}_3$.

Raman

The data obtained by Raman spectroscopy measurements provided the structural information on local scale level and complemented the structural data achieved by the diffraction methods. Typical Raman spectra of the compounds $\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ recorded at room temperature are presented in the [Figure 4](#). The experimentally observed modes of the compounds of both systems are in agreement with a dominance of the rhombohedral phase described by space group $R3c$ which should provide 13 theoretically predicted Raman active modes. The most intensive bands are located at low frequencies and associated with the polar active vibrational modes of Bi and Sm ions, viz. $\sim 140 \text{ cm}^{-1}$ (A_1), $\sim 170 \text{ cm}^{-1}$ (A_1). The intensity of the bands changes with Ti content wherein their position slightly shifts towards higher frequencies thus denoting a shrinkage of the unit cell volume and associated decrease in the chemical bond length Bi(Sm) – O confirmed by the diffraction data. The bands located at $\sim 235 \text{ cm}^{-1}$ (A_1), $\sim 258 \text{ cm}^{-1}$ (E) are characteristic for vibrations of Fe(Ti) ions surrounded by oxygen octahedra, these modes also shift to higher frequencies because of the size effect. The modes located at frequencies higher than $\sim 300 \text{ cm}^{-1}$ are associated with stretching vibrations of Fe(Ti) – O bonds, oxygen motions as well as two-phonon vibrational modes, whereas nearly fixed positions of these modes indicate close to the stoichiometric content of the oxygen ions specific for the all studied compounds. It should be noted that the bands associated with the Bi(Sm) – O and Fe(Ti) – O vibrations modes becomes less split with Ti concentration thus indicating a reduction of the rhombohedral distortion which was previously confirmed by the analysis of the diffraction

results. In spite of the mentioned statement the rhombohedral phase remains in the compound of both systems within the whole concentration range of Ti content.



Magnetization measurements

It is known that structural transformation from the polar rhombohedral phase to the anti-polar orthorhombic phase driven by chemical substitution in $\text{Bi}_{1-y}\text{Sm}_y\text{FeO}_3$ ceramics is accompanied by an increase in remnant magnetization. The remnant magnetization reaches its maximal value of ~ 0.28 emu/g in the solid solutions with a dominance of the orthorhombic phase. The orthorhombic phase (either anti-polar described by s.g. *Pbam* or non-polar – s.g. *Pnma*) is characterized by a disrupted modulated magnetic structure, the concentration range specific for the single phase anti-polar orthorhombic structure in the $\text{Bi}_{1-y}\text{Sm}_y\text{FeO}_3$ ceramics stabilizes in the concentration range $y \sim 0.12 - 0.14$ depending on the synthesis conditions [41]. Maximal value of the remnant magnetization is mainly caused by a release of spontaneous magnetization induced by a non-collinear alignment of the Fe^{3+} magnetic moments due to Dzyaloshinskii-Moriya interactions [48]. Additional component of magnetization is associated with unbounded spins located in the phase boundary regions [22]. Increase in the concentration of Sm ions above ~ 14 mol. %, leads to a slight decrease in spontaneous magnetization and it stabilizes at ~ 0.25 emu/g in the compounds with the single phase non-polar orthorhombic structure [24].

The isothermal $M(H)$ magnetization curves recorded for the initial compounds $\text{Bi}_{1-y}\text{Sm}_y\text{FeO}_3$ with $y = 0.1$ and 0.12 at room temperature are characteristic for BFO-based compounds with weak ferromagnetism [41]. At room temperature, the remnant magnetization values of the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{FeO}_3$ and $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{FeO}_3$ are ~ 0.14 emu/g and ~ 0.16 emu/g respectively (Figures 5, 6). The magnetization loops recorded at room temperature for the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with $x \leq 0.4$ indicate a presence of metamagnetic transition induced by strong magnetic fields and denoted as a mismatch in the positive part of $M(H)$ curves obtained during the first and subsequent cycles (Figure 5). The mentioned field induced modification of the magnetic system of the compounds is most probably caused by a disruption of spatially modulated spin structure partly remained in these compounds at room temperature. The compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with $x \geq 0.6$ denote a complete disruption of the modulated magnetic structure which is accompanied with an increase in the remnant magnetization value as well as in the magnitude of the in-field magnetization measured at $H = 14\text{T}$.

It should be noted that remnant magnetization of the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ do not directly correlate with either rhombohedral or orthorhombic structural phase. The compounds with mixed structural state (i.e. $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with $x < 0.08$ as confirmed by the diffraction data) are characterized by a notable modification of the magnetic state while the magnetic state of the microscopically single phasic rhombohedral compounds ($x \geq 0.08$) does not show prominent changes. A weak if any correlation between the structural state of the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ and their magnetic structure is also confirmed by magnetization measurements performed at low temperatures (Figures 6, S2). Thus, the $M(H)$ magnetization dependencies recorded at 5 K denote significant changes in the magnetic structure, which can be described as antiferromagnetic with mostly remained spatial modulation (Figure S2). In the compound $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{0.94}\text{Ti}_{0.06}\text{O}_3$ the modulated magnetic structure is destroyed by magnetic fields of $\sim 8 - 10$ T as denoted by an explicit deflection in the $M(H)$ curve (Figure S2). The compounds with larger Ti concentration are characterized by partially destroyed modulated magnetic structure occurred in low field ranges. A disruption of the modulated structure leads to a notable increase in the value of in-field magnetization which reaches 1.5 emu/g in the compound with $x = 0.06$ and it further increases with Ti content in the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ (Figure S2).

The $M(H)$ magnetization curves recorded for the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ mainly resemble the results obtained for the system $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$, viz. a presence of partly modulated magnetic structure at room temperature (Figures 5, S2). At low temperature the magnetic structure of the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ is characterized by mostly remained modulation of the magnetic structure and respectively lower value of the remnant magnetization as compared to that observed at room temperature (Figure S2). Analysis of the magnetization data obtained for the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ confirms the absence of direct correlation between the remnant magnetization of the compounds and their structural state – either single or mixed state as well as the symmetry type of structural distortion. In spite of a similarity of the magnetic data obtained for the compounds of both systems there is a difference which is mainly expressed in a lower value of remanent magnetization denoted for the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ as compared to that of $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ system and this difference is well-maintained at low temperature and room temperature measurements (Figures 5, 6).

The magnetization measurements performed in low field regimes (up to 1 Tesla) allowed to attest the initial magnetic structure of the compounds (not subjected to strong magnetic fields) as well as to clarify the origin of different remnant magnetization observed for the compounds in low and high field modes (Figures S2, S3). The low field magnetization measurements performed for the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ testified gradual increase of the remnant magnetization with Ti concentration, while the values of magnetization are multiple times less than the values obtained in high field measurements mode (Figures 6, S2, S3). Thus, remnant magnetization of the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ increases from ~ 0.015 emu/g for the compound with $x = 0.02$ up to ~ 0.132 emu/g for the compound with $x = 0.08$, further increase of Ti content leads to a decrease of the remnant magnetization down to ~ 0.77 emu/g for the compound with $x = 0.1$ (Figure S3). Coercive force of the compounds shows similar tendency, viz. an increase with Ti content with a local maximum of ~ 0.6 T observed for the compound with $x = 0.08$. An evolution of magnetization of the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ shows a monotonous dependence, viz. remnant magnetization gradually increases with Ti content from 0.025 emu/g for the compound with $x = 0.02$ up to ~ 0.134 emu/g for the compound with $x = 0.1$; coercivity of the compounds reaches its maximal value of ~ 0.6 T in the compounds with $x = 0.08$ and $x = 0.1$.

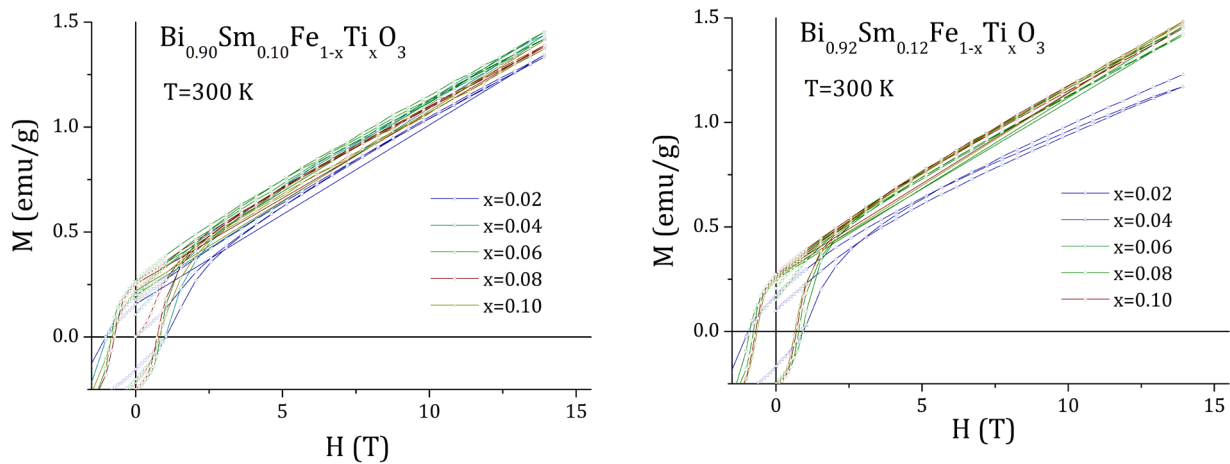


Figure 5. Isothermal magnetization dependencies recorded at room temperatures for compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{0.92}\text{Ti}_{0.08}\text{O}_3$ (left) and $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$.

Careful analysis of the $M(H)$ curves testified the anomalies of the magnetization curves, viz. vertical shift of the magnetization loops and a step-like evolution of magnetization in the vicinity of zero magnetic field (Figures 7, S3). It is known that vertical shift of magnetization loops can be caused by an exchange bias effect associated with complex magnetic structure of the compounds. In the case of $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ system, the magnetic structure of the compounds can be considered as mixed state with the two AFM phases associated with two different structural phases and one extra component associated with unbounded spins located at the phase boundary regions, interaction between these components leads to a shift of the magnetization loops. Along to the mentioned components of the magnetization other possible component can be caused by the interactions between Fe^{2+} and Fe^{3+} ions formed to compensate Ti^{4+} ions and to keep electrical neutrality of the compounds. Formation of Fe^{4+} ions is also possible as declared in the work [49] and related superexchange interactions could notably affect the magnetic state of the compounds. The mentioned exchange interactions could contribute to the mixed magnetic state of the compounds confirmed by the magnetization measurements while these components are unlikely significant as it would contradict with the results obtained by the diffraction data and the Raman spectroscopy results.

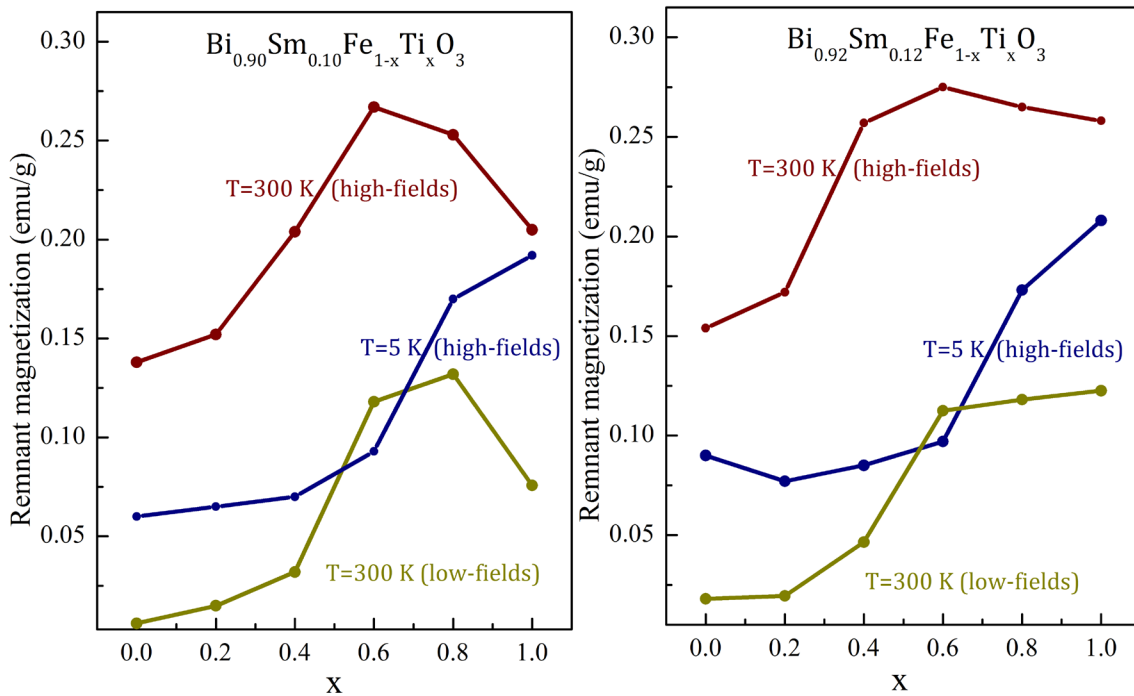


Figure 6. Remnant magnetization values of compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{0.92}\text{Ti}_{0.08}\text{O}_3$ (left) and $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ obtained in low and high field measurements modes.

The compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ also have complex magnetic state as confirmed by an asymmetry in the magnetization loops and a non-monotonous evolution of the remnant magnetization with Ti concentration. The compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with single-phase structural state according to the diffraction data are characterized by a presence of the orthorhombic phase on local scale level as confirmed by the Raman spectroscopy results. The local scale structural inhomogeneities notably affect magnetic state of the compounds leading to observed non-monotonous evolution of the remnant magnetization and coercivity of the compounds. Along with the mentioned inhomogeneities the cations vacancies formed to compensate a residing of Ti^{4+} ions can act as local defects and thus can diminish modulated spin structure and contribute to spontaneous magnetization. The proposed factors can rationally explain a local maximum of remnant magnetization of ~ 0.134 emu/g observed in the compound $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{0.92}\text{Ti}_{0.08}\text{O}_3$ as well as more monotonous trend of the magnetization dependencies observed for the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ (Figures S3, 6). It should be noted that the components of the magnetic state associated with long-range antiferromagnetism (weak ferromagnetism) and unbounded spins have different contribution to the remnant magnetization in low and high field magnetization measurements modes. The most plausible model to describe evolution of the magnetic state of the compounds of both systems consider a significant contribution of the unbounded spins at low field regime and weak ferromagnetism as the key factor of remnant magnetization in high field regime which is confirmed by nearly double value of the remnant magnetization obtained in high field measurements (Figure 6). Analyzing the components of remnant magnetization it should be mentioned a dominant contribution of the component associated with weak ferromagnetism as compared to that associated with the phase boundary spins having minor effect on the spontaneous magnetization as it was determined in our previous study [22].

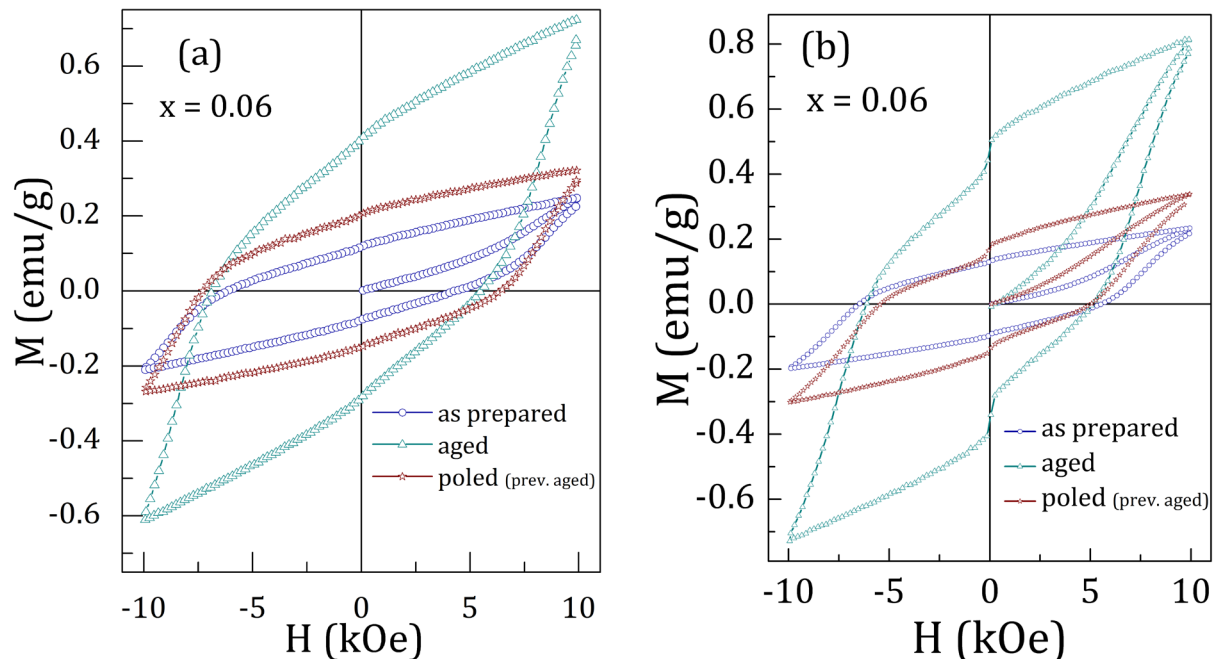


Figure 7. $M(H)$ loops of compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{0.94}\text{Ti}_{0.06}\text{O}_3$ (left) and $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{0.94}\text{Ti}_{0.06}\text{O}_3$ measured for aged samples, before and after electric poling.

The compounds with mixed structural and magnetic states are very sensitive to external stimuli as external magnetic and electric field as well as time aging procedure. Time aging of the compounds performed during ~ 1 year leads to a structural relaxation of the compounds with mixed structural state towards structural state with a dominance of the orthorhombic phase as it was declared in our previous study [50]. The most pronounced effect of the structural relaxation is observed in the compounds with dominant rhombohedral phase with a minor amount of the orthorhombic phase. Structural transformation towards the orthorhombic phase is accompanied with the total disruption of the modulated magnetic structure and related increase in the remnant magnetization. High sensitivity of the mixed structural state is also confirmed by the structural and magnetization data obtained for the compounds subjected to external electric field via poling in the field of 40 kV/cm. Electric poling of the aged compounds leads to a backward transformation of their structural state which assumes a stabilization of the rhombohedral phase as confirmed by the XRD patterns (Figure S4). The mentioned changes in the structural phases ratio causes the related changes of their magnetic state. The magnetization data obtained for the aged compounds subjected to electric poling demonstrate drastic decrease in the remnant magnetization (Figures 7), which is most probably caused by a backward structural transition

which assumes a stabilization of the rhombohedral phase mainly characterized by the modulated magnetic structure with the value of spontaneous magnetization which is less than 0.05 emu/g.

Conclusions

The structural data obtained by the complementary techniques as laboratory and synchrotron X-ray diffraction as well as Raman spectroscopy allowed to conclude about a coexistence of the dominant rhombohedral phase and the antipolar orthorhombic phase in the compounds $\text{Bi}_{0.88}\text{Sm}_{0.12}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ with $0 \leq x \leq 0.1$, wherein the volume fraction of the orthorhombic phase decreases with Ti concentration. The structural state of the compounds $\text{Bi}_{0.90}\text{Sm}_{0.10}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ considered as single phase rhombohedral according to the diffraction data is characterized by the presence of the antipolar orthorhombic phase on local scale level for $x \leq 0.06$ as confirmed by the Raman data, increase of Ti content above 6% leads to a stabilization of the single phase rhombohedral state. Magnetization measurements have testified the absence of direct correlation between the remnant magnetization of the compounds $\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ at the MPB and the symmetry of the structural phases. The evolution of remnant magnetization of the compounds is mainly caused by the unbounded spins and spatially modulated spin structure; the latter term is notably dependent on temperature and chemical homogeneity of the structural state, viz. cation vacancies, presence of the minor structural phase on local scale level etc. The component of magnetization associated with the unbounded spins is mostly pronounced in low field magnetization measurements as the magnetization caused by wF state is notably frustrated. High sensitivity of the structural and magnetic states of the compounds to the external stimuli is confirmed by a modification of the structure and magnetization under external electric field and time aging procedure. Time aging of the compounds leads to a structural relaxation of the mixed phase compounds towards a stabilization of the anti-polar orthorhombic phase, while external electric field causes backward structural transformations associated with a stabilization of the rhombohedral phase. The induced structural transformations are accompanied with the suppression and recovery of the modulated magnetic structure thus affecting remnant magnetization of the compounds.

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Supplementary information: The data providing additional information about the crystal structure and magnetic properties of the compounds under study is presented in Supplementary Materials.

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