PFM and MFM Study of Multiferroics and Magnetoelectric Multiferroics

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Abstract

I this paper, we will review recent developments in fabricating multiferroics and magneto-electric multiferroics. It is shown that the new immiscible composites of multiferroic materials with different engineered structures for instance magnetic nanodots embedded in epitaxially grown ferroelectric matrix can result in magneto-electric (ME) coupling. In other words, one can write the data on material magnetically and read electrically. We focused on the studies that are performed with the help of Piezoresponse Force Microscopy (PFM) and Magnetic Force Microscopy (MFM) at the same time. These tools are able to visualize ferroelectric and magnetic orderings in the material. Therefore they are suitable tools to explore multiferroics that they have both order parameters simultaneously. In these studies different methods have employed to measure ME coupling that we will discuss in detail.

Contents

1 Multiferroics

Materials with both electronic and magnetic functionality have caught a great of interest and are going to have an important role in the modern technology. Ferroics are an example of such materials that show ferroelectricity, ferromagnetism, ferroeleasticity or magnetoeleasticity. They could have one or combination of these properties. Multiferroics are a large class of this kind of materials showing spontaneous ferroelectric and magnetic ordering at the same time. magnetoelectric material is a subclass of multiferroics in which an electric polarization can be induced by an applied magnetic field and vice versa. Magnetism and ferroelectricity coupling can potentially be used in the construction of novel multifunctional spintronic devices. In the following, I will give a brief definition and review of these kind of materials with possible applications regarding to Refs [6,5].

1.1 Definitions and applications

Ferroelectric materials exhibit electrical polarization that could be switchable and stable. This polarization results as a cooperative displacemnet of cations in the crystal. Ferroelectrics are widely used as ferroelectric random access memory (Fe-RAM) in computers.

Ferromagnets show spontaneous magnetization or magnetic order. This ordering is stable and can be switched hysteretically by applying magnetic field. Antiferromagnets possess ordered moments that they cancel each other and then it doen't show pure magnetic moment. The magnetization arises through the quantum mechanical phenomenon of exchange. These materials are extensively used for recording and storing data in hard drive of computers.

Magnetoelectric material show coupling between magnetic and electric ordering at the same time and their magnetic order can be changed by applying electric field and vice versa. Therefore an induced electrical polarization and magnetization can be controlled by applying magnetic and electric field, respectively. This effect allows development of novel tools like new kind of data storages that can be written magnetically (electrically) and read electrically (magnetically). The other interesting application could be the construction of novel spintronic devices such as tunnelling magnetoresistance (TMR) sensors, spin valves with functionality tunable by an electric field [[1]]. Unfortunatly the magnetoelectic effect in this kind of materials is too small to be useful for mentioned applications(the magnetoelectric coupling must be both large and active at room temperature).

Piezoelectrics (Piezomagnetics) are classes of materials in which strain changes linearly as a function of applied electric (magnetic) field. In these materials polarization (magnetization) can be changed by applying electric field. Similar to this definition, we can define the concept of Electrostriction (Magnetostriction) that describes a change in strain as a quadratic function of applied electric field (magnetic field) [6].

Naturally it is difficult to find intrinsic multiferroics because the driving mechanisms of both are different than each other. These mechanisms are incompatible as well. Ferroelectrics are composed of mostly transition metals that have empty d-shell in the crystal, on the other hand in ferromagnets a transition metal with a partially filled d-shell do exist. Scientists are trying to synthesize such a material that could handle two different properties at the same time. For example Smolenskii et al. [2] proposed the doping of paramagnetic cations into known non-magnetic ferroelectric compounds. In this situation if we consider the pervoskites, B site will contains a cation with empty and filled d-shell to produce ferroelectricity and magnetization simultaneously. Also steriochemical activity of Bi^{3+} and Pb^{2+} "lone-pairs" can help to combine ferroelectricity and magnetism [3]. However, the ferroelectricity and magnetism in these types of compounds originate from different ions, it includes both of the properties that is necessary for multiferroic, but the coupling between them is too weak.

There are different suggestions to make multiferroics, but I am not going discuss them here anymore because it is far from goal of this article to include different possibilities for combining electrical and magnetic properties as mentioned before. For more information about these possibilites one can refer [4, 5]

Now a day the classification of the multiferroics is extended to cover antiferroics as well. For example magnetoelectric coupling can occur in paramagnetic ferroelectrics. Figure 1 shows schematically the relationship between all kinds of ferroics that we defined above.

As it shown in Figure 2 a ferroelectric is asymmetric under spatial inversion and invariant under time inversion. This means that the sign of electric field and electric polarization upon inversion of coordinates ($r \rightarrow -r$) changes but is unchanged upon time inversion ($t \rightarrow -t$). Magnetization M and magnetic field H are invariant under spatial inversion and they change their sings under time reversal. These conditions are well showed in the Figure 2. Since a multiferroic include both properties of ferroelectrics and ferromagnetic materials, it will have breaking of both symmetries at the same time. It should be mentioned that coupling between two orders in multiferroic system is often small. Strong coupling will enable us to control the order parameters in different ways. Thus, realization of strong coupling is in the center of researches. Recently some new materials have been discovered that may have opportunity to be a suitable mulferroic. Development in thin film growth techniques and experimental methods, urged the researchers to examine different methods to make magnetoelectric (ME) materials [14].

Magnetoelectric coupling can occur between two order parameters. It can also be raised indirectly by intermediation of the strain. This can happen in composite materials in which magnetic and electric order exist separately, that can be coupled by strain in intimate connection of phases. It is obvious that the size of composite material will play a key role to have a strain-mediated indirect magnetoelectric coupling (Figure 3).

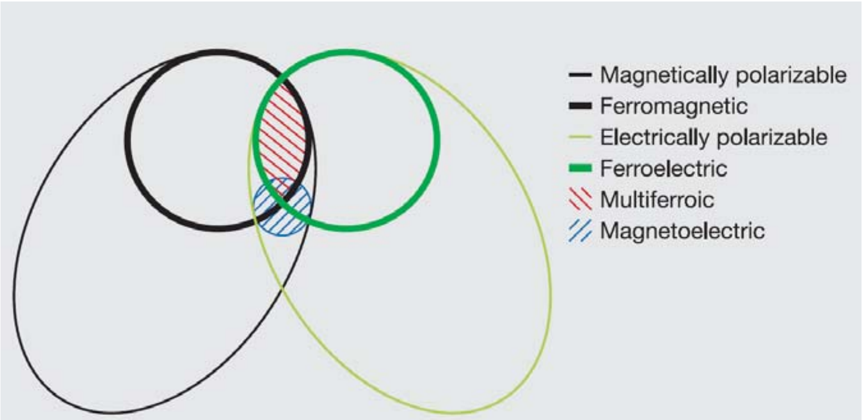

Figure 1- Schematically the relationship of multiferroic and magnetoelectric material is shown. Red hatching part depicts multiferroics. Blue is ME materials that it could occur in all magnetically and electrically polarizable materials either via strain mediated order or not [[6]].

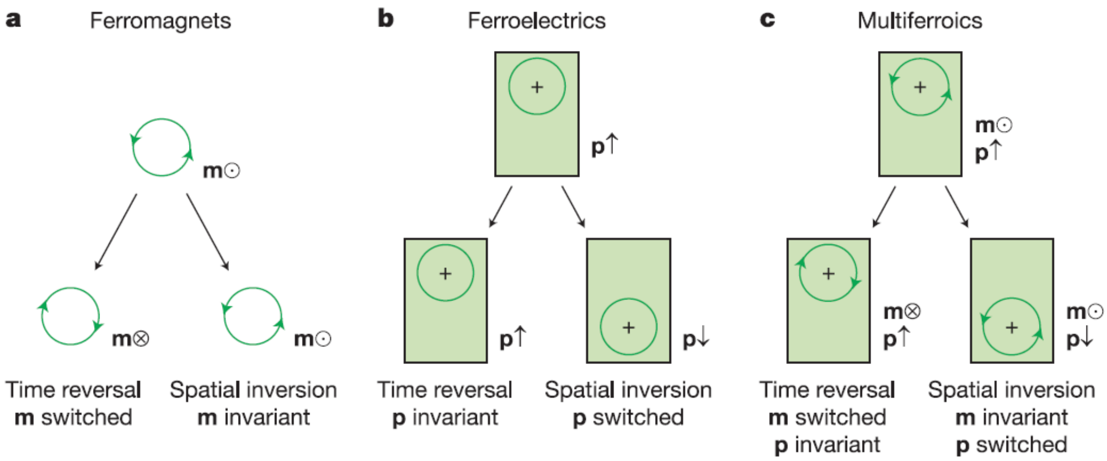

Figure 2- Symmetry operation in ferroics, (a) classically magnetic order, m, comes from orbiting of electron around atom. Thus the symmetry remains unchanged under spatial inversion, changes under time inversion, (b) dipole moment, p, that is asymmetric point charge in the crystal, it is asymmetric under spatial inversion and invariant under time inversion, (c) multiferroics includes both properties at the same time so it breaks all symmetries [6].

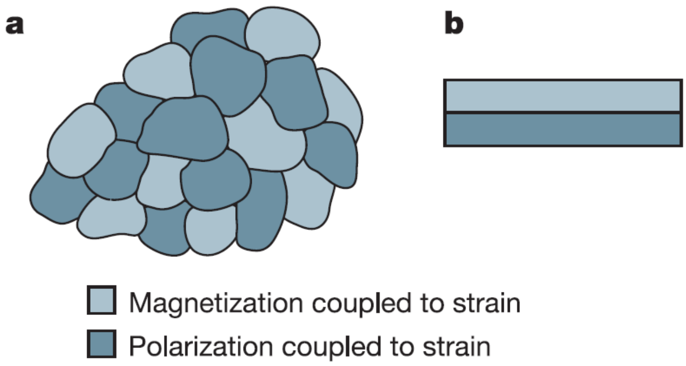

Figure 3- Strain mediated ME coupling can occur in two phase systems via intimate contact of two phase without being miscible in each other [2].

1.2 Magnetoelectric coupling

Magnetoelectric effect can be explained using Landau theory. In this system free energy F is written in terms of an applied magnetic field H and electric field E. Using Einstein summation convention free energy of the system F can be written as

$$-F(E,H)=\frac{1}{2}\varepsilon_0\varepsilon_{ij}E_iE_j+\frac{1}{2}\mu_0\mu_{ij}H_iH_j+\alpha_{ij}E_iH_j+\frac{\beta_{ijk}}{2}E_iH_jH_k+\frac{\gamma_{ijk}}{2}H_iE_jE_k+\ldots \qquad 1$$

Where H_i (E_i) is the i^{th} component of applied magnetic (electric) field. First term of the right hand side of equation is related to the electrical response to an electric field in which ε_0 is the permittivity of the free space and ε_{ij}(T) (a second-rank tensor) is relative permittivity.

The second term is the magnetic equivalent of the first term, where μ_{ij}(T) is the relative permeability and μ_0 is the permeability of free space. Third term is linear coupling via α_{ij}(T). The other terms represent higher order of magnetoelectric coupling coefficients.

By differentiating F one can derive the magnetoelectric effect in the form of Pi(Hj) or Mi(Ej) as follow:

$$P_i(H_j)=\alpha_{ij}H_j+\frac{\beta_{ijk}}{2}H_jH_k+\ldots \qquad 2$$

$$M_i(E_j)=\alpha_{ij}E_i+\frac{\gamma_{ijk}}{2}E_jE_k+\ldots \qquad 3$$

α_{ij} is the parameter that reveals how strong is the linear couling and corresponds to the induction of polarization by magnetic field or vice versa. Ferroelectric and ferromagnetic materials often have large permittivity and permability respectively. Unfortunately the magnetoelectric effect is too small to be used practically as the term α_{ij} is limited by the relation

$$\alpha_{ij}^{2} \leq \varepsilon_{ii}\mu_{jj} \quad 4$$

We have discussed linear coupling above, but nonlinear coupling also is possible in some materials. Materials with small values of either ε_{ij} or μ_{ij} have small linear magnetoelectric coupling (equation 4). for higher order couplings that is described by β_{ijk} and γ_{ijk} ther is not such a limitations and in some material it can dominate the linear part.

As I mentioned before, the coupling can be mediated by a different factor like strain in composites. This kind of coupling that we will discuss about the real experiments in the next sections is known as indirect coupling.

Researchers have tried to make and study different materials that can be classified into two categories, single phase and two phase materials. For example Cr_2O_3 [[7]] value of $\alpha = \partial P / \partial H$ =4.1 psm^{-1}.

Two-phase systems propose an alternative strategy to enhance magnetoelectric effects. As we discussed before indirect strain induced coupling between a ferromagnet and a ferroelectric occurs. Scientists are trying to optimize the factors like their size, shape and thickness to deduce a strong indirect coupling in the room temperature. As it have been discussed strain induced coupling requires intimate contact (Figure 3) between a piezomagnetic (or magnetostrictive) material and a piezoelectric (or electrostrictive) material. This can be achieved in the form of composites[8],[9] , laminates[10] or epitaxial multilayers[11]. Ferroelectric layers can generate strains of the order of 1% in magnetic epilayers owing to structural phase transitions. Alternatively, one may attempt to alter the magnetic structure of a film by applying a voltage to the underlying piezoelectric material[12].

There are few very good review articles that different multiferroics and different ways of combining the ferroelectricity and ferromagnetism have been discussed in detail. For more information one can refer to [[13], [14], [15]]. My goal is to have a look on PFM and MFM application on the multiferroics.

2 Piezo Force response Microscopy (PFM)

Scanning probe microscopy has different variants regarding to the properties of different materials. Of particular interest for the characterization of multiferroic materials is the use of an AFM tip as a movable top electrode, in order to locally measure a sample’s electrical, electromechanical or magnetic properties. For these applications, AFM tips are either coated with a conductive layer or made of a conductive material.

Different types of SPMs can be used to characterize multiferroics including conventional AFM, Conductive probe AFM (CAFM), Electrostatic Force Microscopy (EFM), *Kelvin Probe Microscopy(KPM), Piezoresponse scanning force microscopy (PFM), Magnetic Force Microscopy(MFM).* In the case of multiferroics two latter methods have special advantages because these techniques measure the properties that are critical in multiferroics. Based on this fact nowadays people are interested to observe whether a multiferroic can be manetoelectric or not. These techniques enable us to observe electrical, magnetic and mechanical properties at the same time locally in the nanoscale. In the following we will discuss the techniques and the material briefly.

2.1 PFM Basics

The need for exploring the electromechanical properties and functionalities of materials was the motivation for development of the PFM. It can be used as a tool for local nanoscale imaging, spectroscopy, and probe the coupling between polarization and mechanical displacement of in piezoelectric and ferroelectric materials. By applying an electric field to the sample surface using a conductive tip, PFM will be able to measure the mechanical response with a picometer precision (Figure 4 and 5).

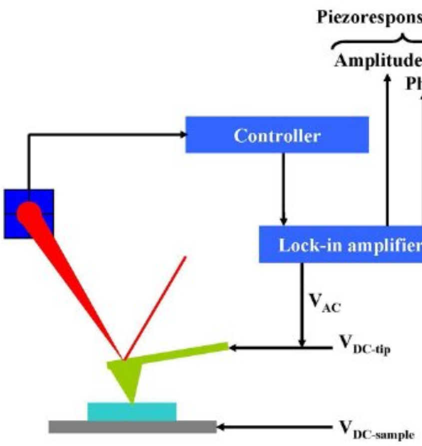

Figure 4- Typical schematic of the PFM that ac and dc voltages are applied to the conductive tip, deflection of the tip from surface due to the origin of deflecting force the (piezo or magnetic) enables to picture the sample property [[16]].

PFM provides a precise method to probe the piezoeffect locally due to high vertical resolution and high localization of electric field at the junction between the conductive tip and the surface. Therefore PFM is a contact mode AFM in due course it biased with a DC voltage to detect the local piezoelectric effect.

Piezoelectricity can occur parallel to the surface of the sample -in plane- that is called lateral effect. Lateral component of tip vibrations can provide the information about the in plane surface displacement, it is known as lateral PFM. Rotating the sample by 90 degrees makes it possible to find the other component of in-plane piezoeffect. If the vertical and lateral PFM signals are calibrated in a proper rout, electromechanically response vector can be derived.

By applying a voltage as a function of DC bias to the tip, the information about ferroelectricity and its polarization switching can be probed.

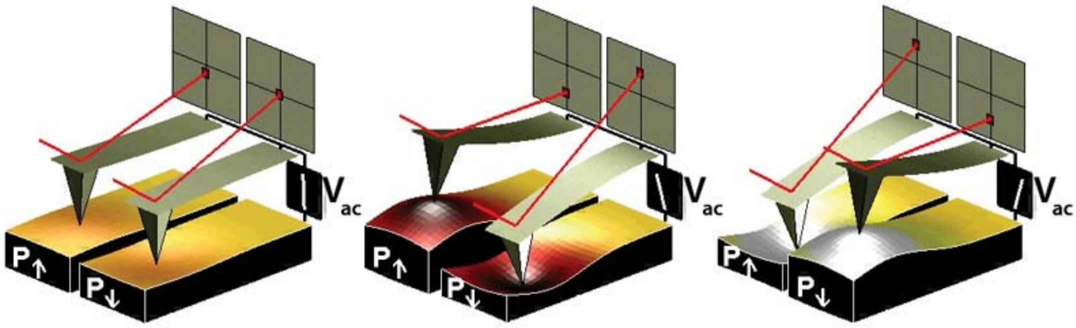

Figure 5 – Strain in ferroelectrics is result of crystal distortion that it induces strain. In downward vertical polarization by applying positive voltage to the tip sample will expand and if the polarization is upward the sample will contract. The reverse occur for negative voltages.

2.2 Piezo Effect

Strain and applied electric field in piezoelectric materials can be formulated by a 3*3 tensor matrix. But the most important element of this tensor is the vertical displacement d_{33}, because it couples directly to the vertical motion of the tip in which mounted on the cantilever.

The voltage is applied to the conductive tip is

$$V_{tip} = V_{dc} + V_{ac} \cos(\omega t) \qquad 5$$

Which V_{dc} is the switch bias and V_{ac} with frequency of ω is the probe bias. Piezoelectric material will expand or contract due to the piezo effect in the material that causes cantilever displacement as below

$$z = z_{dc} + A(\omega, V_{ac}, V_{dc}) \cos(\omega t + \varphi) \qquad 6$$

If ac voltage frequency is far less than contact resonance of the cantilever, the equation 2 can be written as:

$$z = d_{33} V_{dc} + d_{33} V_{ac} \cos(\omega t + \varphi) \qquad 7$$

Where, it clearly relates the mechanical response to the polarization of the material. But it should be noticed that the d33 component is the effective value of displacement. This means that this effective value includes the contribution of other tensor elements and also other effects like crystallographic and real space orientation of the piezo material and so on. d_{33} values is different for different piezoelectric material and varies from 0.1pm/V for (weak) to 500pm/V (strong).

As we can see from the Figure 5, sample polarization direction determines the sign of the tip deflection or response. When the polarization and applied electric field have the same direction and the piezo effect will be positive and it will expand locally, if the local polarization and applied electric field are anti parallel directions, the sample will contract at that position. This sign-dependent behavior means that the phase of the cantilever provides an indication of the polarization orientation of the sample when an oscillating voltage is applied to the sample[17].

2.3 Imaging Modes mechanism in PFM

PFM can only detect the electromechanical response, in other words ferroelectrics are necessarily piezoelectric. Therefore based on this fact the PFM will be a powerful instrument to derive domain patterns. There are three different modes for contrast mechanism in PFM. Cantilever, basically, performs 3 kinds of motion on the sample,

1- vertical deflection - out of plane deflection due to d33 component is measured by detecting the tip-deflection signal at the frequency of modulation, is called vertical PFM
2- Lateral deflection – in plane component of polarization can be measured by this mode is called lateral PFM. In this case, the applied electric field causes a shear deformation of the grain, which is transferred via the friction forces to the torsional movement of the cantilever. Combined with the vertical imaging mode, this technique can be used to reconstruct the 3D distribution of polarization within the domains of single crystal[18],[19] (Figure 6).

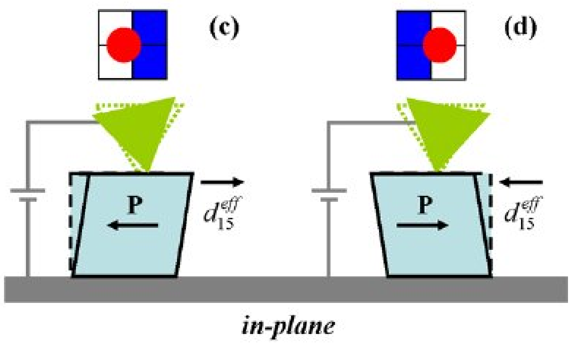

Figure 6- In lateral PFM shear movement is measured as is shown schematically. Torsional deformation causes that cantilever reflect the spot horizontally [16].

2.4 Spectroscopy Modes

PFM technique has another mode that is different from imaging modes in which it is known as spectroscopy mode. It is in fact measuring the hysteresis loops in ferroelectric materials. This hysteresis loop gives some information about local ferroelectric behavior of the materials. It reveals local switching as well as nucleation biases.

Since the most important proof of ferroelectricity is the presence of a switching between at least two stable states, in the PFM technique, the piezoelectric hysteresis is generally recorded using a dc bias source connected in series with the dc voltage source. Hysteresis loops are obtained by sweeping the bias voltage and recording the piezoresponse signal while the PFM tip is kept fixed above the probed nanoscale region of the sample. The result of this procedure is named in-field hysteresis loop[20].

2.5 Magnetic Force Microscopy

Magnetic force microscopy (MFM) is a suitable technique to observe the local magnetization of material on its surface. In MFM a tip with ferromagnetic coated material is attached to the bottom of the cantilever. When it moves on the surface of the sample, depending on the direction of magnetization of the surface, magnetic tip interacts with the surface and will result the deflection of the tip. Figure 7 schematically shows the interaction of the tip with sample. The microscope senses the tip deflection and converts it into images. The system operates in non-contact mode. The force gradient (F′) detected contains information from both the surface structure and surface magnetization[21]:

$$F' = F'_{surface} + F'_{magnetic} \qquad 8$$

$F'_{surface}$ results from tip and surface interaction, and $F'_{magnetic}$ is the magnetic interaction. If the distance between the tip and the sample surface is close enough (typically beyond 100 nm) $F'_{surface}$ will dominate $F'_{magnetic}$ then what we will see would be the topography of the sample instead of magnetic domain effects. Therefore depending on the distance between the surface and the tip, an MFM images will have an image from combination of topography and magnetic signals. Interatomic magnetic forces persist for longer distances from surface compared to short range van der Waals force. This fact reveals that if the tip is too close to the sample (where standard non-contact AFM is operated, the image) the van der waals forces will dominate, if tip is away from surface enough magnetic effects will be revealed. However, some methods have been developed to separate these effects from each other in which one can derive real magnetic images. MFM can image magnetic domains in nano scale. Often the lateral resolution of the MFM is about 10~50 nm that makes it a powerful tool for investigation of magnetization nanostructures. Figure 7 shows magnetic domains map of a hard disk drive derived by MFM technique.

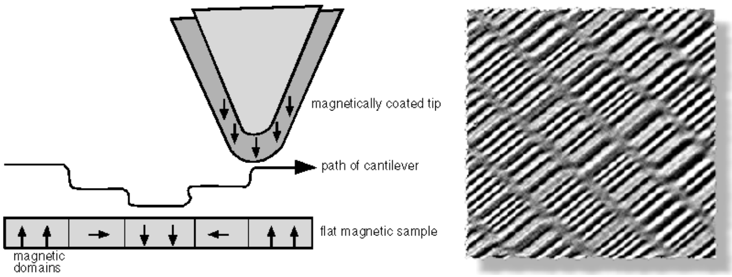

Figure 7- MFM maps the magnetic domains of the sample surface. MFM image is showing the bits of a hard disk (Field of view 30μm) [21].

3 Studies

In this section I am going to review the studies about multiferroics especially magnetoelectric materials that have been studied with combination of PFM and MFM imaging methods. Researchers have used different techniques to study the ferroelectricity and magnetic properties in different kind of matters. Unfortunately the number of articles that magnetoelectric effect was considered in them is limited. For ferroelectric materials the main method to characterize is Piezoresponse Ferroelectric Microscopy, but for magnetic materials except Magnetic force microscopy there are some other methods to characterize and discuss this effect. For example Ying-Hao chu et al[22] have used PFM to reveal piezo effect and X-ray magnetic circular dichroism (XMCD)–photoemission electron microscopy (PEEM) to image the nature of the magnetism and at the end coupling of electric and magnetic property of the matter. In the following I will have a review on the PFM and MFM studies and their results will be discussed.

As it was discussed before thin films and two phase or composite materials has more chance to have higher coefficient of ME. Hetrostructure thin films also are a possible good candidate to explore magnetoelectricity property of them. Ramesh et al[23] have discussed in detail the possibilities for magnetoelectric materials using thin film technology.

3.1 PTFO thin film

Progresses in thin film technology have created many oppurtunity to develope the real two dimaensional physics. It is proven that matrial in the thin film form show different properties than bulk. Thin film material are in stress in comparison to the bulk. Then by using proper method it could be possible to fabricate fuctional material that they could have magnetic and ferroelectricity (piezo effect) at the same time. Nowadays there a lot of efforts to use the advatages of thin films in the different fields. For example, Palkar et al have develpoed room temperature thin films that shows magnetic and ferroelectricity simultaneously[24]. Thin film of $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ was deposited using PLD (Pulsed Laser Deposition) and its magnetic and ferroelectric properties was monitored using MFM and PFM technique at the same time. Figure 8 shows magnetic and ferroelectric hysteresis of the thin film. Saturation magnetization and polarization and also coercive magnetic field can be derived from the graph. The result of these two plot prove the coexistence of the both order parameters at the same time with enough magnitude to be useful.

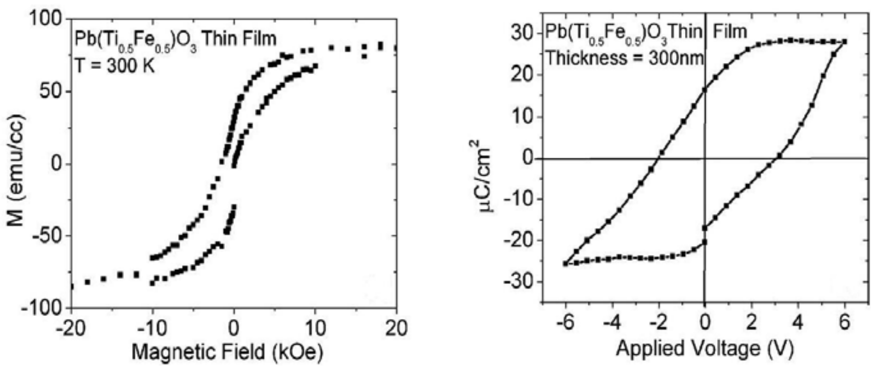

Figure 8- M-H curve for $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ thin film, and Ferroelectric loop obtained on $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ thin film (~3000 Å) [24].

To prove the coexistence of the two magnetic and ferroelectric order at the microscopic scale in the thin film MFM and PFM experiments were done simultaneously. Figure 9a shows topography of the surface and stripe domains of magnetic structure on the surface of the thin film. Simultaneous measurement of topography and piezoresponse is show in the Figure 9b. To observe the effects of polarization on the written magnetic domain, again MFM image was taken from the same area that is shown in Figure 9c. It is obvious that topography remains unchanged during different scans, then this MFM image looks like as a composite of two previous images. The stripe domains are present as Figure 9a so that it is the remnant polarization as in Figure 9b. In other words, this image is a result of both MEM and electric field microscopy (EFM). By the way, thin films of $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ show acceptable coexistence of ferroelectric and magnetic orderings at room temperature at both macroscopic and microscopic levels. This reveals that thin films have great potentiality to make great progresses to synthesize multifunctional materials like multiferroics.

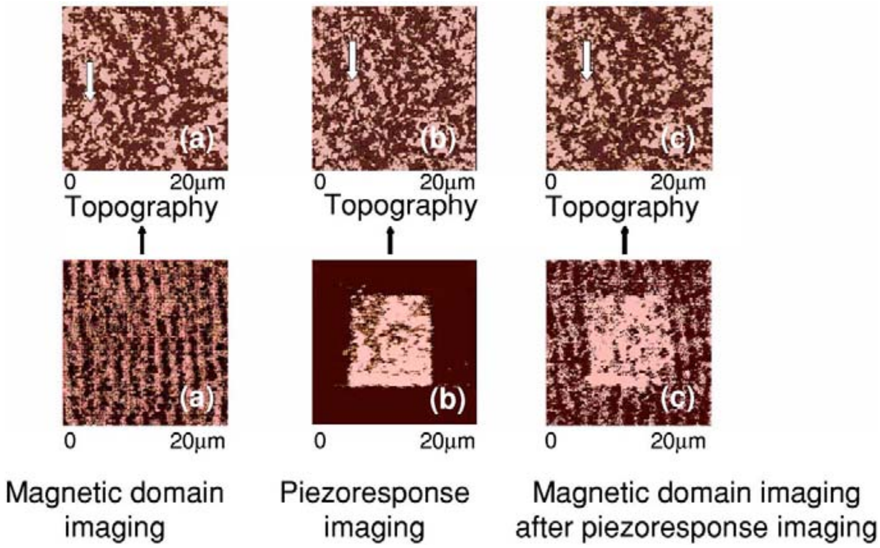

Figure 9- MFM and PFM images of $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ thin film. (a) AFM and MFM images of $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ thin. (b) AFM and PFM images of $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ thin film. (c) AFM and MFM images of $PbTi_{0.5}Fe_{0.5}O_{3-\delta}$ thin film after writing ferroelectric domains in b [24].

3.2 BFO/CFO composite thin films

Li Yan, et al have reported ferroelectric, ferromagnetic and magnetoelectric properties of self assembled epitaxial $BiFeO_3$–$CoFe_2O_4$ (BFO–CFO) nanocomposite thin films that is deposited on variously oriented substrates[25]. They derived that FE and FM properties depend on orientation of BFO phase and the size of CFO phase. What can be understood from this behavior is that ME in addition to dependant on FE and FM properties depends on the structure of phases.
They have deposited two phase $0.65BiFeO_3$–$0.35CoFe_2O_4$ epitaxial thin films using pulsed laser technique on (001), (110), and (111) oriented SrTiO3 (STO) substrates, that SrRuO3 (SRO) is used as bottom electrodes for FE and FM measurements, respectively. FE and FM properties have been studied using PFM and MFM technique. Figure 10a shows 7×7 μm^2 square was poled by -10 V, where a 5×5 μm^2 area was subsequently reversely poled by +10 V. this reveals clear switching of polarization under reverse bias. Figure 10b and 5c shows MFM images of (001) films magnetized by +1 and -1 kOe repectively. These images show clearly that magnetization of sample was reversed fully. These images shows that this composite thin film have the both FE and FM effects at the same time clearly that is necessary for ME effect. They have measured ME coefficient as a function of ac magnetic field for the (001), (110), and (111) BFO–CFO nanocomposite films along both in-plane and out-of-plane directions. Their final results can be summarized as

1- FE properties are similar to BFO single phase and P(111)>P(110)>P(001)
2- FM properties depends on the CFO phase nanostructure, and a trend of (001)>(110)>(111)
3- ME properties that is combination of FE and FM properties have a trend of (001)>(110)>(111),

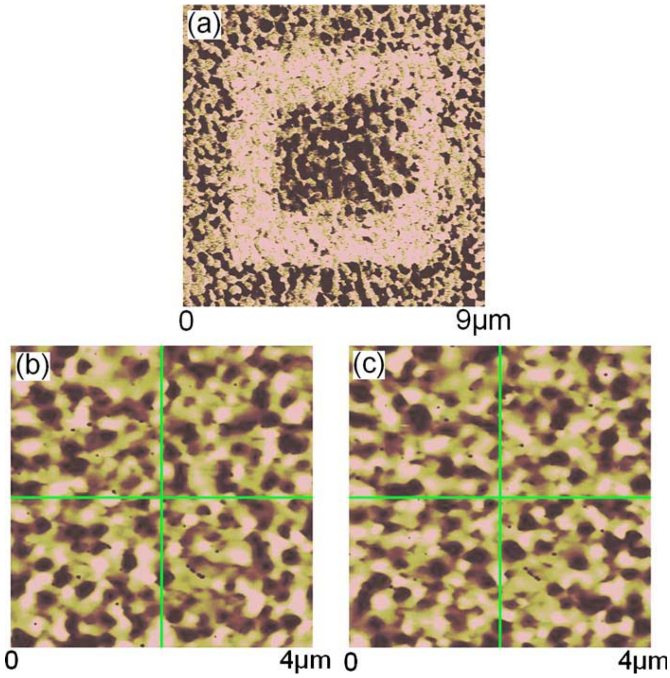

Figure 10- BFO–CFO nanocomposite thin films. a) PFM images of BFO–CFO thin film after poled by E =−10 V applied to a 7×7 μm^2 and E=+10 V applied to a 5×5 μm^2 area, which demonstrate polarization rotation and MFM images of BFOCFO thin films magnetized by b) H=+1 kOe, and (c) H=−1 kOe applied to same regions as those in PFM image, which demonstrate spin rotation [25].

What is clear from these results is that the ME phenomenon depends on different parameters that it needs improvement. Regarding this fact the origin of magnetism is different than ferroelectricity, have led the scientist to synthesize strain mediated functional ME material. As I mentioned before, the composite materials have a great chance due to magnetostriction effect to have magnetoelectric coupling. Therefore most of research works in this field is related to this kind of compounds. To synthesize such a compound there are many options of different kind of piezo and magnetic materials. The point is engineering of the combination and optimizing them regarding to their stochiometric values of elements and structure (like ordinary blend of composites, pillar structure, and multilayer of thin films).

3.3 BFO/CFO columnar nanostructure

One of the ideas to fabricate ME materials is engineering FE and FM materials in different designs. Using this technique one can synthesize FE/FM composites with improved intimate contacts between grains that can increase strain mediated ME. Zavaliche et al[26] synthesized such a material that epitaxial nanostructure (~200 nm film) comprised of ferrimagnetic $CoFe_2O_4$ pillars embedded in a $BiFeO_3$ matrix, with a relative volume ratio of 35/65. They have used PFM and MFM to image locally piezoelectric-magnetic switching of ME composite. Growth at high temperature by Pulsed laser deposition method (PLD) leads phase separation and self assembly of $CoFe_2O_4$ in pillar structure that is surrounded by ferroelectric $BiFeO_3$ that is shown schematically in Figure 11.

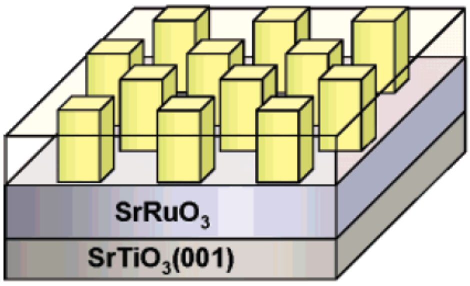

Figure 11- Schematically drawn BiFeO3-CoFe2O4 epitaxial nanostructures. [26].

Figure 12a-c shows MFM and PFM images of this composite and shows that ferroic properties of CFO and BFO are preserved in the composite patterned structure. This means that ferroeletricity and magnetism exist at the same time. Most of the pillars show explicitly uniform magnetic contrast that indicates the pillars are in the single domain state.

In Figure 12a Magnetization points up (negative phase, repulsive interaction) and in Figure 12b it poits down (positive phase, attractive interaction). PFM image of the composite matrix is shown in Figure 12c that poling was performed by applying bias -8V on 5 × 5 μm^2 area, and in its center again probed with applied reverse bias +8V over 3 × 3 μm^2 area. This indicates that polarization that is stable upon switching in the matrix of BFO.

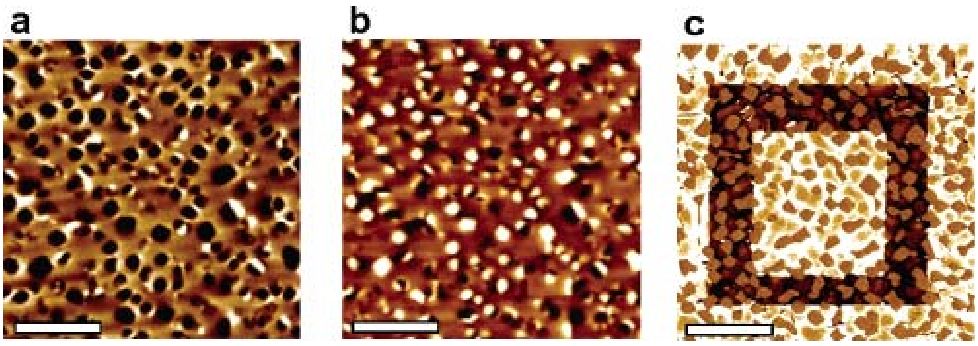

Figure 12- PFM and MFM images of a $(BiFeO_3)0.65$-$(CoFe_2O_4)0.35$ film, (a, b) MFM of the same area of film under perpendicular magnetic fields of 20 kOe to the surface and out of surface. (c) Perpendicular PFM image after the film poled at -8 V (dark frame), and +8 V (white, inside box). (bars = 2 μm) [26].

Like PFM images MFM image of the same area in Figure 12a, b shows magnetization switching occurs on columns after applying sufficiently strong magnetic field. To explore the coupling of two ferroic components in this nanocomposite PFM and MFM imaging were done after every electrical poling or magnetizing. At the first film was magnetized out of plane in 20 kOe magnetic field, that induces upward magnetization in CFO pillar structures (white in Figure 13a) and in the second step the film was poled at -12 and +12V, and polarization was confirmed by PFM. The effect on MFM images is shown in Figure 13a and 13b respectively before and after electrical poling. The result is striking and a large fraction of the magnetic columnar structures reversed from white to black and some of the pillars partially reversed and some of them remained unchanged. in Figure 13c,d line profiles shows magnetic pillars magnetic state before (black curves) and after electrical poling (red and green curves) in which red marked pillar's magnetization sign changed completely but green one partially. Zavaliche et al have attributed this effect to the ME coupling of different phases of composites in the film structure. To be sure about the effect, induced magnetization effect has been observed in reverse procedure. Therefore two magnetization directions in the columnar structure of CFO can be switched perpendicular to the columns by applying an electric field and it is due to the presence of a significant coupling between the ferroelectric matrix and ferrimagnetic pillars. They have quantified the strength of the ME coupling using superconducting quantum interference device (SQUID) magnetometer at room temperature by measuring the hysteresis loops before and after electrical poling that is shown in Figure 13. The electric field induced change in magnetization, ΔM, can be derived from the plots. Then one will able to calculate magnetoelectric coupling strength between the ferroelectric matrix and the ferrimagnetic columnar structures. The estimated value for ΔM/ΔE from the plots is ~1.0×10^{-2} G cm/V that indicates significant coupling in the composite. Observed coupling effect due to electric field application can be explained two initial polarization/magnetization configurations that are schematically shown in Figure 13c. $P_i^{+/-}$, with i = 1-4 and $M^{+/-}$ respectively are indicating the eight possible orientations of polarization in rhombohedral $BiFeO_3$ [27] and two magnetization directions along (001) in spinel $CoFe_2O_4$.

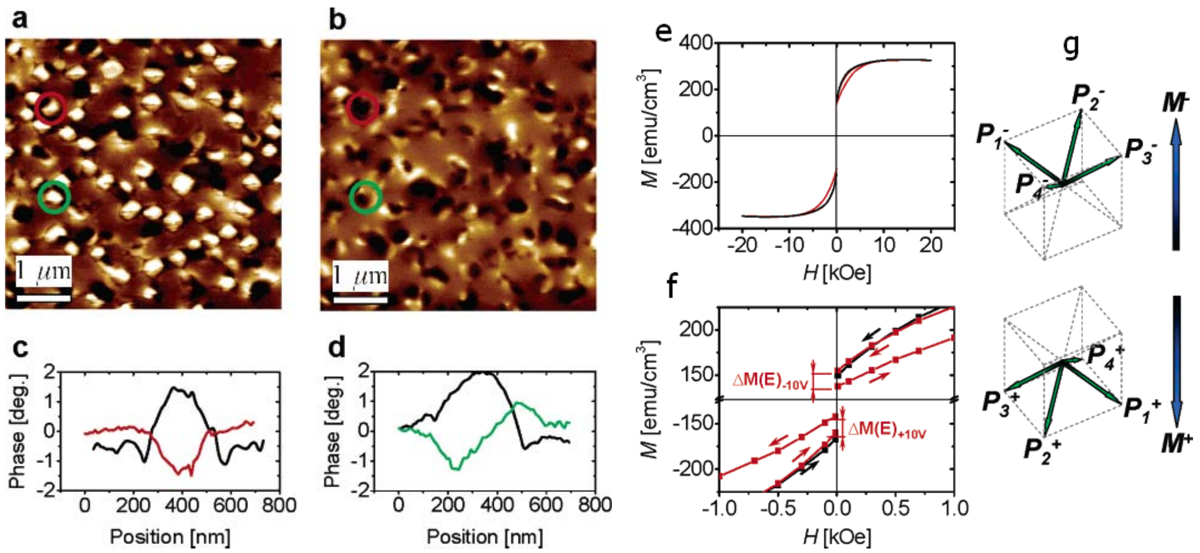

Figure 13- (left a-d) electrical poling effect on the magnetized $(BiFeO_3)0.65$- $(CoFe_2O_4)0.35$ film. MFM image (a) magnetized upward with ~20 kOe perpendicular to the surface, and (b) after electrical poling at +12 V. (c and d) Line profiles of red and green circled $CoFe_2O_4$ pillars. The black curves for the MFM signal before electrical poling. (right e-g) M-H loop after electrical poling. (e) M-H black curves,

and red curves related to before and after electrical poling (f) An enlarged view of the central part of M-H vurve. (g) Possible polarization/magnetization configurations for coupling [26].

3.4 BFO/BTO composite

$BaFe_{12}O_{19}$–$BaTiO_3$ (barium hexaferrite, BaM - barium titanate, BT) is one of different kinds of composite ferroelectric/ferromagnetic ceramics that have been studied by Kaprinsky, et al [[28]] in two different weigh ratios, 50% of each (50BaM-50BT) and 10%BaM-90%BT (10BaM-90BT). Ferroic components of the composite are well known for their excellent magnetic and piezo response. This ceramic were prepared by conventional solid-state sintering method and has higher conductivity in comparison to conventional ferroelectrics. Therefore this conductivity causes degradation of ferroelectricity in comparison to ideal case. Magnetoelectric coupling has been observed in this composite locally using PFM and MFM method.
The magnetic properties of the composites, up to 9T and at different temperature, have been studied and compared with individual pure compounds in ref [28]. The physical properties deviations from pure ones have discussed in it to get idea to optimize the composite due to improvement of FE, FM and dielectric properties. PFM and MFM were done on polished plane – parallel plates of composites to determine the local polarization and magnetic image. Figure 14 shows topography, piezoelectric, and magnetic contrast before and after electric poling. The area marked with square is the poling area. Distinct piezoresponses and magnetic contrasts were observed for both samples (50BaM– 50BT and 10BaM–90BT) and FE grains can be realized from the magnetic ones Figure 14b. Regions with pure FE and FM properties are existed. Therefore magnetic property was analyzed over ferrite grains that are shown in Figure 14b.
Obtained data from PFM experiments shows the local polarization is fully switchable under moderate voltages. This, combined with the excellent magnetic properties, allows us to study ME interactions at the nanoscale.

ME coupling was tested for 50BaM–50BT locally by PFM and MFM. The method is firstly choosing an area in which have both magnetic and piezoelectric/FE responses, where scanning in both PFM and MFM modes was performed before the local switching by PFM. In the next step the small selected area (2 μm^2) was poled by dc voltage 25V. MFM image was taken again after poling and at the end cross-sections of topography and the magnetic signals before and after poling were compared, Figure 15.

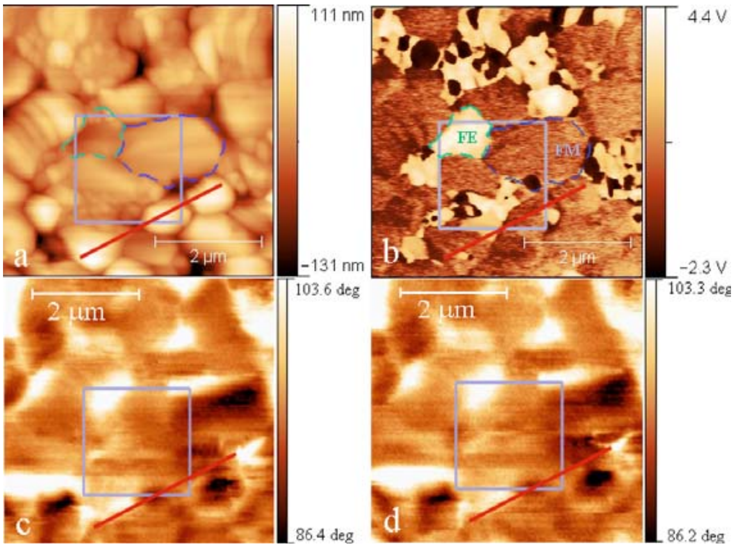

Figure 14- (a) AFM image, (b) PFM amplitude before poling, (c) and (d) MFM contrast before and after poling repectively. Squares show the poled area; solid lines are cross sections. Chain lines show the piezoelectric and magnetic grains with FE and FM abbreviations [28].

From Figure 15 it is clear that topography is unchanged after poling mostly whereas the MFM signals remarkably is different. Three main changes are observable from magnetic signals is shown in the Figure 15. First, change in magnitude, a shift in the peaks of MFM signal, and broadening that is apparent from figure. Kaprinsky and et al[28] have attributed these changes respectively to:

1- Possible variations in electron transfer interactions caused by the charge carrier injection during poling. Carriers experience polarization due to 3*d*-shells of the Fe ions of hexaferrites (RKKY).

2- Shift in maximums of MFM signals and also broadening come from stress mediated ME coupling. Inverse piezoelectric effect causes electromechanical strain and then grain boundaries will changes. If FE and FM grain could have intimate contact then this mechanical interaction will arise. Then can be deduce that piezomagnetism is responsible for change in magnetic signal under induced piezo mechanical stress.

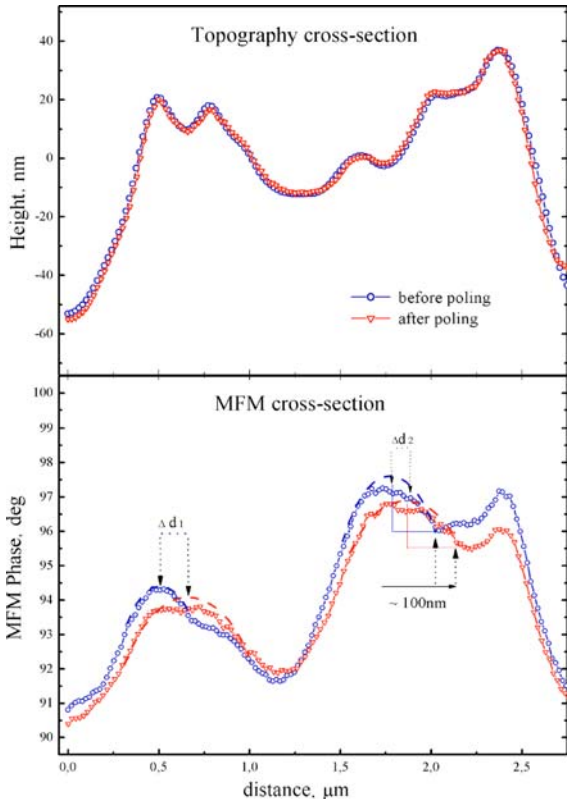

Figure 15- Topography (upper image) and MFM (bottom image) from 50BaM–50B compositebefore and after electrical poling +25 V. The shifts in the MFM peaks are marked by Δd_i (Δd_i~100 nm) [28].

3- Broadening of the MFM cross section signals (~100 nm) could be due to domain wall broadening. By assuming that the case is similar to Bloch wall, Kaprinsky and et al calculated the broadening that is mostly equal to the amount that experiment shows [28].

As I mentioned before the ME coupling is too small in the single phase materials so people are trying to work on the composites that improvement in their structure and nanoscale pattern can help to derive better ME effects due to stress mediation was an example of ability of this kind of materials to be manufacture better and effective ME coupling.

3.5 CFO/PZT nanocomposite

Strain mediated ME coupling can be optimized via self organized immiscible composites. For example synthesizing ferroelectric/magnetic nanopillar structures in the matrix of magnetic/piezoelectric material that can help to achieve larger ME coupling coefficient at room temperature in comparison to single phase multiferroics. ME effect comes from strain transfer of the phase boundaries, thus, are dependent on the geometry on the nanoscale. Gao et al[29] reported such an engineered structure of composite that carries ME effect. To design such a functional composite they have employed pulsed laser deposition and an ultrathin nanoporous anodic aluminum oxide (AAO) membrane. AAO is used as a stencil mask to make regular nanocomposite of various combinations from $CoFe_2O_4$-$PbZr_{0.2}Ti_{0.8}O_3$ (CFO-PZT). That the result is ordered nanodot arrays of one type of material into a matrix of the other type, or bilayered heterostructure dots. CFO is a well-known for lower conductivity and having good magnetic properties and large magnetostriction. PZT is best known ferroelectric and piezoelectric material that shows square hysteresis loop. In the following work that I am going to review, they have tried to demonstrate the concept of different type of matrix structure that is shown in Figure 16. In the Figure 17 SEM and AFM images shows the topography of deposited designed composites.

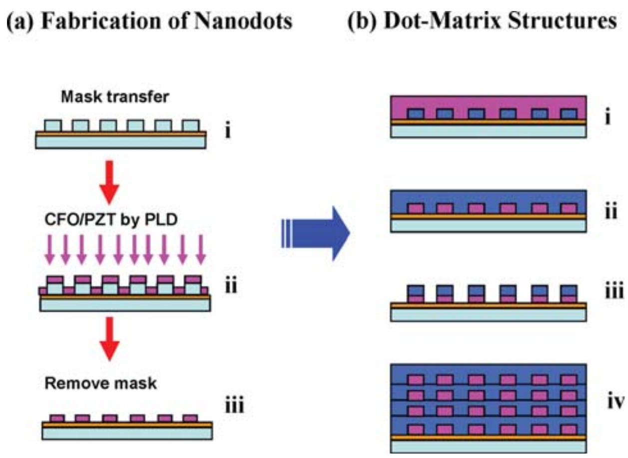

Figure 16- (a) Schematically of the fabrication procedure of nanodot structures: (i) using AAO mask on the SRO/STO substrate, (ii) deposition of the CFO or PZT through the mask, (iii) removal of the mask, obtaining the nanodot structures. (b) pattern of the dot-matrix (continuous film) (i); PZT (dot)-CFO (matrix) structure (ii); heterostructured PZT-CFO nanodot array (iii); complex three-dimensional multiple layers of dot-matrix structures of PZT (dot)-CFO (matrix) or CFO (dot)-PZT (matrix) (iv) [29].

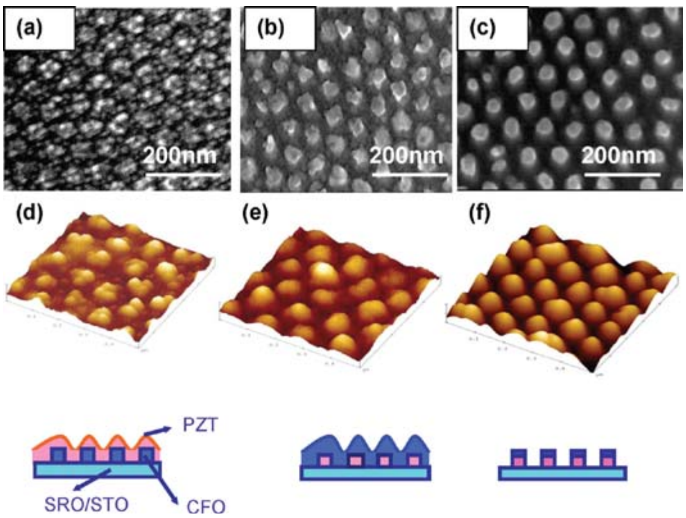

Figure 17- . SEM and AFM images for the three types of multiferroic composites on (100)-orientated SRO/STO substrates: (a,d) CFO dots - PZT continuous layer (b,e) PZT dots- CFO continuous layer CFO dots- CFO dots heterostructure. [29].

The fabricated well ordered composites were studied using MFM and PFM to understand its multiferroic properties. Figure 18 shows magnetic properties of the CFO (dot)/PZT (film) composite that are obtained by SQUID and MFM. Magnetization hysteresis loops shows remnant magnetization values are much smaller than the saturation magnetization due to demagnetization process. MFM images in Figure 18b, c show the switchable well ordered magnetic domains upon upward and downward magnetic field. In these images CFO dots appear as a single domain state.

Ferroelectric properties were investigated using PFM that is shown in Figure 19, where it depicts out of plane piezoelectric response. As it is observable from the figure, polarization is relatively uniform for the composite film and after applying -5V reverse voltage its polarization fully switches into opposite direction (contrast changes in polarized area). Piezoelectric loop confirms switching of polarization as well. It should be note that piezoelectric signal on top of the dots is weaker than the other areas, which cab be attributed to the field decrease across the CFO dots.

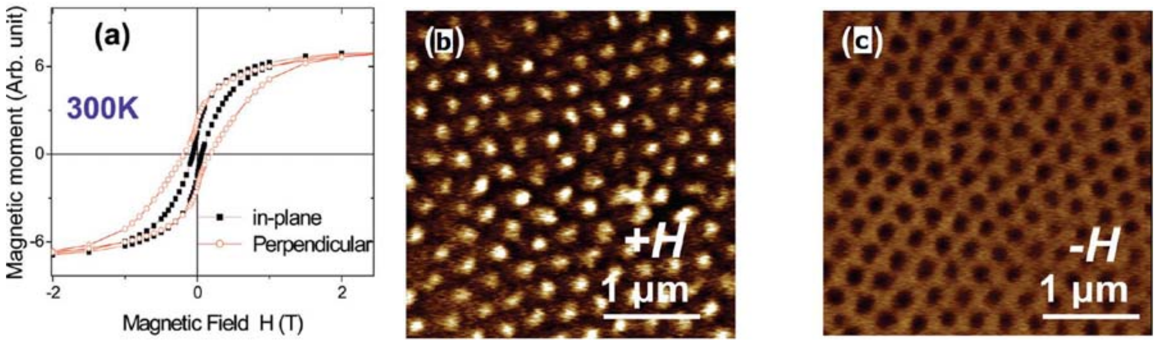

Figure 18- M-H loop of CFO nanodots covered by a layer of PZT, (dot avarage diameter of ~300 nm and height of ~70 nm), measured by SQUID at magnetic field along both in-plane and out of plane directions, (a) at room temperature, (b) MFM images of the premagnetized nanodot along out of plane direction (*c*) MFM after reversing magnetic field [29].

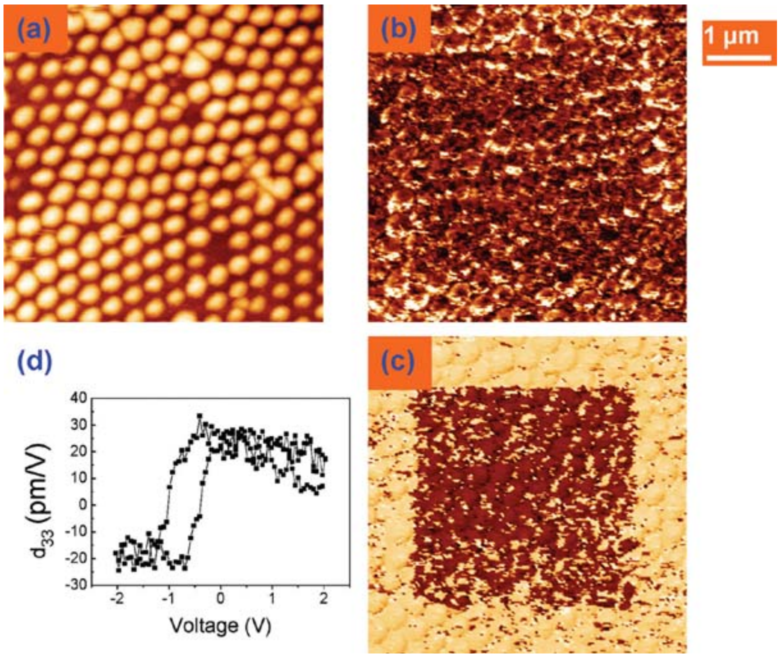

Figure 19- PFM image CFO dots - PZT film: (a) AFM image, (b) amplitude image for PFM response along the vertical direction, (c) phase image for PFM response along the vertical direction, (d) and d_{33} hysteresis loop. In the middle of the scanned area, a reverse voltage (-5 V) was applied leading to the contrast change in both amplitude and phase images [29].

PFM and MFM experiments showed that CFO (dot)/PZT (film) composite can have both magnetic and ferroelectric properties at the same time. But the most expected property is ME coupling. ME coupling tests were performed at the room temperature. To measure the ME coupling on option is measuring the magneto-capacitance of the composite. Figure 20a shows the configuration to measure capacitance using Au as a top electrode. Typical hysteresis P-E loop is shown in Figure 20b from CFO (dot)/PZT (film) composite in which shows relatively large polarization nearly 20 μC/cm^2. It is clear that there is some leakage in the system and it is indication of high polarization relaxation.

To quantify the ME coupling they change in capacitance of the system as a function of external magnetic field was measured. It is clear from the result in Figure 20c capacitance exhibit rather small magnetic field dependency (around 0.03% at 1 T). To be sure that this effect is due to ME coupling, this experiment was repeated several times and also was performed on the pure PZT film at the same conditions in which was not found any detectable magnetic field induced change in capacitance. Actually the origin of magnetocapacitance is not clear yet. It probably comes from strain mediated magnetic and piezoelectric effect or other possibilities that is mentioned in Ref [29].

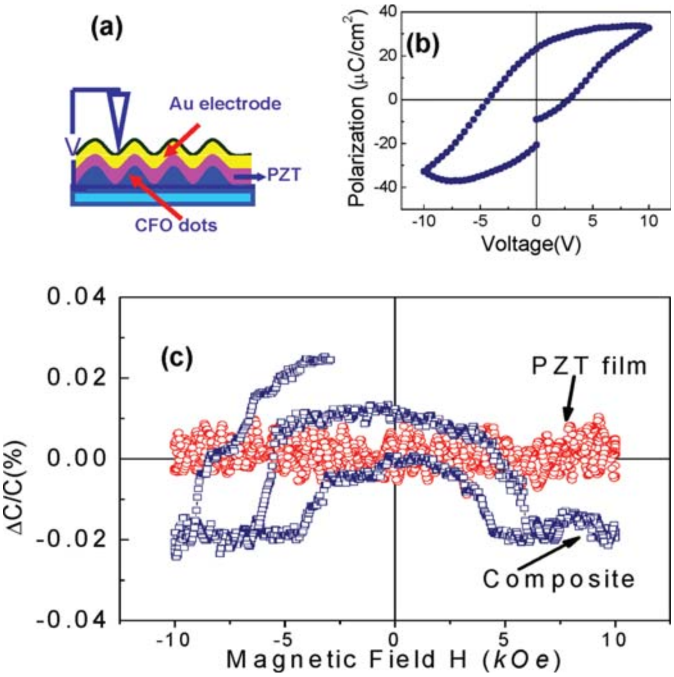

Figure 20- Magneto-capacitance measurment of the CFO - PZT layer. (a) Schematic diagram of the capacitor structure used for electrical measurements; (b) P-E hysteresis loop for a capacitor; (c) Capacitance as a function of magnetic field showing an apparent field dependence of the capacitance change. Magneto-capacitance of a PZT film without CFO dots is also shown [29].

This work was an attempt to develop the functional ME material. As it was shown a family of artificially designed multiferroic nanocomposites can show ME coupling that it can be optimized carefully controlling the deposition parameters and also selecting proper material to use in composite matrix.

3.6 PZT/TDF

S. H. Xie et al[30] have reported ME coupling in PbZrTi/TbDyFe composite. They have used a simple method to derive the ME coupling from such a composite. They have chosen two PZT and TDF disk and bonded both of them to each other in which the outer surface of the disks was polished.

PZT has diameter of 10 mm and thickness of 0.5 mm, with piezoelectric coefficient d_{33} and d_{31} around 350 and -150 pm/V, that longitudinally poled vertical to bonded plane to TDF poly crystal that has diameter of 10 mm and thickness of 0.7 mm. PZT is well-known piezoelectric and material and TDF includes ferromagnetic component and is a magnetstrictive material. The idea is that bonding these two disks with different FE and FM properties to each other can produce ME coupling via strain mediated between them. Two wires were then attached to the edge of the top and bottom surfaces of PZT disk with gold electrode for application of external electric field.

To observe the ME effect in this bilayer composite, PFM image was taken under an external magnetic field provided by variable field module (VFM) that it can be used to apply a series of in-plane magnetic field to the specimen during MFM testing. MFM study was done on TDF under an external electric field that in the following I will briefly review the results.

Figure 21 shows the ferroic properties of each disk separately. The remnant polarization and coercive voltage can be derived from Figure 21b ferroelectric hysteresis loop and PFM image shows that the most of the domains are positive polarized. Figure 21c shows in plane and out of plane magnetization while the corresponding coercive field measured in-plane is smaller, due to the shape anisotropy of the TDF disk. The MFM phase image of TDF disk is shown in Figure 21d in which the typical magnetic domain are observable.

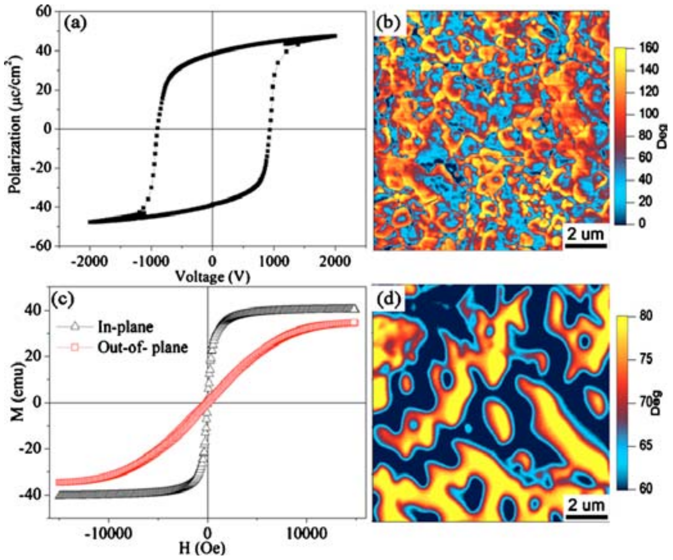

Figure 21- FE and FM properties of individual PZT and TDF disks: (a) P-E hysteresis loop, (b) PFM phase image of PZT disk, (c) magnetic hysteresis loops, and (d) MFM phase image of TDF disk [30].

To examine the local ME response at nanoscale, a series of in plane magnetic field have been applied to the bilayer composit by VFM and PFM signal has been measured in the in the PZT disk that is shown in Figure 22. To understand the effect of topography on PFM image, AFM image is taken to compare with PFM. Figure 22a and 22b comparison shows that there is no correlation between them. Figure 22c shows after applying 2000 Oe dc magnetic field, piezoresponse substantillay increases to the range of 800-1200 pm, indicates changes in polarized domain under magnetic field. It is mentioned that after removal of the magnetic field, polarization is stable. In the next step, opposite magnetic field of -2000 Oe was applied, that is depicted in Figure 22d. The result is that the domain polarizations remain unchanged after reversal of magnetic field. This due to quadratic nature of magnetostrictive effect, the magnetic field induced strain is invariant under reversal of magnetic field. Therefore reversal of magnetic field not only does not change the polarization but also strengthens it as it observable in Figure 22c and d.

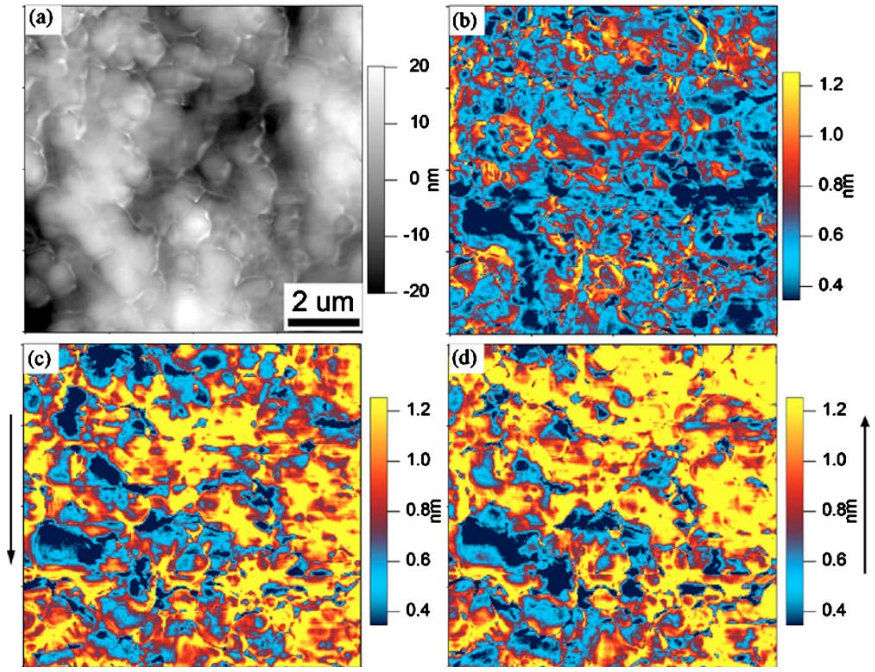

Figure 22- Local ME responses of the bilayer composite under a VFM magnetic field: (a) AFM image, (b) PFM amplitude image in the absence of external magnetic field, (c) PFM amplitude under 2000 Oe, and (d) PFM amplitude under -2000 Oe, arrows shows the direction of magnetic field [30].

The effect of electric field on TDF magnetic domains, in the bilayer composite, was investigated by MFM that is depicted in Figure 23. Topography image is shown in Figure 23a. In the absence of electric field, Figure 23b shows magnetic domains that yello and blue indicates repulsive and attractive interaction between sample and tip that results upward and downward magnetizations. Comparison of topography and MFM images reveals that there is not any correlation between them. Figure 23c shows the effect of 850V applied electric field to PZT disk that causes change in the map of magnetic domain, and area in yellow starts to grow that this means downward magnetization switches upward due to electric field induced stress (Marked areas as 1, 2 and 3). Figure 23d shows the effect of increased electric field that causes upward to downward switch in some area that implies the mutual interaction between two disks is complicated. Removal of electric field does not change the magnetic domain direction that means the magnetic states are stable without external fields.

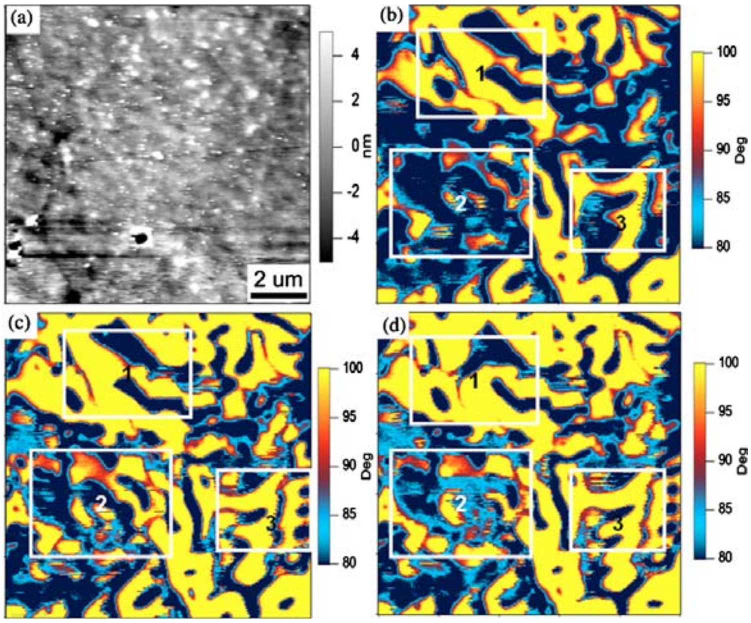

Figure 23- Local ME responses of the bilayer composite under an external electric field: (a) SPM topography, (b) MFM phase image in the absence of electric field, (c) MFM phase image under 850 V, and (d) MFM phase image under 1530 V [30].

In summary, the effect of magnetic/electric field on the polarization/magnetic domain of bilayer composite using MFM and PFM were tested. The results confirmed that the bilayer structure of composite that one is magnetostrictive and other piezoelectric can issue the ME coupling in the nanoscale. So this work shows the usefulness of SPM for detecting ME coupling in the multiferroics.

4 Conclusion

Different experimental works are reviewed in this paper. It will be revealed that it is too difficult to find or synthesize a multiferroic in which it could has magnetic and electrical coupling at the same time. But there is another chance that it can develop such a materials. And this chance is strain mediated magnetism or piezo effect. Thus, the works are done in this field till now and selected works that we discussed about them, proved that it doable. In spite of less studies that are done on multiferroic and magnetoelectric materials using combined MFM and PFM; and It is shown that they are powerful technique to realize the magnetoelectric coupling. Researchers have tried to measure ME coupling via indirect methods like magnetocapacitance that its origin is not so clear. Unfortunately nobody have tried to measure the ME coupling quantitatively using combined MFM and PFM. Maybe it could be a nice idea to do in the future. In summary the studied and discussed compounds about different composites proved that two phase composites have great chance to be a proper magnetoelectic material. Modifying and improving the type of materials and also tailoring them in different suitable patterns can help to improve and develop ME materials.

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