Magnetoelectric phenomena in single-phase and composite systems

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In the present review, the main phenomenology and problematic related some of the most interesting magnetoelectric systems (materials having in the same phase magnetic and ferroelectric order and interaction between them, giving rise to the magnetoelectric effect) is presented. Some single-phase systems as manganites, $BiFeO_3$ and relaxor magnetoelectrics mainly interesting from a fundamental point of view, as well as diphasic composites with a high potentiality in applications are discussed. The coupling between ferroelectric and magnetic activity in magnetoelectric multiferroics opens the possibility of controlling magnetic properties through electric fields and vice versa, giving to these materials a large potentiality for applications in spintronics, multiple state memory elements or novel memory devices which might use electric and/or magnetic fields for read/write operations.

Key Words: Magnetoelectric, Multiferroic, Manganites, $BiFeO_3$, Relaxor, Composite.

Fenómenos magnetoeléctricos en sistemas monobásicos y composites

Resumen: En esta revisión, se presentan la fenomenología y principales problemas relacionados con los sistemas magnetoeléctricos más interesantes. En el efecto magnetoeléctrico el orden magnético y ferroeléctrico se dan en una misma fase con interacción entre ellos. Se abordan sistemas monobásicos como manganitas, $BiFeO_3$ y magnetoeléctricos relaxores y composites difásicos que poseen tanto un interés desde el punto de vista fundamental como un alto potencial de aplicaciones. El acoplamiento entre la actividad ferroeléctrica y magnética en multiferróicos magnetoeléctricos abre la posibilidad de controlar las propiedades magnéticas a través de campos eléctricos y viceversa, dotando a estos materiales de numerosas aplicaciones en espintrónica, elementos de memoria de estados múltiples o novedosas aplicaciones de memoria que pueden emplear campos eléctricos y/o magnéticos en operaciones de lectura/escritura.

Palabras clave: magnetoelectrico, multiferróico, manganitas, $BiFeO_3$, relaxor, composite

1. INTRODUCTION

Multifunctional or smart materials combining several properties in the same structure in order to produce new or enhanced phenomena have stimulated much scientific and technological interest within the scientific community in the last years. One of the most interesting categories of multifunctional systems is the magnetoelectrics, i.e. materials showing magnetoelectric effects. Having simultaneous magnetic and ferroelectric activity, possible attractive functionalities caused by the interactions between electric polarization and spontaneous magnetization can be envisaged. The primary magnetoelectric (ME) effect is defined by the appearance of an electric polarization under a magnetic field P(H): ME output or a magnetization at the application of an electric field M(E): EM output. The ME of second order (or secondary ME) consists on variation of the permittivity under magnetic field $\varepsilon(H)$ or the magnetic permeability at the application of an electric field $\mu(E)$. Materials exhibiting ME properties can be single-phase and composites (di- or poliphasic systems).

A ferroic system has an order parameter switchable by an adequate driving force or field (phenomena normally accompanied by hysteresis). Ferroelectrics, ferromagnetics and ferroelastics are typical examples of ferroics. The electric polarization, magnetic moment and strain can be switched from one ordered state to the opposite one by means of an electric, magnetic or stress field, respectively. If the same system possess two or more ferroic properties in the same phase, is named multiferroic (1.-). Thus, the magnetodielectrics are multiferroic materials.

The history of the ME effect dates back to early 1894, when Pierre Curie stated that it would be possible for an asymmetric crystalline body to polarize directionally under the influence of a magnetic field (2.-). Based on crystal symmetry considerations, Landau and Lifshitz (3.-) demonstrated that a linear ME can occur in magnetically ordered crystals, while Dzyaloshinskii (4.-) predicted the existence of the ME effect in antiferromagnetic Cr_2O_3. This was the first system proved as showing ME coupling, measuring the electric field induced magnetization (5.-) or detection of the magnetic field-induced polarization (6.-). One of the first prepared ferromagnetic ferroelectric material was the weakly

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ferromagnetic nickel iodine boracite, $Ni_3B_7O_{13}I$ (7.-). Following many more multiferroic boracite compounds with the general formula $M_3B_7O_{13}X$, where M is a bivalent cation of Mg^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc. and X a monovalent anion like OH^-, F^-, Cl^-, Br^-, I^- or NO_3^-, all of them having complex structures with many atoms per formula unit and more than one formula per unit cell were synthesized. The large number of inter-ionic interactions in the boracites prevented isolation of the essential factors causing multiferroicity and of the nature of the coupling between the magnetic, electric polarization and structural order parameters. The simultaneous presence of ferroelectricity and ferromagnetism in coexistence with ferroelasticity in nickel boracite $Ni_3B_7O_{13}I$ activates coupling between the spontaneous polarization, spontaneous magnetization and spontaneous deformation. It has been found that a field-induced 180° reversal of the spontaneous polarization causes a symmetry-conditioned 90° reorientation of the spontaneous magnetization (and reciprocally: a magnetic field-induced 90° reorientation of the spontaneous magnetization causes a 180° reversal of the spontaneous polarization) (8,9.-). Another class of early discovered ME materials are the antiferromagnetic-ferroelectrics perovskite ceramics $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) (10.-) and $Pb(Fe_{1/2}W_{1/3})O_3$, PFW (11.-). Later single-crystals of PFN were grown and the presence of a weak spontaneous moment in the ferroelectric phase below 9 K was confirmed (12.-). The ME effect has been found in numerous compounds in the last few decades (13,14.-), in materials with the perovskite structure, rear-earth manganites, yttrium iron garnets, pseudo-ilmenites, $BaMeF_4$ (Me = Mn, Fe, Co, Ni), Cr_2BeO_4 and inverted spinels (14,15).-. The discovery of a linear ME effect in the antiferromagnetic-ferroelectric $BiFeO_3$ (16.-) and in its solid solutions with Bismuth or Barium titanate led to a new class of ME in which the ferroelectric and magnetic phases coexist up to high temperatures (17-21.-). Among the single-phase ME materials, particularly strong ME effects, as initially envisioned, have not so far been measured, so that they have not yet found large scale applications in technology. In order to increase the ME response, a large number of di- or polyphasic composites in various forms have been investigated, as summarized by Ryu et al. (14.-).

The primary requirement for the observance of ME effect is the coexistence of magnetic and electric dipoles. Single-phase materials exhibiting ME effect have an ordered structure and require the presence of a ferroelectric/ferrielectric/antiferroelectric state. They are described by both a dipolar (electric) and a magnetic order parameter. These materials should show two types of phase transitions: one from ferroelectric to paraelectric state and the other one from a magnetic ordered state (ferromagnetic/ferrimagnetic/antiferromagnetic) to a non-ordered paramagnetic state. The ME effect arises due to the local interaction between the ordered magnetic and ferroelectric sublattices. The conditions for the occurrence of ferroelectricity and magnetic order in the same material requires: (i) the presence of adequate structural building blocks permitting ferroelectric-type ionic movements, i.e. off-centre displacement associated to the spontaneous polarization in ferroelectrics, (ii) magnetic-interaction pathways for the magnetic order, usually of the superexchange type, and (iii) to satisfy symmetry conditions (14.-).

To be technologically viable, ME materials must exhibit high ME coefficients, so that an intense activity was dedicated to look for new materials or structures in order to enhance the

ME effect. The possible applications include magnetic-electric sensors in radioelectronics, optoelectronics and microwave electronics and transducers in instrumentation. Apart from the properties of the parent phases (ferro/antiferro/ferrielectricity and ferro/antiferro/ferri-magnetism), the ME effect adds a supplementary freedom degree in designing materials for new applications. The coupling between the ferroelectric and magnetic activity in multiferroics opens the possibility to manipulate the magnetic properties through electric fields and vice versa, giving to these materials large potentiality for applications in spintronics, multiple state memory elements or novel memory devices which might use electric and/or magnetic fields for read/write operations. Although highly exciting for potential applications the single-phase magnetodielectric multiferroism is quite rare, being restricted to only few systems. Although a young topic, the ME multiferroism already put to the scientific community very interesting problems from the point of view of fundamental physics, due to the apparent opposite requirements concerning to the d-orbital occupancy for ferroelectric and magnetic order (N.A. Hill and A. Filippetti, "Why are there any magnetic ferroelectrics?"(9.-). Recently a few different mechanisms have been proposed to explain these contradiction and to find the possible compatibility of the two types of orders (22-24.-).

2. SINGLE-PHASE SYSTEMS

2.1. Manganites: $RMnO_3$ and RMn_2O_5.

The interest in investigating the manganites appeared after the discovery of the colossal magnetoresistance in $(La,Ca)MnO_3$ (26,27.-). The majority of the recent research has focused on manganites in which the large, A-site, cation is a rare earth, R, from the left hand side of the lanthanide series. The manganites of these large rare earth ions (La- to Dy-manganites) all crystallize in the cubic perovskite structure, with the same low temperature orthorhombic distortion. Another type of manganite structure is hexagonal. Both types show A-type antiferromagnetic ordering of the Mn^{3+} ions. In addition to the magnetic ordering, the hexagonal manganites also undergo a phase transition to a non-centrosymmetric low temperature state which has ferroelectric ordering. The family of ME materials with formula RMn_2O_5: $R^{3+}Mn^{3+}Mn^{4+}O_5^{2-}$ (in which R is a rare-earth ion from Pr to Lu, but also can be Y and Bi) are hexagonal manganites showing both magnetic and ferroelectric long-range order at temperatures lower than 30–40 K. At room temperature RMn_2O_5 crystals are characterized by an orthorhombic crystal structure with space group Pbam (28.-), in which Mn^{4+} is at centre of oxygen octahedron and Mn^{3+} is at the centre of the base of a square pyramid. The octahedra share their edges forming a ribbon similar as in rutile structure, a MnO_5 bipyramid forms a bridge connecting these ribbons and a larger R^{3+} ion is surrounded by eight oxygen atoms. The spontaneous polarization lies along the b crystallographic direction. The systems belonging to this family have two low-temperature phase transitions with simultaneous changes in the magnetic and structural states at $T_1 \sim 15 \div 20$ K and $T_2 \sim 35 \div 40$ K. The nature of the first transition is not clear in detail, while the second one is a simultaneous magnetic and ferroelectric phase transition, $T_2 = T_{N,C}$ (29.-). Magnetic, dielectric and magnetoelectric (ME) properties of several crystals with different R ions were studied in the last years (25,30,31.-).

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A very beautiful work proving that a multiferroic system from the family RMn_2O_5 exhibits a profound interplay between electrical polarization and the applied magnetic field was recently published by Hur et al. for $TbMn_2O_5$ (25.-). The authors demonstrated that a highly reversible switching of the electrical polarization can be obtained with moderate magnetic fields of $(0÷2)$ T. By the combined application of electric and magnetic fields, a permanent imprint to the polarization is also obtained (Fig. 1). These results point to new device applications of the multiferroics such as magnetically recorded ferroelectric memory.

The other types of manganite compounds with formula $RMnO_3$: $R^{3+}Mn^{3+}O_3^{2-}$ can also crystallize in two structural phases: hexagonal for R=Ho, Er, Tm, Yb, Lu, or Y, which have small ionic radii, and orthorhombic phase for R=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, or Dy, which possesses a greater ionic radius. In these compounds, the angle Mn-O-Mn is close to 180°, facilitating magnetic ordering via an indirect exchange interaction between the Mn ions through the O ions. While magnetic ordering occurs in both hexagonal and orthorhombic manganites, ferroelectric ordering occurs only in the hexagonal ones, which belong to the non-centrosymmetric P63cm space group. From this family, mostly $YMnO_3$ was investigated (32-35.-). Among the most recent and interesting studies dedicated to $YMnO_3$, is worth to mention the spatial mapping of coupled antiferromagnetic and ferroelectric domains, obtained by imaging with optical second harmonic generation (34.-). The coupling was explained as originating from an interaction between magnetic and electric domain walls, which leads to a configuration that is dominated by the ferroelectromagnetic product of the order parameters.
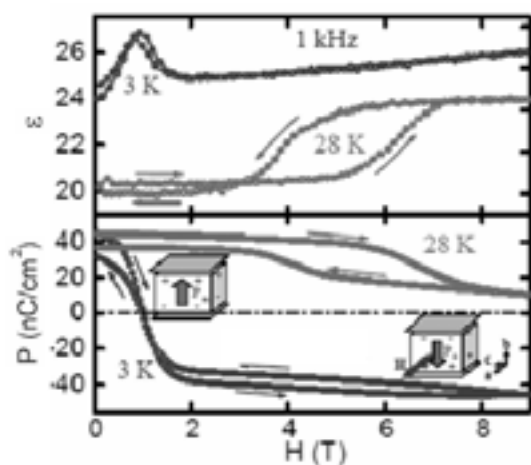

Fig.1.- Dielectric constant and total polarization vs. magnetic field in $TbMn_2O_5$ at 3 and 28 K. The picture shows the orientation of the net polarization at H=0 and high fields (34.-).

Many efforts have been dedicated to understand the mechanisms of ferroelectricity (and the possible ME effect) in perovskite manganites by comparison with the classical ferroelectric perovskites (8,9,22-24.-). The mechanism driving the ferroelectricity in perovskite ferroelectrics such as $BaTiO_3$ and isomorphs is incompatible with the existence of a spontaneous magnetic moment. The central Ti ion in $BaTiO_3$ is shifted from its position in the ideal perovskite structure (the centre of its surrounding oxygen octahedron) along one

crystallographic axis , creating an electric polarization in the ferroelectric state. This off-centring is stabilized by energy-lowering covalent bond formation, in which charge transfers from the filled oxygen 2p orbitals into the d states of the transition metal ion. For this mechanism, the d orbitals must be empty. On the other hand, in order to have magnetic order in transition metal ions, a partly filled d shell is necessary. It results that the classical mechanisms driving the ferroelectricity in perovskites are incompatible with a non-zero magnetic moment and other alternative mechanisms for the off-centre displacement causing ferroelectricity are required in magnetic ferroelectrics (9.-).

A possible way to avoid this incompatibility is proposed by Efremov et al. (22.-) based on the concept of charge ordering in doped perovskite-structure manganites. When $LaMnO_3$ (or related compounds in which the charge on the Mn ions is formally 3+) and $CaMnO_3$ (in which the Mn charge is formally 4+) are alloyed, the resulting arrangement of Mn^{3+} and Mn^{4+} ions can be ordered; this is called charge ordering. In charge-ordered and orbitally ordered perovskites it is possible to make use of the coupling between magnetic and charge ordering to obtain ferroelectric magnets. In particular, in doped manganites with formula $R_{1-x}Ca_xMnO_3$ where R=La, Pr, etc. and $x≠0.5$ there is a type of charge ordering that is intermediate between site-centred and bond centred. Such a state breaks the inversion symmetry and is predicted to be magnetic and ferroelectric (22,23.-). Aken et al. (35.-) proposed another mechanism for the nature of the ferroelectric phase transition in hexagonal $YMnO_3$ using a combination of structural analysis and first-principles density-functional calculations. It was demonstrated that ferroelectricity in $YMnO_3$ arises from a buckling of the MnO_5 polyhedral combined with the unusual Y coordination and the triangular and layered MnO_5 network. The calculations showed that the mechanism originating ferroelectricity is entirely driven by electrostatic and size effects, rather than the usual changes in chemical bonding associated with the ferroelectric phase transitions in other perovskite oxides. In contrast to the chemically stabilized ferroelectrics, this mechanism for ferroelectricity permits the coexistence of magnetism and ferroelectricity (35.-).

2.2 $BiFeO_3$ system

In the eighties, Ismailzade et al. (16,36.-) reported the presence of a linear ME effect in $BiFeO_3$, a compound of antiferromagnetic-ferroelectric nature. Its combination with bismuth titanate and barium titanate forms a family with the general formula $Bi_4Bi_{m-3}Ti_3Fe_{m-3}O_{3m+3}$ (m = 4, 5 and 8) or $Ba_xBi_{1-x}Ti_xFe_{1-x}O_3$ in which the coexistence of ferroelectric and magnetic properties exists up to high temperatures (17,28.-). In its bulk state, $BiFeO_3$ has a rhombohedral-distorted perovskite structure R3c (a=b=c=5.63 Å, α=β=γ=59.4°) at room temperature. It has long been considered an antiferroelectric because of its superstructure and low values of dielectric constant; it was ultimately classified as ferroelectric with a T_C around 1103 K. $BiFeO_3$ is an antiferromagnet with a Néel temperature T_N=310 °C (37,38.-), also showing a weak ferro/ferri magnetic characteristic in some temperature ranges (39.-). Having such a high Curie temperature, it was expected to present a high spontaneous polarization in its ferroelectric state (for example, $PbTiO_3$ with T_C=763 K, has a spontaneous polarization of ~80-100 $\mu C/cm^2$). Practically, only low values of the polarization and of the dielectric constant were determined experimentally at room temperature, mainly due

to the semiconducting properties of $BiFeO_3$, which does not allow proper electrical poling and leads to high dielectric losses. In ferroelectric ceramics the resolution of dielectric anomaly becomes difficult in such cases. Low resistivity of the sample at room temperature makes the observation of the ferroelectric loop very difficult as well, this seriously limits the applications of this material. In order to enhance the resistivity and to observe a P(E) hysteresis loop, measurements were performed on a high purity single-crystal at 80 K (40.-). This experiment allowed to find a spontaneous polarization of 3.5 $\mu C/cm^2$ along the (001), indicating a value of 6.1 $\mu C/cm$ along the (111) direction. Therefore, the saturation of the loop was not observed even at fields as high as 55 kV/cm. Saturated ferroelectric hysteresis loops were observed recently at room temperature in the single-phase $BiFeO_3$ ceramics obtained by rapid liquid phase sintering (41.-), with values of the spontaneous polarization, remanent polarization and coercive field of 8.9 $\mu C/cm^2$, 4.0 $\mu C/cm^2$, and 39 kV/cm, respectively, under an applied field of 100 kV/cm (41.-). The high conductivity and leakage found especially at higher temperatures were considered firstly caused by the high difficulty to produce single phase of $BiFeO_3$ (so that even very small impurities segregated at boundaries could have a doping effect and transform the dielectric into a semiconductor). On the other hand, even in very pure $BiFeO_3$, due to the spontaneous change of the oxidation state of Fe (3+/2+), oxygen vacancies are formed as a result of electrical neutrality requirement, giving rise to thermal activated hoping conductivity.

In order to diminish the mentioned problems, it was adopted the method of forming binary solid solutions with other perovskites with good dielectric properties as $BaTiO_3$ (42-44.-), $PbTiO_3$ (45.-) or systems as $BiFeO_3$–$RFeO_3$–$BaTiO_3$ in which R=La, Dy, Pr (46.-). In the last compounds, remnant polarization P_r=3-7 $\mu C/cm^2$ and remnant magnetization M_r=0.06-0.2 emu/g were reported (45.-). For the solid solutions of $xBiFeO_3$-(1-x)$BaTiO_3$, which was mostly studied, the structure was found as rhombohedral up to x=0.67 mole%, tetragonal at concentrations x<6 mole % and cubic in between (42.-). In the $BiFeO_3$-rich region, these ceramics show a weak ME coupling effect (43.-). Therefore, even in solid solution state, the problems of losses were only partially solved.

Although in single-crystal, ceramics and in solid solutions the properties are strongly affected by high loss and leakage due to nonstoichiometry defects and space charge characteristics, good properties were found in the last years in $BiFeO_3$ films obtained by Pulsed Laser Deposition (PLD), that seems to allow a better control of the composition and oxygen-stoichiometry within the entire volume of the sample (19,47-50.-). Wang et al. (19.-) growth pure heteroepitaxial films of $BiFeO_3$ thin films with thickness in the range of 50 to 500 nm onto (100) single crystal of $SrTiO_3$ substrates. These films had not rhombohedral crystalline state as the bulk material, but tetragonal-like structure with a small monoclinic distortion of about 0.5°. This resulted in a compressive stress imposed by the $SrTiO_3$ substrate electrode, which has an in-plane lattice parameter smaller than of $BiFeO_3$. These films presented both saturate P(E) hysteresis loops with a remnant polarization P_r=55 $\mu C/cm^2$ and magnetic m(H) loops with a saturation of 150 emu/cm^3 and coercivity around 200 Oe. The authors considered the high values of polarization as resulting from the stabilization of the monoclinic phase by the in-plane compressive stress imposed by the epitaxial bottom electrode. The in-plane stress is smaller when the thickness of film is increasing, as proved

by the data of thicker films. The values computed for the total energy and polarization by first-principle calculations using local-spin density approximation of P_s=63.2 $\mu C/cm^2$ for the tetragonal distorted state, by comparison with P_s=6.6 $\mu C/cm^2$ characteristic to the rhombohedral phase were also in favour of this interpretation (19.-).

On the contrary, Eerenstein et al. recently reported much lower values for magnetization and polarization for similar films. (47.-). They concluded that ferroelectric polarization is not enhanced by strain in epitaxial $BiFeO_3$ thin films. In addition, the authors explained the large value of magnetization reported in (19.-) as coming from the possible large percentage of Fe^{2+} in the film volume. But a high density of Fe^{2+} causing a high number of oxygen vacancies required for the neutrality condition would result in low electrical resistivity, unlike reported by Wang et al. (19.-), and thus strongly limiting the ME applications of such films. The authors concluded that an increased thickness-dependent magnetization found in (19.-) is not an intrinsic property of fully oxygenated and coherently strained epitaxial $BiFeO_3$ thin films characterised by a high electrical resistivity. Rather, high magnetizations are possible achieved only in de-oxygenated films, but loosing the ferroelectric performance due to a consequent increasing conductivity (47.-). Although few other explanations were proposed, the mechanism responsible for very different polarization and magnetization characteristics found in different epitaxial $BiFeO_3$ films is still unclear, being a hot topic under debate between various groups (19,47-49.-).
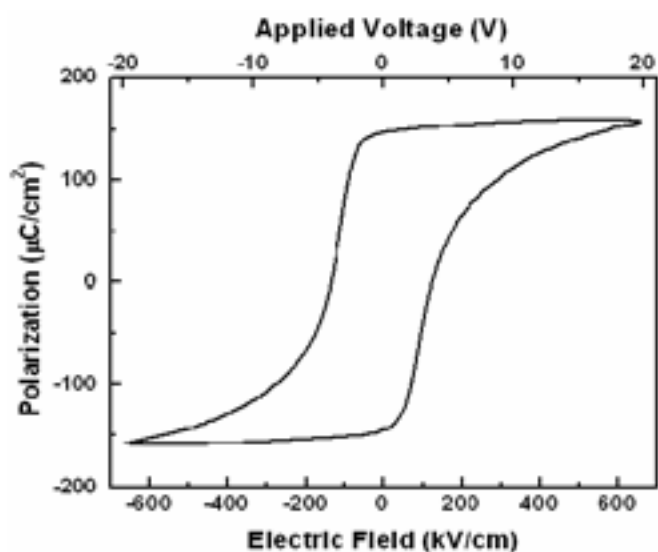

Fig.2.- Ferroelectric hysteresis loop of $BiFeO_3$ polycrystalline film showing giant polarization 49.- (courtesy of Yun et al.)

Moreover, even higher polarization were found in polycrystalline films of $BiFeO_3$ of 300 nm thickness deposited by PLD onto $Pt/TiO_2/SiO_2/Si$ substrates by Yun et al. (49,50.-). The remnant polarization at room temperature was determined as 100 $\mu C/cm^2$, considerably higher than any value previously reported in this system. By decreasing the temperature down to 90 K, a giant switchable polarization with the largest values ever measured for a ferroelectric material, was found (remnant and saturation polarizations P_r=146 $\mu C/cm^2$ and P_s=158 $\mu C/cm^2$ for a 20 V maximum applied voltage, as presented in Fig.

2) (49.-). This extraordinary result suggests that heteroepitaxial growth is not absolutely required for obtaining superior polarization in BiFeO$_3$. The phase symmetry seems to play again a determinant role on the ferroelectric properties (in this case: tetragonal symmetry with the space group P4mm and high tetragonal distortion c/a=1.018).

According to the overall mentioned results, there are few possible causes for the high values of polarization in BiFeO$_3$ films, by comparison with bulk: a) Extrinsic effects, as the constrained structures in epitaxial ultrathin films (19.-); in this case, is not explained the origin of the giant polarization in polycrystalline film reported in ref. (49.-); b) An intrinsic origin characteristic to the pure and defect-free BiFeO$_3$ (the nominal Bi/Fe ratio and oxygen stoichiometry that are controlled during the PLD deposition reduces the leakage in the films by comparison with the bulk samples), as possibly obtained in the polycrystalline BiFeO$_3$ films and not in bulk ceramics (49,50.-); c) The strong ferroelectric response might be associated with the tetragonal phase. In this case, the origin of the tetragonal phase (obtained in constrained and in stress-free epitaxies and in polycrystalline films) instead of the rhombohedral one typical for bulk BiFeO$_3$ system is unclear, as well as its role (maybe determinant) on the high ferroelectric polarization; d) Other new possible switching mechanism activated in thin films and not allowed in bulk structures. This last possibility is supported by large ferroelectric polarizations of 90–100 $\mu C/cm^2$ resulted from calculations within density functional theory with local spin-density approximation, consistent with possible large atomic displacements in the ferroelectric phase (51.-). According to these calculations, all the range of experimental polarizations reported in literature, including the recent exceptional high values, might be correct and not artefacts related to high losses or leakage effects. They can instead correspond to very distinct switching paths and mechanisms in the structural space allowing a simultaneous magnetic and ferroelectric activity and a coupling between them. Anyway, further measurements on well-characterized bulk and film samples are required to confirm this interpretation and to clarify the controversial properties of BiFeO$_3$ system.

2.3 Magnetoelectric relaxors

In the complex perovskite relaxor compounds with formula A(B$_1$B$_2$)O$_3$ the angles in the chain B$_1$-O-B$_2$ are close to 180°. Therefore, when transition element ions lie in the octahedral B positions, they may become ordered via an indirect exchange interaction through the oxygen ions. Since the ferroelectric ordering in the perovskite lattice arises mainly from the displacements of A and B ions, if magnetic ions are introduced into the octahedral B position, simultaneous ferroelectric and magnetic activity and possible ME coupling might appear. This is another route for obtaining ME materials.

Russian researchers started to obtain this type of materials in the period of 1950-1960, based on the idea of replacing some of the d^0 B cations in ferroelectric perovskite oxides by magnetic d^n cations (10,11.-). Using this approach, they produced the first synthetic ferromagnetic-ferroelectric material: (1−x)Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$−xPb(Mg$_{1/2}$W$_{1/2}$)O$_3$, in the early 1960s. In this system, the Mg^{2+} and W^{6+} ions are diamagnetic and their off-centre displacement is responsible for the ferroelectricity, while the formally d^5 Fe^{3+} ion is responsible for the magnetic ordering. Other examples include B-site ordered Pb$_2$(CoW)O$_6$ (52.-) which is ferroelectric and ferromagnetic, B-site disordered Pb$_2$(FeTa)O$_6$ (52.-) which is ferroelectric and antiferromagnetic, with weak ferromagnetism below 10 K. As a result of dilution of the magnetic ions, these materials all have rather low Curie or Néel temperatures. However a number of simple perovskite materials are known to have ferroelectric and magnetic (mostly of the antiferromagnetic type) ordering. The interaction of the ordered subsystems can result in ME effect, where the dielectric properties may be altered by the onset of the magnetic transition or by the application of a magnetic field, and vice versa. Due to their complex chemical structure, many of these systems are ferroelectric relaxors, which are very interesting because of high dielectric, piezoelectric and pyroelectric constants, particularly at the Morphotropic Phase Boundary, MPB, composition, when forming solid solutions with ferroelectrics like PbTiO$_3$, PT, or others.

Among them, a renewal of interest in the last years was particularly oriented to investigate the Pb-based magnetic
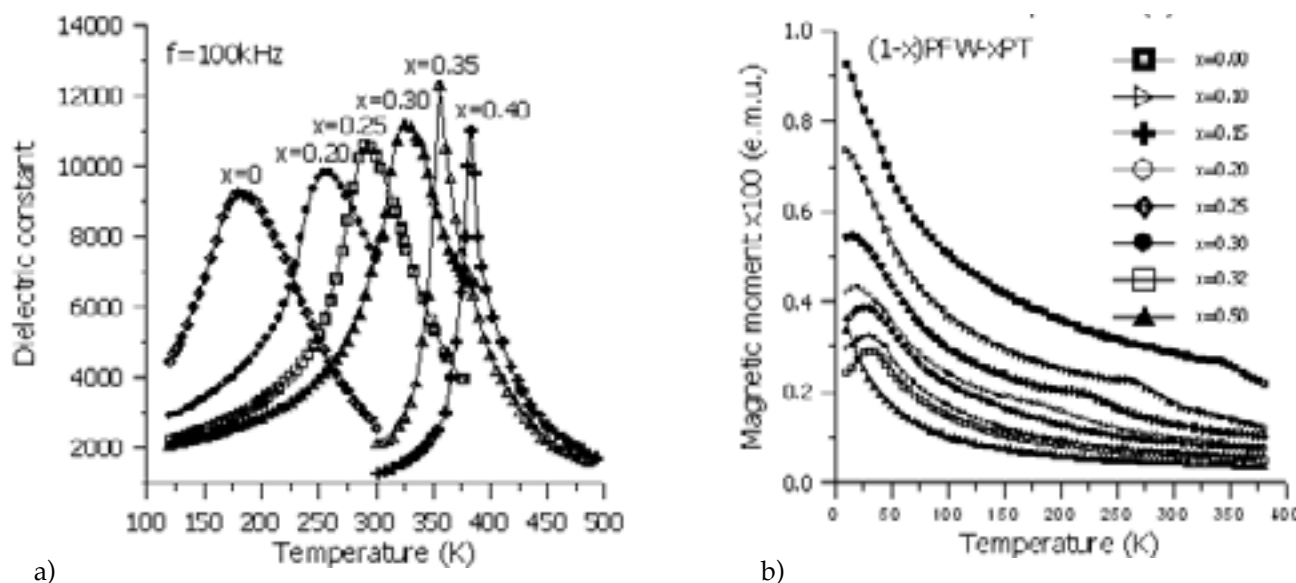

a)

b)

Fig.3.- Ferroelectric-paraelectric (a) and succession of magnetic transitions (b) with composition-dependent characteristic temperatures in (1-x)PFW-xPT (57,58.-).

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relaxors: $Pb(Fe_{2/3}W_{1/3})O_3$, PFW, (53-57.-), $PbNi_{1/3}Nb_{2/3}O_3$, PNN, (57.-) or $PbFe_{1/2}Nb_{1/2}O_3$, PFN, (58.-), $Pb(Co_{1/2}W_{1/2})O_3$ (59.-) and their solid solutions. Particularly, in the case of (1-x)PFW-xPT solid solutions, which were systematically investigated previously by us, both ferroelectric (relaxor)-paraelectric (Fig. 3 a) (55.-) and magnetic phase transitions (Fig. 3 b) were found (56.-).

A succession of magnetic transitions from weak ferromagnetic-antiferromagnetic, T_{N1}, and antiferromagnetic-paramagnetic, T_{N2}, state with increasing temperature take place, with characteristic temperatures T_{N1}, T_{N2} dependent on the composition x. For the pure relaxor composition, PFW, non-linear m(H) was found at low temperatures (Fig. 4). An interesting fact is the change of m(H) towards a triple hysteresis loop with a central loop at ±7 kOe and two lateral loops at (±7, ±45) kOe, in the Curie region for the transition relaxor-ferroelectric at around T_c=175 K. Since the relaxor-to-paraelectric phase transition is not accompanied by structural changes that might influence the magnetic properties via magnetostructural interaction, this fact was interpreted as a demonstration of a magnetoelectric coupling in this ceramic (56.-). The magnetoelectric coupling was explained trough microstructural characteristics of PFW and PFW-PT ceramics, which contain both disordered and partially ordered nanopolar clusters between the off-valence cations on the B-site (59.-). The magnetic interactions giving rise to the observed behaviour might be ascribed as follows: a) in the Fe/W ordered nanopolar domains, a weak superexchange of $- Fe^{3+} - O - W - O - Fe^{3+}$ type of interaction responsible for the magnetic anomaly at low temperature T_{N1} and b) in the Fe/W disordered regions, a stronger superexchange of $- Fe^{3+} - O - Fe^{3+}$ pathway interaction is responsible for the magnetic ordering at higher temperatures T_{N2}. The paramagnetic behaviour indicates the presence of magnetically isolated Fe^{3+} ions: in a perfect ordered system on the B-site of the perovskite cell, all of the magnetic Fe^{3+} ions are isolated. It results a direct relationship between the ferroelectric order degree and the magnetic behaviour (54,56.-). This picture explains
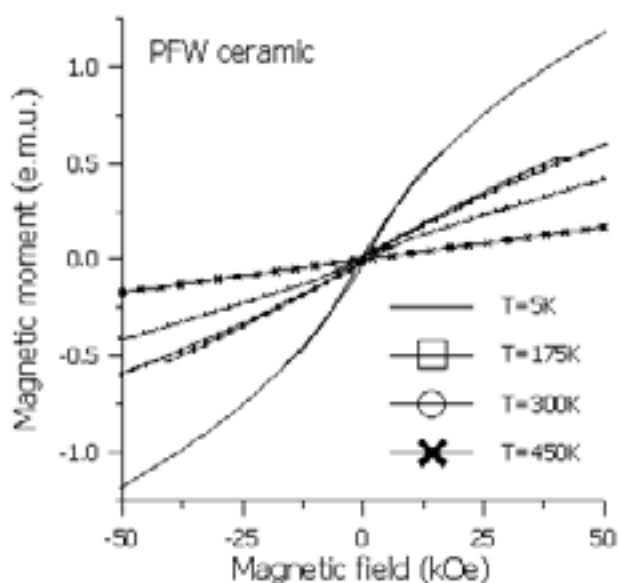

Fig.4.- The magnetic hysteresis loops m(H) for PFW ceramic at a few temperatures. Note the triple hysteresis loop at T_c=175 K (58.-).

the magnetic properties of PFW and of some other complex perovskites, as the ordered $Pb(Co_{1/2}W_{1/2})O_3$ which shows a single magnetic ordering at the temperature T_{N1}=8 K (61.-) and also was applied to obtain information about the degree of order in the relaxor PNN, in connection with the concentration of magnetic ions Ni^{2+} (57.-).

3. MAGNETOELECTRIC COMPOSITES

A second class of magnetoelectric materials consists of two-phase composites. The search for such systems was promoted by practical needs, due to very low values of the magnetoelectric voltage coefficient found in single-phase materials (of the order of 1–20 mV/cm·Oe, far insufficient for practical applications) and by the low temperature range for the ME effect, mostly at cryogenic temperatures. As presented by Ryu et al. (14.-), the ME effect is realized on the basis of the concept of product properties (60.-). According to this principle, a suitable combination of two phases such as a combination of piezomagnetic and piezoelectric phases or a combination of magnetostrictive and piezoelectric phases, can yield a desirable ME property. The conceptual conditions for the ME effect in composites were pointed out by Boomgaard (61.-), as following: i) the individual phases should be in chemical equilibrium, ii) no mismatch between grains, iii) high values for the magnetostriction coefficient of piezomagnetic or magnetostrictive phase and of the piezoelectric coefficient of the piezoelectric phase, iv) no leak of the accumulated charges through the piezomagnetic or magnetostrictive phase and v) deterministic strategy for poling of the composites. Following this principle, various ME composites have been reported, such as $Ni(Co,Mn)Fe_2O_4$-$BaTiO_3$, $CoFe_2O_4$-$BaTiO_3$, $NiFe_2O_4$-$BaTiO_3$, $LiFe_5O_8$-$BaTiO_3$, $CuFeCrO_4$-$BaPbTiO_3$, $CoFe_2O_4$-$Bi_4Ti_3O_{12}$, $NiFe_2O_4$-$Pb(ZrTi)O_3$, $(Ni,Zn)Fe_2O_4$-$Pb(ZrTi)O_3$, etc. (14,60-66.-). Particularly, giant values of the ME coefficients dE/dH of tens to hundreds of V/cm·Oe were obtained in bilayer and multilayer laminate composites of good piezoelectrics (as $Pb(ZrTi)O_3$ or $PbMg_{1/3}Nb_{2/3}$-$PbTiO_3$) with high magnetostrictive materials, as terfenol-D (66-68.-).

It is worth to mention also the recent nanostructured composite of $BaTiO_3$-$CoFe_2O_4$ deposited onto single-crystal $SrTiO_3$ (001) substrates reported by Zheng et al. (69.-), in which a 3D-heteroepitaxy (in-plane and out-of-plane) with self-assembled hexagonal arrays of $CoFe_2O_4$ nanopillars of 20-30 nm embedded in a $BaTiO_3$ matrix was grown. This system showed a strong coupling of the order parameters through the heteroepitaxy of the two lattices. Temperature dependent magnetic measurements illustrated the coupling between the two order parameters, which is manifested as a change in magnetization at the ferroelectric Curie temperature. Quasi-static ferroelectric measurements demonstrate well-defined ferroelectric hysteresis loop with a spontaneous polarization P_s=23 $\mu C/cm^2$ and piezoelectric measurements revealed a clear hysteresis loop with a maximum value of d_{33} around 50 pm/V. The magnetic data show a saturation magnetization of 350 emu/cm^3 with a strong anisotropy between the out-of-plane (001) and in-plane (100) directions. The coupling between the electric and magnetic order parameters in the self-assembled nanostructures was proved by an anomaly (drop) of the magnetization of 16 emu/cm^3 around the ferroelectric Curie temperature of T_C=390 K (69.-).-.

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4. CONCLUSIONS

The field of ME materials is a very active topic, particularly in the last 5 years, when extensive research has been conducted on various types of structures. The dielectric polarization of a material under a magnetic field or an induced-magnetization under an electric field (ME effect) requires the simultaneous presence of long-range ordering of magnetic moments and electric dipoles. The ME effect is particularly low in bulk single-phase materials, thus limiting their applicability in practical devices. This is probably due to the impossibility of controlling in the whole bulk volume the composition, stoichiometry and defect structure. A better control of these characteristics seems to be obtained in PLD films, particularly in the case of $BiFeO_3$ system, in which high values of the spontaneous polarization by comparison with the bulk materials have been reported. The origin of the very scattered (sometimes "author-dependent") values of the ferroelectric characteristics in bulk and epitaxial or polycrystalline films produced by various prestigious groups in the last years is still unclear, although few different (and some of them new and innovative) mechanisms, supported by results of first principle calculations, were proposed. From the fundamental point of view, the single-phase materials, particularly the controversial $BiFeO_3$ system are still very interesting for further studies and far to be understood. On the practical point of view, it seems that a good alternative are the ME composites exploiting the product property of the materials and giving rise to giant values of the ME coefficient.

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