High pressure and Multiferroics materials: a happy marriage

Edmondo Gilioli[a]* and Lars Ehm[bc]*

[a]IMEM-CNR, Area delle Scienze 37/A, Parma, 43124, Italy

[b]Mineral Physics Institute, Stony Brook University, 255 Earth & Space Science Building, Stony Brook, NY, 11794-2100, USA

[c]Photon Sciences Directorate, Brookhaven National Laboratory, 75 Brookhaven Avenue, Upton, NY, 11973-500, USA

Correspondence email: edi@imem.cnr.it; lars.ehm@stonybrook.edu

One or two sentences suitable for the Journal contents listing (style: IUCr synopsis).

Abstract The community of the material scientists is strongly committed in the research area of multiferroic materials, both for the understanding of the complex mechanisms supporting the multiferroism and for the fabrication of new compounds, potentially suitable for technological applications. The use of high pressure is demonstrating to be a powerful tool to synthesize new multiferroic magneto-electric phases, where the pressure stabilization of otherwise unstable perovskite-based structural distortions may lead to promising novel metastable compounds. The *in situ* investigation of the high pressure behaviour of multiferroic materials has provided insight into the complex interplay between magnetic and electronic properties and the coupling to structural instabilities.

1. Introduction

Multiferroism can be generally defined as a phenomena in which two or more of the so-called ‘ferroic’ order parameters (ferroelectricity, ferromagnetism, and ferroelasticity) simultaneously cohexist, in a single phase material.

Among the different interactions, magnetoelectric coupling is the most desirable property; it refers to either the induction of magnetization by an electric field or polarization by a magnetic field. The ultimate goal is a single phase multiferroic (MF), with *strong coupling* between magnetic and electronic order parameters and the potential to mutually manipulate them at *high (ambient) temperature*. Aside from the very promising technological applications (Nan *et al.*, 2008), the fascinating fundamental physics of MF materials certainly deserve further investigation.

Unfortunately, these compounds are extremely rare in nature; the scarcity of magnetoelectric MF can be understood by investigating a number of factors, including symmetry and electronic properties. From the structural point of view, there are only 13 point groups that can give rise to multiferroic

IMPORTANT: this document contains embedded data - to preserve data integrity, please ensure where possible that the IUCr Word tools (available from http://journals.iucr.org/services/docxtemplate/) are installed when editing this document.

behavior. Additionally, ferroelectrics by definition are insulators, while itinerant ferromagnets need conduction electrons. On the other hand, there seems to be an intrinsic contradiction between the conventional mechanism of off-centering in a ferroelectric, related to transition metals with d^0 electronic configuration and the formation of magnetic order which requires the presence of unpaired electrons.

Interestingly, L. Landau and E. Lifshitz in a volume of their Course of Theoretical Physics published in 1959 (Landau & Lifshitz, 1959), stated: *"Let us point out two more phenomena, which, in principle, could exist. One is piezomagnetism…... the other is a linear coupling between magnetic and electric fields in a media... Both these phenomena could exist for certain classes of magnetocrystalline symmetry, but it seems that till present, they have not been observed in any substance"*.

Yet in 2000, Nicola A. Hill, published a paper (Hill, 2000) entitled: "Why are there so few magnetic ferroelectrics?", clearly addressing the complexity of these materials.

Even to probe the magnetoelectric coupling is a complicated issue (Bibes, 2012); it can be measured *indirectly* by simply recording changes in either the magnetization near a ferroelectric transition temperature or the dielectric constant near a magnetic transition temperature ('magnetocapacitance' or 'magnetodielectric" response). *Direct measurements* are more challenging; they record either a magnetic response to an applied electric field [*M(E)*] or an electrical response to an applied magnetic field [*P(H)*].

All these complexities were too puzzling until recently, when the researchers found out that an additional electronic or *structural driving force* must be present for ferromagnetism and ferroelectricity to occur simultaneously.

Undoubtedly, the recent "explosion" in the MF studies is enabled by a combination of theoretical and experimental factors. In particular for the latter, new synthesis techniques such as vacuum-based thin film deposition techniques (for hetero-structures) and *high pressure/high temperature* (HP/HT), allow to obtain new materials by stabilizing metastable or highly distorted structures, that might support ME coupling. Indeed, the use of high pressure (HP) techniques (both for the synthesis and the characterization) is providing important (and somewhat unexpected) results.

Multiferroism is a relatively young field of research; although predicted in the late 50's (Landau & Lifshitz, 1959) and the term coined in 1994 (Schmid, 1994), the attention raised exponentially only after 2003, the "golden year" for MF, concomitant with the discovery of large ferroelectric polarization in epitaxial grown thin films of $BiFeO_3$ (Wang *et al.*, 2003) and the discovery of strong magnetic and electric coupling in orthorhombic $TbMnO_3$ (Kimura *et al.*, 2003) and $TbMn_2O_5$ (Hur *et al.*, 2004). New results are continuously reported and material scientists (and the high pressure community) are working hard to contradict the Landau and Lifshitz's statement and to prove Hill's paper to be outdated. A measure of the activity of the research on MF materials is the large number of

publications; at the date of submission of the present papers, about 4050 papers (2440 from 2010) were published with the term “multiferroic” in the title and 4200 (1780 from 2010) with the term “magnetoelectric” (source: Google Scholar).

Besides the massive literature available on MF ((Spaldin & Fiebig, 2005; Fiebig, 2005; Eerenstein *et al.*, 2006; Khomskii, 2006; Rao & Serrao, 2007) and reference therein), this review paper is limited to discuss the role of HP (synthesis and characterization) in the study of magnetoelectric MF materials, combining a part on HP/HT synthesis (why HP synthesis is so often needed?) and on HP characterization (what kind of information can be derived from HP characterization techniques?).

2. HP/HT synthesis of bulk MF materials

The tremendous rise in the research on MF and magnetoelectric materials pushed the material scientists to search for new materials and mechanisms leading to magnetoelectric coupling and multiferroic behavior. Historically, HP/HT synthesis has proven to be very effective in producing a large number of new phases (Badding *et al.*, 1995; McMillan, 2002, 2003; Brazhkin, 2007), as for example in the fields of super-hard materials (Haines *et al.*, 2001), superconductors (Bos, Penny, *et al.*, 2008), *etc*. For some of them (for example when high density is required, as in the super-hard materials) the role of applied pressure is intuitively easy to understand, while for other systems, often supporting complex electronic, magnetic or transport properties, one can guess that the stabilization of uncommon, metastable phases/structures/coordinations offer a pathway to new properties. Indeed, MF materials belong to this category.

A detailed description of the possible mechanisms supporting the multiferroism can be easily taken from the literature (see, for example, refs in (Khomskii, 2009)) and goes beyond the scope of the present paper; they can be summarized in *Lone-Pair MF* (Es., $BiFeO_3$, (Neaton *et al.*, 2005)), *Geometric Ferroelectric MF* (Es.: hexagonal $RMnO_3$ (Van Aken *et al.*, 2004)), *Charge Ordering Ferroelectrics* (Es.: $LuFe_2O_4$, (Ikeda *et al.*, 2005) or $(Pr,Ca)MnO_3$, (van den Brink & Khomskii, 2008)) or *Spin Spiral Ferroelectrics*, Es.: $TbMnO_3$, (Kimura *et al.*, 2003) or $TbMn_2O_5$, (Mostovoy, 2006)).

Already from this general list, one should ask: why does the perovskite-type structure play such an important role in the search for multiferroic properties? Generally speaking, it’s well known that it’s a very common structure, showing an extraordinary variety of properties. Many different atoms can occupy in particular the cationic sites, allowing a wide tuning of their properties. Moreover, the majority of ferroelectric materials exhibit perovskite structure.

People working with high pressure (and particularly geologists) are well used to perovskites; being a typical HP structure (dense packing, high coordination number, low inter-atomic distances, etc), it’s commonly found in our planet starting from the mantle to the core-mantle boundary, where silicate

perovskites represent the main mineral phases (Murakami *et al.*, 2012). Interestingly, at least part of this depth, corresponds to the thermodynamical conditions accessible to a conventional HP apparatus (piston cylinder, belt apparatus, multi anvil, diamond anvil) used for the HP/HT synthesis and characterization reported in the present paper.

Thus, it's not surprising that the section of this work on HP/HT synthesis of new materials eventually exhibiting MF properties deals mainly with perovskite-based compounds.

As already pointed out, the measurement of the MF properties, and in particular the direct magneto-electric coupling, is not trivial, even on high quality samples available in large quantity. This is usually not the case of HP synthesized metastable compounds, where the ME properties are generally detected (or hypothesized) in an indirect way, when the measurement (or the calculation) of the magnetic and ferroelectric transitions occur simultaneously.

2.1. HP/HT synthesis of simple perovskite bulk MF compounds:

"Simple" perovskite structure (ABO_3) consists of corner sharing BO_6 octahedra, with B ions (usually magnetic, such as Mn or Fe) in the center of the octahedral coordination (coordination number: 6) and A ions at the center of a cube formed by eight BO_6 octahedra (coordination number: 12). The most common structural distortion derives from the mismatch of A-O and B-O bond distances and from the Jahn-Teller (JT) distortion of the BO_6 octahedra; the application of external pressure enhances the ability of the perovskite to accommodate different ionic size, vacancies and structural distortions, by widening the tolerance factor.

In manganites, two crystal phases, hexagonal and orthorhombic, exist for RMnO$_3$ at ambient pressure. The orthorhombic structure (*Pbnm*) is stable for large *R* ions (La, Pr, Nd, Tb and Dy), while small *R* ions (Ho, Er, Yb, Lu, In and Sc) adopts the hexagonal structure ($P6_3cm$, at room temperature). However, orthorhombic RMnO$_3$ with small *R* ion, such as Ho and Lu, can be synthesized as a metastable perovskites by HP/HT synthesis (Wood *et al.*, 1973; Wu *et al.*, 2014; Rodgers *et al.*, 2006).

The simplest method to induce MF is to combine in the same phase a magnetic ion (ferromagnetism) in a non-centrosymmetric structure, enabling the insurgence of ferroelectricity. Ferroelectricity can be inducted by the asymmetrical coordination produced by the stereochemical effect of a "lone-pair" atom such as Bi^{3+} and Pb^{2+}, representing frequent ingredients of the magnetoelectric MF compounds.

$BiFeO_3$ is the prototype material, but it's unusual among the Bi-based perovskites in that it can be made under ambient conditions; most others require HP/HT synthesis. Since Bi_2O_3 melts at 824°C at ambient pressure, HP is necessary in most cases to achieve a high temperature solid state reaction whenever the oxides is used as reagent.

$BiMnO_3$ is an obvious MF magneto electric candidate, requiring HP/HT synthesis (P=4 GPa, T=1273 K). $BiMnO_3$ would deserve a special discussion; in spite of its "simple" perovskite structure, it's a very complex material and we refer to the massive work that has been done to unveil its peculiar structural properties (Belik, Iikubo, *et al.*, 2006), the HP/HT synthesis (P=4 GPa, T=1273 K) and the complex phase diagram at ambient and high temperature (Montanari, Righi, *et al.*, 2005; Montanari, Calestani, *et al.*, 2005) and the magnetic and electric properties (Chou *et al.*, 2009), some of those are also detailed in the second part of this paper on characterization. We emphasize the controversial determination of its MF properties, since a general consensus on the structure and the ferroelectric properties is still lacking (Goian *et al.*, 2012).

The search for polar structure in potentially MF Bi-based perovskites, has been studied in particular by Belik, who reported a series of Bi*M*O_3 oxides with *M*=Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Ga, In, and Rh (Belik, 2012). He also investigated the solid solutions of $BiGa_xM_{1-x}O_3$ (*M* = Cr, Mn, and Fe) prepared at P=6 GPa and T=1700 K (*M* = Cr and Fe) and 1300 K (*M* = Mn) resulting in the formation of a large family of polar materials with *Cm* and *R3c* symmetries. Samples with the *Cm* symmetry have structures similar to $PbVO_3$, $BiCoO_3$ and Bi_2ZnTiO_6 materials, while *R3c* symmetry compounds are isostructural with $BiFeO_3$ and have comparable calculated spontaneous polarization (58 μC/cm^2 for $BiGa_{0.4}Cr_{0.6}O_3$). The calculated polarization is 116 μC/cm^2 for $BiGa_{0.4}Fe_{0.6}O_3$, and 102 μC/cm^2 for $BiGa_{0.3}Mn_{0.3}O_3$. On the contrary, the HP synthesized $BiMnO_3$-type $BiScO_3$, (P=6 GPa, T=1413 K) crystallizes in the space group *C*2/*c* (centrosymmetric, therefore non ferroelectric) (Belik, Iikubo, *et al.*, 2006).

To provide further evidence of the complex and intriguing behavior of $BiMnO_3$, recently Chakrabartty *et al.* reposted a photovoltaic effect exploiting its ferroelectricity (that is the photo carrier separation by the ferroelectricity rather than in a p-n junction as in a conventional solar cell); an external solar power conversion efficiency of ~0.1% was achieved in Bi-Mn-O thin films grown onto Nb doped $SrTiO_3$ single crystal substrate by pulse laser deposition (Chakrabartty *et al.*, 2014).

Ferroelectric behavior associated to lattice distortion is found in single crystals of perovskite-type $YMnO_3$ obtained by high-pressure quasi-hydrothermal condition (P=5.5 GPa) (Ishiwata *et al.*, 2011). Polarization along the *ab*-plane was observed, accompanied by the discontinuous jump of the dielectric constant at T_N=42K, below which P shows a stepwise increase reaching circa 0.22 μC/cm^2 at 2 K, larger than the value for the polycrystalline sample (Taguchi *et al.*, 2012).

By combining dielectric, specific heat, and magnetization measurements and high-resolution neutron powder diffraction, Ye *et al.* investigated the thermodynamic and magnetic and structural properties of the metastable orthorhombic perovskite $ErMnO_3$ prepared at P=3.5 GPa and T=1373 K. The system shows a T_N=42 K and a corresponding sudden increase of the dielectric constant ϵ (Ye *et al.*, 2007).

The monoclinic (*$P2_1/n$*) $ScMnO_3$ perovskite was synthesized by Chen *et al.* from the hexagonal phase at P=12.5 GPa and T=1373 K (Chen *et al.*, 2013). Although indirect evidence of MF properties have been already obtained, the monoclinic phase shows similar structure to the orthorhombic Ho and Lu analogues, stimulating further studies on possibly coupled electrical polarization and magnetism.

Pb^{2+} lone pair asymmetrical coordination was exploited by Shpanchenko *et al.* (Shpanchenko *et al.*, 2004) to search for multiferroism in $PbVO_3$, synthesized at P=4-6 GPa and T= 973-1023 K. Non-centrosymmetric tetragonal *P4mm* structure of corner-shared VO_5 pyramids, instead of octahedra due to a strong tetragonal distortion is found and diffraction data suggest a large ferroelectric polarization above 100 $\mu C/cm^2$ (Belik *et al.*, 2005). Tetragonal perovskite $PbMnO_3$ was obtained by treating the hexagonal perovskite phase at P=15 GPa and T=1273 K (Oka *et al.*, 2009), but surprisingly the structural analysis suggested that $PbMnO_3$ crystallizes in the centrosymmetric space group *P4/mmm*, unlike and $PbVO_3$ and $PbTiO_3$ (Chaudhari & Bichile, 2013). Tetragonal perovskite phases exhibited antiferromagnetic ordering at T_N= 20 K.

Varga *et al.* reported the HP/HT synthesis of $FeTiO_3$ (P=18 GPa, T= 1473 K), isostructural with acentric $LiNbO_3$. Piezoresponse force microscopy and magnetometry demonstrate the coexistence of ferroelectricity and (weak) ferromagnetism below T_N=110 K (Varga *et al.*, 2009).

Other interesting examples are $ScCrO_3$ and $InCrO_3$, synthesized at P=6 GPa and T=1500 K. They crystallize in the $GdFeO_3$-type perovskite structure (space group *Pnma*). Antiferromagnetic transitions occur at T_N=73 K in $ScCrO_3$ and 93 K in $InCrO_3$ and dielectric anomalies were observed in both compounds at T_N, indicating magnetoelectric coupling, contrary to $YCrO_3$ (Belik, Matsushita, *et al.*, 2012).

Aimi *et al.* studied the correlation between structure, magnetic, and dielectric properties in Mn*M*O3 (*M* = Ti, Sn) synthesized in HP/HT conditions (P=7GPa, T= 973 and 1073 K, respectively); both the compounds possess a polar $LiNbO_3$-type structure at room temperature. Weak ferromagnetism due to canted antiferromagnetic interaction was observed at T_N=25 K for $MnTiO_3$ and at T_N=50 K for $MnSnO_3$, with anomalies in the dielectric permittivity indicating the correlation between magnetic and dielectric properties (Aimi *et al.*, 2011).

Similar structure was obtained for $PbNiO_3$ by Inaguma *et al.* at P=3 GPa and T=1073 K. The obtained perovskite-type phase crystallizes as an orthorhombic $GdFeO_3$-type structure (space group *Pnma*) that irreversibly transforms to a $LiNbO_3$-type phase with an acentric space group *R3c* by heat treatment at ambient pressure. The magnetic susceptibility measurement shows that $PbNiO_3$ undergoes an antiferromagnetic transition with T_N=205 K (Inaguma *et al.*, 2011).

2.2. HP/HT synthesis of double perovskite bulk MF compounds:

This paragraph covers the HP/HT synthesis of "double" perovskite MF oxides with general formula $A_2BB'O_6$. The presence of two different magnetic cations on the B-site may lead to different kind of magnetic exchange interactions, favoring the increase of the magnetic ordering temperature and the enhancement of the magnetic properties.

Many combinations of ions bringing either magnetic or electric properties have been attempted in the last years; Shimakawa *et al.* reported that bulk Bi_2NiMnO_6 (monoclinic structure, space group *C2*) synthesized at P=6 GPa, T=1073 K) exhibits ferromagnetic (Tc=485 K) and ferroelectric properties (calculated P= 20μC/cm^2) (Shimakawa *et al.*, 2011). Bi_2FeMnO_6, a potential MF bulk samples was obtained by Delmonte *et al.* at P=6 GPa at T=1373 K, displaying a complex magnetic behavior (magnetic transitions at T=450 and 288 K) and a temperature induced magnetization reversal (Delmonte *et al.*, 2013). The crystal structure is orthorhombic (space group *Pnam*), with no cation order on the *B* site; anomalies in the thermal dependence of the lattice parameters are observed at the magnetic ordering at T=288 K, indicating a spin-lattice coupling and possible magnetoelectric coupling. Cationic disordered of Bi-based double perovskite is also observed in Bi_2FeCrO_3, a recently proposed candidate multiferroic, prepared in a bulk form by HP/HT (Suchomel *et al.*, 2007).

In contrast, a significant degree of ordering of Mn^{4+} and Ni^{2+} ions was observed in In_2NiMnO_6, prepared at P=6 GPa and T=1600 K, characterized by a monoclinic structure (space group $P2_1/n$) and magnetic T_N=26 K. In spite of the interesting magnetic behavior (a field-induced antiferromagnetic-ferromagnetic transition at low T), no magneto electric coupling has been detected (Yi *et al.*, 2013). Liu *et al.* synthesized high purity crystals of Y_2FeMnO_6 and Y_2CrMnO_6, crystallizing in the orthorhombic space group *Pnma*, using a flux method under pressure (P=6 GPa, T=1573 K). An antiferromagnetic transition occurs at T_N=328 K in Y_2FeMnO_6, and a ferrimagnetic one at T_N=74 K in Y_2CrMnO_6; in both cases, the presence of the dielectric anomaly near T_N portends a magnetoelectric effect (Liu *et al.*, 2014).

Other interesting structures have been recently reported; Mathieu *et al.* succeeded in the preparation of Mn_2FeSbO_6 at P=3 GPa and T=1273 K, a rare example of antiferromagnetic double perovskite polymorph (the material also crystallizes as ferrimagnetic ilmenite) with the A site entirely occupied by Mn and Fe/Sb cationic order on the B sites. Theoretical calculations for the perovskite phase suggest a complex magnetic structure, holding an electronic polarization and possible magneto electric properties (Mathieu *et al.*, 2013). Aimi *et al.* reported the synthesis of a novel ferroelectric A-site ordered double perovskite $CaMnTi_2O_6$ at P=7 GPa and T=1473 K, with an uncommon polar space group $P4_2mc$ and a ferroelectric–paraelectric order–disorder type phase transition at 630 K. Similar to the structure of $CaFeTi_2O_6$, the A-site Ca^{2+} is 10-coordinated while Mn^{2+}show alternate tetrahedral and square planar coordination. The square-planar shifts along the c-axis and the usual Ti^{4+} ion displacement account for its polar structure. P-E hysteresis measurement demonstrated that

$CaMnTi_2O_6$ is ferroelectric with a calculated polarization and an observed remnant polarization of 24 and 3.5 μC/cm^2, respectively (Aimi *et al.*, 2014).

Another promising MF is lead iron niobate Pb_2FeNbO_6, possessing simultaneously ferroelectric properties below T≈380 K, antiferromagnetic order at T_N≈150 K and showing one of the largest known value of magnetoelectric coefficient (Levstik *et al.*, 2008). Single-phase (1-x)Pb_2FeNbO_6 - xPb_2FeSbO_6 solid solution ceramics were synthesized at 6 GPa and 1400–1500 K (Raevski *et al.*, 2013).

2.3. HP/HT synthesis of complex (quadruple) perovskite bulk MF compounds:

"Quadruple" perovkites are A-site ordered compounds, derived by the doubling of the conventional ABO_3 axes; their general formula can be written as $AA'_3B_4O_{12}$ to better visualize the site occupation of the different elements. The structure is based on a three dimensional network of corner-sharing tilted octahedra, centered on the *B* site (usually occupied by a magnetic element in MF materials) stabilized under high pressure by the presence of a Jahn-Teller atom (Mn^{3+} or Cu^{2+}) on the A' site, forming an uncommon square planar coordination due to large distortion of the A site coordination.

Among the compounds belonging to this family, $CaMn_7O_{12}$ (or $CaMn_3Mn_4O_{12}$) possess all the requirements for being a good magnetoelectric MF; i) a ferroelectric transition temperature (T_C=90 K) much higher comparing with other magnetic MF manganites, and ii) high polarization values, 450 μC/m^2 at 8 K when using a poling field of 7 kV/cm (Zhang, Dong, *et al.*, 2011). By neutron powder diffraction from $CaMn_7O_{12}$ single crystals, Johnson *et al.* found that the polarization, (along the c-axis of the rhombohedral cell) reaches the remarkable value of 2870 μC/m^2 at low temperatures, one of the largest measured values in magnetic multiferroics (Johnson *et al.*, 2012). $CaMn_7O_{12}$ can be synthesized at ambient pressure although, curiously, was first synthesized under high pressure ((Bochu *et al.*, 1974), P=8GPa, T=1273 K).

Those impressive properties certainly sparked the interest in MF materials belonging to this family of complex perovskites.

Following the consolidated strategy based on the Bi^{3+} substitutions, Mezzadri *et al.* reported the HP/HT (P=4GPa, T=1273 K) synthesis of $BiMn_7O_{12}$ (or $BiMn_3Mn_4O_{12}$) (Mezzadri *et al.*, 2009). As expected, the structural characterization of single-crystal samples shows a distorted and asymmetrical coordination around the Bi atom due to presence of the $6s^2$ lone pair, resulting in noncentrosymmetric space group *Im*, leading to a permanent electrical dipole moment and ferroelectric properties. The dielectric constant shows anomalies, matching the antiferromagnetic transition temperatures (T_N= 22 and 55 K). $BiMn_7O_{12}$ is therefore a promising MF material, with evidence of coupling between magnetic and dielectric properties

By means of neutron diffraction, Gauzzi *et al.* found a large uniform modulation of the antiferromagnetic structure of the Mn^{3+} ions; this modulation (absent in the isovalent compound $LaMn_7O_{12}$) is induced by the internal strain created by the polar Bi^{3+} ion, accounts for a large magnetoelectric coupling. Therefore, the peculiar quadruple perovskite structure, preventing the release of the strain, provides a new degree of freedom to achieve large magnetoelectric couplings (Gauzzi *et al.*, 2013).

Locherer *et al.* reported the HP/HT synthesis (P=7.5 GPa, T=1173-1273 K) of the isostructural and heterovalent $PbMn_7O_{12}$ (or $Pb(Mn^{3+}{}_3)(Mn^{3+}{}_3Mn^{4+})O_{12}$ to appreciate the different mixed valence occupation of Mn on the B-site) (Locherer *et al.*, 2012); as for $BiMn_7O_{12}$, the basic mechanism supporting the FE is supposed to be the stereochemical effect of $6s^2$ lone pair of Pb^{2+} that induces a permanent electric dipole but, surprisingly, $PbMn_7O_{12}$ crystallizes in a centrosymmetric structure (S.G.: *R*-3). However, a sizeable coupling of magnetic, electrical and dielectric properties at T_N=68 K indicates a MF behavior.

This family of compounds is not fully explored yet; new promising properties are awaited, possibly also in non-"lone-pair" materials, for their complex structure leading to unusual magnetic properties, such as in $LaMn_7O_{12}$ (Prodi *et al.*, 2009) and isostructural samples with de-coupling of the magnetic contribution of the A'-B sites, as in $LaMn_3Cr_4O_{12}$ and $LaMn_3Ti_4O_{12}$ (Long *et al.*, 2009).

2.4. HP/HT synthesis of distorted-perovskite bulk MF compounds.

Among the numerous structures derived from various distortions of the perovskite strucure, iron fluorides with tetragonal tungsten bronze (TTB) structure, having general formula of $K_xFe^{2+}{}_xFe^{3+}{}_{1-x}F_3$, deserves a special mention. The structure can be described as a perovskite-like network of $Fe^{2+}O_6$ octahedra surrounded by pentagonal non-perovskite sites. $K_{0.6}Fe^{2+}{}_{0.6}Fe^{3+}{}_{0.4}F_3$ single crystals have been grown by hydrothermal synthesis (P=1.3 Kbar, T=950 K) and below magnetic transition (T_N=118 K) the system, characterized by an ordered arrangement of Fe^{2+}/Fe^{3+}, is suggested to be a rare example of complete MF, being simultaneously ferrimagnetic, ferroelectric and ferroelastic (Mezzadri *et al.*, 2008). In this case, the main role of the (limited) applied pressure is to reach the conditions suitable for hydrothermal synthesis.

A selection of perovskite-based materials, their structural properties, HP/HT syntheses conditions and the corresponding magnetic (T_N, T_C) and electric (polarization) transitions is summarized in Table 1.

Table 1 HP/HT synthesis and magnetoelectric evidences in MF materials with perovskite-based structure.

Material	Synthesis conditions	Space Group	MagnetoElectric properties	Notes

$BiMnO_3$	P: 4 GPa T:1273 K	? (Belik, Iikubo, *et al.*, 2006; Belik, 2012; Montanari, Righi, *et al.*, 2005; Montanari, Calestani, *et al.*, 2005; Chou *et al.*, 2009; Goian *et al.*, 2012)	T_N= 100 K	Still controversial!! Centro/non-centro-symmetric?
$BiGaO_3$	P: 6 GPa T: 1473 K	*Pcca* (Belik, Rusakov, *et al.*, 2012)	P > 100μC/cm^2	Calculated P for $BiGa_{1-x}M_xO_3$, M=Cr, Mn, Fe (S.G.: *R3c*)
$YMnO_3$	P: 5.5 GPa T: 1273 K	*P2$_1$nb* (Wood *et al.*, 1973)	T_N= 42 K P= 0.22 μC/cm^2	Increase of dielectric constant @ T_N
$ErMnO_3$	P: 3.5 GPa T: 1373 K	*Pbnm* (Ye *et al.*, 2007)	T_N= 42 K	Sudden increase of dielectric constant @ T_N
$ScMnO_3$	P: 12.5 GPa T: 1373 K	*P2$_1$/n* (Chen *et al.*, 2013)	T_N= 51 K	Not (yet) direct evidence of M-E coupling
$PbVO_3$	P: 5 GPa T: 1023 K	*Pnma* (Shpanchenko *et al.*, 2004)	P= 100 μC/cm^2 (Varga *et al.*, 2009)	VO_5 pyramids
$PbMnO_3$	P: 5 GPa T: 1023 K	*P4/mmm* (Oka *et al.*, 2009)	T_N= 20 K	Centrosymmetric structure, non FE
$FeTiO_3$	P: 18 GPa, T: 1473 K	*R3c* (Varga *et al.*, 2009)	T_N= 110 K	Evidence of M-E coupling @ T_N
$ScCrO_3$ $InCrO_3$	P: 6 GPa T: 1500 K	*Pnma* (Belik, Matsushita, *et al.*, 2012)	T_N= 73 K (SCO) T_N= 93 K (ICO)	Anomaly in dielectric constant @ both T_N
$MnTiO_3$	P: 7 GPa T: 973 K	*R3c* (Aimi *et al.*, 2011)	T_N= 25 K	Anomaly in dielectric constant @ T_N
$MnSnO_3$	P: 7 GPa T:1073 K	*R3c* (Aimi *et al.*, 2011)	T_N= 50 K	Anomaly in dielectric constant @ T_N
$PbNiO_3$	P: 3 GPa T: 1073 K	*R3c* (Inaguma *et al.*, 2011)	T_N= 205 K	$LiNbO_3$-like acentric structure
Bi_2NiMnO_6	P: 6 GPa, T: 1073 K	*C2* (Shimakawa *et al.*, 2011)	T_C= 485 K P= 20 μC/cm^2	Evidence of M-E coupling

Bi_2FeMnO_6	P: 6 GPa T: 1373 K	*Pnam* (Delmonte *et al.*, 2013)	T_N= 288 K	Reversal magnetization Evidence of M-E coupling
In_2NiMnO_6	P: 6 GPa T: 1600 K	*P2₁/n* (Yi *et al.*, 2013)	T_N= 26 K	Complex magnetic behavior No evidence of M-E coupling
Y_2FeMnO_6	P: 6 GPa T: 1573 K	*Pnma* (Liu *et al.*, 2014)	T_N= 328 K	Evidence of M-E coupling dielectric anomaly @ T_N
Y_2CrMnO_6	P: 6 GPa T: 1573 K	*Pnma* (Liu *et al.*, 2014)	T_N= 74 K	Evidence of M-E coupling dielectric anomaly @ T_N
Mn_2FeSbO_6	P: 3 GPa T: 1273 K	*P2₁/n* (Mathieu *et al.*, 2013)	T_N= 60 K	Possible M-E coupling by theoretical calculation
$CaMnTi_2O_6$	P: 7 GPa T: 1400 K	*P4₂mc* (Aimi *et al.*, 2014)	T_N= K P= 24 μC/cm^2	A-site ordering
Pb_2FeNdO_6	P: 6 GPa T: 1500 K	*P4₂mc* (Raevski *et al.*, 2013)	T_N= 150 K P < 380 K	ME coupling negligibly small (Levstik *et al.*, 2008)
$CaMn_7O_{12}$	P: 8 GPa T: 1273 K	*R3* (Bochu *et al.*, 1974)	T_C=90 K P= 2870 μC/cm^2 (Zhang, Dong, *et al.*, 2011)	Can be synthesized @ AP
$BiMn_7O_{12}$	P: 4 GPa T: 1273 K	*Im* (Mezzadri *et al.*, 2009)	T_N=22 K T_N=55 K	Evidence of M-E coupling (Gauzzi *et al.*, 2013)
$PbMn_7O_{12}$	P: 7.5 GPa T: 1273K	*R*-3 (Locherer *et al.*, 2012)	T_N= 68 K	Evidence of M-E coupling
$K_xFe^{2+}{}_xFe^{3+}{}_{1-x}F_3$	P: 1.3 Kbar T: 1053 K	*Pba2* (Mezzadri *et al.*, 2008)	T_N= 118 K	Complete MF Hydrothermal synthesis

Due to unavoidable limitations of the HP/HT syntheses, such as the scarce amount of obtainable material, alternative methods have been developed to mimic the effect of the external pressure: thin film epitaxial stabilization and chemical substitutions.

2.5. Beyond HP/HT synthesis of MF materials: thin film epitaxial stabilization

This approach, desirable for device fabrication, implies the deposition of the single phase (i.e., non heterostructures formed by a multilayers architecture) in form of a thin film on strained substrates. Interesting results have been achieved for several (potential) magneto-electric MF material as a viable alternative to HP/HT synthesis to get Bi-based perovskites, such as $BiMnO_3$ (dos Santos *et al.*, 2004; Sharan *et al.*, 2004; Eerenstein *et al.*, 2005), $BiAlO_3$ and $BiGaO_3$ (Belik, Wuernisha, *et al.*, 2006) on different substrates.

Analogously, fully epitaxial thin films of $PbVO_3$ were deposited by pulsed laser deposition on a number of single-crystal substrates including $NdGaO_3$ (100) (Kumar *et al.*, 2007) and $LaAlO_3$ (001) (Oh *et al.*, 2014). $PbVO_3$ has been proposed as a good candidate to be a magnetoelectric MF, having an antiferromagnetic ordering ($T_N \approx 200$ K) and a ferroelectric polarization as large as 152 $\mu C/cm^2$.

Concerning the double perovskite structure, the tendency is toward multiferroic heterostructures, that is the combination of layers with different functionalities, by using sophisticated deposition techniques enabling the precise control of the interfaces, as detailed in several topical review papers (Shpanchenko *et al.*, 2004; Ramesh & Spaldin, 2007; Martin *et al.*, 2008; Vaz, 2012).

To the best of our knowledge, no MF properties have been reported for the quadruple-perovskites thin film, although for $NdMn_7O_{12}$, that can be synthesized as bulk at 8 GPa and 1000 °C, 10-nm-thick metastable thin film has been successfully grown on $Nd_{(1-x)}MnO_3$ substrate by pulsed laser method or by injection MOCVD (Bosak *et al.*, 2000; Prellier *et al.*, 2001; Gorbenko *et al.*, 2002) and the isostructural $CaCu_3Ti_4O_{12}$ can be grown onto Pt/Ti/SiO2/Si substrates using pulsed-laser (Fang & Shen, 2003).

2.6. Beyond HP/HT synthesis of MF materials: "chemical" pressure

This approach exploits the well-known effect of the chemical substitution of atoms with different size, simulating the application of external pressure (see: ((Moritomo *et al.*, 1997) for a comparison between chemical (internal) pressure and mechanical (external) pressure on perovskite manganites).

To mention a relevant (but not comprehensive) example, Catalan *et al.* reported the ambient pressure synthesis of bulk Ca-doped $BiFeO_3$ ceramics, for which T_N increases with the Ca concentration (0.66 K per 1% Ca molar). The smaller ionic size of Ca compared to Bi results in a contraction of the lattice, simulating the external pressure at a rate of 1% Ca=0.3 GPa. Thus, hydrostatic pressure increases the magnetic transition temperature of $BiFeO_3$ of 2.2 K/GPa and the interesting conclusion is that that pressure, either chemical or mechanical, may be used to enhance the magnetoelectric coupling in MF materials(Catalan *et al.*, 2009).

The same principle can be applied to thin films; Izquierdo *et al* (Izquierdo *et al.*, 2014) combined the epitaxial strain and the chemical pressure to modify the magnetic response of Al-doped $TbMnO_3$ films grown under compressive/tensile strain using (001)-oriented $SrTiO_3$ and MgO substrates by RF-

sputtering. The chemical pressure generated by Al doping together with the substrate-induced strain modify the subtle competition between magnetic interactions in the system (the films show weak ferromagnetic phase at coexisting with the expected "bulk" antiferromagnetic phase), providing an additional degree of freedom to control the magnetic ordering, for example by varying the film thickness and/or using other substrates.

2.7. Examples of the HP role in the measurements

Besides the HP/HT synthesis, the application of external pressure to thermodynamically stable compounds often helps in the characterization of the MF properties. The comparison between DC-magnetic susceptibility vs. *T* and *H* for the double perovskite Sr_2FeMoO_6 synthesized at ambient pressure and at 2 GPa, evidences an improved cationic ordering and displays a higher saturation magnetization and a sharper ferromagnetic transition at T_C as high as 430 K (Retuerto *et al.*, 2009).

Other examples regard the enhancements in the polarization and magnetic properties in $BiFeO_3$ ceramic prepared by HP/HT synthesis (Su *et al.*, 2007), the improved multiferroic properties in bulk RMn_2O_5 (*R*=Tb, Dy, Ho) (dela Cruz *et al.*, 2007) or Ru-doped $BiFeO_3$ thin films (Feng *et al.*, 2010), or other phenomena such as the HP-induced polarization reversal in multiferroic YMn_2O_5 (Chaudhury, dela Cruz, *et al.*, 2008), the HP-induced spin-liquid phase of bulk $YMnO_3$ (Kozlenko *et al.*, 2008) or the HP-induced increase in the improve microwave absorption properties of bulk $BiFeO_3$ (Wen *et al.*, 2010).

3. *In situ* investigations of MF materials at HP

Pressure is an ideal tool to manipulate the electronic and magnetic structure and the atomic arrangement of a material (Hemley & Ashcroft, 1998; Hemley *et al.*, 2009; Schilling, 2000; Struzhkin *et al.*, 2000). Although some HP phases can be quenched to ambient conditions and be recovered for detailed experimental characterization (as reviewed in the section 2 of this article), the majority of pressure induced structural, electronic and magnetic phase transitions are reversible. Therefore, it is paramount to investigate the high pressure behaviour of materials *in situ*. The advances in HP technology over the past fifty years at large scale facilities (e.g. synchrotron radiation facilities and neutron sources) and in the laboratory (Bassett, 2009; Liebermann, 2011), have provided us with a large number of experimental tools to investigate the response of materials *in situ* at high pressure and variable temperature.

3.1. Multiferroic materials with perovskite structure

The vast majority of investigations at high pressure have been conducted on compounds with perovskite-type structure or variations hereof (we stressed its pivotal role in the synthesis of MF materials in the previous section). The geometrical features of the perovskite structures can be manipulated by the application of high pressure; since there is a direct link between the atomic

structure and the magneto electric properties, dramatic changes in the multiferroic behavior can be expected at high pressure.

3.1.1. $BiFeO_3$ a prototype multiferroic material

As already mentioned, $BiFeO_3$ is the prototype MF material with perovskite structure that is showing magnetic and ferroelectric behavior with a strong polarization at T=300 K (Teague *et al.*, 1970; Wang *et al.*, 2003; Catalan *et al.*, 2009; Shvartsman *et al.*, 2007; Lebeugle *et al.*, 2007). Over the past years, $BiFeO_3$ has developed into the most popular model system for experimental and theoretical investigations of multiferroic materials at high pressure. The pressure induced changes in $BiFeO_3$ have been experimentally investigated by Raman spectroscopy (Haumont *et al.*, 2006; Yang *et al.*, 2009; Guennou, Bouvier, Chen, *et al.*, 2011), X-ray powder and single crystal diffraction (Belik *et al.*, 2009a; Haumont *et al.*, 2009; Zhu *et al.*, 2010; Zhang *et al.*, 2013; Guennou, Bouvier, Chen, *et al.*, 2011; Guennou, Bouvier, Haumont, *et al.*, 2011; Mishra *et al.*, 2013), neutron powder diffraction (Kozlenko *et al.*, 2011), optical absorption spectroscopy (Gomez-Salces *et al.*, 2012; Gavriliuk *et al.*, 2008), resistivity measurements (Gavriliuk *et al.*, 2008), Nuclear Forward Scattering (NFS) (Gavriliuk *et al.*, 2008; Gavriliuk *et al.*, 2005) and X-ray Emission Spectroscopy (XES) (Gavriliuk *et al.*, 2008) as well as theoretically through first principles calculations (Gonzalez-Vazquez & Iniguez, 2009; Shang *et al.*, 2009; Feng *et al.*, 2013; Qiang *et al.*, 2013). $BiFeO_3$ displays a complex response to high pressure with a number of structural phase transitions in the pressure range up to 60 GPa (Belik *et al.*, 2009a; Haumont *et al.*, 2009; Zhu *et al.*, 2010; Guennou, Bouvier, Chen, *et al.*, 2011; Kozlenko *et al.*, 2011; Mishra *et al.*, 2013). However, the number of phase transitions, the atomic structure and the symmetry of the HP phases remain controversial. Gavriliuk *et al,* (Gavriliuk *et al.*, 2008) observed no structural phase transition in the pressure range to 60 GPa. Zhu *et al,* (Zhu *et al.*, 2010) proposed a structural phase transition at about 10 GPa, however based on the low resolution diffraction data no unit cell or space group were proposed for the HP phase. Kozlenko *et al,* (Kozlenko *et al.*, 2011) proposed a phase transition at 3 GPa from *R3c* to an orthorhombic phase with the space group *Pbam* from neutron powder diffraction data. Haumont *et al.* (Haumont *et al.*, 2009) reported two phase transitions at P≈3.5 GPa and 10 GPa and proposed a *R3c→C2/m→Pnma* phase sequence. Mishra *et al* (Mishra et al., 2013) observed two phase transitions at P=4.1 and 11 GPa with a proposed phase sequence of $R3c \rightarrow P222_1 \rightarrow Pnma$. Two phase transitions at P=4 and 7 GPa on compression have been observed by Belik *et al.* (Belik *et al.*, 2009a) and an additional phase transition on decompression, stable in a narrow pressure range between 3.4 to 4.9 GPa. The resulting phase transition sequence is the following *R3c→Pbam→Ibam→Cmmm* proposing three different low pressure phases with orthorhombic symmetry (Belik *et al.*, 2009a). Guennou *et al* (Guennou, Bouvier, Chen, *et al.*, 2011) conducted X-ray single crystal diffraction experiments up pressures of to 60 GPa, reporting six structural phase transitions at P=4, 5, 7, 11, and 38 GPa, respectively. The proposed phase sequence is *R3c→O-I→O-II→O-III→Pnma→Pnmm→Cmcm.* The limited reciprocal space coverage of the HP

single crystal diffraction data did not allow an unambiguous identification of the structure models or space groups of the low pressure orthorhombic O-I, O-II and O-III phase. Gavriliuk *et al.* (Gavriliuk *et al.*, 2008) conducted XES, NFS and resistivity measurements up to P=55 GPa. The results from the XES and NSF measurements suggest a spin crossover from high spin (HS) to low spin (LS) of Fe^{3+} in the region between 45 to 55 GPa and a reversible insulator to metal Mott transition above 55 GPa. The authors suggest that the insulator to metal transition is driven by the HS-LS transition of the Fe^{3+}, by changing the effective correlation energy below the threshold for the insulator to metal transition. First principle calculations (Gonzalez-Vazquez & Iniguez, 2009) confirm the HS-LS transition and the very complex structural-electronic-magnetic interplay during the transformations observed experimentally by Gavriliuk *et al.* (Gavriliuk *et al.*, 2008). Furthermore, an additional transition to a metallic non-spin phase at pressures above 70 GPa was proposed (Gonzalez-Vazquez & Iniguez, 2009).

Haumont *et al.* (Haumont *et al.*, 2006) and Guennou *et al.* (Guennou, Bouvier, Haumont, *et al.*, 2011) find in their experimental results that stress and non-hydrostatic pressure conditions can not only lead to a significant shift in transition pressures, but also to stabilization of new phases. Guennou *et al.* (Guennou, Bouvier, Haumont, *et al.*, 2011) identified a new monoclinic phase at P≈8 GPa under non-hydrostatic pressure conditions. In order to further understand the structural richness of $BiFeO_3$ Dieguez *et al.* conducted a systematic investigation of the stability of potential $BiFeO_3$ phases using first principle methods. The results show a large number of metastable phases, which might explain the observation of large number of HP and different phases reported (Dieguez *et al.*, 2011).

The influence of impurities and defects on the HP behavior of $BiFeO_3$ has been investigated by Chen *et al.* (Chen *et al.*, 2012). Ba-doped $BiFeO_3$ ($Bi_{1-x}Ba_xFeO_{3-0.5x}$) has been compressed to 18.7 GPa and significant changes in the compression behavior, the phase transition pressure and the phase sequence have been reported compared to pure $BiFeO_3$, observing a similar phase sequence, *R3c→C2/m→Pnma*, as Haumont *et al.* (Haumont et al., 2009).

3.1.2. Rare Earth Manganite, $RMnO_3$ (R= Gd, Tb, Dy, Ho, La, Y, Lu, Tm, Sc, Dy)

Rare-earth manganites show a complex correlation between structural, electric and magnetic properties, which can be manipulated through by exchange of the rare-earth ions. As of now, MF properties have only been reported for a subset of the rare-earth manganites and only few have been characterized at high pressure.

The HP behavior of $TbMnO_3$ was investigated by X-ray diffraction and X-ray absorption spectroscopy (XAS). A continuous decrease in the Jahn-Teller distortion well as a decrease in the tilt-angles of the MnO_6 octahedra was observed with increasing pressure. XAS measurements show a shift of the Mn *K*-edge to higher energies while the pre-edge feature shifts to lower energies with

pressure. Chen *et al* (Chen *et al.*, 2009) interpret this as a broadening of the electronic bandwidth of the $e_g\uparrow$ orbitals in $TbMnO_3$.

Chou *et al.* investigated the response of the local and electronic structure of $DyMnO_3$ to pressure by Raman spectroscopy, XAS and XES measurements. A decrease of the Jahn-Teller distortion of the MnO_6 octahedra in combination with gradual breakdown of the high spin magnetism is detected at P=32 GPa suggesting a potential HS to LS transition above 32 GPa. No structural phase transitions were detected in the investigated pressure range (Chou *et al.*, 2013).

$GdMnO_3$ has been investigated to pressures of 63 GPa by X-ray diffraction (Lin, Zhang, *et al.*, 2012) and to pressures of 53 GPa by X-ray diffraction and Raman spectroscopy measurements (Oliveira et al., 2012). A reversible first-order phase transition has been observed at P≈50 GPa. Base on the diffraction data Lin *et al* (Lin, Zhang, *et al.*, 2012) interpret the transition as an isostructural orthorhombic to orthorhombic transition. From X-ray diffraction and Raman spectroscopy measurements, Oliveira *et al.* (Oliveira et al., 2012) conclude that it is an insulator to metal transition with a change in symmetry from orthorhombic (*Pnma*) to cubic ($P2_13$).

Kozlenko *et al.* investigated the crystal and magnetic structure of hexagonal $YMnO_3$ (Kozlenko *et al.*, 2008; Kozlenko, Kichanov, *et al.*, 2010) and $LuMnO_3$ (Kozlenko, Kichanov, *et al.*, 2010) by simultaneous high pressure and low temperature neutron powder diffraction. The reduction of the in-plane splitting of the Mn-O bond with pressure has been identified as the potential reason for the observed enhanced spin fluctuations with increasing pressure in both compounds. Kozlenko *et al* (Kozlenko, Kichanov, *et al.*, 2010) conclude that the reduction in the Mn-O bond splitting with pressure implies a decrease in the magneto-elastic coupling strength.

Wang *et al.* (Wang *et al.*, 2010) investigated the high pressure behavior of hexagonal $TmMnO_3$ by X-ray powder diffraction experiments up to P=28.6 GPa. A hexagonal to orthorhombic transition was detected at 10.2 GPa.

$ErMnO_3$, crystallizes in the hexagonal space group $P6_3cm$. At P≈20 GPa the structure undergoes a irreversible first order transition to orthorhombic phase with space group *Pbnm* (Lin, Liu, *et al.*, 2012).

The structural stability of $RMnO_3$ (R=Y, Ho, Lu) at HP has been investigated by X-ray diffraction, synchrotron IR spectroscopy, XAS and *ab-initio* quantum mechanical calculations (Gao *et al.*, 2011). $YMnO_3$, $HoMnO_3$ and $LuMnO_3$ remain hexagonal up to P≈20 GPa. Above 20 GPa the onset of a structural phase transition to orthorhombic symmetry has been observed. The IR measurements show that the oxygen atoms are the most sensitive to pressure, with vibration modes mainly confined on the *ab*-plane (Gao *et al.*, 2011).

3.1.3. $BiMnO_3$

A lot of work has been done on $BiMnO_3$ as far as the HP characterization concerns, too. The unit cell changes in $BiMnO_3$ with pressure were investigated by energy dispersive diffraction in the pressure range from ambient pressure to 27 GPa (Chi *et al.*, 2008). The measurements showed no evidence for a structural phase transition. The DC magnetization was measured at pressures up to 1.6 GPa by Chou *et al.* (Chou *et al.*, 2008). The T_C=100 K at ambient pressure and the signal associated with ferromagnetic behavior is decreasing with pressure and disappearing at P=1.31 GPa. A second peak in the susceptibility has been detected at 1.17 GPa and has been interpreted as a potential onset of a structural phase transition (Chou *et al.*, 2008). These measurements were followed up by magnetic hysteresis and AC susceptibility to high pressure and low temperature (Chou *et al.*, 2009). Three magnetic phase transition have been detected at ambient pressure and 98 K, 0.87 GPa and 93 K, and 72.5 K and 0.87 GPa. The ambient pressure and 100 K transition can be characterized as a long-range ferromagnetic transition, being suppressed at high pressure and therefore not observed. The transition is accompanied by an anomaly below 90 K, which is attributed to a spin-glass behavior. The second transition is attributed to a long-range soft ferromagnetic to a canted state, while the third is characterized as a canted antiferromagnetic transition. Chou *et al.* (Chou *et al.*, 2009) suggest that both the canted ferromagnetic and the canted antiferromagnetic transition are caused by the structural phase change from *C2/c* to $P2_1/c$ which has been observed by Belik *et al.* (Belik *et al.*, 2009b). This demonstrates the complex interplay between lattice distortion and spin configuration in multiferroic material. Belik *et al* (Belik *et al.*, 2009b) reported two structural phase transitions at 0.9 GPa and at 8 GPa. The phase transition at 0.9 GPa has been characterized as a $C2/c \rightarrow P2_1/c$ transition, however, the structure of the new monoclinic HP phase could not be refined. At 8 GPa $BiMnO_3$ transforms to the non-ferroelectric $GdFeO_3$-type structure with *Pnma* symmetry. The $GdFeO_3$-type structure exhibits a strong Jahn-Teller distortion of the MnO_6 octahedra and long range $d(3y^2\text{-}r^2)$ e_g orbital ordering (Belik *et al.*, 2009b). Kozlenko *et al.* (Kozlenko, Belik, *et al.*, 2010) conducted high pressure neutron powder diffraction measurements on $BiMnO_3$ to 10 GPa and simultaneous high pressure and low temperature neutron diffraction experiments in the pressure region up to 2 GPa. The ferromagnetic ground state is suppressed at moderate pressures of 1 GPa at 90 K with a transition to an antiferromagnetic state with a propagation vector of k= (½ ½ ½) at 90 K. This change in magnetic state is accompanied by a monoclinic to monoclinic structural phase transition. The FM and AFM states are coexisting below pressures of 2 GPa (Kozlenko, Belik, *et al.*, 2010). Mei *et al* (Mei *et al.*, 2010) explored the structural and elastic properties of $BiMnO_3$ by first principles calculations using, LDA+U and GGA+U formalisms. The energies for the monoclinic (*C2/c*) phases and the orthorhombic (*Pnma*) phase were calculated as a function of pressure. The calculations, in contrast to the experimental results by Belik *et al.* (Belik *et al.*, 2009b), show that the orthorhombic phase is the stable structure at ambient pressure. A monoclinic to monoclinic phase transition is predicted at P=10 GPa induced by a magnetic to volume instability in $BiMnO_3$. Recently, Kozlenko *et al.* (Kozlenko *et al.*, 2014) determined the phase diagram of $BiMnO_3$ to pressure of 50 GPa and investigated the phase

relationships as a function of temperature and pressure in the range of T=300-900 K from ambient pressure to 4 GPa using X-ray diffraction and Raman spectroscopy. Two new high pressure phases with *C2/m* symmetry, but distinctly different structural parameters, have been identified at moderate pressures temperatures, as it had been previously suggested based on the results from first principles calculations (Mei *et al.*, 2010). The transition to the high temperature orthorhombic phase is suppressed to room temperature at 8 GPa, consistent with reports from Belik *et al.* (Belik *et al.*, 2009b). Above 20 GPa $BiMnO_3$ undergoes a phase transition from the *Pnma→Imma*, leading to a suppression of the long range $d(3y^2-r^2)$ e_g orbital ordering.

3.1.4. Cobaltite perovskites, ACoO3

Ming *et al.* studied the structural stability the magnetic and electronic properties of $BiCoO_3$ by first-principles calculations up to 30 GPa (Ming *et al.*, 2009). The calculations reproduce the C-type antiferromagnetic structure as a ground state. At P=4 GPa a first-order isostructural transition is observed, accompanied by a HS-LS spin-crossover of Co^{3+} and with an insulator to semimetal transition. The authors conclude that in contrast to the excepted models for insulator to metal transitions, the spin-crossover effect at HP is the driving mechanism in the transition in $BiCoO_3$. Oka *et al.* investigated the HP behavior of $BiCoO_3$ by synchrotron and neutron powder diffraction and X-ray emission spectroscopy (Oka *et al.*, 2010). A first-order tetragonal, $PbTiO_3$-type, to orthorhombic, $GdFeO_3$-type, phase transition has been observed at P=3 GPa, in contrast to the proposed isostructural tetragonal to tetragonal transition by Ming *et al.* (Ming *et al.*, 2009). The transition is accompanied by a HS to LS transition with an intermediate spin state present at the transition as determined from XES data.

3.1.5. $PbNiO_3$

As already mentioned, synthesized two polymorphs of $PbNiO_3$ can be obtained by HP/HT synthesis, with perovskite-type and a $LiNbO_3$-type structure (Inaguma *et al.*, 2011). The unit cell volume for $LiNbO_3$ and the perovskite-type polymorph suggest that perovskite type might be a high pressure polymorph of the $LiNbO_3$ type $PbNiO_3$. The $LiNbO_3$-type $PbNiO_3$ undergoes a pressure induced phase transition to a $GdFeO_3$-type structure, space group *Pnma*, at about 3 GPa. In both polytypes the magnetic interaction of the Ni^{2+} is antiferromagnetic dominated by the Ni-O distances rather than the Ni-O-Ni angles. XPS measurements suggest Pb^{4+}, Ni^{2+} valence states for both polymorphs. Hao *et al* (Hao *et al.*, 2014) performed first principles calculation using the GGA, GGA+U and Heyd-Scuseria-Ernzerhof (HSE) approaches. The observed pressure induced phase transition (Inaguma *et al.*, 2011) from *R3c* to *Pnma* is reproduced although at a slightly higher transition pressure of about 5 GPa. The orthorhombic HP phase shows a considerable anisotropy of the nearest neighbors exchange couplings.

3.1.6. $BiNiO_3$

Azuma *et al* investigated the high pressure behavior of $BiNiO_3$ by neutron diffraction experiments in combination with electronic–state calculations using first principles with the LDA+U approach (Azuma *et al.*, 2007). At 4 GPa a pressure induced phase transition from the *P-1* to $GdFeO_3$-type structure, with the space group *Pbnm* has been observed. Calculation of the changes in the electronic structure with pressure suggest that the pressure induced phase transition is an insulator to metal transition, which occurs via a simultaneous melting of Bi-charge disproportion and charge transfer from Ni to Bi.

3.2. MF materials with non-perovskite structure

Recently, the search for MF has expanded to materials that crystallize in other structure types than the perovskite-type structure and to chemical compositions beyond "simple" oxides such as transition metal oxihalides, transition metal orthotellurides and transition metal chalcogenides. These materials are relatively new and none of them require HP/HT synthesis, but a few have been investigated in situ at high pressure.

3.2.1. $MnWO_4$

$MnWO_4$ crystallizes in the wolframite structure (SG: *P2/c* with *Z*=2) and is ferroelectric showing incommensurate helical spin-density wave (Taniguchi *et al.*, 2006). The pressure dependence of the dielectric properties up to pressure of 1.8 GPa has been measured by Chaudhury *et al* (Chaudhury, Yen, *et al.*, 2008). Pressure suppresses the ferroelectric polarization in the ferroelectric phase suggesting that the stability of the ferroelectric phase is reduced by increasing the pressure. The structural changes in $MnWO_4$ with pressure have been investigated to 8 GPa and the compression mechanism has been derived from X-ray diffraction data (Macavei & Schulz, 1993). *Ab initio* quantum mechanical calculations (Lopez-Moreno *et al.*, 2009) confirm the experimentally determined compression behavior of $MnWO_4$ (Macavei & Schulz, 1993) and suggest no structural phase transition in the pressure range from ambient pressure to 31 GPa. The calculated magnetic moment decreases with pressure confirming the results from Chaundry *et al.* (Chaudhury, Yen, *et al.*, 2008). Recently, Dai *et al.* (Dai *et al.*, 2013) determined the pressure and temperature behavior of $MnWO_4$ by Raman scattering. Changes in the Raman spectrum at P=17.7 GPa at ambient temperature were interpreted as a monoclinic to triclinic structural phase transition.

3.2.2. $Ba_3TaFe_3Si_2O_{14}$

$Ba_3TaFe_3Si_2O_{14}$, a member of the langasite family, crystallizes in the trigonal space group *P321* with one formula unit per unit cell (Lyubutin *et al.*, 2010). Gavriliuk *et al.* (Gavriliuk *et al.*, 2013) investigated the pressure and temperature behavior of $Ba_3TaFe_3Si_2O_{14}$ up to P=38 GPa and down to T=20 K by Nuclear Forward Scattering (NFS) and Raman spectroscopy. At P=19.5 GPa a first-order pressure induced phase transition has been observed. The transition is accompanied by a magnetic

change with a fourfold increase in Néel temperature T_N from 27.2 K to 120 K (Gavriliuk *et al.*, 2013). The authors suggest a strong super-exchange interaction cause by changes in the bond angles as explanation for the strong pressure dependence of the Néel temperature.

3.2.3. $FeTe_2O_5Br$

The relatively new class of multiferroic materials is the group of transition metal oxohalides (Choi *et al.*, 2014). The incorporation of lone-pair cations and halides provides exchange pathways, which lead to magnetic frustration in these materials (Bos, Colin, *et al.*, 2008; Lawes *et al.*, 2003; Pregelj *et al.*, 2009; Zaharko *et al.*, 2006; Zhang, Kremer, *et al.*, 2011). $FeTe_2O_5Br$ is not only a magnetically but geometrically frustrated system as well. The HP behavior of $FeTe_2O_5Br$ has been investigated by Raman and optical absorption spectroscopy up to P=7 GPa (Gnezdilov *et al.*, 2011; Choi *et al.*, 2014). Both, the Raman spectroscopy and the optical absorption measurements show evidence of a structural phase transition between 2.12 and 3.04 GPa. The HP phase exhibits an increased uniformity in the bonding forces, compared to the highly anisotropic ambient pressure phase. The anisotropic Fe(*3d*) orbitals start to overlap with the Br(*4s*) and O(*2p*) orbitals, changing from a two dimensional electronic structure at ambient conditions to a three-dimensional electronic structure at HP.

3.2.4. $HgCr_2S_4$

$HgCr_2S_4$ belongs to the large group of thiospinels and crystallizes in the space group *Fd-3m* at ambient conditions (Hemberger *et al.*, 2006; Weber *et al.*, 2006). The compound exhibits both ferromagnetic and ferroelectric properties together with a pronounced magneto-capacitive coupling with a bond-frustrated magnetic ground state (Hemberger *et al.*, 2006). The ferroelectricity in the chromium thiospinel family is caused by a dynamic disorder of the Cr^{3+} ions, which induces an off-center shift of the Cr^{3+} ions and a change in symmetry of the local structure to the polar space group *F4-3m* (Gnezdilov *et al.*, 2011). The HP behaviour of $HgCr_2S_4$ has been investigated by a combination of X-ray powder diffraction measurements and band structure calculations based on the Linear-Muffin-Tin Orbital method (Efthimiopoulos *et al.*, 2013). Two structural phase transition have been observed at P=20 and 26 GPa, respectively. At 20 GPa $HgCr_2S_4$ undergoes a reversible first-order cubic to tetragonal transition from the space group Fd-3m to $I4_1/amd$. The phase transition has an insulator to metal character and is accompanied by a change in the magnetic to an antiferromagnetic state and the loss of ferroelectric properties. A second-order phase transition to an orthorhombic structure, most likely with *Imma* space group, has been reported at 26 GPa. Based on the diffraction data Efthimiopoulos *et al.*, proposed a third phase transition at P≈37 GPa (Efthimiopoulos *et al.*, 2013). However, strong peak overlap between gasket, the orthorhombic phase and the potentially new HP phase prevented the detailed characterization of this phase.

4. Conclusions

The search for intrinsic magnetoelectric MF, compounds with co-existence and coupling of magnetic and electric order in the same phase, remains challenging despite large effort in the scientific community. Most currently known intrinsic MF only exhibit very small magnetoelectric coupling at low temperature. However, for technological viable applications they are required to show large magnetoelectric effects at ambient conditions. Therefore, it is paramount to broaden the search for MF materials to new classes of materials beyond perovskite-type oxides and to new synthesis techniques.

The HP/HT synthesis has proven to be a powerful tool for the stabilization of metastable HP phases with multiferroic properties. The majority of these new phases crystallize in the perovskite or perovskite-related structure. The investigation of MF materials *in situ* at high pressure and temperature has provided valuable insight into the coupling between electric, magnetic and structural properties. Especially experiments at non-hydrostatic conditions can in the future led to the identification of possible high pressure MF phases that could be stabilized at ambient conditions as highly strained thin films.

Despite the promising results obtained so far, the currently employed high pressure techniques have intrinsic shortcomings, such as comparatively long synthesis times, relatively small sample sizes and vast parameter space in pressure, temperature and composition that needs to be explored. However, these limitations can be overcome by a concerted effort between theoretical (e.g. structure prediction), which could potentially allow targeted synthesis at pressure and temperature, and development of new HP synthesis and characterization approaches.

The availability of such new and more sophisticated synthesis and characterization techniques, combined with theoretical approaches, could lead to an enormous increase in our fundamental understanding of multiferroic materials and potentially a to widespread technological applications.

Acknowledgements EG thanks Francesco Mezzadri, Gianluca Calestani and Davide Delmonte for material synthesis and fruitful discussions. LE acknowledges the support by the National Science Foundation through grant GEO-11-07155. Melissa Sims is acknowledged for her help with editing of the article and the references.

References

Aimi, A., Katsumata, T., Mori, D., Fu, D., Itoh, M., Kyomen, T., Hiraki, K.-i., Takahashi, T. & Inaguma, Y. (2011). *Inorganic Chemistry* **50**, 6392-6398.

Aimi, A., Mori, D., Hiraki, K., Takahashi, T., Shan, Y. J., Shirako, Y., Zhou, J. S. & Inaguma, Y. (2014). *Chemistry of Materials* **26**, 2601-2608.

Azuma, M., Kanda, H., Belik, A. A., Shimakawa, Y. & Takano, M. (2007). *Journal of Magnetism and Magnetic Materials* **310**, 1177-1179.

Badding, J. V., Parker, L. J. & Nesting, D. C. (1995). *Journal of Solid State Chemistry* **117**, 229-235.

Bassett, W. A. (2009). *High Pressure Research* **29**, CP5-186.

Belik, A. A. (2012). *Journal of Solid State Chemistry* **195**, 32-40.

Belik, A. A., Azuma, M., Saito, T., Shimakawa, Y. & Takano, M. (2005). *Chemistry of Materials* **17**, 269-273.

Belik, A. A., Iikubo, S., Kodama, K., Igawa, N., Shamoto, S., Maie, M., Nagai, T., Matsui, Y., Stefanovich, S. Y., Lazoryak, B. I. & Takayama-Muromachi, E. (2006). *Journal of the American Chemical Society* **128**, 706-707.

Belik, A. A., Matsushita, Y., Tanaka, M. & Takayama-Muromachi, E. (2012). *Chemistry of Materials* **24**, 2197-2203.
Belik, A. A., Rusakov, D. A., Furubayashi, T. & Takayama-Muromachi, E. (2012). *Chemistry of Materials* **24**, 3056-3064.
Belik, A. A., Wuernisha, T., Kamiyama, T., Mori, K., Maie, M., Nagai, T., Matsui, Y. & Takayama-Muromachi, E. (2006). *Chemistry of Materials* **18**, 133-139.
Belik, A. A., Yusa, H., Hirao, N., Ohishi, Y. & Takayama-Muromachi, E. (2009a). *Chemistry of Materials* **21**, 3400-3405.
Belik, A. A., Yusa, H., Hirao, N., Ohishi, Y. & Takayama-Muromachi, E. (2009b). *Inorganic Chemistry* **48**, 1000-1004.
Bibes, M. (2012). *Nature Materials* **11**, 354-357.
Bochu, B., Chenavas, J., Joubert, J. C. & Marezio, M. (1974). *Journal of Solid State Chemistry* **11**, 88-93.
Bos, J. W. G., Colin, C. V. & Palstra, T. T. M. (2008). *Physical Review B* **78**, 7.
Bos, J. W. G., Penny, G. B. S., Rodgers, J. A., Sokolov, D. A., Huxley, A. D. & Attfield, J. P. (2008). *Chemical Communications* 3634-3635.
Bosak, A. A., Gorbenko, O. Y., Kaul, A. R., Graboy, I. E., Dubourdieu, C., Senateur, J. P. & Zandbergen, H. W. (2000). *Journal of Magnetism and Magnetic Materials* **211**, 61-66.
Brazhkin, V. V. (2007). *High Pressure Research* **27**, 333-351.
Catalan, G., Sardar, K., Church, N. S., Scott, J. F., Harrison, R. J. & Redfern, S. A. T. (2009). *Physical Review B* **79**, 4.
Chakrabartty, J. P., Nechache, R., Harnagea, C. & Rosei, F. (2014). *Optics Express* **22**, A80-A89.
Chaudhari, V. A. & Bichile, G. K. (2013). *Smart Materials Research* Article ID 147524.
Chaudhury, R. P., dela Cruz, C. R., Lorenz, B., Sun, Y. Y., Chu, C. W., Park, S. & Cheong, S. W. (2008). *Physical Review B* **77**, 4.
Chaudhury, R. P., Yen, F., dela Cruz, C. R., Lorenz, B., Wang, Y. Q., Sun, Y. Y. & Chu, C. W. (2008). *Physica B* **403**, 1428-1430.
Chen, H. Y., Yu, T., Gao, P., Bai, J. M., Tao, J., Tyson, T. A., Wang, L. P. & Lalancette, R. (2013). *Inorganic Chemistry* **52**, 9692-9697.
Chen, J. M., Chou, T. L., Lee, J. M., Chen, S. A., Chan, T. S., Chen, T. H., Lu, K. T., Chuang, W. T., Sheu, H. S., Chen, S. W., Lin, C. M., Hiraoka, N., Ishii, H., Tsuei, K. D. & Yang, T. J. (2009). *Physical Review B* **79**.
Chen, Z. W., Lee, J. S., Huang, T. & Lin, C. M. (2012). *Solid State Communications* **152**, 1613-1617.
Chi, Z. H., You, S. J., Yang, L. X., Chen, L. C., Jin, C. Q., Wang, X. H., Chen, R. Z., Li, L. T., Li, Y. C., Li, X. D. & Liu, J. (2008). *Journal of Electroceramics* **21**, 863-866.
Choi, K. Y., Choi, I. H., Lemmens, P., van Tol, J. & Berger, H. (2014). *Journal of Physics-Condensed Matter* **26**, 8.
Chou, C. C., Huang, C. L., Mukherjee, S., Chen, Q. Y., Sakurai, H., Belik, A. A., Takayama-Muromachi, E. & Yang, H. D. (2009). *Physical Review B* **80**.
Chou, C. C., Taran, S., Her, J. L., Sun, C. P., Huang, C. L., Sakurai, H., Belik, A. A., Takayama-Muromachi, E. & Yang, H. D. (2008). *Physical Review B* **78**.
Chou, T. L., Lee, J. M., Chen, S. A., Haw, S. C., Huang, E., Lu, K. T., Chen, S. W., Deng, M. J., Ishii, H., Hiraoka, N., Lin, C. M., Tsuei, K. D. & Chen, J. M. (2013). *Journal of the Physical Society of Japan* **82**.
Dai, R. C., Ding, X., Wang, Z. P. & Zhang, Z. M. (2013). *Chemical Physics Letters* **586**, 76-80.
dela Cruz, C. R., Lorenz, B., Sun, Y. Y., Wang, Y., Park, S., Cheong, S. W., Gospodinov, M. M. & Chu, C. W. (2007). *Physical Review B* **76**, 7.
Delmonte, D., Mezzadri, F., Pernechele, C., Calestani, G., Spina, G., Lantieri, M., Solzi, M., Cabassi, R., Bolzoni, F., Migliori, A., Ritter, C. & Gilioli, E. (2013). *Physical Review B* **88**, 11.
Dieguez, O., Gonzalez-Vazquez, O. E., Wojdel, J. C. & Iniguez, J. (2011). *Physical Review B* **83**.
dos Santos, A. F. M., Cheetham, A. K., Tian, W., Pan, X. Q., Jia, Y. F., Murphy, N. J., Lettieri, J. & Schlom, D. G. (2004). *Applied Physics Letters* **84**, 91-93.
Eerenstein, W., Mathur, N. D. & Scott, J. F. (2006). *Nature* **442**, 759-765.
Eerenstein, W., Morrison, F. D., Scott, J. F. & Mathur, N. D. (2005). *Applied Physics Letters* **87**.
Efthimiopoulos, I., Yaresko, A., Tsurkan, V., Deisenhofer, J., Loidl, A., Park, C. & Wang, Y. J. (2013). *Applied Physics Letters* **103**, 5.
Fang, L. & Shen, M. R. (2003). *Thin Solid Films* **440**, 60-65.
Feng, H. J., Hu, X. Y. & Chen, H. J. (2013). *Functional Materials Letters* **6**.
Feng, Y., Man-Oh, L., Li, L. T. & Tie-Jun, Z. (2010). *The Journal of Physical Chemistry C* **114**, 6994-6998.
Fiebig, M. (2005). *Journal of Physics D-Applied Physics* **38**, R123-R152.
Gao, P., Chen, Z., Tyson, T. A., Wu, T., Ahn, K. H., Liu, Z., Tappero, R., Kim, S. B. & Cheong, S. W. (2011). *Physical Review B* **83**, 9.
Gauzzi, A., Rousse, G., Mezzadri, F., Calestani, G. L., Andre, G., Bouree, F., Calicchio, M., Gilioli, E., Cabassi, R., Bolzoni, F., Prodi, A., Bordet, P. & Marezio, M. (2013). *Journal of Applied Physics* **113**.
Gavriliuk, A. G., Lyubutin, I. S., Starchikov, S. S., Mironovich, A. A., Ovchinnikov, S. G., Trojan, I. A., Xiao, Y., Chow, P., Sinogeikin, S. V. & Struzhkin, V. V. (2013). *Applied Physics Letters* **103**.
Gavriliuk, A. G., Struzhkin, V. V., Lyubutin, I. S., Hu, M. Y. & Mao, H. K. (2005). *Jetp Letters* **82**, 224-227.
Gavriliuk, A. G., Struzhkin, V. V., Lyubutin, I. S., Ovchinnikov, S. G., Hu, M. Y. & Chow, P. (2008). *Physical Review B* **77**, 155112.
Gnezdilov, V., Lemmens, P., Pashkevich, Y. G., Payen, C., Choi, K. Y., Hemberger, J., Loidl, A. & Tsurkan, V. (2011). *Physical Review B* **84**.
Goian, V., Kamba, S., Savinov, M., Nuzhnyy, D., Borodavka, F., Vanek, P. & Belik, A. A. (2012). *Journal of Applied Physics* **112**.
Gomez-Salces, S., Aguado, F., Rodriguez, F., Valiente, R., Gonzalez, J., Haumont, R. & Kreisel, J. (2012). *Physical Review B* **85**.
Gonzalez-Vazquez, O. E. & Iniguez, J. (2009). *Physical Review B* **79**.
Gorbenko, O. Y., Samoilenkov, S. V., Graboy, I. E. & Kaul, A. R. (2002). *Chemistry of Materials* **14**, 4026-4043.
Guennou, M., Bouvier, P., Chen, G. S., Dkhil, B., Haumont, R., Garbarino, G. & Kreisel, J. (2011). *Physical Review B* **84**.
Guennou, M., Bouvier, P., Haumont, R., Garbarino, G. & Kreisel, J. (2011). *Phase Transitions* **84**, 474-482.
Haines, J., Leger, J. M. & Bocquillon, G. (2001). *Annual Review of Materials Research* **31**, 1-23.
Hao, X. F., Stroppa, A., Barone, P., Filippetti, A., Franchini, C. & Picozzi, S. (2014). *New Journal of Physics* **16**.
Haumont, R., Bouvier, P., Pashkin, A., Rabia, K., Frank, S., Dkhil, B., Crichton, W. A., Kuntscher, C. A. & Kreisel, J. (2009). *Physical Review B* **79**.
Haumont, R., Kreisel, J. & Bouvier, P. (2006). *Phase Transitions* **79**, 1043-1064.

Hemberger, J., Lunkenheimer, P., Fichtl, R., Weber, S., Tsurkan, V. & Loidl, A. (2006). *Phase Transitions* **79**, 1065-1082.
Hemley, R. J. & Ashcroft, N. W. (1998). *Physics Today* **51**, 26-32.
Hemley, R. J., Crabtree, G. W. & Buchanan, M. V. (2009). *Physics Today* **62**, 32-37.
Hill, N. A. (2000). *Journal of Physical Chemistry B* **104**, 6694-6709.
Hur, N., Park, S., Sharma, P. A., Ahn, J. S., Guha, S. & Cheong, S. W. (2004). *Nature* **429**, 392-395.
Ikeda, N., Ohsumi, H., Ohwada, K., Ishii, K., Inami, T., Kakurai, K., Murakami, Y., Yoshii, K., Mori, S., Horibe, Y. & Kito, H. (2005). *Nature* **436**, 1136-1138.
Inaguma, Y., Tanaka, K., Tsuchiya, T., Mori, D., Katsumata, T., Ohba, T., Hiraki, K., Takahashi, T. & Saitoh, H. (2011). *Journal of the American Chemical Society* **133**, 16920-16929.
Ishiwata, S., Tokunaga, Y., Taguchi, Y. & Tokura, Y. (2011). *Journal of the American Chemical Society* **133**, 13818-13820.
Izquierdo, J., Astudillo, A., Bolanos, G., Arnache, O. & Moran, O. (2014). *Journal of Applied Physics* **115**, 3.
Johnson, R. D., Chapon, L. C., Khalyavin, D. D., Manuel, P., Radaelli, P. G. & Martin, C. (2012). *Physical Review Letters* **108**.
Khomskii, D. (2009). *Physics* **2**, 20.
Khomskii, D. I. (2006). *Journal of Magnetism and Magnetic Materials* **306**, 1-8.
Kimura, T., Goto, T., Shintani, H., Ishizaka, K., Arima, T. & Tokura, Y. (2003). *Nature* **426**, 55-58.
Kozlenko, D. P., Belik, A. A., Belushkin, A. V., Lukin, E. V., Marshall, W. G., Savenko, B. N. & Takayama-Muromachi, E. (2011). *Physical Review B* **84**.
Kozlenko, D. P., Belik, A. A., Kichanov, S. E., Mirebeau, I., Sheptyakov, D. V., Strassle, T., Makarova, O. L., Belushkin, A. V., Savenko, B. N. & Takayama-Muromachi, E. (2010). *Physical Review B* **82**.
Kozlenko, D. P., Dang, N. T., Jabarov, S. H., Belik, A. A., Kichanov, S. E., Lukin, E. V., Lathe, C., Dubrovinsky, L. S., Kazimirov, V. Y., Smirnov, M. B., Savenko, B. N., Mammadov, A. I., Takayama-Muromachi, E. & Khiem, L. H. (2014). *Journal of Alloys and Compounds* **585**, 741-747.
Kozlenko, D. P., Kichanov, S. E., Lukin, E. V., Lee, S., Park, J. G. & Savenko, B. N. (2010). *High Pressure Research* **30**, 252-257.
Kozlenko, D. P., Mirebeau, I., Park, J. G., Goncharenko, I. N., Lee, S., Park, J. & Savenko, B. N. (2008). *Physical Review B* **78**, 5.
Kumar, A., Martin, L. W., Denev, S., Kortright, J. B., Suzuki, Y., Ramesh, R. & Gopalan, V. (2007). *Physical Review B* **75**, 4.
Landau, L. D. & Lifshitz, E. M. (1959). *Electrodynamics of continuous media*. Moscow: Pergamon Press.
Lawes, G., Ramirez, A. P., Varma, C. M. & Subramanian, M. A. (2003). *Physical Review Letters* **91**, 4.
Lebeugle, D., Colson, D., Forget, A., Viret, M., Bonville, P., Marucco, J. F. & Fusil, S. (2007). *Physical Review B* **76**, 024116.
Levstik, A., Filipic, C. & Holc, J. (2008). *Journal of Applied Physics* **103**.
Liebermann, R. C. (2011). *High Pressure Research* **31**, 493-532.
Lin, C. L., Liu, J., Li, X. D., Li, Y. C., Chu, S. Q., Xiong, L. & Li, R. (2012). *Journal of Applied Physics* **112**, 6.
Lin, C. L., Zhang, Y. F., Liu, J., Li, X. D., Li, Y. C., Tang, L. Y. & Xiong, L. (2012). *Journal of Physics-Condensed Matter* **24**, 6.
Liu, F., Li, J., Li, Q., Wang, Y., Zhao, X., Hua, Y., Wang, C. & Liu, X. (2014). *Dalton Transactions* **43**, 1691-1698.
Locherer, T., Dinnebier, R., Kremer, R. K., Greenblatt, M. & Jansen, M. (2012). *Journal of Solid State Chemistry* **190**, 277-284.
Long, Y., Saito, T., Mizumaki, M., Agui, A. & Shimakawa, Y. (2009). *Journal of the American Chemical Society* **131**, 16244-16247.
Lopez-Moreno, S., Romero, A. H., Rodriguez-Hernandez, P. & Munoz, A. (2009). *High Pressure Research* **29**, 578-581.
Lyubutin, I. S., Naumov, P. G. & Mill, B. V. (2010). *Epl* **90**.
Macavei, J. & Schulz, H. (1993). *Zeitschrift für Kristallographie* **207**, 193-.
Martin, L., Crane, S. P., Chu, Y. H., Holcomb, M. B., Gajek, M., Huijben, M., Yang, C. H., Balke, N. & Ramesh, R. (2008). *Journal of Physics-Condensed Matter* **20**, 13.
Mathieu, R., Ivanov, S. A., Solovyev, I. V., Bazuev, G. V., Kumar, P. A., Lazor, P. & Nordblad, P. (2013). *Physical Review B* **87**, 5.
McMillan, P. F. (2002). *Nature Materials* **1**, 19-25.
McMillan, P. F. (2003). *High Pressure Research* **23**, 7-22.
Mei, Z. G., Shang, S. L., Wang, Y. & Liu, Z. K. (2010). *Journal of Physics-Condensed Matter* **22**.
Mezzadri, F., Calestani, G., Calicchio, M., Gilioli, E., Bolzoni, F., Cabassi, R., Marezio, M. & Migliori, A. (2009). *Physical Review B* **79**, 4.
Mezzadri, F., Fabbrici, S., Montanari, E., Righi, L., Calestani, G., Gilioli, E., Bolzoni, F. & Migliori, A. (2008). *Physical Review B* **78**, 6.
Ming, X., Meng, X., Hu, F., Wang, C.-Z., Huang, Z.-F., Fan, H.-G. & Chen, G. (2009). *Journal of Physics-Condensed Matter* **21**.
Mishra, A. K., Shanavas, K. V., Poswal, H. K., Mandal, B. P., Garg, N. & Sharma, S. M. (2013). *Solid State Communications* **154**, 72-76.
Montanari, E., Calestani, G., Migliori, A., Dapiaggi, M., Bolzoni, F., Cabassi, R. & Gilioli, E. (2005). *Chemistry of Materials* **17**, 6457-6467.
Montanari, E., Righi, L., Calestani, G., Migliori, A., Gilioli, E. & Bolzoni, F. (2005). *Chemistry of Materials* **17**, 1765-1773.
Moritomo, Y., Kuwahara, H., Tomioka, Y. & Tokura, Y. (1997). *Physical Review B* **55**, 7549-7556.
Mostovoy, M. (2006). *Physical Review Letters* **96**, 4.
Murakami, M., Ohishi, Y., Hirao, N. & Hirose, K. (2012). *Nature* **485**, 90-U118.
Nan, C. W., Bichurin, M. I., Dong, S. X., Viehland, D. & Srinivasan, G. (2008). *Journal of Applied Physics* **103**, 35.
Neaton, J. B., Ederer, C., Waghmare, U. V., Spaldin, N. A. & Rabe, K. M. (2005). *Physical Review B* **71**, 8.
Oh, S. H., Jin, H.-Y., Shin, R. H., Yoon, S., Seo, Y.-S., Ahn, J.-S. & Jo, W. (2014). *Journal of Physics D: Applied Physics* **47**, 245302.
Oka, K., Azuma, M., Chen, W. T., Yusa, H., Belik, A. A., Takayama-Muromachi, E., Mizumaki, M., Ishimatsu, N., Hiraoka, N., Tsujimoto, M., Tucker, M. G., Attfield, J. P. & Shimakawa, Y. (2010). *Journal of the American Chemical Society* **132**, 9438-9443.
Oka, K., Azuma, M., Hirai, S., Belik, A. A., Kojitani, H., Akaogi, M., Takano, M. & Shimakawa, Y. (2009). *Inorganic Chemistry* **48**, 2285-2288.
Oliveira, J., Moreira, J. A., Almeida, A., Rodrigues, V. H., Costa, M. M. R., Tavares, P. B., Bouvier, P., Guennou, M. & Kreisel, J. (2012). *Physical Review B* **85**, 5.
Pregelj, M., Zaharko, O., Zorko, A., Kutnjak, Z., Jeglic, P., Brown, P. J., Jagodic, M., Jaglicic, Z., Berger, H. & Arcon, D. (2009). *Physical Review Letters* **103**, 4.
Prellier, W., Lecoeur, P. & Mercey, B. (2001). *Journal of Physics-Condensed Matter* **13**, R915-R944.

Prodi, A., Gilioli, E., Cabassi, R., Bolzoni, F., Licci, F., Huang, Q. Z., Lynn, J. W., Affronte, M., Gauzzi, A. & Marezio, M. (2009). *Physical Review B* **79**, 10.
Qiang, L., Duo-Hui, H., Qi-Long, C. & Fan-Hou, W. (2013). *Chinese Physics B* **22**, 037101.
Raevski, I. P., Olekhnovich, N. M., Pushkarev, A. V., Radyush, Y. V., Kubrin, S. P., Raevskaya, S. I., Malitskaya, M. A., Titov, V. V. & Stashenko, V. V. (2013). *Ferroelectrics* **444**, 47-52.
Ramesh, R. & Spaldin, N. A. (2007). *Nature Materials* **6**, 21-29.
Rao, C. N. R. & Serrao, C. R. (2007). *Journal of Materials Chemistry* **17**, 4931-4938.
Retuerto, M., Martinez-Lope, M. J., Garcia-Hernandez, M. & Alonso, J. A. (2009). *Journal of Physics-Condensed Matter* **21**.
Rodgers, J. A., Williams, A. J. & Attfield, J. P. (2006). *Zeitschrift fur naturforschung section b-A journal of chemical sciences* **61**, 1515-1526.
Schilling, J. S. (2000). *Hyperfine Interactions* **128**, 3-27.
Schmid, H. (1994). *Ferroelectrics* **162**, 317-338.
Shang, S. L., Sheng, G., Wang, Y., Chen, L. Q. & Liu, Z. K. (2009). *Physical Review B* **80**.
Sharan, A., Lettieri, J., Jia, Y. F., Tian, W., Pan, X. Q., Schlom, D. G. & Gopalan, V. (2004). *Physical Review B* **69**.
Shimakawa, Y., Azuma, M. & Ichikawa, N. (2011). *Materials* **4**, 153-168.
Shpanchenko, R. V., Chernaya, V. V., Tsirlin, A. A., Chizhov, P. S., Sklovsky, D. E., Antipov, E. V., Khlybov, E. P., Pomjakushin, V., Balagurov, A. M., Medvedeva, J. E., Kaul, E. E. & Geibel, C. (2004). *Chemistry of Materials* **16**, 3267-3273.
Shvartsman, V. V., Kleemann, W., Haumont, R. & Kreisel, J. (2007). *Applied Physics Letters* **90**.
Spaldin, N. A. & Fiebig, M. (2005). *Science* **309**, 391-392.
Struzhkin, V. V., Hemley, R. J., Mao, H. K., Timofeev, Y. A. & Eremets, M. I. (2000). *Hyperfine Interactions* **128**, 323-343.
Su, W. N., Wang, D. H., Cao, Q. Q., Han, Z. D., Yin, J., Zhang, J. R. & Du, Y. W. (2007). *Applied Physics Letters* **91**, 3.
Suchomel, M. R., Thomas, C. I., Allix, M., Rosseinsky, M. J., Fogg, A. M. & Thomas, M. F. (2007). *Applied Physics Letters* **90**, 3.
Taguchi, Y., Sakai, H., Okuyama, D., Ishiwata, S., Fujioka, J., Fukuda, T., Hashizume, D., Kagawa, F., Takahashi, Y., Shimano, R., Tokunaga, Y., Kaneko, Y., Nakao, A., Nakao, H., Murakami, Y., Sugimoto, K., Takata, M., Yamauchi, K., Picozzi, S., Baron, A. Q. R., Arima, T. & Tokura, Y. (2012). *Physica B-Condensed Matter* **407**, 1685-1688.
Taniguchi, K., Abe, N., Takenobu, T., Iwasa, Y. & Arima, T. (2006). *Physical Review Letters* **97**.
Teague, J. R., Gerson, R. & James, W. J. (1970). *Solid State Communications* **8**, 1073-1074.
Van Aken, B. B., Palstra, T. T. M., Filippetti, A. & Spaldin, N. A. (2004). *Nature Materials* **3**, 164-170.
van den Brink, J. & Khomskii, D. I. (2008). *Journal of Physics-Condensed Matter* **20**, 12.
Varga, T., Kumar, A., Vlahos, E., Denev, S., Park, M., Hong, S., Sanehira, T., Wang, Y., Fennie, C. J., Streiffer, S. K., Ke, X., Schiffer, P., Gopalan, V. & Mitchell, J. F. (2009). *Physical Review Letters* **103**.
Vaz, C. A. F. (2012). *Journal of Physics-Condensed Matter* **24**, 29.
Wang, J., Neaton, J. B., Zheng, H., Nagarajan, V., Ogale, S. B., Liu, B., Viehland, D., Vaithyanathan, V., Schlom, D. G., Waghmare, U. V., Spaldin, N. A., Rabe, K. M., Wuttig, M. & Ramesh, R. (2003). *Science* **299**, 1719-1722.
Wang, L. J., Feng, S. M., Zhu, J. L., Liu, Q. Q., Li, Y. C., Li, X. D., Liu, J. & Jin, C. Q. (2010). *High Pressure Research* **30**, 258-264.
Weber, S., Lunkenheimer, P., Fichtl, R., Hemberger, J., Tsurkan, V. & Loidl, A. (2006). *Physical Review Letters* **96**.
Wen, F. S., Wang, N. & Zhang, F. (2010). *Solid State Communications* **150**, 1888-1891.
Wood, V. E., Austin, A. E., Collings, E. W. & Brog, K. C. (1973). *Journal of Physics and Chemistry of Solids* **34**, 859-868.
Wu, T., Tyson, T. A., Chen, H., Gao, P., Yu, T., Chen, Z. W., Liu, Z., Ahn, H., Wang, X. & Cheong, S. W. (2014). *arXiv:1403.7998 [cond-mat.str-el]*.
Yang, Y., Bai, L. G., Zhu, K., Liu, Y. L., Jiang, S., Liu, J., Chen, J. & Xing, X. R. (2009). *Journal of Physics-Condensed Matter* **21**.
Ye, F., Lorenz, B., Huang, Q., Wang, Y. Q., Sun, Y. Y., Chu, C. W., Fernandez-Baca, J. A., Dai, P. C. & Mook, H. A. (2007). *Physical Review B* **76**, 4.
Yi, W., Liang, Q. F., Matsushita, Y., Tanaka, M. & Belik, A. A. (2013). *Inorganic Chemistry* **52**, 14108-14115.
Zaharko, O., Ronnow, H., Mesot, J., Crowe, S. J., Paul, D. M., Brown, P. J., Daoud-Aladine, A., Meents, A., Wagner, A., Prester, M. & Berger, H. (2006). *Physical Review B* **73**, 7.
Zhang, D., Kremer, R. K., Lemmens, P., Choi, K. Y., Liu, J., Whangbo, M. H., Berger, H., Skourski, Y. & Johnsson, M. (2011). *Inorganic Chemistry* **50**, 12877-12885.
Zhang, G. Q., Dong, S., Yan, Z. B., Guo, Y. Y., Zhang, Q. F., Yunoki, S., Dagotto, E. & Liu, J. M. (2011). *Physical Review B* **84**, 5.
Zhang, X. L., Wu, Y., Zhang, Q., Dong, J. C., Wu, X., Liu, J., Wu, Z. Y. & Chen, D. L. (2013). *Chinese Physics C* **37**.
Zhu, J. L., Feng, S. M., Wang, L. J., Jin, C. Q., Wang, X. H., Li, L. T., Li, Y. C., Li, X. D. & Liu, J. (2010). *High Pressure Research* **30**, 265-272.