

UNIVERSITA' DEGLI STUDI DI PARMA



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Materiali Innovativi**
Ciclo XXII

Synthesis and characterization of new multiferroic materials

Coordinatore:
Chiar.mo Prof. Anna Painelli

Tutor:
Chiar.mo Prof. Gianluca Calestani

Dottorando: Francesco Mezzadri

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1. Introduction

In human history, technological achievements often deal with the discovery and use of new materials or –in some cases- with a new employment of previously known ones. This statement is particularly evident if related to ancient ages, usually named after the materials having the deepest outcome on the human activities of the time. This choice emphasizes that the use of a particular material is the major influence for a large set of habits, regarding of course activities of subsistence and defense but also, noteworthy, the social, artistic, and even religious fields. In modern era this fact is not that evident, since the number and quality of materials used is much larger with respect to iron-age, for example. Anyway, the development and application of new materials has a strong effect in everyday's life, affecting our relationship with energy saving or production, communications and health care, just to mention some. This is apparent if one considers silicon chips, present in almost any electronic device; light emitting materials, which are at the heart of today's communications; novel liquid crystal displays, providing high performances and low energy consumption; magnetic materials, largely used in recording devices.

The study and development of functional materials (i.e. systems able to perform a certain "function" under a determined stimulus) are thus mandatory, and compounds displaying more than one degree of functionality (multifunctional materials) are promising in particular within the frame of the current rush toward miniaturization. To this wide category belong electro-optic materials, that currently lead the field of data transfer and manipulation; ferromagnetic semiconductors, providing high efficiency in LED structures and offering interesting perspectives in spintronics development; magnetoresistive compounds, bound to become dominant in the market of random access memories in virtue of low power

consumption and high operating frequencies; multiferroic materials, finally, may allow the fabrication of multiple control devices (e.g. electric field-controlled magnetic data storage) and the development of new degrees of freedom in spin transport electronics. Within this picture, it is clear that materials science sets itself as the primary ground for technological development, providing highly optimized matter suitable to be molded by engineers in order to produce effective devices and applications. The present work follows this path, introducing the synthesis processes and fundamental characterizations of new promising multiferroic materials.

1.1 Multiferroism

1.1.1 Historical Background

Briefly cited previously, multiferroism consists in the coexistence in a single material of at least two of the so called ferroic orders: namely ferroelasticity (FEL), ferroelectricity (FE) and ferromagnetism (FM). The interest raised by this class of compounds is related to the intriguing chance of combining in particular ferroelectric and magnetic properties, allowing a single device to perform more than one task. Nevertheless this possibility is subsidiary to the presence of a noticeable interaction between the two ferroic degrees of freedom, which could actually allow the construction of completely new devices, such as electric field-controlled magnetic memories. Besides data storage, the potential applications span from frequency-dependent devices such as filters, oscillators and phase filters to transducers or magnetic (and electric) field sensors. At present, however, spintronics represent the most promising field for the application of multiferroics, since the magnetoelectric coupling offers interesting perspectives for the design of ferroelectric memories with a non-destructive magnetic reading or nonvolatile

magnetic random access memories (MRAM) with an electrical writing procedure (MERAM).

The phenomenon at the basis of all the applications cited here is called “magnetoelectric effect” (i.e. the induction of a magnetization by an electric field, or, vice versa, an electrical polarization generated by the application of a magnetic field). Despite this term was firstly formulated by Peter Debye in 1926 in order to define the interactions between magnetism and ferroelectricity in a crystal, the direct observation of magnetoelectricity took place in 1959 thanks to the work of Astrov,¹ after a prediction made by Dzyaloshinskii.² Research in this field constantly increased up to the 70's, when the scientific community realized that the low magnetoelectric couplings observed in the materials known at that point together with the low magnetic ordering temperatures could not allow technological applications. Nevertheless, in the 90's, the field reacquired large interest, thanks to new characterization and synthesis techniques (in particular thin film deposition), to the formulation of new theories and to the increased computational power essential in order to describe such a complex phenomenon.

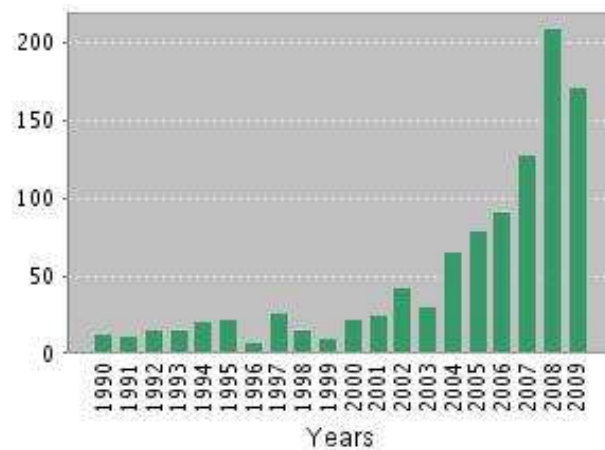


Fig. 1.1: Number of publications presenting the word “magnetoelectric” in the title. Plot taken by “ISI Web of knowledge”.

In 2003 the discovery³ of large electrical polarization in thin films of epitaxially grown BiFeO_3 , coupled to a magnetic ordering temperature above RT gave a definitive burst to the interest in magnetoelectric multiferroics, leading to a flourishing of studies in this field (see Fig. 1.1). Noteworthy is also the concomitant observation of large magnetodielectric coupling in Terbium manganites TbMnO_3 [4] and TbMn_2O_5 [5].

At present magnetoelectric couplings large enough to allow technological applications are reached only in composite materials, where typically a magnetostrictive and a piezoelectric compounds are coupled. In these systems however, the study of the interplay between ferroic degrees of freedom is needed, since linear elasticity models cannot be used to describe the responses on the atomic scale. Experimentally, the use of self-organized nanocomposites could offer particularly efficient coupling between the phases.⁶

Besides the technological interest, should not be forgotten the unique chance offered by multiferroics to the study of solid state physics, for what concerns both the understanding of the ferroic orders separately and their complex interactions.

1.1.2 Conditions of coexistence

The magnetoelectric compounds known to be present in nature are very few: an empirical rule states that ferroelectric materials are usually nonmagnetic, while spin-ordered systems seem not to allow ferroelectric distortions. The understanding of this behavior needs a description of the conditions allowing both ferroelectricity and magnetism to be present in a material.

In a ionic crystal two kinds of interactions are present: short range repulsions between the electronic clouds, that favor a non-ferroelectric symmetric structure, and bonding interactions, which may stabilize the ferroelectric phase. At high temperatures the first one is dominant, inducing high symmetry (paraelectric)

phases also in ferroelectric systems. The lowering of temperature can induce a distortion that, in transition metal (TM) oxides is usually due to the hybridization of TM d orbitals with the oxygen 2p orbitals, inducing the off-centering shift of the cation. Noteworthy is the observation that the most favorable condition, providing d orbital close in energy to the O 2p –thus the insurgence of ferroelectricity- involves a d^0 electronic configuration, proofed by the fact that most of the ferroelectric perovskites show such an electronic configuration (Ti^{4+} , Zr^{4+} and Nb^{5+}). On the other hand it is clear that d orbital occupancy is a fundamental requirement for the occurrence of magnetic ordering.

This limitation to the incidence of magnetoelectricity is quite restrictive, but it is not the only one. The occurrence of both ferroelectricity and ferromagnetism requires symmetry constraints: for example electrical polarization needs the lack of the inversion center. There are 31 point groups that allow a spontaneous electric polarization, and 31 that allow a spontaneous magnetic polarization. Thirteen point groups (1, 2, 2', m , m' , 3, $3m'$, 4, $4m'm'$, $m'm'2'$, $m'm'2'$, 6, and $6m'm'$) result to be in common.

Also electrical considerations must be taken into account: while ferromagnets are often metals, ferroelectrics need to be insulators, otherwise an applied electric field would produce a flow of electric current rather than an electrical polarization. For this reason it is easier to find magnetoelectric compounds in which the ferromagnetic properties are generated by a frustrated antiferromagnetic behavior rather than purely ferromagnetic interactions.

Finally, structural considerations are engaged in the lack of multiferroic compounds: as previously said, ferroelectricity often takes place as a low temperature distortion involving the displacement of an ion from the center of the structure, however in several d^n transition metals, the presence of unpaired electrons in the outer shell induces a Jahn-Teller distortion which results to be a competitive process with respect to the off-centering process.

In brief, we can say that the occurrence of magnetoelectricity is limited in nature by the mutual exclusive conditions of existence for ferroelectricity and ferromagnetism. In fact, as a general rule, magnetic properties are induced by unpaired electrons on the outer electronic shells, while TM d electrons seem to reduce the tendency to ferroelectric distortion.⁷

1.1.3 Occurrence of magnetoelectricity

The extensive list of restraining conditions reported in the preceding section may seem discouraging to the researcher in the field of magnetoelectric materials, however an increasing number of multiferroics has been synthesized in recent years, and this was made possible by the notion that additional structural or electronic driving forces can be present for magnetoelectricity to take place. The applied strategies follow two different paths: the first one leads to magnetoelectricity through the presence of two subsystems carrying electrical and magnetic properties separately; the second way involves ferroelectricity to set in at the same temperature as magnetic ordering and to be driven by it, as sometimes it happens in spiral magnetic systems.

In order to describe the general classes of magnetoelectric materials may be useful to consider the common ways to induce ferroelectric properties in a crystal:

- the presence of a of transition metal (TM) with d^0 configuration, through the process previously described (Fig 1.1a)
- the introduction within the structure of Bi^{3+} or Pb^{2+} ions, that can induce FE through the stereochemical activity of their “lone pair” electrons. The $6s^2$ electronic shell tends to hybridize with the 2p orbitals of oxygen, giving rise to highly directional bonds and electronic cloud polarization (Fig 1.1b)

- the presence of "geometric" ferroelectricity, as it happens in YMnO_3 , where FE is caused by a rigid rotation of the Mn-O coordination polyhedra induced by the small ionic radius of Y^{3+} (Fig 1.1c)
- in some cases FE can be induced by charge ordering, when inequivalent bonds are created between sites displaying different charges, just like in presence of a Peierls transition or magnetostriction. The resulting arrangement is polar, and an electrical dipole moment sets in (Fig 1.1d).

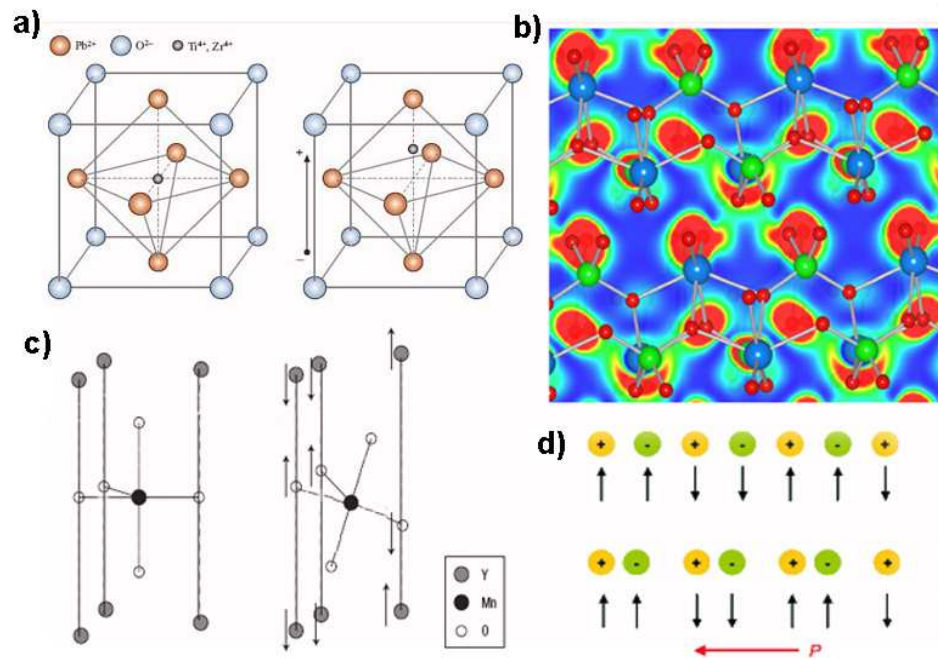


Fig. 1.2: Ferroelectricity mechanisms. a) Ion shift in $\text{Pb}(\text{ZrTi})\text{O}_3$. On the left: paraelectric phase, on the right: offcentering of Ti/Zr ion. b) Representation of BiVO_4 structure and electron density.⁸ Bi blue atom, V green, O red. Electronic clouds are strongly polarized around bismuth ions. c) YmnO_3 paraelectric (left) and ferroelectric(right) phases. The arrows indicate atomic displacements with respect to the centrosymmetric structure. Image taken from reference [9]. d) Stacking of alternate charges in presence (lower panel) and without (upper panel) magnetostriction. Black arrows indicate atomic magnetic moments. In the dimerized structure a nonzero electrical polarization sets in. Image taken from Ref. [10].

Let's now consider some different classes of multiferroics, arranged on the basis of the phenomenon which is likely at the origin of the ME properties.

I. Geometrical frustration

When ferroelectricity is induced by lattice distortions through the off-centering of ions, often magnetoelectricity may be achieved via a geometric frustration (e.g. in Kagomè lattices) of the spin structure, arranged in non-collinear ways. To this class of multiferroics belong the hexagonal manganites RMnO_3 ($\text{R}=\text{RE}, \text{Y}$), where the low size of the R ion yields a large deviation from classical perovskitic structure and is likely at the origin of ferroelectric distortion. In this case, although the ordering temperatures of ferroelectric and magnetic degrees of freedom do not coincide, a large coupling may be expected, since the ion at the origin of both the ferroic phenomena is Mn^{3+} . To this category belong also the series of compounds $\text{K}_x\text{Fe}_5\text{F}_{15}$, which are matter of discussion in the second chapter of this work.

II. Lone pair

As it's been said, the introduction in a nonpolar oxide of a $6s^2$ ion may induce ferroelectricity through the stereochemical activity produced by its electronic lone-pair. The concomitant presence in the crystallographic framework of magnetically active atoms could produce magnetoelectric coupling. Examples include BiFeO_3 [11], BiMnO_3 [12], PbVO_3 [13] and $\text{BiMn}_7\text{O}_{12}$, a new magnetoelectric compound whose synthesis and characterization is discussed in detail in chapter number 3.

III. Charge order

If magnetic ions are present in a dimerized-charge ordered system, the coexistence of magnetism can be established and may be coupled to ferroelectricity.

In the case of LuFe_2O_4 , ferroelectricity is due to the lack of geometrical compensation in a triangular arrangement of mixed valence ions Fe^{2+} and Fe^{3+} [14]. Ferrimagnetic behavior arises from the frustration of the antiferromagnetic interactions within the triangular Fe-O-Fe framework.

For $(\text{Pr,Ca})\text{MnO}_3$ [15] the possibility of charge ordering magnetoelectric behavior has been hypothesized¹⁶ under the name of a "Zener polaron state". In this model one electron is shared by the pair of neighboring Mn ions (which are in formal valence state 3+ and 4+), inducing partial dimerization. Moving back and forth between them, the e_g electron orients in a parallel way the localized spins on the t_{2g} orbitals by the double exchange mechanism, making possible magnetodielectric coupling. However this hypothesis has not been verified by direct experimental observations due to high conductivity of the material at low temperatures.

In addition, charge ordered ferroelectricity is suggested also in the well known ferrimagnetic compound Fe_3O_4 .¹⁷

IV. Magnetically driven ME

In magnetically driven magnetoelectrics, FE is induced by magnetic ordering, so that in this class of materials the largest couplings are expected. The possible origins of this behavior are two. The first involves an inverse Dzyaloshinskii-Moriya effect,¹⁸ which operates in systems with non-collinear, usually spiral magnetic structures (i.e. in which spins rotate around an axis perpendicular to the propagation vector of the spiral),¹⁹ requiring the direct action of the spin-orbit

interaction. The induced electric polarization is orthogonal to the propagation vector and lies in the spiral plane. This mechanism is responsible of ME effect in systems like TbMnO_3 [21], $\text{Ni}_3\text{V}_2\text{O}_8$ [22], MnWO_4 [23] and BaNiF_4 [24].

The second mechanism is based on magnetostriction and can take place also in collinear magnetic structures, not requiring the presence of spin-orbit coupling. In HoMnO_3 [20] magnetostriction gives rise to multiferroic behavior through the presence of a periodic collinear spin arrangement of the up-up-down-down type that can induce electric polarization via exchange striction mechanism (see Fig 1.3).

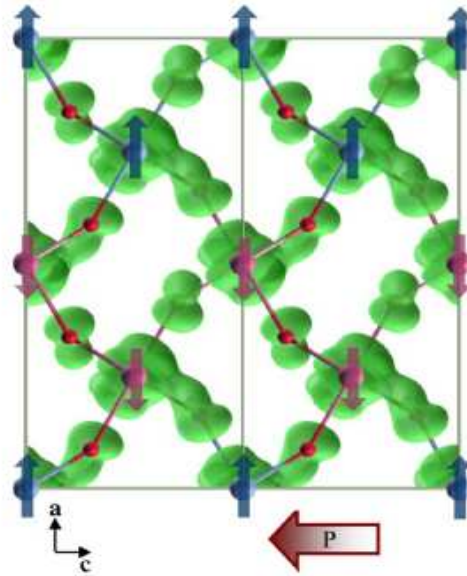


Fig. 1.3: Rendition of orthorhombic HoMnO_3 cell viewed in the ac plane. Blue and pink spheres are Mn ions with different spin directions (drawn as arrows), red ones are Oxygen atoms. Green clouds represent the electronic density, showing an electrical polarization due to anisotropic exchange interactions. From Ref [20].

1.1.4 Synthesis of multiferroics

The choice of the techniques used for the characterization of crystalline solids is often subordinated to the availability of suitable samples, so that a large part of the efforts provided in this work was spent to refine synthesis processes and to the check of the most promising techniques. The choice of the synthesis processes is related to the nature of the compound involved, for this reason a large number of techniques were used: conventional and controlled atmosphere solid state

reactions were carried out in order to obtain crystalline powders; melt and flux synthesis produced large single crystals suitable to structure determination via X-ray diffraction as well as magnetic characterizations performed on oriented samples; hydrothermal syntheses were performed in order to produce single crystals of insoluble phases; finally, high pressure solid state reactions were used to stabilize metastable compounds otherwise not obtainable. Moreover, some efforts were devoted to the refinement of the synthesis processes, fundamental in order to produce single phase compounds that are essential both for bulk characterization and for the possible future realization of technological applications.

1.1.5 Characterization of multiferroics

Since ferroelasticity, ferroelectricity and magnetic ordering are *structural* phenomena, the fundamental characterizations used in this work in order to study the multiferroic properties of the compounds under examination took advantage mainly of diffraction techniques. Of course X-ray diffraction (XRD) is mandatory when materials never synthesized before are to be studied. Besides, fundamental informations on the symmetry and the presence of structural distortions that may give rise to ferroelectricity as well as the observation of displacements of ions inducing a dipole moment (where present), can be obtained thanks to XRD experiments exploited both on single crystals and powder samples. Neutron diffraction, on the other hand, is a fundamental tool for the analysis of spin ordering patterns and determination of magnetic structures. Further structural characterizations were carried out by resonant X-ray diffraction experiments performed using synchrotron radiation, with the aim of gather additional informations about the magnetic ordering and local distortions.

Electrical properties were investigated by resistivity and dielectric measurements, while magnetic behavior was studied via SQUID magnetometry. The study of

ferroelectricity results to be quite complex in particular in semiconductive systems like the ones considered in this work. As a consequence, advantage was taken of indirect observations, based on structural considerations, as said previously. On the other hand, the realization of dedicated measurements should be put forward, also considering that the bulk response of a ferroic system may be considerably different with respect to the one observed on a single crystalline cell, due to hysteretic and microstructure effects or to the presence of domain walls, for example.

Finally, when talking about characterization of multiferroic compounds, it is mandatory to consider ferroic coupling measurements; nonetheless this kind of measures frequently result quite hard to be carried out, since they involve the combination of different techniques (e.g. electrical polarization measurements in an applied magnetic field), requiring the realization up of dedicated measure systems. However, also for this aim indirect probes may give evidence of the interplay between the ferroic degrees of freedom, opening the route to further specific characterizations.

As one can picture itself on the basis of the previous considerations, multiferroics constitute a tricky world where the simple condition $1+1=2$ is not always verified. The concomitant presence of different ferroic properties, indeed, rises the number of degrees of freedom, often making extremely complex the comprehension of the whole picture. However, the challenges provided by this class of materials are unique in the field of solid state sciences, making worth the effort both towards the understanding of the intrinsic nature of ferroic phenomena, their conditions of coexistence and interplay between them, and in the direction of tailoring materials displaying functional properties suitable to the application in technological field.

References

- ¹ D. N. Astrov, *Sov. Phys. JETP* **11**, 708–709 (1960).
- ² I. E. Dzyaloshinskii, *Sov. Phys. JETP* **10**, 628–629 (1959).
- ³ J. 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, R. Ramesh, *Science* **299**(5613), 1719-1722 (2003).
- ⁴ T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, *Nature*, **426**, 55-58 (2003).
- ⁵ N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, S-W. Cheong, *Nature* **429**, 392-395 (2004).
- ⁶ H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, *Science*, **303** (5658), 661 – 663 (2004).
- ⁷ N. A. Hill, *J. Phys. Chem. B* **104**, 6694–6709 (2000).
- ⁸ A. Walsh, *SPIE Newsroom* , 27 May 2009 DOI: 10.1117/2.1200905.1608.
- ⁹ B.B. Van Aken, T.T. M. Palstra, A. Filippetti and Nicola A. Spaldin, *Nature Materials* **3**, 164 - 170 (2004).
- ¹⁰ J. van den Brink and D. I. Khomskii, arXiv:0803.2964v3 [cond-mat.mtrl-sci] 25 Apr 2008.
- ¹¹ J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, *Phys. Rev. B* **71**, 014113 (2005).
- ¹² R. Seshadri, N. A. Hill, *Chem. Mater.* **13**, 2892–2899 (2001).
- ¹³ D. J. Singh, *Phys. Rev. B*, **73**, 094102 (2006).
- ¹⁴ N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, H. Kitô, *Nature* **436**, 1136 (2005).
- ¹⁵ S. W. Cheong and M. Mostovoy, *Nature Materials* **6**, 13 (2007).

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- ¹⁶ A. Daoud-Aladine, J. Rodríguez-Carvajal, L. Pinsard-Gaudart, M. T. Fernández-Díaz, and A. Revcolevschi, *Phys. Rev. Lett.* **89**, 097205 (2002).
- ¹⁷ Y. Miyamoto, S. Ishihara, T. Hirano, M. Takada and N. Suzuki, *Solid State Comm.*, **89** (1), 51-54 (1994).
- ¹⁸ I.A. Sergienko and E. Dagotto, *Phys. Rev. B* **73**, 094434 (2006).
- ¹⁹ M. Mostovoy, *Phys. Rev. Lett.* **96** 067601 (2006).
- ²⁰ S. Picozzi, K. Yamauchi, B. Sanyal, I.A. Sergienko and E. Dagotto, *Phys Rev. Lett.* **99**, 227201 (2007).
- ²¹ T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, *Nature* **426**, 55 (2003).
- ²² G. Lawes, M. Kenzelmann, N. Rogado, K.H. Kim, G.A. Jorge, R.J. Cava, A. Aharony, O. Entin-Wohlman, A.B. Harris, T. Yildirim, Q.Z. Huang, S. Park, C. Broholm and A.P. Ramirez, *Phys. Rev. Lett.* **93**, 247201 (2004).
- ²³ K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa and T. Arima, *Phys. Rev. Lett.* **97**, 097203 (2006).
- ²⁴ C. Ederer and Nicola A. Spaldin *Phys. Rev. B* **74**, 020401(R) (2006).

2. Tetragonal tungsten bronzes

The term “tungsten bronze” was firstly adopted by Wholer in 1824 in order to identify a sodium tungsten oxide belonging to the series Na_xWO_3 , provided of metallic-like appearance and good electrical conductivity. Since then, this name classifies a wide number of compounds that share large compositional stability in spite of remarkably different compositions (the presence of tungsten is not mandatory) and properties. The common feature, however, resides in a sequence of crystallographic structures derived by the perovskitic ABO_3 system: in cubic tungsten bronzes (fig. 2.1 a), the A site of a simple perovskitic framework is partially occupied ($x \approx 0,3\text{-}0,9$) by small-sized alkaline ions like Li^{2+} and Na^{2+} . For larger “A” ions, a tetragonal distortion occurs (fig 2.1 b), yielding the formation of sites displaying pentagonal and triangular section, in addition to the perovskitic ones; this structure is stabilized by values of x ranging from 0,6 to 0,3. Lower occupation of the A site causes the change of symmetry to hexagonal (fig 2.1 c), where the dimension of the sites is suitable to accept larger ions like Rb^+ or Cs^+ .

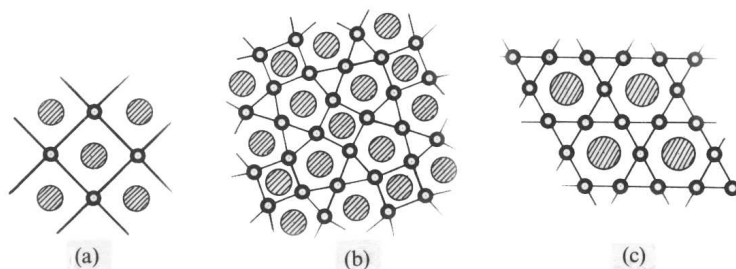


Figure 2.1 Crystal structures of tungsten bronzes viewed in $[001]$ projection. a) Cubic bronze. b) Tetragonal distortion. c) Hexagonal framework.

2.0.1 Structural considerations

In figure 2.2 the common tetragonal tungsten bronze (TTB) structure is schematized. The approximate cell dimensions are $a \approx 12$ and $c \approx 4$ Å, and the general formula may be expressed as $(A1)_2(A2)_4C_4B_{10}O_{30}$. The A1 site derives directly from the perovskitic framework, so that the classical dodecahedral coordination is retained. A2 is the 15-coordinated pentagonal site, while C, generally unoccupied due to its small dimensions, displays 9-fold coordination. Finally, B has a classical octahedral coordination and is usually occupied by transition metal ions.

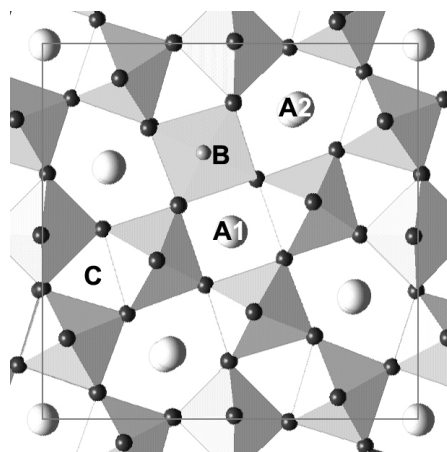


Figure 2.2 TTB crystallographic cell viewed along the $[001]$ direction.

The stacking of planes like the one reported in figure 2.2 causes the formation of channels in the c direction that, as the definition of tungsten bronze implies, can be occupied in nonstoichiometric ratios determined by the valence of the cations in B. This feature can be exploited in order to tune the electric and charge properties of the system, giving rise to a huge number of compounds belonging to this family, which are actually studied and used for different applications.

2.0.2 Multiferroism in tetragonal tungsten bronzes:***Barium Sodium Niobate***

Among TTB compounds, barium sodium niobate $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (BNN), attracted wide attention, being a good ferroelectric¹, piezoelectric² and electro-optic^{3,4} material with nonlinear optic properties⁵ used in technological applications; moreover, due to the aforementioned versatility of the TTB structure, it can be used as a matrix for the insertion of photoluminescent ions,⁶ with applications in the lasing field, while photorefractive effects result to be deeply affected by doping.⁷ The possible chemical substitutions are numerous: a large number of transition metals can replace niobium, while alkaline elements, lead or rare earths can substitute barium and sodium. As a result a wide spread of ferroelectric, piezoelectric and optical behaviors can be obtained, allowing a precise tailoring of the properties.

At room temperature BNN is ferroelectric and ferroelastic, thus multiferroic; however, being Nb^{5+} in d^0 electronic configuration, no magnetic ordering can be observed. Later on this section some routes to the induction of magnetic properties in TTB structures will be suggested. Ferroelectricity sets in below 853 K and is generated by the shift of Nb ions from the center of the coordination octahedra in the c direction. For what concerns ferroelasticity, this phenomenon is originated by the cooperative tilt of the Nb coordination octahedra, which takes place at 573 K with the aim of reducing the compressive stress along the c direction due to the lowering of temperature (fig. 2.3). By the structural point of view this event has two consequences: the doubling of the c lattice parameter (see fig. 2.3), and the definition of a new crystallographic cell, of orthorhombic symmetry, oriented along the diagonals of the fundamental TTB cell: $a \approx 2a_{\text{TTB}}/\sqrt{2}$, $b \approx a_{\text{TTB}}/\sqrt{2}$ e $c = 2c_{\text{TTB}}$. Since two equivalent cells (mutually rotated by 90 degrees and characterized by different tilts of the NbO_6 octahedra) are possible in the ab plane, two types of domains are

formed, which can be mutually converted by the switching of the a and b crystallographic axes (e.g. by the application of an external stress), in line with the definition of ferroelasticity. The averaged ferroelastic structure was firstly determined by Jamieson et al.⁸ at the end of the '60s. The modulation related to the FERroelastic Superstructure (FES) is quasi-commensurate⁹ above 113 K, when it becomes slightly incommensurated, as transmission electron diffraction measurements revealed in 1981 [10].

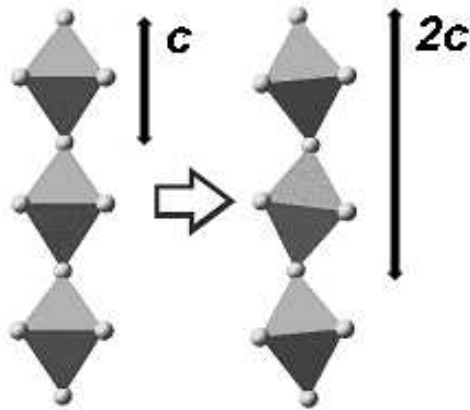


Figure 2.3 Tilt of the NbO_6 octahedra at the origin of ferroelasticity in BNN. The arrows indicate the crystallographic c axis above (left) and below (right) the paraelastic - ferroelastic transition.

2.0.3 Magnetoelectricity in BNN

As pointed out previously, Nb^{5+} is in d^0 configuration and does not allow magnetic ordering, as a consequence magnetoelectricity in BNN can be achieved only by the introduction of magnetically active ions in the TTB matrix. This task is not that easy, since magnetic TM ions often show lower oxidation states with respect to niobium. The possible strategies follow mainly two paths:

- a) substitution of oxygen with fluorine, which displays a similar ionic radius but different oxidation state (-1 instead of -2) and may allow the complete replacement of Nb^{5+} with other lower valence TM. In order to fulfill the charge neutrality conditions, also the A site has to be occupied by a low-valence ion, as for example potassium. The class of compounds obtained has general formula K_xMF_3 ($0.4 \leq x \leq 0.6$), that can be rewritten as $\text{K}_{2+x}\text{M}^{\text{II}}_{2+x}\text{M}^{\text{III}}_{3-x}\text{F}_{15}$ ($0.0 \leq x \leq 1.0$) in order to emphasize the mixed valence nature of the system.
- b) insertion of rare earths in the A1 site. Since the oxidation state of these elements is higher with respect to Ba^{2+} and Na^+ , this allows at the same time a further substitution on site B, with the introduction of a magnetic TM ion. On the one hand rare earths can be magnetically active (although their ordering temperatures are usually very low), on the other hand the possible substitution with a magnetic TM is limited, producing a magnetically diluted system in which the spin interactions are expected to be weak.

This work exploits both the possibilities, dealing with two different materials: iron fluorides $\text{K}_x\text{Fe}_5\text{F}_{15}$, studied in a large range of stoichiometries (in particular for the limit values of x) and iron-substituted BNN oxides, subject of preliminary investigations concerning synthesis methods and control of composition.

2.1 TTB fluorides

2.1.1 History

The study of the structural properties of TTB potassium iron fluorides started in the second half of the '60s;^{11,12} later on, the ferroelectric^{13,35} and magnetic^{14,15} properties were investigated, although in separate ways. Only in 1994 Ishihara et al. suggested the presence of magnetoelectric coupling in $K_3Fe_5F_{15}$ [16].

The crystallographic structure of the compound presenting the highest achievable potassium stoichiometry was firstly solved by Hardy et al. in 1972 by x-ray single crystal diffraction.¹⁷ This work suggested a classical TTB structure (as reported in fig. 2.2) presenting a slight orthorhombic distortion (s.g. Pba2) and lattice parameters $a = 12,637$, $b = 12,750$, $c = 3,986$ Å. Moreover, as may be expected for the formula $K_3Fe^{II}_3M^{III}_2F_{15}$, they observed Fe^{2+}/Fe^{3+} order on the basis of Fe-F interatomic distances. The proposed charge ordering pattern, however, seems to be incomplete, involving a stacking of ions that should increase the structural stress, since in this scheme Fe^{2+} is piled over Fe^{2+} along c , and the same happens for Fe^{3+} . The study of the isostructural compound $K_{2,7}Mn_{2,7}^{2+}Fe_{2,3}^{3+}F_{15}$ carried out by Banks et al. in 1979 cleared the picture,¹⁸ thanks also to the different scattering factors of Manganese and iron and remarkably different ionic radii. The ionic ordering lowers the structural stresses by the doubling of the c axis, induced by the alternate stacking of Mn^{2+} and Fe^{3+} along the [001] direction.

The real structure of one member of the series, finally determined in 2004 making use of x-ray and electron diffraction by Fabbrici et al., revealed the coexistence of two different structural modulations, related to charge ordering and ferroelectricity.¹⁹ The complete description of the system, where stoichiometry was refined from single crystal data as $K_{2,62}Fe_5F_{15}$, required a large orthorhombic cell ($a = 35.73$, $b = 17.872$, $c = 7.903$ Å) in analogy with the ferroelastic superstructure of

BNN described in section 2.0.2. As a result it was evidenced that also TTB fluorides are ferroelastic due to cooperative tilting of the FeF_6 octahedra; moreover the analysis of the fluorine coordination around iron revealed that the metal ions are shifted from the centre of the octahedra, giving rise to a nonzero dipole moment, thus to ferroelectric properties. The second structural modulation is related to charge ordering. Fe^{2+} and Fe^{3+} are arranged in a scheme that fully agrees with the one proposed by Banks et al., which is superimposed to the ferroelastic structure without any modification of the cell symmetry. A representation of the real structure of $\text{K}_{2.62}\text{Fe}_5\text{F}_{15}$ is reported in figure 2.4.

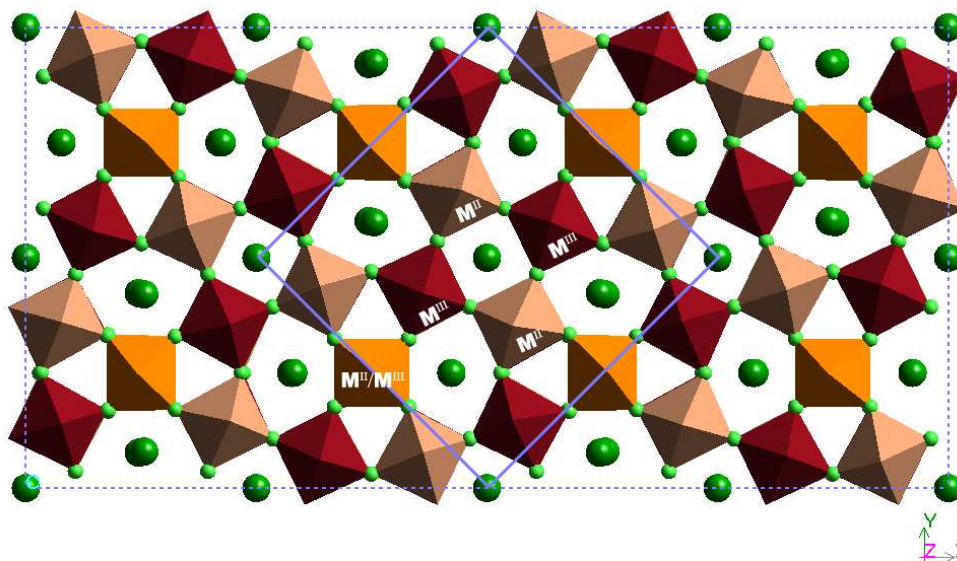


Figure 2.4 Real structure of $\text{K}_{2.62}\text{Fe}_5\text{F}_{15}$. Light and dark green spheres are fluorine and potassium respectively. The octahedra represented in different colors are occupied by Fe ions in different oxidation states. The FES cell is drawn with dashed lines, while the continuous purple line identifies the fundamental TTB structure.

The ferroelectric and structural properties of the system $\text{K}_{3-x}\text{Fe}_5\text{F}_{15}$ were investigated in a series of papers by means of x-ray diffraction and dielectric measurements as a function of composition. The orthorhombic distortion is reported to disappear for $x \leq 0.075$ ²⁰ where the symmetry results to be tetragonal at

room temperature. Anomalies in specific heat and electric permittivity, reported to be present only in the orthorhombic phase, were observed at 490 K and interpreted as the signature of the paraelectric-ferroelectric transition.²¹ In the same way Ravez et al suggest ferroelasticity to be related to the orthorhombic distortion of the fundamental TTB cell, being thus an exclusive feature of the potassium-rich members of the series. However, on the basis of the structural results of Fabbri et al., both these suggestions are doubtful, being $K_{2,62}Fe_5F_{15}$ tetragonal, ferroelectric and ferroelastic. This induced us to undertake a detailed study on the TTB fluorides, which has been extended to the whole composition range.

2.1.2 Synthesis

The synthesis of ceramic fluorides usually takes place by solid state reaction, producing crystalline powder samples; however the success of the reaction is limited by the tendency of elemental fluorides to hydrolysis and oxidation, in particular at high temperatures. In order to overcome this problem the solid state reaction is usually carried out in nitrogen atmosphere. Large single crystals are reported to be produced by high temperature solution growth.¹³ The present work presents some alternative techniques, used in particular to obtain samples suitable to single crystals XRD experiments but also to characterizations performed on oriented samples.

Solid state reaction

The elemental fluorides in stoichiometric ratios are grinded and encapsulated in a mechanically sealed Ag tube. The reactants are then fired under nitrogen atmosphere at 700 °C for a time of about 12 h. The products are crystalline powders displaying a stoichiometry very close to the nominal one.

Melt synthesis

Stoichiometric quantities of reactants are placed in an electron beam sealed Platinum capsule and heated up to 800 °C in N₂ atmosphere; crystal growth is then promoted by cooling at a rate of 50 °C/h in a thermal gradient. This technique allows a precise control of stoichiometry and produces single crystals as thin plates with the TTB c axis perpendicular to the plane.

Hydrothermal synthesis

The term hydrothermal identifies “any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or nonaqueous) above room temperature and at a pressure greater than 1 atm in a closed system”.²² This technique is particularly indicated for the growth of large crystals starting from insoluble materials, since supercritical water is often used as a solvent. Above 218 atm and 374 °C indeed, water shows unusual properties, as lower viscosity and lower dielectric constant, becoming an excellent solvent for the promotion of hydrolysis, able to bring to solution also nonpolar compounds. In these conditions, growth rates result to be quite high since diffusion is inversely proportional to viscosity.

The nutrient material (previously obtained via solid-state reaction), together with 10 µl of HF 40%, is introduced in a platinum tube sealed by electron beam welding. Temperature and pressure are slowly increased up to 680 °C and 1.3 Kbar, respectively. The system is kept in these conditions for 96–144 hours and finally cooled, releasing simultaneously the pressure. Dark red crystals, elongated along the TTB c axis and ranging from few hundredth of micrometers to few millimetres can be obtained, with pink KFeF₃ perovskite crystals as minority phase. The segregation of perovskite lowers the final concentration of potassium in the TTB phase, inducing a variation in the final potassium stoichiometry of about 10%.

2.1.3 $K_3Fe_5F_{15}$

I. Structure

The crystal structure of a melt-grown sample with stoichiometry $K_{2.97}Fe^{2+}_{2.97}Fe^{3+}_{2.03}F_{15}$ (determined by data refinement), was solved with SIR2002²³ and full matrix refined with SHELX97²⁴ software making use of anisotropic thermal parameters for all atoms. Data were collected making use of Mo K_{α} radiation on a SMART Bruker diffractometer equipped with a CCD area detector. Diffraction data were indexed on the basis of an orthorhombic cell $Pba2$ with $a=12.751(1)$, $b=12.660(1)$, and $c=7.975(1)$ Å.

Atom name	x	y	z	s.o.f	U(eq)
Fe(1)	0.5000	0	-0.2074(3)		14(1)
Fe(2)	0.5000	0	0.2932(3)		14(1)
Fe(3)	0.4247(1)	0.2844(1)	0.2939(2)		14(1)
Fe(4)	0.4228(1)	0.2875(1)	-0.2060(2)		14(1)
Fe(5)	0.2142(1)	0.772(1)	-0.2068(2)		14(1)
Fe(6)	0.2120(1)	0.753(1)	0.2928(2)		14(1)
K(1)	0.5000	0.5000	0.422(5)	0.960(3)	21(1)
K(2)	0	0	-0.4533(5)	0.969(3)	21(1)
K(3)	0.6717(2)	0.1703(2)	0.443(6)	1.000(6)	52(1)
K(4)	0.1716(2)	0.3308(2)	0.5421(6)	1.000(7)	56(1)
F(1A)	0.5000	0	-0.4532(18)		40(2)
F(2A)	0.4226(3)	0.2921(4)	-0.4540(12)		34(1)
F(3A)	0.2084(3)	0.769(4)	-0.4611(11)		37(1)
F(4A)	0.2049(3)	0.763(4)	0.548(11)		36(2)
F(5A)	0.4207(3)	0.2950(3)	0.394(12)		32(1)
F(6A)	0.5000	0	0.302(16)		35(2)
F(1B)	0.2786(2)	0.2243(2)	-0.2075(12)		26(1)
F(2B)	0.1403(2)	-0.679(2)	-0.2085(13)		30(1)
F(3B)	0.5029(2)	0.1528(2)	-0.2095(13)		35(1)
F(4B)	0.3482(2)	-0.91(2)	-0.2022(13)		32(1)
F(5B)	0.659(2)	0.1439(2)	-0.2029(12)		32(1)
F(6B)	0.3565(2)	0.4343(2)	0.2883(13)		28(1)
F(7B)	0.2740(2)	0.2159(2)	0.2922(12)		26(1)
F(8B)	0.3408(2)	-0.15(2)	0.3020(14)		36(1)
F(9B)	0.5710(2)	0.3648(2)	0.2933(12)		30(1)
F(10B)	0.5152(2)	0.1545(2)	0.2892(14)		30(1)

Table 2.1 Atomic positions, site occupation factors (s.o.f.) and equivalent thermal parameters for $K_{2.97}Fe^{2+}_{2.97}Fe^{3+}_{2.03}F_{15}$.

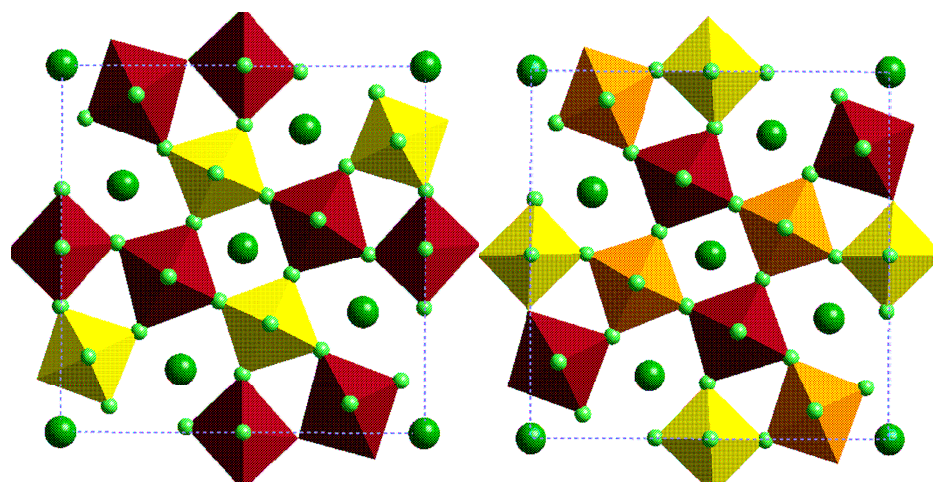


Figure 2.5 Charge ordering pattern viewed in the *ab* plane of the COS cell. The two layers successively stacked along the *c* direction are shown. Coordination octahedra surrounding Fe^{2+} and Fe^{3+} ions are evidenced in dark red and yellow respectively; orange indicates the mixed-valence sites.

The final agreement indices are $R_1 = 0.0397$, $wR_2 = 0.1083$ Goof = 0.997 for 2457 independent reflections and 216 parameters. The refinement indicates that the A2 pentagonal sites are totally occupied by K^+ ions, while the smaller A1 perovskitic sites are partially occupied. As previously seen in $K_{2.65}Fe_5F_{15}$ the doubling of the *c* axis with respect to the classical TTB cell, evidences the presence of a Charge Ordering Superstructure (COS). However the analysis of the Fe-F bond distances and of the charge distribution (calculated with CHARDIS²⁵) reveals a different charge ordering scheme, reported in fig. 2.5. This variation is required to accommodate a higher content of large Fe^{2+} ions and to reduce the structural stress. The analysis of the structural data shows that the iron ions are systematically shifted off the centre of the coordination octahedra, inducing ferroelectric properties to the material. The electrical polarization computed with a simple point-charge model as dipole moment per volume unit results to be $73,4 \mu C/cm^2$, and is completely directed along *c* since symmetry conditions force the other components to zero.

Differently from $K_{2.65}Fe_5F_{15}$, FES satellites are absent at RT; however a peculiar trend of the anisotropic displacement parameters, illustrated in figure 2.6 and consistent in their elongation in the c direction and in the ab plane for the basal and apical fluorine atoms respectively, was pointed out by the refinement.

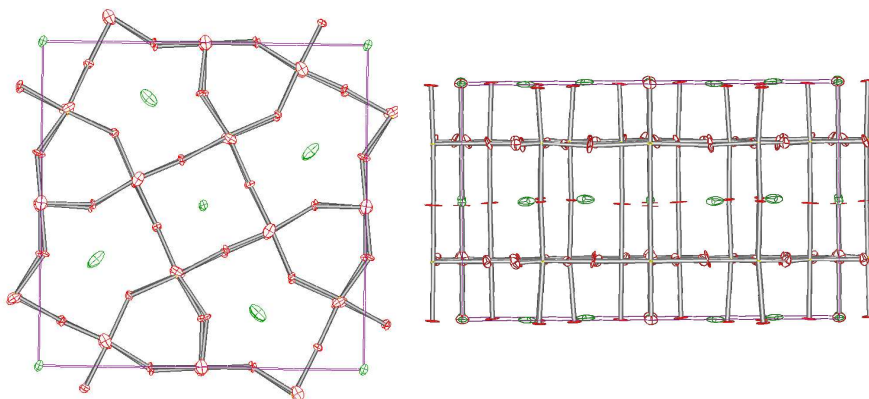


Figure 2.6 Thermal parameters represented in the COS structure viewed along the [001] and [010] directions (left and right respectively). In red are drawn the fluorine atoms, in green potassium and yellow iron.

This behaviour could be explained in terms of static disorder rather than of thermal motion, resulting from an averaged situation in presence of tilted octahedral. However, owing to the absence of FES satellites, the tilt arrangement should be considered as disordered or at least ordered below the coherence length of X-ray diffraction. Transmission Electron Microscopy (TEM) studies allowed the complete understanding of the phenomenon. Data were collected using a Philips TECNAI F20 instrument operating at 200 kV. The samples were prepared by grinding in isopropyl alcohol a small amount of powder and evaporating the suspension on a copper grid covered with a holey carbon film. Due to the shorter coherence length of electrons with respect to X-rays, very weak FES satellites could be detected at RT close to the stronger COS features, as shown in figure 2.7. A temperature dependent single-crystal XRD experiment was therefore performed, making use of the TEM informations relating the FES, COS, and TTB

cells in the reciprocal space. The intensities of one FES and one COS reflections were monitored in the range 300–100 K by decreasing the temperature using an Oxford 600 series cryosystem; the results are reported in Fig. 2.8.

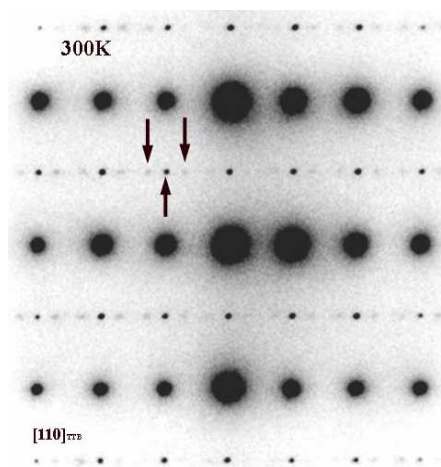


Figure 2.7 Electron diffraction pattern taken at room temperature in TTB $[110]$ zone axis. Upward arrow indicates the COS satellite, while downward arrows are related to the FES modulation.

FES satellites appear just below RT and, as revealed by electron diffraction, their intensity increases by decreasing temperature. No intensity saturation is observed in the examined temperature region, suggesting a progressive increase in the tilt modulation amplitude by decreasing T . On the contrary the intensity of COS satellites remains constant, indicating the persistence of charge order on the whole temperature range.

Differently from the case of the tetragonal $K_{2.62}Fe_5F_5$, discussed in section 2.1.1 and showing an orthorhombic symmetry of the ferroelastic superstructure, the presence in this case of an orthorhombic distortion of the TTB fundamental structure lowers the real structure symmetry (related to FES) to monoclinic.

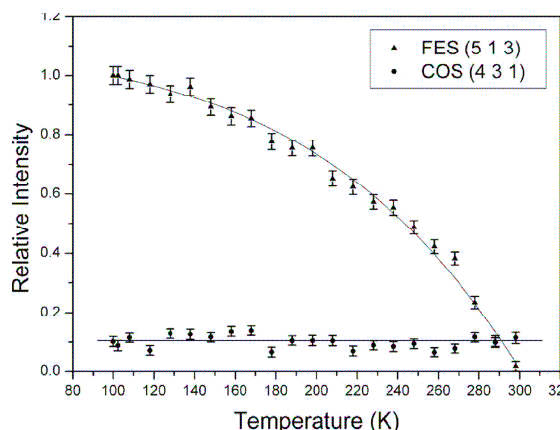


Figure 2.8 Evolution of the FES and COS satellites intensities as a function of temperature.

The appearance of an orthorhombic-monoclinic transition near RT agrees with the results of Ishihara *et al.* They performed optical and magnetic studies on ferroelectric $K_3Fe_5F_{15}$ crystals grown by flux method. In particular the insurgence of a phase transition at about 290 K, characterized by a change in the ferroelastic domains from orthorhombic to monoclinic, was pointed out by polarized light microscopy, in full agreement with the FES characteristics. The domains were found to persist below the magnetic transition and the coupling of ferroelastic and magnetic degrees of freedom was revealed by observation of anomalies in spontaneous linear birefringence at the magnetic ordering temperature.

The evolution of the structural features as a function of temperature was studied by Powder X-Ray Diffraction (PXRD), using a Thermo ARL X'tra powder diffractometer. Data collection was performed using Cu K_α radiation by 0.01 – 0.02° steps and counting times of 3–10 seconds. Temperature-dependent experiments were performed by using an Anton Paar TTK450 chamber in the temperature range 80 - 720 K. The potassium content of the sample, synthesized by solid state reaction, was refined by Rietveld method using GSAS program^{26,27} and resulted to be $K_{2.95}Fe_5F_{15}$, thus very close to the nominal one. In figure 2.9 is reported the behaviour of the 260, 620 and 002 reflections, indexed in terms of TTB structure.

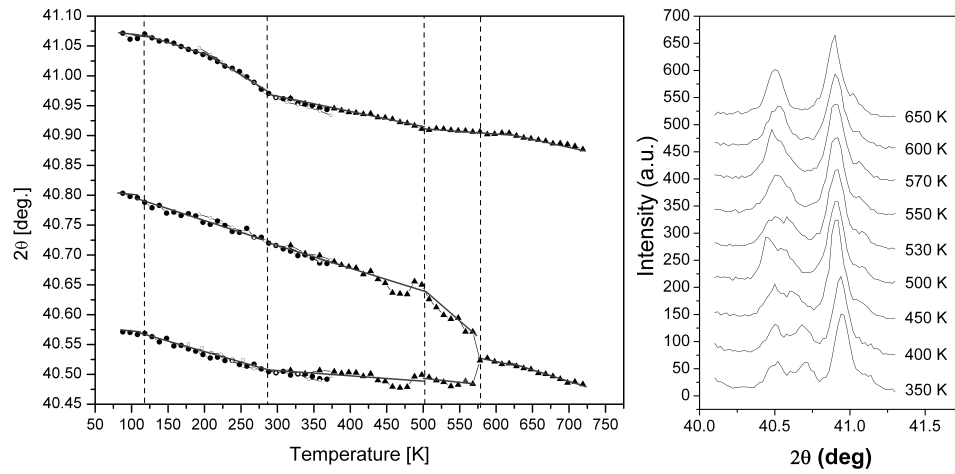


Fig. 2.9 Left: thermal behavior of the 002, 620 and 260 reflections (high to low). Lines are guides to the eye. Right: PXRD patterns in the RT-650 K range, evidencing the splitting of the 620/260 reflections below 600 K.

Several transitions are observed, associated to macroscopic changes of the lattice parameters or to small variations of the linear expansion coefficient. Later on, it will be shown that the transition observed at 120 K is related to the magnetic ordering, whereas, as discussed before, 290 K represents the vanishing of the FES modulation. The orthorhombic-tetragonal transition, detected for the first time in this study, takes place at about 580 K, as indicated by the collapse in a unique peak of the 260/620 reflections at this temperature. This finding, directly evidenced in a diffraction experiment, is in contrast with a study made by Ravez et al. indicating 490 K as the temperature at which three simultaneous ordering transitions (charge order-disorder, para-ferroelectric and para-ferroelastic) take place as the consequences of a supposed orthorhombic-tetragonal structural transition.¹⁴ The loss of charge order, suggested by an inflection in resistivity at this temperature, was also confirmed by Mössbauer measurements²⁸ showing a sharp change in slope of the temperature dependence of the Fe^{3+} quadrupolar splitting and isomer shift. For what concerns the ferroelastic transition, it should be noticed that the typical ferroelasticity of the TTB structure, detected also in tetragonal BNN,

is connected with the cooperative tilt of the FES modulation. In orthorhombic TTB fluorides, the small difference in the a and b parameters could extend the elastic exchange (in this case of different nature) up to the tetragonal-to-orthorhombic structural transition. In large crystals grown from the melt, twinning involving the a and b exchange is observed as a consequence of the crossing of the tetragonal-orthorhombic phase boundary during the cooling process. However the twinning typically occurs on large range and seems to be determined mostly by the nucleation process than by applied stresses.

The ferroelectric transition is surely displaced at higher temperatures (well above 490 K) and further characterizations are needed for its reliable assignment.

II. Ferroelectric characterization

Dielectric measurements performed at different frequencies of the applied field are reported in fig 2.10. The characterization of the $K_xFe_5F_{15}$ compounds results to be difficult in particular at high temperatures due to leaking currents generated by the semiconducting behaviour of the system and by the low density of the samples. For this reason the measurements were experimentally limited to an upper temperature of 500 K.

One maximum in dielectric permittivity can be observed in figure 2.10 (left) at 490 K, its position showing a frequency dependence indicative of relaxor-like behaviour, in line with the presence of Fe^{2+} and Fe^{3+} in the structure. The concomitant presence of a peak in permittivity and of minimum in the dielectric loss may indicate, as suggested by Ravez et al., the occurrence of the ferro-paraelectric transition temperature, ascribed by EPR studies²⁹ to a phonon-assisted transition rather than being of electronic origin, as expected in a displacive ferroelectric. Nevertheless, a careful inspection of the curve collected with applied field frequency 0.1 kHz, suggests that this peak is the shoulder of another peak placed at higher values of T (see inset), in agreement PXRD data (fig 2.9).

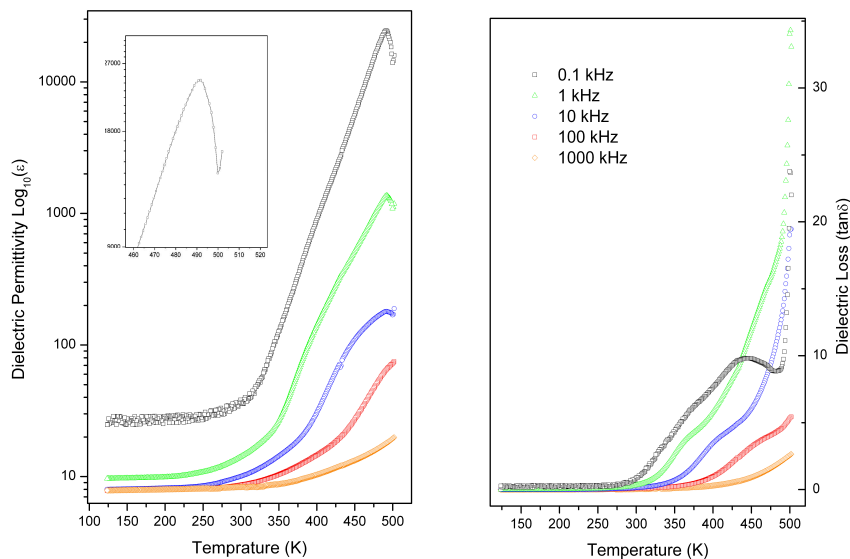


Figure 2.10 Frequency-dependent dielectric permittivity (left) and dielectric loss (right) vs temperature. Inset: High temperature range for applied field frequency 0.1 kHz.

III. Magnetic characterization

The study of the magnetic properties of $K_3Fe_5F_{15}$ was carried out by means of SQUID measurements performed on an oriented single crystal and by powder neutron diffraction. An hydrothermal-grown crystal was placed in the SQUID magnetometer with the c_{TTB} axis parallel (figure 2.11, left) and perpendicular (figure 2.11, right) to the applied magnetic field. The curves relative to Field Cooled (FC) and Zero Field Cooled (ZFC) measurements, performed with applied field $H = 100$ Oe, are reported as black dots and red triangles respectively. A large magnetic anisotropy, resulting in a difference of one order of magnitude in the saturation magnetization (1.15 vs. 0.09 emu/g), is observed in the two different orientations.

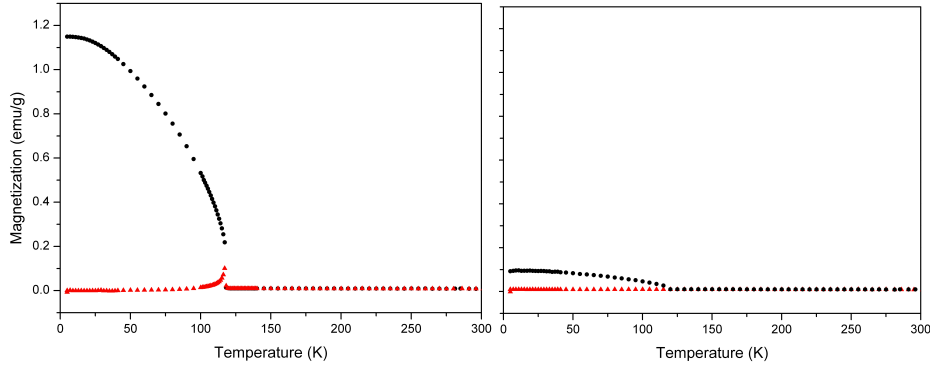


Figure 2.11 Field (black) and zero field (red) magnetization curves with applied field 100 Oe. Left: applied field perpendicular to the [001] crystallographic direction. Right, parallel.

It cannot be excluded *a priori* the anisotropy to be even larger, since the contribution for H parallel to c may be increased by a small misalignment of the sample with respect to the applied field. Inverse susceptibility reveals the antiferromagnetic nature of the exchange interactions, being the Curie-Weiss temperature $\Theta \approx -500$ K. However, the ZFC measure performed with applied field in the ab plane shows the setting of nonzero magnetization below 118 K, evidencing a ferrimagnetic behaviour of the system, originated by frustration of the antiferromagnetic scheme, as confirmed by the value of $\Theta/T_N \approx 4$. Noteworthy is that the inverse susceptibility curve shows a classical Curie-Weiss behaviour only above 200 K, becoming almost temperature-independent below this temperature. This feature suggests the presence of Van Vleck paramagnetism below 200 K, which may be related to a change in the electronic structure of the system.

Neutron powder-diffraction data were collected at different temperatures, ranging from 5 to 300 K at the DB2 beamline at the Laue Langevin Institute in Grenoble. As shown in figure 2.12, below 118 K several magnetic peaks are detected, while in the 16-20 2θ range, a significant increase in the background is observed well above the magnetic transition: this feature is present between 200 and 118 K and can be interpreted as being produced by the presence of short-range magnetic interactions.

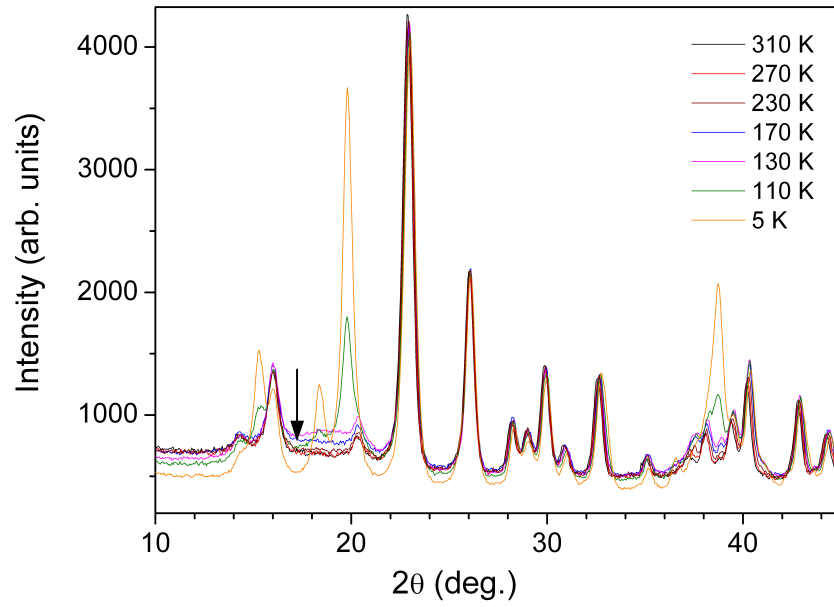


Figure 2.12 Neutron diffraction patterns taken at different temperatures. The arrow indicates the rising of the background ascribed to magnetic short-range order.

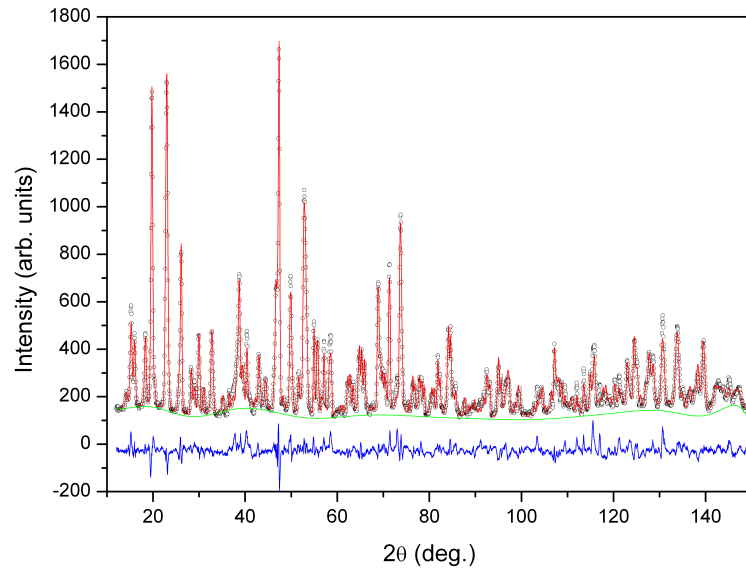


Figure 2.13 Rietveld plot. Black circles: observed data; red line: calculated intensities; green line: background; blue line: difference $F_C - F_O$.

This hypothesis finds confirmation in a series of NMR studies performed on the isostructural compound $K_{2.5}Mn_{2.5}Fe_{2.5}F_{15}$, suggesting the presence of spin glass below 200 K.³⁰ In this system an out-of-plane (*ab*) spin canting was detected and ascribed to the effect of Dzyaloshinskii-Morya interaction. Noteworthy, 200 K represents the temperature for which also the abovementioned change of the magnetic behaviour in the paramagnetic region is observed.

Rietveld refinement of neutron powder diffraction data carried out using GSAS software^{23,24} allowed the definition of the magnetic structure for a sample with stoichiometry $K_{2.93}Fe_5F_{15}$, as obtained by the refinement of the potassium occupancy. Data were collected using wavelength 1.59 Å in the 2θ range 10-150° with resolution 0.05°. The patterns were indexed on the basis of the COS cell, that results to retain the *Pba2* symmetry in the whole temperature range investigated (310-5K). The lattice parameters at 5K are $a=12.70(1)$, $b=12.60(1)$, and $c=7.92(1)$ Å.

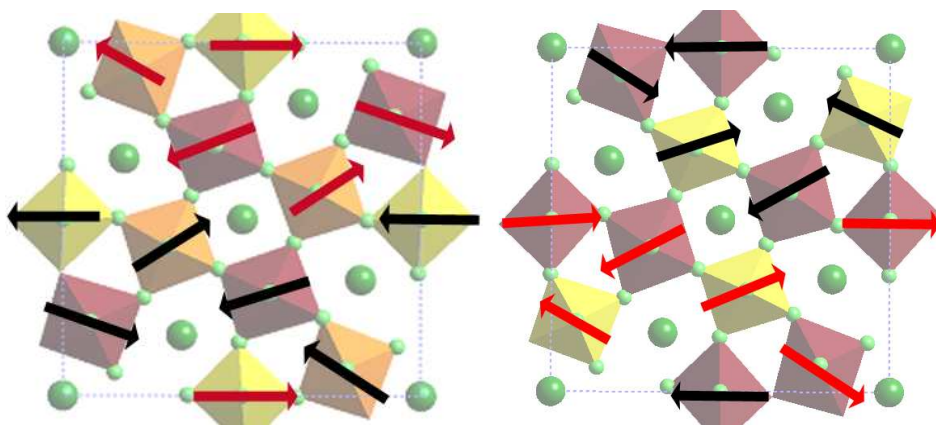


Figure 2.14 Magnetic cell of $K_{2.93}Fe_5F_{15}$. Arrows indicate the orientation of the atomic moments: the use of red and black is related to the presence of time-inversion symmetry operators.

The magnetic peaks can be indexed on the basis of the same cell as the nuclear ones, being the “coloured” space group $Pb'a2'$, in complete agreement with the

results obtained on a Fe/Mn mixed compound.¹² The imposition of constraints was required for the final convergence of the refinement, due to the high number of free parameters. As a consequence the atomic moments components were constrained to be equal, where similar values were obtained. The refinement converged with agreement factors $wRp = 0.078$, and $R(F^2) = 0.084$ and $\chi^2 = 1.502$; Rietveld plot is reported in figure 2.13. The refined moments are listed in table 2.2, the magnetic structure results in a complex scheme, where the spins in the perovskitic cage are coupled in an antiferromagnetic way, while in the triangular block the orientation of the atomic moments is forced by the constraints imposed to follow the ideal configuration (i.e. 120° formed by vectors with equivalent modulus) that gives zero result.

Atom	x	y	z	$M_x (\mu_B)$	$M_y (\mu_B)$	$M_z (\mu_B)$	$ M (\mu_B)$	$\Phi (^\circ)$	$\Theta (^\circ)$
Fe5	$\frac{1}{2}$	0	0.2516	4.29(9)	0	0	4.29(9)	90	0
Fe6	$\frac{1}{2}$	0	0.7505	-4.29(9)	0	0	4.29(9)	90	180
Fe7	0.4250	0.2850	0.2511	-3.43(4)	-2.37(4)	0	4.18(4)	90	-145.4(5)
Fe8	0.4232	0.2877	0.7510	3.43(4)	2.37(4)	0	4.18(4)	90	34.7(5)
Fe9	0.2121	0.0751	0.2508	-3.43(4)	2.37(4)	0	4.18(4)	90	145.4(5)
Fe10	0.2141	0.0771	0.7505	3.43(4)	-2.37(4)	0	4.18(4)	90	-34.7(5)

Table 2.2 Atomic positions and magnetic moments components in cartesian and polar coordinates of $K_{2.93}Fe_5F_{15}$ at 5 K.

The overall structure is antiferromagnetic, giving zero net moment, however it should be considered that the concomitant presence of Fe^{2+} and Fe^{3+} , carrying different atomic moments, modifies the geometric antiferromagnetic structure, and this deviation from the ideal scheme is likely at the origin of magnetic frustration in the system. Indeed, if different values of atomic moments are considered for the Fe^{2+} and Fe^{3+} ions (4.9 and 5.9 μ_B respectively) a nonzero component can be calculated on the basis of the obtained magnetic structure. A spontaneous magnetization equal to 2.6 μ_B for the unit cell is then expected in the y direction, while zero components are given by symmetry constraints along x and z. On the

other hand the magnetization observed by SQUID measurements indicates a magnetic moment per unit cell of $0.58 \mu_B$, about one order of magnitude lower with respect to the one expected by neutron diffraction data. However, since the magnetization measurements were performed with applied field 100 Oe, this difference could depend on the high coercive field needed to orient the magnetic domains, as confirmed by $M(H)$ curves (not reported here), that indicate large values of the coercive field: $H_c = 1.8$ T at 5K.

IV. Phase diagram

The informations collected so far allow the definition of the complete phase diagram of $K_xFe_5F_{15}$, for $x \approx 3$.

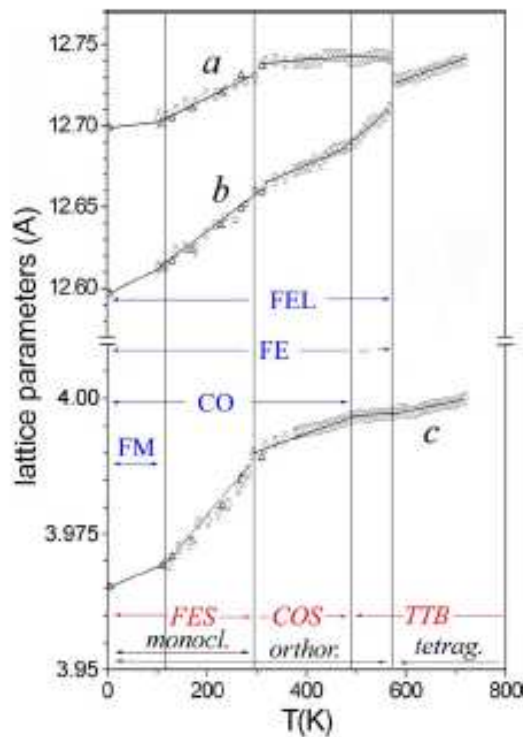


Figure 2.15 Multiferroic phase diagram of $K_3Fe_5F_{15}$.

The ferroelectric/paraelectric transition takes place above RT, probably at 580 K, although the exact temperature should be determined through a specific study. At 580 K the symmetry of the fundamental TTB cell changes from tetragonal to orthorhombic as pointed out by PXRD data, suggesting also the occurrence of the paraelastic-to-ferroelastic transition, whereas charge ordering takes place at 490 K. Short-range magnetic order sets in at about 200 K, followed by the ferromagnetic transition, found for $T_N = 118$ K. Below this temperature $K_3Fe_5F_{15}$ results to be a *complete* multiferroic. This, joined to the presence of charge ordering, makes this compound a unique system for what concerns the study of multiferroism. The whole picture is summarized in figure 2.15, where the trend of the lattice parameters is plotted versus temperature.

V. Occurrence of multiferroic coupling

So far, the ferroic degrees of freedom have been studied independently, thus no mention to any kind of multiferroic coupling was reported. In section 2.1.1, was cited the observation made by Ishihara et al. [13] of anomalies in spontaneous linear birefringence at T_N interpreted as the proof of coupling between ferroelastic domains and magnetism. More recently, Blinc et al. reported the evidence of intrinsic magnetoelectric coupling as a peak in the electric permittivity at the magnetic transition temperature.³¹ A further sign of coupling between elastic and magnetic degrees of freedom was obtained thanks to resonant diffraction performed using synchrotron radiation with incident beam energy tuned at the Fe K-edge (7.112 keV). Data were collected at the ID20 beamline at the European Synchrotron Radiation Facility in Grenoble. The intensity of the ferroelastic (3.75 4.25 1) reflection –indexed on the basis of the TTB fundamental cell- is reported in figure 2.17 as a function of temperature. The incident beam energy was tuned at 7.113 keV, and the polarization analyzer was set in perpendicular configuration with respect to the polarization of the incident radiation (σ - π configuration).

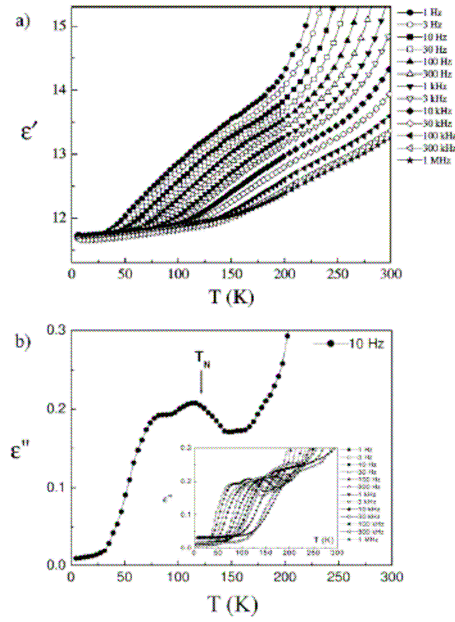


Figure 2.16 Temperature dependence of the real (a) and imaginary (b) part of the dielectric constant around T_N (from Ref. 32).

A large variation of the FES reflection intensity is observed at the Neél temperature, suggesting the coupling of the ferroic orders involved. A similar change of intensity was observed also in the behaviour of the (3 3 1) COS reflection (fig. 2.18). Data were collected in the σ - π channel with incident beam energy 7.113 keV. The intensity shows a peak at T_N , evidencing an interplay between charge and spin degrees of freedom at the onset of ferrimagnetism.

A different COS reflection (Fig. 2.19) shows an interesting feature crossing the temperature which has been ascribed to the onset of spin-glass behaviour. The evolution of the (4 4 1) reflection was followed in temperature without polarization analyser and with beam energy 7.1 keV, thus off resonance. Once again a peak in the diffracted intensity is observed, suggesting a coupling between charge ordering and spin glass state. This may agree with the loss of Van Vleck paramagnetism

above 200 K, that should involve a rearrangement in the energy states of the iron ions, affecting the charge degree of freedom.

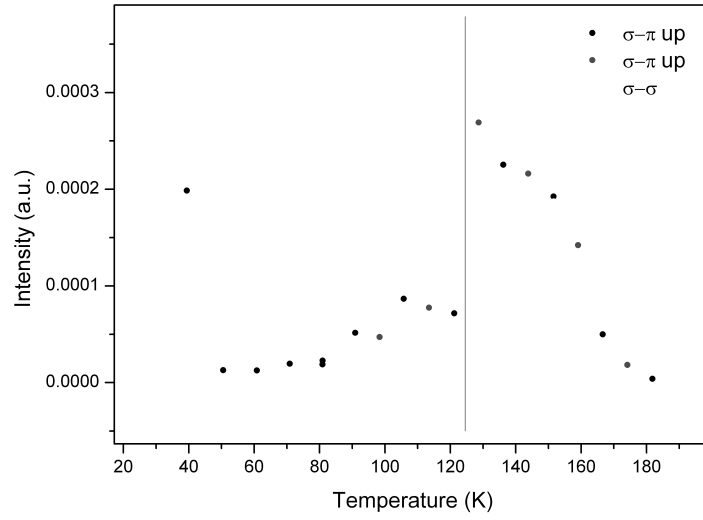


Figure 2.17 Intensity of the (3.75 4.25 1) FES reflection as a function of temperature.

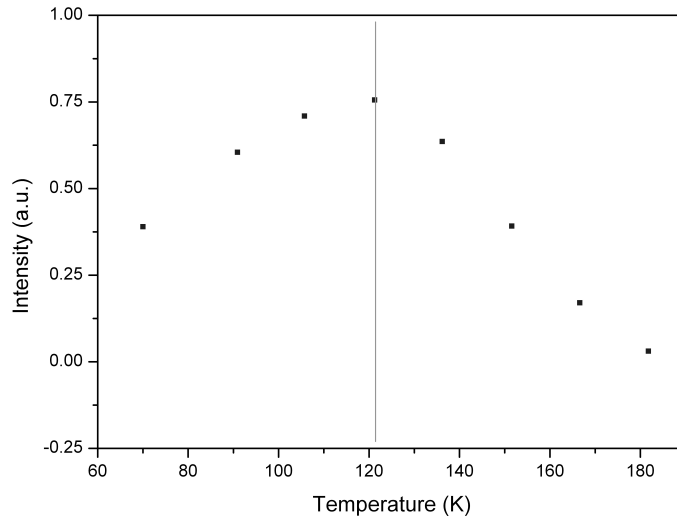


Figure 2.18 Normalized intensity of the 331 reflection as a function of temperature.

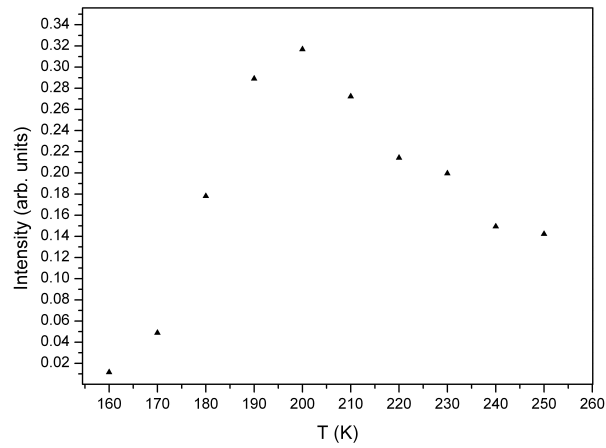


Figure 2.19 Charge Ordering Superstructure 441 reflection vs. temperature.

A strong support to this idea is given by the the structure of the resonant energy scans relative to numerous COS reflections, which happen to change dramatically between RT and 150 K, making clear that a deep modification of the electronic structure takes place well above T_N . In fig. 2.20 the energy scans performed the on the (4 3 0) reflection, above and below the spin-glass transition are shown.

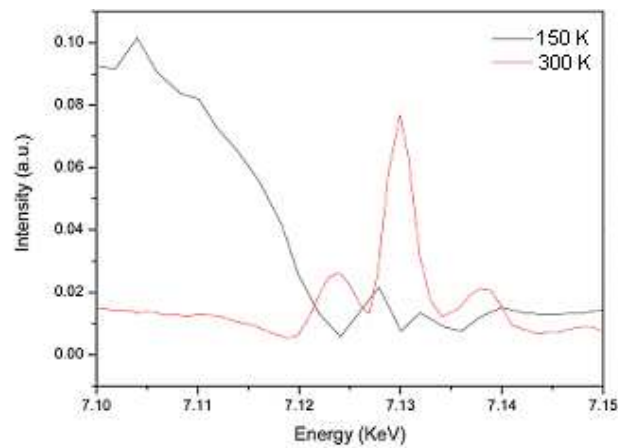


Figure 2.20 Energy scans of the 430 reflection collected above (red) and below (black) the spin-glass transition temperature.

2.1.4 $K_2Fe_5F_{15}$

The present section deals with an extensive characterization of $K_2Fe_5F_{15}$, the compound displaying the lowest potassium content achievable in the TTB structure. It should be reminded that for $x < 2.80$ the fundamental structure becomes tetragonal, so the main structural difference between the two limit compositions will consist in this change of symmetry.

I. Structure

The structure of $K_2Fe_5F_{15}$ was determined by single crystal X-ray diffraction. The data collection was carried out using Mo K_α radiation on a SMART Bruker diffractometer equipped with a CCD area detector on a sample obtained by melt synthesis.

Atom	x	y	z	U(eq)
Fe(1)	1/2	0	0.108(4)	12(1)
Fe(2)	0.2098(1)	-0.727(1)	0.5094(2)	13(1)
Fe(3)	0.2082(1)	-0.726(1)	0.93(2)	12(1)
K(1)	0.1763(2)	-0.323(2)	0.2591(8)	38(1)
K(2)	0	0	0.2540(40)	21(4)
F(1)	0.2788(3)	-0.2117(3)	0.86(18)	31(1)
F(2)	0.3479(2)	-0.32(3)	0.42(13)	47(1)
F(3)	0.5140(3)	-0.1503(2)	-0.17(13)	37(1)
F(4)	0.1558(3)	0.702(3)	0.42(17)	47(1)
F(5)	0.763(3)	-0.1403(3)	0.43(16)	49(1)
F(6)	0.2132(6)	-0.755(7)	0.2420(18)	64(4)
F(7)	0.2112(7)	-0.748(7)	0.7530(20)	69(4)
F(8)	1/2	0	0.2540(20)	61(3)

Table 2.3 Atomic positions, and equivalent thermal parameters ($\text{\AA}^2 \times 10^3$) for $K_{2.11}Fe_5F_{15}$. Site occupation factors of K(1) and K(2) are 0.986(8) and 0.077(5) respectively.

Reflections were indexed using a $P4_2bc$ tetragonal cell, the same seen previously for $K_{2.62}Fe_5F_{15}$,¹⁶ with lattice parameters $a = b = 12.5779(4)$, $c =$

7.7754(3) Å. The structure was solved with SIR2002³² and refined full matrix with SHELX97³³ software making use of anisotropic thermal parameters for all atoms. Refinement agreement indices are $R_1 = 0.0613$, $wR_2 = 0.1592$, Goof = 1.014 for 1526 independent reflections and 107 free parameters. Complete structural data are reported in table 2.3.³⁴ The stoichiometry, determined by the refinement of potassium occupancy, results to be $K_{2.11}Fe_5F_{15}$. Despite a higher vacancy of potassium ions with respect to $K_3Fe_5F_{15}$, as in the previous case the sites presenting partial occupation are the sole A1 perovskitic sites. The observed doubling of the c axis with respect to the “classical” TTB structure evidences the presence of COS modulation, that allows the determination of the charge ordering scheme, reported in figure 2.21. The arrangement is the same observed in $K_{2.62}Fe_5F_{15}$; in this case, however, the extra-perovskite site is completely occupied by Fe^{2+} .

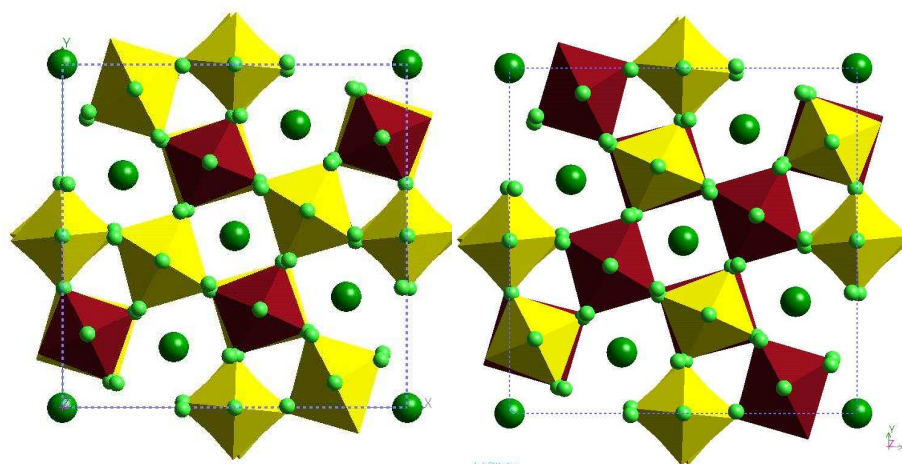


Figure 2.21 COS cell. Dark green spheres correspond to potassium ions while light green ones are fluorine. Yellow and dark red octahedra are occupied by Fe^{3+} and Fe^{2+} respectively.

FES satellites were observed at room temperature; nonetheless a severe twinning deriving from the switching of the a and b axes was detected in all the studied samples, making not possible the unambiguous solution of the FES

structure. Once again, the behaviour of the thermal parameters observed in the COS structure (similar but stronger with respect to $K_3Fe_5F_{15}$) can be interpreted as the fingerprint of the cooperative octahedra tilt.

II. Ferroelectric characterization

The analysis of the Fe-F bond distances reveals that the offcentering of the iron ions is larger than the one observed in $K_3Fe_5F_{15}$ and the correspondent dipole moment is computed as $131.7 \mu\text{C}/\text{cm}^2$. This statement is in contrast with the work of Ravez et al. indicating the sole orthorhombic phase as the one presenting ferroelectricity. Moreover the value of polarization observed is very large, in particular with respect to the one computed for $K_3Fe_5F_{15}$, suggesting that the point charge model used in the calculation could be faulty, making absolutely mandatory a direct measurement of the ferroelectric properties of the whole series of compounds $K_xFe_5F_{15}$.

Dielectric measurements show a peak in the permittivity at about 400K, that can be associated to the COS transition temperature in analogy with $K_3Fe_5F_{15}$. Noteworthy, the data collected with an applied field frequency of 0.1 kHz evidence the certain presence of a peak above 400 K characterized by a high ϵ' value, that strengthens the hypotheses previously presented concerning the ferro-paraelectric transition in $K_xFe_5F_{15}$. Also in this case, however the behavior observed at high temperature may be related to a conductive contribution due to thermally activated carriers. The relaxor-like nature of the compound is confirmed by the large frequency shift displayed by the data.

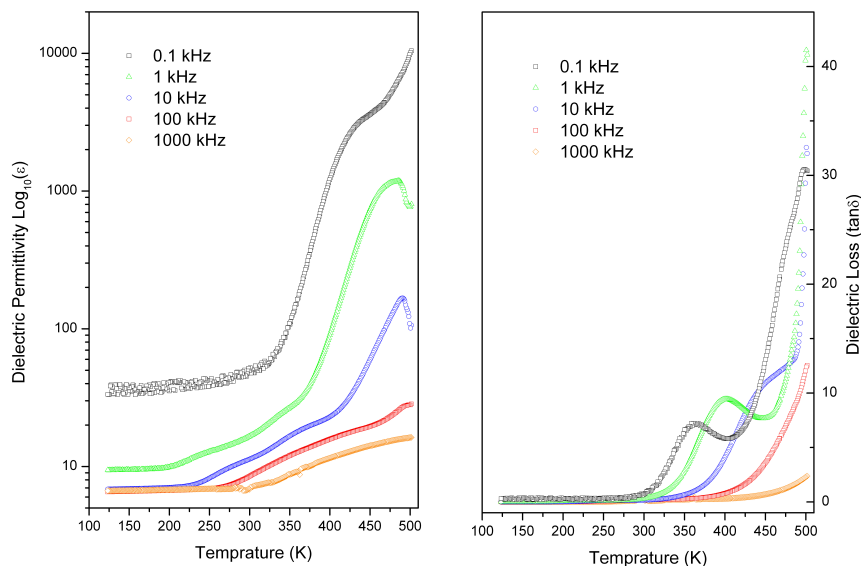


Figure 2.22 Frequency-dependent measurement of the dielectric permittivity (left) and dielectric loss (right) as a function of temperature.

III. Magnetic characterization

SQUID measurements were performed both on powder and oriented single crystal samples. The analysis of the neutron diffraction data is actually in progress and may account for the complex magnetic behaviour observed, probably characterized by several rearrangements of the spin structure.

Field Cooling (FC) and Zero Field Cooling (ZFC) measures were carried out on a powder sample of nominal composition $K_2Fe_5F_{15}$, with applied field $H = 50$ Oe; data are plotted in figure 2.23. At 153 K the setting of nonzero magnetization is observed, reaching the value of $M_s = 0,154$ emu/g at 5 K, one order of magnitude lower with respect to the one observed in $K_3Fe_5F_{15}$ ($M_s = 1,15$ emu/g). A further anomaly is observed in ZFC at $T \approx 100$ K, suggesting a rearrangement of the magnetic structure at this temperature.

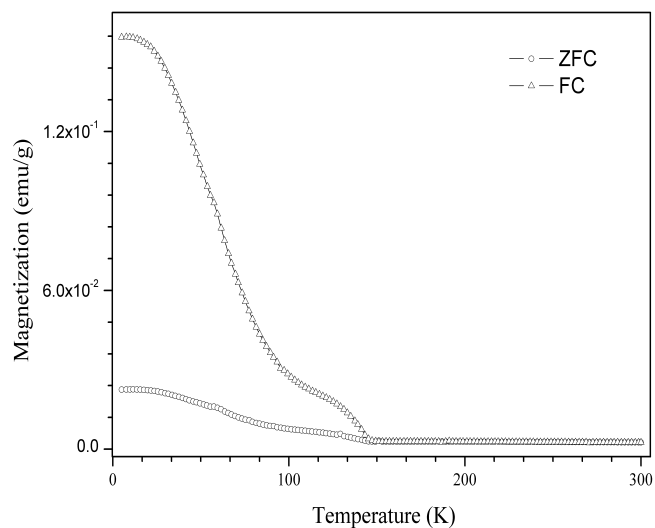


Figure 2.23 FC (Δ) and ZFC ($\circ$) measurements collected with applied field $H = 50$ Oe.

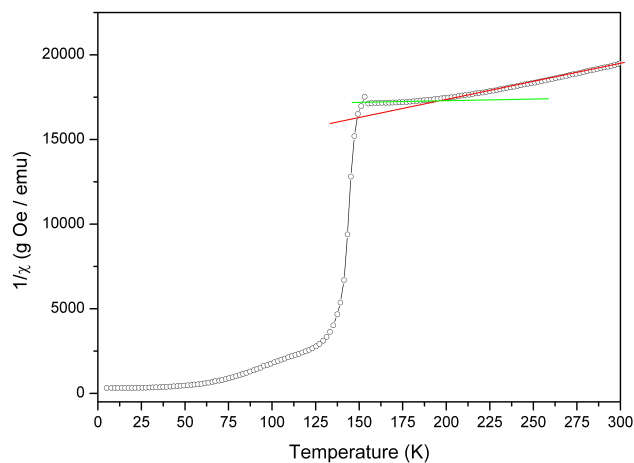


Figure 2.24 Inverse susceptibility plot. Red and Green lines point out the different regimes in the paramagnetic region.

Inverse susceptibility is reported in figure 2.24, where the red line evidences the Curie-Weiss paramagnetic region, while the green line indicates the change to a temperature-independent paramagnetic regime, taking place at about 200 K. This

behaviour is the same observed in $K_3Fe_5F_{15}$, as well as the presumed ferrimagnetic nature of the system, suggested by the high value of $\Theta/T_N \approx 3$.

SQUID measurements carried out on an oriented single crystal give the chance to clarify the complex framework, allowing the uncoupling of the contributions assigned to different crystallographic orientations.

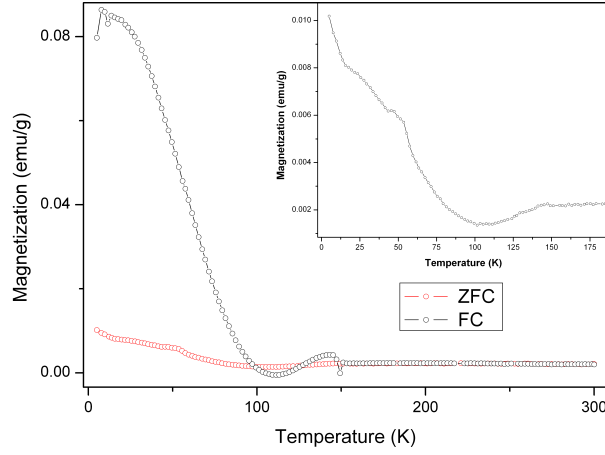


Figure 2.25 FC (black) and ZFC (red) performed on oriented sample with $H=50$ Oe parallel to *a*.

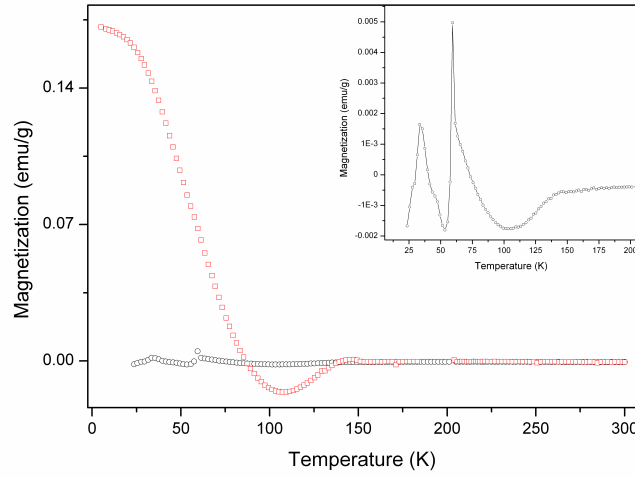


Figure 2.26 ZFC (black) and FC (red) with applied field parallel to *b*.

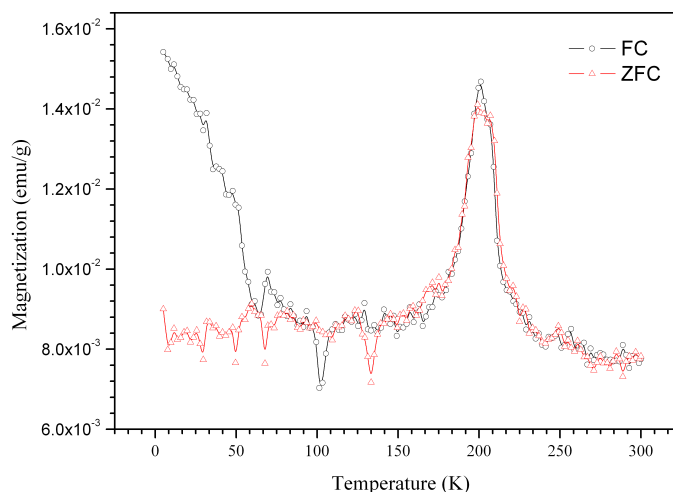


Figure 2.27 ZFC (black) and FC (red) with applied field parallel to c .

FC and ZFC measures were performed on a sample grown by melt technique. The data corresponding to applied field parallel to a , b and c axes are reported in figure 2.25, 2.26 and 2.27 respectively. The magnetic behaviour appears complex, affected by changes in the direction of the measured moment, testified by the negative values of magnetization observed between 150 and 75 K in the a and b orientations. This feature can find its origin in a rearrangement of the magnetic structure, or in the presence of different sublattices, in line with the coexistence of Fe^{2+} and Fe^{3+} in the structure. Completely different are the data relative to the c orientation, where a peak is detected both in FC and ZFC at 200 K, about 50 K above the magnetic ordering transition. The comparison of the data collected in different orientations evidences strong magnetic anisotropy, suggesting –as previously pointed out by neutron diffraction for $K_3Fe_5F_{15}$ – that in terms of magnetic structure, the crystallographic a and b axes (fig. 2.28 and 2.29) are not equivalent, lowering the symmetry of the tetragonal fundamental cell. On the other hand the c orientation, which is of course the axis of hard magnetization, displays a nonzero value of magnetization in the whole investigated temperature range, in particular in the paramagnetic region. This feature is ascribed to the presence of Van Vleck

paramagnetism, as well as the behaviour of the measurements performed with increasing values of the applied field (fig 2.31). Indeed, by passing from an applied field parallel to c of 50 Oe to 1 kOe, a change of about one order of magnitude is observed.

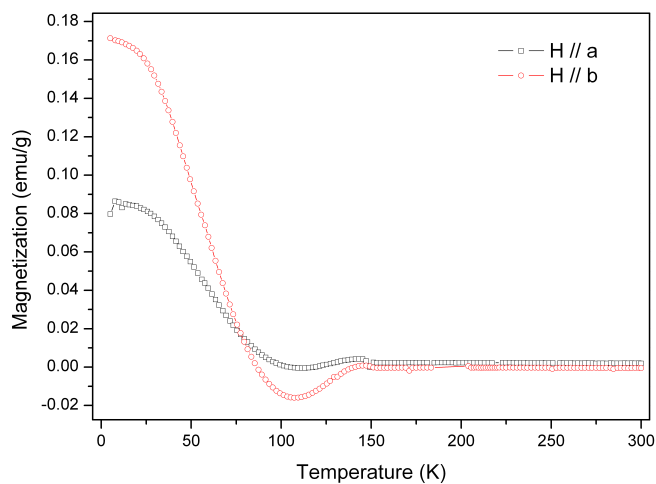


Figure 2.28 Field Cooled SQUID measurements with field $H = 50$ Oe applied along a (black) and b (red).

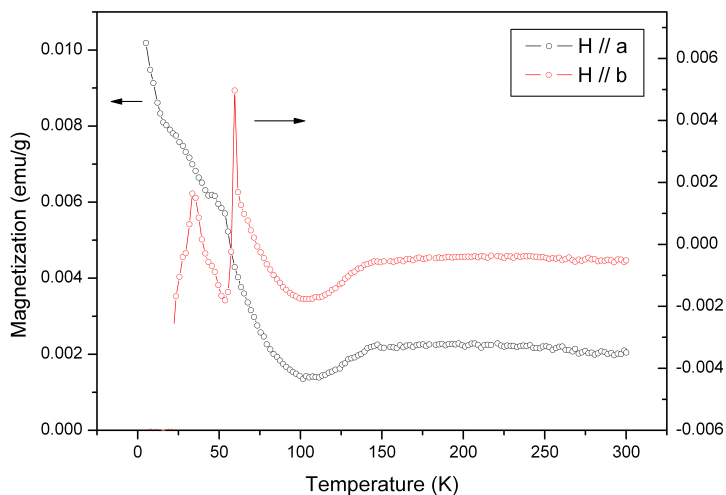


Figure 2.29 Zero Field Cooling curves collected with applied field $H = 50$ Oe, parallel to b (red) and a (black).

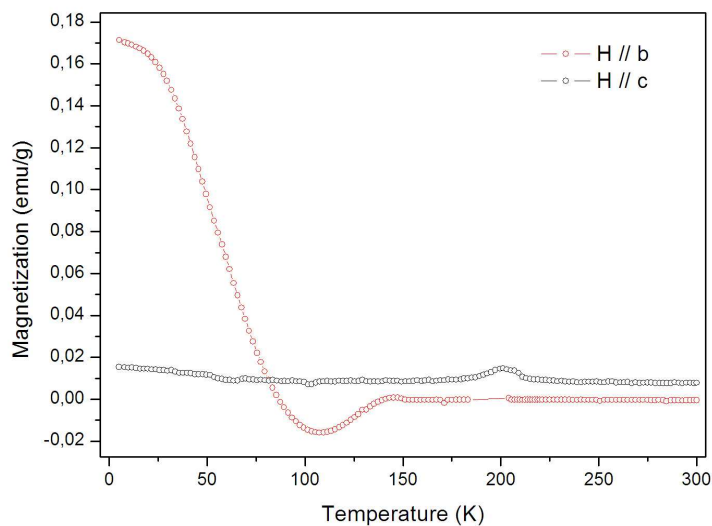


Figure 2.30 FC performed on single crystal with $H = 50$ Oe parallel to b (red) and to c (black).

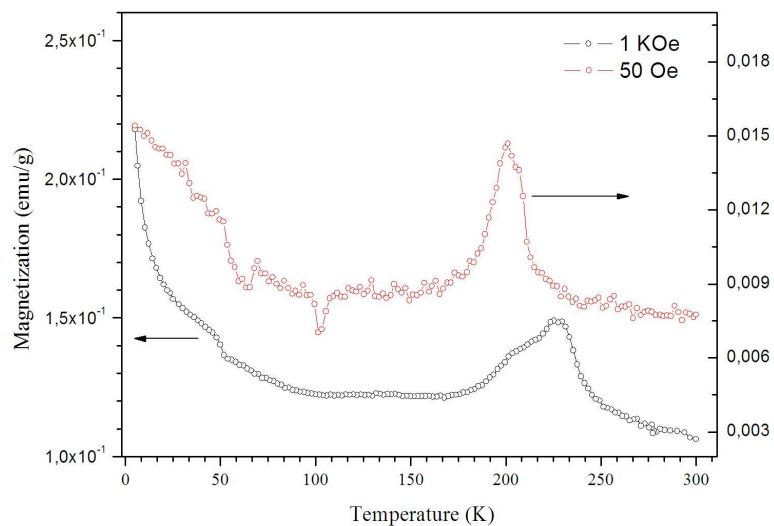


Figure 2.31 FC performed on oriented crystal with applied field parallel to the c axis. In black is reported the measure obtained with $H = 1$ kOe, in red $H = 50$ Oe.

Moreover, the peak observed in c orientation shows temperature dispersion as a function of applied field, displaying complex structure for higher values of H . A smaller effect is detected in the other orientations, suggesting that the Van Vleck-type behaviour observed also in powder samples may be due mainly to the contribution of the c direction. Within this framework seems evident that the response in the paramagnetic region results from the convolution of an “ordinary” Curie-Weiss and a Van Vleck contribution, which becomes predominant below 200 K. Despite nonzero magnetization is observed in the analysed samples, no hysteresis can be detected down to 5 K for all the orientations. $M(H)$ curves (fig. 2.32) show no saturation up to 4 T, revealing a considerably different behaviour with respect to $K_3Fe_5F_{15}$.

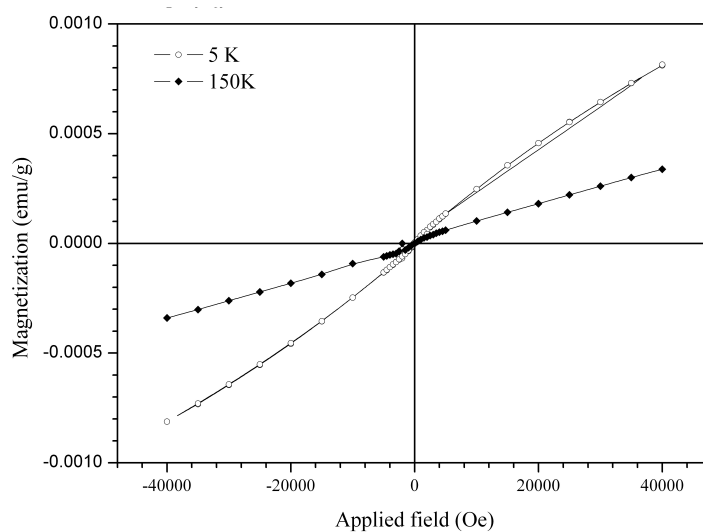


Figure 2.32 $M(H)$ curves with applied field parallel to a . Black dots correspond to $T = 150$ K, white circles $T = 5$ K.

Neutron diffraction data allowed the determination of the magnetic structure of the compound in its low temperature phase. An accurate analysis of the evolution of the magnetic structure should be performed in order to clarify the origin of the

several features appearing in the magnetization measurements. As expected, below 150 K the insurgence of magnetic peaks, shown in figure 2.33, is detected. In analogy with $K_3Fe_5F_{15}$ the growth of the background between RT and the magnetic ordering temperature is ascribed to spin glass, and some relation seems to exist between this phenomenon and the feature observed in $M(T)$ data collected with applied field parallel to the c axis.

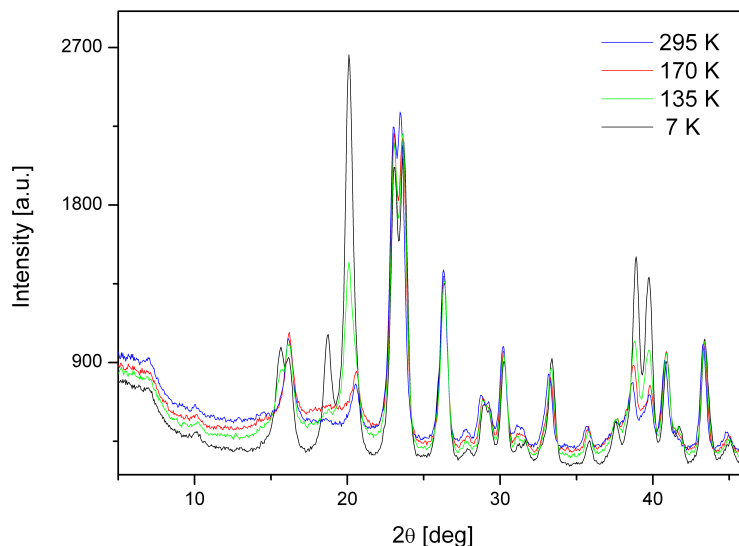


Figure 2.33 Neutron diffraction pattern of $K_{2.2}Fe_5F_{15}$.

Rietveld refinement of data collected using 1.59 Å wavelength in the 2θ range 10-150° was carried out on a sample with stoichiometry -obtained from refinement- $K_{2.2}Fe_5F_{15}$. As in the case of $K_3Fe_5F_{15}$, the patterns were indexed on the basis of the orthorhombic $Pb'a2'$ cell, where the lattice parameters were constrained to be metrically equal: at 7 K the cell results to be $a=b= 12.540(4)$, $c= 7.717(4)$ Å. The refinement was carried out with the same constraints used for $K_3Fe_5F_{15}$, imposed after the partial convergence of the previously seen antiferromagnetic structure. Agreement factors obtained are $wRp = 0.10$, $R(F^2) = 0.11$, $\chi^2 = 3.76$; Rietveld plot is shown in figure 2.34 while the structural data are reported in table 2.3.

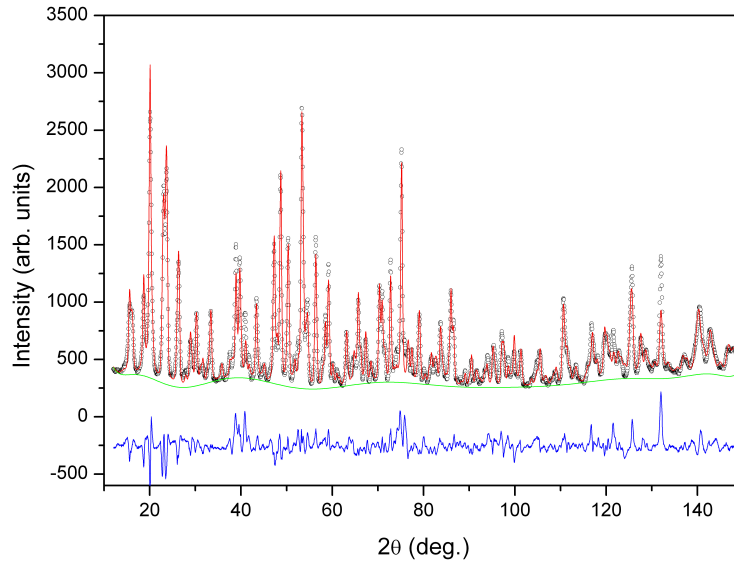


Figure 2.34 Rietveld plot relative to $K_{2.2}Fe_5F_{15}$ collected at 5 K.

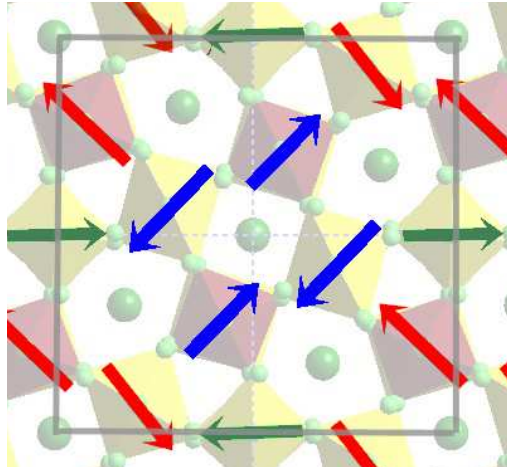


Figure 2.35 Rietveld plot relative to $K_{2.2}Fe_5F_{15}$ collected at 5 K.

The retrieved magnetic structure is exactly the same obtained for $K_3Fe_5F_{15}$, with each of the layers stacked along c having a nonzero resultant along b equal to 0.54

μ_B . However, since in this case the Fe^{2+}/Fe^{3+} ordering pattern observed in the two layers is the same (see figure 2.21), one may expect a complete compensation, thus zero net result. Indeed, magnetization measures evidence a nonzero value of the saturation magnetization, the ferrimagnetic behaviour being ascribed to the slight off-stoichiometry with respect to the ideal $K_2Fe_5F_{15}$, or to a possible deviation from the antiparallel alignment of the spins belonging to the two layers.

Atom	x	y	z	$M_x (\mu_B)$	$M_y (\mu_B)$	$M_z (\mu_B)$	$ M (\mu_B)$	$\Phi (^\circ)$	$\Theta (^\circ)$
Fe1	$\frac{1}{2}$	0	0.25	3.29(8)	0	0	3.29(8)	90	0
Fe2	0.2114	0.0728	0.25	-2.89(3)	2.01(2)	0	3.05(3)	90	138.7(5)
Fe3	$\frac{1}{2}$	0	0.75	-3.29(8)	0	0	3.29(8)	90	180
Fe4	0.2114	0.0728	0.75	2.89(3)	-2.01(2)	0	3.05(3)	90	-41.3(5)
Fe5	0.4272	0.2886	0.25	-2.89(3)	-2.01(2)	0	3.05(3)	90	-138.7(5)
Fe6	0.4272	0.2886	0.75	2.89(3)	2.01(2)	0	3.05(3)	90	41.3(5)

Table 2.4 Atomic positions and magnetic moments components in cartesian and polar coordinates of $K_{2.2}Fe_5F_{15}$ at 7 K.

Since the symmetry of the magnetic structure allows the setting of nonzero magnetization only along the b direction, the magnetization measures performed on oriented crystal, showing comparable values of magnetization along the a and b axes, are apparently not explained. However it must be taken into account that similar refinement results can be obtained in Pba'2', exchanging the effect of the primed operator (and consequently also of the magnetic moment components) between a and b axis.

IV. Multiferroic coupling

Evidences of magnetodielectric exchange were detected as anomalies in the electric permittivity. Figure 2.36 shows the electric permittivity and dielectric loss as a function of temperature in the range 125 - 375 K. A clear singularity –in particular in the dielectric loss- is located at decreasing temperatures as the frequency is

lowered. One may expect that at very low frequency the anomaly will be found at 200 K, in correspondence of the peak observed in magnetization measurements. However, the data collected at 100 Hz are too noisy to confirm this point. Specific studies should be devoted to the study of this phenomenon, which seem to cover an important role in the physics of the whole system.

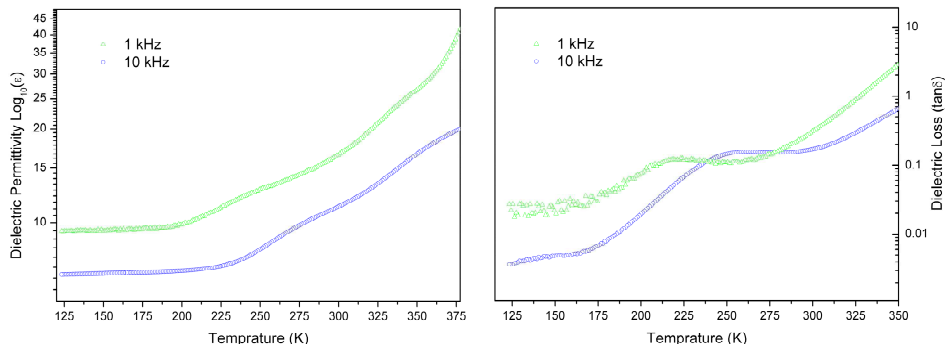


Figure 2.36 Dielectric permittivity and dielectric loss vs temperature for selected frequencies of the applied electric field.

2.1.5 $K_xFe_5F_{15}$

I. Structure

In the previous sections we have shown that the end members of the $K_xFe_5F_{15}$ family display similar properties, so that a detailed study of the intermediate compositions is not strictly required. In this section we will include some information in order to complete the picture, which is not dramatically changed with respect to the one depicted so far.

By the structural point of view the main point is the change of symmetry induced by a potassium content exceeding 2.8. Since the orthorhombic distortion takes

place in order to minimize the tensile stresses originated by the presence of K^+ ions in the perovskite cavity, the raising of the orthorhombic-tetragonal transition temperature is expected by increasing the potassium content.

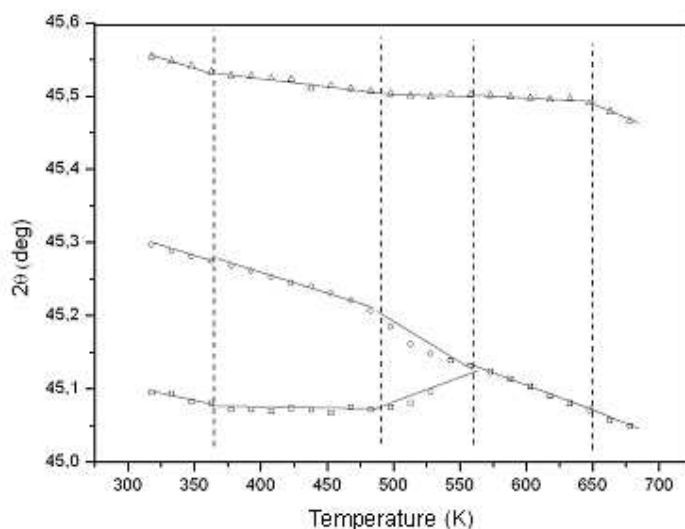


Figure 2.37 Thermal evolution of cell volume in $\text{K}_{2.90}\text{Fe}_5\text{F}_{15}$.

Figure 2.37 shows the behavior of the 002, 620 and 026 reflections in the high temperature range for the composition $\text{K}_{2.9}\text{Fe}_5\text{F}_{15}$. The orthorhombic distortion is clearly visible and disappears at about 560 K, that's to say at a slightly lower temperature with respect to $\text{K}_3\text{Fe}_5\text{F}_{15}$. The same happens for the vanishing of the charge order. Figure 2.37 points out also the existence of a further transition occurring in the tetragonal region (650 K). A similar transition is observed at a comparable temperature in $\text{K}_3\text{Fe}_5\text{F}_{15}$ (but in this case less evident) and at about 600 K in the tetragonal $\text{K}_{2.75}\text{Fe}_5\text{F}_{15}$ (Fig. 2.37). In the latter case the transition can be interpreted as the structural evolution from a ferro- to a paraelectric phase involving the change from $4mm$ to $4/mmm$ point symmetry. Since a similar transition is observed for different compositions in the tetragonal region of the phase diagrams, the hypothesis of a ferro-paraelectric transition occurring in the tetragonal phase

and not connected to the orthorhombic-tetragonal transition should be taken into account also for the potassium-rich members of the family.

Among the properties of the system, the temperature transition ascribed to the onset of FES seems to be the most affected by the stoichiometry and this is explained by the fact that the cooperative tilt of the FeF_6 octahedra (at the basis of the typical ferroelastic properties of the TTB structure) is related to the tensile stresses inside the structure. As said previously, the presence of large potassium ions increases the lattice stress, thus the tendency to structural distortions. This trend is confirmed by the data referring to $\text{K}_{2.75}\text{Fe}_5\text{F}_{15}$ (Fig. 2.38), where the transition is located at 380 K. No temperature variable PXRD data are actually available for potassium stoichiometry lower than 2.75, however a measurement performed on a single crystal sample of composition $\text{K}_{2.65}\text{Fe}_5\text{F}_{15}$ gives further corroboration to the idea that the FES transition temperature rises with the lowering of the potassium content. The FES modulation satellites are monitored in the temperature range 80 - 300 K –the experimental setup did not allow measurements above RT- and the interpolation of the intensity data suggests the FES transition to be located around 400 K (Fig. 2.38).

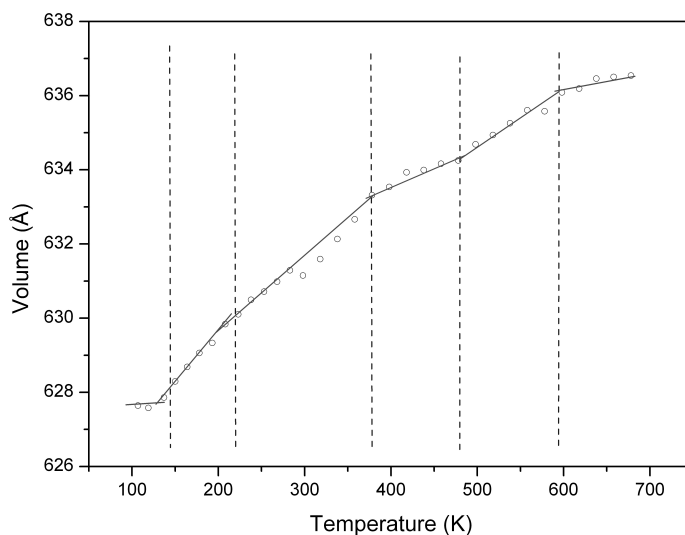


Figure 2.38 Thermal evolution of cell volume in $\text{K}_{2.75}\text{Fe}_5\text{F}_{15}$.

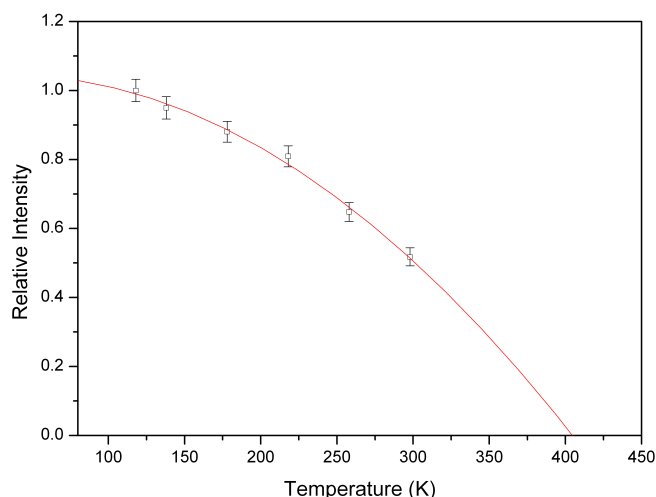
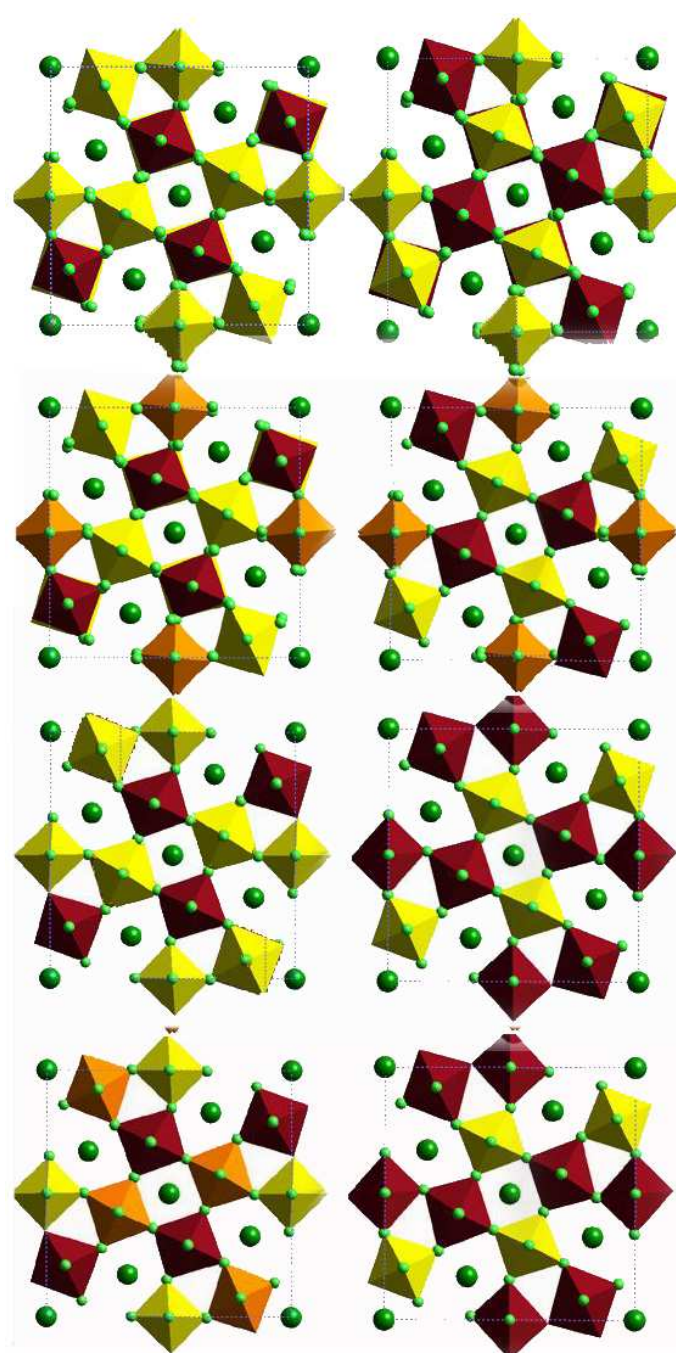


Figure 2.39 FES satellites intensity in $K_{2.65}Fe_5F_{15}$.

By the structural point of view, the possible variation of stoichiometry in $K_xFe_5F_{15}$ influences not only the orthorhombic distortion of the fundamental TTB cell and the appearing of the FES modulation, but also the charge ordering scheme, which varies continuously (Fig. 2.40) going from $K_2Fe_5F_{15}$ to $K_3Fe_5F_{15}$, since to an increase of the potassium content corresponds an increase of the Fe^{2+} content. Considering the TTB cell of $K_2Fe_5F_{15}$, 2/4 of the perovskite sites and both the extraperovskite sites in each layer are occupied by Fe^{3+} , while the other two B sites (perovskite) are occupied by Fe^{2+} . This charge order pattern is rotated of 90° along the c direction in adjacent layers by the effect of the 4_2 screw axis. The introduction of additional Fe^{2+} , corresponding to an increasing content of potassium, produces a mixing of $2+$ and $3+$ ions in the extraperovskite site, located at $(1/2 \ 0 \ z)$, which becomes completely occupied, iron on adjacent layers, by divalent or trivalent for the stoichiometry $K_{2.5}Fe_5F_{15}$. Further introduction of Fe^{2+} seem to be critical for the structure as the large dimensions of the ions tend to stress the system. As a consequence, for $x > 2.5$ the increasing content of iron(II) is distributed in two different sites (in orange in fig. 2.40), that for the potassium rich end member ($x=3$) are occupied by 50% of Fe^{2+} and 50% of Fe^{3+} .

**Fig. 2.40**

a) COS cell relative to the composition $K_2Fe_5F_{15}$, the dark red octahedra are occupied by Fe^{3+} , the yellow ones by Fe^{2+}

b) $K_xFe_5F_{15}$ for $2 < x < 2.5$. Orange octahedra identify the mixed valence sites.

c) COS cell of $K_{2.5}Fe_5F_{15}$.

d) $K_xFe_5F_{15}$ for $2.5 < x < 3$.

II. Phase diagram

The available data allows to define tentatively the complex phase diagram of the $K_xFe_5F_{15}$ system ($2 < x < 3$), reported in figure 2.41, where the ferroic phases are schematized by the use of different colors.

Below T_N the system, characterized by an ordered arrangement of the Fe^{2+} and Fe^{3+} cations, results to be ferrimagnetic, ferroelectric, and ferroelastic in the whole range of compositions. Above this temperature, up to 200 K, the magnetic background observed in neutron-diffraction patterns suggests the presence of short-range ordered magnetic interactions related to the presence of Van Vleck paramagnetism. At 200 K an electronic transition –whose nature should be clarified– takes place. The FES modulation, intrinsically connected to the typical ferroelasticity produced by the cooperative tilting in TTB, disappears at about 290 K in $K_3Fe_5F_{15}$, increasing its onset temperature with the lowering of the potassium stoichiometry. Owing to the orthorhombic distortion of its TTB structure, $K_xFe_5F_{15}$ (for $3 < 2.8$) remains ferroelastic up to the orthorhombic-tetragonal transition. Charge order involving Fe^{2+} and Fe^{3+} disappears below 490 K in $K_3Fe_5F_{15}$ while this transition temperature is placed at slighter lower values for $K_2Fe_5F_{15}$. For other compositions the transition has not been unambiguously located in temperature and Mossbauer studies are currently in progress in order to define the trend. Owing to the relaxor behavior of the system and to the experimental difficulty in performing dielectric characterization at high temperatures, the ferroelectric-paraelectric transition has not been located unambiguously. However, the presence of a structural transition detected for different compositions above 600 K, suggest that it could occur in the tetragonal region by a change from $4mm$ to $4/mmm$ point symmetry.

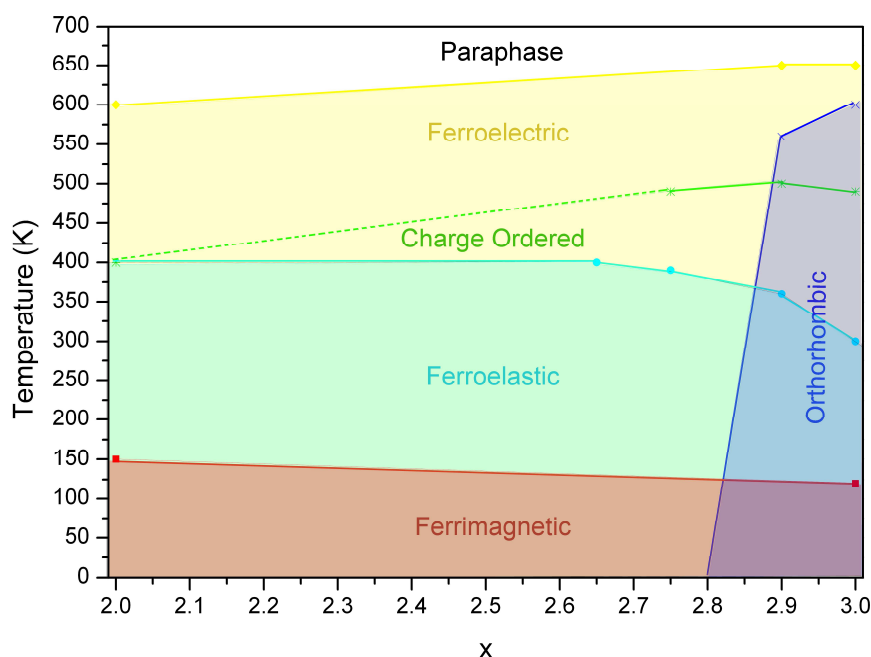


Figure 2.41 Phase diagram of the $K_xFe_5F_{15}$ in the composition range $2 < x < 3$.

III. Conclusions

The family of compounds $K_xFe_5F_{15}$ ($2 < x < 3$) can be considered a prototypic system for the study of multiferroism. Below T_N and for the whole range of compositions, indeed, these compounds are ferroelectric, ferroelastic and ferrimagnetic, thus complete multiferroics. Moreover the mixed valence nature of the system induces charge ordering, adding a further degree of freedom, largely tunable in virtue of the compositional tolerance of the structure. The phase diagram for the whole range of compositions has been tentatively drawn, clarifying some aspects and opening new scenarios, related for example to the dramatic change of properties observed below 200 K, where a spin-glass state is hypothesized. Evidences of couplings between the ferroic and charge degrees of freedom are

acknowledged, opening the way to the crossed study of the phenomena. However, the structural complexity makes the comprehension of the interplay between the ferroic orders quite complex, in particular on the basis of computational models.

2.2 TTB oxides

The introduction of magnetically active ions in a ferroelectric structure is one of the possible routes to the induction of magnetoelectric properties, although the substitution of nonmagnetic ions with magnetic ones may modify the ferroelectric properties of the whole system. In the introductory part of this chapter we illustrated the good ferroelectric properties and versatility of the BNN-derived compounds, which can undergo chemical substitutions in large intervals, without losing their properties. The present section deals with the synthesis and characterization of potential multiferroic compounds belonging to the BNN class in which niobium(V) is partially substituted by the magnetically active ion iron(III).

The research on barium sodium niobates is quite advanced on the technological level. As a consequence a large number of synthesis routes are employed in order to produce devices with suitable shape, dimensions and properties. Crystalline powders are usually obtained via solid state reaction or sol-gel route,^{35,36} the former technique allowing also the production of good quality thin films.³⁷ Molten salt technique allows the synthesis of large single crystals,^{38,39} as well as the micro pulling-down method.⁴⁰ The ones mentioned here are just the most popular techniques, however different routes can be exploited in order to obtain effective devices.

2.2.1 $RE_3Fe_2Nb_3O_{15}$

I. Synthesis

In section 2.0.3 we introduced the possibility of inducing magnetic properties in BNN by the substitution of niobium with iron and sodium with a rare earth element,

that should carry the positive charges lost with the substitution of Nb^{5+} with Fe^{2+} . Several TTB niobates containing rare earths in small concentrations are known, studied in particular for their optical properties, and the RE ions result to occupy preferentially the perovskitic A1 site of the TTB cell. However, in principle the maximum stoichiometry reachable implies the complete occupation of both the square and pentagonal channels with the rare earth ions, yielding a general formula $RE_3Fe_2Nb_3O_{15}$, with a 2/3 ratio of iron and niobium in the B sites. Only the member of the series with RE = Neodymium is reported to be synthesized in literature⁴¹ by solid state reaction. The ferroelectric properties were studied but no mention to magnetic characterization was made. As a consequence some attempts were performed in order to obtain this compound in which the magnetic ions may be not too diluted to induce spin order.

Stoichiometric quantities of highly pure Nd_2O_3 , Fe_2O_3 and Nb_2O_5 were grinded together and pressed into a pellet, the reaction temperature was initially taken from Ref[38], so that solid state reaction was carried out at 1300 °C for 1 hour in air. The samples obtained were analyzed by Rietveld method applied to powder x-ray diffraction data, which evidences the formation of $FeNbO_4$ (50%), $NdNbO_4$ (40%) and Fe_2O_3 (10%). Reaction temperatures and times were then explored systematically, without producing any improvement: no TTB phase was detected in any of the synthesis batches. Lower reaction temperatures (800-900 °C) partially change the products, giving $FeNb_2O_6$, $NdFeO_3$, $NdNbO_7$, $NdNbO_4$ and Fe_2O_3 , however, these conditions seem to be too mild to produce the TTB phase, also taking into account that $Ba_2NaNb_5O_{15}$ is obtained via solid state reaction at about 1250 °C.

In general $NdNbO_4$ seems to be a very stable phase, in particular at high T, subtracting niobium to the reactants, thus avoiding the crystallization of the $Nd_3Fe_2Nb_3O_{15}$ phase. Moreover, it is possible that the Nd^{3+} ions are not suitable to fit the large A2 sites: in BNN containing rare earths the small trivalent ions are observed to occupy the perovskitic site A1 rather than the pentagonal one. A

further possibility is thus to place larger ions in the A2 site (e.g. Ba^{2+}), while the RE ions should occupy the sole A1 site, consequently reducing the maximum reachable stoichiometry of iron from 2 to 1.

2.2.2 $Ba_2NdFeNb_4O_{15}$

I. Solid state reaction synthesis

A short study regarding $Ba_2NdFeNb_4O_{15}$ dated back in 1960 suggests this material as a magnetic ferroelectric, though the authors do not provide any characterization nor synthesis conditions or further informations.⁴² Krainik et al. report the synthesis and ferroelectric characterization of several iron-substituted TTB niobates,³⁸ among them appears $Ba_2NdFeNb_5O_{15}$, which is reported to be synthesized at 1260 °C for 1 hour of reaction time.

Following these indications, stoichiometric amounts of $BaCO_3$, Nd_2O_3 , Fe_2O_3 and Nb_2O_5 were grinded and pelletized, fired in air up to 1200 °C for 12 h. Pale yellow powders were obtained, characterized by the presence of inhomogeneous, darker, regions. PXRD evidenced the presence of TTB phase, suggesting that the different chromatic tonalities may correspond to different concentrations of iron. Consequently, the sample was grinded and thermally treated at the same conditions in order to homogenize the composition. Rietveld refinement indicates the presence of small amounts of segregated phases as barium ferrite $BaFe_{12}O_{19}$ besides the majority TTB phase (see inset in figure 2.24). The refinement of the occupation within the perovskitic A1 site suggests that the Neodymium stoichiometry is 0.95, while the A2 site is 100% occupied by barium ions, leading to the composition $Ba_2Nd_{0.95}Fe_{0.94}Nb_{4.06}O_{15}$, very close to the nominal one. The Rietveld plot is reported in figure 2.24, the agreement indices result to be $wRp = 0.087$, $R(F^2) = 0.039$.

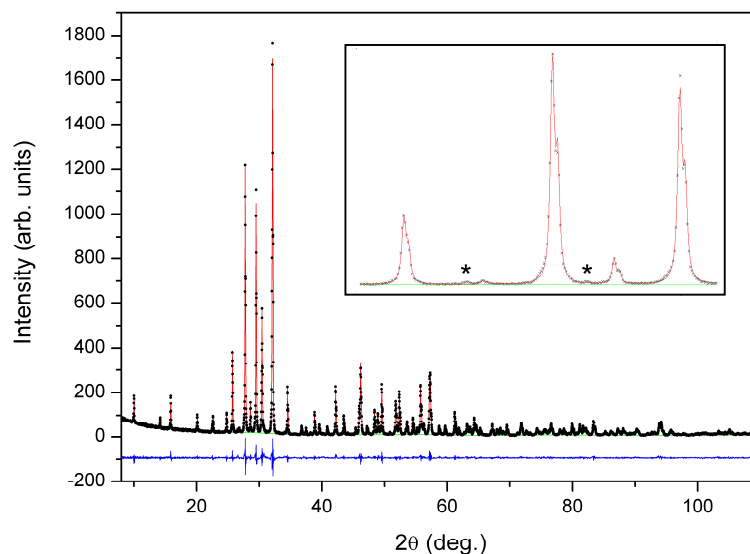


Figure 2.24 Rietveld plot of a sample of $\text{Ba}_2\text{Nd}_{0.96}\text{Fe}_{0.94}\text{Nb}_{4.06}\text{O}_{15}$.

A couple of recent works^{43,44} concerning the series $\text{Ba}_2\text{LnFeNb}_4\text{O}_{15}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) show that at room temperature several of these compounds are ferroelectric, with $P_s = 0.5 - 1.2 \mu\text{C}/\text{cm}^2$, and ferromagnetic, although it has been demonstrated that the magnetic properties are induced by barium ferrite, which always appears as segregated phase for nominal stoichiometry of rare earth close to 1. These compounds are claimed to be room-temperature “composite multiferroics”, however no real coupling can be assured by the segregation of one phase into another, since the dispersion should be extremely homogeneous in order to have a linear response of the system. In any case, the low-temperature magnetic behaviour of the system was not investigated, making worth a specific study in this region.

II. Magnetic characterization

Preliminary SQUID measurements were performed on polycrystalline samples of $Ba_2Nd_{0.96}Fe_{0.94}Nb_{4.06}O_{15}$ with applied field $H = 100$ Oe.

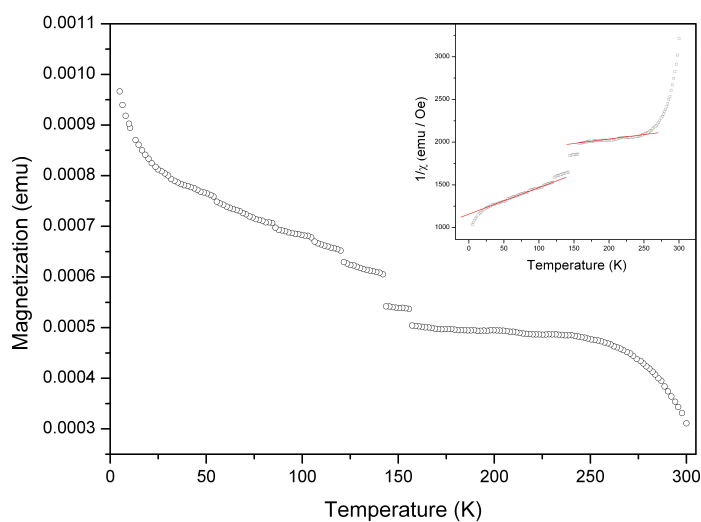


Figure 2.25 Field cooled magnetization curve of a polycrystalline sample.

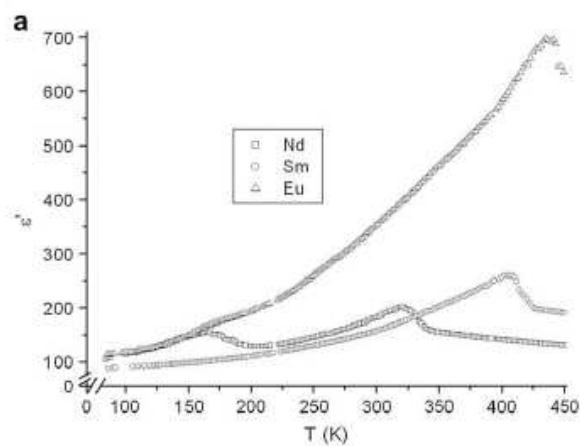


Figure 2.26 Real part of the electric permittivity of different $Ba_2LnFeNb_4O_{15}$ compounds. Squares correspond to $Ln = Nd$. Taken from reference 42.

The measurements reported in figure 2.25 show in the whole range of investigated temperatures the presence of nonzero magnetization, probably induced by barium ferrite, whose Curie temperature is placed well above RT. Nevertheless an anomaly, consisting in an increase of magnetization not ascribable to the high temperature magnetic ordering of Barium Ferrite, is observed at about 300 K, in agreement a peak in the dielectric constant detected by Josse et al. [42] just above room temperature. In the same way some discontinuous variations of the magnetization are detected around 150 K, matching a further peak of the electric permittivity reported in the same paper. These latter features we observed could be related to experimental problems, but the change in the slope of the inverse susceptibility (inset in figure 2.25) suggests an intrinsic contribution to the phenomenon. In this case the successive jumps observed in the magnetization could be related to compositional inhomogeneities, each one with a different transition temperature. The detected anomalies suggest the presence of magnetodielectric effects intrinsic in this compound.

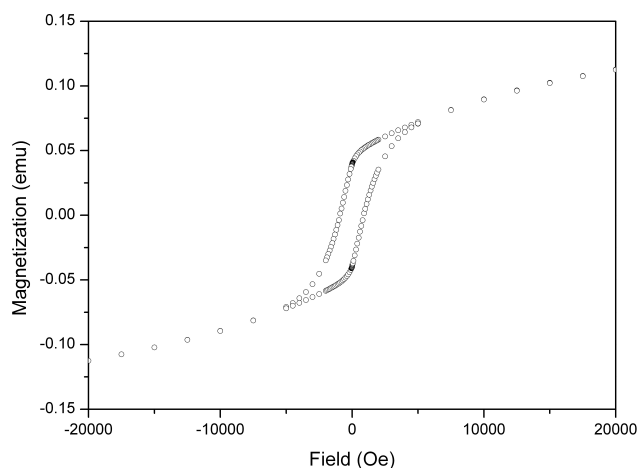


Figure 2.27 Room temperature hysteresis cycle.

. A $M(H)$ measure carried out on a powder sample at 300 K, showing the presence of hysteresis, with coercitive field $H_R \approx 900$ Oe and nonzero remanence, is reported in figure 2.27,. The paramagnetic contribution of the BNN phase is

clearly detected at high fields, where no saturation is reached up to $H = 2$ T. Even if the presence of barium ferrite is surely at the origin of the ferromagnetic component observed here, the magnetic transition detected just above room temperature makes worth the attempt to disentangle the contributions of BNN and barium ferrite. In the following section some efforts are provided in order to obtain single crystals, which could allow the study of the properties of the sole Tetragonal Tungsten Bronze phase.

III. High temperature solution growth

The availability of single crystal samples may allow the uncoupling of the contribution coming by TTB phase and barium ferrite, making also possible the characterization of oriented samples. Among the synthesis techniques cited previously, high temperature solution growth allows the production of single crystals characterized by high purity and large dimensions. Moreover it is particularly appropriate for the synthesis of materials presenting high melting temperatures and non eutectic systems, since a molten salt is used in order to solubilize the reactants without reaching their melting temperatures. However, the complexity of the technique resides in the large number of variables involved, since the presence of the flux can in principle influence the reaction products. Indeed, the molar ratio reactants/flux should be explored in order to obtain single phase products, as well as temperature, cooling rates and reaction times. In this case a mixture of B_2O_3 and Li_2CO_3 was chosen as flux medium for the promotion of crystal growth, considering that none of the elements involved in the formation of the flux should take place in the reaction. Only Li^+ is reported to be present in TTB structures, occupying the triangular C site in virtue of its small dimensions, however this feature is limited to particular cases, in which the structural and chemical conditions are particularly favourable.

High purity grade BaO , Nb_2O_5 , Nd_2O_3 and Fe_2O_3 were used as starting materials. The reactants, mixed together, were put in platinum crucibles and fired in air up to 1120 °C, the reaction temperature was kept constant for all the synthesis batches. Crystallization was promoted by slow cooling to room temperature and the crystals were separated from the glassy solidified salt by immersion in hydrochloric acid at about 50 °C. The products were analysed both by powder x-ray diffraction performed on grinded samples and by single crystal diffraction experiments. The TTB phases usually look like pale yellow prisms elongated in the direction of the c axis.

The syntheses carried out with reactants in stoichiometric ratios yielded the formation of the TTB phase, $NdNbO_4$ and $FeNbO_4$. The stoichiometry was determined by the refinement of both the occupancy of Nd and the ratio Nb/Fe in the B sites, suggesting the composition $Ba_2Nd_{0.55}Fe_{0.32}Nb_{4.68}O_{15}$. In general, the control over composition in presence of a solvent results to be more complex with respect to solid state reactions: in dynamical conditions indeed, the crystallization of phases thermodynamically or kinetically favored cannot be avoided. However, in order to maximize the quantity of iron in the structure several attempts were carried out using molar excess of iron and neodymium equal to 2 and 3. Some improvements to the final stoichiometry were obtained, despite the segregation of further unwanted phases was detected: $Ba_3Fe_2Nb_6O_{21}$ and Fe_2O_3 crystals are formed. The best result was obtained with an excess of 1 mole of Neodymium: in these conditions crystals with stoichiometry $Ba_2Nd_{0.73}Fe_{0.59}Nb_{4.41}O_{15}$ were produced; higher excess of rare earth do not improves the results, evidencing that a 50% occupation of the A1 site is probably the most favored configuration. Besides the stoichiometry of the starting reagents, also charge and dimensions of the ion sitting in the pentagonal site were explored, substituting BaO with SrO or K_2CO_3 . The iron composition within the TTB phase could not be increased, and additional phases were produced, like $LiNbO_3$ in presence of Strontium oxide.

IV. Structure

Single crystal X-ray diffraction data were collected using a SMART Bruker diffractometer equipped with a CCD area detector and Mo K α radiation. The structure solution was carried out using SIR2002²³ and data were refined full matrix using SHELX97²⁴ with anisotropic thermal parameters for all atoms except oxygen. Here is reported the structure of the compound displaying the highest stoichiometry of iron reached (Ba₂Nd_{0.73}Fe_{0.59}Nb_{4.41}O₁₅). The 2105 reflections collected were indexed on the basis of a cell with space group P4bm and lattice parameters a=b=12.488(15) c=3.921(2). On the two independent B sites the complementary ratio of Nb and Fe was refined, while Nd appeared to occupy only the perovskitic cavity; the overall stoichiometry was constrained in order to obtain the electroneutrality of the system. The thermal parameters of Nd1 and Nb2/Fe2 appear to be particularly small, evidencing that occupancy and atomic displacements strongly correlate, however this inconvenient can not be overcome since the occupancy of the A1 perovskitic site can in principle range between 1 to 0. The final agreement indices are R₁=0.0576 for 500 F_o>4sig(F_o) and 0.0605 for all 541 data; wR₂ = 0.1473, GooF=1.155. The niobium/iron atoms appear to be displaced from the centre of the coordination octahedra all in the same direction, being 2.01 and 1.93 Å the bond distances for Nb1/Fe1 along the c direction and 1.99-1.93 Å for Nb2/Fe2. This observation is likely caused by the ferroelectric properties of the system. In the other directions the overall dipole moment is forced to zero by symmetry constraints. As reported previously, the dielectric response of a Nd-rich phase of the compound is known [42] suggesting ferroelectric properties.

However specific polarization measurements are needed in order to describe the ferroelectric behaviour of the system, also considering that the stoichiometry is reported to affect considerably the dielectric properties of the Europium-substituted compound Ba_{6-2x}Eu_{2x}Fe_{1+x}Nb_{9-x}O₃₀.⁴⁵

Atom	x	y	z	sof	U_{eq}
Nd1	0.000	0.000	0.539(1)	0.181(2)	0.009(6)
Ba2	0.329(1)	0.172(1)	0.543(1)	0.500	0.019(1)
Nb1	0.074(1)	0.212(1)	0.044(9)	0.899(8)	0.007(1)
Fe1	0.074(1)	0.212(1)	0.044(9)	0.101(8)	0.007(1)
Nb2	0.000	0.500	0.046(2)	0.816(7)	0.009(7)
Fe2	0.000	0.500	0.045(2)	0.184(7)	0.009(7)
O1	-0.006(8)	0.342(9)	0.993(3)	1.000	0.009(3)
O2	0.217(1)	0.283(1)	0.069(7)	0.500	0.010(3)
O4	0.135(1)	0.067(1)	0.103(4)	1.000	0.031(4)
O3	0.000	0.500	0.554(2)	0.250	0.032(6)
O5	0.075(1)	0.200(2)	0.550(1)	1.000	0.043(4)

Table 2.1 Refined atomic coordinates, site occupancy and equivalent displacement parameters.

V. Magnetic characterization

The availability of large single crystals allowed the magnetic characterization of oriented samples. The orientation of the crystal was determined using an eulerian single crystal diffractometer, then the specimen was glued on a quartz sample holder easily allowing the orientation of the crystal with respect to the applied field into the SQUID magnetometer. $M(T)$ measurements were performed with an applied field of 50 Oe, evidencing that no magnetic ordering takes place down to 5 K. The system results to be paramagnetic in the whole range of temperatures investigated, pointing out that the magnetic ions are too diluted in the structure to interact, as a consequence further studies may be devoted to clarify the nature of the features observed in the magnetization measurements performed on iron-rich powder samples of composition $Ba_2NdFeNb_5O_{15}$.

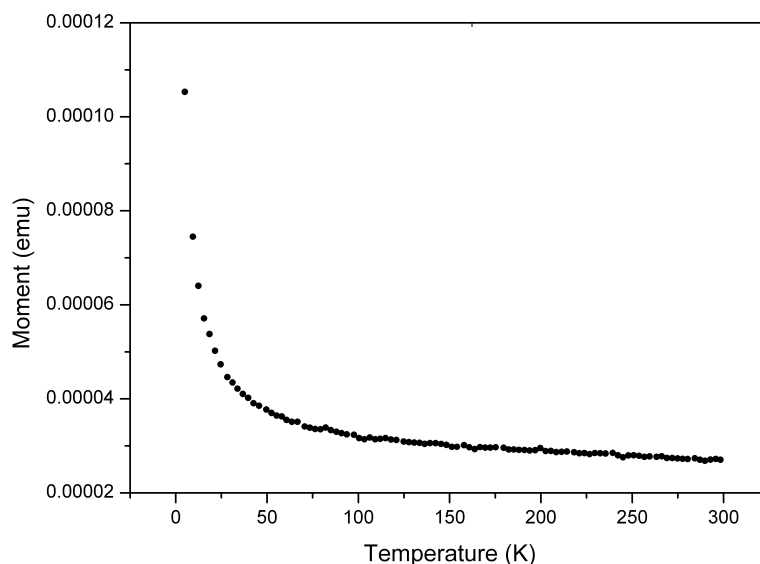


Figure 2.28 Magnetic moment vs temperature for a single crystal sample of stoichiometry $Ba_2Nd_{0.73}Fe_{0.59}Nb_{4.41}O_{15}$.

VI. Conclusions

The preliminary studies performed on the class of compounds with general formula $Ba_{6-2x}Nd_{2x}Fe_{1+x}Nb_{9-x}O_{30}$ suggest that these materials are not single phase multiferroics. However the investigation of the magnetodielectric behavior may be interesting in order to understand the nature of two different feature observed both on dielectric and magnetization measurements at about 300 and 150 K.

The solid state reaction allows the synthesis of crystalline powders with stoichiometry approaching the nominal one, although for concentrations of Rare Earth close to 1 the segregation of small amounts of Barium Ferrite seems unavoidable. On the other hand, molten salt technique assures a good homogeneity of the grown crystals, but the control of the final composition results quite complex and determined more by the relative thermodynamic stability and

growth kinetics of the different compositions rather than by the starting batch stoichiometry. Nevertheless further attempts should be devoted to the optimization of this synthesis route which allows the availability of single crystals, particularly interesting in the study of highly anisotropic systems like Niobates with Tetragonal Tungsten Bronze structure.

References

- ¹ J. J. Rubin, L. G. Van Uitert, H. J. Levinstein, *J. Cryst. Growth* **1**, 315 (1967).
- ² S. Singh, D. A. Draegert, J. E. Geusic, *Phys. Rev. B* **2**, 2709 (1970).
- ³ D. Trivedi, P. Tayebati, M. Tabat, *Appl. Phys. Lett.*, **68** (23), 3227 (1996).
- ⁴ J. E. Geusic, H. J. Levinstein, S. Singh, R. G. Smith, L. G. Van Uitert, *Appl. Phys. Lett.* **12**, 306 (1968).
- ⁵ R. G. Smith, J. E. Guesic, H. J. Levinstein, J. J. Rubin, S. Singh, L. G. Van Uitert, *Appl. Phys. Lett.* **12**, 308 (1968).
- ⁶ M. O. Ramirez, D. Jaque, L. Ivleva, L. E. Bausa, *Journal of Applied Physics* , **95** (11), 6185 (2004).
- ⁷ Y. Tomita, J. Bergquist, M. Shibata, *Journal of the optical society of America b-optical physics* **10**, 94 (1993).
- ⁸ P. B. Jamieson, S. C. Abrahms, J. L. Bernstein, *J. Chem. Phys.* **48**, 5048 (1968).
- ⁹ P. Labbè, H. Leligny, B. Raveau, J. Scheck, J. C. Toledano, *J. Phys.: Condens. Matter* **2**, 25 (1990).
- ¹⁰ J. Schneck, F. Denoyer, *Phys. Rev. B* **23**, 383 (1981).
- ¹¹ R. De Pape, *C. R. Hebd. Seances Acad. Sci.* **260**, 4527 (1965).
- ¹² A. Tressaud et al., *Bull. Soc. Chem. de France.* **10**, 3411 (1970).
- ¹³ J. Ravez, A. Simon, S. C. Abrahams, A. M. Mercier And R. De Pape, *Phase Transitions* **33**, 81 (1991).
- ¹⁴ E. Banks, M. Shone, R. F. Williamson, and W. O. J. Boo, *Inorg. Chem.* **22**, 3339 (1983).
- ¹⁵ P. Lacorre, J. Pannetier, G. Ferey, *J. Magn Magn. Mat.* **94**, 331 (1991).
- ¹⁶ S. Ishihara, J.-P. Rivera, E. Kita, Z.-G. Ye, F. Kubel, H. Schmid, *Ferroelectrics* **162**, 51 (1994).

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- ¹⁷ A. M. Hardy, A. Hardy, G. Ferey, *Acta Cryst. B* **29**, 1654 (1973).
- ¹⁸ E. Banks, S. Nakajima, G. J. B. Williams, *Acta Cryst. B* **35**, 46 (1979).
- ¹⁹ S. Fabbri, E. Montanari, L. Righi, G. Calestani, A. Migliori, *Chem. Mater.* **16**, 3007 (2004).
- ²⁰ J. Ravez, S.C. Abrahams, A.M. Mercier, L. Rabardel, R. de Pape, *J. Appl. Phys.* **67** (5), 2681 (1990).
- ²¹ J. Ravez, S.C. Abrahams, R. de Pape, *J. Appl. Phys.* **65** (10), 3987 (1989).
- ²² K. Byrappa and M. Yoshimura, *Handbook of hydrothermal technology*, Noyes Publications, (2001).
- ²³ A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *SIR2002, Program for Crystal Structure Solution and Refinement* IRMEC-CNR, Bari, Italy (2002).
- ²⁴ G. M. Sheldrick, *SHELXL93, Program for the Crystal Structure Refinement* University of Göttingen, Germany, (1993).
- ²⁵ M. Nespolo, G. Ferraris, H. Ohashi, *Acta Crystallogr., Sect. B: Struct. Sci.* **55**, 902 (1999).
- ²⁶ A.C. Larson, R.B. Von Dreele, "General Structure Analysis System (GSAS)", *Los Alamos National Laboratory Report LAUR 86-748* (2000).
- ²⁷ B. H. Toby, *EXPGUI*, a graphical user interface for GSAS, *J. Appl. Cryst.* **34**, 210-213 (2001).
- ²⁸ Y. Calage, S.C. Abrahams, J. Ravez, R. de Pape, *J. Appl. Phys.* **67** (1), 430 (1990).
- ²⁹ R. Blinc, B. Zalar, P. Cevc, A. Gregorovič, B. Žemva, G. Tavčar, V. Laguta, J.F. Scott, N. Dalal, *J. Phys. : Condens. Matter* **21**, 045902 (2009).
- ³⁰ S. Giri, K. Ghoshray, A. Ghoshray, N. Chatterjee, *Phys. Rev. B* **56**, 3347 (1997).
- ³¹ R. Blinc, G. Tavčar, B. Žemva, D. Hanžel, P. Cevc, C. Filipič, A. Levstik, Z. Jagličič, Z. Trontelj, N. Dadal, V. Ramachandran, S. Nellutla, J.F. Scott, *J. Appl. Phys.* **103**, 074114 (2008).

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- ³² A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *SIR2002, Program for Crystal Structure Solution and Refinement* IRMEC-CNR, Bari, Italy (2002).
- ³³ G. M. Sheldrick, *SHELXL93, Program for the Crystal Structure Refinement* University of Gottingen, Germany, (1993).
- ³⁴ C. Sezzi, *Thesis: Crescita, proprietà strutturali e diagramma di fase del sistema multiferroico $K_xFe_5F_{15}$ per $2 \leq x \leq 2.25$* (2008).
- ³⁵ A. V. P. Rao, D. S. Paik, S. Komarneni, *Journal Of Sol-Gel Science And Technology*, **10** (2), 22 (1997).
- ³⁶ M. Prades, H. Beltrán, N. Masó, E. Cordoncillo, A.R. West *Journal Of Applied Physics*, **104**, 104118 (2008).
- ³⁷ T. Yogo, W. Sakamoto, T. Isaji, M. Ichida, A. Nakamura, S. Hirano, *Journal Of The American Ceramic Society* **82** (10), 2672 (1999).
- ³⁸ Q.W. Huang, J. Xu, L.H. Zhu, H. Gu, P.L. Wang, *Journal Of The American Ceramic Society*, **88** (2) 447 (2005).
- ³⁹ Q.X. Bao, L.H. Zhu, Q.W. Huang, J. Xv, *Ceramics International*, **32** (7), 745 (2006).
- ⁴⁰ A. Yoshikawaa, H. Itagakia, T. Fukudaa, K. Lebboub, A. El Hassounib, A. Brenierb, C. Goutaudierb, O. Tillementb, G. Boulonb *Journal of Crystal Growth* **247**, 148 (2003).
- ⁴¹ N.N. Krainik, V.A. Isupov, M.F. Bryzhina, A.I. Agranovskaya, *Soviet Physics – Crystallography*, **9** (3), 281 (1964).
- ⁴² P.H. Fang, R.S. Roth, *J. Appl. Phys.*, **31** (5), 278S (1960).
- ⁴³ M. Josse, O. Bidault, F. Roulland, E. Castel, A. Simon, D. Michau, R. Von der Muhll, O. Nguyen, M. Maglione, *Solid State Sciences*, **11** (6), 1118 (2009).
- ⁴⁴ E. Castel, M. Josse, F. Roulland, D. Michau, L. Raison, M. Maglione, *Journal of Magnetism and Magnetic Materials* **321**, 1773 (2009).
- ⁴⁵ F. Roulland, M. Josse, E. Castel, M. Maglione, *Solid State Sciences*, **11**, 1709 (2009).

3. “Lone pair” driven multiferroism

The previous chapter of this thesis was devoted to the study of multiferroism in TTB systems where magnetoelectricity is achieved by the insertion of magnetic ions in a strongly ferroelectric structure. An alternative possibility is given by the presence of a stereochemically active ion in a system with magnetic properties: in this case magnetic and ferroelectric features are driven by different ions, making the mechanism for the (possible) coupling completely different in nature with respect to the previous example. It is well known that $6s^2$ ions (e.g. Tl^+ , Pb^{2+} , Bi^{3+}) carrying a “lone pair” on the electronic outer shell display strongly distorted coordinations, in virtue of intra-atomic hybridization of the metal s and anion p orbitals.¹ However, in lone-pair ferroelectrics, the electrical polarization is often induced not only by the asymmetrical coordination of the ion carrying the lone pair, but also by a polarization of the electronic cloud, producing a dipole moment that in some cases may be comparable in magnitude to the “point charge” contribution.

Several magnetoelectric compounds are known in which the presence of bismuth or lead is at the origin of ferroelectricity: $BiFeO_3$ is widely studied and appears to be one of the most promising magnetoelectric multiferroics, being both ferroelectric and magnetic at RT, displaying weak ferrimagnetism due to spin canting of an antiferromagnetic structure.^{2,3,4} Epitaxial $BiFeO_3$ films grown on $SrTiO_3$ revealed an enhancement both of the ferroelectric polarization (about one order of magnitude) and of the magnetic properties with respect to bulk samples,⁵ making of this compound a promising candidate to technological applications.

Another example is $PbVO_3$, firstly synthesized in 2004 [6] and hypothesized to be ferroelectric on the basis of structural considerations.⁷ Although no ferroelectric characterization is available, piezoelectricity was revealed in 2007 as well as the evidence of magnetic ordering below 130 K.⁸ Density functional electronic structure

studies suggest that PbVO_3 may be a magnetoelectric multiferroic;⁹ however, further characterizations are needed in order to define the ferroic features of the system.

One different topic regards BiMnO_3 , which for years was considered a promising ferromagnetic ferroelectric,¹⁰ but in recent years the possible presence of electrical polarization has been excluded on the basis of structural considerations indicating the compound as centrosymmetric. However this subject is still matter of debate.

All the lone pair multiferroics discussed so far display simple perovskite (of general formula ABO_3) structure. The present chapter of this work deals with the possibility of inducing ferroelectric properties in a peculiar class of manganites derived by simple perovskites, whose complex structure may easily bear the distortion induced by the lone pair ions. Moreover the distortion observed in these systems, the so-called quadruple perovskites, is often at the origin of ferromagnetic components, essential for magnetoelectric properties to set in, which are rarely observed in simple perovskites.

3.1 Quadruple perovskite manganites

3.1.1 Structure

The first compound to be synthesized displaying the “quadruple perovskite” structure is $\text{NaMn}_7\text{O}_{12}$, obtained in 1973 by a solid state reaction carried out in high pressure and high temperature conditions.¹¹ The symmetry was observed to be cubic, $a = 7.3036 \text{ \AA}$, space group $Im\bar{3}$ with two formula weights per unit cell. The description of the structure requires the doubling of the simple perovskite ABO_3 crystallographic axes, caused by the buckling of the MnO_6 octahedra centered on the B sites (see figure 3.1). This structure is stabilized only by the presence of Mn^{3+} ions with high Jahn-Teller distortion within $\frac{3}{4}$ of the A sites. In these conditions

manganese (III) shows a coordination that can be considered square planar, induced by the application of high pressure during the synthesis process; for this reason quadruple perovskite manganites are to be considered metastable compounds.

The general formula of the whole class of compounds can be written -in analogy with simple perovskites- as $(AA'_3)B_4O_{12}$, where is pointed out the “quadruple” nature with respect to ABO_3 . As it's been said, the A' site must be occupied by a strong Jahn-Teller ion, such as Mn^{3+} or Cu^{2+} , so that the oxidation state of the cation sitting in A tunes the valence of the transition metal (TM) ions on the B site, inducing charge ordering. This is a fundamental difference with respect to simple perovskites, where mixed valence causes an inhomogeneous distribution of charge, at the origin of most of the relevant properties displayed by these systems, such as giant magnetoresistance, metal-insulator transitions and structural features. Moreover the mixed valence ions in B occupy well defined crystallographic sites, making possible the direct observation, besides charge ordering, of orbital and spin orderings.

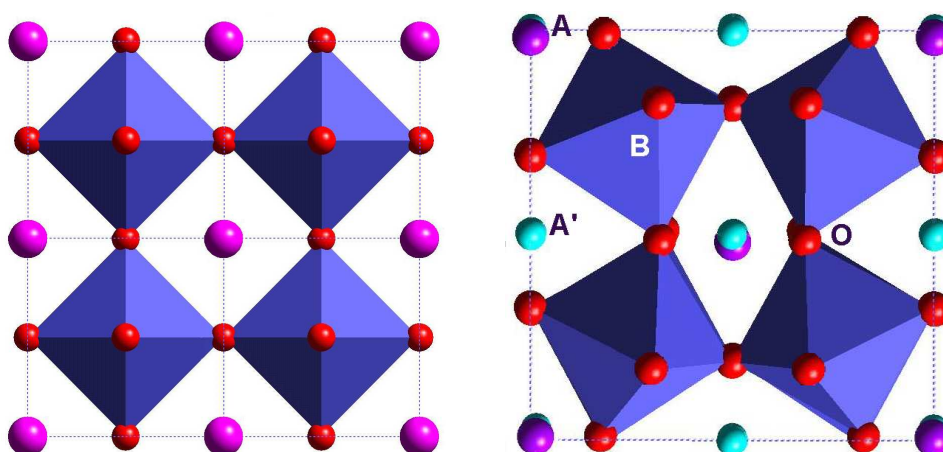


Fig. 3.1: Simple perovskite (left) and quadruple perovskite structure (right). The site are identified in relation to the general formula $AA'_3B_4O_{12}$.

3.1.2 Fundamental interactions

The physics related to strongly correlated materials are at the basis of the complex interactions displayed by several TM oxides, leading to peculiar properties such as superconductivity, metal-insulator transitions or half-metallicity. Typically, strongly correlated materials have incompletely filled *d* or *f* electron shells with narrow bands. Within this framework, the Coulomb interaction between electrons and the effect of exchange on their motion must be taken into account in order to describe the system, since each single electron has a complex influence on its neighbors. The interest related to the study of this kind of compounds is double: on the one hand the challenge derives by the theoretical difficulties related to effective modeling of the correlations; on the other hand the interplay and competition between the degrees of freedom given by spin, orbital and charge often leads to a large number of fascinating properties and collective phenomena.

Since quadruple perovskite manganites belong to the class of strongly correlated materials, the comprehension of the physical properties displayed by these compounds requires a large number of complex interactions to be considered collectively. Charge localization induces orbital ordering, driving the electronic and spin interactions, so that the study of magnetic and electrical phenomena requires the precise knowledge of the structural features. Consequently, the present work is mainly based on the definition of the structural attributes of $\text{BiMn}_7\text{O}_{12}$, a new member of the quadruple perovskites family, displaying the coexistence of both ferroelectric and ferromagnetic properties.

The fundamental interactions and physical effects observed in these compounds are briefly summarized in the following.

I. Jahn-Teller distortion

Jahn-Teller effect involves the interaction between valence electrons of a TM and the neighboring anions, inducing local distortions that can be cooperative in nature -thus becoming a collective phenomenon-, which modifies the scheme of interactions that may be hypothesized for the undistorted system.

It is well known that in octahedral coordination the degenerate d ground state of a TM undergoes an energy splitting yielding the formation of three t_{2g} low energy orbitals and two e_g orbitals with higher energy.

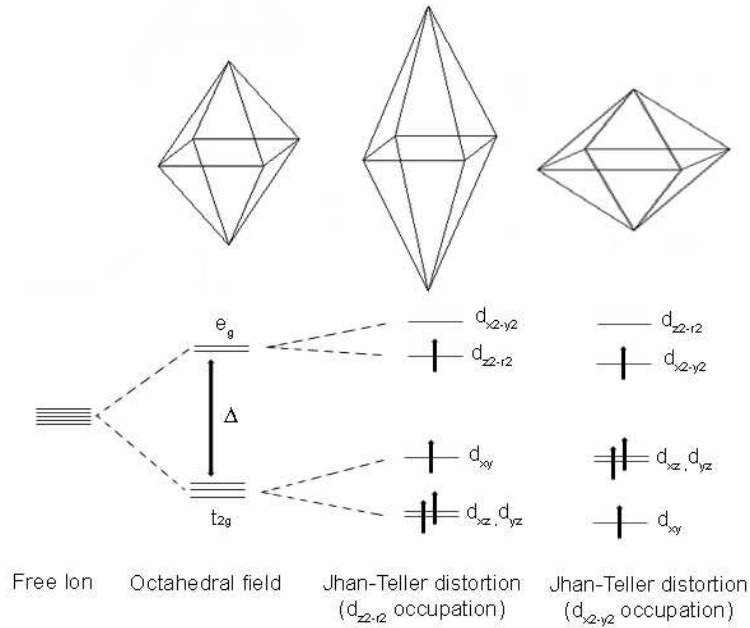


Fig. 3.2: Effect on the degeneracy of a TM d orbitals in octahedral crystal field and in presence of Jahn-Teller distortion for a d^4 ion.

The width of the induced gap (Δ) is a function of the crystal field applied to the cation. Manganese (IV) is in d^3 electronic configuration, so that the three t_{2g} orbitals (d_{xy} , d_{xz} , d_{yz}) are occupied by one electron, making the interactions with the coordination anions isotropic. In manganese (III) the additional electron can in

principle occupy one high energy e_g state, determining an high spin configuration, or be coupled with a t_{2g} electron (low spin). The setting of one of the two configurations depends on the energy balance between the crystal field splitting and the Coulomb repulsion related to the coupling of two electrons in t_{2g} . The Jahn-Teller theorem states that in presence of one (or three) electrons in e_g orbitals (as it happens in Mn^{3+}), it can be energetically favorable a distortion of the octahedral environment that lowers the crystal field splitting allowing the high spin configuration. Within this framework, if the d_{r2-z2} orbital is occupied, the repulsion between the high energy electron and the coordination anions produces an elongation of the octahedra in the z direction, while the occupation of the d_{x2-y2} orbital yields an elongation of the basal bonds (see figure 3.2).

II. Double exchange and superexchange

In mixed-valence simple perovskites the exchange interactions are determined by a process involving charge transfer between two different valence states on the same atom. The theory of “double exchange” was formulated by Zener in 1951 in order to describe the magnetic behavior of doped manganites with perovskite structure.¹² In these systems the states $Mn^{3+}O^{2-}Mn^{4+}$ and $Mn^{4+}O^{2-}Mn^{3+}$ are degenerate and the two configurations are connected by the double exchange matrix element, related to the transfer of one electron from Mn^{3+} to the O^{2-} , simultaneous with the transfer from O^{2-} to Mn^{4+} . Because of strong Hund's coupling, the transfer matrix element has finite value only when the core spins of the Mn ion are aligned ferromagnetically. The coupling of the degenerate states lifts the degeneracy and the system resonates between the two states if the core spin are parallel, leading to a conducting ground state.

While double exchange involves a real electron transfer between two ions with different charge, superexchange (Kramers-Anderson exchange) is the mechanism usually adopted to interpret the interactions between two next-to-nearest

neighboring positive ions through a non-magnetic anion, via a virtual charge transfer.^{13,14} When the direct overlap of *d* orbitals is weak, their superposition with the *s* and *p* wave functions of the ligands must be considered: since no effective hopping is involved, the interaction yields an antiferromagnetic coupling of the spins. However, if the two next-to-nearest neighbor positive ions are connected at 90 degrees to the bridging non-magnetic anion, the interaction can be a ferromagnetic.

III. Goodenough-Kanamori semiempirical rule

The Goodenough-Kanamori rule defines the nature of the spin-spin interactions between two atoms on the basis of the orbital occupation and orientation, taking into account the superexchange or semicovalent exchange interactions.

J.B. Goodenough introduced in the second half of the '50s the concept of semicovalency for the Mn-O bonds: the length of the bond is characteristic of the degree of the covalency and the magnetic, structural and electronic properties resulted to be deeply affected by the nature and the relative orientation of these bonds.¹⁵ Later on, Kanamori developed mathematically the theory suggesting that to one given orbital ordering scheme (derived by the observation of the structural distortions) corresponds a defined scheme of magnetic interactions.¹⁶

The coupling is antiferromagnetic when superexchange interactions take place between overlapping orbitals that are each half-filled, while ferromagnetic exchange is a consequence of virtual electron transfer between one half-filled and one empty orbital or filled/half filled orbital. In this picture superexchange and semicovalent exchange are considered equivalent. This empirical rule is verified in perovskitic structures where interactions take place with 180° bond angles. Nonetheless in some cases the validity of the Goodenough-Kanamori theory may be extended to distorted systems.

3.1.3 State of the art

Several compounds of the family $(A^xMn^{3+}_3)(Mn^{3+}_{1-x}Mn^{4+}_{3-x})O_{12}$ are known. The general formula is written here in a proper form to point out how the valence of the ion in A tunes the ratio between trivalent and tetravalent manganese ions in the B site. As said previously, the A' site can accommodate only the highly Jahn-Teller distorted Mn^{3+} ions. Although all the members of the series display similar structural and physical properties, some remarkable differences make worth the description of the fundamental features of the known systems.

In $NaMn_7O_{12}$ the presence of the monovalent ion Na^+ in A yields a ratio Mn^{3+}/Mn^{4+} equal to 1:1 in the B site.⁸ At room temperature the symmetry is cubic $Im\bar{3}$ and no charge ordering is observed. At 180 K a cubic to monoclinic transition is reported to take place¹⁷ related to the localization of the e_g electron of manganese, inducing Jahn-Teller distortion as a consequence of the occupation of the $d_{x^2-y^2}$ orbital.

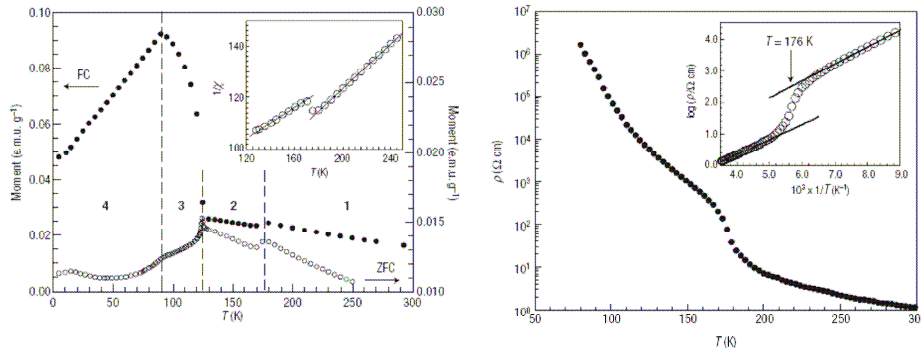


Fig. 3.3: Left: $M(T)$ curve of $NaMn_7O_{12}$. In inset is reported the inverse susceptibility in correspondence of the charge order-disorder transition. Right: increase of resistivity due to the charge localization. Inset: Arrhenius plot in the transition region. Both Images taken from Ref. 18.

This transition is accompanied by a change in the susceptibility –evidencing a variation of the paramagnetic properties of the system, reported in the inset in figure 3.3- and an increase below 180 K of the resistivity due to the localization of

the carriers (fig. 3.3, right). At 125 K the magnetization measurements (reported in figure 3.3, left panel) show the setting of nonzero magnetization¹⁸ due to the ordering of the manganese ions sitting in the B site, yielding a magnetic structure of the CE type.¹⁹ At 90 K an antiferromagnetic transition related to the spin ordering of the A' site is reported.

The introduction of the divalent cation Ca^{2+} in the A site yields a symmetry change in the charge ordered phase -that in this case is observed at room temperature- related to the need to accommodate Mn^{4+} and Mn^{3+} ions in a ratio 6:2. The crystallographic cell is rhombohedral $R\bar{3}$, and the Jahn-Teller undistorted Mn^{4+} ions are placed on the threefold axis suggesting that the symmetry of the charge ordered phase may be related to the relative concentration of tri- and tetravalent manganese ions. The apical compression of the Mn^{3+}O_6 octahedra²⁰ suggests the occupation of the $d_{x^2-y^2}$ orbitals, in analogy with $\text{NaMn}_7\text{O}_{12}$. The magnetic behavior results to be complex, characterized by the presence of ferrimagnetic ordering²¹ between 86 and 50 K, while below 50 K the magnetic structure is modulated.²² Noteworthy is the recent observation of magnetoelectric effect in $\text{CaMn}_7\text{O}_{12}$ polycrystalline samples, ascribed to improper ferroelectricity due to the coexistence of charge ordering and magnetostriction.²³

Two compounds having trivalent ions in the A site are reported. $\text{LaMn}_7\text{O}_{12}$ is monoclinic $I2/m$ at room temperature, displaying charge localization related to the ordering of the $d_{z^2-r^2}$ orbitals.²⁴ At high temperature ($T > 803$ K) the system undergoes a monoclinic to cubic transition related to the loss of orbital ordering. The space group of the high symmetry phase is $I\bar{3}m$, the same observed at room temperature in $\text{NaMn}_7\text{O}_{12}$, suggesting that the cubic structure is a common feature of the high temperature phases for all the $(\text{AMn}^{3+}_3)\text{Mn}_4\text{O}_{12}$ compounds. The magnetic behavior is similar to the one observed in the Sodium substituted member of the series, displaying two transitions –localized at 78 and 21 K– ascribed, on the basis of neutron diffraction data, to the ordering of the spins on the manganese ions placed in the A' and B sites respectively. Magnetization

measurements are reported in figure 3.4, evidencing the presence of nonzero magnetization in the field cooled curves between 78 and 21 K, interpreted as the evidence of Dzyaloshinsky-Moriya interaction yielding spin canting of a collinear antiferromagnetic structure. The analysis of the neutron diffraction data supported this hypothesis revealing an antiferromagnetic ordering of the magnetic moments on the B sites producing a C-type structure. The low-temperature transition corresponds to the ordering of the Mn ions in the A' site in purely AFM fashion, as confirmed by the magnetization measures.

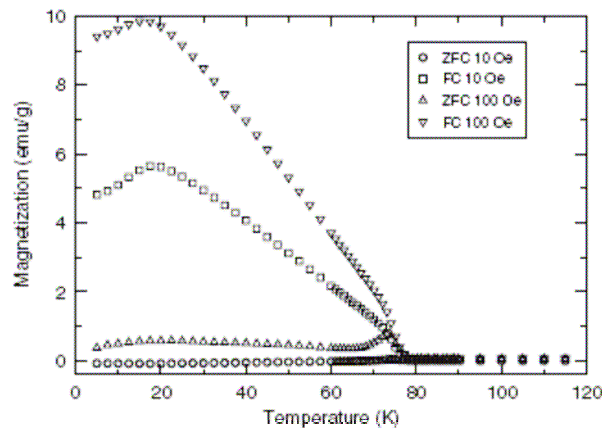


Fig. 3.4: Magnetization vs. temperature curved for different values of the applied field. Image taken from Ref. 24.

The second reported quadruple perovskite manganite with a trivalent ion in the A site is $\text{PrMn}_7\text{O}_{12}$.²⁵ This compound is the sole member of the family showing polymorphism, specifically the coexistence of one monoclinic $I2/m$ and one rhombohedral $R-3$ structure, attributed to different electronic configurations of the octahedrally coordinated manganese (III) ions. The monoclinic phase is similar to the one observed in $\text{LaMn}_7\text{O}_{12}$, with evidence of orbital ordering at room temperature, related to the occupation of the $d_{z^2-r^2}$ state. The magnetic characterizations performed on the $I2/m$ phase show the presence of DM interaction yielding nonzero magnetization below 70 K, in analogy with $\text{LaMn}_7\text{O}_{12}$.

However, the second transition, likely related to the ordering of the A' site, is not detected. For what concerns the rhombohedral phase, should be pointed out that 1/4 of the Mn ions in B are placed in the undistorted 3e sites, so that in the charge localized phase (observed at RT) the Jahn-Teller Mn^{3+} ions in high spin configuration cannot be placed in these sites. As a consequence, since the presence of Mn^{4+} due to oxygen stoichiometry or vacancy of praseodymium are excluded due to the high density of the structure, the low-spin configuration for 1/4 of the Mn^{3+} ions was hypothesized. This statement is supported by the magnetization data, which shows different slopes for the inverse susceptibility curves of the two phases, corresponding to Bohr magnetons contents in line with the calculated ones. One single AFM transition placed at 44 K is observed, evidencing the drastic variation of properties related to the symmetry change.

Noteworthy is the fact that, in general, the ratio of distorted/undistorted ions in the B sites seem to be the driving force to the setting of the crystal structure in the charge ordered phase. This is a remarkable difference with respect to simple perovskite systems, where the structure is mainly determined by the size of the "A" ion. This variable seems to affect primarily the strength of the magnetic interactions by changing the Mn-O-Mn bond angle, thus determining different degrees of overlap of the manganese *d* and oxygen *p* orbitals. In particular, can be stated that for smaller A ions the deviation of the angle from 180° increases, yielding a lowering of the magnetic ordering transitions.

3.2 BiMn₇O₁₂

BiMn₇O₁₂ represent the third known member of the series with a trivalent ion on the A site; however it differs from the lanthanum and praseodymium-based compounds for the fundamental properties induced by the Bi lone pair. As will be discussed later on, in fact, this is the sole quadruple perovskite compound known so far to crystallize in a noncentrosymmetric space group, allowing in principle the insurgence of ferroelectricity. This feature, as well as the peculiar magnetic structure, is ascribed uniquely to the stereochemical effect produced by the Bi³⁺ ion, that can be considered the driving force for the whole variety of interesting phenomenology observed in BiMn₇O₁₂.

3.2.1 Synthesis

The effects of pressure in solid state chemistry are mostly unexplored, both for the technical difficulty related to the achievement of well controlled high hydrostatic pressures and for drastically changes induced by high pressure on the physical properties at the solid state with respect to ambient conditions. As a consequence high pressure can be considered one of the most promising routes for the discovery of new materials, through modifications of the structure of already known compounds or the synthesis of completely new materials thermodynamically stable only at HP-HT. Besides a dramatic increase in density, changes in orbital hybridization and coordination number can be induced by HP, with deep modification of the electronic structure and transport properties. Examples include insulator-metal transitions and induction of superconductive properties.

In general the effects of pressure are numerous, involving structural, physical and chemical properties: the strongest distortions may be expected between atoms

separated by the weakest bonds, on the other hand compression increases the covalent character of the bond involved. The increase of pressure favours close packing, increases the coordination number and oxidation state. The change in coordination number is usually accompanied by an elongation of the bonds and by an increase in the ionic character. Anions are more compressible than the cations, undergoing deep modifications of their electronic and bond properties.

As anticipated in section 3.1.1, the synthesis of manganites with quadruple perovskite structure requires High Pressure/High Temperature (HP/HT) conditions. Despite the generation of high uniaxial pressures (up to 300 GPa) is quite easy, as it happens Large Volume Presses or Diamond Anvil Cells, the application of hydrostatic forces in the high pressure region is extremely complex. In fact the adoption of any gaseous or liquid medium to distribute the pressure applied by a piston, anvil or screw into an isotropic pressure would produce the solidification of the medium itself for very high pressures; in general 20 kbar is maximum pressure reached with this technique. As a consequence, the synthesis of compounds requiring high isotropic pressure has to be carried out using a solid-medium technique as the multi-anvil pressure system available at the IMEM Institute. The apparatus, shown schematically in figure 3.5, consists of a 1000 ton hydraulic press and a Walker multi-anvil module at the centre of which the sample assembly is placed. The reactants are inserted into a cylindrical graphite furnace, protected by a platinum or gold foil, which may also separate different samples if more than one reactions need to be carried out in identical PT conditions. A thermocouple is placed in proximity of the samples for accurate temperature determination. An octahedron of variable size –in relation to the maximum pressure desired- contains the graphite furnace. Pyrophyllite is used as final pressure medium in order to avoid any conductive contact between graphite and the surrounding set of tungsten carbide cubes, whose corners are truncated with the aim of accommodate the pyrophyllite octahedron. The cubes in turn are nested within six cylindrical wedges fabricated from tool steel placed inside a containment ring and it converts the

uniaxial loading of the two large hydraulic rams in to a quasi-hydrostatic force converging on the small octahedral sample assembly. Pressure and temperature determination are guaranteed by programmable controllers through an accurate calibration using standard compounds with well known phase transitions. The maximum operating conditions are 250 kbar and temperatures as high as 3000°C, depending upon sample size.

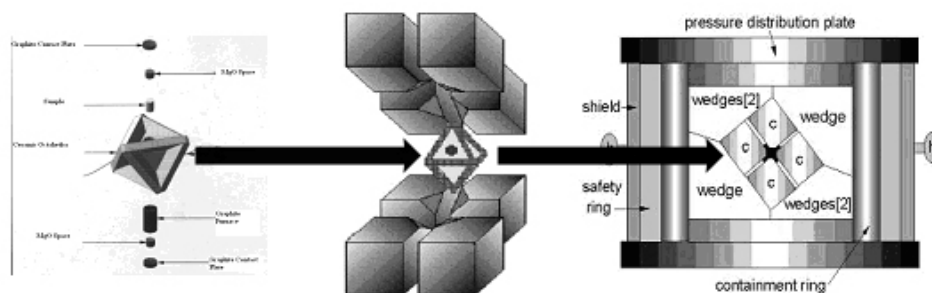


Fig. 3.5: Schematic representation of the Multianvil apparatus.

Left to right: Cylindrical graphite furnace and MgO octahedron.

System of eight Tungsten Carbide cubes containing the MgO octahedron.

Walker module composed of six steel wedges and pressure distribution plates.

BiMn₇O₁₂ was obtained by solid state reaction synthesis in high pressure/high temperature (HP/HT) conditions. Mn₂O₃ (Ventron 98%) and Bi₂O₃ (Merck 99%) in stoichiometric amounts were mixed, finely grounded in glove box and encapsulated in a Pt foil inserted in the MgO octahedral cell and in the multi anvil apparatus. The pressure was increased at a rate of 160 bar/min and then the sample was heated up to the reaction temperature at a rate of 50±C/min. The optimal conditions for the synthesis of a mixture of bulk material and single crystals were identified as 40 kbar and 1000°C. After 2 hours in these conditions the sample was cooled down to room temperature by switching off the heater. The pressure was finally slowly released at 0.4 bar/min. The reaction products, checked by x-ray powder diffraction, evidence the presence of BiMn₇O₁₂ as the majority phase, bismuth oxycarbonate or Mn₃O₄ being the unique impurities detected. The formation of

carbonate is likely due to the interaction of the reactants with the graphite heater. A rough refinement of the intensities of a PXRD pattern referring to an average synthesis (see fig 3.6) suggests that the amount of unwanted phase (in this case Bi₂CO₅) is about 4%.

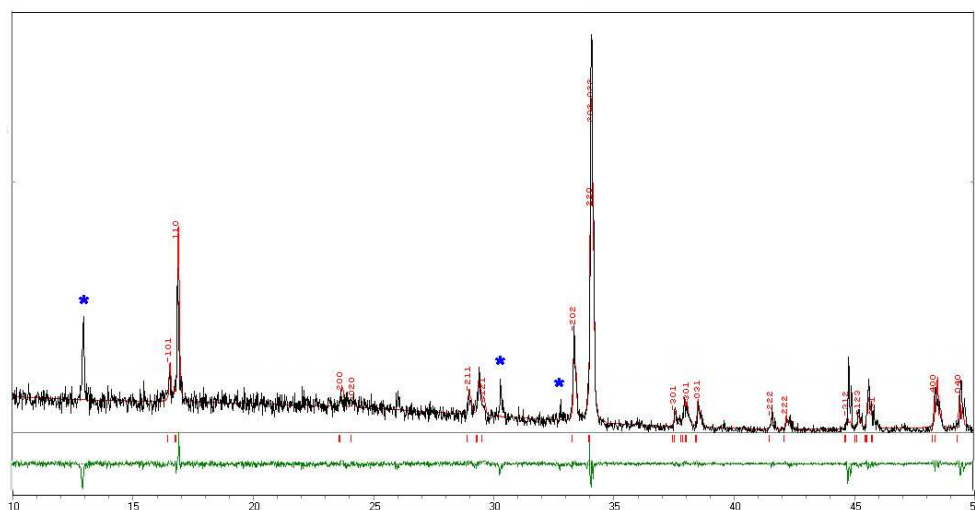


Fig. 3.6: Powder x-ray diffraction pattern of a BiMn₇O₁₂ sample (black). In red are plotted the calculated intensities while in green is shown the difference $F_c - F_o$. Blue stars indicate the contribution due to Bi₂CO₅.

3.2.2 Structure

The crystal structure of BiMn₇O₁₂ was determined at room temperature by single crystal X-ray diffraction. The MoK α wavelength was used as incident radiation for the data collection, carried out using a Bruker ASX Smart diffractometer equipped with a CCD area detector. Intensities were integrated in the 2θ range 3.79 - 28.83 ° on the basis of a monoclinic unit cell with parameters $a = 7.5351(15)$, $b = 7.3840(15)$, $c = 7.5178(15)$ Å and $\beta = 91.225(3)$ °. The structure was solved using SIR2002²⁶ and then refined with the SHELX97²⁷ software. Initially the refinement was carried out using the space group $I2/m$, in analogy with the other known

monoclinic quadruple perovskite manganites. The refinement converged to good values of the agreement indices: $R_1 = 0.0535$, $wR_2 = 0.1413$ and $g.o.f = 1.101$ for 562 data and 59 parameters. However a peculiar behaviour of the anisotropic displacement parameters (a.d.p.) was observed, reported in figure 3.7, evidencing an elongation in a common direction of the ellipsoids corresponding to oxygen atoms. The unusual trend of the displacement parameters evidences the presence of static disorder taking place mainly in the ac plane, and was interpreted as the necessity to lower the space group symmetry in the refinement process. As a consequence the refinement in the noncentrosymmetric space group $I2$ was carried out, also taking into account the possible occurrence of polar domains, thus employing the twin option of the refinement software. The results obtained were comparable in term of agreement indices and behaviour of the adp's to those obtained in the centrosymmetric space group.

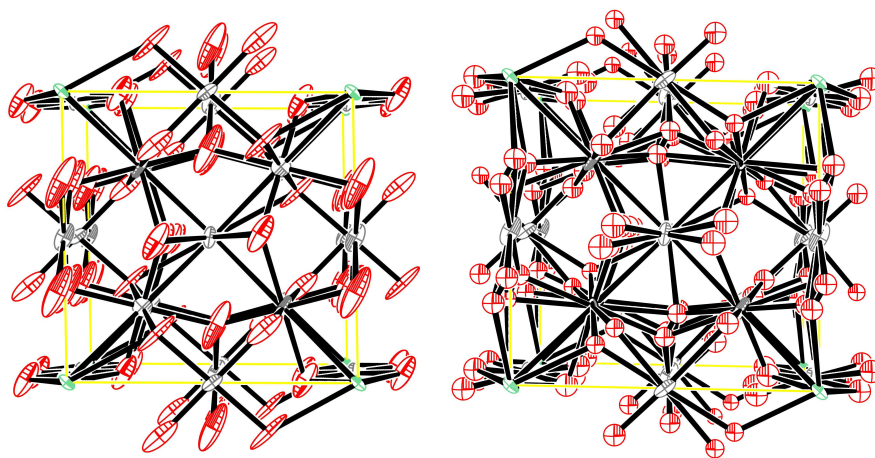


Fig. 3.7: BiMn₇O₁₂ cell viewed in the $[010]$ projection where the anisotropic displacement parameters are represented by ellipsoids drawn at the 50% probability level. In red are shown the oxygen atoms, in grey manganese and green bismuth.

Left: refinement in the centrosymmetric space group $I2/m$.

Right: refinement in the noncentrosymmetric space group Im .

The refinement obtained using the Im space group yielded a noticeable improvement both of the refinement indices ($R_1 = 0.0391$, $wR_2 = 0.0928$ and $g.o.f =$

1.113 for 1082 data and 103 parameters) and a normalization of the anisotropic displacement parameters (see figure 3.5, right panel).

Atom	x	y	z	U _{eq}	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Bi1	0.0284(6)	0	0.0173(6)	0.0255(3)	0.0247(8)	0.0307(3)	0.0210(5)	0	-0.0028(4)	0
Mn1	0.0030(30)	0	0.4951(3)	0.0106(6)	0.0066(15)	0.0185(10)	0.0066(16)	0	-0.0041(10)	0
Mn2	0.4997(4)	0	0.5019(4)	0.0102(6)	0.014(2)	0.0101(9)	0.0069(13)	0	-0.0041(11)	0
Mn3	0.4955(2)	0	-0.0022(4)	0.0101(6)	0.0034(14)	0.0082(9)	0.0185(14)	0	-0.0049(10)	
Mn4	0.2542(3)	0.7419(3)	0.2540(3)	0.0083(4)	0.0080(10)	0.0076(6)	0.0093(8)	-0.0020(7)	-0.0031(7)	-0.0030(8)
Mn5	0.2476(2)	0.74930(17)	0.74590(18)	0.0067(5)	0.0066(12)	0.0084(6)	0.0049(10)	-0.0016(5)	-0.0046(7)	0.0006(6)
O1	0.3366(19)	½	0.1827(18)	0.015(2)	0.006(5)	0.023(5)	0.015(6)	0	-0.007(4)	0
O2	0.1916(19)	0	0.6755(19)	0.017(2)	0.010(6)	0.023(5)	0.017(6)	0	-0.007(4)	0
O3	0.1742(18)	0	0.3031(18)	0.017(2)	0.004(5)	0.029(6)	0.017(6)	0	-0.001(4)	0
O4	0.825(2)	0	0.3094(19)	0.020(3)	0.012(6)	0.029(6)	0.017(6)	0	-0.010(5)	0
O5	0.4910(16)	0.8086(13)	0.3282(14)	0.0196(19)	0.016(4)	0.028(4)	0.015(4)	-0.015(3)	-0.006(3)	-0.006(4)
O6	0.3081(15)	0.8259(10)	-0.0105(14)	0.0192(15)	0.019(4)	0.016(4)	0.023(4)	0.001(3)	-0.009(3)	-0.001(3)
O7	0.0167(14)	0.6830(13)	0.1765(15)	0.0197(19)	0.009(4)	0.031(4)	0.019(4)	-0.010(3)	-0.006(3)	-0.010(4)
O8	0.6796(15)	0.1800(10)	0.0112(13)	0.0162(15)	0.017(4)	0.015(4)	0.016(4)	0.000(3)	-0.008(3)	-0.002(3)

Table 3.1: List of ccoordinates and atomic displacement parameters. U_{eq} is one third of the orthogonoalized U_{ij} tensor, which is defined as $\exp(-2\pi^2(U_{11}h^2(a^*)^2+...+2U_{12}hk(a^*)(b^*)+...))$.

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Bi1-O3	2.392(14)	Mn2-O7	2x1.887(11)	Mn5-O8	1.897(10)
Bi1-O6	2x2.481(9)	Mn2-O5	2x1.925(10)	Mn5-O6	1.961(11)
Bi1-O7	2x2.631(10)	Avg	1.906(11)	Mn5-O2	1.969(6)
Bi1-O5	2x2.697(10)	Q(ij)	3.039	Mn5-O4	1.986(6)
Bi1-O4	2.706(13)			Mn5-O5	2.087(12)
Bi1-O2	2.872(15)	Mn3-O6	2x1.910(10)	Mn5-O7	2.163(11)
Bi1-O1	2.874(14)	Mn3-O8	2x1.923(10)	Avg	2.01(9)
Bi1-O8	2x2.945(11)	Avg	1.916(10)	Q(ij)	3.013
Avg	2.497(11)	Q(ij)	3.031		
Q(ij)	2.973			Atoms	Angle (°)
		Mn4-O7	1.920(12)	Mn4-O1-Mn4	130.24
Mn1-O1	1.907(14)	Mn4-O5	1.922(13)	Mn4-O3-Mn4	138.94
Mn1-O4	1.916(16)	Mn4-O1	1.969(6)	Mn4-O5-Mn5	2x 136.21
Mn1-O2	1.943(16)	Mn4-O3	2.035(5)	Mn4-O6-Mn5	2x 137.95
Mn1-O3	1.956(13)	Mn4-O8	2.076(11)	Mn4-O7-Mn5	2x 138.32
Avg	1.931(15)	Mn4-O6	2.130(11)	Mn4-O8-Mn5	2x 137.22
Q(ij)	2.933	Avg	2.009(10)	Mn5-O2-Mn5	140.21
		Q(ij)	2.998	Mn5-O4-Mn5	135.97

Table 3.2: List of interesting interatomic distances and angles. "Avg" indicates the averaged distance, Q(ij) is the charge computed using CHARDIS99 [28].

The cations occupancy was checked by refining the occupation factor, retrieving a value very close to 1; this result agrees with the peculiar characteristics of the structure, where no particular deviations from the stoichiometric concentration of the ions are expected due to the high density of the system. The results of the refinement are summarized in Table 3.1, where atom positions and thermal

parameters are reported. Table 3.2 gathers the informations about the Bi-O and Mn-O bond distances, Mn-O-Mn angles, and the estimated cationic charges on the basis of charge distribution calculations implemented on the CHARDIS99²⁸ program, which result to be equal to 3+ for all the cations. Mn1, Mn2 and Mn3 are the square coordinated ions in the A' site displaying equivalent bond lengths. Mn4 and Mn5 occupy the B site and are characterized by an apical elongation, ascribed to the occupation of the e_g $d_{x^2-y^2}$ orbital, yielding an ordering pattern that implies a checkboard-like scheme in the ac plane. The distortion of the two octahedra is comparable, as confirmed by the similar values of the coefficient $\sigma_{JT} = \sqrt{1/3} \sum_i [(d_{Mn-O})_i - (d_{Mn-O})]^2$ [29], which quantifies the strength of the Jahn-Teller distortion. The values obtained for Mn4 and Mn5 are 11×10^{-2} and 13×10^{-2} respectively: quite large values if compared to the other compounds of the family. Along b the orbital ordering pattern -a schematic representation is reported in figure 3.8- repeats itself due to the presence of the mirror plane perpendicular to this direction.

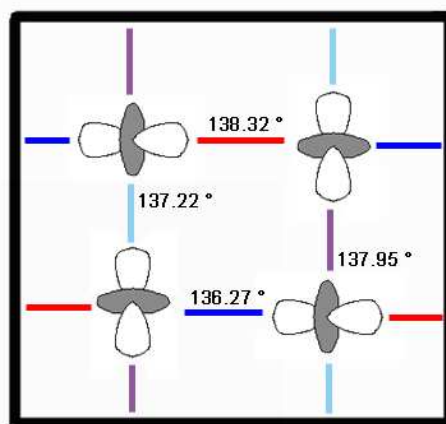


Fig. 3.8: Representation of the quadruple perovskite cell in the ac plane. The orbital ordering scheme of the B site is reported, and the different Mn-O-Mn angles are highlighted by different colours.

Within this framework one may expect, on the basis of the Goodenough-Kanamori rules, the magnetic interactions to be ferromagnetic in the ac plane, while the coupling along the b direction should be of antiferromagnetic kind.

However, despite a regular orbital ordering scheme, the overlap between the orbitals may not be isotropic in the *ac* plane, since the Mn-O-Mn angles in the different directions are affected by a variation of about 2 °; a small amount which nevertheless is large enough to affect the scheme of magnetic interactions -when angles assume intermediate values between 90 and 180 °, as the solution of the magnetic structure, illustrated in section 3.2.6, will testify. A combined representation of the orbital order and bond angles is drawn in figure 3.8.

Another fundamental indication can be obtained by the analysis of the bond distances: the oxygen coordination around the Bi³⁺ ions is highly distorted, with the longer bonds sitting on the opposite side with respect to the shorter ones. Noteworthy the rest of the structure almost is almost centrosymmetric, suggesting that –as expected- the bismuth steric properties are at the origin of the symmetry lowering observed in this compound if compared to the other quadruple perovskites.

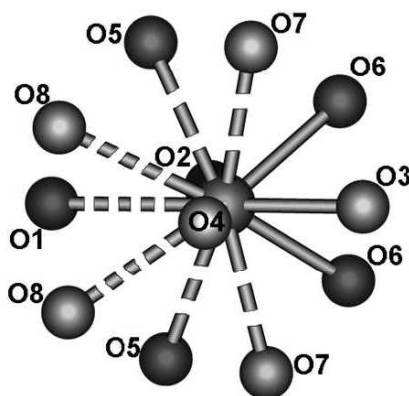


Fig. 3.9: Bismuth-oxygen coordination polyhedron. The shorter bonds are drawn as continuous lines, while dashed lines evidence the longer ones.

At room temperature an electrical polarization equal to 7.33 $\mu\text{C}/\text{cm}^2$ can be computed by a simple point charge model as dipole moment for volume unit. This value is only indicative, since further effects can take place in the settlement of the overall electrical polarization. However, this observation suggests that BiMn₇O₁₂ is

a ferroelectric compound, making of it a good candidate to magnetoelectric multiferroism.

Transmission Electron Microscopy (TEM) measurements, performed on a Philips TECNAI F20 instrument operating at 200 KV, give corroboration to this hypothesis, showing the presence of domains which can be interpreted as ferroelectric domains, characterized by different shift directions of the Bi ions. Samples were prepared by grinding the powders in isopropyl alcohol and evaporating the suspension on a copper grid covered with a holey carbon film. The bright field image shown in figure 3.10, evidences the presence of twinning domains extending on a few tens of nanometers corresponding to sharp contrast variations. The High Resolution Transmission Electron Microscopy (HREM) image, taken in the same orientation of the crystal, allowed the definition of the zone axis of observation through the indexing of its Fast Fourier Transform (FFT). Since the lattice parameters are too similar to allow the indexation on the basis of metrical relations, the Electron Diffraction (ED) pattern was simulated in order to identify the reflections on the basis of their intensities. The projection of observation is thus defined as $[11\bar{1}]$, indicating that the twin domains boundaries in the Bright Field image are normal to the $[112]$ reciprocal lattice vector. However the characteristic features of the contrast variation of the twin boundaries and the alternate sequence of sharp and blurred zone in the HREM image suggest the twinning boundaries to be inclined with respect to the observation axis. Twinning should then occur in the (111) plane, which is the direction of elongation of the a.d.p.'s observed when the structure is refined in the centrosymmetric $I2/m$ space group.

Therefore TEM investigations confirm the hypothesis of ferroelectric properties in BiMn₇O₁₂; however a series of characterizations with the specific aim to quantify the polarization of the system are needed.

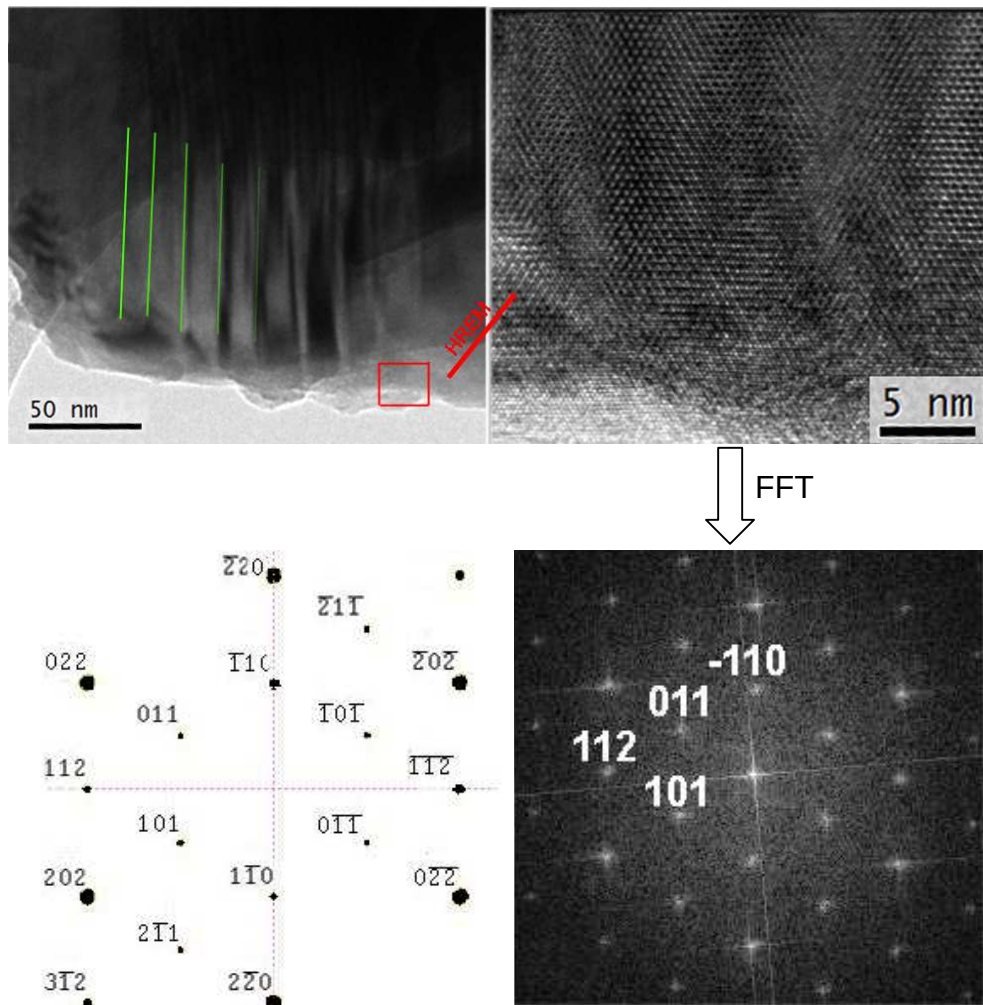


Fig. 3.10: From top-left corner, clockwise order; the orientation of the images is consistent.
 Bright filed image where some of the twin boundaries are highlighted in green.
 Selected Area Electron Diffraction (SAED) image taken in $[11\bar{1}]$ zone axis.
 Indexed Fast Foureier Transform of the SAED pattern.
 Simulated ED used in the indexation process.

3.2.3 Magnetic characterization

The magnetic properties of BiMn₇O₁₂ have been studied using a Quantum Design SQUID magnetometer in the temperature range 5-300 K. The Field Cooled (FC) and Zero Field Cooled (ZFC) magnetization curves obtained for a polycrystalline sample with applied field $H = 10$ Oe are reported in figure 3.11.

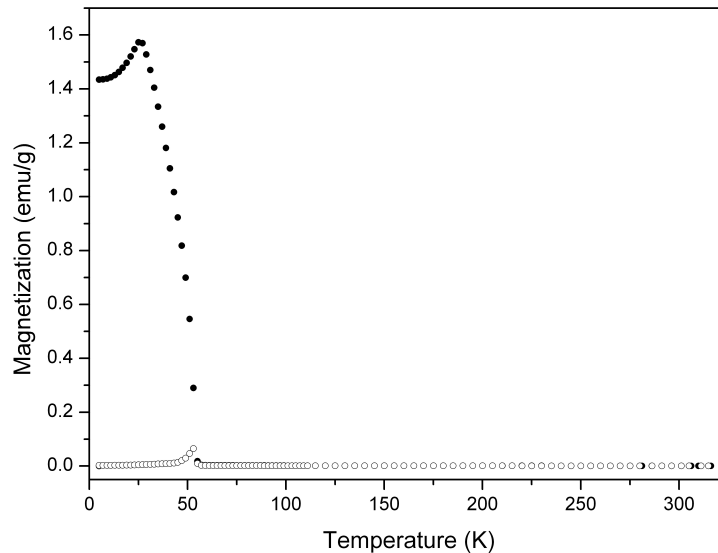


Fig. 3.11: Field Cooling (●) and Zero Field Cooling (○) magnetization curves with applied field $H = 10$ Oe.

A sharp transition is observed at $T = 50$ K ascribed, in analogy with the isostructural compounds to the ordering of manganese ions placed in the B site. The FC curve displays the setting of nonzero magnetization reaching the value $M = 1.6$ emu/g at 25 K. However, the antiferromagnetic nature of the ordered phase is revealed by the trend of the inverse susceptibility shown in Fig.3.12, that allows to estimate the Curie-Weiss temperature $\Theta = -206$ K, suggesting that the exchange interactions are antiferromagnetic in nature. The slope of the inverse susceptibility yields $6 \mu_B$ per Mn ion, while the expected value for Mn^{3+} would be $4.9 \mu_B$. The anomaly clearly seen in this figure at $T = 100$ K could be ascribed to the possible

presence of BiMnO₃ impurities, whose monoclinic phase undergoes a ferromagnetic transition at $T_c = 99$ K. On the basis of the magnetization measurements performed on BiMnO₃ [30] the impurity can be estimated to be less than 1%. For this reason the presence of perovskitic bismuth manganite was not detected by PXRD. The sharp drop of the inverse susceptibility at T_c has the shape usually observed in stoichiometrically pure Dzyaloshinskii- Moriya (DM) compounds.^{31,32} similar magnetization curves are observed in the structurally related compounds PrMn₇O₁₂ [22] and LaMn₇O₁₂ [14].

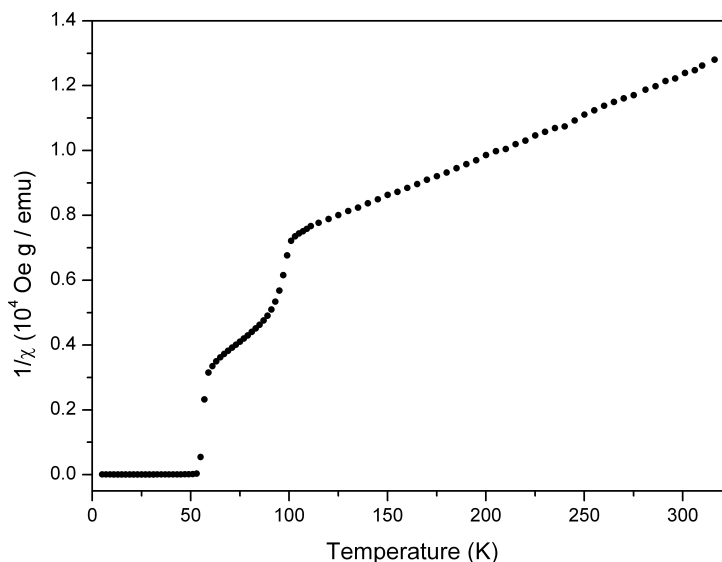


Fig. 3.12: Inverse susceptibility curve.

The DM interaction, which is an antisymmetric exchange interaction between two spins S_i and S_j of the form $D \cdot (S_i \times S_j)$ arising from the spin-orbit coupling, produces a nonzero net result only if S_i and S_j are not related by a centre of inversion. This condition is fulfilled because of the sizeable tilting of the MnO₆ octahedra in quadruple perovskites, in contrary to the case, for instance, of BiMnO₃, where a completely different magnetic behaviour is detected.

The peak observed in FC at 26 K is purely antiferromagnetic and should correspond, in analogy with the other known quadruple perovskite compounds, to the ordering of the Mn ions in the planarly coordinated A' sites.

3.2.4 Electric characterization

Resistivity measurements have been performed using standard four-probe method with DC current, using a close cycle cryostat. Data were collected in the range 100-400 K, but due to the high resistance and capacitive components present at low temperature due to the semiconducting nature of the sample, the informations coming from the low temperature region are not reliable. At 340 K an anomaly is detected, both in cooling and in heating ramps, displaying a small hysteresis. The Arrhenius plot (reported in figure 3.13) allows the determination of the activation energies of the phases above and below the transition: 300 and 210 meV respectively.

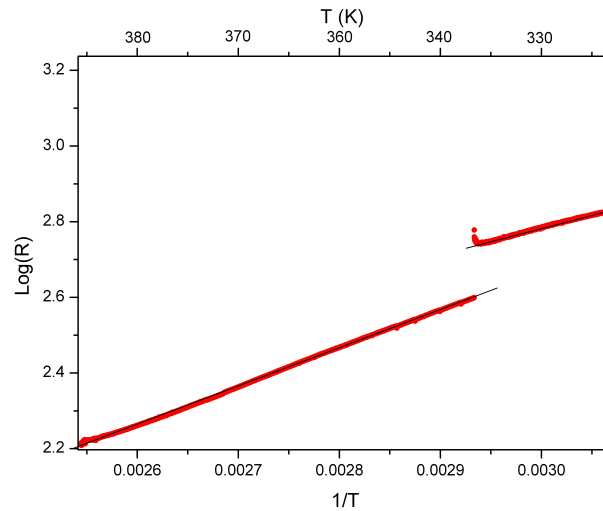


Fig. 3.13: Arrhenius plot of $\text{Log}(R)$ vs. $1/T$. Black lines are guides to the eye.

The nature of the transition observed here has not been clarified, even if it may be related to a structural change similar to the one observed in LaMn₇O₁₂ at higher temperatures (803 K), or in NaMn₇O₁₂ at 160 K, in both cases related to the loss of charge/orbital ordering.

3.2.5 Dielectric characterization

The electric permittivity was measured applying mica linings to the sample in order to remove the extrinsic contribution coming from contact junctions.³³ In figure 3.14 is reported the measurement performed on a polycrystalline sample with applied field frequency 3 kHz. The dielectric permittivity rises up to 200 K where an inflection probably due to the leaking currents deriving from the semiconducting nature of the compound can be observed.

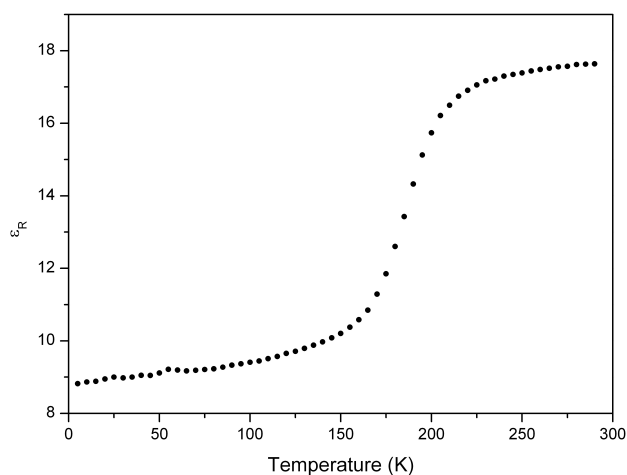


Fig. 3.14: Dielectric permittivity as a function of temperature measured with applied field frequency 3 kHz.

The trend of the curve suggests that the dielectric peak related to the ferroelectric Curie temperature is placed above room temperature, indirectly

confirming the presence of ferroelectric properties at RT. Some small variation of the permittivity can be observed in the low temperature region of the graph: an enlarged portion of the curve is reported in fig. 3.15 together with measurements collected at different frequencies of the applied field. Two distinct anomalies matching the magnetic transitions temperatures evidence the coupling between magnetic and dielectric properties thus the presence of magnetodielectric effect in BiMn₇O₁₂. The temperature position of the peaks is not frequency dependent suggesting the absence of any kind of dielectric dispersion in this compound.

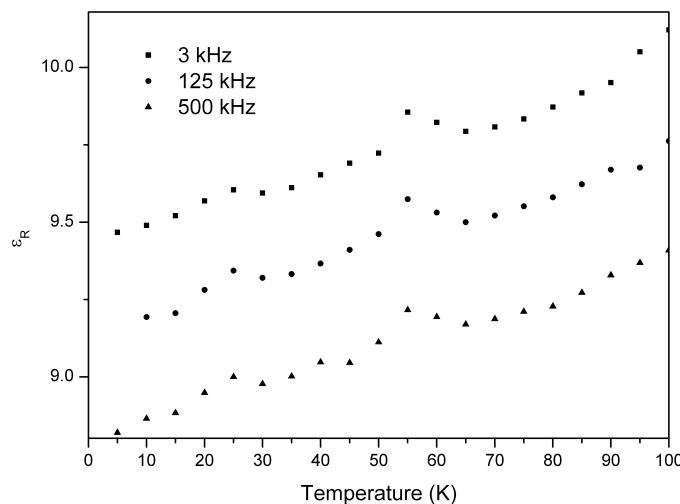


Fig. 3.15: Dielectric permittivity vs temperature for different frequencies of the applied field: ■ = 3 kHz, ● = 125 kHz, ▲ = 500 kHz.

3.2.6 Magnetic structure

Neutron diffraction data were collected in the low temperature region at the G4.1 beamline of the Laboratoire Léon Brillouin in Saclay (France), using a radiation with wavelength 2.42 Å in the 2θ range 3 – 95°.

The analysis of the diffraction patterns, where the only phases detected are BiMn₇O₁₂ and a small amount of Hausmannite Mn₃O₄ (about 4%), reveals that no structural transition takes place between RT and 1.5 K. Some of the patterns are reported in figure 3.16, where the rise of magnetic peaks can be noticed at 55, 35, and 24 K. It is well known that Hausmannite undergoes a magnetic transition at 41.8 K, so that the peaks appearing below 35 K can be easily ascribed to the magnetic ordering of this phase.

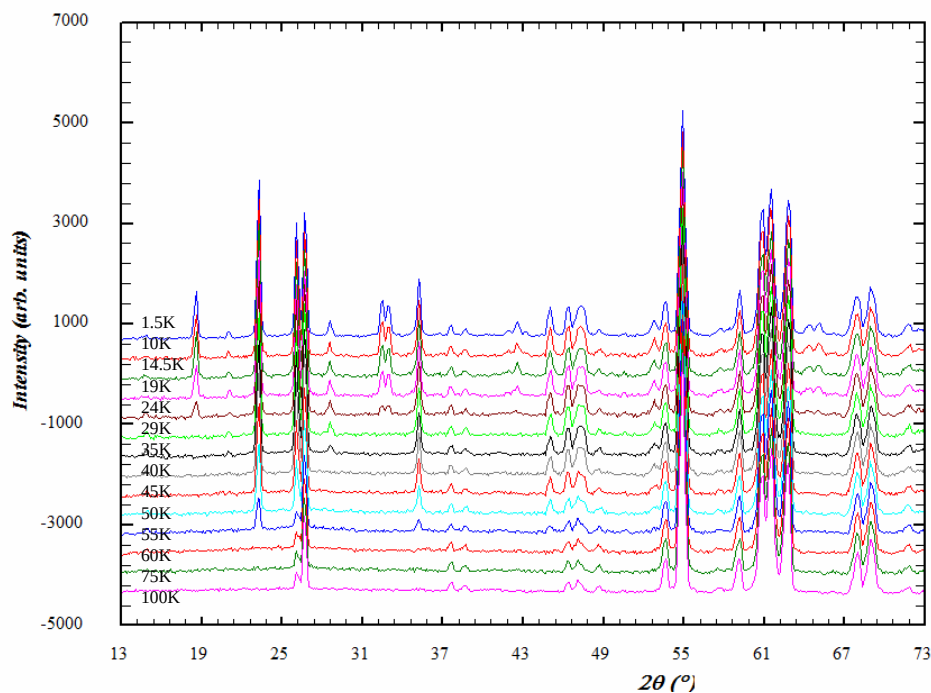


Fig. 3.16: Neutron diffraction patterns collected in the temperature range 100 - 1.5 K.

The assignment of the magnetic peaks of BiMn₇O₁₂ was attempted in analogy with the other known quadruple perovskites so that the first transition (50 K) was ascribed to the ordering of the octahedrally coordinated Mn³⁺ ions in the B site, while the second one (at 25 K) was assigned to the magnetic ordering of the spins on the manganese sitting in the A' site.

I. B site

A careful inspection of the peaks appearing between 55 and 45 K indicates two distinct temperature behaviours of the magnetic intensities, shown in Fig. 3.17, suggesting the presence of two distinct transitions in this interval.

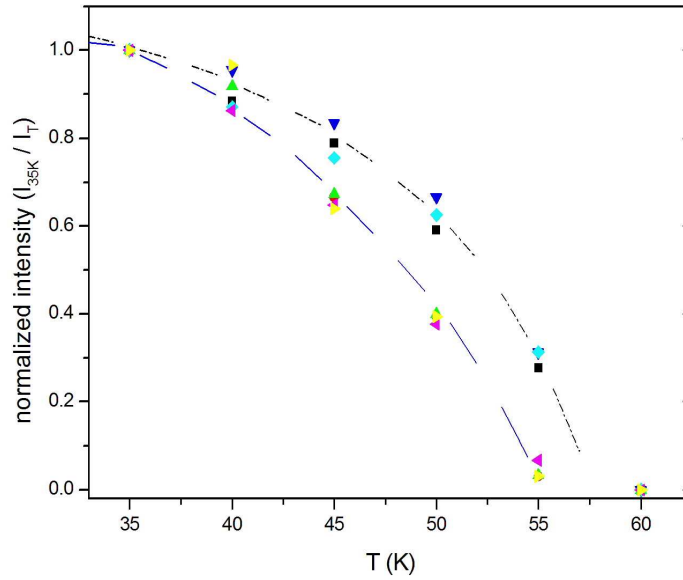


Fig. 3.17: Thermal behavior of the normalized intensity of the magnetic contribution, appearing in the temperature range 55 - 45 K, of some selected neutron diffraction peaks.

As shown in Fig. 3.18, the peaks appearing at 55 K have propagation vector $(\frac{1}{2} 0 \frac{1}{2})$, while the ones raising at 50 K can be indexed on the basis of the fundamental cell, the propagation vector being $(0 0 0)$. Basing on the analysis of reflection indices, microstructure effects and preferred orientation of domains were excluded for the interpretation of the phenomenon. The possible presence of two transitions is supported by the specific heat measure published by Iamamura et al., showing a double peak at about 50 K with strong magnetic field dependence.³⁴

SQUID measurements in AC configuration were performed in order to clarify this point, shown in figure 3.19, but despite the presence of a weak shoulder over the main peak, no evident features supporting the existence of two transitions was detected. However, in the refining process the presence of two transitions was considered, in order to describe the peculiar behaviour of the magnetic peaks intensities and their different propagation vectors.

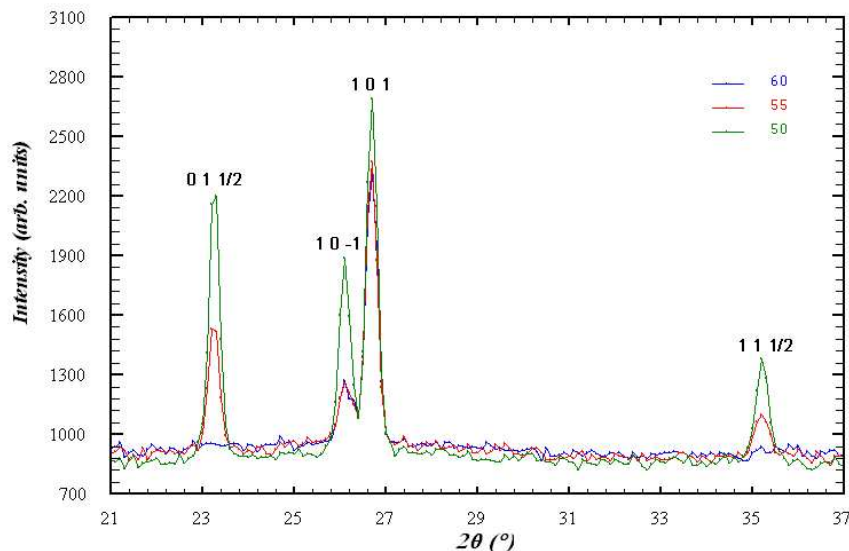


Fig. 3.18: Neutron diffraction patterns in the 2θ range $21\text{--}37^\circ$ indexed on the basis of the fundamental Im cell. The peaks appearing at 55 K and 50 K have propagation vector $(\frac{1}{2} 0 \frac{1}{2})$ and $(0 0 0)$ respectively.

The two transitions were initially ascribed to sequential ordering of two sublattices on the B site involving symmetry independent manganese ions described by a cell with propagation vector $(\frac{1}{2} 0 \frac{1}{2})$. As a consequence the data collected at 55 K were refined using the GSAS program^{35,36} by adding one magnetic phase with cell parameters $a = 10.778$, $b = 7.352$, $c = 10.530$ and space group Im , the a and c vectors being directed along the diagonals of the fundamental quadruple perovskite cell in the ac plane. One half of the magnetic moments were included and all the components were refined independently. Good

agreement indices were obtained and the magnetic structure, shown in figure 3.20, displays a precise antiferromagnetic order, so the components were constrained following the observed scheme. In this hypothesis the second sublattice should order at 55 K.

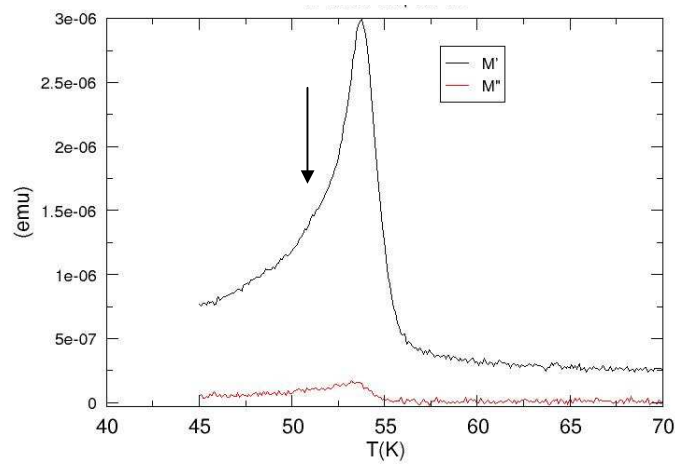


Fig. 3.19: AC Magnetization measurements collected with applied field $H = 0.2$ Oe and frequency 997 Hz. The black curve corresponds to the real part of the magnetization, the red one is the imaginary part. The arrow indicates the possible second transition.

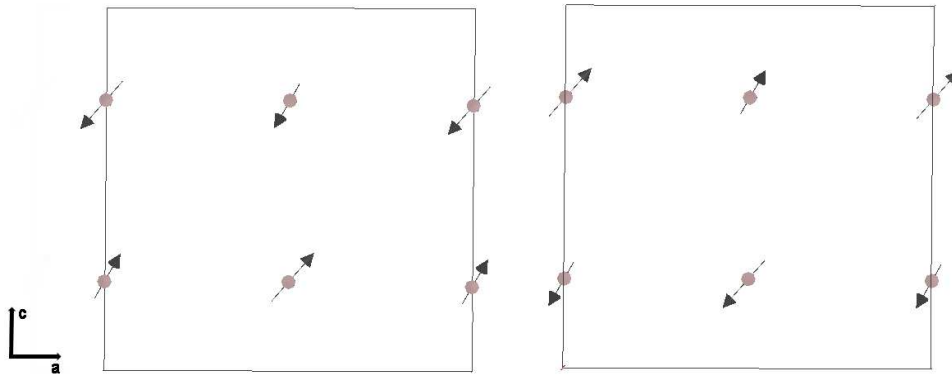


Fig. 3.20: Magnetic cell obtained by the refinement of the data collected at 55 K in the large cell by using $\frac{1}{2}$ of the magnetic ions on the B site. The two pictures correspond to the ac layers stacked along the b direction.

However, despite the peaks involved in the second transition should have propagation vector (0 0 0), no good solution for the second sublattice was found in the conventional cell. The best refinement was obtained again in the larger cell, indicating that the ordering of both sublattices requires a propagation vector ($\frac{1}{2}$ 0 $\frac{1}{2}$). An indication was obtained by letting free all the components of the second sublattice and later imposing the constraints on the basis of the obtained results.

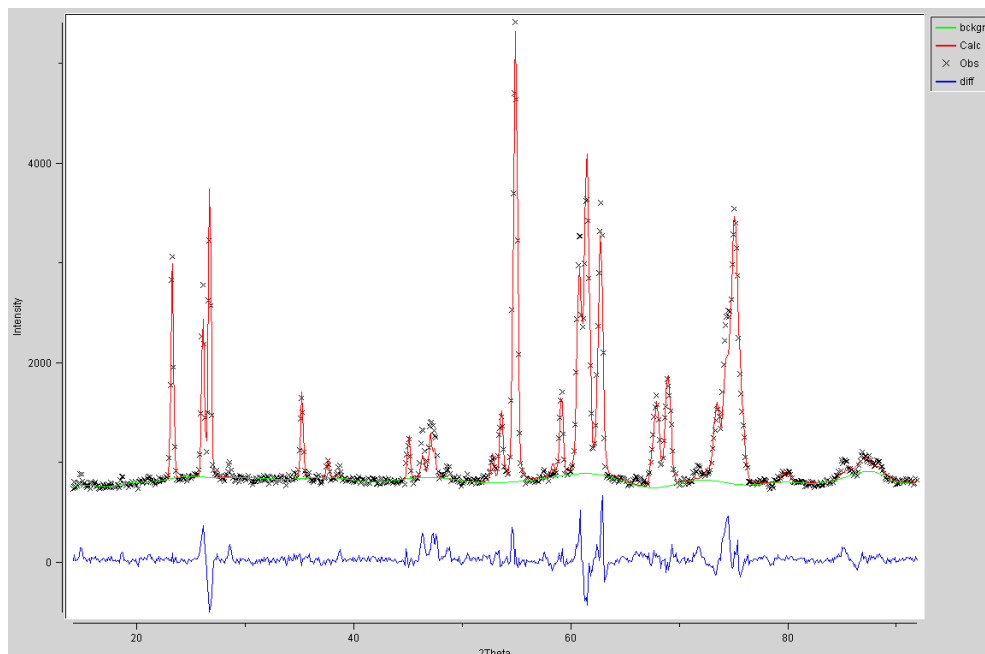


Fig. 3.21: Rietveld plot relative to the data collected at 50 K.

The refinement converged with $R(F^2)=10.2\%$. Although both the background and intensities in the Rietveld plot are not satisfactory, should be noted that all the magnetic peaks are indexed and no extra peaks are observed. The final results are shown in figure 3.21, where the two layers at $z=1/4$ and $z=3/4$ are reported. On the right the fundamental “quadruple perovskitic” cell is highlighted in blue. The pink lines correspond to the Mn-O-Mn bonds that form angles of 138° , while in yellow the ones for which the angles are equal to 137° and 136° are pointed out.

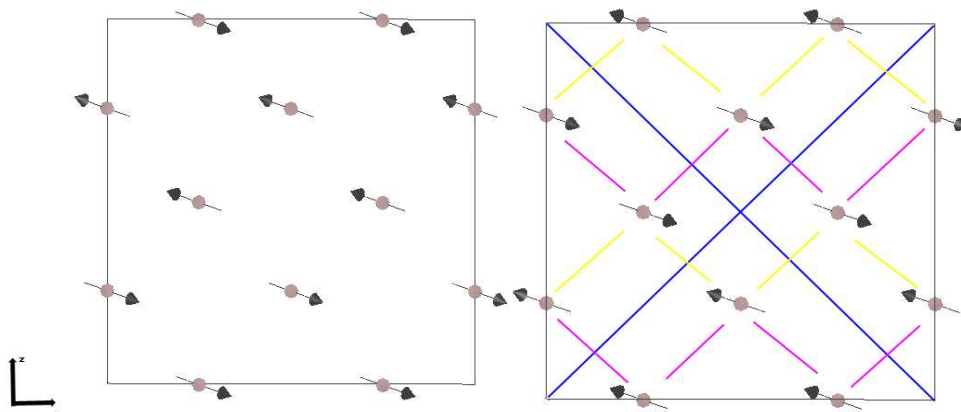


Fig. 3.22: Projection along the b direction of the magnetic moments of the manganese ions (B sites) in the large cell with propagation vector $(\frac{1}{2} 0 \frac{1}{2})$. The two images correspond to layers stacked along the b direction. In the right image the ferromagnetic interactions are highlighted in pink while the antiferromagnetic ones in yellow. Blue lines identify the nuclear cell.

Noteworthy is the fact that the bonds with equivalent angles yield the same kind of interaction in the ac plane suggesting a correspondence of the obtained magnetic structure with the nuclear features of the system (in particular here pink = ferromagnetic and yellow = antiferro). Moreover as it was shown in section 3.2.2, the orbital ordering scheme suggests a ferromagnetic coupling of the spins in the ac plane, antiferromagnetically coupled along b (in case the Goodenough-Kanamori rules are valid). This condition is almost fulfilled here: if the fundamental cell is considered, $\frac{3}{4}$ of the spins follow this path, only one of them breaking the rule. Within this framework, it would be of fundamental importance the accurate determination of the atomic positions, bond lengths and angles; however the low resolution of the available data do not allow a study of this kind. Powder x-ray diffraction using synchrotron radiation or neutron diffraction performed using high resolution optics should be clarifying in this direction. The proposed magnetic structure is not collinear, since all the components along b are non-zero (see figure 3.22, where the bc plane is drawn). Any trial to force them to zero value, imposing

a collinear arrangement, results in a drastic deterioration of the fit. Note that in this model, as all the components along b are constrained to be equal in modulus, the overall moment is zero. This statement agrees with the observation of antiferromagnetic behaviour in zero field cooling measurements between 50 and 25 K.

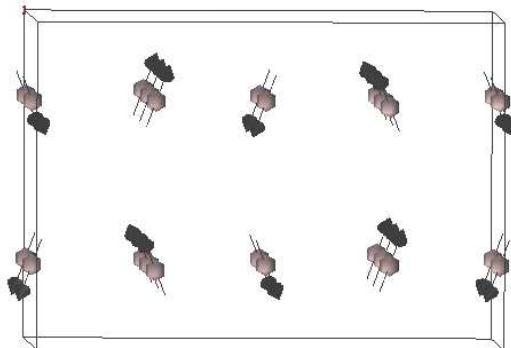


Fig. 3.23: BiMn₇O₁₂ magnetic cell relative to the B site viewed along the $[1\ 0\ 0]$ direction .

As a consequence of the spin canting along b , the whole picture is quite complex and requires the components of the spins in the three directions to be considered independently. In figures 3.24 and 3.25 are drawn the orientations of the spin components in the ac plane and b direction respectively. The coupling of the components in the ac plane is the same pointed out in figure 3.22, where the ferromagnetic interactions as well as the antiferromagnetic ones form a zigzag chain along the diagonal of the large non conventional cell. The ac components are coupled antiferromagnetically along the b direction, the b component being antiparallel in the ac plane, while the coupling between the layers is ferromagnetic. Noteworthy, whereas the representation of the ac components ordering pattern requires a propagation vector $(\frac{1}{2}\ 0\ \frac{1}{2})$, the b components can be described using a propagation vector $(0\ 0\ 0)$.

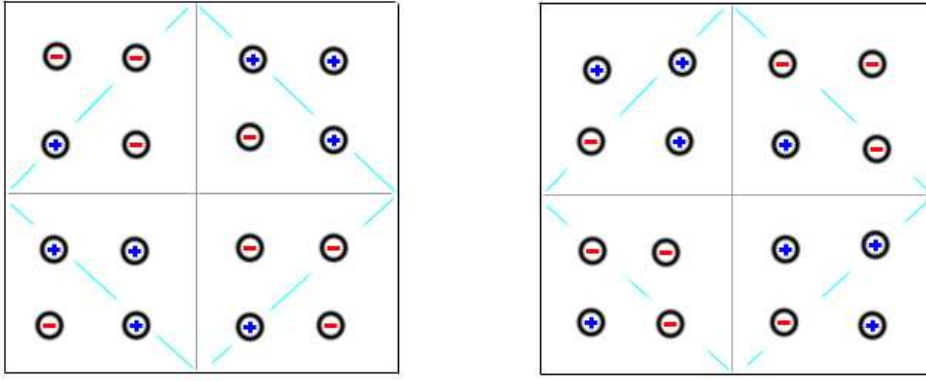


Fig. 3.24: Magnetic interactions among the ac components of the magnetic moments. The structure is viewed along the 010 direction of the fundamental cell, in light blue is highlighted the magnetic cell having propagation vector $(\frac{1}{2} \ 0 \ \frac{1}{2})$.

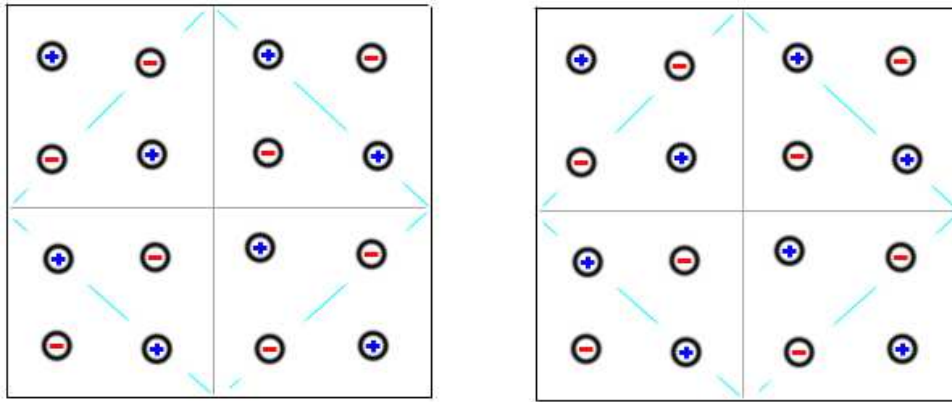


Fig. 3.25: Interactions of the magnetic moments b component.

These considerations suggest that the reflections having different propagation vectors correspond to the ordering of the different components of the magnetic moments. In order to verify this hypothesis the 55 K data were refined with the model of large cell obtained at lower temperature including all the Mn atoms occupying the B site, setting to zero the b components. Good results were obtained

in term of agreement indices and quality of the fit. A second model including only the *b* components in the fundamental cell was added to the previous to refine the lower temperature data. Therefore, on the basis of this interpretation, a single transition is present, involving the moments of the Mn atoms occupying the B sites to be at first AF coupled in the *ac* plane (as usual in quadruple perovskites) with a propagation vector ($\frac{1}{2}$ 0 $\frac{1}{2}$) and then progressively tilted along the *b* axis with a propagation vector (0 0 0). In table 3.3 are reported the results of the refinement carried out on the data collected at 35 K, the lowest temperature in which only the Mn ions on the B site are ordered.

Space group: Im				
Lattice parameters: a = 7.5416(9), b = 7.3526(7), c = 7.5313(9) Å, β = 91.17(1)° R(F ²) = 10.2% Rwp = 6,19% Rp = 4.36				
Atom	x	y	z	U _{iso}
Bi1	0.0284	0	0.0173	0.0255
Mn1	0.003	0	0.4951	0.0573
Mn2	0.4997	0	0.5019	0.0573
Mn3	0.4955	0	-0.0022	0.0573
Mn4	0.2542	0.7419	0.254	0.0573
Mn5	0.2476	0.7493	0.7459	0.0573
O1	0.3366	0.5	0.1827	0.0484
O2	0.1916	0	0.6755	0.0484
O3	0.1742	0	0.3031	0.0484
O4	0.8247	0	0.3094	0.0484
O5	0.491	0.8086	0.3282	0.0484
O6	0.3081	0.8259	-0.0105	0.0484
O7	0.0167	0.683	0.1765	0.0484
O8	0.6796	0.18	0.0112	0.0484

Tab. 3.3: Refinement parameters, atom positions and isotropic displacement parameters corresponding to the nuclear cell of BiMn₇O₁₂ at 35K.

Space group: Im									
Lattice parameters: a = 10.778(3), b = 7.352(1), c = 10.530(30) Å, $\beta = 90.21(5)^\circ$									
$R(F^2) = 10.2\%$ Rwp = 6.19% Rp = 4.36									
Atom	x	y	z	Mx (μ_B)	My (μ_B)	Mz (μ_B)	M (μ_B)	Φ ($^\circ$)	Θ ($^\circ$)
Mn4a	0.7492	0.2493	0.4968	1.32(4)	1.11(3)	-0.46(10)	1.79(3)	105(3)	40.1(9)
Mn4b	0.2492	0.2507	0.4968	1.32(4)	1.11(3)	-0.46(10)	1.79(3)	105(3)	40.1(9)
Mn5a	0.4999	0.2581	0.7541	1.32(4)	-1.11(3)	-0.46(10)	1.79(3)	105(3)	-40.1(9)
Mn5b	0.4999	0.2419	0.2541	-1.32(4)	-1.11(3)	0.46(10)	1.79(3)	75(3)	-139.9(9)

Tab. 3.4: Refinement parameters, magnetic moments component in cartesian and spherical coordinates relative to manganese ions in the B site at 35 K.

The atomic positions were not refined, therefore the sigma values are not indicated. The isotropic thermal parameters relative to atoms of the same species were constrained to be equal. Manganese (III) oxide was refined as supplementary phase.

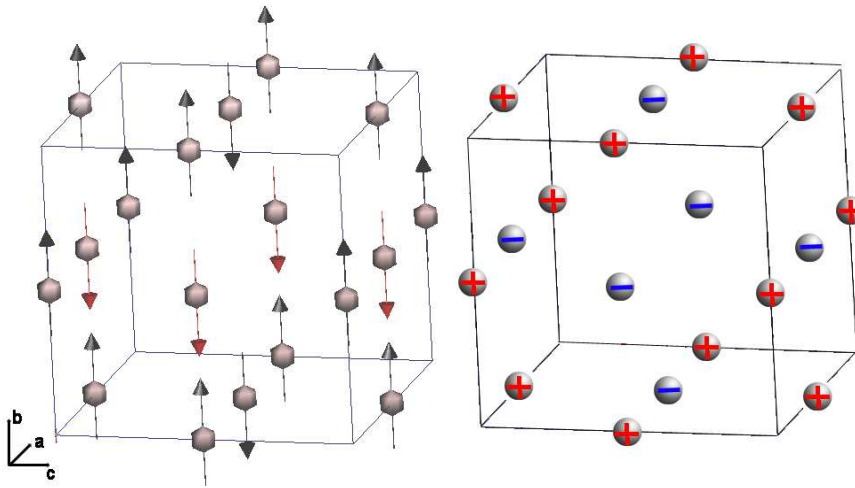


Fig. 3.26: Magnetic structure corresponding to the A' site in BiMn₇O₁₂. Left: spin orientation in the fundamental quadruple perovskite cell. Right: simplified view of the magnetic order.

II. A' site

The refinement of the atomic moments of the A' manganese ions results quite complex due to the scarce number of peaks appearing below the ordering temperature, as evidenced by figure 3.16. As a consequence the possible reasonable solutions are several, none of them excluding the others.

Space group: <i>I'm</i> Lattice parameters: $a = 7.5462(7)$, $b = 7.3579(5)$, $c = 7.5376(8)$ Å, $\beta = 91.17(1)^\circ$ $R(F^2) = 13.9\%$ $R_{wp} = 7.81\%$ $R_p = 0.51$											
Atom	x	y	z	U _{iso}	M _x (μ _B)	M _y (μ _B)	M _z (μ _B)	M (μ _B)	Φ (°)	Θ (°)	
Bi1	0.0284	0	0.0173	0.0255							
Mn1	0.003	0	0.4951	0.0573	0.000	2.33(5)	0.000	2.33(5)	90	90	
Mn2	0.4997	0	0.5019	0.0573	0.000	-2.33(5)	0.000	2.33(5)	90	-90	
Mn3	0.4955	0	-0.0022	0.0573	0.000	2.33(5)	0.000	2.33(5)	90	90	
Mn4	0.2542	0.7419	0.254	0.0573							
Mn5	0.2476	0.7493	0.7459	0.0573							
O1	0.3366	0.5	0.1827	0.0484							
O2	0.1916	0	0.6755	0.0484							
O3	0.1742	0	0.3031	0.0484							
O4	0.8247	0	0.3094	0.0484							
O5	0.491	0.8086	0.3282	0.0484							
O6	0.3081	0.8259	-0.0105	0.0484							
O7	0.0167	0.683	0.1765	0.0484							
O8	0.6796	0.18	0.0112	0.0484							

Tab. 3.5: Refinement parameters, atom positions and isotropic displacement parameters corresponding to the nuclear cell of BiMn₇O₁₂ and magnetic A' site at 1.5K.

However the magnetization data suggest unambiguously that the magnetic structure setting in below 25 K is purely antiferromagnetic; moreover the indices of peaks corresponding to this phase break the body centering of the fundamental quadruple perovskite cell (space group *Im*), as a consequence two refinements were carried out both in the coloured space groups *I'm'* and *I'm*. Although both models yielded comparable agreement indices values, *I'm'* causes the appearance of unobserved peaks displaying low intensity. On the other hand the refinement

carried out in $I'm$ is not completely satisfactory in terms of intensity fitting, but no extra peaks are observed, and the obtained magnetic structure, drawn in figure 3.26 consists of a collinear antiferromagnetic arrangement, producing zero net moment. The components of the spins along b were constrained to be equal and result to be quite small ($2.33 \mu_B$), but comparable to those obtained for the B site. The components in the other directions are forced to zero by symmetry. Noteworthy is the fact, particularly evident in the right panel in figure 3.26, that the ordering of the A' site is the same observed in NaMn₇O₁₂.¹⁸ The results of the refinement are resumed in table 3.5 and 3.6.

Space group: Im Lattice parameters: $a = 10.811(4)$, $b = 7.395(2)$, $c = 10.563(8)$ Å, $\beta = 90.32(8)^\circ$ $R(F^2) = 13.9\%$ $Rwp = 7.81\%$ $Rp = 0.51$									
Atom	x	y	z	Mx (μ_B)	My (μ_B)	Mz (μ_B)	M (μ_B)	Φ ($^\circ$)	Θ ($^\circ$)
Mn4a	0.7492	0.2493	0.4968	1.69(6)	1.46(3)	-1.07(9)	2.47(3)	115(2)	41(1)
Mn4b	0.2492	0.2507	0.4968	1.69(6)	1.46(3)	-1.07(9)	2.47(3)	115(2)	41(1)
Mn5a	0.4999	0.2581	0.7541	1.69(6)	-1.46(3)	-1.07(9)	2.47(3)	115(2)	41(1)
Mn5b	0.4999	0.2419	0.2541	1.69(6)	-1.46(3)	1.07(9)	2.47(3)	65(2)	-139(1)

Tab. 3.6: Refinement parameters, magnetic moments component in cartesian and spherical coordinates relative to manganese ions in the B site at 1.5 K.

3.2.4 Low temperature structural evolution

The refinement of the lattice parameters making use of the neutron diffraction data collected at different temperatures reveals a strong dependence of the structural parameters on temperature. The behaviour retrieved evidences a noticeable variation of the cell parameters a and b (about 1%) in correspondence of the magnetic transition, while β and V show smaller but still relevant features. These data clearly put in evidence the presence of a negative magnetostriction yielding a cell increase in the ac plane that produces an enlargement of the cell volume in correspondence of the magnetic transition located at 55 K.

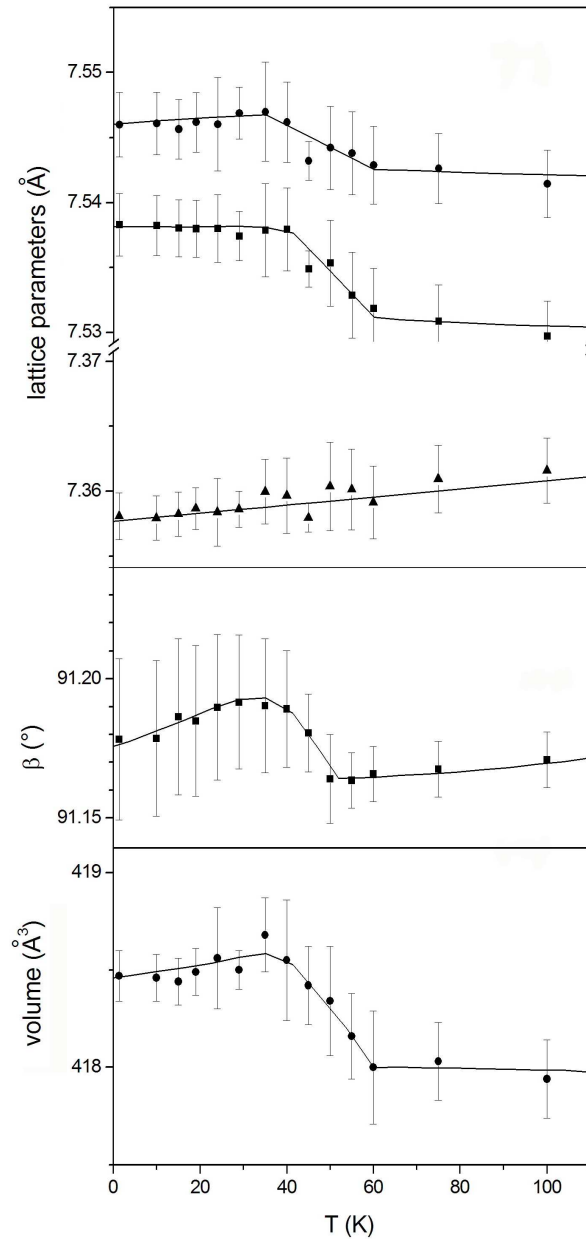


Fig. 3.27: Evolution of the lattice parameters and volume of the fundamental quadruple perovskite cell as a function of temperature. Lines are guides to the eye.

Another anomaly in the lattice parameters is detected at about 30 K, thus at slightly higher temperature with respect to the A' site ordering transition: below 30 K the a , c and β parameters and the volume reduce as the temperature is lowered. In general, the b lattice parameter seem not to be affected by the presence of the magnetic transitions in the whole range of temperatures investigated, showing a decreasing trend as expected as a consequence of the shrinking due to the lowering of temperature. On the contrary, suggesting an anisotropic scheme of interactions, all the magnetostrictive effects observed take place in the ac plane, in which also the dipole moment lays. This fact may account for the observed magnetic behaviour: the rising of the b component of the magnetic moments could be the effect of the coexistence of the two ferroic orders. In absence of electric dipole one may imagine the moments to lay in the ac plane, being coupled to the lattice parameters via conventional magnetostrictive effects. Within this picture, the presence of electric polarization, may represent a perturbation to magnetostriction, yielding the off-plane canting of the spins.

The interpretation of the complex behaviour observed, in particular below the magnetic ordering temperature, is in progress, the modelization of the system being perhaps the most effective technique for this specific purpose. However, besides the comprehension of the mechanisms involved in the coupling process, their phenomenology is particularly interesting, making worth further general studies of the system and specific characterizations of the ferroic exchange.

3.2.5 Conclusions

The synthesis of BiMn₇O₁₂ was carried out with the aim of studying the introduction of a stereochemically active atom into a known magnetic system, in order to induce magnetoelectric properties. The consequent choice of quadruple perovskites manganites as “host” matrices for the Bi³⁺ ions is related to the large

structural tolerance to chemical substitutions of these compounds. The structural analyses revealed that BiMn₇O₁₂ crystallizes in the noncentrosymmetric space group *Im*, differently from all the other known quadruple perovskite manganites, thus allowing the onset of a nonzero dipole moment. Electrical polarization is likely produced by the observed asymmetrical coordination around the bismuth atom; TEM measurements confirmed the idea of ferroelectricity in this system by showing the presence of twin domains probably generated by the switching of the polarization vector.

The magnetic characterization revealed a weakly ferromagnetic behaviour -due to Dzyaloshinsky-Moriya interaction- below 55 K, related to the ordering of the spins on the Mn ions in octahedral coordination. At T=25 K a purely antiferromagnetic transition is detected, corresponding to the ordering of the A' square planar manganese ions. The magnetic structure, obtained by the analysis of neutron powder diffraction data, appears to be complex, and probably affected by the presence of ferroelectricity in the compound.

Evidence of magnetoelectric coupling was revealed by the observation of anomalies in the electric permittivity as well as variations of the lattice parameters in correspondence of the magnetic transition temperatures, making further studies on this compound particularly interesting for the comprehension of the exchange mechanisms among ferroelectricity and magnetism in multiferroics.

References

- ¹ D.J. Payne, R.G. Egdell, A. Walsh, G.W. Watson, J. Guo, P.-A. Glans, T. Learmonth, K. E. Smith, *Phys. Rev. Lett.* **96**, 157403 (2006).
- ² F. Kubel, H. Schmid, *Acta Cryst.* **46**(6), 698 (1990).
- ³ M.M. Kumar, V.R. Palkar, K. Srinivas, S.V. Suryanarayana, *Appl. Phys. Lett.* **76** (19), 2764 (2000).
- ⁴ C. Ederer, N.A. Spaldin, *Phys. Rev. B* **71**(6), 060401 (2005).
- ⁵ J. 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, R. Ramesh, *Science* **299**, 1719 (2003).
- ⁶ R.V. Shpanchenko, V.V. Chernaya, A.A. Tsirlin, P.S. Chizhov, D.E. Sklovsky, E.V. Antipov, E.P. Khlybov, V. Pomjakushin, A.M. Balagurov, J.E. Medvedeva, E.E. Kaul, C. Geibel, *Chem. Mater.* **16** (17), 326 (2004).
- ⁷ A. Belik, M. Azuma, T. Saito, Y. Shimakawa, M. Takano, *Chem. Mater.*, **17**, 269 (2005).
- ⁸ A. Kumar, L.W. Martin, S. Denev, J.B. Kortright, Y. Suzuki, R. Ramesh, V. Gopalan *Phys. Rev. B* **75**, 060101(R) (2007).
- ⁹ D.J. Singh, *Phys. Rev. B* **73**, 094102 (2006).
- ¹⁰ A.F. Moreira dos Santos, A.K. Cheetham, T. Atou, Y. Syono, Y. Yamaguchi, K. Ohoyama, H. Chiba, C.N.R Rao, *Phys. Rev. B* **66**, 064425 (2002).
- ¹¹ M. Marezio, P.D. Dernier, J. Chenavas, J.C. Joubert, *Journal of Solid State Chemistry* **6** (1), 16 (1973).
- ¹² C. Zener, *Phys. Rev.* **82**, 403 (1951).
- ¹³ H.A. Kramers, *Physica* **1**, 182 (1934).
- ¹⁴ P.W. Anderson, *Phys. Rev.* **79**, 350 (1950).
- ¹⁵ J.B. Goodenough, *J. Phys. Chem. Solids* **6**, 287 (1958).

-
- ¹⁶ J. Kanamori, *J. Phys. Chem. Solids* **10**, 87 (1959).
- ¹⁷ J. Chenavas, F. Sayetat, A. Collomb, J.C. Joubert, M. Marezio *Solid State Communications* **16**(10-11), 1129 (1975).
- ¹⁸ A. Prodi, E. Gilioli, A. Gauzzi, F. Licci, M. Marezio, F. Bolzoni, Q. Huang, A. Santoro, J.W. Lynn *Nature Mater.* **3**, 48 (2004).
- ¹⁹ E.O Wollan, W.C. Koehler, *Phys. Rev.* **100**(2), 545 (1955).
- ²⁰ B. Bochu, J.L. Buevoz, J. Chenavas, A. Collomb, J.C. Joubert, M. Marezio. *Solid State Commun.* **36**, 133 (1980).
- ²¹ R. Przeniosło, I. Sosnowska, D. Hohlweinb, T. Haußb, I.O. Troyanchuke, *Solid State Comm.* **11**(1), 687 (1999).
- ²² R. Przeniosło, I. Sosnowska, M. Zołtek, D. Hohlwein, I.O. Troyanchuk, *Physica B* **241**, 730 (1998).
- ²³ M. Sanchez-Andujar, S. Yanez-Vilar, N. Biskup, S. Castro-Garcia, J. Mira, J. Rivas, M.A. Senaris-Rodriguez, *Jour. of Magn. Magn. Mater.* **321**, 1739 (2009).
- ²⁴ A. Prodi, E. Gilioli, R. Cabassi, F. Bolzoni, F. Licci, Q. Huang, J.W. Lynn, M. Affronte, A. Gauzzi, M. Marezio *Phys. Rev. B* **79**, 085105 (2009).
- ²⁵ F. Mezzadri, M. Calicchio, E. Gilioli, R. Cabassi, F. Bolzoni, G. Calestani, F. Bissoli *Phys. Rev. B* **79**, 014420 (2009).
- ²⁶ A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *SIR2002, Program for Crystal Structure Solution and Refinement* IRMEC-CNR, Bari, Italy (2002).
- ²⁷ G. M. Sheldrick, *SHELXL93, Program for the Crystal Structure Refinement* University of Gottingen, Germany, (1993).
- ²⁸ M. Nespolo, G. Ferraris, H. Ohashi, *Acta Crystallogr., Sect. B: Struct. Sci.* **55**, 902 (1999).
- ²⁹ M.W. Lufaso, P.M. Woodward, *Acta Crystallogr., Sect. B: Struct. Sci.* **60**, 10 (2004).

-
- ³⁰ E. Montanari, G. Calestani, L. Righi, E. Gilioli, F. Bolzoni, K.S. Knight, P.G. Radaelli, *Phys. Rev. B* **75**, 220101(R) (2007).
- ³¹ J. Topfer, J.B. Goodenough, *J. Solid State Chem.* **130**, 117 (1997).
- ³² J. Hemberger, F. Schrettle, A. Pimenov, P. Lunkenheimer, V. Yu. Ivanov, A.A. Mukhin, A.M. Balbashov, A. Loidl, *Phys. Rev. B* **75**, 035118 (2007).
- ³³ R. Cabassi, F. Bolzoni, A. Gauzzi, E. Gilioli, A. Prodi, F. Licci, *Phys. Rev. B* **74**, 045212 (2006).
- ³⁴ N. Imamura, M. Karppinen, T. Motohashi, D. Fu, M. Itoh, H. Yamauchi, *J. Am. Chem. Soc.* **130**, 14948 (2008).
- ³⁵ A.C. Larson, R.B. Von Dreele, "General Structure Analysis System (GSAS)", *Los Alamos National Laboratory Report LAUR 86-748* (2000).
- ³⁶ B.H. Toby, *EXPGUI*, a graphical user interface for GSAS, *J. Appl. Cryst.* **34**, 210-213 (2001).

4. Conclusions

The present Ph.D thesis deals with the synthesis and characterization of new multiferroic materials, in which different approaches are exploited in order to induce the coexistence of magnetic and ferroelectric properties in the same material. Particular attention was paid to the understanding of structure-properties relationships, fundamental topics in particular when new structures are involved.

The first class of materials studied is the tetragonal tungsten bronze (TTB) family, whose structure derives from a variation of the simple perovskitic framework. Being the TTB oxides generally good ferroelectrics, but having at the same time diamagnetic properties, the goal of the research was to introduce in the structure magnetic (iron) ions. Two different routes were followed: the first yielding the maximum number of magnetically active ions acceptable by the system ($K_xFe_5F_{15}$), while the second involves a dilution of the magnetic ions in the TTB matrix ($Ba_2GdFeNb_4O_{15}$).

When this work in the research group was started, the study of $K_xFe_5F_{15}$ fluorides was an open research field, for which some important results have been obtained, as for example the definition of the real structure of one member of the series ($K_{2.62}Fe_5F_{15}$) and the establishment of the connection between structural modulations, charge order and ferroelasticity. However, an accurate characterization of the physical properties of the system was missing, in particular relating to the effect of the potassium content on properties. The present work allowed the definition of the structural, magnetic, elastic and electric phase diagram of the whole system ($2 < x < 3$), which shows a complete multiferroic behaviour below the magnetic ordering temperature for all the stoichiometries. The nature of the magnetic ordering has been established by magnetization measurements and the magnetic structure has been determined by powder neutron diffraction

experiments. The ordering of Fe^+ and Fe^{3+} in the crystal lattice was established for different composition by single crystal X-ray diffraction and its influence on the physical properties discussed. The dielectric characterization was performed for both the end members, pointing out a relaxor behaviour connected with the charge order-disorder transition located just below 500K. Beside polycrystalline powders, produced by solid state reaction in controlled atmosphere, single crystals suitable for physical measurements were produced by different growth techniques, including hydrothermal growth in hydrofluoric acid solution, used for the first time for similar compounds. Besides fluorides, iron substituted TTB niobates were synthesized and characterized. However, their study was limited by the difficulty encountered in producing single phase samples showing the higher (and more interesting) iron concentrations.

The second structural class of materials studied is the so called “quadruple perovskites” manganites family, derived from simple perovskites through the buckling of the MnO_6 coordination octahedra. All the known manganites presenting quadruple perovskite structure are centrosymmetric and present antiferro- or weakly ferromagnetic properties. Noteworthy, in this case, the adopted “philosophy” was somehow opposite with respect to the one that brought magnetoelectricity in TTBs and involved the introduction of a “ferroelectrically” active ion in a magnetic matrix. Bismuth (III), well known for its stereochemical properties, was selected to produce the metastable $\text{BiMn}_7\text{O}_{12}$ phase, produced by high pressure/high temperature synthesis. The structure was determined by single crystal X-ray diffraction, evidencing an asymmetrical coordination around the Bi^{3+} ions, which result to be systematically shifted off the centre of their coordination polyhedra. As a consequence a dipole moment can be observed, likely giving rise to ferroelectric properties, which may be enhanced by the polarization of the bismuth $6s^2$ electronic cloud. TEM experiments pointed out the presence of twin domains ascribed to the shift of Bi ions in opposite directions, giving boost to the hypothesis of ferroelectricity in this compound. This statement is particularly

interesting if joined to the fact that the magnetic characterizations evidenced the presence of weakly ferromagnetic behaviour, suggesting that $\text{BiMn}_7\text{O}_{12}$ is a magnetoelectric multiferroic. Indeed, below 55 K nonzero magnetization is observed, ascribed to Dzyaloshinsky-Moriya interaction, yielding the spin canting of an antiferromagnetic structure which involves the Mn ions in octahedral coordination. The ordering of the spins on the square planar manganese ions takes place at lower temperature ($T=25$ K) and is of purely antiferromagnetic nature. The analysis of powder neutron diffraction data allowed the solution of the magnetic structures of the two manganese sublattices (octahedral and square planar coordination). The former, in particular, is the result of a complex scheme of interactions, in which the effect of the electrical polarization cannot be excluded. This feature, if confirmed, would give certain evidence to the coupling of ferroelectric and magnetic degrees of freedom, which nonetheless is suggested by the observation of anomalies in the electric permittivity at the magnetic transition temperatures. A further confirmation to this hypothesis is given by the detection of noticeable variations of the lattice parameters in correspondence of the magnetic ordering temperatures, evidencing the presence of magnetostrictive effects in the system.