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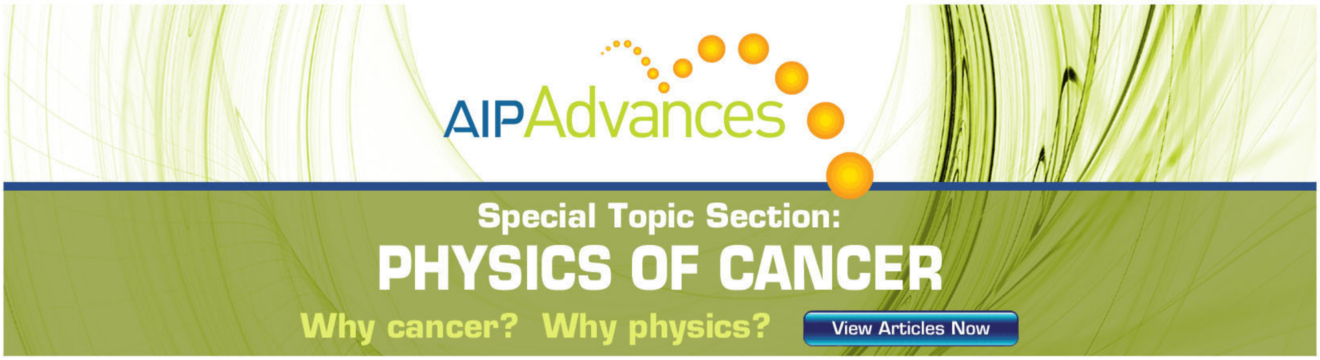

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Rhombohedral-to-orthorhombic transition and multiferroic properties of Dy-substituted $BiFeO_3$

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Investigation of crystal structure, ferroelectric, and magnetic properties of polycrystalline $Bi_{1-x}Dy_xFeO_3$ $(0.1 \leq x \leq 0.2)$ samples was carried out. X-ray diffraction study revealed composition-driven rhombohedral-to-orthorhombic $R3c \rightarrow Pnma$ phase transition at $x \sim 0.15$. Both structural phases were found to coexist in a broad concentration range. Piezoresponse force microscopy found suppression of the parent ferroelectric phase upon dysprosium substitution. Magnetometric study confirmed that the A-site doping induces appearance of a weak ferromagnetic behavior. Both the ferroelectric and magnetic properties were shown to correlate with a structural evolution. © *2010 American Institute of Physics*. [doi:10.1063/1.3486500]

I. INTRODUCTION

Despite the persistent attempts to develop novel single-phase multiferroics, exhibiting simultaneous spin and electric dipole ordering at relatively high temperatures,[1–3] bismuth ferrite,[4] in fact, remains the only noncomposite material (which can be obtained via conventional ceramic technology) with the proven room temperature multiferroic behavior. Below the ferroelectric Curie temperature of 1100 K, $BiFeO_3$ possesses rhombohedral $R3c$ symmetry characterized by antiphase $a^-a^-a^-$ octahedral tilting[5] and off-center ionic displacements along $[111]_C$ direction of the parent cubic perovskite cell.[6,7] Below the magnetic Neel temperature of 640 K, the compound becomes antiferromagnetic with the G-type structure (i.e., each Fe^{3+} ion is surrounded by six nearest neighbors with antiparallel magnetic moments) modified by a long-wavelength spiral modulation.[8] This modulation prevents the presence of any net magnetization and the linear magnetoelectric effect.[9] Lanthanide (Ln) A-site substitution of $BiFeO_3$ is known to suppress the spin modulation to yield a weak ferromagnetism in the $Bi_{1-x}Ln_xFeO_3$ compounds.[10–12]

In spite of the numerous investigations performed for $Bi_{1-x}Ln_xFeO_3$ multiferroics in recent years, a clear understanding of evolution of crystal structure, ferroelectric, and magnetic properties of the solid solutions upon A-site substitution is still not achieved.[11] Recent structural investigation of $Bi_{1-x}Ln_xFeO_3$ $(Ln=La,Nd,Sm,Gd)$ systems[13,14] showed that an antiferroelectric $PbZrO_3$-like orthorhombic structure ($Pbam$ symmetry of $PbZrO_3$ perovskite combines $a^-a^-c^0$ octahedral tilting with antipolar displacements of Pb cations along $[110/\bar{1}\bar{1}0]_C$ directions of the parent cubic cell[15]) can be stabilized at the phase boundary between the rhombohedral $R3c$ and the orthorhombic $Pnma$ structures (the latter is characterized by $a^-b^+a^-$ octahedral tilting), typical of the end members of the $(BiFeO_3)_{1-x}-(LnFeO_3)_x$ series[6,16] (schematic representations of the mentioned structures can be found, for instance, in Refs. 11 and 15). It was found that single-phase compounds with the intermediate antiferroelectric structure can be obtained in Nd-doped and Sm-doped systems in a narrow concentrational range near $x \sim 0.2$ and $x \sim 0.15$, respectively.[13,14] As far as we know, no systematic study of mechanism of the composition-driven $R3c \rightarrow Pnma$ transition in polycrystalline $BiFeO_3$-based series doped by the lanthanides with the smaller ionic radii was carried out so far. To contribute to solution of this problem as well as to investigate peculiarities of multiferroic behavior of the compounds belonging to concentrational range of this phase transition, we performed synthesis and characterization of crystal structure, local ferroelectric and magnetic properties of $Bi_{1-x}Dy_xFeO_3$ $(0.1 \leq x \leq 0.2)$ samples. The results obtained suggest that the concentrational rhombohedral-to-orthorhombic phase transition in $Bi_{1-x}Dy_xFeO_3$ system is realized via the formation of an intermediate structurally-inhomogeneous state to give rise to a ferroelectromagnetic phase separation.

II. EXPERIMENTAL

Polycrystalline samples $Bi_{1-x}Dy_xFeO_3$ $(x=0.1, 0.15, 0.2)$ were prepared by a two-stage solid-state reaction method using the oxides Bi_2O_3, Dy_2O_3, and Fe_2O_3 taken in desired cation ratio. The synthesis was carried out in air in closed alumina crucibles at 850 °C for 6 h and 930 °C for 5

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h with heating/cooling rates of 5 °C/min. A negligible loss (∼0.1%) of the samples weight was detected after the synthesis. It indicates that no significant evaporation of Bi_2O_3 oxide took place during the heat treatment and chemical compositions of the obtained ceramics correspond to nominal values. Phase analysis of the samples and investigation of their crystal structure were performed by x-ray diffraction (XRD) technique using automated Philips PW 1050/35 diffractometer with Cu K_α radiation. XRD patterns were collected over an angular range $20° \leq 2\theta \leq 100°$ with step of 0.02° and exposition intervals of 25 s/step. The data were analyzed by the Rietveld method using the FULLPROF program.[17] Local ferroelectric properties of the samples were investigated with piezoresponse force microscopy (PFM) using a commercial setup NTEGRA Aura (NT-MDT) equipped with an external lock-in amplifier (SR-830, Stanford Research) and a function generator (FG-120, Yokogawa). A commercial tip-cantilever system Arrow™ Silicon SPM Sensor (NanoWorld) was used. Domain visualization was performed under an applied ac voltage with the amplitude $V_{ac}=4$ V and frequency $f=50$ kHz. Magnetic measurements were performed with a superconducting quantum interference device magnetometer (MPMS-5, Quantum Design).

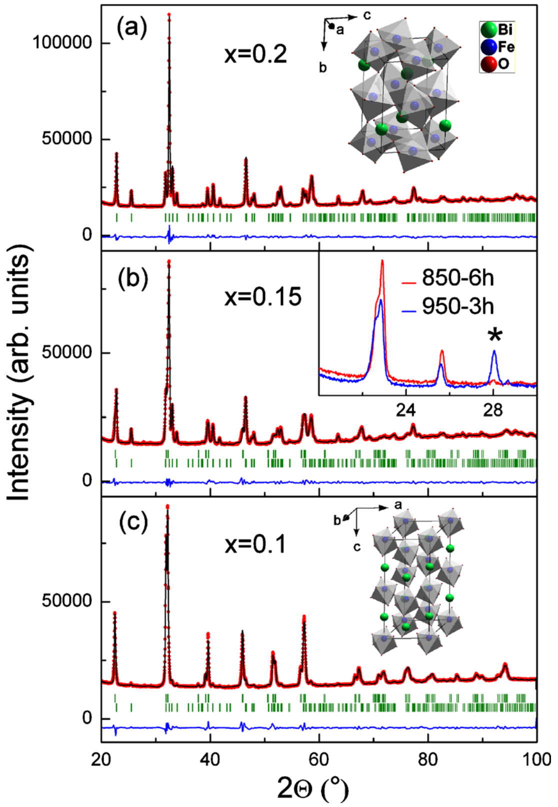

FIG. 1. (Color online) Observed, calculated, and difference XRD patterns for (a) $Bi_{0.8}Dy_{0.2}FeO_3$ (*Pnma* model), (b) $Bi_{0.85}Dy_{0.15}FeO_3$ ($R3c+Pnma$ model), and (c) $Bi_{0.9}Dy_{0.1}FeO_3$ ($R3c+Pnma$ model) samples at room temperature. Insets in parts (a) and (c) show schematic representations of the corresponding dominant structures (*Pnma* and *R3c*, respectively). Inset in part (b) demonstrates the effect of the annealing temperature on the crystal structure of $x=0.15$ compound (* indicates a peak from impurity phase).

III. RESULTS AND DISCUSSION

Rietveld refinement of the diffraction pattern obtained for $x=0.2$ samples confirmed that the compound is single-phase and possesses the orthorhombic $LnFeO_3$-like structure (space group *Pnma*) [Fig. 1(a)]. XRD experiment performed for the $x=0.15$ and $x=0.1$ compounds revealed a more complex character of the diffraction spectra, suggesting a multiphase structural state of these samples [Figs. 1(b) and 1(c)]. A thorough analysis of the spectra allowed us to conclude that the resulting XRD profiles corresponded to a superposition of two main structural components. For $x=0.15$ samples, the dominant contribution (∼70%) is related to an orthorhombic phase typical of $LnFeO_3$ orthoferrites.[16] The second component is attributed to a rhombohedral phase (∼30%) characteristic of $BiFeO_3$.[6] It is worth noting that very slight traces of a $PbZrO_3$-like orthorhombic structure[13,14] were also detected but the corresponding contribution was too small to be taken into consideration during the Rietveld refinement. Attempts to homogenize the structure of the compound by its annealing at higher temperatures result in decomposition of the perovskite phases [see inset in Fig. 1(b)]. Such a behavior is routinely observed in $BiFeO_3$-based compounds, if the synthesis is performed at too high temperature or during too long periods of time.[18,19] The coexistence of the rhombohedral (94%) and orthorhombic (6%) phases is also observed for the $x=0.1$ compound [Fig. 1(c)]. Results of the phase identification performed for the samples annealed at higher temperatures confirmed that $Bi_{0.9}Dy_{0.1}FeO_3$ compound cannot be obtained in a single-phase state. The conclusion is consistent with data of previous structural investigations of $x=0.1$ ceramics.[20,21] Thus, the observed *Pnma*/*R*3*c* phase separation, taking place for $Bi_{1-x}Dy_xFeO_3$ system in a rather broad concentrational range, is not due to inappropriate synthesis conditions and is probably attributed to the large difference in ionic radii of Bi^{3+} and Dy^{3+} ions, hampering the formation of homogeneous solid solutions.[22] The results of the present work confirm the tendency revealed during the previous structural investigations of $Bi_{1-x}Ln_xFeO_3$ multiferroics[14] and suggest that the intermediate $PbZrO_3$-like orthorhombic structure becomes less stable with decreasing ionic radius of the substituting element.

Previous investigations[21,23,24] show that 10%–20% lanthanide substitution does not significantly improve electrical properties of $BiFeO_3$ compound, which is known to be rather leaky. Room temperature dielectric losses ($\tan\delta \sim 0.1$) typical of the substituted compounds remain too high to ignore their influence during a ferroelectric research. Polarization hysteresis loops obtained for the lossy dielectrics,[21,23,24] in fact, say nothing about their actual ferroelectric properties.[25] Taking into account that in a case of the macroscopic *P-E* (polarization versus electric field) measurements intrinsic ferroelectric behavior can be masked by rather large leakage currents characteristic of $Bi_{1-x}Dy_xFeO_3$ multiferroics,[21] ferroelectric investigation of our samples was performed using a PFM, which was proven to be an appropriate technique for the ferroelectric testing of semi-insulating materials.[26,27] PFM measurements of the $Bi_{0.9}Dy_{0.1}FeO_3$ compound revealed the behavior characteristic of ferroelectrics [Fig. 2(a)]. Indeed, a clear piezoresponse was observed on the surface of $x=0.1$ samples (in our experiments, bright and dark

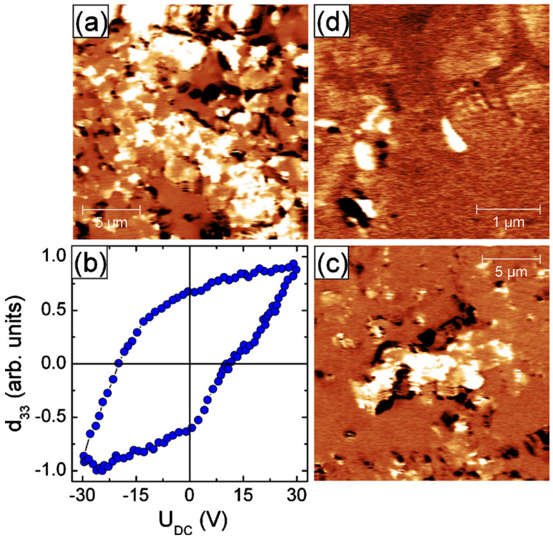

FIG. 2. (Color online) Scanning probe microscopy measurements of $Bi_{1-x}Dy_xFeO_3$ samples at room temperature: (a) and (b) PFM image and local piezoresponse hysteresis loop obtained for the $x=0.1$ compound; (c) and (d) PFM images for the $x=0.15$ and $x=0.2$ compounds, respectively.

contrast corresponded to domains with polarization vectors directed normally to the free surface of the ceramics and to their bulk, respectively). The shape of the PFM hysteresis loops obtained inside individual grains by applying the consecutive voltage pulses and measuring the piezoelectric response as a function of the voltage was typical of ferroelectric materials [Fig. 2(b)]. Local piezoresponse is approximately three times weaker as compared to undoped $BiFeO_3$ ceramics, thus pointing out a smaller value of the spontaneous polarization [the parent compound has the spontaneous polarization $P_S \sim 75\ \mu C/cm^2$ (Ref. 28)]. In accordance with the results of structural study [Fig. 1(b)], a coexistence of the regions demonstrating a distinct PFM contrast with the areas showing a zero piezoresponse was observed for the $x=0.15$ compound [Fig. 2(c)]. Small regions exhibiting the inhomogeneous contrast were also found on the surface of $x=0.2$ samples [Fig. 2(d)]. The contrast regions demonstrate a switchable behavior typical of ferroelectric materials (however, the measured signal is approximately order of magnitude smaller than that characteristic of $x=0.1$ samples). Previous PFM investigations of $Bi_{0.8}Ln_{0.2}FeO_3$ (Ln=Sm, Gd, Dy) compounds gave rather similar results.[11,12,29] Taking into consideration data of the XRD experiments showing no additional reflections, which might be attributed to any secondary phase, it was concluded that the observed polar clusters might have a $Pn2_1a$ structure ($a^-b^-a^-$ tilt system; b axis is polar) with cell parameters very close to those characteristic of the main nonpolar $Pnma$ phase (noncentrosymmetric $Pn2_1a$ and centrosymmetric $Pnma$ space groups give the same reflection conditions[30]). On the other hand, we cannot rule out the possibility that the detected PFM contrast is originated from the clusters having the initial $R3c$ structure characteristic of lightly-doped $Bi_{1-x}Ln_xFeO_3$ compounds (corresponding low-intense diffraction peaks can be completely masked by the reflections from the main orthorhombic phase). It is impossible to distinguish these possibilities in the framework of our experiment: the question about the nature of the polar regions observed in orthorhombic $Bi_{1-x}Ln_xFeO_3$ samples deserves a separate research.

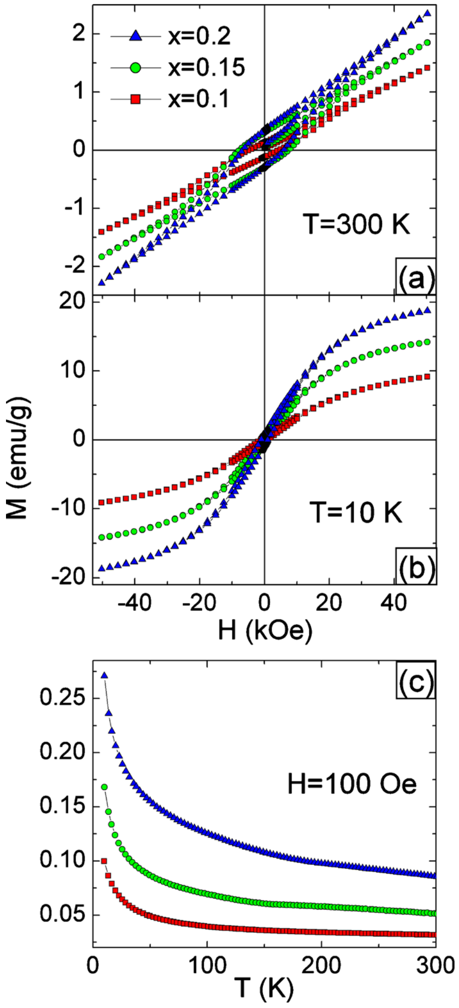

FIG. 3. (Color online) Field dependences of the magnetization obtained for $Bi_{1-x}Dy_xFeO_3$ ($x=0.1, 0.15, 0.2$) samples at $T=300$ K (a) and $T=10$ K (b), and temperature dependences of the magnetization measured at $H=100$ Oe in the field-cooled mode (c).

Magnetometric investigations of the $Bi_{1-x}Dy_xFeO_3$ compounds revealed appearance and enhancement of a room temperature net magnetization with increasing dysprosium concentration [Fig. 3(a)]. It is worth noting that magnetically-active rare-earth (RE) subsystem in $REFeO_3$ ferrites orders magnetically below 5–10 K. Above this temperature, the RE ions are paramagnetic but experience the molecular field of the weak ferromagnetic iron subsystem, which partially magnetizes them.[31] Due to the paramagnetic contribution from Dy ions, the room temperature field dependencies of the magnetization do not exhibit any saturation [Fig. 3(a)]. It is interesting to note that remnant magnetization of $x=0.2$ and $x=0.15$ samples (0.32 emu/g and 0.3 emu/g, respectively) is several times larger that obtained for the $x=0.1$ compounds (0.13 emu/g) possessing a dominant rhombohedral structure. The same feature was also found in La, Nd, Eu, Sm, and Gd-doped compounds,[10–12] thus implying that such a behavior reflects a common tendency observed in $Bi_{1-x}Ln_xFeO_3$. The appearance of the net magnetization in the doped compounds can be understood in terms of the substitution-driven modification of the spiral *G*-type antiferromagnetic ordering characteristic of $BiFeO_3$ to the collinear *G*-type antiferromagnetic structure, in which the canted component of the antiferromagnetically ordered spins becomes measurable.[32] Results of nuclear magnetic resonance and Mössbauer spectroscopy measurements show that suppression of the spatially-modulated spiral spin structure in $Bi_{1-x}La_xFeO_3$ correlates with the substitution-induced structural transformation from a rhombohedral to an orthorhombic phase.[33,34] Recent investigation of crystal structure and magnetic properties of the $Bi_{1-x}Ln_xFeO_3$ (Ln =La, Nd, Eu) compounds suggest that the coexistence of spontaneous magnetization and polarization in these materials is due to the mixed structural state.[10] According to Troyanchuk *et al.*,[10] the doping-driven nonferroelectric orthorhombic phase with the homogeneous weak ferromagnetic spin structure gives rise to the spontaneous magnetization, while the initial ferroelectric antiferromagnetic rhombohedral phase remains responsible for the spontaneous polarization. Results of the present investigation of crystal structure, local ferroelectric and magnetic properties of $Bi_{1-x}Dy_xFeO_3$ samples (i.e., structural phase separation, polar/nonpolar phase separation, and significant increase in the magnetization upon the transition to an orthorhombic phase) are basically consistent with this hypothesis, however, alternative mechanism, consisting in the possibility of existence of an intermediate polar weak ferromagnetic state in $Bi_{1-x}Ln_xFeO_3$ multiferroics ($Pn2_1a$ phase),[11,35] should be also carefully examined during a further research. Moreover, closeness of the remnant magnetization of $x=0.15$ and $x=0.2$ samples as well as rather large remnant magnetization obtained for the $x=0.1$ compound [Fig. 3(a)] give indirect proof that some net magnetization in $Bi_{1-x}Dy_xFeO_3$ can apparently start to develop even in the rhombohedral phase. Dramatic increase in the magnetization takes place with decreasing temperature [Figs. 3(b) and 3(c)]. Field dependencies begin to exhibit some saturation of the magnetization in the highest magnetic fields but remnant magnetization remains extremely small [Fig. 3(b)]. Similar effects, associated with a magnetic contribution from RE ions possessing a large own magnetic moment, were also observed in $Bi_{1-x}Gd_xFeO_3$ system.[11]

IV. CONCLUSIONS

In conclusion, solid-state synthesis and investigation of multiferroic properties of $Bi_{1-x}Dy_xFeO_3$ ($x=0.1, 0.15, 0.2$) ceramic samples were performed. A correlation between the structural, ferroelectric, and magnetic behavior of the compounds was found. The samples possessing the main parent rhombohedral $R3c$ structure are shown to be ferroelectrics. The dysprosium substitution results in $R3c \rightarrow Pnma$ phase transition, which is realized via the formation of an inhomogeneous structural state and is accompanied by a vanishing of ferroelectric behavior and appearance of enhanced magnetization. The results are important from the viewpoint of searching for strategy for the developing $BiFeO_3$-based materials with improved ferroelectromagnetic characteristics and constructing the phase diagram of $Bi_{1-x}Ln_xFeO_3$ multiferroics.

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