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## ADVERTISEMENT



## Enhanced piezoelectric and magnetic properties of $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ solid solutions

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An investigation of the crystal structure, the magnetic and the piezoelectric properties of polycrystalline  $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$  (I) and  $Bi_{1-x}Pb_xFe_{1-x/2}Nb_{x/2}O_3$  (II) systems was performed by x-ray diffraction, Mössbauer spectroscopy, vibrating sample magnetometry, and piezoresponse force microscopy. It is shown that an increasing niobium content induces a polar-to-nonpolar morphotropic boundary near x = 0.19 (I) and x = 0.3 (II). Within the polar region of the system (I),  $(0.15 \le x \le 0.18)$ , the solid solutions are homogeneous weak ferromagnets whereas compounds of the system (II) do not exhibit an appreciable spontaneous magnetization. It is assumed that chemical substitutions leading to a decrease of the initial volume of the unit cell favor the stabilization of the weak ferromagnetic state within the rhombohedral ferroelectric phase. The piezoresponse is significantly enhanced near the morphotropic boundary. The piezoelectric properties of the parent antiferromagnet BiFeO<sub>3</sub>, harboring a cycloidal spatially modulated spin structure, are compared with those of the polar weak ferromagnet  $Bi_{0.82}Ca_{0.18}Fe_{0.91}Nb_{0.09}O_3$ . (© 2011 American Institute of Physics. [doi:10.1063/1.3594251]

#### I. INTRODUCTION

BiFeO<sub>3</sub> is a single phase material in which both magnetic and ferroelectric ordering occurs at temperatures much higher than room temperature. Antiferromagnetic ordering arises at  $T_N = 643$  K whereas, dipole ferroelectric ordering appears at a much higher temperature, at 1100 K.<sup>1,2</sup> Below 1100 K the unit cell is described by the polar space group R3c whereas, above 1100 K one finds the orthorhombic nonpolar space group *Pbnm*.<sup>3</sup> The dipole order occurs owing to the stereochemical activity of the lone  $6s^2$  electron pair of the bismuth ion. The antiferromagnetic ordering is of the basic G-type modified by cycloidal modulation with a large period, i.e., 62 nm.<sup>4,5</sup> It was argued<sup>6</sup> that the presence of the cycloidal modulation prevents both a spontaneous magnetization and a linear magnetoelectric effect. However, it has been found that BiFeO<sub>3</sub> undergoes a metamagnetic transition at 5 K and in an external magnetic field of 18 T - from a spatially modulated antiferromagnetic state to a homogeneous weakly ferromagnetic one.<sup>6,7</sup> Therefore, it is interesting to compare the physical properties of the compounds which show a homogeneous weak ferromagnetic state with those which show an inhomogeneous incommensurate antiferromagnetic one. According to published data, the incommensurate magnetic structure can be destroyed not only by applying high external magnetic fields, but also by the epitaxial stresses<sup>8</sup> and chemical substitutions.<sup>9-12</sup> Epitaxial

BiFeO<sub>3</sub> films show a large spontaneous polarization and magnetization. Here, a tetragonal or monoclinic symmetry (due to the epitaxial stresses) was observed instead of the rhombohedral one.<sup>2,8</sup> The magnetic moment array in these films could be characterized as homogeneous magnetic G-type structure. However, further investigations have shown that the high spontaneous magnetization may result from a parasitic magnetic phase of the spinel structure, i.e.,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Ref. 13), the small amount of which cannot be detected by x-ray measurements. On the other hand, some papers reported that the weak ferromagnetic properties could be due to the partial substitution of the bismuth ions by rareearth<sup>9,10</sup> or alkali earth<sup>11,12</sup> ions. Also, the Fe ions could be replaced by other 3d or 4d ions.<sup>14,15</sup> However, a closer analysis of the published data show that the spontaneous magnetization appearing in the rare-earth doped samples can be attributed to the admixture of nonpolar orthorhombic phases with other symmetry type than that observed in BiFeO<sub>3</sub> (Refs. 16 and 17). These orthorhombic phases (Pbam and Pnma) are weak ferromagnets due to the Dzyaloshinskii-Moriya interaction, which is also responsible for the weak ferromagnetism of orthoferrites such as LaFeO<sub>3</sub> (Ref. 18). Some more reliable results have been obtained in the case of BiFeO<sub>3</sub> doped with titanium.<sup>19</sup> As it was shown in Ref. 19, both solid solutions Bi<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.8</sub>Ti<sub>0.2</sub>O<sub>3</sub> and BiFe<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub> exhibit a spontaneous magnetization up to 0.25 emu/g at room temperature within the polar R3c-type phase. Recently, examples of solid solutions of Bi1-xCaxFe1-x/2Nbx/2O3 have been studied.<sup>20</sup> It was shown that the compound with the

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composition x = 0.3 exhibits a spontaneous magnetization of about 0.3 emu/g. This effect has been attributed to the existence of a nonpolar orthorhombic structure (space group *Pnma*) which allows weak ferromagnetism. However, so far the magnetic properties of those compounds, which also reveal the ferroelectric properties under light doping, have not been studied extensively.

In this work, we report on the crystal structure, piezoelectric and magnetic properties of solid solutions Bi<sub>1-</sub> $_xA_xFe_{1-x/2}Nb_{x/2}O_3$  (A – Ca, Pb) in the lightly doped ferroelectric phase regime. As a particular result we show that a homogeneous weakly ferromagnetic state is observed only within the polar structure (space group R3c) and in the case of Bi<sub>1-x</sub>Ca<sub>x</sub>Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>O<sub>3</sub> with 0.15  $\leq x \leq 0.18$ . Specifically, it was shown that Nb substitution leads to an enhancement of the local piezoelectric properties near the ferroelectric– paraelectric morphotropic boundary with  $x \approx 0.19$ .

#### II. EXPERIMENTAL

Polycrystalline samples of Bi<sub>1-x</sub>Ca<sub>x</sub>Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>O<sub>3</sub>  $(0 \le x \le 1)$  and  $Bi_{1-x}Pb_xFe_{1-x/2}Nb_{x/2}O_3$   $(0 \le x \le 0.5)$  solid solutions were obtained from the basic oxides Bi<sub>2</sub>O<sub>3</sub>, PbO, Fe<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>3</sub> and carbonate CaCO<sub>3</sub> 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 I). After synthesis the samples were rapidly cooled (500 C/h) to room temperature. To enhance the chemical homogeneity, all Nb-doped samples were synthesized during 15 h. The x-ray diffraction patterns were recorded using a diffractometer (DRON-3M) and  $CuK_{\alpha}$  radiation. The data analysis was performed using the FullProf software package. Only 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 and

TABLE I. Crystal symmetry and unit cell parameters of  $Bi_{1-x}A_xFe_{1-x/2}$  $Nb_{x/2}O_3$  (A = Ca, Pb) systems.

x	T <sub>syn</sub> , °C	S. G.	<i>a</i> , Å	$b, \mathrm{\AA}$	<i>c</i> , Å	$\alpha$ , $\beta$ , deg.	<i>V</i> , Å <sup>3</sup>
		E	Bi <sub>1-x</sub> Ca <sub>x</sub> Fe	$e_{1-x/2}Nb_{x/2}$	03		
0	870	R3c	5.630			59.35	124.3
0.15	990	R3c	5.611			59.50	123.5
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	5.452	5.546	7.761		234.7
1	1350	$P2_1/n$	5.439	5.551	7.751	90.01	234.1
		E	Bi <sub>1-x</sub> Pb <sub>x</sub> Fe	$e_{1-x/2}Nb_{x/2}$	$O_3$		
0.1	900	R3c	5.642			59.51	125.6
0.2	900	R3c	5.644			59.53	125.8
0.3	920	R3c	5.649			59.62	126.3
0.4	920	Pm3m	3.991				63.6
0.5	950	Pm3m	3.992				63.7

a <sup>57</sup>Co in Rh source. The spectra were recorded in transmission geometry at room temperature. The Mössbauer spectra were fitted using the NORMOS software. All isomer shifts were related to the  $\alpha$ -Fe standard.

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

The local ferroelectric properties of the samples were investigated using a scanning force microscope in the piezoresponse (PFM) mode. Specifically, a commercial setup NTEGRA Aura (NT-MDT) equipped with an external lockin amplifier (SR-830A, Stanford Research) and a function generator (FG-120, Yokogawa) were used. For detection, a commercial tip-cantilever system, Arrow<sup>TM</sup> Silicon SPM Sensor (Nano World) was used. Domain visualization was performed under an applied AC-voltage of 5V peak-to-peak and a frequency of 50 kHz. The set-up was calibrated using commercial PZT (52/48) films (Inostek).

#### **III. RESULTS AND DISCUSSION**

Solid solutions of the  $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$  ( $0 \le x \le 1$ ) series were studied by x-ray diffraction at room temperature. The refinement of the unit cell parameters of compounds with x < 0.18 was carried out, based on the space group R3c, in which parent BiFeO<sub>3</sub> crystallizes (Table I, Fig. 1). For the x = 0.19 sample, the x-ray diffraction patterns show additional reflections indicating the formation of a superstructure of the type  $\sqrt{2} a_p \times \sqrt{2} a_p \times 2 a_p$ , 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 original 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 a composition with a dominant phase of rhombohedral structure (space group R3c). As the synthesis temperature increases up to 1010 °C, the amount of the rhombohedral phase decreases, whereas the amount of the orthorhombic phase increases. Simultaneously, foreign perovskite phases containing bismuth and iron oxides appear. A sample with x = 0.2 has been obtained in a pure orthorhombic phase at a synthesis temperature of 1010 °C. Its unit cell is well described by the space group *Pbnm* (Table I, Fig. 1). Note that this space group is characteristic of many compounds with perovskite structure, such as LnMnO3 and LnFeO3 (Lnlanthanide). Using this space group, we could describe the unit cell of Ca|Nb doped solid solutions up to x = 0.9 rather well. The volume of the unit cell gradually decreases with increasing Ca content (Table I). The determination of the type of unit cell distortions in the case of  $Bi_{1-x}Pb_xFe_{1-x/2}Nb_{x/2}O_3$ solid solutions is more complicated. A rhombohedral type of distortion (space group R3c) remains up to x = 0.3 (Fig. 2, Table I). For higher lead concentrations the superstructure reflections are no longer observed; the basic reflections in x-ray diffraction patterns are broadened and not well resolved, which strongly complicates the choice of a proper space group. The indication is that the real symmetry is not cubic.



FIG. 1. Observed (circles), calculated (solid line) and difference patterns resulting from the Rietveld analysis of the x-ray powder diffraction data of  $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$ . Bragg reflections are indicated by tick marks.

Varying the synthesis conditions and duration of annealing, we could achieve a notable narrowing of the peaks. However, this effect was marginal. So the average unit cell parameters of the x = 0.4 and x = 0.5 samples were formally refined using the cubic space group  $Pm\bar{3}m$  taking into account that the real symmetry could be lower. In contrast to the Bi<sub>1-x</sub>Ca<sub>x</sub>Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>O<sub>3</sub> series, the doping with Pb|Nb leads to the increase of the volume of the unit cell (see Table I).

The magnetization as a function of magnetic field of the  $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$  compounds is presented at room temperature in Fig. 3. For the parent compound BiFeO<sub>3</sub> (x = 0) the M–H dependence at room temperature shows a metamagnetic-like behavior in magnetic fields above 11 T. A magnetic hysteresis is observed and associated with the metamagnetism, suggesting a first order magnetic transition. Below 11 T both up and down magnetization curves practically coincide and a remanent magnetization is practically absent. According to the Ref. 6, a similar metamagnetic transition takes place in single crystal BiFeO<sub>3</sub> in a magnetic field around 18 T at helium temperature and leads to a release of 0.25 emu/g of additional magnetization. The critical field inducing this transition should decrease with increasing temperature. This is actually observed for  $BiFeO_3$  (Fig. 3). The remanent magnetization and coercive field of the 10% Ca (5% Nb) doped sample, as estimated from the magnetization



FIG. 2. Observed (circles), calculated (solid line) and difference patterns resulting from the Rietveld analysis of the x-ray powder diffraction data of  $Bi_{1-x}Pb_xFe_{1-x/2}Nb_{x/2}O_3$ . Bragg reflections are indicated by tick marks.

curves, evidence a partial collapse of the initial magnetic structure which is also inherent to the parent BiFeO<sub>3</sub>. The spontaneous magnetization reaches a maximum ( $M_s \sim 0.3$  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



FIG. 3. Magnetization as a function of magnetic field for  $Bi_{1\text{-}x}Ca_xFe_{1\text{-}x/2}$   $Nb_{x/2}O_3.$ 

because the Nb ions are diamagnetic. It is important to note that the magnetization for the sample with x = 0.1 is not saturated even under a field of 8 T, thus indicating an incomplete magnetic transition into a new magnetic state. In fact, the magnetization versus field curves for the x = 0.1 and x = 0.15 samples practically coincide above 8 T, i.e., in the magnetic field regime where the new magnetic state would be 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<sub>3</sub> to the homogeneous canted G-type antiferromagnetic ordering, in which a small ferromagnetic component of noncollinear ordered spins yields the spontaneous magnetization.<sup>18</sup> The obtained data indicate that the sample with x = 0.1 possesses a mixed magnetic state whereas the samples in the compositional range of 0.15 < x < 0.2 reveal a homogeneously canted weak ferromagnetic state.

The magnetization versus field dependencies for the  $Bi_{1-x}Pb_xFe_{1-x/2}Nb_{x/2}O_3$  series are depicted in Fig. 4. As can be seen, the substitution of the  $Bi^{3+}$  ions by  $Pb^{2+}$  and the Fe<sup>3+</sup> ions by Nb<sup>5+</sup>, does not lead to the appearance of a significant spontaneous magnetization, however, a very small ferromagnetic component was observed. At low doping levels ( $x \le 0.3$ ; rhombohedrally distorted samples) the magnetization versus field curve is nonlinear in a wide range of



FIG. 4. Magnetization as a function of magnetic field for  $Bi_{1\text{-}x}Pb_xFe_{1\text{-}x/2}$   $Nb_{x/2}O_3.$ 

magnetic field. Apparently, there exists a magnetic hysteresis associated with the gradual destruction of the cycloidal modulated antiferromagnetic structure in an external magnetic field. However, the weakly ferromagnetic state seems to be unstable without an external magnetic field. The heavily doped samples with pseudocubic structure (x > 0.3) exhibit a linear magnetization versus field dependence, which is typical for conventional collinear antiferromagnets. Therefore, we conclude that for solid solutions of  $Bi_{1-x}Pb_xFe_{1-x/2}$  $Nb_{x/2}O_3$  the Pb|Nb doping does not lead to an appreciable release of a spontaneous magnetization and that these compounds have cycloidal spatially modulated spin structures in the absence of external fields. The transition from a modulated antiferromagnetic structure to a homogeneous antiferromagnetic structure can be evidenced by <sup>57</sup>Fe Mössbauer spectroscopy. Indeed, the existence of the spatially modulated magnetic structure results in a specific distribution of hyperfine fields P(B) with two peaks corresponding to the Fe ions with the spins directed along and perpendicular to the propagation wave vector [Fig. 5(d)]<sup>21</sup>. On the other hand, a collinear magnetic structure is characterized by a singlepeak distribution [Fig. 5(b)].<sup>21</sup> The same behavior is observed in <sup>57</sup>Fe nuclear magnetic resonance experiments.<sup>22</sup> The Mössbauer spectra of both rhombohedral Bi<sub>0.82</sub>Ca<sub>0.18-</sub> Fe<sub>0.91</sub>Nb<sub>0.09</sub>O<sub>3</sub> and orthorhombic Bi<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.9</sub>Nb<sub>0.1</sub>O<sub>3</sub> compounds were found to be very similar [Fig. 5(a) and 5(c), respectively]. These spectra show only one component: a sextet attributed to the magnetically-ordered perovskite-type phase. The hyperfine parameters characteristic of the sextet are: an isomer shift of 0.37 mm/s, a quadrupole shift of -0.146(2) mm/s, and a hyperfine field of 47.0 T for the sample with x = 0.18; an isomer shift of 0.37 mm/s, a quadrupole shift of -0.153 mm/s, and a hyperfine field of 47.0 T for the sample with x = 0.2. These data suggest that these compounds contain high- spin  $(t_{2g}^3 e_g^2)$  Fe<sup>3+</sup> ions in octahedral coordination. No other valence state of iron has been detected. The hyperfine magnetic field distribution for both spectra reveals an asymmetric single peak, thus indicating the suppression of a spiral modulation. The asymmetry can be related to a lightly inhomogeneous Nb-ion distribution over the lattice. That is very often observed in diamagnetically diluted magnetic compounds. Therefore, one can conclude that both the rhombohedral and the orthorhombic phase demonstrate a similar magnetic behavior, i.e., the transition into a canted weak ferromagnetic state. The spontaneous magnetizations observed for the polar and nonpolar orthorhombic phases are almost equal, thus indicating the same magnetic structure and mechanism of the magnetic interaction responsible for the magnetization behavior. Hence, it can be suggested that canting of the magnetic moments results from the Dzyaloshinskii-Moriya antisymmetric interaction as it is commonly accepted for the majority of weak ferromagnets.<sup>18</sup> It is worth noting that similar systems doped with large Pb ions do not exhibit a transition into the weak ferromagnetic state (Fig. 4). For example, the weak ferromagnetic state has not been found in the case of  $Bi_{1-x}Ba_xFe_{1-x}Ti_xO_3^{19}$  and of  $Bi_{1-x}Pb_xFe_{1-x}Ti_xO_3^{23}$  compounds within concentration range with x < 0.3 where a rhombohedral ferroelectric phase is realized. In accordance



FIG. 5. Mössbauer spectra (a), (c) and hyperfine field distributions (b), (d) for  $Bi_{1-x}Ca_xFe_{1-x/2}Nb_{x/2}O_3$  samples at room temperature.

with a neutron diffraction study, the  $Bi_{1-x}Pb_xFe_{1-x}Ti_xO_3$  system pertains a cycloidal spatially modulated spin structure in the whole range of rhombohedrally distorted compositions.<sup>23</sup> As it was shown in Ref. 23, the period of the magnetic structure depends on the Pb content and increases from 79 nm to 84 nm for x = 0.1 and x = 0.25, respectively. Therefore, it can be suggested that the type of doping ion is very important for the stabilization of the weakly ferromagnetic state. Taking into account the results obtained in the present work and those reported in the literature<sup>19,23</sup> it is reasonable to assume that the chemical substitutions of the bismuth ions, which lead to a decrease of the initial volume of the unit cell, favor the stabilization of the weak ferromagnetic state within the rhombohedral ferroelectric phase.

Due to the significant conductivity of the samples, a piezoresponse force microscope<sup>24</sup> was used as a suitable tool for studying the local ferroelectric properties of the BiFeO<sub>3</sub> compounds which are doped with Ca- and Nb- ions. In order to improve the reliability of the data, the measurements were made at different parts of the samples. This also eliminates the effect of grain orientation. Well saturated local piezoresponse hysteresis loops were acquired for the parent compound BiFeO<sub>3</sub> under a maximum bias voltage of 50 V (Fig. 6). The measured piezoelectric coefficient  $d_{33}$  of about 65 pm/V (evaluated using commercial PZT samples) is in good agreement with published data.<sup>25</sup> Similar results have been obtained for other granules. Hysteresis loops of the piezoelectric coefficient measured using the same parameters as for the parent compound BiFeO<sub>3</sub> testify to significantly enhanced piezoelectric parameters of the  $Bi_{0.82}Ca_{0.18}$ - $Fe_{0.91}Nb_{0.09}O_3$  compound under a considerably smaller bias voltage (Fig. 6). It is worth noting that the coercive force is much smaller for the doped compound as that of undoped



FIG. 6. Local piezoelectric loops for  $BiFeO_3$  and  $Bi_{0.82}Ca_{0.18}Fe_{0.91}Nb_{0.09}O_3$  at room temperature.

BiFeO<sub>3</sub> compound, thus demonstrating the advantage of doping in regard to applications. The piezoelectric coefficient measured for x = 0.18 ( $d_{33} \approx 120$ pm/V) correlates with the maximal  $d_{33}$  values obtained for Sm-doped BiFeO<sub>3</sub> near the morphotropic phase boundary ( $d_{33} \approx 110$ pm/V for  $x = 0.14^{26}$ ), Tb-doped BiFeO<sub>3</sub> ( $d_{33} \approx 140$ pm/V,  $x = 0.11^{27}$ ) films and ceramic Bi<sub>1-x</sub>La<sub>x</sub>FeO<sub>3</sub> ( $d_{33} \approx 190$ pm/V for  $x = 0.16^{28}$ ). However, these rare-earth doped BiFeO<sub>3</sub> compounds are not homogeneous weak ferromagnets within the polar phase.<sup>28</sup>

The large piezoelectric response as observed for the compound with x = 0.18 is in line with the general notion that ferroelectric properties are maximum for the compositions near a morphotropic phase boundary.<sup>29,30</sup> However, it is worth noting that the compound x = 0.18 is in the single phase rhombohedral structural state, while the orthorhombic phase of x = 0.2 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 known to enhance the piezoelectric properties.<sup>31</sup> The first mechanism is associated with the rotation of the polarization, whereas the second one is related to a polarization enhancement that is appreciable only near the Curie point or near the polar/nonpolar morphotropic boundary.<sup>31</sup> Hence, it is concluded that the large piezoelectric parameters of the Bi<sub>1-x</sub>Ca<sub>x</sub>Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>O<sub>3</sub> compound result from the polarization extension which occurs near the polar-nonpolar morphotropic boundary.

#### **IV. CONCLUSIONS**

We investigated the crystal structure, the magnetic and piezoelectric properties of  $Bi_{1-r}Ca_rFe_{1-r/2}Nb_{r/2}O_3$  and  $Bi_{1-r}$ Pb<sub>x</sub>Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>O<sub>3</sub> solid solutions as prepared by a standard ceramic solid state reaction method. A morphotropic phase boundary between a polar rhombohedral (R3c) and a nonpolar orthorhombic (*Pbnm*) phase was found in the  $Bi_{1-x}Ca_x$  $Fe_{1-x/2}Nb_{x/2}O_3$  system at the doping level x = 0.19. According to magnetization and Mössbauer studies, Bi<sub>1-x</sub> Ca<sub>x</sub>Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>O<sub>3</sub> shows a homogeneous weak ferromagnetic state within the concentration range  $0.15 \le x \le 0.18$  of the polar phase. An enhancement of the piezoelectric activity was observed near the polar-nonpolar morphotropic boundary. According to the magnetization versus field measurements, the Bi<sub>1-x</sub>Pb<sub>x</sub>Fe<sub>1-x/2</sub>Nb<sub>x/2</sub>O<sub>3</sub> solid solutions show cycloidal modulated antiferromagnetic structures within the concentration range ( $0 \le x \le 0.3$ ) of the rhombohedral polar phase. It is suggested that the chemical substitutions of bismuth, which lead to a decrease of the volume of the unit cell, favor the stabilization of the weak ferromagnetic state within the rhombohedral polar phase.

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- <sup>1</sup>M. Fiebig, J. Phys. D: Appl. Phys. **38**, R123 (2005).
- <sup>2</sup>G. Catalan and J. F. Scott, Adv. Mater. **21**, 2463 (2009).
- <sup>3</sup>D. C. Arnold, K. S. Knight, F. D. Morrison and P. Lighfoot, Phys. Rev. Lett. **102**, 027602 (2009).
- <sup>4</sup>I. Sosnowska, T. Peterlin-Neumaier, and E. Steichele, J. Phys. C 15, 4835 (1982).
- <sup>5</sup>I. Sosnowska, M. Loewenhaupt, W. I. F. David, and R. M. Ibberson, Physica B 180, 117 (1992).
- <sup>6</sup>A. M. Kadomtseva, A. K. Zvezdin, Yu. F. Popov, A. P. Pyatakov, and G. P. Vorob'ev, JETP Lett. **79**, 571 (2004).
- <sup>7</sup>G. P. Vorob'ev, A. K. Zvezdin, A. M. Kadomtseva, Yu. F. Popov, V. A. Murashov, and D. N. Rakov, Phys. Solid State **37**, 1793 (1995).
- <sup>8</sup>D. Ricinschi, K. -Y. Yun and M. Okuyama, J. Phys. Condens. Matter 18, L97 (2006).
- <sup>9</sup>G. L. Yuan, S. W. Or, J. M. Liu, and Z. G. Liu, Appl. Phys. Lett. **89**, 052905 (2006).
- <sup>10</sup>S. T. Zhang, Y. Zang, M. H. Lu, Ch. L. Du, Y. F. Chen, Z. G. Liu, Y. Y. Zhu, N. B. Ming, and X. Q. Pan, Appl. Phys. Lett. 88, 162901 (2006).
- <sup>11</sup>V. A. Khomchenko, D. A. Kiselev, E. K. Selezneva, J. M. Vieira, A. M. L. Lopes, Yu. G. Pogorelov, J. P. Araujo, and A. L. Kholkin, Mater. Lett. **10**, 044 (2007).
- <sup>12</sup>I. O. Troyanchuk, M. V. Bushinsky, A. N. Chobot, O. S. Mantytskaya and N. V. Tereshko, JETP Lett. 89, 180 (2009).
- <sup>13</sup>H. Bea, M. Bibes, S. Fusil, K. Bouzehouane, E. Jacquet, K. Rode, P. Bencok, and A. Barthelemy, Phys. Rev. B 74, 020101(R) (2006).
- <sup>14</sup>Y.-K. Jun, W.-T. Moon, C.-M. Chang, H.-S. Kim, H. S. Ryu, J. W. Kim, K. H. Kim, and S.-H. Hong, Solid State Comm. **135**, 133 (2005).
- <sup>15</sup>Y.-K. Jun and S.-H. Hong, Solid State Comm. **144**, 329 (2007).
- <sup>16</sup>G. L. Bras, D. Colson, A. Forget, N. Genand-Riondet, R. Tourbot, and P. Bonville, Phys. Rev. B 80, 134417 (2009).
- <sup>17</sup>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).
- <sup>18</sup>C. Ederer and C. J. Fennie, J. Phys.: Condens. Matter 20, 434219 (2008).
- <sup>19</sup>I. O. Troyanchuk, N. V. Tereshko, A. N. Chobot, M. V. Bushinsky, K. Bärner, Physica B 404, 4185 (2009).
- <sup>20</sup>I. O. Troyanchuk, M. V. Bushinsky, A. N. Chobot, O. S. Mantytskaya, N. V. Pushkarev, and R. Szymczak, JETP **107**, 245 (2008).
- <sup>21</sup>V. S. Pokatilov, V. V. Pokatilov, and A. S. Sigov, Phys. Solid State 51, 552 (2009).
- <sup>22</sup>A. V. Zalesskii, A. A. Frolov, T. A. Khimich, and A. A. Bush, Phys. Solid State 45, 141 (2003).
- <sup>23</sup>T. Stevenson, T. P. Comyn, A. Daoud-Aladine, and A. J. Bell, J. Magn. Magn. Mater. **322**, L64 (2010).
- <sup>24</sup>N. Balke, I. K. Bdikin, S. V. Kalinin, and A. L. Kholkin, J. Am. Ceram. Soc. **92**, 1629 (2009).
- <sup>25</sup>S. Y. Yang, F. Zavaliche, and L. Mohaddes-Ardabili, Appl. Phys. Lett. 87, 102903 (2005).
- <sup>26</sup>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).
- <sup>27</sup>X. Chen, G. Hu, W. Wu, C. Yang, and Xi Wang, J. Am. Ceram. Soc. 93, 948 (2010).
- <sup>28</sup>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).
- <sup>29</sup>D. Damjanovic, N. Klein, J. Li, and V. Porokhonskyy, Functional Materials Letters 3, 5 (2010).
- <sup>30</sup>D. Damjanovic, Appl. Phys. Lett. 97, 062906 (2010).
- <sup>31</sup>E. Aksel and J. L. Jones, Sensors **10**, 1935 (2010).