Perovskite solid solutions with multiferroic morphotropic phase boundaries and property enhancement

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Recently, large phase-change magnetoelectric response has been anticipated by a first-principles investigation of phases in the BiFeO₃–BiCoO₃ perovskite binary system, associated with the existence of a discontinuous morphotropic phase boundary (MPB) between multiferroic polymorphs of rhombohedral and tetragonal symmetries. This might be a general property of multiferroic phase instabilities, and a novel promising approach for room temperature magnetoelectricity. We review here our current investigations on the identification and study of additional material systems, alternative to BiFeO₃–BiCoO₃ that has only been obtained by high pressure synthesis. Three systems, whose phase diagrams were, in principle, liable to show multiferroic MPBs have been addressed: the BiMnO₃–PbTiO₃ and BiFeO₃–PbTiO₃ binary systems, and the BiFeO₃–BiMnO₃–PbTiO₃ ternary one. A comprehensive study of multiferroism across different solid solutions was carried out based on electrical and magnetic characterizations, complemented with mechanical and electromechanical measurements. An in-depth structural analysis was also accomplished when necessary.

Keywords: Multiferroics; magnetoelectrics; perovskite solid solutions; morphotropic phase boundary; ceramic technologies.

1. Introduction

The search of single-phase multiferroics with large room temperature (RT) magnetoelectric response has concentrated and increasing activity during the last 10 years,^{1–3} for they are an enabling material technology for a wide range of potentially disruptive related technologies that would make use of the ability of controlling electrical polarization with the magnetic field, and magnetization with an electric one. Among the different applications proposed, electrically tunable magnetic microwave components and spintronic devices, high sensitivity magnetic sensors with RT operation, and above all, the long time chased electrical-writing magnetic-reading random access memory stand out.^{4–6}

Although the first multiferroic compounds were described as early as in 1966,⁷ these materials became highly topical at the dawn of the 21st century after a number of reports of large magnetoelectric effects, basically changes of permittivity and reorientation of polarization, even direction reversal, under high magnetic fields in several magnetic (or spin induced) ferroelectrics.^{8,9} These are improper ferroelectrics, in which a small ($<< 1 \mu\text{C cm}^{-2}$) spontaneous polarization develops as

a byproduct of a magnetic transition, often involving complex incommensurate antiferromagnetic states like sinusoidal or spiral spin configurations.¹⁰ First reported materials were orthorhombic terbium manganites like TbMnO₃ and TbMn₂O₅ with ordering temperatures around 40 K, which developed a ferroelectric state at low temperature and successive magnetic transitions involving spin reorientation. Large magnetoelectric effects were phase-change responses associated with the shift of the antiferromagnetic state instability with the magnetic field.^{8–10} Following works concentrated on finding systems that showed similar phenomenology but higher magnetic ordering temperatures, among which CuO at 230 K,¹¹ and Sr₃Co₄Fe₂₄O₄₁ at 670 K deserved being highlighted.¹² However, a comparable electrical control of magnetization has not been achieved. Therefore, and though research goes on covering an ever wide range of manganites, ferrites, chromites and cobaltites,¹³ alternative material concepts need to be (and are being) investigated.

A second set of materials under extensive research are ABO₃ perovskites in which multiferroism is chemically

engineered by placing ferroelectrically and magnetically active cations in the A- and B-site, respectively. Pb^{2+} or Bi^{3+} with stereochemically active $6s^2$ electron lone pairs are usually selected for the A-site, while magnetically active Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} and Cr^{3+} are located at the B-site, like for the ferroelectric antiferromagnets $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and BiFeO_3 .¹⁴ This A-site-based ferroelectricity would result from a different mechanism to that responsible of the ferroic order in model ferroelectric compounds like BaTiO_3 and PbTiO_3 , for which the hybridization between the Ti 3d and O 2p electronic states and thus, covalency plays a major role.¹⁵ Recall that an intrinsic contradiction has been pointed out to exist between B-site-based ferroelectricity, which involves a transition metal in a d^0 configuration, and magnetism that requires the same metals with partially filled (with an odd number of electrons) d levels.¹⁶

Indeed, BiFeO_3 stands out as the most topical multiferroic at present, not only for it is one of the rare compounds that show independent but coupled electrical and magnetic orders at RT,^{17,18} but for its magnetic and ferroelectric domain configurations are related, which enables the reorientation of the antiferromagnetic domains following the electrical switching of the ferroelectric/ferroelastic ones.^{19,20} A large effort is being put in order to tailor down its high RT conductivity, while enhancing its weak ferromagnetism.²¹ Besides, this material is a basic component of multiferroic film epitaxial heterostructures under extensive investigation for magnetoelectricity.²²

Recently, partially reversible ferroelectric domain reorientations under magnetic fields have been described for $(1-x)\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3-x\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ with $x = 0.4$ at RT.²³ This is an example out of a number of perovskite solid solutions between ferroelectric phases and relaxor compounds containing magnetically active cations which show weak ferromagnetism in coexistence with a range of polar states, and different magnetoelectric coupling phenomena.²⁴ Spin clustering is thought to be responsible for the ferromagnetic component, while elastic interactions between the magnetic nanoregions and the ferroelectric matrix would cause the magnetoelectric effects.

Also involving perovskite solid solutions, strong phase-change magnetoelectric response has been anticipated by a first-principles investigation of phases in the BiFeO_3 – BiCoO_3 binary system, associated with the existence of a discontinuous morphotropic phase boundary (MPB) between multiferroic polymorphs of rhombohedral and tetragonal symmetries.²⁵ Mechanism would be the discrete rotation of the magnetization easy axis following that of the spontaneous polarization, during the electric field induced transformation from one ferroelectric (multiferroic) polymorphic phase to the other.

Furthermore, a recent experimental study reported the existence of a monoclinic *Cm* phase between the rhombohedral and tetragonal polymorphs in the BiFeO_3 – BiCoO_3 system, and polarization rotation within this phase with

temperature and composition.²⁶ The phase diagram would be then analogous to that described for high sensitivity piezoelectric $\text{Pb}(\text{Zr,Ti})\text{O}_3$, which shows lattice transverse softening and very high polarizability and piezoelectric response by the mechanism of continuous polarization rotation.^{27,28} The finding of the same intermediate monoclinic phase in the multiferroic system raises the possibility of also obtaining an enhanced magnetoelectric response by the same mechanism.

Indeed, these distinctive magnetoelectric effects might be a general property of multiferroic MPBs; this understood as a boundary in the phase diagram separating two perovskite polymorphic phases both multiferroic, but with different symmetry and thus, spontaneous polarization (and coupled magnetization easy axis) along different crystal directions, and a novel promising approach for obtaining RT magnetoelectricity. However, the in-depth exploration of this approach requires the identification and study of additional material systems. A serious issue when addressing this task is the low thermodynamical stability of most of the suitable candidates, anticipated by their low perovskite tolerance factor. BiFeO_3 – BiCoO_3 , for instance, has only been obtained by high pressure synthesis. We review in this paper our current investigations on the identification of such material systems, in which mechanosynthesis in high energy planetary mills is playing a major role as an alternative to high pressure synthesis for obtaining these oxides.²⁹

2. The BiMnO_3 – PbTiO_3 Binary System

BiMnO_3 is one of the rare ferromagnetic insulators with an ordering temperature of 100 K,³⁰ which has also been claimed to be ferroelectric. Ferroelectricity was initially proposed after structural studies that showed this oxide to have a heavily distorted perovskite structure with monoclinic symmetry and *C2* space group,³¹ and the independent reports of ferroelectric hysteresis loops³² and second harmonic generation.³³ Contemporary first-principles calculations indicated the off-center distortions to be driven by the stereochemically active Bi^{3+} lone pair.³⁴ Indeed BiMnO_3 was considered until recently as a prototype of multiferroics, in which independent electric and magnetic ferroic orders are obtained by placing ferroelectrically and magnetically active cations at the A-site and B-site of the ABO_3 perovskite. Therefore, it seemed a suitable perovskite edge member to be combined with the PbTiO_3 tetragonal perovskite, in order to obtain a multiferroic MPB.

There was a single previous report of the $x\text{BiMnO}_3$ – $(1-x)\text{PbTiO}_3$ perovskite solid solutions series when we started working on the system.³⁵ These authors succeeded in obtaining perovskite single phases up to an x value of 0.7 by conventional solid-state synthesis, and described a tetragonal *P4 mm* phase for x below 0.4, and a pseudocubic phase for x values above this threshold. No phase coexistence was found for any composition that might indicate the existence of a

Fig. 1. XRD patterns of highly crystalline $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ powders obtained by (a) wet chemistry (adapted with permission from Ref. 37. Copyright (2010) American Chemical Society), and (b) mechanosynthesis (adapted from Ref. 38, Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). Peaks associated with the coexisting tetragonal (T) and pseudocubic (pc) polymorphic phases are indicated with Miller indices. *Second phases.

MPB, so the structural evolution was proposed to be associated with the disruption of the long range ferroelectric order with increasing x , and the appearance of a relaxor state.³⁶

However, our own investigations clearly showed the existence of a compositional range between $x = 0.36$ and 0.44 , where coexistence of two perovskite polymorphic phases was found, which suggested the targeted MPB to exist. Consistent results were obtained on two independent set of powdered samples synthesized by a nonconventional wet chemistry approach³⁷ and by mechanosynthesis,³⁸ respectively. High chemical homogeneity is provided by these alternative advanced synthesis techniques, which is thought to have been the key to uncovering the MPB. In summary, two perovskite polymorphic phases are present in the system: (1) a tetragonal $P4mm$ phase for $0 \leq x < 0.36$, and (2) an apparently cubic, yet we will see later that this is not the case, phase for $x > 0.44$, while a region where these tetragonal and pseudocubic phases coexist is found for intermediate compositions, namely $0.36 \leq x \leq 0.44$. This is illustrated in Fig. 1, where X-ray diffraction (XRD) patterns of the two sets of powders are provided.

Note the presence of traces of second phases for $x > 0.74$ in the case of the powders synthesized by wet chemistry. This method involved a final thermal treatment at 1273 K in the case of materials with x up to 0.6, which was decreased down to 1223 K above this value and up to 0.8. No perovskite phases were obtained above this composition. Indeed, the magnetic characterization clearly showed the presence of a magnetic impurity for x values as low as $x = 0.2$.

Traces of the same second phase were found for the material with $x = 0.8$ obtained by mechanosynthesis. Nanocrystalline powders result from the mechanochemical activation and thus, a thermal treatment at 1223 K was required to increase crystallinity for the structural characterization. The second phase appears after this thermal treatment,

for its magnetic signature was not found in the nanocrystalline powders that were perovskite single phase according to both XRD and selected area electron diffraction (SAED) in transmission electron microscopy (TEM). It is remarkable that the technique allowed perovskite phases to be obtained all across the binary system beyond 0.8, including BiMnO_3 ($x = 1$), which had only been obtained before by high pressure synthesis. However, these nanocrystalline perovskites were unstable under heating, and thermal decomposition was triggered at a temperature that decreased when x increased, such as it was 1173 K for $x = 0.5$,³⁸ and 673 K for $x = 1$.³⁹

Perovskite structure evolution across the system. Perovskite lattice parameters were obtained as a function of composition for the two polymorphs, and are shown in Fig. 2. Consistent trends were found in the two sets of powders, so as the tetragonal distortion, c/a , maintained a constant value around 1.07 up to $x = 0.2$, above which it started decreasing on approaching the phase coexistence region down to ~ 1.03 for $x = 0.44$. Slightly smaller c parameters and thus, tetragonal distortions were obtained in the case of the mechanosynthesized powders. Perovskite cell volume is also shown in the figure for the two polymorphs. Note the small volume difference between the tetragonal and pseudocubic phases within the coexistence region, which seems to suggest a discontinuous MPB. This difference is noticeable in the case of the materials synthesized by wet chemistry, but not for those obtained by mechanosynthesis. Like the differences in c/a , this is most probably related to the remnant microcrystalline strain; that is, a high level of perovskite disorder characteristic of the mechanosynthesis, which is not fully removed during subsequent thermal treatments, and that is thought to play a major role in the stabilization of the low tolerance factor perovskites.^{29,40}

The actual symmetry of the pseudocubic phase was studied on highly crystalline samples of $x = 0.5$ and 0.6 by

Fig. 2. (a) Perovskite lattice parameters of the tetragonal (a_T and c_T) and pseudocubic (a_{pc}) polymorphic phases across the $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ solid solution series for the powders obtained by either wet chemistry: WC (from Ref. 37) or mechanosynthesis: MS (from Ref. 38), and (b) evolution of the perovskite cell volume.

precession electron diffraction, and found to be orthorhombic $Pnma$. Details of the space group determination can be found elsewhere.³⁸ This is the same crystal structure of the high temperature phase of BiMnO_3 , which transforms into the monoclinic one at 770 K.^{41,42} The monoclinic to orthorhombic transformation can be also induced by high pressures,⁴³ and by oxygen hyperstoichiometry,⁴⁴ as well as by the simultaneous substitution of Pb^{2+} for Bi^{3+} and Ti^{4+} for Mn^{3+} as shown here. This might be an example of chemical pressure effects, like those described in the $\text{Pb}(\text{Zr,Ti})\text{O}_3$ system that have been proposed to be responsible of the appearance of the MPB.⁴⁵ Multiferroic BiFeO_3 also presents a high temperature orthorhombic $Pnma$ phase that transforms into the rhombohedral $R3c$ phase at ~ 1100 K.¹⁸ Note that $Pnma$ is a centrosymmetrical group and thus, ferroelectricity is not allowed. Indeed the $Pnma$ to $C2$ transition at 770 K has

been proposed to be the ferroelectric transition of BiMnO_3 , likewise the $Pnma$ to $R3c$ transition of BiFeO_3 . It seems contradictory, however, that the substitutions of ferroelectrically active Pb^{2+} and Ti^{4+} for Bi^{3+} and Mn^{3+} result in the transformation of a polar phase into a nonpolar one. We will come back to this point in Sec. 3.

Magnetism across the system. Though BiMnO_3 is distinctively ferromagnetic, the increasing Mn^{3+} dilution with decreasing x along the system readily transforms it into a canted antiferromagnetic with a Néel temperature that decreases with x , from 22 K at $x = 0.9$ to 7 K for $x = 0.3$. A weak paramagnetic state has been described below this temperature.

Details of the magnetic characterization and all results can be found somewhere else.^{37,38} We will focus here on analyzing possible differences between the magnetism of the two polymorphs within the coexistence region. Magnetization after zero field cooling (ZFC), measured during heating and subsequent field cooling (FC) between 2 and 120 K are shown in Fig. 3 for the powders obtained by mechanosynthesis. Curves for $x = 0.3$ (tetragonal at RT), $x = 0.4$ (phase coexistence) and $x = 0.5$ (orthorhombic) are provided. No qualitative changes are found across the structural evolution, and all materials show a distinctive upturn of magnetization below 50 K, along with well-defined maxima in the ZFC curve that indicate the Néel temperature, and a significant irreversibility or separation of the ZFC and FC curves, associated with the occurrence of spin canting and of weak ferromagnetism within the antiferromagnetic state.³⁸ Actual changes are an expected increase of magnetization with x ,

Fig. 3. Magnetization for the $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ powders with $x = 0.3$ (Δ), $x = 0.4$ (∇) and $x = 0.5$ ($\circ$) obtained by mechanosynthesis (adapted from Ref. 38, Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). Measurements were carried out between 2 and 300 K after ZFC (open symbols) and during subsequent FC (full symbols) under an applied field of 100 Oe. The evolution of the Néel temperature across the solid solution series is provided in the inset, along with that obtained for powders synthesized by wet chemistry.

i.e., with the concentration of Mn^{3+} cations, and shift of the Néel temperature. Consistent results were attained for the powders synthesized by wet chemistry.³⁷

The shift of the Néel temperature with x is illustrated in the inset of the figure for the two types of powder. No distinctive change of the slope of the T_N versus x curve is found across the phase coexistence, in spite of the described structural evolution. Recall that a small volume difference existed between the coexisting polymorphs, and so the $\text{Mn}^{3+}\text{--O}^{2-}\text{--Mn}^{3+}$ superexchange interactions must be slightly modified.

Finally, note the presence of a magnetization step at ~ 44 K for all samples, associated with the previously discussed magnetic impurity.

Ferroelectricity across the system. The vanishing of ferroelectricity, anticipated by the perovskite structural evolution from a tetragonal $P4mm$ phase to an orthorhombic $Pnma$ one, was independently confirmed by following the ferroelectric transition from PbTiO_3 with increasing x . This was done by measuring the temperature dependence of a number of physical quantities, such as enthalpy changes, dielectric permittivity and Young's modulus that show distinctive signals and critical behavior at the transition.

The ferroelectric transition was initially followed by differential thermal analysis in the powdered samples synthesized by wet chemistry.³⁷ The transition for PbTiO_3 takes place at ~ 765 K and is first order, so it has associated a distinctive reversible thermal signal readily identified in DTA. Analogous endothermic reversible effects that could be directly related to the transition were found for low x values and up to $x = 0.25$, so as the transition temperature, T_c , seemed to maintain a constant value around 770 and 760 K on heating and cooling, respectively, up to $x = 0.2$, above which it started decreasing. However, the thermal signals were not observed above $x = 0.25$, in spite of the tetragonal phase persisting up to $x = 0.44$.³⁷ This indicates the presence of a tricritical point in the binary system; that is a composition at which the ferroelectric transition changes from first order to second order. This x value seems to be between 0.25 and 0.30 for $x\text{BiMnO}_3\text{--}(1-x)\text{PbTiO}_3$, and it is the composition at which the perovskite tolerance factor that continuously decreases with x across the solid solution series takes a value of 1. Analogous tricritical points have been described for a number of perovskite systems, such as $\text{Bi}(\text{Mg}_{3/4}\text{W}_{1/4})\text{O}_3\text{--PbTiO}_3$.⁴⁶ Note also that this specific composition is that above which the tetragonal distortion starts a fast decrease towards the region of phase coexistence.

The ferroelectric transition was also followed by measuring the temperature dependence of the dielectric permittivity, after the processing of ceramics. In the case of materials processed by conventional sintering of the powders synthesized by wet chemistry, consistent transition temperatures were obtained up to $x = 0.25$. However, conductivity was an issue above this value, and the dielectric anomaly associated with the transition vanished for higher values,

Fig. 4. Temperature dependence of the relative permittivity at 1 MHz of two $x\text{BiMnO}_3\text{--}(1-x)\text{PbTiO}_3$ ceramics with $x = 0.15$ and 0.3^* , processed by conventional sintering of powders obtained by wet chemistry: WC (from Ref. 37), and of a second material with $x = 0.3$, this processed by hot pressing of the nanocrystalline powder obtained by mechanosynthesis: MS (from Ref. 47). *The frequency dispersion for this sample is provided in the inset.

basically buried in a strong high temperature dielectric relaxation and the conduction background (see inset of Fig. 4). Conductivity in this system is thought to be associated with the presence of an oxygen hyperstoichiometry, or rather of Mn vacancies and thus, Mn^{4+} , by a mechanism of electron hopping between Mn^{3+} and Mn^{4+} .⁴⁷ Conduction tailoring has been demonstrated by modifying synthesis and processing, and so microstructure, so as ceramics with $x = 0.3$ processed by hot pressing of powders obtained by mechanosynthesis did show the dielectric anomaly at 678 K,⁴⁷ as illustrated in Fig. 4.

Beyond $x = 0.3$, the ferroelectric transition could only be followed by measuring the temperature dependence of the low frequency Young's modulus by dynamical mechanical analysis. This is a powerful means of studying phase transitions that has been widely applied to ferroelectrics complementing electrical measurements, especially useful when conduction becomes an issue like for $\text{BiMnO}_3\text{--PbTiO}_3$.^{37,47} The technique has also been key to provide a description of the development of ferroelectric long range order in relaxor systems,^{48,49} and is also sensitive to the dynamics of the ferroelectric/ferroelastic domain walls.⁵⁰

The temperature dependences of the dielectric permittivity and the Young's modulus across the ferroelectric transition of the ceramic material with $x = 0.3$, processed by hot pressing of mechanosynthesized powders, are given in Fig. 5. Note the presence of a distinctive minimum in Young's modulus at the ferroelectric transition, readily identified by the characteristic dielectric anomaly. This is accompanied by a maximum in mechanical losses (not shown) that reflects the appearance of highly mobile ferroelectric/ferroelastic domains at the

Fig. 5. (a) Temperature dependences of the relative permittivity and low frequency Young's modulus of one $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ ceramic with $x = 0.3$, processed by hot pressing of the nanocrystalline powder obtained by mechanosynthesis, across its ferroelectric transition, and (b) Temperature dependence of the Young's modulus of five $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ ceramics with $x = 0.3, 0.4$ and 0.5 , processed by conventional sintering of powders obtained by wet chemistry: WC (from Ref. 37), and of two materials with $x = 0.3$ and $x = 0.4$, these ones processed by hot pressing of the nanocrystalline powder obtained by mechanosynthesis: MS (from Ref. 47 and unpublished, respectively).

transition; 90° domains in the case of the tetragonal $P4mm$ phase.

The Young's modulus for ceramic materials with x values up to 0.5 , processed from powders obtained by both wet chemistry and mechanosynthesis, are also given in the figure. The minima associated with the ferroelectric transition are easily identified in the curves of all materials with $x = 0.3$ and 0.4 , so as the transition temperature further decreased down to 485 K in the latter case. However, an elastic anomaly that could be unambiguously associated with the transition was not observed for $x = 0.5$.

Note also the presence of a low temperature mechanical effect consisting of a sharp increase of the Young's modulus for all materials, at a temperature that increases with x . This hardening has been also observed in rhombohedral $\text{BiScO}_3-\text{PbTiO}_3$, and related to a low temperature phase transition.⁵¹ Its actual nature is not known, but it has clearly associated the disappearance, or at least freezing of the ferroelectric/ferroelastic domains.

All critical temperatures, whatever technique has been used to determine them, for the materials prepared by wet chemistry or mechanosynthesis are collected in Fig. 6, where the transition temperatures of the ceramic samples with $x = 0.2$ and 0.3 , prepared by conventional means in Ref. 35 are included for completeness. A distinctive trend is obtained for the ferroelectric transition: initially, it maintains a constant value around 765 K up to $x = 0.2$, composition at which the ferroelectric transition changes from first order to second order. Above this value, the transition temperature readily decreases down to a value of 485 K for $x = 0.4$. Note that slightly higher T_c s are obtained for the mechanosynthesized samples, yet this does not modify the trend. At the same time, the low temperature hardening takes place at an increasing

temperature, so as it occurs at 330 K for $x = 0.5$. This is above RT, at which an orthorhombic $Pnma$ has been described. Therefore, one can conclude that the low temperature transition is a $P4mm$ to $Pnma$ transition, which involves the vanishing of ferroelectricity (and so of the improper ferroelasticity) and that it is shifted up with composition. Note that the $Pnma$ phase appears at a temperature above the extrapolation of the T_c curve for $x = 0.5$. Therefore, a direct cubic $Pm3m$ to orthorhombic $Pnma$ can be assumed in this case.

Fig. 6. Experimentally determined ferroelectric transition temperatures (T_c^h determined on heating, T_c^c on cooling and T_c no thermal hysteresis), and temperatures of the second polymorphic transition (LTtran) across the $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ solid solution series for the samples obtained by conventional means: SS (from Ref. 35), wet chemistry: WC (from Ref. 37), and mechanosynthesis: MS (from Ref. 38).

Indeed, this transition has been reported for BiFeO_3 at high temperature.¹⁸ Recent high temperature XRD measurements have revealed that the coexisting polymorphs in powders with $x = 0.4$ undergo independent structural transitions to a cubic phase on heating. This demonstrates the actual existence of a MPB in the system, though between a ferroelectric and a nonferroelectric phase, and bent at low temperatures towards PbTiO_3 .

Analysis of multiferroism. Summing up, antiferromagnetic order exists in the system for x values as low as 0.3 that is also ferroelectric, but with an ordering temperature of 7 K. This is well below the temperature at which the $P4\text{mm}$ to $Pnma$ transition takes place, and ferroelectricity is lost. Therefore, and though ferroelectric and antiferromagnetic orders develop for $x = 0.3$ and 0.4, ferroelectricity vanishes before the magnetic one sets in, so they do not coexist at any temperature. Multiferroism then does not exist in the system.

Actually, note that magnetic ordering always takes place in orthorhombic phases, which explains the lack of discontinuities in the T_N versus x curve shown in Fig. 3. Recall that even if $x = 0.3$ is tetragonal at RT, it transforms into the orthorhombic phase at 167 K.

3. Revisiting BiMnO_3

The vanishing of ferroelectricity in the $x\text{BiMnO}_3-(1-x)\text{PbTiO}_3$ system for $x \geq 0.5$, which is when the orthorhombic $Pnma$ phase develops, questions the actual ferroelectric nature of BiMnO_3 . Indeed, density functional calculations have shown that the ground state of this perovskite oxide is monoclinic $C2/c$, and thus centrosymmetric.⁵² BiMnO_3 would be then isostructural to BiScO_3 , and a comparative Rietveld study of neutron diffraction data seemed to suggest this to be the case.⁵³ Subsequent additional neutron diffraction experiments confirmed this space group determination,⁴⁴ but an independent report using SAED indicated the presence of long-ranged monoclinic $C2$ order, in coexistence with short ranged $P2$ or $P2_1$ distortions, and thus, of a polar state.⁵⁴ The length of the short range order seems to increase with the oxygen hyperstoichiometry,³⁹ but a $P2_1/c$ space group has been determined for $\text{BiMnO}_{3.08}$.⁴⁴

Further insight into this issue can only be gained by a sound electrical characterization, which requires the processing of high quality ceramics. This is challenging for BiMnO_3 that thermally decomposes into a mixture of $\text{Bi}_2\text{Mn}_4\text{O}_{10}$, $\text{Bi}_{12}\text{MnO}_{20}$ and MnO_2 above 673 K. Note that $\text{Bi}_2\text{Mn}_4\text{O}_{10}$ is ferromagnetic with a T_c of 42 K, and most probably the magnetic impurity in Fig. 3.

We figured out the processing of dense (92% densification) ceramics of BiMnO_3 by using spark plasma sintering and the nanocrystalline powders obtained by mechanosynthesis.³⁹ Oxygen hyperstoichiometry was controlled by XPS and magnetic measurements, by comparing the Néel temperature of 80 K to previous reports on the evolution of the magnetism

with stoichiometry.⁴⁴ A composition of $\text{BiMnO}_{3.04}$ was estimated, so monoclinic $C2/c$ phase can be assumed.³⁹

A full electrical characterization was carried out.³⁹ The temperature dependence of the dielectric permittivity is shown in Fig. 7. Samples thermally decomposed when heated above 673 K, so the temperature of the monoclinic to orthorhombic transition at 770 K could not be reached. Results basically show up to three successive dielectric relaxations on heating from 77 K, but no reversible nondispersive anomaly that could be associated with a phase transition. Note the relaxation peaks in the 375–475 K range that had been previously confused with the ferroelectric transition, for BiMnO_3 shows a first structural phase transition between two

Fig. 7. Temperature dependences of the dielectric (a) permittivity, and (b) losses at several frequencies of a dense ceramic of $\text{BiMnO}_{3.04}$, processed by spark plasma sintering of nanocrystalline powder obtained by mechanosynthesis. High field response at 77 K typical of a lossy dielectric is shown in the inset. Adapted from Ref. 39 with permission from The Royal Society of Chemistry.

monoclinic $C2/c$ phases at around 475 K. However, this is not the case.

Absence of ferroelectricity was also confirmed by measuring ferroelectric hysteresis loops at 77 K, below the onset of conductivity. The typical behavior of lossy dielectrics with no hint of ferroelectricity was found. This is in agreement with an independent study of the lattice dynamics on samples obtained by high pressure that also showed no ferroelectricity.⁵⁵

4. The BiFeO_3 – PbTiO_3 Binary System

BiFeO_3 is unambiguously multiferroic, and unlike BiMnO_3 , an actual example of perovskite oxides, in which independent electric and magnetic ferroic orders are obtained by placing ferroelectrically and magnetically active cations at the A-site and B-site of the ABO_3 structure, respectively.¹⁸ This compound is a proper ferroelectric with a transition temperature of ~ 1100 K^{18,56} a rhombohedral structure with space group $R3c$,⁵⁷ and a RT spontaneous polarization close to $100 \mu\text{C cm}^{-2}$.⁵⁸ Besides, the oxide is a G-type antiferromagnet with an ordering temperature of 643 K.⁵⁹ Crystal magnetoelectric coupling exists, and results in spin canting but also in a long range incommensurate cycloid superstructure.^{60,20} Weak ferromagnetism is obtained when the latter spin cycloid is destroyed by doping ($M_s = 1.2 \text{ emu g}^{-1}$ for $\text{Bi}_{0.7}\text{Ba}_{0.3}\text{FeO}_3$ ceramic materials).²¹ Therefore, it seemed an especially suitable second perovskite edge member to be combined with the PbTiO_3 tetragonal perovskite, in order to obtain the targeted multiferroic MPB, not found in BiMnO_3 – PbTiO_3 .

Indeed the $x\text{BiFeO}_3$ – $(1-x)\text{PbTiO}_3$ perovskite solid solutions series concentrates an increasing attention, and coexistence of rhombohedral $R3c$ and tetragonal $P4mm$ polymorphic phases has been described in a compositional range that varies from $0.6 \leq x \leq 0.8$ to $0.69 < x < 0.73$ for powders obtained by conventional solid-state synthesis.^{61–64} These coexisting polymorphs would be then isostructural with the edge ferroelectric oxides, which strongly suggests a ferroelectric MPB to exist. Our own results on chemically homogenous powders obtained by mechanosynthesis are shown in Fig. 8.⁶⁵ A region of phase coexistence was found for $0.625 \leq x \leq 0.75$, slightly wider than that reported in Ref. 64. The reason of this discrepancy cannot be chemical homogeneity that is very high in the mechanosynthesized samples, but differences of particle size or even the temperature and/or cooling profile used in the synthesis or crystallization treatments, for these parameters have been shown to strongly affect the phase distribution in the coexistence region.⁶⁵

Note the absence of traces of second phases for all x values, not only in the nanocrystalline powders that result from the mechanochemical activation, but also after the thermal treatments carried out to increase crystallinity for the structural characterization. A temperature of 1323 K could be used for materials with x from 0 up to $x = 0.75$, which had to

Fig. 8. XRD patterns of highly crystalline $x\text{BiFeO}_3$ – $(1-x)\text{PbTiO}_3$ powders obtained by mechanosynthesis. Peaks associated with the coexisting rhombohedral (R) and tetragonal (T) polymorphic phases are indicated with Miller indices. Adapted from Ref. 65 with permission from The Royal Society of Chemistry.

be decreased down to 1273, 1123 and 1063 K for $x = 0.8$, 0.9 and 1, respectively to avoid triggering the perovskite decomposition.

Perovskite structure evolution across the system. Perovskite lattice parameters were obtained as a function of composition for the two polymorphs, and are shown in Fig. 9. Trends were consistent with previous reports on powders synthesized by high temperature solid-state reactions.^{63,66} Unlike most related binary systems, such as BiScO_3 – PbTiO_3 and BiMnO_3 – PbTiO_3 itself, the tetragonal distortion did not decrease on approaching the coexistence region, but continuously increased up to reach a value as high as 1.19 for $x = 0.75$. This suggests a very high spontaneous polarization, as it was confirmed by electrical measurements. Perovskite cell volume is also shown in the figure. Note the large volume difference between the tetragonal and rhombohedral phases of 3.45 Å^3 within the coexistence region; to be compared with $\Delta V \sim 0.25 \text{ Å}^3$ for BiMnO_3 – PbTiO_3 , which clearly indicates a discontinuous MPB.

The actual symmetry of the rhombohedral phase close to the coexistence region is currently under debate. Evidences of an intermediate phase were firstly provided by electron diffraction,⁶² and subsequent Rietveld analysis of XRD data claimed this phase to be monoclinic Cc , and to extend up to $x = 0.9$.⁶⁶ This has deep implications, for it opens the possibility of not only having high field phase-change responses in the system, but also enhanced low field ones by polarization rotation.^{27,28}

Magnetism across the system. A number of reports also addressed the evolution of magnetism across the perovskite solid solution series. Antiferromagnetic order is maintained across the whole rhombohedral and/or monoclinic fields between $x = 1$ and $x = 0.72$, with a Néel temperature that decreases from 630 K for $x = 1$ down to ~ 520 K for $x = 0.72$, as determined from ZFC magnetization curves.⁶³

Fig. 9. (a) Perovskite lattice parameters of the tetragonal (a_T and c_T) and rhombohedral (a_R and β) polymorphic phases across the $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ solid solution series for the powders obtained by mechanosynthesis, and (b) evolution of the perovskite cell volume. Adapted from Ref. 65 with permission from The Royal Society of Chemistry.

G-type antiferromagnetism and a Néel temperature of 592 K were obtained in an independent neutron diffraction study of a material with $x = 0.9$.⁶⁷ Tetragonal compositions are also antiferromagnetic at least until $x = 0.45$, but with ordering temperatures below RT.⁶³ Therefore, the coexisting polymorphs at the MPB region have well-differentiated antiferromagnetic order and Néel temperature,⁶⁸ the latter being above and below RT for the rhombohedral and tetragonal phases, respectively.⁶⁹

Compositions claimed to be monoclinic present a second magnetic anomaly in their ZFC curves, below the ordering temperature,^{63,70} which has been related to a spin reorientation transition.⁷⁰ A significant irreversibility, that is divergence of the ZFC and FC curves has been recently described for a material with $x = 0.675$ at the spin reorientation transition, which strongly suggests the appearance of spin canting and weak ferromagnetism at the magnetic instability.⁷¹ This effect is illustrated in Fig. 10, where the spin reorientation transition at 380 K is marked with an arrow. Note the persistence of significant magnetization above this temperature,

Fig. 10. Magnetic behavior of $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ with $x = 0.675$, prepared by mechanosynthesis. (a) Magnetization between 2 and 300 K, measured after ZFC and during subsequent FC under an applied field of 500 Oe. The spin reorientation transition of the monoclinic polymorphic phase (T_{SRT}^M), and the Néel temperature of the coexisting tetragonal phase (T_N^T) are indicated. (b) RT magnetization. Reprinted with permission from Ref. 71. Copyright [2014], AIP Publishing LLC.

indicating the Néel temperature to be above the measuring range. This composition shows phase coexistence, so the magnetic anomaly associated with the ordering temperature of the tetragonal polymorph can also be seen below RT. A RT magnetization loop is also given in the figure, which shows a small, but measurable ferromagnetic component.

Ferroelectricity across the system. The ferroelectric character of the two polymorphic phases, anticipated by their crystal symmetries, was confirmed and their main parameters determined by electrical measurements, including the temperature dependence of the dielectric permittivity for determining the position of the ferroelectric transition, and ferroelectric hysteresis loops in ceramics samples processed from the nanocrystalline powders.^{71,72}

Nevertheless, the ferroelectric transition temperatures were also determined by differential thermal analysis in the powdered samples obtained by mechanosynthesis.⁶⁵ Distinctive endothermic reversible effects that could be directly related to the transition were found for all compositions from $x = 0$ to 1. A tricritical point then does not seem to exist in the binary system, and the ferroelectric transition is first order all across the solid solution series. The evolution of T_C with x is shown in Fig. 11, where a continuous increase with x , along with a distinctive change of the slope within the phase coexistence region is evident.

Fig. 11. (a) Temperature dependence of the relative permittivity at 1 MHz of six $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ ceramics with $x = 1, 0.9, 0.8, 0.7, 0.675$ and 0.6 , processed from the nanocrystalline powders obtained by mechanosynthesis (adapted with permission from Ref. 71. Copyright [2014], AIP Publishing LLC), and (b) ferroelectric transition temperatures (T_C^h determined on heating, T_C^c on cooling, and T_C not specified) across the $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ solid solution series for samples obtained by mechanosynthesis: MS (from Refs. 65 and 71), and by conventional means: SS (from Ref. 73), experimentally determined either by differential thermal analysis: DTA, or from the temperature dependence of permittivity: $\epsilon(T)$.

The ferroelectric transition was further studied by measuring the temperature dependence of the dielectric permittivity, after the processing of ceramics by hot pressing of the nanocrystalline powders for $1 \geq x \geq 0.65$, or by spark plasma sintering of the same powder followed by a thermal treatment for $x < 0.65$. The latter procedure was necessary for compositions in the tetragonal field, next to the MPB because of the very high tetragonal distortion that made hot pressed samples to disintegrate during cooling. Like for $\text{BiMnO}_3\text{-PbTiO}_3$, conductivity was an issue, this time associated with the presence of oxygen vacancies and Fe^{2+} , so as both low temperature electron hopping between Fe^{2+} and Fe^{3+} and high temperature ionic conduction, along with a number of related dielectric relaxations contributed to the electrical response. As a consequence, a stringent control of the processing conditions was necessary to obtain materials with minimized conduction related phenomena (and also enhanced dielectric breakdown resistance), which allowed the ferroelectric parameters to be determined. Details of this sample tailoring can be found in Ref. 71.

The temperature dependence of the permittivity for six materials covering the rhombohedral/monoclinic field, the coexistence region, and a tetragonal composition with very high tetragonal distortion are given in Fig. 11 at 1 MHz. The obtained evolution of T_C with x is compared with that of powders measured by DTA in the same figure. The transition temperature for a ceramic material with $x = 0.7$, processed from powders synthesized by conventional solid-state reactions, and taken from an independent report is included for completeness.⁷³ Note the discrepancy between the transition temperatures of powders and ceramics in the coexistence region that suggests a higher percentage of tetragonal phase in the former samples for a given composition, in agreement with XRD results.^{65,72} This is most probably an effect of the ceramic stress field, and nicely illustrates how close the two polymorphs are in the free energy space.

Ferroelectric hysteresis loops for the same six materials are shown in Fig. 12. As processed ceramics did not show ferroelectric switching up to breakdown fields, and a thermal treatment consisting of heating above the Curie temperature, followed by quenching was required to obtain saturated loops. This has been proposed to result in the release of the ferroelectric domain walls, initially clamped by the presence of aligned Fe^{2+} -oxygen vacancy dipolar defects.^{71,72} Indeed, this treatment was not efficient enough to obtain fully saturated loops for $x = 1$, that is BiFeO_3 , because the transition temperature of 1100 K could not be exceeded in this case. Perovskite decomposition was already triggered at a temperature as low as 1063 K for the multiferroic edge member. A somehow similar problem was found for $x = 0.6$, whose very high transition strain characteristic of the tetragonal phase made the quenching treatment to result in microcracking. However, saturated loops were obtained all across the rhombohedral/monoclinic field, and within the coexistence region.

Fig. 12. (a) Ferroelectric hysteresis loops at 0.1 Hz of six $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ ceramics with $x = 1, 0.9, 0.8, 0.7, 0.675$ and 0.6 , processed from the nanocrystalline powders obtained by mechanosynthesis (from Ref. 71 but for $x = 0.7$ that is unpublished), and (b) the obtained ferroelectric parameters (P_R remnant polarization, and E_C coercive field) across the $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ solid solution series. *From unsaturated loops.

The ferroelectric parameters across the binary system are given in the same figure. Recall that those of $x = 1$ and $x = 0.6$ correspond to unsaturated loops. Remnant polarization, P_R , seemed to maintain a constant value around $45 \mu\text{C cm}^{-2}$ for materials with $x = 0.9, 0.8$ and 0.7 and rhombohedral or monoclinic symmetry. However, the coercive field continuously decreased from 12 kV mm^{-1} for $x = 0.9$, down to 8 and 5 kV mm^{-1} for $x = 0.8$ and 0.7 , respectively. A fairly constant spontaneous polarization thus exists in this compositional range, which would be $\sim 90 \mu\text{C cm}^{-2}$ under the assumption that only inversion domains contribute to switching (we will see later this to be the case). The figure is very close to that reported for rhombohedral BiFeO_3 single crystals.⁵⁸ However, coercive field does change, which suggests a strong modification of the domain configuration with increasing x . This might be a consequence of the reported rhombohedral to monoclinic transition for $x = 0.9$ ⁶⁶ that could be also responsible of the significant modification of the dielectric anomaly when x was decreased from 0.9 down to 0.8 (see Fig. 11). It is worth noting that the ferroelectric transition is from an orthorhombic $Pnma$ phase to a rhombohedral $R3c$ one for $x = 1$, but from a cubic $Pm3m$ phase to monoclinic Cc for $x = 0.73$.⁶⁶

A main result of the electrical study was the significant increase of P_R when entering the phase coexistence region, up to a value as high as $63 \mu\text{C cm}^{-2}$, while the coercive field remained basically unchanged. This cannot be associated with a sudden increase of the spontaneous polarization in the monoclinic component, for the previous evolution with x does not indicate it. It cannot be associated with the tetragonal component either, for only incipient switching is obtained in this phase at the applied fields, as shown by the loop of the material with $x = 0.6$. A possibility might be the onset of a ferroelectric/ferroelastic contribution, but this should be accompanied by an increase of E_C . Besides, the RT

electromechanical response of ceramics with $x = 0.675$, shown for fields up to 2 kV mm^{-1} in Fig. 13, is very linear and hysteresis-free, which seems to exclude this mechanism. Therefore, this very high number can only be understood if a significant phase-change contribution to switching is assumed.^{71,72} Indeed, a distinctive phase-change electromechanical response was revealed when temperature was raised above 425 K , and the threshold field was decreased below the applied ones.⁷²

The evolution of the electrical and electromechanical linear coefficients across the perovskite solid solution series was outstanding too.⁷¹ Permittivity and the charge piezoelectric coefficient are also given in Fig. 13. A distinctive enhancement of the ϵ_{33} dielectric permittivity and the d_{33} piezoelectric coefficient at the phase coexistence region, similar to that described at the ferroelectric instabilities of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ and a range of related perovskite solid solutions, was found.^{27,74} In the case of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, this enhancement is known to be the combination of two effects: (1) the presence of a lattice transverse instability at the monoclinic Cm -tetragonal $P4mm$ boundary,²⁸ and (2) an enhanced ferroelectric/ferroelastic domain wall activity within the monoclinic phase.⁷⁵ In the case of $\text{BiFeO}_3\text{-PbTiO}_3$, however, no ferroelectric/ferroelastic contribution to the electromechanical response has been found up to electric fields as high as 2 kV mm^{-1} . Therefore, the enhancement of the piezoelectric coefficient at the MPB must only reflect the presence of lattice transverse softening and thus, the enabling of the associated polarization rotation mechanism in the multiferroic system. Indeed, the actual figure of 87 pC N^{-1} for MPB $\text{BiFeO}_3\text{-PbTiO}_3$ favorably compares with the single crystal contribution to the coefficient of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics, reported to be 80 pC N^{-1} (raised up to 245 pC N^{-1} by domain wall contribution).⁷⁶ Note that this mechanism requires the presence of the monoclinic polymorph, so these results support

Fig. 13. (a) Electric field induced strain for one $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ ceramic with $x = 0.675$, processed by hot pressing of nanocrystalline powders obtained by mechanosynthesis (adapted with permission from Ref. 72. Copyright [2012], AIP Publishing LLC), and (b) relative permittivity (ϵ_r) and charge piezoelectric coefficient (d_{33}) across the $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ solid solution series (adapted with permission from Ref. 71. Copyright [2014], AIP Publishing LLC).

the structural characterizations that indicated the presence of the Cc phase.

A similar exercise can be done with permittivity. The figure for MPB $\text{BiFeO}_3\text{-PbTiO}_3$ of 335 is also comparable to the single crystal contribution to the permittivity of $\text{Pb}(\text{Zr, Ti})\text{-O}_3$ ceramics, this reported to be 350 (raised up to 1200 by domain wall contributions).⁷⁶ It is clear that inversion domains do move in $\text{BiFeO}_3\text{-PbTiO}_3$; there would be no ferroelectric switching otherwise, but the very high coercive fields, one order of magnitude larger to those of $\text{Pb}(\text{Zr, Ti})\text{O}_3$, hint their very low contribution to the linear coefficient.

Analysis of multiferroism and the potential magnetoelectric response. In summary, and unlike $\text{BiMnO}_3\text{-PbTiO}_3$, the perovskite $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ solid solution series shows multiferroic states for all compositions from $x = 1$ down to 0.45. This comprises the phase coexistence region between the monoclinic and tetragonal polymorphs that is thus a multiferroic phase boundary like targeted. A distinctive characteristic of the system is that both polymorphic phases have the electrical ordering temperatures above RT, but only the monoclinic one has the magnetic ordering temperature above RT, while the Néel temperature of the tetragonal component is below 298 K.

Besides, strong RT phase-change electrical and electro-mechanical responses have been found for $\text{BiFeO}_3\text{-PbTiO}_3$ ceramics at the MPB. This involves the partially reversible electrical field induced transformation between a canted antiferromagnet and a paramagnet and thus, a distinctive phase-change magnetoelectric response can be expected.

Moreover, the system shows transverse lattice softening at the multiferroic monoclinic–tetragonal boundary, and related enhancement of permittivity and piezoelectric coefficient by the polarization rotation mechanism. An analogous enhancement of the magnetoelectric coefficients might be expected if the ferroelectric and magnetic orderings are

coupled like in BiFeO_3 .^{19,20} This coupling has been suggested to exist in $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ with $x = 0.73$, based on the observation of a dielectric anomaly at the antiferromagnetic transition.⁷⁷

5. Final Considerations and Future Trends

Here we have put together our investigations on two systems, whose phase diagrams were, in principle, liable to show multiferroic MPBs. Design concept was quite straightforward, namely to form perovskite solid solutions with one edge member of crystal symmetry other than tetragonal, which included stereochemically active Bi^{3+} at the A-site and a magnetically active cation in the B-site, and tetragonal PbTiO_3 as the second edge member. Pb-based perovskites like $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ were avoided, for the low concentration of the magnetic species anticipated very low magnetic ordering temperatures.

Indeed, MPBs were found for both cases, but of very different nature. A multiferroic instability does not exist for $\text{BiMnO}_3\text{-PbTiO}_3$, but a MPB between a ferroelectric tetragonal $P4mm$ polymorphic phase and a nonpolar orthorhombic $Pnma$ phase. Magnetic order sets in for the latter polymorph but at very low temperature. Besides, tetragonal phases next to the MPB transform into the orthorhombic phase on cooling. Therefore, multiferroic states do not exist across the system at any temperature.

Contrarily, a multiferroic instability unambiguously exists for $\text{BiFeO}_3\text{-PbTiO}_3$ that shows a MPB between ferroelectric, canted antiferromagnets of monoclinic Cc and tetragonal $P4mm$ symmetries. Furthermore, electric field induced phase transformations between the two polymorphic phases, as well as lattice transverse softening at the monoclinic–tetragonal boundary have been demonstrated. A main issue of this

multiferroic instability is its antiferromagnetic nature, and the very weak ferromagnetism provided by the spin canting. Novel systems thus need to be found with a ferromagnetic character, or at least enhanced weak ferromagnetism.

A promising candidate that we are currently investigating is the $\text{BiFeO}_3\text{--BiMnO}_3\text{--PbTiO}_3$ ternary system, and specifically the line across the phase diagram that joins the morphotropic phase boundaries of the $x\text{BiFeO}_3\text{--}(1-x)\text{PbTiO}_3$ and $x\text{BiMnO}_3\text{--}(1-x)\text{PbTiO}_3$ perovskite solid solution series, located at $x = 0.7$ and $x = 0.4$, respectively. It has been proposed after an study of the strongly related ternary $\text{BiScO}_3\text{--BiFeO}_3\text{--PbTiO}_3$ that a Vegard-type relationship exists for the MPB compositions, so as the line that joins the MPBs of two binary $\text{BiMO}_3\text{--PbTiO}_3$ and $\text{BiM}'\text{O}_3\text{--PbTiO}_3$ systems across the phase diagram of the corresponding $\text{BiMO}_3\text{--BiM}'\text{O}_3\text{--PbTiO}_3$ ternary is a line of MPBs.⁴⁰ Indeed,

this is the case for $\text{BiFeO}_3\text{--BiMnO}_3\text{--PbTiO}_3$, for which phase coexistence, initially between a rhombohedral $R3c$ and tetragonal $P4\text{mm}$ polymorphic phases that subsequently evolves towards a coexistence between tetragonal $P4\text{mm}$ and orthorhombic $Pnma$ ones, has been recently described along such a line.⁷⁸ This is illustrated in Fig. 14.

A consistent evolution of the magnetism and ferroelectricity has also been found along the line, with distinctive features at selected compositions, such as decrease of the temperature of the spin reorientation transition, accompanied by an increase of the irreversibility and thus, an enhancement of the weak magnetism.⁷⁸ Moreover, an unambiguous RT phase-change magnetoelectric response has been obtained for a chemically engineered composition at a monoclinic Cc tetragonal $P4\text{mm}$ boundary, which also shows a significant magnetoelectric linear coefficient by polarization rotation.⁷⁹

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References

- W. Eerenstein, N. Mathur and J. F. Scott, Multiferroic and magnetoelectric materials, *Nature* **442**, 759 (2006).
- G. Lawes and G. Srinivasan, Introduction to magnetoelectric coupling and multiferroic films, *J. Phys. D: Appl. Phys.* **44**(24), 243001 (2011).
- J. F. Scott, Room temperature multiferroic magnetoelectrics, *NPG Asia Mater.* **5**, E72 (2013).
- M. Bibes and A. Barthelemy, Multiferroics: Towards a magnetoelectric memory, *Nature Mater.* **7**(6), 425 (2008).
- J. F. Scott, Applications of magnetoelectrics, *J. Mater. Chem.* **22** (11), 4567 (2012).
- D. Sando, A. Barthelemy and M. Bibes, BiFeO_3 epitaxial thin films and devices: Past, present and future, *J. Phys.: Condens. Matter.* **26**(47), 473201 (2014).
- E. Ascher, H. Rieder, H. Schmid and H. Stössel, Some properties of ferromagnetoelectric nickel-iodine boracite $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$, *J. Appl. Phys.* **37**, 1404 (1966).
- T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, Magnetic control of ferroelectric polarization, *Nature* **426**, 55 (2003).
- N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha and S. W. Cheong, Electric polarization reversal and memory in a multiferroic material induced by magnetic fields, *Nature* **429**, 392 (2004).
- S. W. Cheong and M. Mostovoy, Multiferroics: A magnetic twist for ferroelectricity, *Nat. Mater.* **6**(1), 13 (2007).
- T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist and A. P. Ramirez, Cupric oxide as an induced-multiferroic with high- T_C , *Nat. Mater.* **7**, 291 (2008).

Fig. 14. (a) Line of MPBs across the $\text{BiFeO}_3\text{--BiMnO}_3\text{--PbTiO}_3$, expressed as $x(0.4\text{BiMnO}_3\text{--}0.6\text{PbTiO}_3)\text{--}(1-x)(0.7\text{BiFeO}_3\text{--}0.3\text{PbTiO}_3)$. (b) XRD patterns of selected highly crystalline powders along this line. Peaks associated with the coexisting monoclinic, tetragonal and orthorhombic polymorphic phases are indicated with M, T and O, respectively. Adapted from Ref. 78 with permission from The Royal Society of Chemistry.

- ¹²Y. Kitagawa, Y. Hiraoka, T. Honda, T. Ishikura, H. Nakamura and T. Kimura, Low-field magnetoelectric effect at room temperature, *Nat. Mater.* **9**, 797 (2010).
- ¹³K. R. S. Preethi-Meher, C. Martin, V. Caignaert, F. Damay and A. Maignan, Multiferroics and magnetoelectrics: A comparison between some chromites and cobaltites, *Chem. Mater.* **26**, 830 (2014).
- ¹⁴M. Fiebig, Revival of the magnetoelectric effect, *J. Phys. D: Appl. Phys.* **38**(8), R123 (2005).
- ¹⁵R. E. Cohen, Origin of ferroelectricity in perovskite oxides, *Nature* **358**(6382), 136 (1992).
- ¹⁶N. A. Hill, Why are there so few magnetic ferroelectrics? *J. Phys. Chem. B* **104**(29), 6694 (2000).
- ¹⁷J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig and R. Ramesh, Epitaxial BiFeO₃ multiferroic thin film heterostructures, *Science* **299**(5613), 1719 (2003).
- ¹⁸G. Catalan and J. F. Scott, Physics and Applications of bismuth ferrite, *Adv. Mater.* **21**(24), 2463 (2009).
- ¹⁹T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom and R. Ramesh, Electrical control of antiferromagnetic domains in multiferroic BiFeO₃ films at room temperature, *Nat. Mater.* **5**, 823 (2006).
- ²⁰D. Lebeugle, D. Colson, A. Forget, M. Viret and A. M. Bataille, Electric-field-induced spin flop in BiFeO₃ single crystals at room temperature, *Phys. Rev. Lett.* **100**, 227602 (2008).
- ²¹V. A. Khomchenko, D. A. Kiselev, J. M. Vieira, L. Jian, A. L. Kholkin, A. M. L. Lopes, Y. G. Pogorelov, J. P. Araujo and M. Maglione, Effect of diamagnetic Ca, Sr, Pb and Ba substitution on the crystal structure and multiferroic properties of the BiFeO₃ perovskite, *J. Appl. Phys.* **103**, 024105 (2008).
- ²²S. M. Wu, S. A. Cybart, P. Yu, M. D. Rossell, J. X. Zhang, R. Ramseh and R. C. Dynes, Reversible electric control of exchange bias in a multiferroic field-effect device, *Nat. Mater.* **9**, 756 (2010).
- ²³D. M. Evans, A. Schilling, A. Kumar, D. Sanchez, N. Ortega, M. Arredondo, R. S. Katiyar, J. M. Gregg and J. F. Scott, Magnetic switching of ferroelectric domains at room temperature in multiferroic PZTFT, *Nat. Commun.* **4**, 1534 (2013).
- ²⁴D. Sánchez, N. Ortega, A. Kumar, G. Sreenivasulu, R. S. Katiyar, J. F. Scott, D. M. Evans, M. Arredondo-Arechavala, A. Schilling and J. M. Gregg, Room-temperature single phase multiferroic magnetoelectrics: Pb(Fe,M)_x(Zr,Ti)_{1-x}O₃ [M=Ta, Nb], *J. Appl. Phys.* **113**, 074105 (2013).
- ²⁵O. Dieguez and J. Iniguez, First-principles investigation of morphotropic transitions and phase-change functional responses in BiFeO₃-BiCoO₃ multiferroic solid solutions, *Phys. Rev. Lett.* **107**, 057601 (2011).
- ²⁶K. Oka, T. Koyama, T. Ozaaki, S. Mori, Y. Shimakawa and K. Azuma, Polarization rotation in the monoclinic perovskite BiCo_{1-x}Fe_xO₃, *Angew. Chem. Int. Ed.* **51**, 7977 (2012).
- ²⁷R. Guo, L. E. Cross, S. E. Park, B. Noheda, D. E. Cox and G. Shirane, Origin of the high piezoelectric response in PbZr_{1-x}Ti_xO₃, *Phys. Rev. Lett.* **84**, 5423 (2000).
- ²⁸D. Damjanovic, Comments on origins of enhanced piezoelectric properties in ferroelectrics, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **56**, 1574 (2009).
- ²⁹M. Algueró, J. Ricote, T. Hungria and A. Castro, High-sensitivity piezoelectric, low-tolerance-factor perovskites by mechanosynthesis, *Chem. Mater.* **19**(20), 4982 (2007).
- ³⁰A. Moreira dos Santos, A. K. Cheetham, T. Atou, Y. Syono, Y. Yamaguchi, K. Ohoyama and H. Chiba, Orbital ordering as the determinant for ferromagnetism in biferroic BiMnO₃, *Phys. Rev. B* **66**, 064425 (2002).
- ³¹T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi and Y. Syono, Structure determination of ferromagnetic perovskite BiMnO₃, *J. Solid State Chem.* **145**, 639 (1999).
- ³²A. Moreira dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham and C. N. R. Rao, Evidence for the likely occurrence of magnetoferroelectricity in the simple perovskite BiMnO₃, *Solid State Commun.* **122**, 49 (2002).
- ³³A. Sharan, J. Lettieri, Y. Jia, W. Tian, X. Pan, X. Pan, D. G. Scholm and V. Gopalan, Bismuth manganite: A multiferroic with a large nonlinear optical response, *Phys. Rev. B* **69**, 214109 (2004).
- ³⁴R. Seshadri and N. A. Hill, Visualizing the role of Bi 6s "lone pairs" in the off-center distortion in ferromagnetic BiMnO₃, *Chem. Mater.* **13**, 2892 (2001).
- ³⁵D. I. Woodward and I. M. Reaney, A structural study of ceramics in the (BiMnO₃)_x-(PbTiO₃)_{1-x} solid solution series, *J. Phys.: Condens. Matter* **16**, 8823 (2004).
- ³⁶A. A. Bokov and Z. G. Ye, Dielectric relaxation in relaxor ferroelectrics, *J. Adv. Dielect.* **2**(2), 1241010 (2012).
- ³⁷A. Castro, E. Vila, R. Jiménez, J. Hernández-Velasco, T. Hungria and M. Algueró, Synthesis, structural characterization and properties of perovskites belonging to the x BiMnO₃-(1-x) PbTiO₃ system, *Chem. Mater.* **22**, 541 (2010).
- ³⁸T. Hungria, C. Correias, F. Houdellier, O. Peña, E. Vila and A. Castro, Study of nanocrystalline BiMnO₃-PbTiO₃: Synthesis, structural elucidation, and magnetic characterization of the whole solid solution, *Chem. Eur. J.* **18**, 9075 (2012).
- ³⁹A. Castro, C. Correias, O. Peña, A. R. Landa-Cánovas, M. Algueró, H. Amorín, M. Dollé, E. Vila and T. Hungria, Nanostructured BiMnO_{3+δ} obtained at ambient pressure: Analysis of its multiferroicity, *J. Mater. Chem.* **22**, 9928 (2012).
- ⁴⁰M. Algueró, P. Ramos, R. Jiménez, H. Amorín, E. Vila and A. Castro, High temperature piezoelectric BiScO₃-PbTiO₃ synthesized by mechanochemical methods, *Acta Mater.* **60**(3), 1174 (2012).
- ⁴¹T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano and Y. Tokura, Magnetocapacitance effect in multiferroic BiMnO₃, *Phys. Rev. B* **67**, 180401 (2003).
- ⁴²E. Montanari, G. Calestani, A. Migliori, M. Dapiaggi, F. Bolzoni, R. Cabassi and E. Gilioli, High-temperature polymorphism in metastable BiMnO₃, *Chem. Mater.* **17**, 6457 (2005).
- ⁴³A. A. Belik, H. Yusa, N. Hirao, Y. Ohishi and F. Takayama-Muromachi, Peculiar high pressure behavior of BiMnO₃, *Inorg. Chem.* **48**, 1000 (2009).
- ⁴⁴A. A. Belik, K. Kodama, N. Igawa, S. Shamoto, K. Kosuda and E. Takayama-Muromachi, Crystal and magnetic structures and properties of BiMnO_{3±δ}, *J. Am. Chem. Soc.* **132**, 8137 (2010).
- ⁴⁵M. Ahart, M. Somayazulu, R. E. Cohen, P. Ganesh, P. Dera, H. K. Mao, R. J. Hemley, Y. Ren, P. Liermann and Z. G. Wu, Origin of morphotropic phase boundaries in ferroelectrics, *Nature* **451** (7178), 545 (2008).
- ⁴⁶C. J. Stringer, R. E. Eitel, T. R. Shrout, C. A. Randall and I. M. Reaney, Phase transition and chemical order in the ferroelectric perovskite (1-x)Bi(Mg_{3/4}W_{1/4})O₃-xPbTiO₃ solid solution system, *J. Appl. Phys.* **97**, 024101 (2005).
- ⁴⁷H. Amorín, R. Jiménez, E. Vila, M. Dollé, A. Castro and M. Algueró, Electrical properties of ferroelectric BiMnO₃-PbTiO₃

- under tailored synthesis and ceramic processing, *Phase Transit.* **86**(7), 681 (2013).
- ⁴⁸M. Algueró, B. Jiménez and L. Pardo, Transition between the relaxor and ferroelectric states for $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ with $x=0.2$ and 0.3 polycrystalline aggregates, *Appl. Phys. Lett.* **87**(8), 082910 (2005).
- ⁴⁹R. Jimenez, B. Jimenez, J. Carraud, J. M. Kiat, B. Dkhil, J. Holc, M. Kosec and M. Algueró, Transition between the ferroelectric and relaxor states in $0.8\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.2PbTiO_3 ceramics, *Phys. Rev. B* **74**(18), 184106 (2006).
- ⁵⁰M. Algueró, B. Jiménez and L. Pardo, Rayleigh type behavior of the Young's modulus of unpoled ferroelectric ceramics and its dependence on temperature, *Appl. Phys. Lett.* **83**(13), 2641 (2003).
- ⁵¹M. Algueró, R. Jiménez, H. Amorín, E. Vila and A. Castro, Low temperature phenomena in ferroic BiMO_3 - PbTiO_3 (M: Mn and Sc), *Appl. Phys. Lett.* **98**(20), 202904 (2011).
- ⁵²P. Baettig, R. Seshadri and N. A. Spaldin, Anti-polarity in ideal BiMnO_3 , *J. Am. Chem. Soc.* **129**(32), 9854 (2007).
- ⁵³A. A. Belik, S. Ikubo, K. Kodama, N. Igawa, S. Shamoto, M. Maie, T. Nagai, Y. Matsui, S. Y. Stefenovich, B. I. Lazoryak and E. Takayama-Muromachi, BiScO_3 : Centrosymmetric BiMnO_3 -type oxide, *J. Am. Chem. Soc.* **128**(3), 706 (2006).
- ⁵⁴T. Yokosawa, A. A. Belik, T. Asaka, K. Kimoto, E. Takayama-Muromachi and Y. Matsui, Crystal symmetry of BiMnO_3 : Electron diffraction study, *Phys. Rev. B* **77**, 024111 (2008).
- ⁵⁵V. Goian, S. Kamba, M. Savinov, D. Nuzhnyy, F. Borodavka, P. Vaněk and A. A. Belik, Absence of ferroelectricity in BiMnO_3 ceramics, *J. Appl. Phys.* **112**, 074112 (2012).
- ⁵⁶W. Kaczmarek, Z. Pajak and M. Polomska, Differential thermal analysis of phase transitions in $(\text{Bi}_{1-x}\text{La}_x)\text{FeO}_3$ solid solution, *Solid State Commun.* **17**, 807 (1975).
- ⁵⁷F. Kubel and H. Schmid, Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite BiFeO_3 , *Acta Crystallogr. Sect. B* **46**, 698 (1990).
- ⁵⁸D. Lebeugle, D. Colson, A. Forget and M. Viret, Very large spontaneous polarization on BiFeO_3 single crystals at room temperature and its evolution under cycling fields, *Appl. Phys. Lett.* **91**, 022907 (2007).
- ⁵⁹J. M. Moreau, C. Michel, R. Gerson and W. J. James, Ferroelectric BiFeO_3 X-ray and neutron diffraction study, *J. Phys. Chem. Solids* **32**, 1315 (1971).
- ⁶⁰C. Ederer and N. A. Spaldin, Weak ferromagnetism and magnetoelectric coupling in bismuth ferrite, *Phys. Rev. B* **71**, 0604401(R) (2005).
- ⁶¹R. T. Smith, G. D. Achenbach, R. Gerson and W. J. James, Dielectric properties of solid solutions of BiFeO_3 with $\text{Pb}(\text{Ti,Zr})\text{O}_3$ at high temperature and high frequency, *J. Appl. Phys.* **39**, 70 (1968).
- ⁶²D. I. Woodward, I. M. Reaney, R. E. Eitel and C. A. Randall, Crystal and domain structure of the BiFeO_3 - PbTiO_3 solid solution, *J. Appl. Phys.* **94**, 3313 (2003).
- ⁶³W. M. Zhu, H. Y. Guo and Z. G. Ye, Structural and magnetic characterization of multiferroic $(\text{BiFeO}_3)_{1-x}(\text{PbTiO}_3)_x$ solid solutions, *Phys. Rev. B* **78**, 014401 (2008).
- ⁶⁴S. Bhattacharje, S. Tripathi and D. Pandey, Morphotropic phase boundary in $(1-x)\text{BiFeO}_3$ - $x\text{PbTiO}_3$: Coexistence region and unusually large tetragonality, *Appl. Phys. Lett.* **91**, 042903 (2007).
- ⁶⁵C. Correas, T. Hungria and A. Castro, Mechanosynthesis of the whole $x\text{BiFeO}_3$ -($1-x$) PbTiO_3 multiferroic system: Structural characterization and study of phase transitions, *J. Mater. Chem.* **21**, 3125 (2011).
- ⁶⁶S. Bhattacharje and D. Pandey, Stability of the various crystallographic phases of the multiferroic $(1-x)\text{BiFeO}_3$ - $x\text{PbTiO}_3$ system as a function of composition and temperature, *J. Appl. Phys.* **107**, 124112 (2010).
- ⁶⁷T. P. Comyn, T. Stevenson, M. A. Al-Jawad, S. L. Turner, R. Smith, A. J. Bell and R. Cywinsky, High temperature neutron diffraction studies of 0.9BiFeO_3 - 0.1PbTiO_3 , *J. Appl. Phys.* **105**, 094108 (2009).
- ⁶⁸S. Bhattacharje, A. Senyshyn, P. S. R. Krishna, H. Fuess and D. Pandey, Simultaneous changes of nuclear and magnetic structures across the morphotropic phase boundary in $(1-x)\text{BiFeO}_3$ - $x\text{PbTiO}_3$, *Appl. Phys. Lett.* **97**, 262506 (2010).
- ⁶⁹T. Comyn, T. Stevenson, M. Al-Jawad, S. L. Turner, R. I. Smith, W. G. Marshall, A. J. Bell and R. Cywinski, Phase-specific magnetic ordering in BiFeO_3 - PbTiO_3 , *Appl. Phys. Lett.* **93**, 232901 (2010).
- ⁷⁰S. Bhattacharje, A. Senyshyn, H. Fuess and D. Pandey, Morin-type spin-reorientation below the Neel transition in the monoclinic compositions of $(1-x)\text{BiFeO}_3$ - $x\text{PbTiO}_3$ ($x=0.25$ and 0.27): A combined dc magnetization and x-ray and neutron powder diffraction study, *Phys. Rev. B* **87**, 054417 (2013).
- ⁷¹H. Amorín, C. Correas, C. M. Fernández-Posada, O. Peña, A. Castro and M. Algueró, Multiferroism and enhancement of materials properties across the morphotropic phase boundary of BiFeO_3 - PbTiO_3 , *J. Appl. Phys.* **115**, 104104 (2014).
- ⁷²H. Amorín, C. Correas, P. Ramos, T. Hungria, A. Castro and M. Algueró, Very high remnant polarization and phase-change electromechanical response of BiFeO_3 - PbTiO_3 at the multiferroic morphotropic phase boundary, *Appl. Phys. Lett.* **101**, 172908 (2012).
- ⁷³T. P. Comyn, S. P. McBride and A. J. Bell, Processing and electrical properties of BiFeO_3 - PbTiO_3 ceramics, *Mater. Lett.* **58**, 3844 (2004).
- ⁷⁴R. E. Eitel, S. J. Zhang, T. R. Shrout, C. A. Randall and I. Levin, Phase diagram of the perovskite system $(1-x)\text{BiScO}_3$ - $x\text{PbTiO}_3$, *J. Appl. Phys.* **96**, 2828 (2004).
- ⁷⁵R. Theissmann, L. A. Schmitt, J. Kling, R. Schierholz, K. A. Schöna, H. Fuess, M. Knapp, H. Kungl and M. J. Hoffmann, Nanodomains in morphotropic lead zirconate titanate ceramics: On the origin of the strong piezoelectric effect, *J. Appl. Phys.* **102**, 024111 (2007).
- ⁷⁶Q. M. Zhang, H. Wang, N. Kim and L. E. Cross, Direct evaluation of domain-wall and intrinsic contributions to the dielectric and piezoelectric response and their temperature dependence on lead zirconate-titanate ceramics, *J. Appl. Phys.* **75**, 454 (1994).
- ⁷⁷S. Bhattacharje, V. Pandey, R. K. Kotnala and D. Pandey, Unambiguous evidence for magnetoelectric coupling of multiferroic origin in 0.73BiFeO_3 - 0.27PbTiO_3 , *Appl. Phys. Lett.* **94**, 012906 (2009).
- ⁷⁸C. M. Fernández-Posada, H. Amorín, C. Correas, O. Peña, M. Algueró and A. Castro, Mechanosynthesis and multiferroic properties of the BiFeO_3 - BiMnO_3 - PbTiO_3 ternary system along the morphotropic phase boundary, *J. Mater. Chem. C* **3**, 2255 (2015).
- ⁷⁹C. M. Fernández-Posada, A. Castro, J. M. Kiat, F. Porcher, O. Peña, M. Algueró and H. Amorín, in preparation.