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Structural evolution and magnetic properties of $Bi_{0.86}Nd_{0.14}Fe_{1\mbox{-}x}Ti_xO_3$ ceramics

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ABSTRACT

Ceramic $Bi_{0.86}Nd_{0.14}Fe_{1-x}Ti_xO_3$ (0.02 $\leq x \leq 0.1$) compounds were prepared to study the structural evolution, microstructure, and magnetic properties. The structural analysis by X-ray diffraction and Rietveld refinement revealed a coexistence of the polar rhombohedral (*R3c* symmetry) and antipolar orthorhombic (*Pbam* symmetry) structures over the entire composition range, while Raman scattering spectroscopy detected not only the phonon vibrations of the *R3c* and *Pbam* but also the *Pbnm* symmetries. The microstructure investigation showed the small and large grain size regions corresponding to the *R3c* and *Pbam/Pbnm* phases, respectively. The dependence of magnetization on the Ti concentration suggested that the weak ferromagnetism observed in the compounds arised from the intrinsic collapse of cycloidal order rather than defect-induced magnetism. The magnetic aging observed at room temperature was explained on the basic of phase switching and spin frustration at the phase boundary. The influence of phase switching induced by an external electric field on the magnetic properties was also studied to reveal the contribution of phase boundary spins to the net magnetization.

1. Introduction

A simultaneous combination of ferroelectricity and ferromagnetism of BiFeO₃ (BFO) above room temperature is fascinating in the research of multiferroic materials to make possible applications in novel multifunctional devices [1,2]. This compound has a noncentrosymmetric rhombohedral structure with space group R3c, permitting the polar ionic displacements along the [111] direction [3]. The polar displacement induced by the stereochemical activity of Bi³⁺ lone pair electrons provides a very large spontaneous polarization of 100 μ C cm⁻¹ and high Curie temperature T_C (~1100 K) [4]. Nevertheless, the groundstate cycloidal-type antiferromagnetic structure with an incommensurate period of about 62 nm in the bulk BFO seriously limits the net magnetization and magnetoelectric coupling [5,6]. Thus, an improvement of the magnetic properties is a key for practical use of BFO. In general, the weak ferromagnetism arising from the antisymmetric spin coupling can be observed by suppressing the cycloidal spin structure via epitaxial strain [7], chemical substitution [8,9], or particle size-reduction

[10]. In addition, recent investigations on the correlation between the crystal structure and magnetic properties have shown an improvement of magnetization at a morphotropic phase boundary (MPB) [11-13]. The enhancement of magnetic properties in the vicinity of MPB has been ascribed to several mechanisms, such as the percolating exchange pathway of Nd element and Fe ions [11], the superior magnetization of the bridging phase [12,14], and the phase boundary ferromagnetism [15,16]. It is worth mentioning that the magnetization enhancement is not only observed with the substitution of magnetic elements but also with nonmagnetic element doping [17]. Actually, the magnetic properties of BFO-based compounds are mainly related to the structural phase evolution rather than other mechanisms [12,14,18]. Therefore, the percolating exchange pathway between dopant and Fe ions is possibly not a universal behavior for explaining the enhancement of the magnetization in the diversity of MPB systems. The evolution of magnetic properties in Ref. 11 can be explained by considering the reorientation of magnetic dipoles as the phase transition from the PbZrO3-type to Pbnm structures [19]. A hypothesis of the higher magnetization of the bridg-

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ing phase (e.g., *Pna2*₁ symmetry) than other phases may be not suitable to elucidate the magnetic properties of other MPB systems [20–23]. It is reasonable to consider the ferromagnetic ordering at the phase boundary (PB) because the difference in the magnetic structure and magnetic anisotropy of two phases can rise the frustration of spins via the percolating exchange interaction through the PB. In the vicinity of MPB, we have observed the exchange bias effect [16], vertical hysteresis shift [24], field step-dependent hysteresis loop [15,16], and magnetic aging behavior [25]. These observations can only be fulfilled by considering the existence of the PB spins and magnetic interaction of the PB spins with the antiferromagnetic ground-state of material. Besides the aforementioned mechanisms, the defect chemistry also plays a critical role in the emergence of the weak ferromagnetism in BFO-based ceramic compounds [26,27]. The remanent magnetization induced by cation vacancies is about 0.25 emu/g which is comparable to that of the collapse of the cycloidal spin structure of BFO under a high magnetic field [28]. Considering the Nd and Ti codoped BFO, few studies regarding the connection between the structural evolution and magnetic properties have been reported [11,28,29]. In addition, there is no consensus regarding the origin of the weak ferromagnetic behavior in Nd and Ti codoping compounds [11,28]. Thus, in this work, we investigated the crystal structure, microstructure, and magnetic properties of $Bi_{0.86}Nd_{0.14}Fe_{1-x}Ti_xO_3$ (0.02 $\leq x \leq 0.1$) polycrystalline ceramics. The phase coexistence of the polar rhombohedral (R3c symmetry), antipolar and nonpolar orthorhombic (Pbam and Pbm symmetries) structures was revealed by a combination of X-ray diffraction, Rietveld refinement, and Raman scattering spectra. The magnetic studies showed the weak ferromagnetism arising from the collapse of the cycloidal spin structure, eliminating the interplay of the cation vacancies on the magnetic properties of our samples. The influence of the isothermal structural transition and electric field-induced phase transition on the magnetic properties was also investigated in detail.

2. Experimental details

The samples of $Bi_{0.86}Nd_{0.14}Fe_{1-x}Ti_xO_3$ (BNFTO) with x varying from 0.02 to 0.1 were prepared by a conventional solid-state reaction using high-purity oxides Bi₂O₃, Nd₂O₃, Fe₂O₃, and TiO₂. The reagents were taken in a specific composition, mixed, carefully ground, and pressed into pellets. The samples were synthesized at 900 °C in air for 24 h. Then, the samples were re-ground, pressed into pellets, and finally sintered in air at 960 °C for 12 h. X-ray diffraction (XRD) patterns were measured by using a D2 Phaser diffractometer equipped with a Cu-K α radiation source ($\lambda = 1.5405$ Å). Raman scattering (RS) spectra were collected by using an XploRa-Plus micro-Raman spectrometer with an excitation wavelength of $\lambda = 532$ nm. The morphology of the samples was examined by scanning electron microscope (Hitachi S - 4800). The XRD data were analyzed by the Rietveld method using the GSAS-2 program. Magnetization measurements were performed in a VSM LakeShore 7400. All investigations were carried out at room temperature. The BNFTO samples was stored in the laboratory condition with controlled relative humidity of 40–50% and temperature (T \sim 300 K). The electric poling process was done by applying a high voltage supply between parallel-plate electrodes, where the sample was placed between them.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BNFTO samples with various Ti contents. All the major peaks of the x = 0.02 sample can be indexed to the *R3c* rhombohedral structure (isostructural with BiFeO₃) [8]. In comparison to the standard pattern of BFO, the double peaks at 20 around 32° merge into a single peak. Such type of peak merging implies a phase coexistence of the rhombohedral and orthorhombic structures [30]. Indeed, the XRD peaks of the BNFTO samples at 20 around 22.7,



Fig. 1. Room temperature XRD patterns of BNFTO samples.

28.9, 40.1, and 46.5° belongs to diffraction peaks of the Pbam orthorhombic structure, as denoted in Fig. 1. The previous reports revealed that the Bi1-vNdvFeO3 compounds have two polymorphs of the polar rhombohedral-antipolar orthorhombic (R3c-Pbam) and antipolar orthorhombic-nonpolar orthorhombic (Pbam-Pbnm) structures at around 10% and 16% Nd doping concentration, respectively [14,19,31]. So, the substitution of Ti at the Fe site of the Bi_{0.86}Nd_{0.14}FeO₃ compound possibly contains a nonpolar Pbnm orthorhombic structure. Unfortunately, Fig. 1 shows no trace of the diffraction peak profiles of the nonpolar Pbnm symmetry [31]. The BNFTO compounds thus presents a biphasic of the R3c and Pbam symmetries, which is general consensus with previous reports [11,14]. Besides the aforementioned phase mixture, a small amount of Bi₅FeTi₃O₁₅ impurity (Aurivillus phase) is observed in the samples with $x \ge 0.06$ (marked by the circle symbol). In general, the impurity phase generally hampers the multiferroic properties of BFO-based compounds. But, the Bi₅FeTi₃O₁₅ impurity is a multiferroic material and often appears in Ti doped BFO-based compounds [32,33]. Therefore, a composite of two multiferroic materials would enhance the multiferroic properties of our samples. To further clarify the current phase mixture, the crystal structure of all the samples is refined by using the Rietveld refinement approach for XRD patterns of the BNFTO samples. The refinement is performed adopting the R3c + Pbam models for x = 0.02-0.04 and $R3c + Pbam + A2_1am$ models for x = 0.06-0.1 samples, where the A21am is the crystal symmetry of Bi5FeTi3O15 impurity. The typical refinement results obtained for x = 0.02 and 0.1 samples are shown in Fig. 2. The lattice parameters and phase percentage are listed in Table 1. It is seen in Fig. 2 that all the diffraction peaks are well fitted to the suggested phase models, as indicated by the Bragg peaks (vertical bars) and the residue (solid lines). According to the refinement results, the percentage of the R3c phase reduces from 56% for x = 0.02-38% for x = 0.1, while that of the *Pbam* phase increases from 44% to 55% with an increase in Ti concentration. Therefore, the substitution of Ti ions for Fe ions in the Bi_{0.86}Nd_{0.14}FeO₃ compound can retain the biphasic state in the composition range of $0.02 \le x \le 0.1$ and thus it influences strongly the distortion of the crystal lattice of the R3c and Pbam phases. The incorporation of Ti⁴⁺ ions into the Bi_{0.86}Nd_{0.14}FeO₃ lattices allows the investigation of the structural distortion, microstructure, and magnetic properties, which would highly differ in the physical properties in



Fig. 2. Rietveld refined XRD patterns of (a) x = 0.02 and (b) x = 0.1 samples.

Table 1

The crystal symmetry and lattice parameters of $^{Bi0.86Nd0.14Fe1-xTixO3}$ compounds. The $A2_{1}am$ space group corresponding to the $Bi_{5}FeTi_{3}O_{15}$ impurity.

Composition	Space group	a (Å)	b (Å)	c (Å)	V (Å) ³
x = 0.02	R3c (56%)	5.5692	5.5692	13.8169	371.14
	Pbam (44%)	5.5938	11.2003	7.8209	489.99
x = 0.04	R3c (54%)	5.5722	5.5722	13.8156	371.48
	Pbam (46%)	5.5981	11.2126	7.8245	491.15
x = 0.06	R3c (49%)	5.5708	5.5708	13.8167	371.35
	Pbam (48%)	5.5999	11.2148	7.8258	491.48
	$A2_1 am$ (3%)	5.4577	5.4120	40.8951	1207.92
x = 0.08	R3c (46%)	5.5707	5.5707	13.7958	370.76
	Pbam (49%)	5.5994	11.2088	7.8497	492.66
	$A2_1 am$ (5%)	5.4572	5.4105	40.8931	1207.41
x = 0.1	R3c (38%)	5.5697	5.5697	13.7947	370.61
	Pbam (55%)	5.5999	11.2062	7.8514	492.71
	A2 ₁ am (7%)	5.4563	5.4095	40.8961	1207.08

comparison with Ti induced defect chemistry in $B_{1-y}Nd_yFeO_3$ compounds [26,28,31,34].

RS spectra have been proved to be a very useful method to study the structural evolution. Any change in the frequency, bandwidth, intensity, and number of Raman modes reflects the modulation of crystal structure or structural transition. To further confirm the phase coexistence in the BNFTO compounds, we measured the RS spectra of all samples at an excitation wavelength of 532 nm. Fig. 3 shows the results for RS spectra of two-phase coexistence and the inset Fig. 3 reveals the RS spectra of $Bi_5FeTi_3O_{15}$ impurity [35]. All the Raman peaks in Fig. 3 can be well classified into nine representative modes for the *R3c* phase in the frequency ranging from 60 to 700 cm⁻¹, which is in good agreement with the previous report [11]. No individual Raman mode of the *Pbam*



Fig. 3. RS spectra of BNFTO samples. The inset shows the RS spectra of $Bi_5FeTi_3O_{15}$ impurity phase measured for x = 0.1 sample.

symmetry is relevant in Fig. 3. This implies that the phonon vibration of the R3c and Pbam symmetries strongly overlaps in the Raman spectra of BNFTO samples, which inhibits the observation of individual modes for each symmetry at the MPB [11,24]. According to group theory, the R3c rhombohedral symmetry of BFO has 13 Raman active modes but the angular dispersion of oblique phonon modes in BFO dedicates a total of 22 distinct modes [36,37]. In the sample with x = 0.02, nine representative modes for the R3c symmetry located at around 86, 142, 174, 225, 276, 374, 475, 540, and 623 cm⁻¹ can be assigned to the E-1 (LO), A₁-1 (TO), E-2 (LO), A1-2 (TO), E-5 (TO), E-7 (TO), E-8 (LO), E-9 (TO), and E-9 (LO), respectively [36]. Nine Raman modes are clearly visible throughout the composition range $(0.02 \le x \le 0.1)$, meaning that the R3c symmetry still exists in all samples. The evolution of peak position of nine Raman modes in the BNFTO samples can be easily visualized in Fig. 4, where the spectra are deconvoluted into nine individual Lorentzian components. The shifting and broadening of Raman peaks in BN-FTO compound mean that the crystal structure is distorted with the substitution of Ti ion at Fe site, as seen in Figs. 3 and 4. From the vibrational point of view, the activation of Bi 6s² lone pair contributes to the E-1 (LO), A_1-1 (TO), and E-2 (LO) modes, while the vibration of Fe and O atoms leads to the phonon vibrations at a higher frequency [37,38]. Thus, the intensity reduction and peak broadening observed in the A_1 -1 (TO) and E-2 (LO) modes are evidence for a suppression of the ferroelectric properties of the BNFTO compounds [8,39,40]. A similar scenario was observed in Ti-doped Bi_{0.9}Nd_{0.1}FeO₃ ceramics [28]. It is accepted that the A1-2 (TO) is a tilt mode and its frequency is strongly dependent on the oxygen octahedral tilts of the R3c symmetry [8,37,40]. The shifting of the tilt mode can be used to evaluate the change of the tilt angle and the deviation of Fe³⁺-O²-Fe³⁺ bond angle from 180° [8]. The tilt mode frequency of the sample with x = 0.02 is about 225 cm⁻¹, which is consistent with the earlier reported data [39,41]. Upon increasing the amount of Ti, the A₁-2 (TO) tilt mode shifts from 225 cm⁻¹ for x = 0.02 to 232 cm⁻¹ for x = 0.1. Such type of behavior suggests that the tilt angle and the deviation of $Fe^{3+}-O^{2-}$ Fe³⁺ bond angle from 180° increase monotonically with an increase in Ti concentration. A recent investigation on the structural evolution of $Bi_{1-y}Nd_yFe_{0.97}Ti_{0.03}O_3$ (0.1 $\leq x \leq 0.2$) compounds revealed that the Pnma orthorhombic structure (equivalent to Pbnm) can be presented



Fig. 4. Deconvoluted Raman spectra for (a) x = 0.02, (b) x = 0.04, (c) x = 0.06, (d) x = 0.1 samples.

along with the R3c and Pbam phases around 15% Nd doping concentration [11]. Surely, the XRD analysis shows no evidence for the presence of the Pbnm phase. This can be a limitation of X-ray diffractometer for detecting a crystal structure less than 3% of the total amount. Therefore, we measured the RS spectra at different positions on the sample surface for finding the phonon vibration of the Pbnm symmetry. Actually, we observe solely the phonon vibration of the Pbnm symmetry in the samples with x = 0.08 and 0.1 but could not find a single phonon vibration of the Pbnm symmetry because the Raman modes of the Pbnm phase highly overlaps with some active modes of the R3c and/or Pbam phases, as seen in Fig. 5. The other samples show no resemblance with the RS spectra of x = 0.08 and 0.1 samples; thus, we belive that the Pbnm symmetry appears only in these two samples. Our observation is in good agreement with the work of Bielecki, where three distinct spectra belonging to the R3c, Pbam, and Pbnm (Pnam) were clearly demonstrated [37]. Although the Raman active modes of the R3c, Pbam, and Pbnm symmetries strongly overlap, several unique modes in the spectra of the samples with x = 0.08 and 0.1 are helpful to assign the phonon vibrations of each symmetries, as seen in Fig. 5. For instance, the Raman peak at 407 cm⁻¹ is a characteristic mode of the *Pbam* and *Pbnm* symmetries and it does not present in Figs. 3 and 4 [42-44]. Fig. 5 shows that the phonon vibrations of the R3c + Pbam symmetries, the samples with $x \le 0.06$, have a double peaks in the frequency range of 450–550 cm⁻¹ or 574–700 cm⁻¹, while the RS spectra of the x = 0.08and 0.1 samples displays a single peak belonging to the *Pbam* + *Pbnm* symmetries. There are total five Raman active modes of the Pbnm symmetry in the BNFTO compounds, which is in good agreement with previous papers [37,42-44]. Accordingly, the structural analysis by X-ray diffraction, Rietveld refinement, and RS spectroscopy confirms the polymorphs of the R3c/Pbam for x = 0.02-0.06 and R3c/Pbam/Pbnm for $x \ge 0.08$.

Fig. 6 shows the SEM micrographs of the sample with x = 0.02 for illustrating the microstructure of BNFTO compounds. The other samples exhibit a similar morphology that we do not show here. It is accepted that the structural transition is along with the reduction of grain size [28,34,45]. Therefore, the phase coexistence expects to show a different grain size regions in the SEM micrograph. Kothai et



Fig. 5. RS spectra of x = 0.02, 0.08, and 0.1 samples representing the phonon vibrations of: (a) R3c + Pbam and (b) and (c) R3c + Pbam + Pbnm.

al. indeed observed a large and small grain regions corresponding to the rhombohedral and tetragonal coexistence in a singe compound [46]. In the BNFTO samples, we clearly observe two distinct grain size regions with a large difference in the average grain size, which are about 2 μ m and 0.4 μ m, as seen in Fig. 6(b) and (c). A close relationship between the structural transformation and the grain size distribution helps us to identify the large and small grain regions corresponding to the *R3c* rhombohedral and *Pbam/Pbnm* orthorhombic structures, respectively.



Fig. 6. (A) SEM micrographs of samples with x = 0.02 showing coexistence of the large and small grains. Selected area demonstrating the grain size for (b) the large grain and (c) the small grain.

Fig. 7(a) shows the magnetic hysteresis loops of the BNFTO samples, which were measured within a day after synthesis (as-prepared samples). All the samples show a clear open loop with small remanent magnetization (M_r) and coercivity (H_c), meaning that the weak ferromagnetism emerges in the intrinsic antiferromagnetic ground-state. The magnetic parameters extracted from the magnetic hysteresis loops are listed in Table 2. The magnetic properties of BNFTO compounds slowly increase with increasing Ti concentration up to x = 0.06 and then decrease with further increasing x to 0.1. A slight enhancement of the M_r and H_c with x for $x \le 0.06$ can be explained by the gradual sup-

pression of the cycloidal spin structure with increasing *x* as the tilt angle and the deviation of Fe³⁺-O²-Fe³⁺ bond angle from 180° increase continuously in these samples. The reduction of the H_c and M_r in the x = 0.08 and 0.1 samples is attributed to several parameters: i) A small amount of the *Pbnm* phase, which has a cancellation of macroscopic magnetization, reduces the net magnetization [11,47]; ii) The nonmagnetic Ti⁴⁺ ions substituting for Fe³⁺ ions dilute the exchange interaction of the magnetic sublattice [23]; iii) An increase in Bi₅FeTi₃O₁₅ content, an intrinsic antiferromagnetic material, reduces the total amount of the magnetization [48]. The dependence of the



Fig. 7. The magnetic hysteresis loops measured for (a) the as-prepared samples and (b) the 24-months samples.

Table 2

The magnetic parameters of the as-prepared and 24-months samples.

Composition	M_r (emu/g)		H_c (kOe)	
	as-prepared	24 months	as-prepared	24 months
x = 0.02	0.0205	0.0175	0.572	1.689
x = 0.04	0.0240	0.0225	0.621	1.508
x = 0.06	0.0330	0.0295	0.827	2.468
x = 0.08	0.0250	0.0220	0.677	1.612
x = 0.10	0.0270	0.0250	0.743	1.237

magnetic properties on the Ti concentration approves that the weak ferromagnetism observed in the BNFTO compounds originates from an intrinsic collapse of the cycloidal order rather than the defect-induced magnetism. The structural defect surely plays a crucial role for the weak ferromagnetism of Ti-doped BFO-based compounds [28,49,50]. A characteristic of defect-induced ferromagnetism is that the magnetic properties undergo an abrupt change at a threshold doping concentration [28,49-51], which is far different from the magnetic properties of the BNFTO samples. The defect and defect-free in Ti and Nd codoped BFO were both reported [11,29] but it is unclear what is the key factor for its appearance? Actually, we have tried to sinter the BNFTO samples at a higher temperature; the crystal structure of compounds remains unchanged but the coercivity and magnetization increase drastically (not shown). Hence, we believe that the synthesis process strongly affects the magnetic properties as well as the local structure of Ti and Nd codoped BFO. Fig. 7(b) shows the magnetic hysteresis loops of the BNFTO samples, of which there were measured after 24 months synthesis (24-months samples). The hysteresis loops of the 24-months samples show a rigorous change in the coercivity, while the remanent magnetization is slightly reduced as compared with the as-prepared samples, as shown in Table 2. It is reported that the magnetic aging behavior in BFO-based ceramics is induced by the isothermal structural transition and the frustration of spin structure at the boundary of two structures [25,52–54]. The isothermal structural transition was previously observed in BFO-based compounds with a self-transformation of the crystal structure from the metastable R3c rhombohedral to the stable Pbam orthorhombic structures. This effect is always along with the reorientation of the spin structure and hence the magnetic aging can be exploited in MPB systems. Besides, a competition in the lattice strain and Gibbs free energy of coexisting phase also induces a reorientation of spin structure and causes a spin frustration at the PB [25,55]. In the present work, the XRD patterns measured after 24 months systhesis show no clear evidence of the isothermal structural transition in the BNFTO samples, as shown in Fig. 8. Therefore, the magnetic aging behavior should concern the instability of spin state at the PB [25]. As mentioned in the introduction section, the difference in the magnetic structure and magnetic anisotropy of two phases can rise a frustration of spins at the PB via the percolating exchange interaction through the PB, which in turn possibly produces the ferromagnetic ordering at the PB. Thus, the magnetic interaction of the PB ferromagnetism and the intrinsic antiferromagnetic of two phases could be formed to enhance the coercivity of BNFTO compounds [56,57]. In fact, this proposal has been proved in various MPB systems and the magnetic coupling in polycrystalline ceramics can drive not only the classical exchange bias effect but also the vertical hysteresis shift and the field step-dependent hysteresis loop [15,16,24,32].

It is known that the electric field can induce an irreversible and/or reversible phase transition between the antipolar orthorhombic and polar rhombohedral structures of BFO-based compounds [12,58–61]. Therefore, the electric field-induced phase switching could cause a disorder of spin at the PB and leave evidence in the magnetic hysteresis loop. Unfortunately, a direct measurement of the magnetic hysteresis loop after and before poling in an electric field has been rarely reported [12,14]. We believe that the abnormality of the coercivity enhancement after poling in the works of X. Shi and J. Chen may relate to the



Fig. 8. (A) XRD patterns of the BNFTO samples measured after 24-months synthesis. (b) Comparison of XRD profiles of the x = 0.02 measured for the asprepared and after 24-months samples.

magnetic interaction because the phase transition to the cycloidal spin structure of the *R3c* symmetry is expected to reduce the coercivity [12,14]. Besides, the asymmetry hysteresis loop before and after poling in the work of X. Shi et al. should be considered as the exchange bias effect. In the present work, to get more insight into the spin frustration induced by phase switching, we measured the hysteresis loops after and before poling in an electric field of 40 kV/cm for 24-months samples. The results are shown in Fig. 9 for four typical samples. A remarkable



Fig. 9. The magnetic hysteresis loops of 24-months samples: (a) x = 0.02; (b) x = 0.04; (c) x = 0.06; (d) x = 0.1 before and after poling in an electric field.

decrease of the H_c and M_r observed in all samples after poling indicates that the electric field leads a partial phase transition from the canted antiferromagnetic to the cycloidal spin structure. An unusual hysteresis loop behavior is observed in the sample with x = 0.06 where the loop is pinched around the low field region, as seen in Fig. 9(c). The pinched hysteresis loop is generally observed in the material possessing a coexistence of the hard and soft magnetic phases [16,62,63]. The pinched hysteresis loop observed in the x = 0.06 sample can be attributed to a coexistence of the ferromagnetic (soft phase) and antiferromagnetic (hard phase) orders. It is worth mentioning that the pinched hysteresis loop cannot be related to the inhomogeneous distribution of two structure phases otherwise it can be observed in the other samples. Thus, it is no doubt that the ferromagnetic order should be originated from the PB ferromagnetism. We have reported that the appearance of the pinched loop concerns the disorder of spins and the net magnetic moment of the PB [24]. The change in the Ti concentration has changed the free energy of the R3c and Pbam phases, which in turn affects the frustrated spin at the PB. Therefore, the PB ferromagnetism would have different values in each sample. This explains why the pinched loop does not appear in all the samples.

4. Conclusions

In conclusion, the effect of Ti doping on the crystal structure, microstructure, and magnetic properties of the Bi_{0.86}Nd_{0.14}FeO₃ ceramics have been reported in the vicinity of the MPB. The polycrystalline ceramics BNFTO crystallizes into two crystal structures of the R3c rhombohedral and *Pbam* orthorhombic for $x \le 0.06$, while a ternary phase of the R3c, *Pbam*, and *Pbnm* structures is observed for x > 0.06. A small amount of the Aurivillus Bi5FeTi3O15 impurity phase is detected at a high Ti concentration. The study on the microstructure by scanning electron microscope shows two-grain size regions. The weak ferromagnetism observed in the BNFTO is attributed to the intrinsic collapse of the cycloidal spin structure. All the samples show the aging of the magnetic properties for which the coercivity undergoes an abruption change after 24 months synthesis. The studies on the electric fieldinduced structural transition reveal a change of the coercivity and remanent magnetization. The change of the magnetic properties of the BNFTO compounds is explained in term of the magnetic interaction of the PB ferromagnetism and intrinsic antiferromagnetic of two phases.

Data availability statements

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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