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2008 J. Phys.: Condens. Matter 20 155207

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Coexistence of spontaneous ferroelectricity and weak ferromagnetism in $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ perovskite

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Received 9 January 2008, in final form 5 March 2008

Published 25 March 2008

Online at stacks.iop.org/JPhysCM/20/155207

Abstract

Polycrystalline samples with the nominal composition $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ have been studied via x-ray diffraction, Mössbauer spectroscopy, dielectric, magnetic, and local ferroelectric measurements. It has been found that the heterovalent Pb^{2+} substitution in $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_y$ is realized through the formation of oxygen vacancies. The crystal structure of the compound has been shown to be described by the non-centrosymmetric space group $R3c$. Investigations of local ferroelectric and magnetic properties have confirmed that spontaneous polarization and weak ferromagnetism coexist in this material at room temperature. The nature of the weak ferromagnetic moment in this compound is discussed in terms of a doping-induced change in the magnetic anisotropy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Spontaneous magnetic ordering and ferroelectric polarization combined in a single phase material has been a subject of growing interest in both ferroelectric and magnetic scientific communities. Indeed, the coupling between the corresponding order parameters can find numerous applications in multiply controlled devices [1]. Despite their evident technological potential, none of the single phase multiferroic materials has been used in practical applications so far. Typical reasons constricting potential applications of multiferroics are due to either low temperature of the magnetic ordering [2–6] or to weak response to the magnetic field. The latter is the main factor that hampers the application of the most studied multiferroic material BiFeO_3 . Despite the fact that BiFeO_3 exhibits both antiferromagnetic and ferroelectric orders at very high temperatures ($T_N = 643$ K; $T_C = 1143$ K) [7], its long

range cycloidal spin structure [8], incommensurate with the lattice parameters, prevents any net magnetic signal and linear magnetoelectric response being observed [9]. Suppression of this spin configuration has been recognized as a necessary condition for the spontaneous magnetization and the linear magnetoelectric effect in BiFeO_3 [10]. An enhancement of the magnetization has been reported in epitaxial BiFeO_3 films [11], in bulk BiFeO_3 materials under application of a high magnetic field [9, 10, 12], or upon doping [13–20], indicating three possible ways to suppress the spin modulation.

Spontaneous magnetization has been revealed both for BiFeO_3 -based solid solutions doped by the rare-earth (RE) ions possessing their own magnetic moment (for instance, $\text{Bi}_{1-x}\text{RE}_x\text{FeO}_3$, where $\text{RE} = \text{Nd}^{3+}$, Sm^{3+} , Tb^{3+} etc) [14–16] and for diamagnetically doped samples (for instance, $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$, where $\text{A} = \text{La}^{3+}$, Ba^{2+}) [13, 17], whose magnetic properties are entirely determined by the magnetically active iron sublattice. Due to the fact that possible

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superexchange interactions $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ or $\text{Fe}^{3+}\text{-O-Fe}^{4+}$ in these compounds are antiferromagnetic [21], the only intrinsic reason for the appearance of spontaneous magnetization in $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ is a canting of the antiferromagnetic sublattices (weak ferromagnetism) [22, 23]. Taking into account that the value of the net magnetization in these solids depends strongly on the substituting element (in other words, there is a correlation between the ionic radii of the substituting elements and the magnetic properties of the corresponding solid solutions) [24], the $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ compounds doped with diamagnetic ions might be a model object for the investigation of the influence of crystal chemistry on the weak ferromagnetic moment value, thus contributing to the understanding of the relationship between the processing, crystal structure, magnetic properties and magnetoelectric coupling in the BiFeO_3 -based multiferroics.

Net magnetization has been recently reported in Pb^{2+} -doped BiFeO_3 -based compound [24]. In this paper, we present the results of a detailed investigation of the crystal structure, defect chemistry, ferroelectric properties, and magnetization behavior of the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ solid solution and discuss the reasons for the appearance of the doping-induced weak ferromagnetic moment in diamagnetically substituted $\text{Bi}_{1-x}\text{A}_x\text{FeO}_y$ compounds.

2. Experiment

The polycrystalline samples with nominal chemical composition $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ were prepared by a rapid two-stage solid-state reaction method using high-purity Bi_2O_3 , Fe_2O_3 and PbO oxides. The compacted mixture of reagents taken in the desired cation ratios was annealed at 800°C for 30 min in air to obtain a single phase perovskite structure. Final heat treatment was performed at $T = 840^\circ\text{C}$ for 10 min to produce dense ceramics followed by quenching of the samples. The synthesis temperature was close to the melting point of the compound. This rapid synthesis method allowed us to prevent intensive evaporation of Bi_2O_3 and PbO and to obtain a single phase solid solution, as was confirmed by a careful x-ray powder diffraction (XRD) analysis. XRD patterns were collected at room temperature using a Rigaku D/MAX-B diffractometer with $\text{Cu K}\alpha$ radiation. The data were analyzed by the Rietveld method using the FullProf program [25]. Mössbauer measurements were performed using a conventional constant acceleration spectrometer with a ^{57}Co -in-Rh source. The dielectric characteristics were measured in the temperature range from 80 to 400 K using a HP4194A impedance analyzer. Ferroelectric hysteresis loops were obtained with the conventional Sawyer–Tower method using a LT322 oscilloscope (LeCroy). Local ferroelectric properties of the samples were investigated with piezoresponse force microscopy (PFM). PFM measurements were performed with a commercial setup multimode nanoscope IIIA (Veeco) equipped with a lock-in amplifier (SR-830A, Stanford Research) and a function generator (FG-120, Yokagawa). A commercial tip-cantilever system NSG11 (NT-MDT) with a spring constant of 10 N m^{-1} and TiN-coated tip with apex radius less than 10 nm was used. The dielectric and ferroelectric measurements were performed using cylindrical samples with

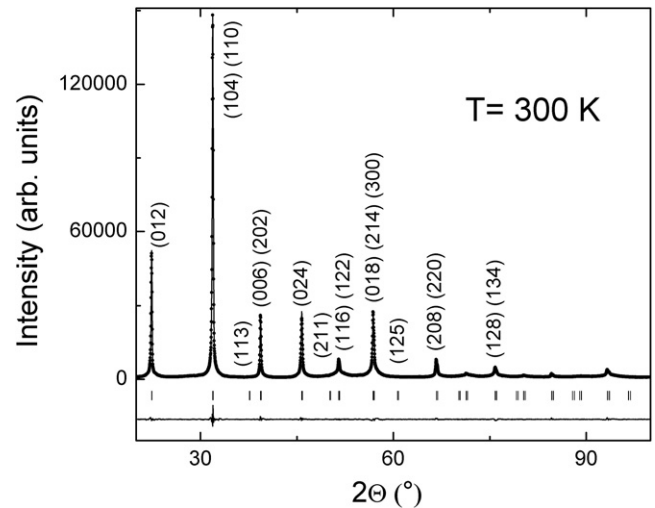


Figure 1. Observed (solid circles) and calculated (solid line) XRD patterns of the Pb-doped sample obtained at room temperature. The difference between these spectra is plotted at the bottom. Bragg reflections are indicated by ticks.

a diameter (d) of 10 mm and a height (h) of 0.8 mm. Measurements of the field dependencies of the magnetization were performed with a SQUID magnetometer (MPMS-5, Quantum Design) using cylindrical samples with $d = 1\text{ mm}$ and $h = 5\text{ mm}$. Ferromagnetic resonance measurements were performed with a Bruker ESP 300E spectrometer equipped with an Oxford Instruments continuous-flow helium cryostat using samples in the form of thin plates $3\text{ mm} \times 3\text{ mm} \times 0.1\text{ mm}$.

3. Results and discussion

The crystal structure of pure BiFeO_3 is known to be described within the space group $R3c$ [26], in which the cations are displaced from their centrosymmetric positions along the threefold symmetric hexagonal $[001]$ axis, thus giving rise to a ferroelectric polarization along this direction. In accordance with the structural data obtained for the parent compound, Rietveld refinement of the x-ray powder diffraction pattern of the Pb-doped sample has been performed using the same space group. The structural model allowed us to reproduce adequately all the observed reflections. Observed and calculated XRD patterns of the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ sample collected at room temperature are shown in figure 1. The diffraction data were fitted with a hexagonal perovskite-type cell with lattice parameters $a = 5.5995(1)\text{ \AA}$ and $c = 13.7274(1)\text{ \AA}$. Unlike a number of publications reporting substitution-induced structural phase transitions to orthorhombic or even triclinic phase in lanthanide-doped samples [13–15], no splitting or extra reflections indicative of the necessity to reduce the lattice symmetry of the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ compound were detected. In spite of the fact that the ionic radius of the Pb^{2+} ions is appreciably bigger than that of the Bi^{3+} ones [27], the unit cell volumes of the Pb-doped compound ($V = 372.75(5)\text{ \AA}^3$) and pure BiFeO_3 samples ($V = 372.5\text{--}374.3\text{ \AA}^3$ [28, 29]) are very similar. This can be explained by taking into account that

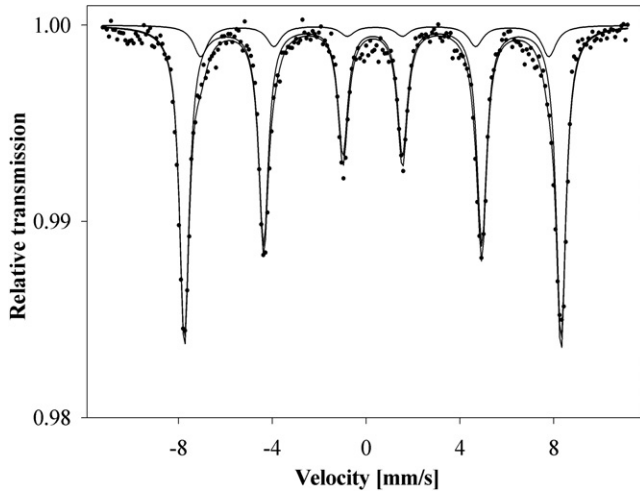
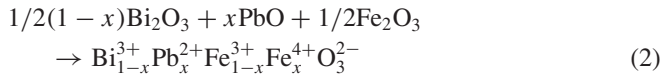
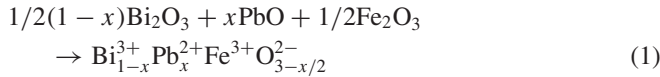


Figure 2. Mössbauer spectrum for the Pb-doped sample at room temperature.

the heterovalent Bi^{3+} to Pb^{2+} substitution in $\text{Bi}_{1-x}\text{Pb}_x\text{FeO}_3$ requires the appearance of oxygen vacancies or/and Fe^{4+} ions in the host lattice, thus leading to the unit cell reduction.

The corresponding models of the defect chemistry:



have been tested with Mössbauer spectroscopy measurements. If the substitution is realized through the appearance of Fe^{4+} ions, the Mössbauer spectrum of the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ sample should contain two subspectra corresponding to Fe^{3+} ($\sim 80\%$) and Fe^{4+} ($\sim 20\%$) in an octahedral coordination. In the magnetically ordered phase, the subspectra should be distinguished both by the value of the hyperfine field (~ 50 T for Fe^{3+} and ~ 40 T for Fe^{4+}) and by the isomer shift (0.05 – 0.5 mm s^{-1} for Fe^{3+} and -0.15 – 0.05 mm s^{-1} for Fe^{4+} (relative to the α -Fe standard)) [30]. In the case of the oxygen vacancies model, the subspectra corresponding to Fe^{3+} in octahedral and pentahedral coordinations should have very similar parameters. The Mössbauer spectrum obtained for the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ compound at room temperature consists of two six-line magnetic hyperfine patterns (figure 2), indicating that the sample is in a magnetically ordered state. The Zeeman sextets were fitted with hyperfine fields of $H_1 = 50$ T and $H_2 = 46.1$ T and isomer shifts of $\delta_1 = 0.394$ mm s^{-1} and $\delta_2 = 0.484$ mm s^{-1} (the spectral fractions of the sextets with hyperfine fields of 50 T and 46 T were about 88% and 12%, respectively). The values are typical of the high-spin Fe^{3+} [30]. No indication of the presence of Fe^{4+} in the lattice was detected. Thus, the results of the Mössbauer spectroscopy experiment support the hypothesis that the Pb^{2+} substitution in $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_3$ is realized through the formation of oxygen vacancies (we believe that the minor spectral contribution corresponds to Fe^{3+} ions in non-octahedral coordination), so the correct chemical formula of the investigated sample should be written as $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$.

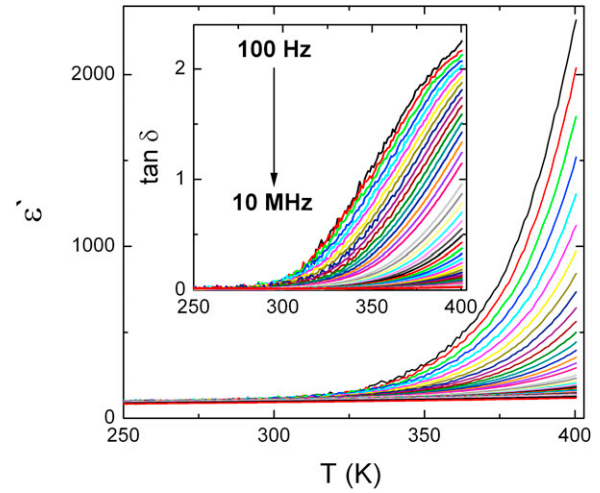


Figure 3. Temperature dependence of the dielectric constant and dielectric loss (in the inset) for the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ sample at different frequencies.

The presence of the oxygen vacancies in the lattice of the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ perovskite manifests itself in the frequency/temperature dependencies of the dielectric permittivity and loss factor (figure 3) where both of these quantities sharply increase with decreasing frequency or increasing temperature. The behavior can be qualitatively explained in the following way [15, 31]: the oxygen vacancy-related dipoles follow the alternating field at low frequencies, providing high values of ϵ' , but lag behind the field in the high frequency range, giving $\epsilon'_\infty \sim 100$ (at room temperature), which is comparable with that observed in pure BiFeO_3 and isovalently substituted $\text{Bi}_{1-x}\text{RE}_x\text{FeO}_3$ ceramics [14, 15]. The increase in the apparent dielectric permittivity and loss factor with increasing temperature is then related to the thermally induced enhancement of the conductivity contribution.

Measurements of the ferroelectric hysteresis loops by the conventional Sawyer–Tower method have been undertaken to confirm the existence of spontaneous polarization in the studied samples at room temperature, but no saturation of the polarization has been observed up to the fields of dielectric breakdown (~ 100 kV cm^{-1}). This is quite typical of the polycrystalline BiFeO_3 -based materials which are commonly known to possess very high coercive fields [32]. Due to the fact that no definitive conclusion proving the existence of spontaneous polarization in the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ sample could be made on the basis of the P – E measurements, we have used the PFM technique (see, e.g. [33] and references therein) for the visualization of the ferroelectric domain structure in this material to clarify this question. The PFM method is based on the detection of thickness oscillations of ferroelectric materials under an *ac* voltage applied between the conductive tip and the bottom electrode. The amplitude of the vibration signal provides information on the magnitude of the effective piezoelectric coefficient, while the phase signal determines the polarization direction. Domains with oppositely oriented polarization are distinguished by a different contrast on the PFM image. In our experiment, domain

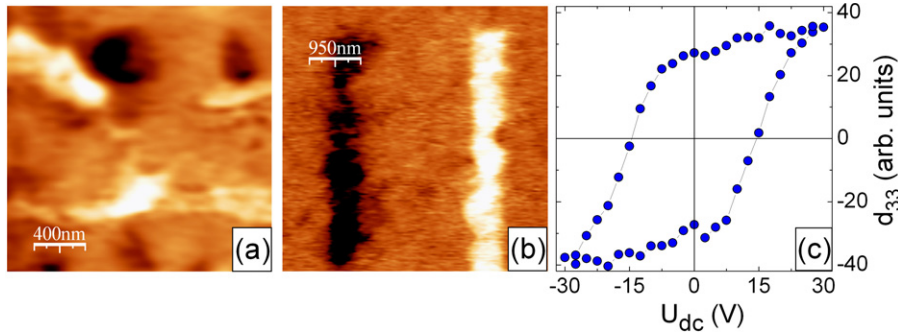


Figure 4. Piezoresponse force microscopy measurements of the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ sample: (a) PFM image showing the ferroelectric domains; (b) electric-field-induced PFM contrast; (c) local piezoresponse hysteresis loop.

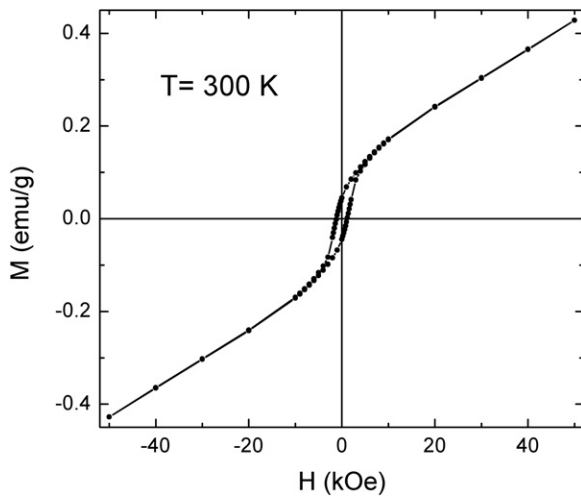


Figure 5. Field dependence of the magnetization for the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ compound at room temperature.

visualization was performed under an applied *ac* voltage with amplitude $V_{ac} = 2.5$ V and frequency $f = 50$ kHz. It has been found that areas with intermediate contrast corresponding to regions with defect structure suppressing any PFM signal coexist with areas exhibiting clear piezoresponse (figure 4(a)). In spite of the appreciable roughness of the surfaces, masking the contribution of the piezoelectric deformation to the PFM contrast, only weak correlation is found between the topography and piezoresponse, pointing to a weak contribution of the electrostatic signal. Piezoelectric contrast appears also after scanning with a *dc* voltage (± 10 V) applied to the tip (figure 4(b)). This provides an additional proof that the spontaneous polarization can be switched upon application of an electric field and that the induced polarization is quite stable. The existence of ferroelectric polarization was also confirmed by local piezoresponse hysteresis loop measurements (figure 4(c)) in which the application of consecutive voltage pulses causes clear polarization reversal as judged from the measured local piezoelectric signal.

Unlike pure BiFeO_3 , which exhibits a linear magnetization versus magnetic field dependence in accordance with its antiferromagnetic nature [28], a $M(H)$ curve obtained for the Pb-doped sample indicates the existence of a spontaneous magnetization (0.1 emu g^{-1}) at room temperature

(figure 5). The magnetic properties of the diamagnetically doped $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ compound are entirely determined by the magnetically active iron sublattice. Due to the fact that the superexchange interaction $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ is antiferromagnetic, the only intrinsic reason for the appearance of spontaneous magnetization in $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ is a canting of the antiferromagnetic sublattices through weak ferromagnetism [22, 23], permitted by the $R3c$ symmetry if the magnetic moments of the Fe^{3+} ions are oriented perpendicular to the [001] axis [34]. The net magnetization originating from the canting can naturally exist only if the spin modulation peculiar to BiFeO_3 is suppressed [34]. Thus, the discovery of spontaneous magnetization in $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ confirms that doping with A-site impurities can change the anisotropy constant to an extent that the presence of a spatially modulated structure becomes energetically unfavorable, as was recently proposed in order to explain the appearance of the doping-induced magnetization in the BiFeO_3 - PbTiO_3 -based ceramics [20].

In BiFeO_3 , as in the common case of the transition metal-based compounds, the interaction energy of the orbital moment of 3d-electrons with an external magnetic field, Δ_H , is significantly less than the value of the crystal field-induced level splitting, Δ_{cryst} [35]. This means that the magnetic field is only a weak perturbation in comparison with the electric field of the crystal lattice. It is thus not able to influence the orientation of the orbital moment, so that the total magnetic moment contains only the spin moment contribution. However, the spin-orbit interaction with energy Δ_{LS} ($\Delta_H < \Delta_{\text{LS}} < \Delta_{\text{cryst}}$) prevents the complete ‘freezing out’ of the orbital moment and induces a minor magnetic moment [$\sim(\Delta_{\text{LS}}/\Delta_{\text{cryst}})\mu_B$] related to the electron orbital motion. This moment determines the orientation of the spin moment in the crystal lattice, thus causing magnetic anisotropy. Thus, the magnetic anisotropy in the spin magnets is the result of the joint action of the anisotropic crystal field and spin-orbit interaction [35]. The appearance of the spin-orbit interaction-induced magnetic moment will evidently shift the *g*-factor from the value predicted for the spin-only moment ($g = 2.0023$). This shift is actually observed in the ferromagnetic resonance experiment performed on $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ ceramics (figure 6). The *g*-factor, calculated in accordance with the relation $g = h\nu/(H_{\text{eff}}\mu_B)$, where h is Planck’s constant, ν the resonance frequency, H_{eff} the effective magnetic field, and μ_B the Bohr magneton, is equal to 2.49. The result

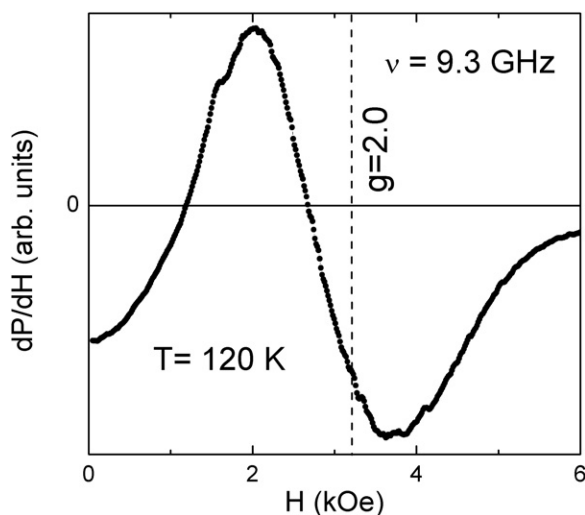


Figure 6. FMR spectrum of the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ compound at $T = 120$ K. The vertical line corresponds to the calculated position for $g = 2$.

conforms to the increase of the g -factor above the spin-only value peculiar to BiFeO_3 and the simultaneous appearance of spontaneous magnetization in La-doped BiFeO_3 [36]. Thus, having an influence on the parameters controlling the magnetic anisotropy in the spin magnets, A-site doping can induce a transition from a spatially modulated G-type antiferromagnetic spin structure to a homogeneous weak ferromagnetic state. In the light of a correlation observed between the ionic radii of the substituting elements and the magnetic properties of the corresponding $\text{Bi}_{1-x}\text{A}_x\text{FeO}_y$ solid solutions [24], the role of the crystal and defect chemistry in the initiation of this transition should be investigated in future in more detail.

4. Conclusions

In this work, we report on the observation of coexisting spontaneous ferroelectric polarization and weak ferromagnetism in a Pb-doped BiFeO_3 -based perovskite. Polycrystalline $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ samples were investigated by x-ray diffraction, Mössbauer spectroscopy, dielectric spectroscopy, magnetometry, piezoresponse force microscopy, and ferromagnetic resonance techniques. X-ray diffraction data show that the $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ is crystallized in the perovskite structure described by the space group $R3c$. Mössbauer spectroscopy measurements confirm that the Pb^{2+} substitution results in the formation of oxygen vacancies in the lattice. Piezoresponse force microscopy data reveal the existence of spontaneous polarization in the compound at room temperature. Magnetic studies indicate that net magnetization is also present at room temperature. The origin of the weak ferromagnetic moment in $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{FeO}_{2.9}$ samples is explained by doping-induced changes in the magnetic anisotropy.

Acknowledgments

The authors thank Dr M Maglione for help in performing the dielectric measurements and useful discussions.

V A Khomchenko is grateful to the Foundation for Science and Technology of Portugal (FCT) for financial support (grant SFRH/BPD/26163/2005). The work was done within the EC-funded project ‘Multiceral’ (NMP3-CT-2006-032616) and the Network of Excellence ‘FAME’ (NMP3-CT-2004-500159).

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