Improved multiferroic properties in \((1-x)\text{BiFeO}_3-x\text{BaTi}_{0.95}(\text{Yb}_{0.5}\text{Nb}_{0.5})_{0.05}\text{O}_3\) system \((0 \leq x \leq 0.3)\)

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**A B S T R A C T**

Polycrystalline samples of \((1-x)\text{BiFeO}_3-x\text{BaTi}_{0.95}(\text{Yb}_{0.5}\text{Nb}_{0.5})_{0.05}\text{O}_3\) \((x=0, 0.1, 0.2 \text{ and } 0.3)\) were prepared by the conventional solid state reaction method. The phase purity and composition were checked using powder X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The grain size and morphology of the ceramics were confirmed by scanning electron microscopy (SEM). X-ray diffraction showed that these compounds crystallized, at room temperature, in the Rhomboedral R3c for \(x=0\) and in tetragonal P4mm for compositions \(0.1 \leq x \leq 0.3\) distorted perovskite structures. The \(\text{BaTi}_{0.95}(\text{Yb}_{0.5}\text{Nb}_{0.5})_{0.05}\text{O}_3\) substitution led to an improvement of magnetic and ferroelectric properties at room temperature. The highest magnetization was reported for composition \(x=0.2\) which was due to the enhancement of canting angles and the suppression of cycloid spin structure, as confirmed by \(^{57}\text{Fe}\) Mössbauer spectroscopy and the presence of \(\text{Fe}^{3+}\), as detected by XPS. The electric polarization increased significantly for doped samples, which proves the enhancement of the ferroelectric behavior and resistivity of our ceramics. Large electric field induced strains were observed for 0.7BiFeO\(_3\)-0.3BaTi\(_{0.95}(\text{Yb}_{0.5}\text{Nb}_{0.5})_{0.05}\text{O}_3\), as an evidence of piezoelectric behavior. These results show that BaTi\(_{0.95}(\text{Yb}_{0.5}\text{Nb}_{0.5})_{0.05}\text{O}_3\) doped BiFeO\(_3\) is a promising multiferroic material.

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1. Introduction

An immense interest has been attributed to multiferroic materials which simultaneously exhibit two or more ferroic properties in the same phase. Such materials show an important potential, specially for applications in innovative technological devices, such as electromagnetic devices, or optoelectronics and spintronics [1–3]. Nevertheless, the coupling interaction between multiferroic orders, especially ferroelectric and ferromagnetic ones rarely co-exist. This scarcity of such materials in nature stems from the fact that while ferroelectricity requires the presence of unpaired electrons in them, Bismuth ferrite, BiFeO\(_3\), is currently the most extensively investigated material in this respect. It is the only material that presents a coupling between the magnetic and electric ordering at room temperature [4]; BiFeO\(_3\) exhibits a high ferroelectric curie temperature \(T_c=1100\) K and high G-type antiferromagnetic ordering temperature \(T_N=643\) K [5].

Bulk BiFeO\(_3\) crystallizes in a Rhomboedral distorted perovskite structure with an R3c space group: the ferroelectricity arises mainly from the lone pair 6s\(^2\) of Bi\(^{3+}\). The partially filled d orbital of Fe ions leads to a G-type antiferromagnetic spin configuration. Each Fe\(^{3+}\) ion is surrounded by six Fe\(^{3+}\) nearest neighbors with antiparallel moments in this ferromagnetic BiFeO\(_3\) structure. The latter is a spiral arrangement of the magnetic moments of Fe\(^{3+}\) ions and the canted spins arising from Dzyaloshinskii–Moriya (DM) interaction. This interaction causes a slight deviation from ideal antiferromagnetic behavior giving rise to weak ferromagnetism in BiFeO\(_3\) [6–8].

Synthetic BiFeO\(_3\) ceramics are still ambiguously understood and require more investigation to avoid the formation of second phases [9,10]. Its low electric resistivity at room temperature is also a serious drawback limiting the application of these materials because the measurement of ferroelectric loop is very difficult [11]. BiFeO\(_3\)–ABO\(_3\) perovskite is a major solution used to obtain pure phase and enhance resistivity [12–14].

However, BaTi\(_{0.95}(\text{Yb}_{0.5}\text{Nb}_{0.5})_{0.05}\text{O}_3\) is a classical ferroelectric exhibiting excellent electrical properties: a high dielectric permittivity of about 11,420 at 1 kHz at \(T_c=358\) K [15] better than BaTi\(_3\) (\(e'_c\) around 9000 and \(T_c=457\) K) [16].

In order to ameliorate the electrical and magnetic properties of...
BiFeO₃, we prepared \((1-x)\) BiFeO₃-xBaTiO₃ (Yb₀.₅Nb₀.₅)₀.₀₅O₃ polycrystalline samples via a solid–solid reaction. The structural, dielectric and magnetic properties were analyzed. Especially, the magnetic order was deeper investigated by XPS and ⁵⁷Fe Mössbauer spectroscopy.

2. Experimental techniques

\[ \begin{align*}
X \text{BaCO}_3 + (1-x)/2\text{Bi}_2\text{O}_3 + 0.95x\text{TiO}_2 + \left(0.05x/4\right)\text{Yb}_2\text{O}_3 \\
+ (0.05x/4)\text{Nb}_2\text{O}_5 + (1-x)/2\text{Fe}_2\text{O}_3 \\
\to (1-x)\text{BiFeO}_3 - x\text{BaTiO}_{3.95}(\text{Yb}_0.5\text{Nb}_0.5)_{0.05}\text{O}_3 + x\text{CO}_2
\end{align*} \]

The solid state reaction method was used to prepare different compositions of \((1-x)\)BiFeO₃-xBaTiO₃ (Yb₀.₅Nb₀.₅)₀.₀₅O₃ ceramics. Barium carbonate (BaCO₃ - 99.9% purity, Aldrich), Bismuth oxide (Bi₂O₃ - 99.9% purity, Aldrich), Titanium oxide (TiO₂ - 99.9% purity, anatase phase, Aldrich), Ytterbium oxide (Yb₂O₃ - 99.9% purity, Aldrich), Niobium oxide (Nb₂O₅ - 99.9% purity, Aldrich), and Iron oxide (Fe₂O₃ - 99.9% purity, Aldrich) powders were weighed according to stoichiometric proportion of Eq. (1).

Mixtures were wet milled for 4 h with rotation speed of 600 rot./min. by agate balls (3 mm diameter) in an agate jar. The ball-to-sample mass ratio was 100:1. Samples were dried, pre-calcined at 873 K during 12 h, calcined at high temperature at 1023 K during 3 h and cooled to room temperature. After calcination, the product was milled again for 4 h. The powder was then shaped into pellets of 8 mm in diameter by uniaxial pressing of 1023 K during 3 h and cooled to room temperature. After calcination, the resulting sample was covered by an aluminosilicate glass cap, followed by a capsule of silica. The capsules were placed in a furnace and sintered for 2 h at 1103 K for undoped BiFeO₃ and at 1123 K; 1143 K and 1173 K for all our samples. The state of the faces was monitored with the C₁s photo-electron microprobe ESCALAB 250. The spectra were excited according to the stoichiometric proportion of Eq. (1).

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of \((1-x)\)BiFeO₃-xBaTiO₃ (Yb₀.₅Nb₀.₅)₀.₀₅O₃ compositions \(x=0, 0.1, 0.2\) and 0.3 ceramics, at room temperature. For BiFeO₃ \((x=0)\), the X-ray diffractogram indicated low intensity peaks attributed to the Bi₂Fe₃O₉ impurity phase (shown by asterisks in Fig. 1). The identification of this impurity was based on the data base of «X-Pert HighScore». The percentage determined by the ratio of the intense peak of the principal phase by that of the impurity was around 0.16%. The formation of impurity phases was omitted in the doped samples (Fig. 1). Thus, simultaneous substitutions of Barium in A site and Ytterbium/Niobium/Titanate in B site into BiFeO₃ stabilized single-phase prepared samples.

This result could be confirmed by Energy-dispersive X-ray microanalysis using the EDX equipment. SEM micrographs of \((1-x)\)BiFeO₃-xBaTiO₃ (Yb₀.₅Nb₀.₅)₀.₀₅O₃ (x=0, 0.1, 0.2 and 0.3) samples are shown in Fig. 3: those performed in secondary modes are designated with the index “Sec” and those done in retodufus modes with the index “Retod”. No constraint between secondary and retodufus modes was noticed, which reveals uniform doping like other perovskite ABO₃ [[17–21]]

Furthermore, EDX analysis done for Bi, Ba, Fe, Ti, Yb and Nb elements, for compositions \(x=0.1, 0.2\) and 0.3 of \((1-x)\)BiFeO₃-xBaTiO₃ (Yb₀.₅Nb₀.₅)₀.₀₅O₃ revealed close correspondence of expected amounts, considering the gap error, which implied a good range of stoichiometric synthesis and confirmed stabilization of single-phase prepared samples. However, measurements for our prepared BiFeO₃ ceramic showed a deficit of Bismuth as signal of second phase: an estimation of Bi₂Fe₃O₉ percentage second phase was 0.17%, which is consistent with X-ray results.

As illustrated in Fig. 3, SEM images showed bimodal grain size. For \(x=0.1\) compositions were noted to vary from 0.5 µm to 1.4 µm, it ranged from 0.6 µm to 1.2 µm for \(x=0.3\) compositions. This implies the development of lattice strain inside the lattice due to ionic size mismatch between host and substituent cations which led to a local structural disorder and reduced the rate of nucleation resulting in the decrease of average crystallite size (Table 1).

Rietveld refinement of X-ray diffraction patterns was carried out for all compositions using the Fullprof program [20]. At room temperature, BFO crystalized in Rhomboedral structure R3c. However, \(x=0.1, 0.2\) and 0.3 compositions were indexed on tetragonal symmetry with space group P4mm. The goodness of fit was obvious by an agreement between the observed and calculated interplaner spacing. Also, small R-values of refinement were obtained. Fig. 2(a) and (b) shows, as examples, X-ray Rietveld refinement patterns for compositions \(x=0\) and 0.3, respectively.
Compared to undoped BiFeO$_3$, tetragonal symmetry of compositions $x=0.1, 0.2$ and 0.3 is confirmed by the emergence of three doubled peaks $(110) \langle 104 \rangle$; $(006)$ and at $-32^\circ$ and $39^\circ$ in $2\theta$ (Fig. 1(b) and (c)), respectively of each one into one peak. A similar type of phase transition was reported [22-24].

The refinement results, lattice parameters, and unit cell volume of ceramic compositions at room temperature are reported in Table 1. These results revealed a significant increase in volume with an increase of substitution rates in A and B sites, which were fully compatible with the shift observed for the reflection peaks to $2\theta$ lower angles (Fig. 1).

This evolution could be understood considering the variation of both average radii of cations occupying A $<r_A>$ and B $<r_B>$ sites determined by the following relationships:

\[ <r_A> = (1-x)r(Bi^{3+}) + x r(Ti^{4+}) \]  
\[ <r_B> = (1-x)r(Fe^{3+}) + x r(Nb^{5+}) \]

In fact, the ionic radius of Bismuth, Bi$^{3+}$, $r(Bi^{3+})=1.38$ Å [26] is smaller than that of Barium, Ba$^{2+}$, $r(Ba^{2+})=1.61$ Å [25] in co-ordination XII occupying the A site. The ionic radius of iron, Fe$^{3+}$, $r(Fe^{3+})=0.645$ Å [25] (this ionic valence was confirmed by Mössbauer spectroscopy and XPS analysis) was greater than that of Niobium, Nb$^{5+}$, $r(Nb^{5+})=0.65$ Å [25] but smaller than that of ytterbium, Yb$^{3+}$, $r(Yb^{3+})=0.868$ Å [25] in the B site in co-ordination VI. Theoretical calculation showed ($r_B$) increase from 1.38 Å to 1.449 Å and ($r_A$) decrease from 0.645 Å to 0.6352 Å for BiFeO$_3$ and 0.7BiFeO$_3$-0.38BaTi$_{0.95}$Yb$_{0.05}$O$_3$ ($x=0.3$) ceramics, respectively. It is clear that the increase of unit cell volume was dominated by ($r_A$) increase.

In Rhomboedral distorted perovskite structure with $R3c$ space group, for undoped BiFeO$_3$ samples, cations were located at 6b $(0, 0, 0)$ and $(0, 0, 0.2198)$ whereas oxygen occupied 18b positions at $(0.909, 0.203, 0.6205)$ and their symmetry equivalent positions. However, for doped samples with space group P4 mm tetragonal structure, cations were located for A site at 1a $(0, 0, 0)$ and for B site at 1b $(0.5, 0.5, 0.4692)$ whereas oxygen occupied non symmetrical positions O$_1$ at 1b $(0.5, 0.5, 0.2213)$ and O$_2$ at 2c $(0.5, 0.5, 0.5256)$. Atomic bond length and angles were obtained. The Fe–O–Fe bond angles have a crucial role in magnetic properties [27-29]. These angles are tabulated in Table 1 by means of Rietveld refinement. It can be noted that Fe–O–Fe bond angles increased compared to BiFeO$_3$.

3.2. Mössbauer spectroscopy

$^{57}$Fe Mössbauer spectroscopy is one of the most efficient tools to investigate the hyperfine magnetic behavior and oxidation state of the iron atoms. Fig. 4 shows the Mössbauer spectra of $(1-x)$BiFeO$_3$-$x$BaTi$_{0.95}$Yb$_{0.05}$O$_3$ $(x=0, 0.1, 0.2$ and 0.3) ceramics recorded at room temperature. All spectra were composed of six absorption line patterns indicating an Fe$^{3+}$ magnetic environment. We could also conclude that the Neel temperature $T_N$ was above room temperature.

Fig. 4(a) displays the BiFeO$_3$ Mössbauer spectrum at room temperature. The spectra asymmetry, which is associated with the heterogeneous line broadenings, was due to the spiral magnetic structure of BiFeO$_3$ [30,31]. The differential broadening of the spectral lines with respect to the experimental line width is explained in terms of the presence of different non-equivalent Fe sites in the crystal structure [30,31]. Fig. 4(b), (c) and (d) shows room temperature Mössbauer spectra of compositions $x=0.1, 0.2$ and 0.3, respectively. Compared to BiFeO$_3$, as substitution rate increased, more symmetrical shape and broadening of the six line spectra were noted. This observation could be interpreted as an increase of the modulation of the hyperfine energies suggesting the continuous deletion of modulated spiral spin structure as rate of substitution in A and B sites increase.
change of the magnetic nearest neighbors of Fe$^{3+}$ [34,35], as substituted by Yb$^{3+}$/Nb$^{5+}$/Ti$^{4+}$ leading to a distortion of FeO$_6$ octahedral origin of structural transition. This could lead to modulation spin structure which contributed to the improvement of magnetization.

According to Table 2, the isomer shift of all the sextets was around 0.38–0.42 mms$^{-1}$. This indicates that iron was in high-spin 3+ order state for all our ceramics [39]. Compared to BiFeO$_3$, these parameters for sextets 1 and 2 (S$_1$ and S$_2$) were reduced gradually as substitution rate increased indicating an increase of the density of s-electrons around the Fe nucleus. Such results led to the enhancement of the DM interaction resulting in stronger canting spins [40]. The isomer shift of sextets 3 was mainly constant indicating that the s-electrons density around the Fe nucleus was constant. This could be interpreted as the fact of non-magnetic B ions surrounding Fe ions.

The magnetic hyperfine field ($B_{hf}$) showed a slight decrease which could be due to Ytterbium/ Niobium/ Titanium substituted at the Fe site: these values of (sextet1; $B_{hf} = 50$ T sextet2; $B_{hf} = 49$ T) for $x = 0$ became of (sextet1; $B_{hf} = 41$ T sextet2; $B_{hf} = 40$ T sextet3; $B_{hf} = 42$ T) for $x = 0.3$. This could be attributed to local magnetic disorder as increasing the rate of substitution leads to the distortion of spin cycloid [40].

As the substitution rate increased, the difference between the three values of the quadrupole splitting QS, corresponding to the three sextets, indicating three different octahedral environment of Fe site were modulated. This was due to the difference in the electric field gradient or the difference of spin orientations [31]. In fact, all the magnetic hyperfine $^{57}$Fe Mössbauer parameters clearly showed the modulation of magnetic cycloid corresponding to high spin ordered iron Fe$^{3+}$.

The Lorentz doublet with different line intensities is a signature of the secondary phase. The minority phase was identified based on its hyperfine interaction parameters [31] as dibismuth-non-auxotetraferrate Bi$_3$Fe$_4$O$_9$ which showed a paramagnetic behavior at room temperature [36–38]. Thus, this impurity had no contribution to magnetic order, especially because its hyperfine field $B_{hf}$ was null. Therefore, the fraction area of such components is minor, the secondary phase detection showed the limit of XRD data microanalyses and improved our knowledge of microstructure.

The area fraction of spectra component allows a good estimation of the percentage of pure and parasitic phases as listed in Table 2. The area fraction of spectral component S$_1$ and S$_2$ of 46% site population for undoped BiFeO$_3$ decreased gradually to become of 41% and 40% for sextets S$_1$ and S$_2$, respectively, for composition $x = 0.3$. However, the population site determined for sextets S$_3$ increased as the rate of substitution increased. This third site population is undoubtedly representative of Fe site strongly surrounded by Ytterbium/ Niobium/ Titanate.

### 3.3. XPS

XPS studies were done to check their composition and to extract chemical state and electronic charge transfer information. Fig. 5(a) and (b) show a wide range spectrum analysis for BiFeO$_3$ and 0.7BiFeO$_3$–0.3BaTiO$_{3.95}$(Yb$_{0.5}$Nb$_{0.5}$)$_{0.05}$O$_3$, respectively. Detection of Bi; Ba; Ti; Fe and O binding energy peaks confirm the chemical composition of the samples (Yb, Nb and Ti with low concentration could not be detected because of background noise). Except for a small amount of absorber Cs I at 285 eV, which was used to calibrate the system, the spectrum did not show any other impurity peaks. Therefore, the purity samples were confirmed by the absence of impurity peaks in XPS.

High resolution XPS was zoomed to investigate the oxidized state and concentration of the Fe, Bi and O elements, via
calculation of the integral areas of peaks, for composition \(x = 0, 0.1, 0.2\) and 0.3 of \((1-x)\text{BiFeO}_3-x\text{BaTi}_{0.95}\text{Yb}_{0.5}\text{Nb}_{0.5}\text{O}_3\) ceramics. Fig. 5(c); (d) and (f) shows high resolution XPS spectra of Fe2P, Bi4f and O1s.

XPS analysis of Fe2P binding energy shows the existence of two valence states of iron Fe\(^{2+}\)/Fe\(^{3+}\). The Fe2P binding energy around
714 eV for Fe2P1/2 and 726 eV for Fe2P3/2 was consistent with trivalent valence Fe3+ [23,24,41,42]. A weak satellite peak corresponding to Fe2+ [43] around 718 eV binding energy was also found, indicating valence change of the Fe from Fe3+ to Fe2+. The ratio of Fe2+ to Fe3+ was obtained by fitting narrow scan spectra area peaks. The evolution of relative % of Fe2+ to Fe3+, as the rate of substitution increases shows an increase, passing through a relative maximum for composition x=0.2, which did not exceed 9.9 %, followed by a decrease of this relative ratio as illustrated in Fig. 6.

This trend is in correlation with changes in the full width at half maximum (FWHM) of O1S X-ray photoelectron binding peak strongly linked to the amount of oxygen vacancies [44]. Indeed, the oxygen peak got wider as the compound got more deficient in oxygen. Contrarily, the narrower the peak, the greater the stoichiometry was respected. This evolution of the oxygen vacancy concentrations probably had an influence on the leakage current density which had an impact on ferroelectric properties. The O1s binding energy was around 529.43 eV, 531.01 eV and 532.69 eV. The spectra showed a pronounced modification mainly related to the difference of electronegativity [22,42] due to the substitution of Bi3+ by Ba2+ in A site and of Fe3+ by Nb5+/Yb3+/Ti4+ in B site. A close focus showed that the full width at half maximum (FWHM), was of 2.45 eV, 2.89 eV, 3.52 eV and 3.08 eV for compositions x=0, 0.1, 0.2 and 0.3, respectively. Moreover, as illustrated in Fig. 6, the behavior of the integral breadth was similar; its tendency presented an extreme for the composition x=0.2. This confirms the difference of electronegativity oxygen environment due to the substitution of BiFeO3 by BaTi0.95(Yb0.5Nb0.5)0.05O3. As shown in Fig. 6, both evolutions of the full width at half maximum (FWHM) and the integral breadth of O1S peak were very proportional to the shift position of Bi4f binding energy for doped ceramics compared with that around 164.17 eV, in the case of BiFeO3, reflecting Bismuth fluctuations.

Indeed, the creation of oxygen vacancies to neutralize the charge due to the volatility of Bismuth and the substitution of Bi3+ by Ba2+ could be an appropriate explanation for this phenomenon. Thus, The fluctuations of Bismuth could have caused the deficiency of oxygen leading to the appearance of Fe2+. It is well known that the unavoidable Fe2+ ions may play a fundamental role in the enhanced magnetization via double exchange between Fe2+ and Fe3+ ions [23,24]. Undoubtedly, Fe2+ ions detected by XPS influenced the magnetic properties of our samples.

3.4. Magnetic measurements

Magnetic hysteresis loops (M–H) at room temperature of (1–x)BiFeO3–xBaTi0.95(Yb0.5Nb0.5)0.05O3 ceramic (0 ≤ x ≤ 0.3) are

<table>
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<tr>
<th>Table 2</th>
<th>Mössbauer spectroscopic hyperfine interaction parameters extracted from the fitting of the hyperfine data for (1–x)BiFeO3–xBaTi0.95(Yb0.5Nb0.5)0.05O3 ceramics with compositions x=0.3, 0.2, 0.1 and 0 collected at room temperature.</th>
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<td>Fe site</td>
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<td>x=0.1</td>
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shown in Fig. 7. However, the unsaturated hysteresis magnetic loops indicate the signature of antiferromagnetic basic nature with weak ferromagnetic. Such a result is an evidence for the enhancement of magnetization. The magnetic properties of BiFeO₃ at room temperature were enhanced by the introduction of BaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃.

Previous reports attributed the appearance of magnetic hysteresis loop through A and/or B-sites substitution in BiFeO₃ to the following factors:

- The breakdown of the balance between the anti-parallel sublattice magnetization of Fe³⁺ by structural distortion [45,46].
- the modulation of spin spiral structure [19,47–49].
- the effect of grain size [50–52]: with dimension less than 62 nm, the probable modification of cycloid spin structure of BiFeO₃ can lead to weak ferromagnetism, and
- the presence of Fe²⁺ ions probably leading to a double-exchange interaction between Fe³⁺ and Fe²⁺ (Fe³⁺–O–Fe²⁺) influenced magnetization [17,23].

Compared to these works, in our system, the enhancement of ferromagnetic properties of BiFeO₃ as a results of doping non-magnetic Ba²⁺ and Yb³⁺/Nb⁵⁺/Ti⁴⁺ in A and B sites, respectively, could be attributed to the contribution of the above mentioned factors.

In fact, the dependent magnetic properties in grain size should be discussed. Certainly, the effect of decreasing grain size, as substitution rate increased, observed by SEM micrograph, could lead to little increase of the total magnetic moment of uncompensated spins at the surface. Nevertheless, for the synthesized ceramic, Grain size (~µm, as indicated in Table 1) were still greater than the antiferromagnetically cycloid spin length (~62 nm). So, grain size effect cannot be the primary reason for the observed magnetization in this case.

Hence, the magnetic property enhancement, caused by a co-substitution in A and B sites, led to ferromagnetic ordering. This was mainly due to the canting of antiferromagnetic ordered Fe³⁺–O–Fe³⁺ angle proved by XRD refinement data, the suppression of modulated spin spiral structure as confirmed by ⁵⁷Fe Mössbauer spectroscopy, and the presence of Fe²⁺ as detected by XPS, rather than grain size effect.

This is consistent with the increase of the Goldschmidt tolerance factor of our synthetized ceramics as concentration of substituted elements increased (Table 1). In fact, as substitution rate

![Fig. 5. XPS wide range spectrum analysis for (a) BiFeO₃ (b) 0.7BiFeO₃-0.3BaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃; High resolution XPS zoomed in (c) Fe2p; (d) Bi4f and (e) O1s core levels of (1-x)BiFeO₃-xBaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃ (x = 0, 0.1, 0.2 and 0.3) ceramics.](image-url)
increased, the evolution of ionic radii of cations occupying A and B sites led to the increase in the octahedral tilt and the Fe–O–Fe band angles. In turn, the antiferromagnetically canted angle of ordered adjacent planes increased with the suppression of the cycloid spin structure.

Focusing on the evolution of magnetic hysteresis loops, (Fig. 7) we reported an increase and subsequent decrease of the maximum of magnetization with increasing the BaTi$_{0.95}$(Yb$_{0.5}$Nb$_{0.5}$)$_{0.05}$ substitution content. The saturated magnetization $M_s$, at 29 kOe, of the samples with $x=0.1$, 0.2 and 0.3 were 1.454, 2.381 and 2.011 emu g$^{-1}$ The remnant magnetization $M_r$ were of 0.266, 0.89 and 0.594 emu g$^{-1}$ and the coercive field $H_c$ of those ceramics were 2.434, 4.349 and 2.566 kOe, respectively. Interestingly, the highest magnetization, coercive field and $M(H)$ magnetization loop area were found for the critical composition $x=0.2$. So, the progressive enhancement on magnetization, for low substitution rate up to $x=0.2$ composition, could be attributed to the canting of antiferromagnetically ordered spins, as the substitutes (Ba and Yb/Nb/Ti in A and B sites, respectively) were non-magnetic: low substitution could not completely destroy the spin cycloid structure. However, for the critical composition $x=0.2$, the maximum reached indicated almost broken spin cycloid structure. Further reduction of magnetization while increasing concentration could be explained by the appearance of complete antiferromagnetic ordering. Similar behavior was reported by other authors [24,52–54].

Closely followed trend saturated magnetization and coercive field show a similar evolution as Fe–O–Fe canted angles determined by XRD Rietveld refinements and proportional growth of the ratio of Fe$^{2+}$ to Fe$^{3+}$. Thus, we could deduce the dominance
contribution of both factors to the enhancement of magnetic order.

Comparing the magnetic results for our ceramic \((1-x)\text{BiFeO}_3-x\text{BaTiO}_{3.95}\) \((Yb_{0.5}N_{0.5}O_3)_{x}\) \((x=0.1, 0.2, 0.3)\) prepared samples to those of pure single crystalline nanocubes \((\text{BiFeO}_3)_{0.7}\) \((\text{BiFeO}_3)_{0.8}\) \((\text{BiFeO}_3)_{0.9}\) nanocubes \((\text{BiFeO}_3)_{0.1}\) exhibited the largest magnetic response as a function of applied magnetic field. As expected, the saturated magnetization \(M_s\) for our three doped ceramics were higher than that of undoped \(\text{BiFeO}_3\) at 164.17 ev depending on the composition.

This assumption remains unrestricted seen that the value of \(H_c\) for \(0.9\text{BiFeO}_3-0.1\text{BaTiO}_{3.95}(Yb_{0.5}N_{0.5}O_3)_{0.05}\) was of 2.434 kOe still lower than that of \((\text{BiFeO}_3)_{0.5}(\text{BaTiO}_3)_{0.3}\) which presented an \(H_c\) value equal to 3400 Oe [56]. Thus, in contrast with \(x=0.1\), the high corrective field made both compositions \(x=0.2\) and 0.3 difficult to pole.

3.5. Hysteresis loops

Polarization hysteresis loop measurements were performed, as a function of applied field, to characterize the ferroelectricity of composition \(x=0.1, 0.2\) and 0.3 for \((1-x)\text{BiFeO}_3-x\text{BaTiO}_{3.95}\) \((Yb_{0.5}N_{0.5}O_3)_{x}\) ceramics.

Electric hysteresis loops at room temperature are given in Fig. 8 and show attainable remnant polarizations of 0.229, 0.942 and 3.279 \(\mu C/cm^2\) for \(x=0.1, 0.2\) and 0.3 composition of \((1-x)\text{BiFeO}_3-x\text{BaTiO}_{3.95}(Yb_{0.5}N_{0.5}O_3)_{x}\) ceramics, respectively, while the saturated polarization cannot be achieved in either case before electrical break down because of important conductivity in this material family as explained in previous reports [23,54]. A similar hysteresis loop with an unsaturated remnant polarization of 0.01 \(\mu C/cm^2\) was observed for the \(\text{BiFeO}_3\) ceramic [55]. As evidenced in Fig. 8, the compositions \(x=0.1, 0.2\) and 0.3, reported in our present work, could sustain a higher measuring field than \(\text{BiFeO}_3\) and 0.98BiFeO$_3$–0.18BaTiO$_{3.95}$, confirming that the increase of the BaTi$_{0.95}$Yb$_{0.5}$N$_{0.5}$O$_3$ percentage in the solid solution \((1-x)\text{BiFeO}_3-x\text{BaTiO}_{3.95}(Yb_{0.5}N_{0.5}O_3)\) can reduce electric leakage and thus improve polarization and prove the ferroelectric behavior (Table 3). This deduction can be clearly observed for the composition \(x=0.3\) where the evolution of polarization as a function of applied field showed a nonlinear behavior from the field \(E=1 \text{ kV/cm}\) : a saturation beginning aspect was detected, as shown in Fig. 9.

Fig. 10 shows the bipolar strain curves for 0.7BiFeO$_3$–0.3BaTi$_{0.95}$Yb$_{0.5}$N$_{0.5}$O$_3$ sample measured at a maximum electric field of 37 kV/cm. A characteristic ‘butterfly’ strain loop was found. However, this loop is dissymmetrical as a function of positive and negative electric field. This demonstrates a piezoelectric behavior.

4. Conclusion

We could achieved enhanced multifurcations properties of \((1-x)\text{BiFeO}_3-x\text{BaTiO}_{3.95}(Yb_{0.5}N_{0.5}O_3)_{x}\) \((0 \leq x \leq 0.3)\) ceramics prepared by the solid state reaction method. XRD patterns showed that this material crystallizes in a perovskite-type single phase
tetragonal structure with space group P4mm for (0.1 ≤ x ≤ 0.3) and Rhomboedral R3c for BiFeO₃. According to SEM microscopy, the grain size decreased, as substitution rate of BaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃ increased. This induced weak ferromagnetism but cannot be considered the primary origin for magnetization loops. Thus, Magnetic hysteresis loop measured at room temperature is an evidence of magnetic properties improvement as a result of the canting of antiferromagnetic ordered Fe⁵⁺–O–Fe⁵⁺ angle, proved by XRD Riveted refinement data, suppression of modulated spin spiral structure, as confirmed by ⁵⁷Fe Mössbauer spectroscopy and probably by double-exchange interaction Fe³⁺–O–Fe³⁺, as the presence of unavoidable Fe²⁺ was evidenced by XPS, rather than grain size effect. The incorporation of BaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃ in BiFeO₃ presented a maximum of spontaneous magnetization Mₛ and coercive magnetic field Hₛ of about 2.045 emu g⁻¹ and 4.369 kOe, respectively, for composition x=0.2 then a decrease. These results indicate that as substitution rate increases, above this critical composition, complete antiferromagnetic ordering appears.

Comparing the results dependence of magnetic response to the applied magnetic field of (1–x)BiFeO₃–xBaTiO₃ shows that the composition 0.9BiFeO₃–0.1BaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃ exhibited improved magnetic properties than (BiFeO₃)ₓBaTiO₃(1−x), which is appreciable for mass memory applications. For composition x=0.2 and x=0.3, the magnetic characteristics are still debatable since saturated magnetization Ms has improved compared to (BiFeO₃)ₓBaTiO₃(1−x) and (BiFeO₃)ₓBaTiO₃(1−x), respectively, however, their higher corrective field makes them difficult to pole, which limits their fields of application.

Although the saturated polarization could not be achieved, the increase of the BaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃ percentage reduced electric leakage and thus improved polarization and proved the ferroelectric behavior. Our doped samples had better ferroelectric properties than undoped BiFeO₃. The electric field-induced strain is an evidence of piezoelectric behavior. The results show clearly that (1–x)BiFeO₃–xBaTi₀.₉₅(Yb₀.₅Nb₀.₅)₀.₀₅O₃ ceramics exhibit much better multiferroic properties compared to undoped BiFeO₃ samples.

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