Electromechanical and magnetic properties of BiFeO$_3$-LaFeO$_3$-CaTiO$_3$ ceramics near the rhombohedral-orthorhombic phase boundary

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Electromechanical and magnetic properties of BiFeO$_3$-LaFeO$_3$-CaTiO$_3$ ceramics near the rhombohedral-orthorhombic phase boundary

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BiFeO$_3$-LaFeO$_3$-CaTiO$_3$ ceramics have been studied by X-ray diffraction, magnetization measurements, and piezoresponse force microscopy (PFM). The compositional ranges of the polar, antipolar, and non-polar phases have been estimated. PFM measurements testify gradual decrease of piezoelectric response in Bi$_{0.85\ x}$La$_{0.15}$Ca$_x$Fe$_{1\ x}$Ti$_x$O$_3$ system with Ca/Ti content increase, except a narrow concentration region near polar-antipolar phase boundary where piezoelectric signal shows maximum value. It is found that increase of dopant concentration leads to apparent decrease of the off-center Bi-O displacement and, consequently, causes a reduction of piezoelectric response. It is concluded that notable remanent magnetization in polar and non-polar structural phases is a result of the Dzyaloshinsky-Moria interaction. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4801960]

I. INTRODUCTION

Remarkable physical properties of the multiferroic compounds based on BiFeO$_3$ attract significant attention in the last years.[1–3] Theoretically predicted improvement of the electromechanical properties of the BiFeO$_3$-based solid solutions near the morphotropic phase boundary (MPB) essentially increased a number of studies on these systems.[4,5] Improved ferroelectric properties of the compounds near the MPB were experimentally attested in a number of studies on Bi$_{1\ x}$RE$_x$FeO$_3$ ceramics and thin films.[6–9]

The highest electromechanical response among the compounds of Bi$_{1\ x}$RE$_x$FeO$_3$ systems was observed so far for La-doped solid solutions of the compositions near the rhombohedral-orthorhombic phase boundary.[9–12] The piezoresponse estimated for Bi$_{0.85}$La$_{0.15}$FeO$_3$ compound was found to be almost three times higher than that for pure BiFeO$_3$ and comparable to piezoelectric activity of Pb(Zr,Ti)O$_3$ (PZT) films.[2,8,9,13,14] Similar evolution of the electromechanical properties of BiFeO$_3$-based solid solutions was found for aliovalent substitution by ions with 2+ valence state. In the case of alkali-earth ion substitution the highest piezoelectric response was also revealed for the compounds close to the MPB.[15,16] In Ca-doped BiFeO$_3$ system ($x \sim 0.1$) the maximum piezoresponse was identified to be 2.5 times higher as compared with pure (undoped) BiFeO$_3$.[15]

The magnetoelectric coupling is another phenomenon of primary importance in BiFeO$_3$, and it also depends on chemical substitution. The magnetic structure of pure BiFeO$_3$ is defined by a cycloidal modulation superimposed on antiferromagnetic G-type structure which can be disrupted by a substitution into the A and/or B-sites of the perovskite

structure. Therefore, the enhanced remanent magnetization can potentially increase magnetoelectric coupling. However, the proposed chemical doping results in a significant leakage problem because of the creation of charged defects, viz., oxygen and/or cation vacancies.[17,18] One of the methods to overcome the leakage increase is a simultaneous co-doping in A- and B-sites by the ions having 2+ and 4+ oxidation states, respectively. Chemical doping according to Bi$_{1\ x}$Ca$_x$Fe$_{1\ x}$Ti$_x$O$_3$ formula was used to prepare highly resistive ceramics with active polar structure and enhanced magnetic properties.[19] The highest magnetoelectric coupling revealed in this system for $x = 0.25$ was observed close to a boundary between rhombohedral and orthorhombic phases. Enhanced ferroelectric properties were also achieved in co-doped multiferroic films Bi$_{1\ x}$Ca$_x$Fe$_{1\ x}$Mn$_x$O$_3$ with the dopants concentration of $x = 0.1$.[20]

There are two major models describing improved electromechanical properties of ferroelectrics at the MPB. According to the first model, enhanced piezoelectric response of the compounds is explained by the increased shear and hence effective longitudinal piezoelectric coefficients; in the second, better electromechanical properties are associated with a softening of the polar phase as a result of instability of the structural phases near the MPB.[21–23]

In present work, we used co-doped Bi$_{0.85\ x}$La$_{0.15}$Ca$_x$Fe$_{1\ x}$Ti$_x$O$_3$ system to follow evolution of the crystal structure, electromechanical, and magnetic properties of the solid solutions across the phase boundary between polar rhombohedral and non-polar orthorhombic phases. To clarify an origin of the enhanced electromechanical response of the ferroelectrics near the MPB, Bi$_{0.85}$La$_{0.15}$FeO$_3$ ceramics with rhombohedral structure close to the rhombohedral-orthorhombic phase boundary was used as a starting compound. Simultaneous doping with Ca and Ti ions is expected to decrease electric conductivity of the compounds, to stabilize the polar rhombohedral phase, and

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TABLE I. The unit cell parameters for Bi$_{0.85-x}$La$_{0.15}$Ca$_x$Fe$_{1-x}$Ti$_x$O$_3$ solid solutions.

	Space group	a (Å)	b (Å)	c (Å)	Volume (per f.u., Å³)	Bi(La) O (Å)	Fe(Ti) O (Å)	Fe(Ti) O Fe(Ti) (deg)
BiFeO$_3$	R3c	5.5714 (5)	5.5715 (5)	13.8502 (7)	62.09	2.27; 2.52	1.95; 2.11	154.9
Bi$_{0.85}$La$_{0.15}$FeO$_3$	R3c	5.5697 (4)	5.5697 (4)	13.7471 (6)	61.55	2.29; 2.52	2.03; 2.02	154.9
Bi$_{0.83}$La$_{0.15}$Ca$_{0.02}$Fe$_{0.98}$Ti$_{0.02}$O$_3$	R3c	5.5678 (6)	5.5678 (6)	13.7449 (8)	61.50	2.30; 2.51	2.02; 2.01	155.9
Bi$_{0.8}$La$_{0.15}$Ca$_{0.05}$Fe$_{0.95}$Ti$_{0.05}$O$_3$	R3c	5.5594 (5)	5.5594 (5)	13.7263 (4)	61.23	2.41; 2.48	1.91; 2.10	155.3
Bi$_{0.75}$La$_{0.15}$Ca$_{0.1}$Fe$_{0.9}$Ti$_{0.1}$O$_3$	R3c	5.5572 (3)	5.5572 (3)	13.6995 (5)	61.06	2.32; 2.47	1.89; 2.21	153.7
Bi$_{0.72}$La$_{0.15}$Ca$_{0.13}$Fe$_{0.87}$Ti$_{0.13}$O$_3$	R3c+	5.5538 (4)	5.5538 (4)	13.6754 (7)	60.88	2.39; 2.45	1.84; 2.29	153.6
	Pnma	5.5529 (7)	7.8243 (5)	5.5629 (8)	60.42			
Bi$_{0.7}$La$_{0.15}$Ca$_{0.15}$Fe$_{0.85}$Ti$_{0.15}$O$_3$	Pnma	5.5217 (5)	7.8254 (7)	5.5609 (4)	60.07			

to improve magnetic properties keeping oxygen stoichiometry and iron ions in a 3+ oxidation state.

II. EXPERIMENTAL

Ceramic samples of Bi$_{0.85-x}$La$_{0.15}$Ca$_x$Fe$_{1-x}$Ti$_x$O$_3$ (x = 0, 0.02, 0.05, 0.1, 0.15) system were prepared by the solid-state reaction technique using high-purity oxides and carbonates taken in a stoichiometric ratio. The powders were thoroughly mixed using a planetary ball mill (Retsch PM 200). Initial BiFeO$_3$ was also prepared as a reference compound at a sintering temperature 870 °C during 10 min. Doped compounds were sintered at 930 1030 °C during 15 h (the synthesis temperature was increased with increasing calcium and titanium content) followed by a fast cooling down to room temperature. The X-ray diffraction patterns were collected at room temperature using DRON-3M and Rigaku D/MAX-B diffractometers with CuK$_\alpha$ radiation. The XRD data were analyzed by the Rietveld method using the FullProf software package.[24] Local ferroelectric and piezoelectric properties were studied by the piezoresponse force microscopy (PFM) using a commercial setup (NTEGRA Prima, NT-MDT). PFM setup was calibrated using commercial PZT (52/48) films (Inostek, Inc.) as a standard. The measurements were performed under an applied *ac* voltage with the amplitude $V_{ac} = 5$ V and frequency $f = 50$ kHz. Piezoresponse versus *dc* voltage hysteresis loops (d$_{33eff}$ (V)) were measured in the pulse mode.[25] Magnetic properties of the samples were investigated with a SQUID-magnetometer (MPMS-5, Quantum Design) and vibrating sample magnetometer (Cryogenic Ltd.).

III. RESULTS AND DISCUSSION

A. Crystal structure

The crystal structure of doped BiFeO$_3$ was analyzed using X-ray diffraction measurements performed at room temperature. The XRD pattern of Bi$_{0.85}$La$_{0.15}$FeO$_3$ solid solution was successfully refined using a rhombohedral space group R3c with the unit cell parameters slightly reduced in comparison with pure BiFeO$_3$ (see Table I). The aliovalent substitution according to Bi$_{0.85-x}$La$_{0.15}$Ca$_x$Fe$_{1-x}$Ti$_x$O$_3$ chemical formula results in the significant changes of the unit cell parameters. A co-doping with Ca and Ti ions causes a decrease of the rhombohedral distortion accompanied with a reduction of the unit cell volume.

It should be noted that in Bi$_{1-x}$La$_x$FeO$_3$ system an increase of dopant content accompanied with a reduction of the unit cell volume (~1%) triggers a structural phase transition. For Bi$_{0.85-x}$La$_{0.15}$Ca$_x$Fe$_{1-x}$Ti$_x$O$_3$ solid solutions the rhombohedral phase remains stable at much lower unit cell volume (see Table I). The crystal structure of the Bi$_{0.85-x}$La$_{0.15}$Ca$_x$Fe$_{1-x}$Ti$_x$O$_3$ is characterized by rhombohedrally distorted lattice up to a concentration of x $\approx$ 0.12
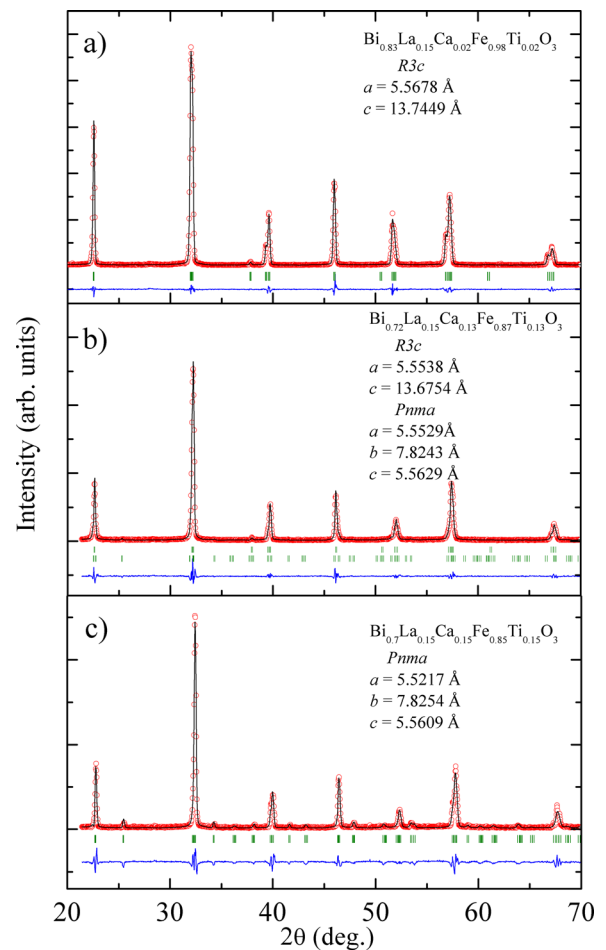

FIG. 1. The XRD patterns obtained for Bi$_{0.85-x}$La$_{0.15}$Ca$_x$Fe$_{1-x}$Ti$_x$O$_3$ compounds at room temperature (circles are experimental data, lines are calculated ones). Bragg reflections are indicated by vertical ticks: (a) the XRD data for x 0.02 compound fitted with R3c space group; (b) the XRD for x 0.13 solid solution refined within two phase model R3c+Pnma; (c) x 0.15, Pnma space group.

(Figure 1). It can be concluded that a co-doping with Ca and Ti ions expands concentration range of the structural stability of the polar rhombohedral phase in contrast to subsequent doping of $BiFeO_3$ with RE ions.[9,26] The concentration phase transition to nonpolar orthorhombic phase is another crucial difference of the Ca/Ti doping strategy.

The XRD patterns of the compounds in the concentration range $0.13 \leq x < 0.15$ were successfully refined using a two-phase model assuming coexistence of the polar rhombohedral and nonpolar orthorhombic phases. The XRD data of the $x = 0.15$ solid solution were considered assuming single *Pnma* space group (Figure 1). Further increase in the dopant concentration leads to a stabilization of the nonpolar orthorhombic phase, and a crystal structure of the compounds with $x > 0.15$ was also refined using *Pnma* space group. Based on the structural data the preliminary phase diagram has been constructed (Figure 2). The structural data for the compounds with chemical compositions not mentioned in the present study but necessary to construct the phase diagram have been taken from our previous works.[9,19,26] The phase diagram shows concentration regions of the structural stability as well as piezoelectric activity of the $Bi_{0.85-x}La_{0.15}Ca_xFe_{1-x}Ti_xO_3$ solid solutions, and the dotted line depicts the compositions under the proposed chemical formula.

Close inspection of the XRD patterns for the compounds near the phase boundary and in the two-phase region did not reveal any evidence of the structural phases with symmetries lower than the above-mentioned ones. Certain broadening and asymmetry of the diffraction peaks was observed for the compound within the rhombohedral phase region with concentration $x = 0.05$. Gradual increase in the grain size of sintered samples with doping as observed by SEM measurements (not shown) cannot give rise to the observed broadening of the XRD peaks for this particular compound. We suggest that the broadening can be caused by nonuniform strain induced by random polar displacements. Most probably, at this concentration a critical amount of defects produced by doping occurs throughout the sample. Similar evolution of the peaks width caused by random polar displacements accompanied with inhomogeneous strains was observed for $Bi_{1-x}Ca_xFeO_{3-x/2}$ solid solutions for concentration $x \sim 0.1$.[15]

B. Piezoelectric properties

The changes in the structural parameters observed in the studied ceramics should inevitably modify ferroelectric and magnetic properties of these solid solutions. The diffraction data testify a decrease of the rhombohedral distortion with doping accompanied by a reduction of the off-center displacement of the A-site ions (Table I). The coordinates calculated for Fe/Ti ions prove an increase of the off-center displacement with dopants concentration. A reduction of the off-center displacement of bismuth ions as well as a decrease in the amount of the polar active ions in A-site position with doping should, in principle, diminish polarization and piezoelectric response in the studied compounds. However, an observed evolution of the electromechanical response for the lightly doped compounds contradicts the expected behavior.

Due to the notable conductivity of the sintered samples, conventional polarization measurements were difficult to perform. Therefore, piezoresponse force microscopy method was used to attest ferroelectric properties of the compounds. Prior to PFM measurements, the surface of the samples was mechanically polished, and the samples were annealed at a temperature of $\sim 500\,°C$ during 1 h to remove residual stress. A switchable character of the polarization was tested by measurements of local piezoresponse versus *dc* voltage dependencies.[27] Local piezoelectric loops were measured in a broad range of the applied bias voltages. The measurements were performed in multiple locations in different grains in order to exclude an apparent effect of grain orientation, and presented data are the averaged ones. All measurements were carried out using the same instrumental setup parameters, so the results obtained for different samples could be directly compared in magnitude.

Well saturated local piezoresponse hysteresis loops were obtained for the initial $BiFeO_3$ under application of high dc bias (up to 70 V) (Figure 3). Almost three-fold increase in the piezoresponse observed for the $Bi_{0.85}La_{0.15}FeO_3$ compound in comparison with pure $BiFeO_3$ is consistent with the recent results reported in Refs. 9 and 11. Structural instability of the rhombohedral phase near the phase boundary and concomitant ease of the polarization extension caused by the free energy flattening can be the main reason of the enhanced electromechanical response.[9,28] Light doping with Ca/Ti ions results in significantly enhanced piezoresponse confirmed by a large number of PFM measurements (Figure 3). The piezoelectric response observed for $x = 0.02$ compound is about 25% higher than the maximum signal obtained for compounds of parent $Bi_{1-x}La_xFeO_3$ system (inset of Figure 3). It worth noting that the measured piezoresponse signal is comparable with that obtained in optimized thick PZT films of the morphotropic phase boundary composition (Inostek, Inc.). Further increase in the concentration of non-polar Ca ions leads to a decrease of the rhombohedral c/a ratio and hence to a rapid reduction in the piezoelectric response. The piezoresponse signal for the composition with $x = 0.05$ is close to that of
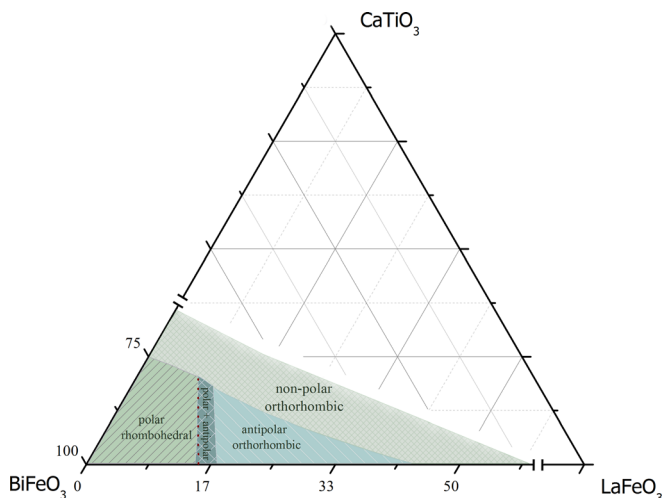

FIG. 2. The part of the structural phase diagram of $BiFeO_3$ $LaFeO_3$ $CaTiO_3$ system showing regions of piezoelectric activity of solid solutions.

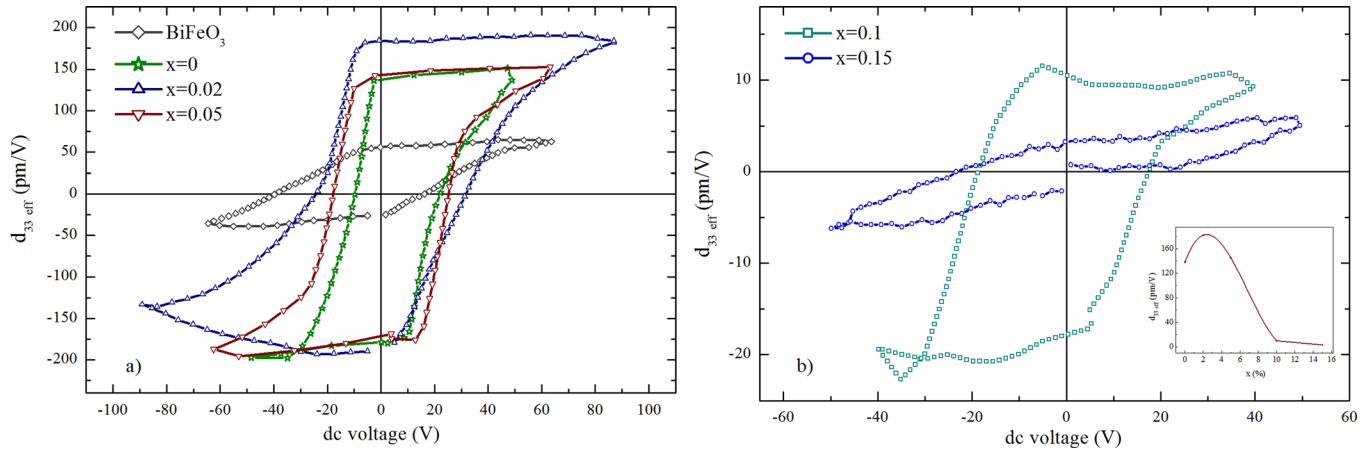FIG. 3. The local piezoelectric hysteresis loops: (a) for initial $BiFeO_3$ and $Bi_{0.85-x}La_{0.15}Ca_xFe_{1-x}Ti_xO_3$ compounds with x = 0, 0.02, 0.05; (b) for x = 0.10 and 0.15 compounds. The dependence of the piezoelectric coefficient on the dopant content is shown in the inset.

the starting compound $Bi_{0.85}La_{0.15}FeO_3$. A small amount of non-polar orthorhombic phase estimated for $x = 0.13$ compound promotes further deterioration of electromechanical response (Figure 3). The piezoelectric response observed for the compounds in two-phase structural region is almost zero (not shown). The PFM measurements for the $x > 0.15$ solid solutions did not reveal any piezoresponse signal over the entire sample surface, which is consistent with the non-polar orthorhombic structure estimated from the diffraction data.

It was noted that the structural changes induced by the chemical substitution with Ca and Ti ions should lead to a decrease of polarization and piezoelectric coefficient, while experimentally observed behavior contradicts to this assumption. It is well known that moderate doping of $BiFeO_3$-based compounds with titanium ions results in an increase of the resistivity via compensation of some Fe^{2+} ions and elimination of oxygen vacancies.[29,30] Therefore, increased resistivity expected for the $x = 0.02$ sample allowed an application of *dc* bias voltage of 100 V during PFM measurements, whereas similar voltage is destructive for the other samples. However, enhanced piezoresponse observed for the $x = 0.02$ sample cannot be explained only by a better poling and is due to the additional contribution to polarization coming from Ti ions with higher polarizability. Higher peizoelectric response observed at the same voltage for $x = 0.02$ sample in comparison with that specific for $x = 0$ compound testifies apparent additional extrinsic contribution to the electromechanical signal.

Assuming the observed evolution of the piezoelectric signal near the phase boundary between polar rhombohedral and anti-polar orthorhombic phases one cannot explain enhanced piezoresponse for these compounds assuming increased longitudinal piezoelectric coefficients near the MPB.[22] The maximal electromechanical response is observed for the $x = 0.02$ compound with pure rhombohedral crystal structure where a flattening of the Gibbs free energy profile is not so pronounced as for the compounds with compositions closer to the phase boundary. High piezoelectric response for the compounds with apparently reduced intrinsic contributions can be explained by significant extrinsic contribution caused by domain wall effects. Most probably, the doping level of $x = 0.02$ promotes optimal domain wall

density which results in the significant contribution to the piezoelectric effect via easier domain walls displacements and related effects.[31,32]

An evolution of the piezoresponse observed for $Bi_{0.85-x}La_{0.15}Ca_xFe_{1-x}Ti_xO_3$ compounds within the rhombohedral range ($x < 0.12$) can be explained by the following reasons. Both flattening of the Gibbs free energy profile near the phase boundary and extrinsic piezoelectric contributions due to enhanced mobility of the domain walls give a contribution to electromechanical response. On the other hand, chemical dilution of the highly polarizable Bi ions with calcium ions and concomitant decrease of the off-center displacement of A-site ions reduce the piezoelectric activity. The trade-off between these trends actually defines the observed dependence.

C. Magnetic properties

Magnetization vs. magnetic field dependencies for the $x < 0.15$ compounds (Figure 4) represent an evolution of the magnetic properties with increasing dopant concentration at
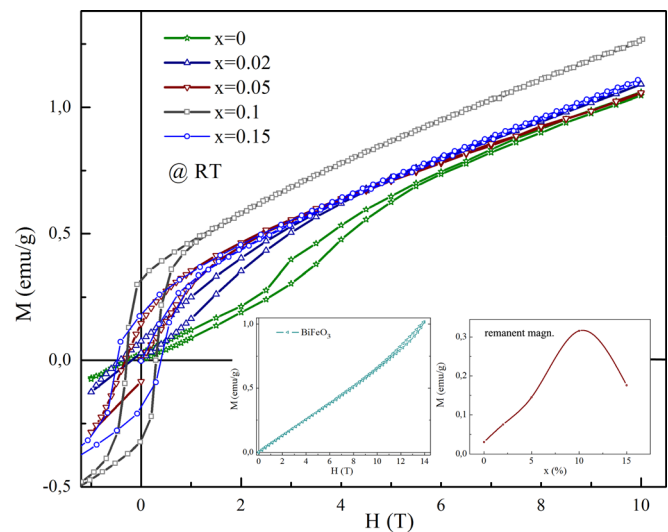

FIG. 4. The magnetic field dependencies of the magnetization obtained for $Bi_{0.85-x}La_{0.15}Ca_xFe_{1-x}Ti_xO_3$ compounds (x = 0, 0.02, 0.05, 0.10, 0.15) at room temperature. The M(H) dependence of $BiFeO_3$ and the evolution of remanent magnetization are shown in the insets.

room temperature. The metamagnetic transition characteristic for pure $BiFeO_3$ at $H_c \approx 130$ kOe (inset of Figure 4) is strongly shifted to lower field for x = 0 compound. Small remanent magnetization (~ 0.03 emu/g) observed for the $Bi_{0.85}La_{0.15}FeO_3$ compound is most probably caused by local inhomogeneities (lattice defects, domain walls) within partly disrupted spatially modulated structure.

Doping with Ca and Ti ions drastically changes magnetic properties of the compounds. The spatially modulated magnetic structure becomes completely destroyed in the x = 0.02 compound, and canted antiferromagnetic structure is stabilized at zero magnetic field. The remanent magnetization increases with doping for the compounds with rhombohedral crystal structure (inset of Figure 4). The maximal value of the remanent magnetization of about 0.3 emu/g observed for the x = 0.1 compound is most probably caused by changes in Fe $3d$ O $2p$ orbital hybridization within antiferromagnetic canted structure.

Doping with nonmagnetic Ti ions in the B-site dilutes magnetic sublattice, whereas this effect becomes pronounced for titanium ions concentrations higher than 10% what is in accordance with data for similar systems.[18,33,34] A doping according to the chemical formula $Bi_{0.85-x}La_{0.15}Ca_xFe_{1-x}Ti_xO_3$ assumes a majority of the iron ions in 3+ oxidation state. A small amount of Fe^{4+} ions possibly generated upon synthesis process cannot contribute to remanent magnetization via Fe^{3+}-Fe^{4+} interactions as was noted in Ref. 35. An increase in the remanent magnetization observed for the compounds in the concentration range $0.02 < x \leq 0.10$ can be explained considering a shift in coordinates of both oxygen and iron ions. As magnetic properties of these compounds are related to the bond overlapping of the oxygen p orbitals and iron d orbitals, the structural changes in the relative positions of corresponding ions modify Fe $3d$ O $2p$ orbital hybridization as well as the remanent magnetization of the compounds. An observed decrease in Fe O bond length estimated for x = 0.1 compound (see Table I) promotes larger spin canting and concomitant remanent magnetization increase. Similar mechanism of magnetization increase was proposed in Refs. 36 and 37 for strained $BiFeO_3$ films.

For the compounds with higher Ca/Ti ions concentration the magnetic dilution effect becomes more pronounced, and gradual magnetization reduction takes place (Figure 4). The magnetization of the compounds in the range $0.02 < x < 0.15$ is characterized by gradual transformation of the remanent magnetic moment across the phase transition from the rhombohedral to the orthorhombic phase, whereas net magnetization is nearly equal for the doped compounds. Continuous changes of the magnetization across the phase boundary testify the same origin of the remanent magnetization in both structural phases. Assuming the magnitude of the magnetization and symmetry constraints for weak ferromagnetism, we conclude that the remanent magnetization in both structural phases is caused by the Dzyaloshinsky-Moria interactions. An origin of the magnetic moments canting is similar to that in rare-earth orthoferrites and is explained by the combined action of the antisymmetric exchange interactions and spin-orbital coupling in accordance with Refs. 38 and 39.

IV. CONCLUSIONS

Simultaneous co-doping with Ca/Ti ions of multiferroic $Ba_{0.85}La_{0.15}FeO_3$ leads to a stabilization of the polar rhombohedral phase of the compounds near the phase boundary. A gradual transformation of the magnetization across the structural transition from the rhombohedral to the orthorhombic phase testifies the same origin of the spontaneous magnetization in both structural phases. An increase of the remanent magnetization observed for x = 0.02 compound can be explained by a change in Fe O orbital hybridization; the magnetic properties of the compounds are described assuming canted G-type antiferromagnetic structure. Weak piezoresponse signal observed for the solid solutions with composition close the $R3c$-$Pnma$ phase boundary is caused by strong reduction of the off-center displacement of the polar active ions. The enhanced electromechanical response observed for the lightly doped compounds can be explained by several mechanisms: (i) more effective poling due to reduced conductivity, (ii) increased longitudinal piezoelectric coefficients caused by a flattening of Gibbs free energy profile near the phase boundary, and (iii) additional extrinsic contribution to piezoelectric response from domain wall effects. Local PFM measurements are able to follow the evolution of electromechanical response across the phase boundaries. The preliminary phase diagram showing concentration regions of the structural stability as well as piezoelectric activity of the $Bi_{0.85-x}La_{0.15}Ca_xFe_{1-x}Ti_xO_3$ solid solutions has been constructed. The results can be useful for further development of magnetoelectric devices based on $BiFeO_3$.

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