Magnetoelectric Based Multiferroics

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Introduction

This present minireview gives a brief introduction, basic principles of multiferroics and its related parameters. Multiferroics, are the multifunctional materials in which existence of two or more ferroic orders, have become one of the hottest topics in this new era. The coexistence of different order parameters brings out new physical phenomena and are useful for new device fabrications. In multiferroics the experimental and theriotical concepts are evidenced by research activities, discoveries, and concepts. The creation of novel materials is one of the challenging approache i.e., to combine 2 or 3 different physical properties in single material to achieve multifunctional behaviors. The rare existence of magnetic and ferroelectric (FE) materials [1] was the starter of an exciting development in the physics of multiferroics [2]. In particular, the magnetoelectric (ME) effect, viz. the cross coupling of the order parameters, e.g., magnetization M and polarization P, to their conjugate fields, H and E [3] play an important role in applications [4]. The electrically and magnetically polarizable materials and their coexistence [5,6]. Particular interest has been aroused by the possibility of new magnetoelectric coupling mechanisms and the potential for exploitation in technical applications [7-9]. The objective of this thesis was to study the structural, magnetic, dielectric and ferroelectric properties of multiferroic materials and provide insight into these coupling mechanisms. We highlight the indirect evedinces of magnetoelectric and spin lattice coupling in Pb based multiferroics and special attention is paid to three novel mechanisms to understand the magnetoelectric coupling: (i) through the structural dynamics around the Neel temperature; (ii) dielectric anomalies around the Neel temperature; and (iii) low temperature magnetic susceptibility.

Magnetoelectric multiferroics

Recently, the coexistence of magnetization and electrical polarization in a single material play an important role and so called magnetoelectric (ME) multiferroics (now onwards stated as multiferroics) are currently center of attraction [6,10,14]. There exist several different classes of multiferroics [9] a very interesting type being the recently discovered [15,19] systems in which ferroelectricity appears only in certain magnetically ordered states [10] Some of the ME multiferroics show polarization only when applied to the magnetic field and others in zero magnetic field [20,22]. These multiferroics systems fit in to different crystallographic classes, and although some general rules governing their behavior are already established [10] yet there is no clear idea or general understanding of the origin of multiferroic properties. In the current developments in device shrinking and high-density data storage, the integration of multifunction's into one material system has become highly desirable. From magnetic and ferroelectric materials, emergence the extensive applications, it is natural to pursue a new generation of applications like, Memories, sensing, and actuating devices tailored by materials that combine magnetism and ferroelectricity in an effective and intrinsic manner One way to improve the magnetoelectric response in single-phase compounds significantly is to make use of strong internal electromagnetic fields in the components with large dielectric and magnetic susceptibilities. It is well known that ferroelectric/ferromagnetic materials have the largest dielectric/magnetic susceptibility, respectively. Ferromagnetism and ferroelectrics, i.e., magneto - ferroelectric [2] would be primary candidates for an enhanced magnetoelectric effect. Except for the coexistence of ferroelectricity and ferromagnetism, materials with strong coupling between primary ferro elastic and ferromagnetic order parameters, in the class of ferromagnetic martensitic systems, were also studied about 10 years ago [23].

The origin of multiferroicity

Dzyloshinsky [25] and Astrov [26] (1959 - 1960) theoretically and experimentally showed the ME effect, means magnetic or

electric induction of polarization P or magnetization M. Since then numerous magnetic materials have been established to show this ME effect [27]. In general, ME effect describes the coupling between electric and magnetic fields in matter (i.e., induction of magnetization (M) by an electric field (E) or polarization (P) generated by a magnetic field (H). Thermodynamically, the ME effect can be understood within the Landau theory framework, approached by the expansion of free energy for a magnetoelectric system, i.e.,

$$F(\vec{E},\vec{H})=F_0- P_i^s\, E_i -\ M_i^s\, H_i -\ \tfrac{1}{2}\ \varepsilon_0\varepsilon_{ij}E_iE_j -\ \tfrac{1}{2}\ \mu_0\mu_{ij}H_iH_j -\ \alpha_{ij}E_iH_j -\tfrac{1}{2}\beta_{ijk}E_iH_jH_k -$$
$$\tfrac{1}{2}\gamma_{ijk}H_iE_jE_k - \cdots \qquad (1.1)$$

where F_0 is the ground state free energy and subscripts (i, j, k) refer to the three components of a variable in spatial coordinates. E_i and H_i are the components of the electric field and magnetic field , respectively; and are the components of the spontaneous polarization and magnetization ; ε0 and μ0 are the dielectric and magnetic susceptibilities, β_{ijk} and γ_{ijk} are the third-order tensor coefficients and, most importantly αij is the component of tensor . The tensor corresponds to induction of polarization by a magnetic field or of magnetization by an electric field which is designated as the linear magnetoelectric effect. The rest of the terms in the preceding equations correspond to the high-order magnetoelectric effects parameterized by tensors β and γ [7]. The differentiation of equation (1.1) leads to the polarization and to the magnetization.

$$P_i(E,H) = \frac{\partial F}{\partial E_i} = P_i^s + \varepsilon_0\varepsilon_{ij}E_j + \alpha_{ij}H_j + \tfrac{1}{2}\beta_{ijk}H_jH_k + \tfrac{1}{2}\gamma_{ijk}H_iE_j + \cdots \qquad (1.2)$$

$$M_i(E,H) = -\frac{\partial F}{\partial H_i} = M_i^s + \mu_0\mu_{ij}H_j + \alpha_{ij}E_j + \beta_{ijk}H_jE_i + \tfrac{1}{2}\gamma_{ijk}E_jE_k + \cdots \qquad (1.3)$$

Different Routes to Multiferroicity

A detailed summary of classification of multiferroics based on the mechanism underlying the ME phenomena can be found in references [7,34,35].

a)   Geometrically driven ferroelectricity in hexagonal manganites

b)   Ferroelectricity induced by spiral spin-order

c)   Independent System

d)   Ferroelectricity Induced by lone pair electrons

Geometrically driven ferroelectricity in hexagonal manganites

In ferroelectrics the driving force for ferroelectricity is structural instability towards the polar state associated with electronic pairing. Such ferroelectrics were coined as 'proper' ferroelectrics. Along this by product of a complex lattice distortion will induce polarization. This class of materials, together with all other ferroelectrics with their polarization originating from by–product of order configurations, were coined as 'improper' ferroelectrics. The hexagonal manganites ($RMnO_3$) with R the rare – earth element (Ho – Lu, or Y), fall into the latter category, and are often cited as typical examples that violate the d^0 – ness rule.

Ferroelectricity induced by spiral spin-order

In the above systems the magnetoelectric coupling is rather weak as the ferroelectricity and magnetism basically originate from different ions or subsystems. There are few exceptional compounds in which ferroelectricity is induced directly by the spin order, meaning that an intrinsic magnetoelectric coupling occurs between the ferroelectric and magnetic order parameters. Two mechanisms are being considered to understand such a magnetoelectric effect:

Symmetry consideration

The inter-exclusion between ferroelectricity and magnetism originates not only from the d^0 -ness rule, also they depend on the spatial and time reversal symmetry. Ferroelectricity needs the broken spatial-inversion symmetry and invariant time reversal symmetry. Whereas the broken time-reversal symmetry is the prerequisite for magnetism. Consequently, a multiferroic system requires the simultaneous breaking of the spatial-inversion and time-reversal symmetries. The ME coupling between polarization and magnetization is derived from this general symmetry argument [25,40 41].

Microscopic mechanism

In addition to the symmetry restrictions, a microscopic mechanism responsible for ferroelectricity in magnetic spiral systems is required. It remains unclear whether the spiral spin order (spiral SDW) is a prerequisite for generating ferroelectricity. It was predicted that the acentric dislocated SDW may also drive a ferroelectric polarization [41]. Currently, three theories on microscopic aspect of magnetoelectric coupling in magnetic spiral multiferroics have been proposed: the inverse Dzyaloshinskii-

Moriya (DM) model [42-44], the spin current model (KNB model) [68] and the electric current cancelation model [45].

Independent system

To combine ferroelectricity and magnetism is to synthesize multiferroics with two structural units functioning separately for the ferroelectricity and magnetism and well known examples are borates, such as $GdFe_3(BO_3)_4$, which contain ferroelectricity active BO_3 groups and magnetic ions Fe^{3+} [46,47]. In addition to multiferroicity, these materials exhibit interesting optical properties. Boracites, such as $Ni_3B_7O_{13}I$, are also in this category [48,49]. $Fe_3B_7O_{13}Cl$ and $Mn_3B_7O_{13}Cl$ they belong to a same category. All the above compounds are non-perovskite compounds. Pervoskite multiferroics were first prepared by Russian scientists. They proposed to mix both transition metal (TM) ion with *d* electrons and ferroelectrically active TM ions with d^0 configurations at B–sites. The idea was that the magnetic ions and d^0 – shell TM ions separately favor a magnetic order and a ferroelectric order. The typical compound is $Pb (Fe_{0.5}Nb_{0.5}) O_3$ (PFN) in which Nb^{5+} ions are ferroelectrically active and Fe^{3+} ions are magnetic, respectively. The coupling between magnetic and ferroelectric order in this kind of multiferroic is very week because these two order parameters originate from different kinds of ions, hence the name independent multiferroic materials. In addition to PFN, other multiferroics falling in this category of $A(B'_{1-x}B''_x) O_3$, such as $Pb (Fe_{0.5}Ta_{0.5}) O_3$ [50] and $Pb (Fe_{0.67}W_{0.33}) O_3$ [51] which also showed weak magnetoelectric coupling.

Ferroelectricity induced by lone-pair electron

In the magnetic perovskite structure oxides and related materials, multiferroics is most commonly achieved by making use of the stereochemical activity of the lone pair on the large (A-site) cation to provide the ferroelectricity, while keeping the small (B-site) cation magnetic. The ions with lone–pair of electrons, such as Bi^{3+} and Pb^{2+}, always locate at A-site in an ABO_3 perovskite structure. This allows TM ion to locate at B-site so that the incompatibility for TM ions to induce magnetism and ferroelectricity is partially avoided. The typical examples are (and the most widely studied) $BiFeO_3$ and $BiMnO_3$ where B–site ions contribute to magnetism and the A–site ions via the lone pair mechanism lead to ferroelectricity. Considerable research has been carried out recently on independent Pb based multiferroic systems. Among the independent systems $Pb (Fe_{0.5}Nb_{0.5}) O_3$ (PFN), $Pb (Fe_{0.67}W_{0.33}) O_3$ (PFW) and solid solutions of the $Pb (Fe_{0.5}Nb_{0.5}) O_3$ - $Pb (Fe_{0.67}W_{0.33}) O_3$ are taken for the studies.

$Pb (Fe_{0.5}Nb_{0.5}) O_3$ Magnetoelectric Multiferroics

Recent years, single phase multiferroic materials have attracted much attention as they provide means to explore and understand details about the coexistence of magnetic and electric ordering [62]. The search for these materials is driven by the prospect of controlling charges by applying magnetic field and controlling spins by applying electric field. Such inter-controllability helps in developing new forms of multifunctional devices [62]. Among the single-phase lead based multiferroic materials, $Pb (Fe_{0.5}Nb_{0.5}) O_3$

(PFN) exhibits high dielectric constant and diffuse ferroelectric phase transition. PFN is an attractive candidate for the potential applications, such as multilayer ceramic capacitors and other electronic devices [63]. PFN exhibits ferroelectric phase transition (Curie temperature, T_C) at ~ 380 K and antiferromagnetic ordering below its Néel temperature (T_N ~ 143 K) [63]. Although multiferroic properties have been well characterized both in single crystal [64 – 66] and ceramic form [67–69], there exists controversy about the structure of PFN. In a study using synchrotron x-ray diffraction for powder and single crystals of PFN, Bonny et al. [66] have reported a monoclinic ferroelectric structure at 293 K, which undergoes a structural transition at 355 K (for single crystals) to another ferroelectric phase with tetragonal symmetry. At 376 K a phase transition to a paraelectric phase with cubic symmetry takes place. Some reports show PFN with rhombohedral structure (space group *R3m*) at room temperature, which undergoes a diffuse phase transition at 387 K to cubic Pm3m symmetry [70]. A recent work on single crystals has suggested a small monoclinic distortion away from rhombohedral symmetry at room temperatures, along with the existence of an intermediate phase of tetragonal symmetry at temperatures between 355 K and the ferroelectric Curie point of 376 K [66]. Moreover, antiferromagnetic G-type spin ordering has been found in powder PFN samples at temperatures below T_N =143 K [63, 70]. However, the T_N values for PFN have been reported to be widely scattered from lowest value of 143 K [71] to the highest value of 200 K [72]. The large scattering of T_N (143 -200 K) in PFN is mainly due to the fluctuations in the local ordering of Nb and Fe ions [72] and/or to local clustering of Fe ions. It may also be due to the varied synthesis methods adopted, which leads to grain growth with lattice strain/stress in the material and these parameters affect the T_N.

These results of structural complexity are consistent with the study of Lampis et al., [73] who performed neutron and x-ray diffraction experiments in PFN powders obtained by grinding single crystals, although the authors have shown a monoclinic distortion ("pseudo- rhombohedral" structure) in the ferroelectric phase i. e. at 80, 250, and 363 K. On the other hand, it has been pointed out that the structure of PFN ceramic samples corresponds to a rhombohedral symmetry [74]. In agreement with these results, Ivanov *et al.*, refined the structure from neutron diffraction measurements in rhombohedral symmetry at 10 and 300 K [75]. However, more recently, it has been reported that PFN exhibits monoclinic structure with *Cm* space group from 12 K up to room temperature [2]. However, the nature of magnetic and nuclear structure is still not clearly understood, as Ivanov *et al.* [75] discussed the structure only at 10 and 300 K, while Singh et al. [63] reported only nuclear structure using synchrotron powder XRD. The disagreements in the earlier reports are the propelling reasons for present study. In the light of above considerations, further investigation is required to confirm the existence of structural symmetry in this synthesis conditions and method. We have applied neutron diffraction technique in order to resolve the structural complexity of PFN. Neutron diffraction experiments measured at

different temperatures from 290 K to 2 K for better understanding of the nuclear and magnetic structure of the controversial PFN along with dielectric and magnetic properties. Detailed understanding of the structural properties is very important because all magnetic and ferro-dielectric properties are structural dependent. From the analysis of the structural refinements, it is shown that the lattice parameters and unit cell volume show distinct anomaly at T_N, with unambiguous evidence of small negative thermal expansion and a large thermal expansion below and above the T_N, respectively. These structural anomalies are well reflected in magnetic, ferro-dielectric properties which indicates the presence of strong correlation between the structural properties and magnetic, ferro-dielectric properties and this is the direct evidence of spin-lattice coupling.

Pb (Fe$_{0.67}$W$_{0.33}$) O$_3$ Magnetoelectric Multiiferroics:

Pb based multiferroics have been attracted researcher attention to develop the fabrication of magnetoelectric multiferroic materials at ambient temperature [76-78]. Materials that have a simultaneous existence of ferroic ordering such as ferroelectricity and ferromagnetism in single phase materials would be the tremendous interest in not only for practical applications but also for understanding the fundamental physics [76-80]. Ferroelectricity occurs from change in dipoles which relative shifts of negative and positive ions that induce surfaces charges and is favoured by empty d orbitals in covalent oxides such as perovskite tungstate; on the other hand, magnetism is related to ordering of spin of electrons in incomplete electron shells, resulting from partially filled d orbitals. Single phase and other composite oxide multiferroics are discovered by the Smolenskii. et al in the late 1959s, among which Pb Pb (Fe$_{2/3}$W$_{1/3}$) O$_3$ (PFW) was one of the promising candidates. PFW is showing a complex perovskite-type structure with ferroelectric and antiferromagnetic ordering at room temperature. In which the two kinds of cations (Fe^{3+} and W^{6+}) are randomly distribute at the octahedral B-site positions. PFW has the unique properties of having a high degree of order parameter and practically viable magnetic ordering at $T_N \sim 350 – 380K$ (paramagnetic-to-antiferromagnetic); with paraelectric to ferroelectric phase transition temperature (T_C) $\sim 150 – 200K$ [782]. Recently, *M-E* coupling between the ferroelectric and antiferromagnetic orders in PFW (and related materials) was observed through an anomaly in the lattice parameters variation anomaly of dielectric constant at T_N and through a change in the dielectric constant induced by an external magnetic field The exact T_C depends on the measuring conditions of the samples tested, principally whether they are in the form of single crystals or ceramic powders [84]. Ye et al reported on single crystals of PFW remain optically isotropic down to 4 K and, thus there is no indication of any structural phase transition related to the Curie temperature (T_C) at 150 – 200K, structure remains cubic only. Although multiferroic properties have been well characterized on PFW both in single crystal and ceramic form [79], but there exists a controversy regarding the structure. Agranovskaya et al reported the PFW exhibits rhombohedral structure below T_C and above T_C is cubic structure. Ivanov et al [80] studied the PFW through XRD

(90 – 700K) and ND (10 – 700K), reported the existence of cubic structure throughout the sample. According to an early report PFW adopt a *cubic* perovskite structure (*Pm-3m*) at room temperature (RT), with Fe^{3+} and W^{6+} statistically distributed over B-sites. The cubic symmetry was also reported for PFW at low temperatures. It has also been proposed that the Fe ions in PFW give rise to an antiferromagnetic structure below T_N The structural properties of PFW have been studied in less detail and the role of the structure change upon the magnetic and dielectric properties is not clear. The basis of this structural study around T_C, has not been clearly investigated and becomes the first purpose of this work. Ivanov et al reported the existence of relaxor nature due to the polar clusters but they have not discussed origin of relaxor nature. The disagreements in the earlier reports are the propelling reasons for the present study. In the light of above considerations, further investigation is required to confirm the existence of structural symmetry in this synthesis conditions and method. We have presented a detail synthesis method to obtain single phase PFW at lower sintering conditions through the columbite method. We have performed neutron diffraction technique in order to resolve the structural complexity of PFW. Neutron diffraction experiments measured at different temperatures from 300 to 2 K for better understanding of the nuclear and magnetic structures of the controversial PFW along with dielectric and magnetic properties. Detailed understanding of the structural properties is very necessary because all magnetic and ferro-dielectric properties are structural dependent. From the analysis of the structural refinements, it is shown that the lattice parameters and unit cell volume show distinct anomaly at T_C, with unambiguous evidence of small negative thermal expansion and a large thermal expansion below and above the T_C, respectively. From the ND data, diffuse scattering observed above the ferroelectric ordering temperature and it suggesting the existence of polar domains in the paraelectric state, due to the relaxor nature. Magnetic, ferroelectric and dielectric measurements were done to gain broad insight into the origin and presence of phase transitions and instabilities in PFW. This is first detailed investigation of PFW system including structural, magnetic and electrical properties. These structural anomalies are well reflected in magnetic, ferro-dielectric properties which indicates the presence of strong correlation between the structural properties and magnetic, ferro-dielectric properties and this is the direct evidence of spin–lattice coupling.

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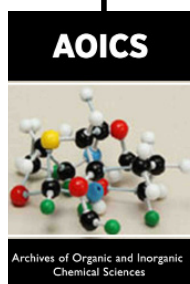
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