Crystal Structure and Magnetic Properties of $Bi_{1-y}Ba(Sr)Fe_{1-y}Ti_yO_3$ Solid Solutions

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Abstract: Usages of various chemical substitution schemes of the initial multiferroic $BiFeO_3$ can significantly reduce known drawbacks specific for the functional oxides based of iron ions and thus foster a creation of novel magnetoelectric compounds perspective for various technological applications. In the present study the co-doped compounds of the system $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ (x = 0.0 – 1.0; y ≤ 0.4) synthesized using sol-gel technique were analyzed focusing on the crystal structure stability and the correlation between the structure and magnetic properties. The concentration driven evolution of the crystal structure as well as the unit cell parameters were investigated based on the X-ray diffraction data, the correlation between the crystal structure and the magnetic properties of the compounds has been studied by magnetometry techniques. The compounds $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ with x = 0; y = ≤ 0.2 are characterized by single-phase rhombohedral structure, and increase in the dopant concentration to y = 0.4 leads to the stabilization of the pseudocubic phase. An increase in the Sr content leads to the phase transition in the compounds to the single phase state with the cubic structure which is accompanied by an increase in the value of the remanent magnetization.

Keywords: Multiferroics, Magnetometry, Crystal structure, Magnetic structure.

INTRODUCTION

Materials based on bismuth ferrite attract great attention of the scientific community due to a wide range of structural and magnetic phase transitions [1-4]. In spite of the attracting physical parameters as high temperatures of the ferroelectric and antiferromagnetic transitions (T_C ~ 1100 K, T_N ~ 650 K) [5-7] there are significant drawbacks (low residual magnetization, high conductivity, small magnetoelectric interaction) which notably limits the scope of their possible applications [4, 8-10]. Some of these problematic issues can be overcome by various chemical substitution schemes [7, 11-13]. The present work is aimed at the creation and study of new electroceramics based on bismuth ferrite and characterized by a metastable structural state with polar active clusters which are most probably located in a nonpolar matrix with a (pseudo)cubic structure. According to the available data [14-16] the crystal structure of the mentioned clusters should have rhombohedral symmetry. The proposed chemical substitution scheme for the solid solutions $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ make it possible to obtain the materials with polar active clusters coexisting in a nonpolar matrix, thus the dipole interactions between the clusters should be weak because of the distance, wherein the size and structure of the clusters can be controlled via chemical doping.

It is shown that the usage of the mentioned chemical substitution scheme makes it possible to control not only the electric dipole parameters but also the magnetic structure of the $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ solid solutions. The proposed chemical substitution scheme allows to reach the main goal of the study, viz. to create novel electroceramic materials possessing relaxor-like properties; while the main objectives assume a formation of the metastable state due to the coexistence of the polar active clusters in the nonpolar pseudocubic matrix which can be considered as structural analog of classic relaxors. The obtained compounds can be considered as weakly coupled relaxors which is a promising direction in the development of functional materials for capacitors, the obtained materials can also be used in the field of information and energy saving technologies [17, 18].

EXPERIMENTAL

Compounds $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$, where x = 0.0 – 1.0; y ≤ 0.4 were synthesized using the sol-gel technique similar to the procedure described in the Ref. [16]. The initial nitrates $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Fe(NO_3)_3$, $Bi(NO_3)_3$ taken the ratio of 1:for the metal ions and citric acid were dissolved in distilled water. After, the obtained compositions were mixed with ethylene glycol keeping the ratio 1:10 and then the mixture was homogenized at T~ 90°C during about 1 hour. The obtained gel was dried for 12 hours at T~180°C, the resulting compound was ground and annealed at T~ 1000°C.

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The phase purity and the structural state of the compounds were analyzed based on the X-ray diffraction results recorded at room temperature in the 2Θ range of 20–80° with a step of 0.02° using a diffractometer Bruker D8 with Cu-Kα radiation. The diffraction data were calculated by the Rietveld method using the FullProf program. The magnetic properties were studied using a Cryogenic vibrating magnetometer ltd.

RESULTS AND DISCUSSION

X-ray patterns obtained for the compounds $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ with x = 0; y = ≤ 0.2 are characterized by a single-phase rhombohedral structure. An increase in the concentration of substituent ions leads to a decrease in the rhombohedral distortions, and the structure of compounds with y = 0.25 – 0.33 can be refined assuming the coexistence of the rhombohedral and the pseudocubic phases. It should be noted that the pseudocubic phase is observed in the compounds in the concentration range $0.25 < y < 0.40$. The chemical substitution causes a steady decrease in the volume fraction of the rhombohedral phase and related unit cell parameters, which can be judged from the evolution of characteristic reflections associated with the distortion of oxygen octahedra in the *ab* plane of the rhombohedral lattice.

Figure **2** denotes the X-ray diffraction patterns of the compounds $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ with x = 0.25 – 1, y = 0.3. Analysis of the diffraction data points at only minor structural changes occurred in the compounds with the dopant concentrations up to 0.75. The most intensive diffraction reflection located at 2θ = 32° for the composition with x = 1.0 has an asymmetric profile, which indicates the presence local distortion most probably inheriting the rhombohedral symmetry.

It is noted that an increase in the concentration of Sr ions leads to a distortion of the rhombohedral symmetry specific for the undoped compound, thus fostering the structural transition to the single phase state with the cubic or pseudocubic symmetry (Figures **1**, **2**). The refined structural parameters testify the decrease in the unit cell parameter a as well as in the unit cell volume with the increase of Sr content, viz. the value of the unit cell volume decreases from V=62.61 Å^3 for the compound with a substitution concentration x = 0.25 to V=61.22 Å^3 for the compound with x = 1.0. The noted structural changes in the parameters are caused by a replacement of the Ba ions having large radius by the Sr ions with a lesser ionic radius (the ionic radii for the mentioned ions having 2+ oxidation state and six coordination are 1.35 Å and 1.18 Å respectively).

Measurements of the magnetization allowed to clarify the correlation between the crystal structure and the magnetic properties of the compounds. The results of measurements of the magnetization of the compounds $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ with y = 0.3 indicate the predominantly antiferromagnetic character of the G -type magnetic structure. The dependence of the magnetization curves M(H) obtained for the compound with x = 0 is characterized by the absence of residual magnetization, which is caused by the spatially modulated spin structure wherein the crystal structure of the compounds changes from the rhombohedral to (pseudo)cubic phase. In the compound $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ with x = 0 the

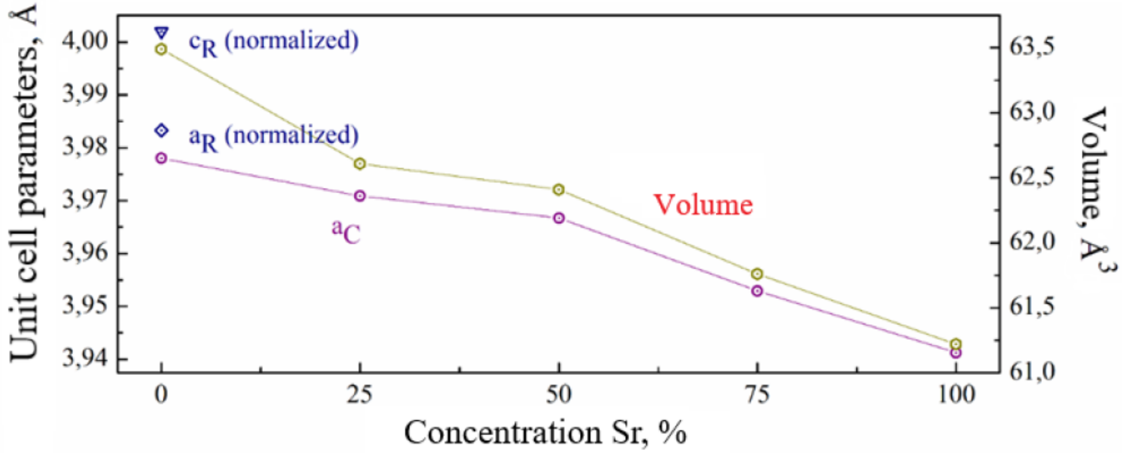

Figure 1: The unit cell parameters calculated for compounds $0.7BiFeO_3$-$0.3Ba_{1-x}Sr_xTiO_3$ with x = 0.0 - 1.0 based on the XRD data.

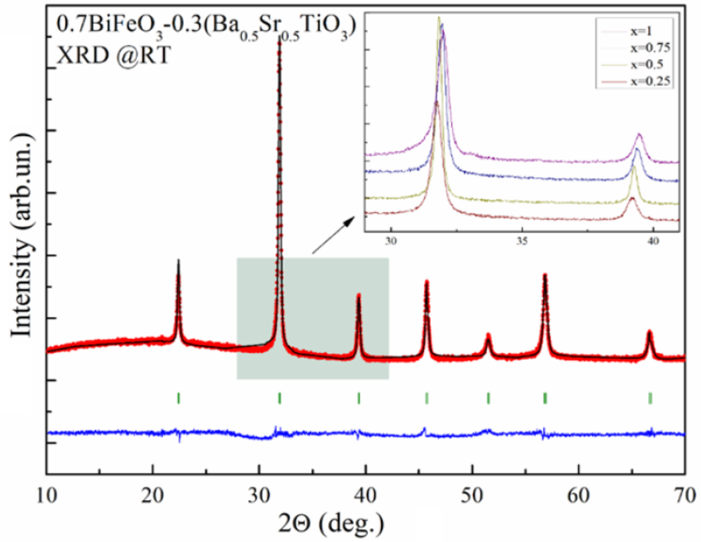

Figure 2: X-ray patterns obtained for the compounds $0.7BiFeO_3$-$0.3Ba_{1-x}Sr_xTiO_3$ at room temperature. The inset shows the concentration dependent evolution of the reflections for the solid solutions with x = 0.25 – 1.

sublattice formed by the magnetically active Fe^{3+} ions is sufficiently diluted with diamagnetic ions Ti^{4+} and thus makes the exchange interactions negligible. An increase in the Sr content leads to an increase in the remanent magnetization due to the modification of the crystal structure as the Sr ions have smaller ionic radius than the Ba ions. The remanent magnetization reaches the highest value of ~0.006 emu/g in the compound $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ with x = 1, y = 0.3 (Figure **3**).

CONCLUSIONS

Compounds $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ with x = 0.0 and y = ≤ 0.2 are characterized by the single-phase rhombohedral structure. An increase in the concentration of the dopant ions leads to a decrease in the rhombohedral distortions, and the structure of compounds with y = 0.25 – 0.33 can be refined assuming the coexistence of the rhombohedral and the pseudocubic phases. An increase in the concentration of Sr ions leads to the transition of the compound to a single-phase cubic state, and also causes a decrease in the magnitude of the parameter ***a*** as well as the unit cell volume of the crystal lattice, for the compound with the concentration level of the dopant ions x= 0.25 the unit cell volume equals to 62.61 $Å^3$, while for x = 1 the volume is 61.22 $Å^3$. The noted changes in the structural parameters are caused by the replacement of the Ba ions having large radius by the Sr ions with a lesser ionic radius assuming their stable oxidation state of 2+. The substitution of initial compound with the Sr and Ti ions in accordance with the proposed chemical formula causes a stabilization of the metastable structural state characterized by the very close values of the unit cell parameters of the both *R*- and *C*- structural phases and

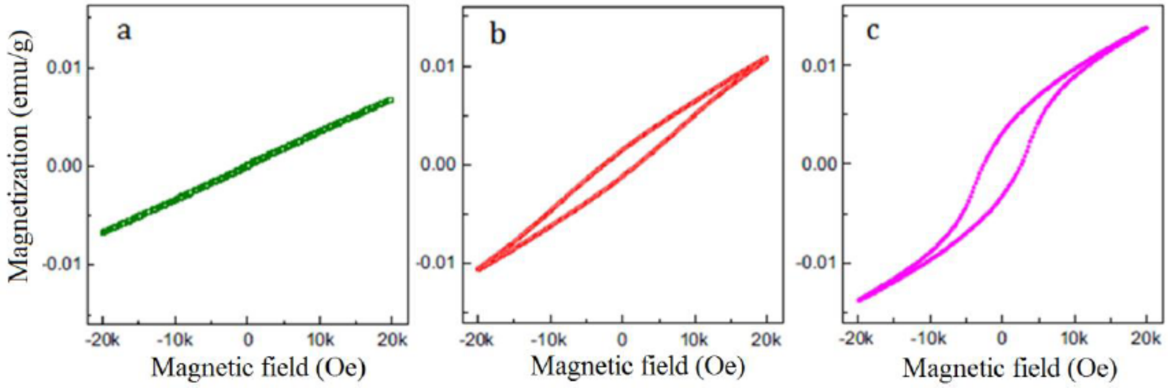

Figure 3: Isothermal dependences of the magnetization obtained at room temperature for the compounds $0.7BiFeO_3$-$0.3Ba_{1-x}Sr_xTiO_3$ with x= 0.0 (**a**), 0.5 (**b**), 1.0 (**c**) at T = 5 K.

thus leads to a decrease in the distortion of the chemical bond angles O – Fe(Ti) – O as well as a shrinkage of the chemical bond lengths Fe(Ti) – O which fosters a strengthening of the exchange interactions between magnetically active iron ions and thus increases the remanent magnetization. The residual magnetization reaches its maximum value (~0.006 emu/g) at the substitution level $Bi_{1-y}(Ba_{1-x}Sr_x)_yFe_{1-y}Ti_yO_3$ x = 1, y = 0.3.

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