

## Structural phase relations in perovskite-structured BiFeO<sub>3</sub>-based multiferroic compounds

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**Abstract:** In this review, the state of the art in understanding the structural phase relations in perovskite-structured BiFeO<sub>3</sub>-based polycrystalline solid solutions is presented and discussed. Issues about the close relation between the structural phase and overall physical properties of the reviewed systems are pointed out and discussed. It is shown that, by adjusting the structural symmetric arrangement, the ferroelectric and magnetic properties of BiFeO<sub>3</sub>-based polycrystalline solid solutions can be tuned to find specific multifunctional applications. However, an intrinsic mechanism linking structural arrangement and physical properties cannot be identified, revealing that this subject still deserves further discussion and investigation.

**Keywords:** bismuth ferrite; ferroelectrics; multiferroics

### 1 Introduction

Multifunctional compounds are materials whose two or more physical properties can be exploited simultaneously or separately for the same or different purposes. The advancement of processing multifunctional materials needs to meet a range of revolutionary technologies, such as shape memory, electrostriction, solid-state transformer and magnetorheological device [1,2]. In this context, perovskite-structured polycrystalline compounds, i.e., BiFeO<sub>3</sub>-ABO<sub>3</sub>-type materials can potentially be applied for constructing or developing multifunctional

smart devices. In fact, compounds with perovskite structure may have more than one applicable property (e.g., ferroelectricity, (weak, ferri) magnetism, piezoelectricity, and magnetoelectric coupling) to be classified as multifunctional. Furthermore, materials with perovskite structure that present ferroelectricity, ferroelasticity and/or some magnetic order simultaneously, are known as multiferroics; for multiferroic compounds, such properties can be intrinsically coupled, as the case of magnetoelectric materials. In these materials, an electric field can induce an electric polarization and a magnetic order simultaneously, or a magnetic field can induce a magnetization and an electric order simultaneously [3,4]. These materials can also be used in advanced electro-electronic devices, such as multiple-state non-volatile memory [5,6] and high-power solid-state transformer, by fundamentally exploiting the

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magnetoelectric coupling [7]. In recent years, some multiferroic materials have emerged as potential candidates for these specific applications, e.g., perovskite-structured polycrystalline BiFeO<sub>3</sub> (BF) and BF-based compounds.

In fact, BF is a well-known multiferroic magnetoelectric material presenting two ferroic orders, i.e., antiferromagnetic and ferroelectric states in the same phase [8,9]. BF possesses a rhombohedral distorted perovskite structure (*R3c* space group). It is ferroelectric (Curie temperature  $T_C \approx 830$  °C) and antiferromagnetic at room temperature (with  $T_N \approx 367$  °C) [10,11], and it shows a strong magnetoelectric coupling ( $dE/dH$  as high as 3 V/(cm·Oe)) [12]. Despite being a promising candidate for multifunctional applications, polycrystalline BF shows serious problems related to electric conductivity, and a cycloidal disposition of the magnetic moments forms a typical weak-ferromagnetic arrangement that prevents practical application of BF samples. In this sense, the mixing of BF with other perovskite-structured materials (forming pseudo-binary systems), which focuses on obtaining high-resistive solid solutions with magnetic moment and magnetoelectric coupling, has been employed with good results.

In this work, a careful review concerning the state of the art about the structural phase relations in binary perovskite-structured BF-based polycrystalline compounds is presented and discussed. Furthermore, some unpublished results are added and discussed with the objective to point out the open issues relative to the intrinsic and unrevealed mechanism that links structural arrangements and ferroic properties in these systems, and show their potential for practical applications.

## 2 BiFeO<sub>3</sub>-based systems

The three most investigated BF-based polycrystalline solid solutions that can be found in the literature are (1-*x*)BiFeO<sub>3</sub>-*x*PbZrO<sub>3</sub> (BF-PZ), (1-*x*)BiFeO<sub>3</sub>-*x*BaTiO<sub>3</sub> (BF-BT), and (1-*x*)BiFeO<sub>3</sub>-*x*PbTiO<sub>3</sub> (BF-PT) systems. BF-PZ system is less studied among them, and its potential for multifunctional applications is only recently investigated [13]. Initially, this system was synthesized focusing on PZ's effects on the overall physical properties of BF compound. However, these studies were abandoned because of the enormous

difficulty for obtaining single-phase polycrystalline samples and the strong tendency of the formation of non-perovskite phases during the synthesis process [13]. BF-BT system is the most widely studied and shows potential to be applied in ferroelectric, magnetic and piezoelectric devices. As BF-BT solid solutions are processed from BiFeO<sub>3</sub> and BaTiO<sub>3</sub> that are known to be lead-free, BF-BT solid solutions form a continuous series of compounds that also show environmental interest. Finally, BF-PT system shows the highest potential of multifunctional applications, because it presents very good ferroelectric, piezoelectric and weak ferromagnetic properties, and a strong magnetoelectric coupling. In fact, the development of BF-PT compounds can trigger the onset of a new family of multifunctional devices focusing on several advanced applications.

## 3 (1-*x*)BiFeO<sub>3</sub>-*x*PbZrO<sub>3</sub> system

BF-PZ solid solutions show triclinic crystal symmetry (rhombohedral, *R3c* space group) and perovskite structure (ABO<sub>3</sub> type) at room temperature [13], and low PZ concentration ( $x < 0.2$ ). Increasing PZ concentration ( $x > 0.2$ ), the compound acquires a pseudo-cubic symmetry, which can be represented by a rhombohedral structure whose angles between lattice parameters are close to 90°. When *x* is above 0.7, BF-PZ system acquires an orthorhombic symmetry (*Pba2*) [14]. Apparently, the lattice symmetry is derived from BF compound and does not change with the increase of PZ content until  $x \approx 0.2$  [13]. The related lattice parameters are: for  $x = 0.1$ ,  $a \approx 5.59$  Å and  $c \approx 13.9$  Å; for  $x = 0.2$ ,  $a \approx 5.63$  Å and  $c \approx 13.98$  Å. The magnetic properties of BF-PZ system are also investigated by magnetic and neutron diffraction measurements. The magnetic field dependency of the magnetization indicates a typical weak-ferromagnetic behavior, revealing that the spiral spin arrangement of BF end member is effectively broken by introducing PZ into BF structure. However, the magnetic moments, obtained from the neutron diffraction experiments, indicate an antiferromagnetic/paramagnetic phase transition around 635 K for  $x = 0.1$ , and 500 K for  $x = 0.2$ , respectively. Figure 1 shows the sketch of magnetic structure of the  $x = 0.1$  sample.

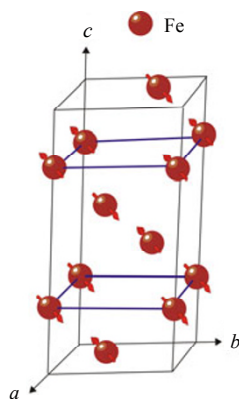


Fig. 1 Schematic magnetic structure of the  $0.9\text{BiFeO}_3\text{-}0.1\text{PbZrO}_3$  sample at 10 K ( $R3c$  space group with a G-type antiferromagnetic structure, adapted from [13]).

The magnetic phase revealed by neutron diffraction data is best described by an antiferromagnetic G-type magnetic structure model, as those reported for BF compound. Anyway, considering that few BF–PZ compositions are investigated, a close relation between the structure and magnetization has not been identified in this case, suggesting that further investigations need to be conducted to elucidate/reveal the true mechanism in this correlation.

#### 4 $(1-x)\text{BiFeO}_3\text{-}x\text{BaTiO}_3$ system

X-ray diffraction (XRD) and high-resolution XRD studies show that the symmetric structural arrangements of BF–BT compounds can be controlled by changing BT content in the solid solutions. In fact, for  $x$  ranging from 0 to 0.27, BF–BT solid solutions exhibit a rhombohedral distortion ( $R3c$  space group) [15,16]. However, a monoclinic phase ( $Cm$  space group) is also reported as coexisting with the  $R3c$  symmetry in the polycrystalline sample of  $x=0.2$  [17]. The coexistence of cubic and rhombohedral phases is reported to occur near  $x=0.3$  [16]. For samples with  $x$  ranging from 0.27 to 0.93, a cubic phase (Fig. 2), and a tetragonal symmetric arrangement for  $x>0.92$  [15,16], are also reported.

The change in BF–BT structural symmetry, as a function of temperature, was investigated by Wang *et al.* [16] by performing high-resolution XRD measurements. For pure BF samples, a rhombohedral phase is observed until  $825^\circ\text{C}$ , where the symmetry changes to an orthorhombic arrangement and persists until  $850^\circ\text{C}$ , and then the sample becomes cubic. For

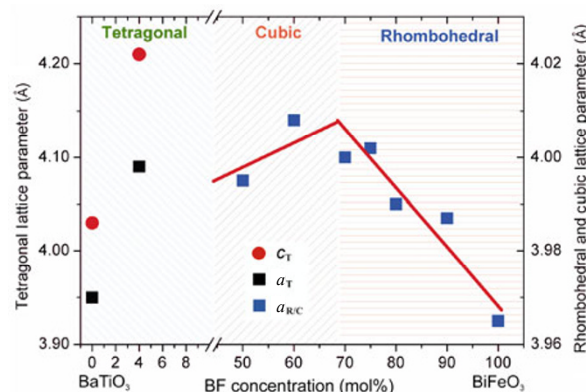


Fig. 2 Lattice parameters and space groups of BF–BT system obtained from the XRD results, as a function of BF molar concentration; the left and right scales are the values of the tetragonal ( $a_T$ ,  $c_T$ ) and rhombohedral/cubic ( $a_{R/C}$ ) lattice parameters, respectively (adapted from [15]).

$x=0.1$ , a transition from rhombohedral to cubic phase is observed in the temperature range of  $700\text{--}760^\circ\text{C}$ . A similar behavior is also observed for the  $x=0.2$  sample, which reveals a rhombohedral-to-cubic phase transition near  $740^\circ\text{C}$ . For samples with  $x=0.3$ , a “cubic + rhombohedral” (where the cubic phase is the majority phase) to cubic transition takes place near  $680^\circ\text{C}$ .

The dielectric, ferroelectric and magnetic properties of BF–BT solid solutions also show a strong dependence with BF–BT composition, and consequently, with the structural symmetry in each case. The electrical properties are improved with the increase of BT content, generally by increasing the dielectric response and reducing the dielectric losses [18]. In fact, Wang *et al.* [18] observed an increase of the dielectric constant in the  $x=0\text{--}0.3$  samples, from 30 ( $x=0$ ) to 500 ( $x=0.3$ ), at 1 MHz and room temperature.

Considering magnetic properties, it is reported a considerable change in the magnetic behavior of BF–BT solid solutions with the increase of BT content, by changing the structural symmetric arrangements of the samples [15,17,19,20]. As observed by Kumar *et al.* [15], BF–BT system exhibits an improvement of magnetic response for the  $x=0.1$  and 0.2 samples, showing a high hysteretic behavior. However, a decrease is observed as BF–BT symmetry becomes more and more symmetric, showing almost no hysteresis for  $x=0.75$  and so on. The  $x=0.1$ , 0.2 and 0.3 samples, analyzed by Kumar *et al.* [15] and Shi *et al.* [21], exhibit an antiferromagnetic behavior with a

field-induced ferromagnetic ordering. In fact, these authors reaffirmed that, through electron spin resonance measurements, the ferromagnetic behavior is shown for the  $x=0.1$ , 0.2 and 0.25 samples, while for samples with  $x=0.3$  and 0.996 at room temperature, resonance peaks at different fields reveal the absence of magnetic ordering, confirming that as BT content increases, the antiferromagnetic ordering gets to be suppressed, giving order to a paramagnetic state [22].

## 5 $(1-x)\text{BiFeO}_3-x\text{PbTiO}_3$ system

The first published work, regarding the synthesis of BF–PT solid solutions, was reported by Fedulov *et al.* [23] in 1962. Later, in 1964, Fedulov *et al.* [24] proposed the first structural, magnetic and ferroelectric phase diagrams for these solid solutions. In fact, it reported the coexistence of rhombohedral and tetragonal symmetries at  $x=0.7$ , consisting in a morphotropic phase boundary (MPB). In the early 1990s, the magnetic properties of BF–PT solid solutions were investigated once more [25]. However, it was only with the resurgence of the academic interest in the multiferroics driven by works of Spaldin *et al.* [12,26] at the beginning of this century, that the studies of BF–PT solid solutions gained a renewed impulse [27–30]. In this way, structural aspects of these compounds began to be investigated in order to find magnetoelectric applications, understand the magnetic [31], ferroelectric and piezoelectric behaviors [32], and even the magnetoelectric coupling [33]. Currently, studies are being conducted in order to understand the nature of the physical properties observed in these compounds in both single and polycrystalline formats. These studies are intended to discover the relationship of the physical properties of these compounds with their structure, in order to control these properties through doping/modifying the A and B perovskite sites [34,35].

In fact, BF–PT solid solutions acquire magnetoelectric, ferroelectric and piezoelectric properties from their end members, i.e., BF and PT compounds [36,37]. Furthermore, similar to the previous systems, their properties can be tuned/controlled by changing the concentration of each end member. In this way, by increasing PT concentration the ferroelectric and piezoelectric properties are enhanced, while by decreasing PT concentration the magnetic properties tend to be enhanced.

These degrees of freedom for tuning BF–PT physical properties are intrinsically linked to the structural arrangement/group symmetry, which also can be controlled by PT concentration with a still unrevealed mechanism. As BF compound shows a rhombohedral perovskite structure ( $R3c$  space group) [36], when PT compound is added into BF, the  $R3c$  space group is maintained at low PT concentrations, as shown in Fig. 3. However, with increasing PT concentration (always reported for  $x=0.3$ , here precisely for  $x=0.31$ – $0.32$ ), the structural symmetry of these solid solutions changes to a tetragonal symmetry ( $P4mm$  space group), arising from PT end member.

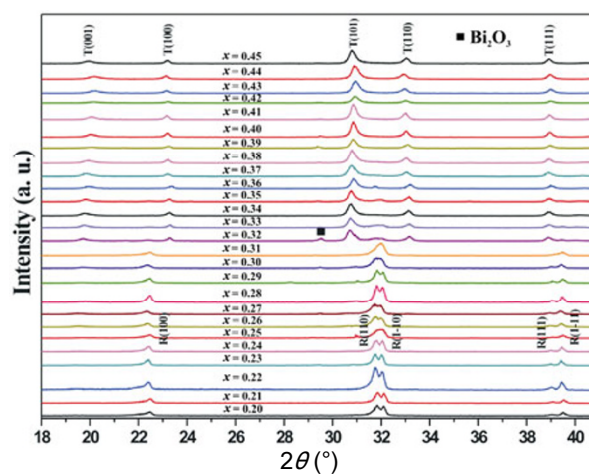


Fig. 3 XRD patterns for BF–PT polycrystalline compounds. The PT concentration is ranged from 20 mol% to 45 mol% (from bottom to top).

The structural transition is also a region of coexistence of both symmetric phases ( $R3m$  and  $P4mm$ ). This MPB region can vary with the method and parameters of synthesis (processing protocol), and occur in our samples for  $x$  ranging from 0.20 to 0.45 (Fig. 4). Systems showing MPB region have been pointed out as promising candidates for practical applications, because they present enhanced ferroelectric and piezoelectric properties as, for example, those observed in  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  samples [38].

The structural, electric and magnetic properties of BF–PT system have been studied since the middle of the 20th century. The first paper reporting BF–PT phase diagram was published in 1964 [24]. In this work, the authors observed a structural phase transition from rhombohedral to tetragonal symmetry and the presence of MPB region. Recently, in 2008, a complete structural and magnetic study of BF–PT system was conducted by Zhu *et al.* [39]. The structural



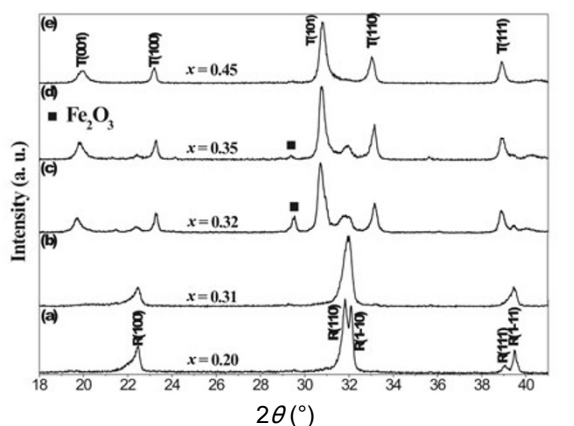


Fig. 4 XRD patterns for BF–PT solid solutions, evidencing an MPB region for  $x$  ranging from 0.20 to 0.45.

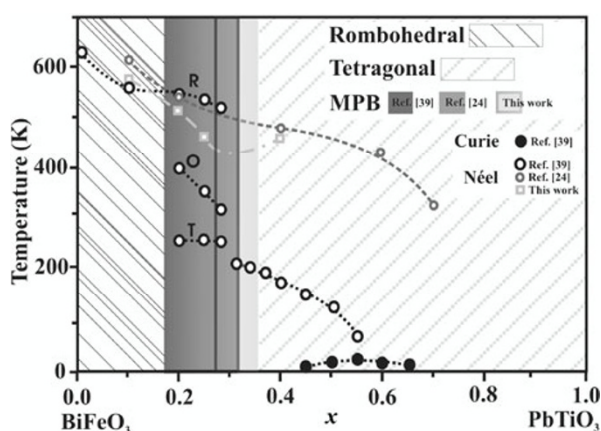


Fig. 5 Structural and magnetic phase diagrams for BF–PT system (R: rhombohedral; O: orthorhombic; T: tetragonal, adapted from [24,39]).

and magnetic data, comparing with current phase diagrams, is shown in Fig. 5. In fact, unlike the first authors [24], Zhu *et al.* claimed that they have found an orthorhombic phase in MPB region by deconvoluting XRD peaks [39]. In this way, three phases are proposed for MPB region and three magnetic phase transition temperatures (antiferromagnetic–paramagnetic Néel temperatures) are identified. However, divergent Néel temperatures can be observed for high PT concentrations, probably as a consequence of the different synthesis protocols employed for samples processing. In addition, at high PT concentrations and very low temperatures, a ferromagnetic state was also proposed.

In 2009, Bhattacharjee *et al.* [40] showed evidences for a monoclinic phase ( $Cc$  space group) in MPB region of the BF–PT system by associating Rietveld analysis with some magnetic anomalies observed in

magnetization curves. The experimental evidence of the existence of a monoclinic phase separating or coexisting with tetragonal and rhombohedral phases means a bridge connecting the different directions of polarization in this system, as similarly described by Noheda *et al.* [38] for PZT (lead zirconate titanate) samples. In other works, it was shown that the change in the electric polarization direction does not occur abruptly, from [111] (rhombohedral symmetry) to [001] (tetragonal symmetry) direction [41]. Instead, an intermediate direction in a monoclinic arrangement was proposed (Fig. 6).

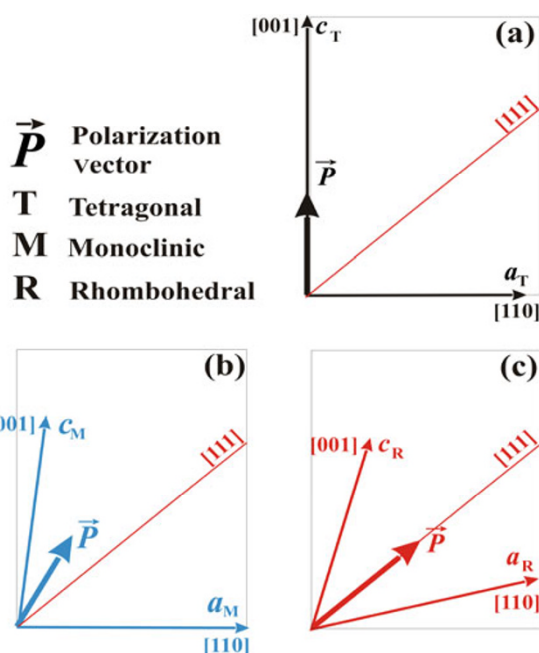


Fig. 6 Schematic illustration of (a) tetragonal, (b) monoclinic, and (c) rhombohedral distortions of the perovskite unit cell projected on the pseudo-cubic (110) plane with the respective polarization directions (adapted from [41]).

The magnetic and nuclear structure of BF–PT solid solutions were also recently investigated by neutron diffraction. In 2009, Comyn *et al.* [31] investigated the  $x=0.1$  composition by neutron diffraction and observed a perovskite structure with rhombohedral symmetry ( $R3c$  space group) and an antiferromagnetic G-type magnetic arrangement. Recently, in 2011, two works by Ranjan *et al.* [42] and Comyn *et al.* [34], reported neutron diffraction investigations in BF–PT samples. In the first work [42], an interesting study about the sensible change in the structure of the  $x=0.2$  composition was conducted as a function of temperature. The authors reported a change in the

chemical bonds of the compound at the magnetic Néel temperature and related this change to the force that the magnetic arrangement promotes in the structure. These observations suggest that this system exhibits some kind of coupling between spin, strain and structural degrees of freedom.

The second work [34] conducted at low temperatures ( $T < 4$  K), and reported an antiferromagnetic ordering in the tetragonal arrangement of the  $x=0.3$  sample. Figure 7 shows the tetragonal structure (eight unit cells) with the antiferromagnetic G-type magnetic arrangement. In

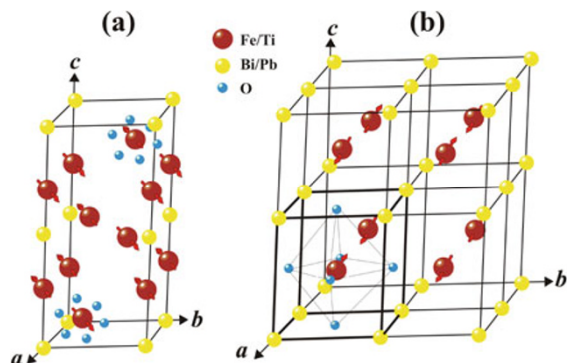


Fig. 7 Simulation of the magnetic and structural arrangements from neutron diffraction data: (a)  $0.9\text{BiFeO}_3-0.1\text{PbTiO}_3$ , and (b)  $0.7\text{BiFeO}_3-0.3\text{PbTiO}_3$  unit cells (adapted from [22]).

this scheme, the ferroelectric polarization vector, pointing in  $[001]$  direction ( $c$ -direction), is approximately  $50^\circ$  misaligned to the antiferromagnetic magnetization vector, which points in the  $[111]$  direction of tetragonal unit cell.

## 6 Structure–property relations

The three BF-based compounds presented in this paper have advantages for some practical applications and disadvantage for others (see Table 1). For example, BF–PZ ceramics have high dielectric constants (at room temperature) in comparison with those found in BF–PT and BF–BT ones, being apparently more suitable for applications in areas where elevated capacitances are required, as in information or electric field storage. On the other hand, the magnetic coercive fields of BF–BT samples are smaller than those found for BF–PZ and BF–PT samples. Therefore, magnetic devices constructed with BF–BT materials will tend to require less energy for operation. However, for all other possible practical applications (magnetic, ferroelectric, piezoelectric and magnetoelectric), BF–PT samples seem to be more adequate. In fact, the results found for BF-based ceramics in the framework of multiferroic properties and applications, are listed in Table 1.

**Table 1 Comparison between physical properties of  $(1-x)\text{BiFeO}_3-x\text{ABO}_3$  solid solutions**

Feature	$x\text{PbZrO}_3$	$x\text{BaTiO}_3$	$x\text{PbTiO}_3$
Structural behavior	$R3c$ ( $x < 0.2$ ) [13] $P-C$ ( $0.2 < x < 0.7$ ) [14] $Pba2$ ( $x > 0.7$ ) [14]	$R3c$ or $R3c+Cm$ ( $0 < x < 0.27$ ) [15,17] $Pm-3m$ ( $0.30 < x < 0.92$ ) [16] $P4mm$ ( $x > 0.92$ ) [15,16]	$R3c$ ( $0 < x < 0.18$ ) [24,39] $R3c+P4mm$ ( $0.18 < x < 0.35$ ) [24,39] $P4mm$ ( $x > 0.35$ ) [24,39]
Magnetic behavior	G-type antiferromagnetic	G-type antiferromagnetic with weak ferromagnetism	G-type antiferromagnetic with weak ferromagnetism
$T_N$ (K)	500 ( $x=0.2$ ) [13]	267 ( $x=0.3$ ) [15]	630 ( $x=0.3$ ) [29]
$M_r$ ( $10^{-3}$ emu/g)	0	1.76 ( $x=0.3$ ) [12]	9.91 ( $x=0.4$ ) [37]
$H_c$ (Oe)	0	182 ( $x=0.3$ ) [12]	754 ( $x=0.4$ ) [37]
Electric property	Ferroelectric	Ferroelectric	Ferroelectric and piezoelectric
$T_{C-FE}$ (K)	423 (MPB)	645 (MPB)	933 (MPB)
$P_s$ ( $\mu\text{C}/\text{cm}^2$ )	4.0 ( $x=0.8$ , 100 kHz) [14]	4.4 ( $x=0.3$ , 46 Hz) [16]	22.5 ( $x=0.4$ , 30 Hz) [37]
$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	0.7 ( $x=0.8$ , 100 kHz) [14]	1.8 ( $x=0.3$ , 46 Hz) [16]	17.5 ( $x=0.4$ , 30 Hz) [37]
$E_c$ (kV/cm)	Uninformed [14]	19.0 ( $x=0.3$ , 46 Hz) [16]	18.1 ( $x=0.4$ , 30 Hz) [37]
$K'$ (room temp.)	800 ( $x=0.8$ , 100 kHz) [14]	500 ( $x=0.3$ , 1 MHz) [16]	330 ( $x=0.3$ , 1 kHz) [29]
$\alpha_{33}$ (mV/(cm·Oe))	—	0.11 ( $x=0.2$ , 300 K) [20]	0.90 ( $x=0.5$ , 298 K) [33]
$d_{33}$ ( $10^{-12}$ m/V)	—	—	49.1 ( $x=0.4$ ) [32]

From top to bottom: structural behavior ( $R3c$ =rhombohedral,  $P-C$ =pseudo-cubic,  $Pba2$ =orthorhombic,  $Cm$ =monoclinic,  $Pm-3m$ =cubic, and  $P4mm$ =tetragonal); magnetic behavior ( $T_N$ =antiferro-paramagnetic (Néel) transition temperature,  $M_r$ =remnant magnetization, and  $H_c$ =coercive magnetic field); electric property ( $T_{C-FE}$ =ferro-paramagnetic (Curie) transition temperature,  $P_s$ =polarization of saturation,  $P_r$ =remnant polarization,  $E_c$ =coercive electric field, and  $K'$ =real dielectric constant); magnetoelectric property ( $\alpha_{33}$ =magnetoelectric coefficient); piezoelectric property ( $d_{33}$ =piezoelectric coefficient).

The structural phase relations in this system appear to be coincident because all structural transitions occur with their specific modifier concentration increasing. Moreover, MPB is observed in all systems ( $x \approx 0.8$  to BF–PZ,  $x \approx 0.3$  to BF–BT and BF–PT), where there is an improvement of the ferroic properties. Interestingly, these MPB regions appear to be intrinsic of perovskite structures, since other known compounds, as  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  and  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ , also present intriguing MPBs [43].

Likewise, all revised systems present an antiferromagnetic G-type structure. However, only BF–PT and BF–BT systems exhibit a small ferromagnetic hysteresis, indicating a weak-ferromagnetic state. The weak ferromagnetism is closely linked to the structural symmetry of the compound. In fact, according to Dzyaloshinsky and Moriya's prevision [44,45], in systems with rhombohedral symmetry and antiferromagnetic order, a small canting in antiparallel magnetic dipole moments results in a localized magnetization. Among those systems mentioned in this work, BF–PT has the best magnetic parameters ( $T_N$  and  $M_r$ ), which can be attributed to specific changes in the superexchange angle and to the disposition of the magnetic ions caused by specific modifications in A and B sites of the compound.

Ferroelectric properties are present in all BF–PT samples, independently of PT concentration. Like other properties, the best ferroelectric parameters are found in BF–PT system. The highest ferroelectric/paraelectric (Curie) transition temperature for the saturation and remnant polarizations, with the lowest coercive fields, are found in samples of the BF–PT system. As the ferroelectric properties are directly linked to the structural distortions, they are more pronounced in BF–PT than in other systems due to the strong and directional chemical bonds (active lone-pairs and/or hybridization [46]) between  $\text{Pb}^{2+}-\text{O}^{2-}$  and  $\text{Ti}^{4+}-\text{O}^{2-}$  ions.

The magnetoelectric coefficients  $\alpha_{33}$  for BF–PT (0.90 mV/(cm·Oe)) and BF–BT (0.11 mV/(cm·Oe)) systems were obtained in the same order of magnitude. The requirements for showing magnetoelectric coupling (MC), according to Hill [47], are mainly the existence of ferroelectric response and some magnetic order. However, other requirements are also needed, as having a polar point group (1, 2, 2',  $m$ ,  $m'$ , 3,  $3m'$ , 4,  $4m'm'$ ,  $m'm'2'$ ,  $m'm'2'$ , 6 e  $6m'm'$ ) adequate for both magnetic and electric orders [47]. Another requirement,

specific for polycrystalline samples, is that they own electrical resistivities that proportionate electric polarization. At this point, an enormous difficulty arises because magnetic systems generally tend to be electrically conductive.

Thus, by meeting the requirements listed above, two of the three systems discussed in this work need to be highlighted, i.e., BF–PT and BF–BT solid solutions. In fact, both systems show high electrical resistivity, ferroelectric polarization and weak ferromagnetic order, as facilitators of the MC [47]. From another point, which highlights the relation between MC and atomic structure, is that both systems show point groups belonging to those cited above ( $3m$  to BF–PT,  $3m$  and/or  $4mm$  to BF–BT). In fact, their high electrical resistivities are linked to the hybridization which distorts the  $d^n$  electronic sublayer and induces the magnetoelectric coupling [33]. In both cases, Ti–O bonds are hybridized [46], distorting the  $d^n$  sublayer and allowing, in some way, the coexistence of magnetic and electric (with high electrical resistivity) orders. However, Pb–O bonds are also hybridized in BF–PT system, enhancing its ferroelectric properties. In this way, the magnetoelectric coupling of BF–PT compounds (0.9 mV/(cm·Oe)) tends to be stronger than that of BF–BT compounds (0.1 mV/(cm·Oe)) (better electric and magnetic responses for BF–PT samples ( $P_r = 17.5 \mu\text{C}/\text{cm}^2$  and  $M_r = 9.91 \times 10^{-3} \text{ emu/g}$ ) in comparison with BF–BT ones ( $P_r = 1.8 \mu\text{C}/\text{cm}^2$  and  $M_r = 1.76 \times 10^{-3} \text{ emu/g}$ )).

## 7 Close remarks

Perovskite-structured BF-based multiferroic compounds appear as important candidates to be applied in smart advanced multifunctional devices, as solid-state transformers, multiple state nonvolatile memories, magnetic tunable piezodevices, magnetic field sensing and actuators, and so on. In fact, a complete understanding of the close relations between structure and physical properties in these solid solutions is highly desirable. However, it seems to be clear that the physical properties of the perovskite-structured BF-based compounds are highly dependent of the structural symmetric arrangement in each case. Depending on the solid solution end member, i.e.,  $\text{PbZrO}_3$ ,  $\text{BaTiO}_3$  or  $\text{PbTiO}_3$ , and the physical nature of the atoms in A site of the perovskite structure, the compound can assume a specific group

symmetry that can favor specific physical properties, as weak ferromagnetism and piezoelectricity. In this way, new ideas and investigations, focused to identify the intrinsic mechanisms that link the structural and physical properties of multifunctional multiferroic materials, especially those composed by BF compound, are still necessary, and demonstrate that this subject is still open for discussion.

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