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Morphotropic phase boundary in $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ multiferroics

Abstract. *Investigation of crystal structure, magnetic and piezoelectric properties of polycrystalline $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ system was performed by X-ray diffraction, Mössbauer spectroscopy, Vibrating Sample Magnetometry (VSM), and Piezoresponse Force Microscopy (PFM). It is shown that increasing niobium content induces a polar-to-nonpolar morphotropic boundary near the x=0.19. The piezoresponse is significantly enhanced near the morphotropic boundary. The piezoelectric properties of parent antiferromagnet $BiFeO_3$ with a cycloidal spatially modulated spin structure and polar weak ferromagnet $Bi_{0.82}Ca_{0.18}Fe_{0.91}Nb_{0.09}O_3$ are compared and analyzed.*

Streszczenie. *Struktura krystaliczna oraz właściwości magnetyczne i piezoelektryczne polikryształu $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ zostały zbadane przy użyciu dyfrakcji rentgenowskie, spektroskopii Mosswbauera, magnetometrii z wibrującą próbką (VSM) oraz mikroskopii odpowiedzi elektrycznej (PFM). Wykazano, że rosnąca zawartość niobu wymusza powstanie granicy morfotropowej pomiędzy obszarem polarnym i nie polarnym w pobliżu x=19. Odpowiedź piezoelektryczna jest znacząco lepsza w pobliżu granicy morfotropowej. Zbadano i porównano właściwości piezoelektryczne macierzystego antyferromagnetyka $BiFeO_3$ z cykloidalnym modulowanym przestrzennie momentem spinowym oraz słabego ferromagnetyka polarnego $Bi_{0.82}Ca_{0.18}Fe_{0.91}Nb_{0.09}O_3$. (**Morfotropowa granica fazowa w multiferroikach $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$**).*

Keywords: multiferroics, morphotropic phase boundary, piezoelectricity, magnetization.
Słowa kluczowe: multiferroiki, morfotropowa granica fazowa, piezoelektryczność, magnesowanie.

Introduction

$BiFeO_3$ is a single phase material in which both magnetic and ferroelectric orderings occur at temperatures much higher than room temperature. Antiferromagnetic ordering arises at T_N=643 K whereas dipole ferroelectric ordering appears at much higher temperature of about 1100 K [1]. Below 1100 K the unit cell is described by the polar space group $R3c$ whereas above 1100 K it belongs to the orthorhombic nonpolar space group $Pbnm$ [2]. The dipole order occurs owing to the stereochemical activity of the lone electron pair $6s^2$ of the bismuth ions. The antiferromagnetic ordering is of the basic G-type modified by cycloidal modulation with a large period of 62 nm [3]. It was argued [4] that a presence of the cycloidal modulation prevents both the spontaneous magnetization and linear magnetoelectric effect. It has been found that $BiFeO_3$ in an external magnetic field of 18 T at 5 K undergoes a metamagnetic transition from a spatially modulated antiferromagnetic state to a homogeneous weakly ferromagnetic one [5]. It is interesting to compare physical properties of the compounds with homogeneous weak ferromagnetic state and those with inhomogeneous incommensurate antiferromagnetic one. According to the published data the incommensurate magnetic structure can be destroyed not only by applying external high magnetic field but also by the epitaxial stresses [6] and chemical substitutions [7].

Recently, the examples of solid solutions of $Bi_{1-x}Ca_{-x}Fe_{1-x/2}Nb_{x/2}O_3$ have been studied [8]. It was shown that the compound with the composition x=0.3 exhibits spontaneous magnetization of about 0.3 emu/g. This effect has been attributed to nonpolar orthorhombic structure (space group $Pbnm$) which allows weak ferromagnetism. However, the magnetic properties of the lightly doped compounds with the ferroelectric order have not been studied.

Experimantal

Polycrystalline samples of the $Bi_{1-x}Ca_{-x}Fe_{1-x/2}Nb_{x/2}O_3$ ($0\leq x\leq 1$) solid solution were obtained from raw oxides Bi_2O_3, Fe_2O_3, Nb_2O_3 and carbonate $CaCO_3$ taken in stoichiometric proportion and thoroughly ground in a planetary ball mill (RETSCH, PM-100). The synthesis temperature was increased with increasing niobium content (see Table 1). After synthesis the samples were rapidly cooled (500 C/h) to room temperature. To enhance the chemical homogeneity all the Nb-doped samples were synthesized during 15 h. The X-ray diffraction patterns were recorded with a diffractometer DRON-3M using CuK_α radiation. Data analysis was performed using FullProf software package. The samples with small content of impurity phases (less than 1-2%) were selected for magnetic and piezoelectric measurements. The Mössbauer measurements were performed using a conventional constant acceleration spectrometer with ^{57}Co in Rh source. The spectra were recorded in transmission geometry at room temperature. The Mössbauer spectra were fitted using the NORMOS program. All the isomer shifts were related to the α-Fe standard.

The magnetization was measured in magnetic fields up to 14 T with a universal system for the measurement of physical properties (CRYOGENIC Ltd).

Local ferroelectric properties of the samples were investigated with a scanning force microscopy in piezoresponse (PFM) mode using a commercial setup NTEGRA Aura (NT-MDT) equipped with an external lock-in amplifier (SR-830A, Stanford Research) and a function generator (FG-120, Yokogawa). A commercial tip-cantilever system Arrow^{TM} Silicon SPM Sensor (Nano World) was used. Domain visualization was performed under an applied AC voltage with the amplitude of V_{AC}=5V and frequency f=50 kHz. The setup was calibrated using commercially available PZT(52/48) films (Inostek).

Result and discussion

Solid solutions of the $Bi_{1-x}Ca_{-x}Fe_{1-x/2}Nb_{x/2}O_3$ ($0 \leq x \leq 1$) series were studied by X-ray diffraction at room temperature. The refinement of the unit cell parameters of compounds with $x\leq 0.18$ was carried out based on space group $R3c$ in which parent $BiFeO_3$ crystallizes (Table 1). For x=0.19 sample the X-ray diffraction patterns show additional reflections indicating the formation of a superstructure of the type $\sqrt{2}\,a_p\times\sqrt{2}\,a_p\times 2a_p$, where a_p is the lattice parameter of the primitive cubic unit cell. A superstructure of this type may correspond to orthorhombic distortions of the unit cell. We succeeded in interpreting the *X*-ray diffraction pattern for x=0.19 only assuming that the sample consists of two different crystalline phases, namely, rhombohedral (space group *R3c*) and orthorhombic (space group *Pbnm*). Synthesis at low temperature (950°C) results in the formation of composition with a dominant rhombohedral structure (space group *R3c*). As the synthesis temperature increases up to 1010°C the amount of the rhombohedral phase decreases whereas quantity of the orthorhombic phase increases with the appearance of second phases containing bismuth and iron oxides. A sample with x=0.2 has been obtained in pure orthorhombic phase at a synthesis temperature of 1010°C. Its unit cell is well described by the space group *Pbnm* (Table 1). Note that this space group is characteristic of many compounds with perovskite structure, such as $LnMnO_3$ and $LnFeO_3$ (Ln - lanthanide). Using this space group, we could describe well the unit cell of Ca (Nb) doped solid solutions up to x=0.9. The volume of the unit cell gradually decreases with increasing calcium content (Table 1).

Table 1. Crystal symmetry and unit cell parameters of $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ system

x	T_{syn}, °C	S. G.	a, Å	b, Å	c, Å	α, β, deg.	V, Å^3
0	870	*R3c*	5.630			59.35	124.3
0.15	990	*R3c*	5.611			59.50	126.5
0.18	1000	*R3c*	5.600			59.51	122.8
0.20	1010	*Pbnm*	5.507	5.588	7.857		241.8
0.3	1050	*Pbnm*	5.488	5.587	7.841		240.5
0. 5	1100	*Pbnm*	5.475	5.576	7.812		238.5
0.7	1180	*Pbnm*	5.463	5.576	7.792		237.4
0.9	1180	*Pbnm*	5.425	5.546	7.761		234.7
1	1350	$P2_1/n$	5.439	5.551	7.751	90.01	234.1

The magnetization dependencies as a function of magnetic field at room temperature for $Bi_{1-x}Ca_{x}Fe_{1-x/2}Nb_{x/2}O_3$ compounds are presented in Fig. 1. For the parent compound $BiFeO_3$ (x=0) the M–H dependence at room temperature shows a metamagnetic-like behavior in magnetic fields above 11 T. Magnetic hysteresis associated with the metamagnetic transition is clearly observed indicative of the first order magnetic transition.

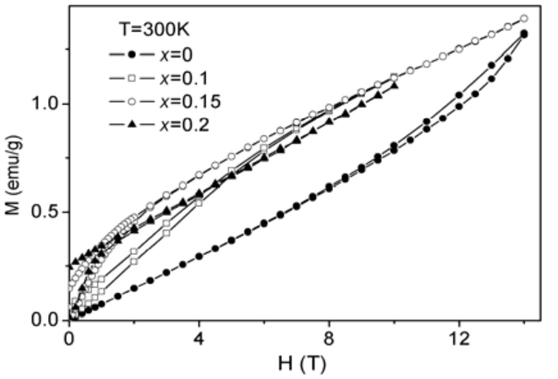

Fig.1. Magnetization as a function of magnetic field for $Bi_{1-x}Ca_{x}Fe_{1-x/2}Nb_{x/2}O_3$

Remanent magnetization and coercive field estimated from the magnetization curves for 10 % Ca (5 % Nb) doped sample evidence partial collapse of the initial magnetic structure inherent for parent $BiFeO_3$. The spontaneous magnetization reaches a maximum (M_s ~ 0.3 emu/g) for the rhombohedrally distorted samples in the range 0.15<x<0.18 whereas for the orthorhombic samples with x>0.18 the spontaneous magnetization is slightly lower because Nb ions are diamagnetic. It is important to note that the magnetization for sample with x=0.1 is not saturated even under the field of 8 T thus indicating an incomplete magnetic transition into a new magnetic state. In fact, the magnetization versus field curves for x=0.1 and x=0.15 samples are practically coincident above 8 T in the magnetic field regime where the new magnetic state is established for both samples. The appearance of the spontaneous magnetization can be understood in terms of the modification of the incommensurate spiral *G*-type antiferromagnetic ordering characteristic of $BiFeO_3$ to the homogeneous canted *G*-type antiferromagnetic ordering, in which a small ferromagnetic component of non-collinearly ordered spins gives spontaneous magnetization [9]. The data obtained indicate that the sample with x=0.1 possesses a mixed magnetic state whereas the samples in the composition range of 0.15<x<0.2 reveal a homogeneous canted weak ferromagnetic state.

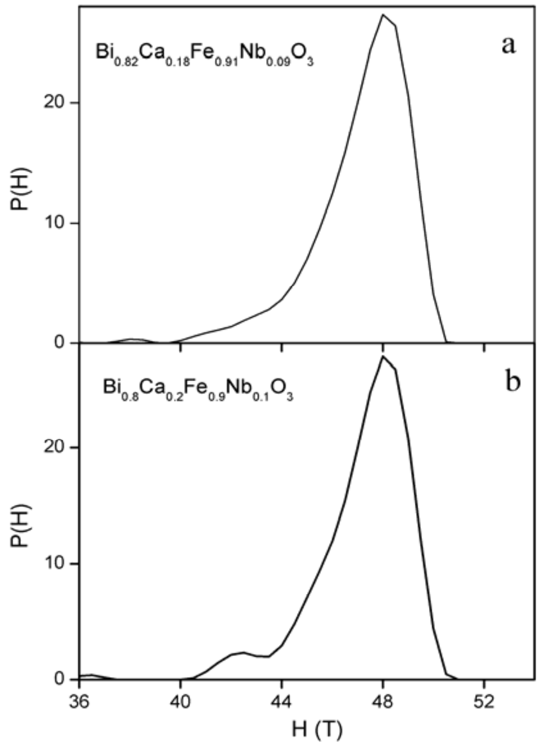

Fig.2. Hyperfine field distributions at room temperature

The transition from modulated antiferromagnetic structure to homogeneous antiferromagnetic structure can be evidenced by ^{57}Fe Mössbauer spectroscopy. Indeed, the existence of the spatially modulated magnetic structure resulted in a specific distribution of hyperfine fields *P(H)* with two peaks corresponding to the Fe ions with the spins directed along and perpendicular to the propagation wave vector (Fig. 2b). In turn, a collinear magnetic structure is characterized by a single- peak distribution (Fig. 2a). The same behavior is observed in the ^{57}Fe nuclear magnetic resonance experiments. The hyperfine magnetic field distribution for both spectra reveals an asymmetric single peak, thus indicating suppression of a spiral spin modulation. The asymmetry can be related to slightly inhomogeneous Nb ions distribution over lattice that is very often observed in diamagnetically diluted magnetic compounds. Therefore, one can conclude that both rhombohedral and orthorhombic phase demonstrate similar magnetic behavior as a result of the transition into canted weak ferromagnetic state. The spontaneous magnetizations observed for polar and nonpolar orthorhombic phases are almost equal thus indicating the same magnetic structure and mechanism of the magnetic interaction responsible for magnetization behavior. Hence, it can be suggested that canting of the magnetic moments results from Dzyaloshinskii-Moriya antisymmetric interaction as it is commonly accepted for the majority of weak ferromagnets [9].

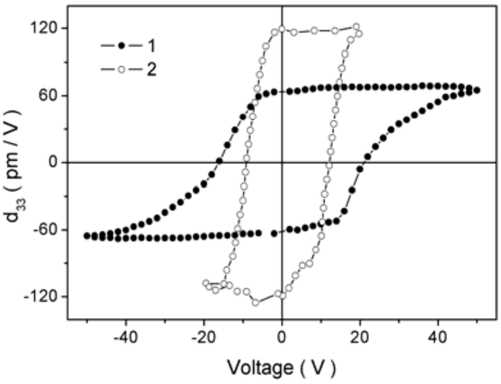

Fig.3. Local piezoelectric loops for $BiFeO_3$ (1) and $Bi_{0.82}Ca_{0.18}Fe_{0.91}Nb_{0.09}O_3$ (2) at room temperature

Due to the significant conductivity of the samples piezoresponse force microscopy was used as a suitable tool for studying the local ferroelectric properties of the $BiFeO_3$ co-doped with Ca and Nb ions. In order to improve the reliability of the data the measurements have been made on different parts of the samples and averaged to eliminate the effect of grain orientation. Well saturated local piezoresponse hysteresis loops were acquired for parent $BiFeO_3$ under a maximum bias voltage of 50 V (Fig. 3). The measured piezoelectric coefficient $d_{33}\approx 65$ pm/V (evaluated using standard PZT samples) is in a good agreement with the published data. Hysteresis loops of piezoelectric coefficient measured using the same parameters as for parent $BiFeO_3$ testify significantly enhanced piezoelectric properties of the $Bi_{0.82}Ca_{0.18}Fe_{0.91}Nb_{0.09}O_3$ compound using a considerably smaller bias voltage (Fig. 3). It is worth noting that the coercive force is much smaller for the doped compound as compared with that for the undoped $BiFeO_3$ thus demonstrating the advantage of doping for possible practical applications. Significantly larger piezoelectric response observed for x=0.18 is in line with the general notion that ferroelectric properties are maximal for the compositions near a morphotropic phase boundary. However, it is worth noting that the compound with x=0.18 is in the single phase rhombohedral structural state, in addition, the orthorhombic phase revealed for x=0.2 composition is nonpolar. As a rule, a larger piezoresponse is expected in the case when two different ferroelectric phases coexist. However, there are two different mechanisms of enhancement of piezoelectric properties. The first mechanism is associated with rotation of polarization whereas the second one is related to polarization extension that is pronounced near the Curie point or polar-nonpolar morphotropic boundary. Hence, it is concluded that the enhancement of the piezoelectric properties in $Bi_{1-x}Ca_{-x}Fe_{1-x/2}Nb_{x/2}O_3$ compounds results from the polarization extension occurring near the polar-nonpolar morphotropic boundary.

Conclusions

We investigated the crystal structure, magnetic and piezoelectric properties of $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ solid solutions prepared by standard solid state reaction method. Morphotropic phase boundary between polar rhombohedral ($R3c$) and nonpolar orthorhombic ($Pbnm$) phase was revealed in $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ system at the doping level x=0.19. In accordance with magnetization and Mössbauer studies $Bi_{1-x}Ca_{-x}Fe_{1-x/2}Nb_{x/2}O_3$ indicates the existence of homogeneous weak ferromagnetic state within concentration range $0.15\leq x\leq 0.18$ of the polar phase. The enhancement of the piezoelectric activity was observed near the polar-nonpolar morphotropic boundary. It was suggested that the chemical substitutions of bismuth which lead to decreasing the volume unit cell, favor stabilization of the weak ferromagnetic state within rhombohedral polar phase.

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