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The Polar/Antipolar Phase Boundary of BiMnO₃-BiFeO₃-PbTiO₃: Interplay among Crystal Structure, Point Defects and Multiferroism

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A highly topical material is the ferromagnetic perovskite oxide BiMnO₃, and also the solid solutions it forms with antiferromagnetic/ferroelectric BiFeO₃ and with ferroelectric PbTiO₃ that result in distinctive polar/non-polar morphotropic phase boundaries (MPBs). The exploitation of such type of MPBs could be a novel approach to engineer novel multiferroics with phase-change magnetoelectric responses, in addition to ferroelectrics with enhanced electromechanical performance. We report here the interplay among crystal structure, point defects and multiferroic properties of the BiMnO₃-BiFeO₃-PbTiO₃ ternary system at its line of MPBs between polymorphs of tetragonal *P4mm* (polar) and orthorhombic *Pnma* (antipolar) symmetries. A strong dependence of the phase coexistence on thermal history was found, so as phase percentage significantly changes whether the material is quenched or slowly cooled from high temperature. The origin of this phenomenon is investigated with temperature dependent structural and physical property characterizations. A major role of the complex

defect chemistry, where a Bi/Pb-deficiency allows Mn and Fe ions to have a mixed-valence state, in the delicate balance between polymorphs is proposed, and its influence in the magnetic and electric ferroic orders is defined.

1. Introduction

Magnetoelectric multiferroics are compounds that simultaneously present ferroelectricity and magnetic order, either ferromagnets or antiferromagnets with canted ferromagnetism, and that are liable to show coupling between polarization and magnetization.^[1] Research activity in this field is being extensive and driven toward novel approaches for obtaining compounds with large linear magnetoelectric effect or crossed switching phenomena at room temperature:^[2,3] the generation or reversal of the magnetization with an electric field and of the polarization with a magnetic one.^[4] This is required for their incorporation into a range of proposed technologies,^[5] like voltage tunable microwave components, spintronic devices, and non-volatile magnetoelectric memories.^[6,7]

One of the most promising approaches for the design of new multiferroics is the engineering of functionality on a site-by-site basis in model systems such as ABO_3 perovskite oxides, in which one makes use of the stereochemical activity of an *A*-site cation (*e.g.*, $6s^2$ lone-pair electrons of Bi^{3+} or Pb^{2+}) to induce the required structural distortion for ferroelectricity, while magnetism is achieved by placing a magnetically active cation at the *B*-site.^[8] Many examples of these *A*-site driven ferroelectric perovskites can be found in the literature,^[9] among which BiFeO_3 stands out as the most topical one.^[10] This is because it shows both antiferromagnetic ordering and ferroelectricity at room temperature, and also because coupling of ferroelectric and antiferromagnetic domains has been demonstrated.^[11]

Alternative *A*-site driven ferroelectric perovskites are also under focus, in particular those in which multiferroicity comes from materials with ferromagnetic ordering.^[12] A number of Mn-based perovskite oxides has been reported, among which BiMnO_3 stands out as one of the

rare ferromagnetic insulators with an ordering temperature of ~ 105 K.^[13] A first-principles investigation has indicated heavy perovskite distortions in this material to be driven by the stereochemically active Bi^{3+} lone pair,^[14] resulting in a non-centrosymmetric monoclinic structure ($C2$ space group).^[15] However, later detailed structural and electrical characterizations of bulk materials have indicated it to crystallize in space group $C2/c$,^[12] and thus not to be ferroelectric at room temperature.^[16-18] This is in contrast with the case of epitaxial thin films under a compressive bi-epitaxial stress, in which ferroelectricity is strain engineered.^[19] From the synthesis point of view, the stoichiometric compound is rarely obtained free of point defects due to the volatility of bismuth oxide and the resulting lack of phase stability. Indeed, compositions with oxygen hyper-stoichiometry have often been reported, which showed different centrosymmetric structures depending on the actual composition.^[20] $\text{BiMnO}_{3+\delta}$ has been shown to tolerate oxygen excesses as high as $\delta = 0.16$, for which strong effects on functionality are anticipated.^[21] This non-stoichiometry is likely related to cation vacancies compensated by a mixed valence state of manganese.^[22] The role of the defect chemistry on the multiferroic behavior of Mn-containing perovskites has already been demonstrated, particularly in the context of strained films.^[23]

Among different approaches under investigation for enhancing the phase stability of Bi-containing perovskites while improving their multiferroic properties, the preparation of solid solutions stands out as a very promising route.^[24-26] It can lead to the appearance of morphotropic phase boundaries (MPBs), at which property enhancement take place and phase-change functional responses can be obtained.^[27,28] Indeed, the occurrence of phase-change magnetoelectric phenomena has been experimentally demonstrated for specific compositions of the BiFeO_3 - BiMnO_3 - PbTiO_3 ternary system placed at MPBs between polymorphs of monoclinic Cc and tetragonal $P4mm$ symmetries.^[29] The underlying mechanism is the discrete rotation of the magnetization due to an electric field induced transformation between the ferroelectric (multiferroic) polymorphs. This is a well-known

phenomenon in ferroelectric perovskite solid solutions based on PbTiO_3 , in which the resulting enhancement of the piezoelectric properties at the MPB makes them of special interest for applications. Analogous multiferroic MPBs could be then the basis of a promising approach for obtaining room-temperature magnetoelectricity.

BiMnO_3 also forms a solid solution with the ferroelectric PbTiO_3 , which provides improved stability to this low-tolerance factor perovskite.^[30-32] Interest in this binary system is fostered by the presence of a potentially multiferroic MPB at composition 0.4BiMnO_3 - 0.6PbTiO_3 , characterized by the coexistence of a tetragonal $P4mm$ phase, isostructural with PbTiO_3 , and an apparently pseudo-cubic one, so that it would be a polar/non-polar MPB.^[30,31] A later study by precession electron diffraction suggested the pseudo-cubic phase to be orthorhombic $Pnma$ for compositions at the BiMnO_3 -rich region (away from the MPB).^[32] This polymorph is also present in BiMnO_3 under high pressure, above 8.6 GPa,^[33] and also in partially oxidized $\text{BiMnO}_{3+\delta}$ phases, with $\delta \geq 0.14$.^[21] Although fundamentally different to the widely exploited MPBs between two polar polymorphs, such type of MPBs between polar and non-polar phases might also result in large piezoelectric response from a polarization extension mechanism,^[34] and could thus be a novel approach to engineer novel ferroelectrics that match or even surpass the electromechanical performance of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$. Moreover, $Pnma$ can be turned into ferroelectric under an applied electric field, with the potential to be used in energy storage devices.^[35] Large phase-change magnetoelectric response has also been anticipated as a result of the antipolar to polar transition.^[36]

We report here an in-depth study on the interplay among crystal structure, point defects and multiferroic properties of two compositions of the BiMnO_3 - BiFeO_3 - PbTiO_3 ternary system lying in the line of polar/non-polar MPBs recently reported in its phase diagram.^[37] Materials are $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ (hereinafter binary-system composition) and $\text{Bi}_{0.47}\text{Pb}_{0.53}\text{Fe}_{0.17}\text{Mn}_{0.3}\text{Ti}_{0.53}\text{O}_3$ (ternary-system one). Mechano-synthesis was chosen as the synthesis method, which has been demonstrated to be optimal for the preparation of BiMnO_3 ,

BiFeO₃, and also the solid solutions they form with PbTiO₃. The high chemical homogeneity provided by this synthesis technique has been the key to uncover the actual MPB phases of these materials, and to correlate phase coexistence with point defects. Temperature dependant crystal structure and physical property characterizations were carried out. Results of the electrical and magnetic characterizations, along with mechanoelastic studies, allowed establishing the structure-property relationships, and the role of the defect chemistry on the multiferroic nature of phases at the polar/antipolar MPB.

2. Results

2.1. Crystal Structure

Mechanosynthesized powders consisted of submicron-sized agglomerates of nano-sized crystals with average size of 35 nm, as measured by transmission electron microscopy (TEM), in which only pseudocubic perovskite-type structure could be identified by x-ray diffraction (XRD) because of the low crystal size.^[37] Thermal treatments were then necessary to increase crystallinity for structural characterization. Two cooling profiles were used: (i) a slow cooling with rate of 3 °C min⁻¹ and (ii) a fast cooling (quenching) down to room temperature, both in air, that lead to different results.

Figure 1a shows the high-resolution XRD patterns of powdered samples corresponding to the binary-system composition after thermal treatments with the two different cooling profiles. In both cases, the powder was fully crystallized into a single perovskite-type structure (no secondary phases were found), which appears to be cubic (at least on average) after the slow cooling (red pattern), while it is clearly tetragonal after the quenching (blue pattern). Results indicate that different polymorphs can be stabilized at room temperature in the same powdered sample depending on the cooling profile used.

A first step was establishing the actual crystal symmetry of the two polymorphic phases at this MPB. The diffraction profiles were analyzed by the Rietveld method, implemented in

Jana2006 package,^[38] for which the orthorhombic *Pnma* and tetragonal *P4mm* symmetries, among others such as cubic *Pm-3m* and monoclinic *C2/c* and *C2* space groups, were selected as structural models (typical space groups reported within the binary system). Anisotropic strain broadening models, such as that proposed by Stephens,^[39] were implemented, which take into account crystal stresses and difference in transition strain between the polymorphs. Anisotropy factors due to presence of polar axes were also considered. The initial lattice parameters and atom coordinates were taken from reported data (Supporting Note S1).

The best fits between the observed and calculated profiles were obtained when using *Pnma* and *P4mm* symmetries for the slowly cooled and quenched powders, respectively (Supporting Figure S1 and Table S1). In the latter case, improved fits resulted when a model involving coexistence of *P4mm* (75%) and *Pnma* (25%) phases was considered. Note, however, that even though best statistical parameters were obtained for refinements using *Pnma*, differences with those including cubic *Pm-3m* instead are not large enough to fully rule out the latter symmetry ($R_{wp} = 10.18$, $R_p = 8.93$ and goodness-of-fit indicator $GOF = 1.53$ for *Pnma* to be compared with $R_{wp} = 10.26$, $R_p = 9.07$ and $GOF = 1.55$ for *Pm-3m*).

Neutron diffraction was then carried out to better distinguish between these two symmetries in the slowly cooled powdered sample. Pattern is shown in Figure 1b, along with Rietveld refinement using the orthorhombic *Pnma*. Results of the refinement for either *Pnma* or *Pm-3m* symmetries are given in **Table 1**. It can be seen that statistical parameters obtained, in particular the R_{wp} factor and GOF indicator, are clearly better for the *Pnma* space group.

The study was also accomplished in the ternary-system composition, in which a similar MPB between a tetragonal polymorph and an apparently cubic phase was obtained. The high-resolution XRD patterns after thermal treatments with either slow cooling or quenching are given in Supporting Figure S2, along with the Rietveld refinements using orthorhombic *Pnma* and tetragonal *P4mm* symmetries. A model involving coexistence of *P4mm* (85%) and *Pnma* (15%) phases was also necessary to fit the pattern of the quenched sample. Also in this case,

best fits were obtained when using these two space groups, among different symmetries. The refined structural and statistical parameters are summarized in Supporting Table S2.

To further investigate the actual symmetry of the pseudo-cubic phase, the evolution of phases with temperature was studied in the binary-system composition. **Figure 2** shows the temperature evolution of the XRD profiles around the $(110)_p$ diffraction peak (referring to pseudocubic index), along with the lattice parameters for both the tetragonal phase (a_T, c_T) and the apparently cubic one assuming a pseudo-cubic parameter (a_{ps}). In the case of the powder quenched from high temperature, tetragonality (ratio of lattice parameters c_T/a_T) decreases on heating indicating decrease of perovskite distortion, until the profile finally merges into a single 110 peak above 227 °C (Figure 2a). It should be noted that peak splitting above this temperature is due of CuK_α doublet. At higher temperature, a progressive shift of the 110 reflection towards lower angles takes place indicating the cell thermal expansion. Besides, a distinctive discontinuity seems to happen around 600 °C (see evolution of a_{ps} in Figure 2c, where a sharp cell contraction is evident). This could indicate the transition towards the high-temperature parent phase. It should be noted that most ferroelectric perovskites convert into cubic $Pm-3m$ at high temperatures.^[40]

On the contrary, only pseudo-cubic phases are observed in the slowly cooled powder on heating up to 750 °C, according to the XRD profiles in Figure 2b. No clear phase transitions are found, though two regions can be differentiated from the evolution of the a_{ps} parameter with temperature (see inset of Figure 2c), which shows a distinctive change of the cell thermal expansion rate at about 300 °C. The question is whether this change of slope might be associated with the transition towards the high-temperature cubic phase. Note that results indicate the actual symmetry of the polymorph in coexistence with the tetragonal one at the MPB to be orthorhombic $Pnma$ at room temperature. Note also that the low temperature slope of the a_{ps} parameter (27 - 300 °C) for the slowly cooled sample (orthorhombic $Pnma$) has the same value than that for the quenched sample at intermediate temperatures (250 - 600 °C).

Note finally that the quenched sample has larger cell parameters than the slowly cooled one in this intermediate range, and that the parameters converge to the same values above 600 °C.

This is the temperature, at which the quenched sample has been proposed to undergo the transition to the $Pm-3m$ phase. Therefore, one could assume that the slope discontinuity at 300 °C in the case of the slowly cooled sample is associated with the same transition. We will see how the temperature dependence of the physical properties supports this scenario.

2.2. Dielectric and Mechanoelastic Properties

Fully dense ceramics (final densification levels above 98%) with tailored microstructures and no traces of secondary phases (as checked by scanning electron microscopy and energy dispersive x-ray spectroscopy) were prepared by hot-pressing (see Supporting Figure S3).

This is a requirement for a sound ferro-/dielectric characterization, which is not easily fulfilled in the case of low tolerance factor perovskites, and especially in BiMnO₃-based materials owing to the poor stability of the perovskite structure in this oxide.^[18]

The temperature dependences of the relative permittivity (K') and dielectric losses ($\tan \delta$) for the ceramic materials under study showed large dielectric dispersion from room temperature up to 600 °C (Supporting Figure S4 and S5), which is likely related to conductivity effects. Indeed, the high conductivity is evident already at room temperature with $\tan \delta$ values above 0.1 and large frequency dispersion. This was confirmed by measurements of the temperature dependence of the dc conductivity (σ) obtained from impedance spectroscopy analysis. Results for the binary- and ternary-system compositions are shown in **Figure 3a**. Both samples presented Arrhenius-type behavior with similar room-temperature resistivity below $10^6 \Omega \text{ cm}$, which are not high enough to withstand the high electric fields required for ferroelectric characterization (resistivity values of bulk ferroelectric materials typically exceeds $10^9 \Omega \text{ cm}$ and even reaches up to $10^{12} \Omega \text{ cm}$).^[3,29] Besides, a

single mechanism seems to dominate the total σ along the whole temperature range, with activation energy of 0.4 - 0.45 eV. These values are typical of hopping of electrons/holes between mixed-valence state in transition metals, such as those of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$, which seem to be the origin of the high conductivity of these materials, as checked by x-ray photoelectron spectroscopy (XPS) analysis.^[37]

Figure 3b shows the temperature dependence of K' at 1 MHz (heating/cooling cycle) for the ceramic corresponding to the binary-system composition after quenching from 750 °C. The curves clearly indicate a different sequence of phase transitions on heating and cooling. High frequency data is shown to minimize contributions from conductivity that might mask the dielectric anomalies (data at several frequencies are given in Supporting Figure S5). It should be noted that the predominant room-temperature phase in this sample is ferroelectric tetragonal $P4mm$, which fully disappears at about 250 °C according to the XRD results (Figure 2). Therefore, none of the anomalies on permittivity that are observed on heating at ~450 °C and ~615 °C can be related with the disappearance of the tetragonal phase. The first anomaly shows a strongly dispersive height, yet its position does not change with frequency and thus, it is likely related to a sudden release of trapped charge. Note that it is not observed on cooling. The high temperature anomaly above 600 °C has the typical shape of a ferroelectric or antiferroelectric transition, and actually it coincides with the described change in the evolution of the pseudo-cubic cell parameter that has been associated with the transition to a parent phase, most probably cubic $Pm-3m$. Note the irreversible character of the transition, for it is not observed on cooling. Indeed, the transition from the orthorhombic $Pnma$ phase to the cubic one was proposed to take place below 300 °C in slowly cooled powders, based on a change of slope of the pseudo-cubic parameter. However, no dielectric anomaly was observed at this temperature during the slow cooling of the ceramic.

Similar overall dielectric behavior was found for the ternary-system composition, yet few differences are worth noting, as shown in Figure 3c for the ceramic quenched from 750 °C

(see also Supporting Figure S5). In this case, a dielectric anomaly can be associated with the disappearance of the tetragonal phase at ~ 320 °C (only in the heating curves), which means a shift of 80 °C towards higher temperature in relation to that of the binary-system composition. Furthermore, the high temperature anomaly associated with the transition towards the parent cubic phase was found at ~ 530 °C, which indicates a shift of 85 °C towards lower temperature. Note also the presence of the anomaly at ~ 450 °C on heating related to the release of trapped charge, as discussed for the binary system.

Mechanoelastic effects that might be associated with this phase sequence were investigated by dynamical mechanical analysis, a powerful technique for studying ferroelastic transitions, widely applied to ferroelectrics,^[41-43] and especially useful when high conductivity becomes an issue, like the materials under study.^[31,43] Young's modulus (Y) and mechanical losses ($\tan \delta$) as a function of temperature for ceramic bars quenched from 750 °C are shown in **Figure 4**. Measurements were carried out during two successive heating/cooling cycles. In both materials, an irreversible elastic anomaly was found during the first heating, at ~ 220 °C for the binary-system composition and at ~ 300 °C for the ternary-system one (Figure 4a,c). This asymmetric minimum in Young's modulus is typically of a ferroelectric transition, and it is accompanied by a maximum in $\tan \delta$ that reflects the appearance of highly mobile ferroelectric/ferroelastic domains (90° domains in the case of tetragonal phase).^[41] Results are in a good agreement with those of XRD and dielectric data, indicating that both systems undergo a transition from quenched ferroelectric tetragonal to orthorhombic phase on heating.

Furthermore, a second anomaly consisting in a sudden stiffening of Young's modulus is also observed during the first heating, which starts at ~ 600 °C and ~ 550 °C for the binary- and ternary-system compositions, respectively. These are the temperatures at which a dielectric anomaly was associated with the transition to the high-temperature cubic phase (Figure 3b,c), and suggests that this transition might be a ferroelastic one, as one may anticipate for an orthorhombic to cubic transition. Note again the pronounced irreversible character of these

transitions, for only a broader and more symmetric minimum was obtained on cooling, and at the same temperature (~ 150 °C) in both samples. Recall that the room-temperature phase after cooling is *Pnma*, so this is not a transition towards the ferroelectric tetragonal phase initially present prior to heating curves, but most probably towards the orthorhombic one. Indeed, a tight reversibility of the curves was found during a second heating/cooling cycle in both materials, that is, when the starting phase is the *Pnma* one, in which only a minimum at ~ 150 °C is observed during both heating and cooling stages (Figure 4b,d). This confirms a different sequence of polymorphic transitions in the first and second heating/cooling cycles, due to the different polymorphs stabilized at room temperature with either quenching or slow cooling.

An additional study of the irreversibility of phase transitions was carried out in a ceramic of the ternary-system composition quenched from high temperature, consisting in successive thermal cycles between room temperature and an increasingly higher temperature, as shown in Figure 4e. First measuring cycle up to 350 °C showed the tetragonal-orthorhombic phase transition in both the heating and cooling curves, though with a significant thermal hysteresis of ~ 30 °C between heating and cooling runs. This indicates the partial (or complete) recovering of the tetragonal phase at room temperature after this first thermal cycle. Therefore, heating up to 350 °C is not enough to stabilize the *Pnma* polymorph in the later cooling, and the system evolves back to the tetragonal one. A next measuring cycle up to 500 °C indicates a different phase evolution on heating and cooling curves, more similar to that already showed in Figure 4c, though the minimum in Young's modulus on cooling is not so broad and symmetric. There seems to be a correlation between irreversibility and the previously discussed charge release event at 450 °C. We will come back to this point in the discussion.

2.3. Magnetic Properties

Magnetization was measured during conventional zero-field-cooling (ZFC)/field-cooling (FC) cycles under a *dc* magnetic field of 100 Oe. **Figure 5a,b** shows the temperature dependence

of the molar magnetic susceptibility (M/H ratio) of powdered samples with the two different cooling profiles, either slowly cooled or quenched. In both compositions, the overall magnetic behavior is similar regardless of the cooling profile used, despite the different polymorphs stabilized at room temperature in each treatment. The curves clearly display paramagnetic behavior down to very low temperatures, indicating the absence of any magnetic ordering at least until ~ 12 K. This must be associated with a similar disposition, and thus interactions, of magnetic ions in both tetragonal and orthorhombic structures for each composition.

In both materials, susceptibility curves exhibit a cusp-like anomaly in ZFC along with divergence of the ZFC and FC curves below 12 K, with a nearly constant magnetization in the FC one (see insets of Figure 5a,b). These are typical features of systems undergoing spin-glass or cluster-glass transitions, in which the maximum in ZFC curves corresponds to the critical temperature of the freezing process.^[44] The spin dynamics was studied by measuring the temperature dependence of the in-phase (χ') and out-of-phase (χ'') components of the *ac* susceptibility at several frequencies. Figure 5c,d shows the results for the binary-system composition (similar curves were obtained for the ternary-system one). The maxima of both χ' and χ'' were frequency dependent, so that their positions shifted toward higher temperatures on increasing frequency. Besides, around the maximum, χ' decreases and χ'' increases with frequency. These are common features of both spin- and cluster-glass systems that definitely rules out the possibility of a long-range magnetic ordering.

Useful information on the dynamics of a magnetic system that exhibit critical slowing down can be obtained from the *ac* susceptibility data, by comparing the dependence of the temperature of maximum susceptibility, T_m , on the characteristic relaxation time, $\tau = (2\pi f)^{-1}$, with the predictions of the dynamic scaling theory.^[44] According to this theory, the spin-glass transition temperature, T_{sg} , can be pinpointed from the divergence of τ related T_m using the power law expression of critical dynamics,^[45]

$$\tau = \tau_0 \left(\frac{T_m - T_{sg}}{T_{sg}} \right)^{-zv} \quad (1)$$

where zv is the dynamic critical exponent and τ_0 is the shortest relaxation time available to the system. The nonlinear fitting of the χ' data with Equation 1 is shown in Figure 5e for the two compositions under study, and the parameters obtained are given in **Table 2**. In both cases, the value of T_{sg} obtained is in a good agreement with the peak location in the ZFC curve (Figure 5a,b), as expected in the dynamic scaling theory, and the critical exponents fall within the usual range for glassy systems ($zv \sim 4 - 12$).^[46] However, the resulting τ_0 is several orders of magnitude smaller than the values expected for cluster glasses ($10^{-9} - 10^{-6}$ s), and rather lies within the range of values typical of spin glasses ($10^{-11} - 10^{-13}$). Note τ_0 is either determined by the atomic spin-flip time or by the flip time of noninteracting clusters.^[47] Results clearly pointed to canonical spin-glass behavior in both materials.

3. Discussion

A first issue that deserves discussion is the actual existence of the orthorhombic *Pnma* as one of the polymorphs at the MPB of the compositions under study. First structural data reported for the $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ binary system already indicated coexistence of a pseudo-cubic polymorph with the tetragonal *P4mm* one at the MPB (at about $x = 0.4$).^[30,31] The macroscopically pseudo-cubic phase reported for $x > 0.4$ was initially associated with a frustration effect coming from the different preferred environments of the cations, which results in the absence of long-range coupling of ionic displacements.^[30] Our combined structural and physical property characterizations strongly support this phase to be of orthorhombic *Pnma* symmetry in both the binary- and ternary-system compositions. This is also consistent with our previous TEM studies on $x = 0.5$ and 0.6 that indicated this phase.^[32]

Note that *Pmna* is a centrosymmetric space group and thus ferroelectricity is not allowed. Therefore, this MPB separates a ferroelectric tetragonal phase and a non-ferroelectric

orthorhombic one. This type of MPB has been reported, for instance, in rare-earth (RE) substituted BiFeO_3 (RE = Sm, Dy, Gd),^[48] and in solid solutions containing BiFeO_3 ,^[49] among others, leading in some cases to exceedingly large piezoelectric properties. In the former, a boundary between a rhombohedral $R3c$ and $Pnma$ phase was established, in which $Pnma$ was claimed to be antiferroelectric. This is one of the most common space groups in perovskite oxides,^[50] and deviation of the ideal structure originates from the ability of the corner-sharing octahedral framework to undergo cooperative tilting distortions due to the size mismatch between the A - and B -cations.^[51] Indeed, $Pnma$ symmetry is antipolar in nature,^[52] and can be turned into a functional ferroelectric under an applied electric field.^[35]

A second issue worth discussing, and actually the main topic of the article, is the finding of a strong thermal history dependence of the phase coexistence, so percentages of coexisting $Pnma$ and $P4mm$ components significantly change for the same powdered sample whether the material is quenched or slowly cooled from 950 °C. Insight into this thermal history effects can be gained from the temperature dependent structural and physical property characterizations, which clearly revealed a different sequence of polymorphic transitions during heating and cooling runs. Specifically, and in the case of the quenched powders, the structure evolves on heating from ferroelectric $P4mm$ to $Pnma$ phase, which involves the vanishing of ferroelectricity, and then finally transforms into the paraelectric cubic one. This is accompanied by distinctive dielectric and mechanical anomalies at the transitions. On the contrary, and on subsequent slow cooling, a single transformation into the $Pnma$ polymorph is found, in good agreement with the temperature evolution of the lattice parameters.

Note that the occurrence of the material coefficient anomalies (dielectric permittivity and Young's modulus) at the transition between the orthorhombic and high-temperature cubic phases indicates its ferroic character: from antiferroelectric/ferroelastic to paraelectric/elastic in this case. Elastic stiffening has been anticipated for this type of phase transition.^[53] It is remarkable that opposite softening during cooling takes place over a large temperature

interval, and that a minimum in the Young's modulus (accompanied by a maximum in the mechanical losses) is reached at ~ 150 °C. This indicates the completion of the transition towards the *Pnma* phase at room temperature.^[54] The higher values of the Young's modulus in the 200 - 600 °C temperature range is an indication of the gradual transformation into *Pnma* on cooling, and thus of a wide range of phase coexistence.

The same sequence of phase transitions applies to both compositions, only difference being the specific temperatures at which the transitions take place, as shown by the electrical and mechanical characterizations. Additionally, we have also found memory effects in relation to the phase stabilized at room temperature after thermal cycling, so as the material stabilizes into *Pnma* or evolves back to the tetragonal phase depending on the temperature reached in the heating step. As already advanced, there seems to be a correlation between the loss of memory and the charge release event observed in the electrical measurements at 450 °C. This strongly suggests a major role of the defect chemistry in the described phase evolution.

The complicated synthesis and processing of these materials, where Bi/Pb-deficiency usually arises during sintering and causes the Mn ions to change their oxidation state, result in a complex defect chemistry. The corresponding defect reaction could be expressed as:

where Bi(g) refers to evaporation of gaseous Bi. In this case, charge compensation after the formation of a Bi vacancy (which also applies to Pb) is only accomplished by oxidation of three Mn ions, though it could also be partially compensated by oxygen vacancies.

The explanation for the two different phases that are stabilized in the same material depending on the cooling profile might thus be related with the presence of Mn^{4+} and variations in oxidation state at *B*-sites. For instance, it is expected a high-temperature random occupancy of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions at this perovskite site. This disorder state might be frozen at room temperature with the quenching. This would imply that the disordered state would favor

the tetragonal ferroelectric phase. On the contrary, $\text{Mn}^{3+}/\text{Mn}^{4+}$ cation ordering could take place during slow cooling. This would yield an increased lattice periodicity and favor the tiny distortion that results in the *Pnma* phase. The occurrence of charge ordering is quite a common phenomenon in transition metal oxides, like the half-doped Mn-containing perovskites,^[55] and strongly interacts with the elastic behavior even in cases where crystals are not ferroelastic (*e.g.*, for symmetry reasons).^[53]

A noteworthy aspect related to this is the resulting high conductivity, in which electron/hole hopping mechanisms linked to the mixed valence of Mn seem to dominate. Indeed, previous XPS analysis indicated the presence of $\text{Mn}^{4+}/\text{Mn}^{3+}$ with ratio of 0.26 for the binary-system composition, which might be compensated by either Bi/Pb (*A*-site) or Mn (*B*-sites) vacancies, or both, giving rise to oxygen hyper-stoichiometry.^[37] The ratio increased to 0.31 for the ternary-system composition, in which Fe cations also showed a mixed valence ($\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.57). Nevertheless, in spite of the higher amount of carriers provided by the combined mixed-valence states of Mn and Fe, the total σ decreased, indicating it to be mainly dominated by the Mn mixed valence. Formally, a single Bi vacancy is compensated by three Mn^{4+} , which would be equivalent to a hole doping (*p*-type conductivity).

An additional aspect must be considered. It is common that the defect chemistry of these oxides is dominated by oxygen vacancies formed due to thermally induced reduction of the transition metal,^[22,56] which might also play a role in the phase coexistence dependence on cooling profile. For instance, the equilibrium oxygen content at high temperature might be frozen at room temperature by quenching, in addition to order/disorder phenomena. The slow cooling, however, provides more time for equilibration of the oxygen content of the samples, and this involves oxidation and reduction of cations, which results in changes in the tolerance factors. This would imply a different $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio that might push the system across the MPB. In this case, the point defect equilibrium using Kröger-Vink notation would be:

where $\text{Mn}_{\text{Mn}}^{\bullet}$ and Mn_{Mn} refers to Mn^{4+} and Mn^{3+} , respectively, $\text{V}_\text{O}^{\bullet\bullet}$ is an oxygen vacancy and O_O is an oxygen anion. Here, the kinetics would be controlled by diffusion of oxygen vacancies and oxygen anions during the thermal treatments.

Note that lattice parameters, and therefore the unit cell volumes, of the quenched and slowly cooled samples converge to the same value above 600 °C, indicating same thermal expansion coefficient in both cases. At room temperature, however, the difference in the unit cell volume of the resulting phases is about 0.75%, so as a chemical expansion was obtained as a result of the quenching treatment, which favored the formation of the tetragonal phase. This chemical expansion can be understood from the difference in the cation radii of Mn^{3+} (0.645 Å) and Mn^{4+} (0.53 Å), both with CN = 6, and the resulting changes in the size of the MnO_6 octahedra.^[56] The smaller lattice parameters for the slowly cooled sample then suggest that chemical contraction due to Mn oxidation took place, whereas a frozen oxygen vacancy state, achieved with the quenching, must hinder Mn oxidation. This would also explain the larger lattice parameters for the latter sample at intermediate temperatures (250 - 600 °C), which showed greater unit cell volume in about 0.5%.

The absence of ferroelectricity in one of the two polymorphs at the MPB is also worth mentioning. In this case, the occurrence of the antipolar orthorhombic phase may also be related to the presence of Mn^{4+} and the specific distortions that it introduces. It is known the Jahn-Teller character of Mn^{3+} ($t_{2g}^3 e_g^1$), with a single e_g electron with orbital degeneracy that is responsible of the high deformation of different perovskites.^[57] Presumably, Mn^{4+} decreases such distortion and favors the presence of a centrosymmetric structure. Indeed, the role of $\text{Mn}^{3+}/\text{Mn}^{4+}$ on the multiferroic characteristics has recently been described for $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_{3+\delta}$ compositions with $x \leq 0.3$.^[24] A dependence of the δ value on the sample thermal history was found, like a higher $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio in air-cooled samples than in air-quenched ones, with

significantly smaller perovskite distortions in the former. In our case, the question is whether the presence of only Mn^{3+} in a defect-free perovskite would likely result in two ferroelectric polymorphs at the MPB, such as the tetragonal $P4mm$ and, for instance, a monoclinic structure like the one anticipated for the stoichiometric BiMnO_3 (S.G. $C2$).^[15]

The presence of mixed-valence states might give rise to a double-exchange mechanism similar to that observed in A -substituted perovskites, thus inducing short-range ferromagnetism with spin-glass character. Random orientation of frozen spins occurs when the concentration of magnetic ions is diluted or the magnetic exchange interactions are frustrated.^[58] It is known that BiMnO_3 is an orbitally ordered ferromagnetic insulator below 105 K, via superexchange interactions.^[15] In our case, however, superexchange pathways involving nonmagnetic cations of the type Mn-O-Ti-O-Mn result in suppression of the long-range magnetic order. Indeed, the maximum M/H ratio decreases by three times for the ternary-system composition with respect to the binary-system one, indicating a decrease of magnetic interactions due to the further dilution of Mn ions.

Manganese oxides and doped manganese oxides can be easily found having mixed valence states, for which spin-glass behavior has been reported.^[59,60] This has been described as a low-temperature electronic phase separation, in which large ferromagnetic domains are present within an antiferromagnetic matrix. In this kind of systems, a strong competition between superexchange of positive ferromagnetic ($\text{Mn}^{4+}\text{-O-Mn}^{3+}$) and negative antiferromagnetic ($\text{Mn}^{4+}\text{-O-Mn}^{4+}$ and $\text{Mn}^{3+}\text{-O-Mn}^{3+}$) interactions can be found. This would lead to freezing of the local magnetic moment and spin-clustering with random orientations. This effect should be present in both the binary- and ternary-system compositions under study. In the latter, perovskite B -sites occupied by Fe^{3+} do also participate in both interactions, becoming predominant those which are antiferromagnetic between Fe^{3+} and its nearest Mn^{3+} or Fe^{3+} , while the ferromagnetic interactions would appear from $\text{Fe}^{3+}\text{-O-Mn}^{4+}$.

4. Conclusion

We have provided a detailed study of the crystal structure and physical properties of two compositions of the $\text{BiMnO}_3\text{-BiFeO}_3\text{-PbTiO}_3$ ternary system placed at its line of polar/antipolar MPBs. High-resolution x-ray and neutron diffraction studies indicated the actual phases coexisting at this MPB to be tetragonal $P4mm$ and orthorhombic $Pnma$ polymorphs. We have also found a strong thermal history dependence in the phase coexistence, so that the same powdered sample crystallizes into $P4mm$ or $Pnma$ phases depending on whether the material is quenched or slowly cooled from 950 °C. This results in a strong irreversible sequence of polymorphic phase transitions during subsequent thermal cycling, as shown by temperature dependant structural characterization and dielectric and mechanoelastic studies. Specifically, the perovskite phase evolves from ferroelectric $P4mm$ to antiferroelectric $Pnma$ on heating, wherein ferroelectricity is vanished, and finally to the high-temperature paraelectric $Pm-3m$ phase. However, on cooling, the $Pnma$ polymorph is the one stabilized at room temperature.

The origin of this phenomenology is correlated with the defect chemistry and possible order/disorder features of this complex system, in which the formation of cation vacancies are charge compensated by the combined presence of mixed-valence states in both Mn/Fe ions and oxygen vacancies. Results indicate the essential role of defects on the polar/antipolar phases present at the MPB and, hence, on their ferroelectric/antiferroelectric and magnetic behaviors. The mixed-valence state is responsible not only of the high p -type conductivity, but also of the relative stability of the phases and the canonical magnetic glass freezing obtained. The presence of Mn^{4+} presumably decreases distortion and favors the presence of the centrosymmetric structure when the sample is slowly cooled. Moreover, mixed-valence state gives rise to a double-exchange mechanism that might induce a ferromagnetic-like behavior, but it is suppressed by the superexchange pathways involving nonmagnetic cations.

5. Experimental Section

Synthesis of Nanopowder and Ceramic Processing: Mechano-synthesis was used to obtain nanocrystalline powders of the $(1-x-y)\text{BiMnO}_3-x\text{PbTiO}_3-y\text{BiFeO}_3$ system, with $x = 0.6$; $y = 0$ (binary-system composition), and $x = 0.53$; $y = 0.17$ (ternary-system one), from stoichiometric mixtures of analytical grade oxides Bi_2O_3 , PbO , Fe_2O_3 , Mn_2O_3 and TiO_2 . Details of the procedure and of the mechanisms taking place during the mechanical treatments can be found elsewhere.^[32,37] Initial mixtures were homogenized in an agate mortar, after which 10 g of each mixture were mechanically treated during 18 h in a planetary mill (Fritsch Pulverisette 6) operating at 300 rpm. Tungsten carbide grinding vessels of 250 cm³ with seven balls of 2 cm in diameter and 63 g in weight (powder-to-ball weight ratio of 1:44) were used. The milling conditions were tailored so as negligible contamination levels resulted. Ceramic materials were prepared by hot-pressing at 900 °C for 1 h under 60 MPa, using heating/cooling rates of 3 °C min⁻¹. Both the mechano-synthesis and the ceramic processing experiments were carried out in air. Archimedes's method was used to measure the density of the pellets.

Structural and Physical Property Characterizations: Crystal structure of powdered samples was assessed via x-ray diffraction and neutron diffraction experiments. A highly accurate two-axis diffractometer with a Rigaku RA-HF18 rotating anode generator, in Bragg-Brentano geometry and coupled with a furnace, was used in the range of 15° to 150° (2 θ), in steps of 0.02° and counting time of 20 s per step. $\text{CuK}\alpha$ doublet ($\lambda = 1.5418 \text{ \AA}$) was used in these experiments, and a monochromator producing $\text{CuK}\beta$ ($\lambda = 1.39225 \text{ \AA}$) was occasionally used for higher resolution. Neutron diffraction experiments were carried out on the 3T2 high-resolution diffractometer using the Orphée reactor facilities at Laboratoire Léon Brillouin (Saclay, France). The patterns were recorded in the range of 5° to 122° (2 θ) in steps of 0.02° for 24 h, using a wavelength of 1.2252 Å obtained from the Ge (335) reflection. Further details of the crystal structure investigations may be obtained from the

Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on

quoting the depository numbers CSD-434318 and CSD-434319 for the S.G. *Pnma* and *P4mm*.

See also Supporting Information for additional information of the refinements.

Electrical properties were measured on ceramic discs, on which Ag electrodes were painted and annealed at 750 °C for 1 h. The temperature dependence of the dielectric permittivity was dynamically measured under heating/cooling cycles at 1.5 °C min⁻¹ with a HP4284A precision LCR Meter in the frequency range 20 Hz - 1 MHz. Additionally, measurements were also carried out in static conditions, at temperature steps of 20 °C in the same temperature and frequency range, for impedance spectroscopy analysis with the commercial Zview software. Magnetic properties were characterized with a Quantum Design MPMS-XL5 SQUID magnetometer on powdered samples. Magnetization was measured between 2 and 400 K under zero-field-cooling and field-cooling conditions with a magnetic field of 100 Oe, and the complex magnetic susceptibility was measured with a magnetic field of 1 Oe at frequencies between 1 Hz and 1000 Hz. Mechanical properties were characterized by dynamical mechanical analysis in three-point bending geometry with a Perkin Elmer DMA7 apparatus. A stress sine wave of 2.5 MPa amplitude superimposed on a static stress of 3.5 MPa was applied to ceramic bars of 12×2×0.5 mm dimensions. Measurements were accomplished at 40 Hz during heating/cooling cycles at 2 °C min⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Crystal structure. (a) High-resolution XRD patterns using $\text{CuK}\beta$ for powdered samples of the $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ composition, after thermal treatment at 950 °C for 12 h followed by two different cooling rates: slow cooling (red pattern) and quenching (blue pattern), pseudocubic indices are given (**T** - tetragonal). Small diffraction peaks arising from $\text{CuK}\alpha$ are indicated. (b) Neutron diffraction pattern for the slowly cooled sample along with Rietveld refinement using orthorhombic $Pnma$ space group. Y_{Obs} and Y_{Cal} refer to measured and calculated intensities, respectively.

Figure 2. XRD profiles using $\text{CuK}\alpha$ around the $(110)_p$ diffraction peak (pseudocubic index) at increasing temperatures for $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ powdered sample with (a) quenching and (b) slow cooling. (c) Evolution of lattice parameters with temperature obtained from Le Bail analysis assuming tetragonal (a_T , c_T) and pseudo-cubic parameters (a_{ps}).

Figure 3. Dielectric properties. (a) dc conductivity (σ) vs inverse absolute temperature of the $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ (binary-system) and $\text{Bi}_{0.47}\text{Pb}_{0.53}\text{Fe}_{0.17}\text{Mn}_{0.3}\text{Ti}_{0.53}\text{O}_3$ (ternary-system) ceramics after quenching from 750°C (activation energy, E_a , values are indicated, RT - room temperature). Temperature dependence of permittivity (K') at 1 MHz during a heating/cooling cycle for samples of the (b) binary-system and (c) ternary-system compositions after quenching from 750°C (dashed lines indicate phase transition temperatures).

Figure 4. Dynamical mechanical analysis. Young's modulus (Y) as a function of temperature at 40 Hz for (a,b) $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ and (c,d) $\text{Bi}_{0.47}\text{Pb}_{0.53}\text{Fe}_{0.17}\text{Mn}_{0.3}\text{Ti}_{0.53}\text{O}_3$ ceramic bars, both with quenching treatment from 750 $^{\circ}\text{C}$, and measured during two successive heating/cooling cycles. Insets (a,b) show mechanical losses ($\tan \delta$) as a function of temperature. (e) Successive thermal cycles between room temperature and an increasingly higher temperature for the $\text{Bi}_{0.47}\text{Pb}_{0.53}\text{Fe}_{0.17}\text{Mn}_{0.3}\text{Ti}_{0.53}\text{O}_3$ ceramic with quenching.

Figure 5. Magnetic properties. Zero-field-cooled (ZFC)/Field-cooled (FC) susceptibility curves under a dc magnetic field of 100 Oe for (a) $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ and (b) $\text{Bi}_{0.47}\text{Pb}_{0.53}\text{Fe}_{0.17}\text{Mn}_{0.3}\text{Ti}_{0.53}\text{O}_3$ powdered samples, with different thermal treatments from 900 °C: slow cooling ($Pnma$) and quenching ($P4mm$). Temperature dependence of the (a) in-phase (χ') and (b) out-of-phase (χ'') components of ac susceptibility, at several frequencies, for the $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ powdered sample. (c) Fitting of the χ' data with the power law expression of critical dynamics, Equation 1, for the $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ (binary-system) and $\text{Bi}_{0.47}\text{Pb}_{0.53}\text{Fe}_{0.17}\text{Mn}_{0.3}\text{Ti}_{0.53}\text{O}_3$ (ternary-system) samples.

Table 1. Crystallographic parameters for the $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ composition on the powdered sample slowly cooled. Rietveld refinements carried out on the neutron diffraction pattern, using cubic $Pm-3m$ and orthorhombic $Pnma$ symmetries. Refined structural parameters and reliability R -factors are given (GOF for goodness-of-fit indicator), along with position coordinates (x, y, z) for the $Pnma$ symmetry.

S.G.	<i>Pm-3m</i>	<i>Pnma</i>
Statistical parameters	$R_{\text{wp}} = 3.74$; $R_{\text{p}} = 2.69$; $R_{\text{Bragg}} = 5.62$; GOF = 2.67	$R_{\text{wp}} = 3.48$; $R_{\text{p}} = 2.55$; $R_{\text{Bragg}} = 5.58$; GOF = 2.49
Lattice parameters [Å]	$a = 3.966(2)$	$a = 5.609(7)$ $b = 7.924(3)$ $c = 5.610(4)$

S.G.	<i>Pnma</i>			
	Bi/Pb	Mn/Ti	O1	O2
x	-0.002(6)	0	0.505(6)	0.249(2)
y	0.25	0	0.25	0.001(7)
z	-0.000(5)	0.5	-0.000(6)	0.750(9)

Table 2. Parameters from the power law fitting of critical dynamics, Equation 1, for the $\text{Bi}_{0.4}\text{Pb}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ (binary-system) and $\text{Bi}_{0.47}\text{Pb}_{0.53}\text{Fe}_{0.17}\text{Mn}_{0.3}\text{Ti}_{0.53}\text{O}_3$ (ternary-system).

Sample	binary-system	ternary-system
τ_0 [s]	10^{-13}	10^{-13}
$z\nu$	11.3	8.1
T_{sg} [K]	9.4	11.7

Interplay among crystal structure, point defects and multiferroism at the polar/antipolar MPB of the $\text{BiMnO}_3\text{-BiFeO}_3\text{-PbTiO}_3$ ternary system. The origin of the phenomenon is investigated with temperature dependent structural and physical property characterizations. A major role of the complex defect chemistry in the delicate balance between polymorphs is proposed, and its influence in the magnetic and electric ferroic orders is defined.

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The Polar/Antipolar Phase Boundary of $\text{BiMnO}_3\text{-BiFeO}_3\text{-PbTiO}_3$: Interplay among Crystal Structure, Point Defects and Multiferroism