MultiferroicPhenomenon in Bulk, Nanostructures and Thin Films

Samta Manori and Ramesh Chandra

Abstract The development of composite systems of multiferroic or magnetoelectric materials made from magnetic and ferroelectric subsystems has attracted interest as well as increased a large number of research activities. Multiferroics have found a special place in various technological applications based on novel multifunctional devices, like multi-state memories, spintronics, sensors, and transducers. Single phase multiferroics are rare and the coupling between various ferroic orders is either weak or occurs at low temperatures in these materials. The composite multiferroic materials, however, combine both ferroelectric and ferromagnetic phases and show a giant magnetoelectric effect even at high temperatures that are well above room temperature. In this view, various bulk composites have been studied and developed both experimentally and theoretically. Also, the high demand for on-chip integration in electronic and memory devices has accelerated the development of nanostructured ferroelectric and magnetic oxide materials in the form of thin films. With a high-quality thin film, it becomes easy to tailor the properties by epitaxial strain and interfacial coupling. This chapter will take the reader through the journey of evolution of multiferroic materials starting from the bulk form to nanostructures and thin films.

Keyword Bulk composites · Thin film · Epitaxial strain · Sputtering · Pulsed laser deposition

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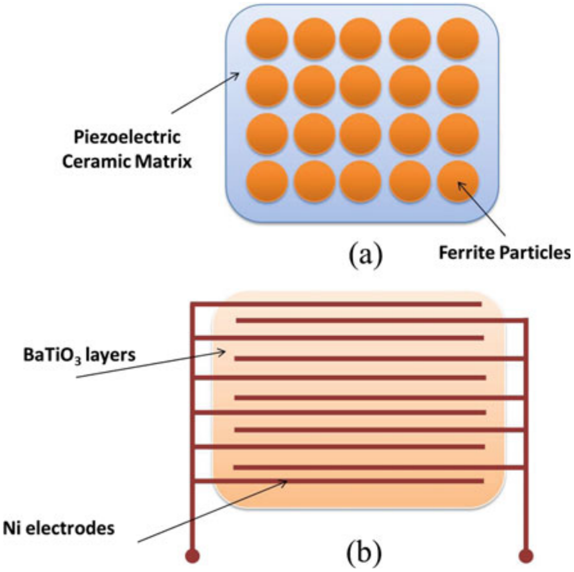
1 Multiferroism in Bulk Materials

The development of bulk multiferroic structures started in the form of bulk composites of magnetoelectric materials started in 1972 and was first proposed by van Suchtelen [1]. Experimental findings further accelerated the theoretical work on magnetoelectric composite structures and hence most of the work on these systems was theoretical before 2000 [2]. These theoretical modelings provided a quantitative knowledge of the magnetoelectric effect in bulk ceramic compounds. At the onset of the year 2000, a sudden rise in the research related to multiferroic magnetoelectric composite structures was observed. And the biggest turning point in the development of these composites in bulk form came in 2001 with the findings of materials with a giant magnetostrictive rare-earth alloy like Terfenol-D$Tb_{1-x}Dy_xFe_2$. The giant magnetoelectric effect observed in bulk materials of Terfenol-D was studied both theoretically [3] and experimentally [4, 5]. Let us now discuss some of the different types of bulk forms of multiferroic or magnetoelectric materials.

1.1 Composite of Ceramic Materials

Bulk magnetoelectric materials of ceramic composites can be made by various possible combinations of ferroelectric and magnetic oxides (especially ferrites), more commonly by co-sintering at high temperatures. It is to be noted here, that bulk magnetoelectric ceramic composites were expected to show a larger magnetoelectric effect, but on the contrary composites of ceramic materials co-sintered at high-temperature show magnetoelectric effect that is around ten times lower than expected. This results largely from the problems during their preparation, like reaction problems, and mismatch between thermal expansions of two ceramic phases during high-temperature treatment. In the case of ceramic composites with 0–3 type particulate structure, it is better to use a piezoelectric ceramic matrix in which ferrite particles are dispersed with high concentration (Fig. 1a). This is desired for the reason that mostly ferrites are conducting or semiconducting, this property can degrade the insulation of the composites with a leakage problem. A core–shell structure is an effective solution to this problem, with ferrite core and piezoelectric shell [6, 7], this approach can prevent the ferrite core particles from direct contact with the shell during sintering. However, because of the difficulties faced in preparing a core–shell structured system, such microstructured ceramics have not yet been attained. Recently developed techniques like chemical solution processing and sintering methods e.g. spark plasma sintering [8] and microwave [9] sintering have made it possible to fabricate improved quality of these particulate ceramics. However, there is still some more work is to be done to get adequate dispersion of ferrite particles with high concentration in the matrix of piezoelectric ceramic, coherent interfaces, and adequate bulk density while escaping any reaction or diffusion at the interface between the two ceramic phases.

Fig. 1 **a** 0–3 type bulk magnetoelectric composite with magnetic (Ferrite) particles immersed in a piezoelectric matrix, **b** 2–2 type alternate layers of ferroelectric ($BaTiO_3$) and ferromagnetic (Ni) materials



The 2–2 type laminate composite ceramics have high magnetoelectric coefficients as compared to particulate composite ceramics. This is attributed to the structure of these composites which comprises alternate layers of ferrite and piezoelectric oxide materials, which eliminates any leakage problem. However, the ferrite layers in these laminate composite ceramics do not perform as a good conductive electrode which results in the loss of magnetoelectric output signal induced by the alternate piezoelectric layers. This signal loss can be greatly reduced by introducing internal electrodes made up of materials like Ag, Ni, and Ag–Pd, between the alternate layers of piezoelectric and magnetic materials. These interface electrodes can improve the response by directly collecting the output charges that are produced from the piezoelectric layers. The phenomenon is well explained in a trilayered NCZF/PZT/NCZF (NCZF: $Ni_{0.6}Cu_{0.2}Zn_{0.2}Fe_2O_4$, PZT: $Pb(ZrTi)O_3$) with the internal electrodes made up of Ag–Pd at the interface [11]. The multilayer ceramic capacitors (MLCCs) are made up of precisely fabricated magnetoelectric sensors [12] which consist of thin layers of $BaTiO_3$ (BTO) and ferromagnetic Ni internal electrodes (Fig. 1b). The magnetoelectric coupling is enhanced due to the laminar structure which further simplifies the strain field, and the magnetically induced output charge is increased by their large capacitance. The greatest advantage of these MLCC magnetoelectric sensors which are produced on a massive scale is that they can be operated at room temperature with highly reproducible cross-field cycles and temperature cycles [12]. The sensitivity of these magnetoelectric materials can be improved in a significant manner by connecting these capacitor plates in series. In this way, these MLCCs can be used as magnetic field sensors in various fields due to their low cost. As discussed in the case of 0–3 type particulate composites, the biggest challenge in the case of bulk magnetoelectric laminate composites is their processing by controlled cofiring of ferrite

and piezoelectric layers at high temperatures so as to obtain an interfacial contact without any inter-diffusion or reactions. Thus, to get rid of these problems, low temperature processing of these ceramics is desirable. Recently, various techniques used for the deposition of thin films have been employed to overcome the challenges imposed by high temperature sintering [13]. When ferroelectric films are deposited on dense ferrite ceramics by methods like pulsed laser deposition (PLD) or spin coating technique, then the ceramics can be easily annealed at much lower temperatures (~600–700 °C) than co-sintering temperatures. Also, with these methods, an improved interfacial bonding between the ferroelectric and ferrite layers is obtained which gives a large direct magnetoelectric effect. However, the obtained values of the magnetoelectric coefficient are still much lower than that calculated using the theoretical continuum model [14]. On the other hand, as mentioned earlier, the ferrite ceramics are not good enough to be used as conductive electrode because of their not so low resistance, and hence a bottom electrode in between the layers of ferrite and ferroelectric materials would be beneficial to improve the magnetoelectric response of these systems made up of layers-on-ceramics composites via low temperature processing.

1.2 Composite Materials from Magnetic Alloys

Bulk magnetoelectric composites which are based on magnetostrictive alloys like Terfenol-D and Metglas are reported to show a strong magnetoelectric effect. The modified Terfenol-D based ME composites, like a piezoelectric transformer with a Rosen-type structure, can magnify the input signal by more than 100 times [15]. Some better configurations of these bulk composites can also be made by considering their mechanical properties. However, magnetoelectric composites based on Terfenol-D are not so promising for low field applications because of their low permeability and high saturation field. As an alternate option, soft magnetic alloys, like Ni (Mn–Ga), Permendur and Metglas, can also be utilized. Among these alloys, Metglas is the widely used alloy. It is an amorphous alloy ribbon prepared by a rapid solidification process [16]. The process of rapid annealing is advantageous from the perspective that it creates remarkable properties in the ribbon alloy so that it can undergo magnetization and de-magnetization swiftly and effectually, giving low coercivity and saturation fields, and high magnetic permeability. A large magnetoelectric response of about 10 $\text{Vcm}^{-1}\ \text{Oe}^{-1}$ at low frequency and several hundred $\text{Vcm}^{-1}\ \text{Oe}^{-1}$ at resonance have been observed, when the applied magnetic field is low, in a laminate of Metglass ribbon and a PZT-fiber actuator layer [5]. The optimization of some structural parameters of metglas based composites can be done to improve the magnetoelectric response and the sensitivity towards the applied field. Metglas is also advantageous as it shows magnetic flux concentration effect ascribed to its high permeability which in turn affects magnetostriction. In addition, the planar aspect ratio of the metglas ribbon is large enough that it can remarkably enhance the flux density near the central region [17]. The high permeability of metglas allows it to be used as a third phase in the Terfenol-D/piezoelectric laminates, which in turn significantly increases the effective permeability of the resulting three-phase system, thus giving a strong magnetoelectric response at lower applied fields. The piezoelectric layer and the magnetic alloys in these magnetic alloy-based magnetoelectric composites are joined together with polymer binders. These binders affect the magnetoelectric response in a significant manner [18]. The aging effect and adhesive fatigue of these composites are mainly determined by the interfacial binders. Another alternative to prevent these issues is to deposit the magnetic alloys directly onto the piezoelectric layer by using magnetron sputtering or electro-deposition [19–21].

1.3 Composite Materials from Polymers

Polymer based magnetoelectric composites are easy to fabricate as compared to ceramic and magnetic alloy based composites. They can be produced in various forms like thin sheets and molded shapes using conventional low-temperature processes and give improved mechanical properties. It has been reported that a single PZT ceramic rod embedded in Terfenol-D/epoxy (TDE) matrix can give a much larger magnetoelectric response as compared to other polymer based magnetoelectric composites, due to effective coupling interaction between PZT rod and TDE medium [22, 23]. The studies on this magnetoelectric composite confirm that smaller (micro)-sized rods with large magnetoelectric response can be processed using a single PZT fiber which can prove to be a promising future micro-magnetoelectric device. The aging test performed on these composites shows that the response remains the same even for two years duration, thus indicating that no degradation occurred under the normal environment. Fatigue measurements also show good stability of the magnetoelectric response. Moreover, magnetoelectric composites which are derived from polymer based compounds with magnetic particles like $CoFe_2O_4$(CFO), $NiFe_2O_4$ (NFO), Fe_3O_4, Ni, and Terfenol-D, that are embedded in a matrix of polymers such as PVDF and Polyurethane, are technologically important for their easy processing. Some experimental investigations reveal that in these polymer-based composites, the magnetostriction produced by magnetic nano-fillers does not have any direct effect on the magnetoelectric response. However, the source of magnetoelectric coupling in these nanocomposites is still not clear.

1.4 Converse Magnetoelectric Effect in Bulk Composites

The Sects. 1.1, 1.2 and 1.3 mainly discussed the direct magnetoelectric effect, where the electric polarization is induced by an applied magnetic field. A converse magnetoelectric effect, in which magnetization is controlled by applied electric field is also another fascinating and technically important phenomenon in bulk composites [24–26]. Also, the magnetic hysteresis loops of some composite materials reveal the dependence of magnetic anisotropy on applied electric field. Magneto-optical Kerr effect (MOKE) measurements in PZT/metglas laminate show that the local magnetization vector can be easily switched by an applied electric field [27]. The ferromagnetic resonance frequency can be easily tuned by applying a bias voltage through the converse magnetoelectric effect by controlling the magnetic response at high frequencies in these magnetoelectric structures. The electrostatically tunable microwave multiferroic devices are more energy-efficient, less noisy, compact in size, and lightweight as compared to their conventional tunable microwave magnetic devices.

2 Multiferroism in Nanostructures and Thin Films

With the advancement in techniques for thin film deposition and with improved theoretical calculations, the studies on nanostructured thin films of multiferroic materials have taken a new height. These deposition techniques provided a new path to grow different structures with the characteristics of parent functional materials which are tailored by strain engineering. The last few years have seen a surge in the number of studies on composite magnetoelectric thin films. Various physical deposition methods like sputtering, PLD, molecular beam epitaxy, and chemical methods like spin coating, metal–organic chemical vapor deposition (MOCVD) have been used to grow a large number of multiferroic thin films with ferroelectric materials like BTO, $PbTiO_3$ (PTO), PZT, and BFO and magnetic materials like CFO, NFO, Fe_3O_4, $La_{1-x}Sr_xMnO_3$ (LSMO), and also certain metals with different types of composite structures (0–3 type, 2–2 type and 1–3 type). Multiferroic thin films are far superior to their bulk counterpart owing to their unique properties. The main advantage of multiferroic thin films is the ease of combining different phases at the atomic level, and the possibility to grow epitaxial and superlattice composite films by precisely controlling the lattice match between different layers. This way, the understanding of magnetoelectric coupling becomes more simplified at an atomic level. Multiferroic thin films have proved to be promising candidates for applications in integrated magnetoelectric devices, high-density memory systems, microelectromechanical systems, and spintronics. This can be achieved by synthesizing high-quality thin films of multiferroic materials using the techniques mentioned above.

Among these techniques, spin coating is a simple and low-cost chemical method to produce polycrystalline or textured films with some preferred orientations and is also flexible enough to develop thick films with large areas [28–31]. But, these conventional techniques are unable to provide high structural perfection, epitaxy, and growth of atomic level layers. The physical vapor deposition techniques, on the other hand, provide the flexibility to produce epitaxial thin films on an atomic scale with coherent interfaces. In the growth of thin films using physical vapor deposition techniques (PLD, sputtering, etc.), there is a large number of factors that need to be controlled for a better quality thin film. The most important factor is the choice of the substrate as it controls the orientation and strain in the epitaxial films. Orientation of the substrate with respect to the thin film decides the inherent properties of multiferroic materials and also affects the crystallization and morphology of nanostructures with multiple components. These deposition techniques allow the atoms to acquire low-energy configurations so that the single crystal substrate can be extended to an epitaxial layer.

Another deciding factor for thin film growth, specifically for 2–2 type heterostructures, is strain-induced because of differences in the lattice constants and thermal expansion coefficients between the film and substrate. In heteroepitaxial structures, film and substrate are of different materials which usually have the same type of structure with a difference in their lattice parameters. To grow an ideal heteroepitaxial structure, one can select a suitable substrate with a little mismatch between lattice parameters of the substrate and desired materials to be grown. This way, a fully coherent and epitaxial film can be deposited with only a little structural distortion across the interface of substrate and film. However, if the mismatch between the lattice parameters of film and substrate is slightly higher, then it results in a strained or relaxed epitaxial layer, depending upon the lattice parameters [32]. These conditions can create some defects such as dislocations at the interface which in turn degrades the ferroelectric or other properties of the film.

For a good quality thin film, another important factor is the pre-treatment of substrates before deposition. For successful growth of epitaxial thin film with controllable atomic layers, the substrate must undergo specific chemical treatment at the surface. In addition to these factors, other deposition parameters like energy density and frequency of laser beam in PLD, target-substrate distance, rate of arrival of adatoms, the temperature of substrate, pressure, etc. in techniques like PLD and sputtering and surface diffusion also need to be monitored for the deposition of thin films with desired compositions, morphology, and other properties. However, as compared to their bulk counterpart, there is still a narrow understanding of physics involved in multiferroic thin films. There are still many questions that remain unanswered, like, what is the exact effect of a stiff substrate on the multiferroic properties of a thin film? How to improve the magnetoelectric response in a multiferroic thin film? Is the magnetoelectric coupling strain-mediated in multiferroic thin films like a bulk counterpart? Let us try to find the answers to these questions in the next section!

2.1 Magnetic Field Controlled Electric Polarization

(a) *Direct Magnetoelectric Coupling*

In bulk multiferroic composites, the magnetoelectric coupling is strain mediated where strain induced in the magnetic or ferroelectric component by an applied magnetic or electric field, respectively, is transferred mechanically to the ferroelectric or magnetic component, which further induces a direct polarization or magnetization. However, the source or mechanism behind the observed magnetoelectric effect in multiferroic thin films is still not determined in an absolute manner.

To understand the origin of the direct magnetoelectric effect in multiferroic thin films, it is worth considering some properties of the film like residual stress or strain which results from the mismatch between lattice parameters or thermal expansion coefficient between film and substrate. Theoretical calculations on the magnetoelectric coupling and magnetic field induced polarization in the nanostructured multiferroic thin films done using Green's function technique [33] revealed the following observations: If leakage problem is prevented, then 1–3 type heterostructures can show larger magnetoelectric response as compared to their bulk counterpart, and by assuming complete in-plane constraint effect, the 2–2 type alternate layered heterostructures give a weaker response. Other theoretical calculations suggested that the magnetic field-induced polarization depends on the thickness of the film, morphology, and substrate stiffness. Some studies on the effect of constraint stress on the magnetoelectric response suggest that in magnetoelectric thin films, the strain-mediated magnetoelectric coupling is suppressed due to mechanical clamping imposed by the substrate [33, 34]. And if some how this mechanical clamping is relaxed in these layered structures, then the strain-mediated coupling is still not vanished.

(b) *Methods to Enhance Direct Magnetoelectric Response*

It is always desired to have a high output signal from the magnetoelectric effect for various practical applications. In the previous section, we have already discussed that the direct magnetoelectric coupling in the case of multiferroic thin films does not depend only on its structural parameters (thickness of the layers, ratio of thickness between ferroelectric and magnetic layers, orientation of the grown films, etc.), but is highly modified by the interfaces and constraint imposed by the substrate. Thus, to get high output, it is well desired to control the growth orientation of ferroelectric and magnetic layers as well as coherent interfaces and relaxation of strain constraint in the magnetic layer. In the case of two-layered composite thin films made by a ferroelectric material like PZT or BTO and a magnetic material like spinel ferrites, with both the materials having different lattice match with the substrates due to their different crystal structures, the sequence of deposition of these layers on the substrates greatly influences the properties of the resulting composite thin films [31, 35]. It is found that the relaxation of constraint from the magnetic layer imposed by the substrate can largely enhance the magnetoelectric response. This relaxation from substrate constraint can also be attained by deposition of a buffer layer. For this purpose, some conductive perovskite materials like $LaNiO_3$ (LNO), $SrRuO_3$ (SRO), and LSMO can be used preferably as their lattice parameters are close to various perovskite ferroelectric materials. These materials serve the purpose of both, buffer layer as well as the bottom electrode layer on which the thin films of desired magnetoelectric bilayers can then be deposited [29, 36]. In addition to bringing relaxation from the constraint imposed by the substrate, the buffer layer also helps in the growth of thin films with preferential orientation and further improves the properties of the bottom ferroelectric layer. The mechanical transfer of strain between the layers becomes a major concern as magnetoelectric coupling is established at the interface. It is to be mention here that the deposition techniques like PLD and sputtering produce coherent interface in the magnetoelectric bilayered epitaxial films which enhances the magnetoelectric response as compared to the films deposited by sol–gel methods which produce incoherent interfaces. Interface density also plays an important role in enhancing the magnetoelectric response. One solution to increase the interface density is growing multilayers or superlattices [37–39]. The magnetic and ferroelectric properties are also influenced by interface density. As the interface density is increased, the ferroelectric hysteresis loops show less remanent polarization mainly due to the dilution created by the ferrite layer. The resistance of the ferrite layer is also not sufficiently low to act as conductive electrodes, and this prevents the effective transport of polarization charges which are induced by magnetoelectric coupling leading to loss of polarization charges in these films. The understanding of the nature of magnetoelectric coupling in multilayer thin films is still lacking and needs vast investigation. On the other hand, the choice of a suitable ferroelectric or magnetic layer and controlled orientation of bottom ferroelectric layer can greatly enhance the magnetoelectric coupling [26, 30]. A strong and efficient mechanical coupling across the interface gives an extraordinary magnetoelectric effect in heterostructures. The magnetostrictive properties of manganite crystals give a very strong temperature-dependent magnetoelectric effect.

The 1–3 type vertical heterostructures with magnetic spinel nanopillars embedded in the ferroelectric film matrix with an epitaxial structure are found to show a much larger magnetoelectric response as compared to thin films. Such a larger response in these structures could arise due to the following reasons [40, 41]: (i) the substrate clamping is reduced in the heterostructures, (ii) larger interfacial areagives stronger strain coupling. But, the measurement of direct magnetoelectric response is difficult to measure in these 1–3 type heterostructures due to leakage problems because of the low resistance of magnetic nanopillars embedded in the ferroelectric film matrix. However, the leakage problems can be reduced to a large extent by increasing the film thickness. Even after all these considerations, getting rid of the leakage problems in these heterostructures is still a challenging task.

After discussing all the approaches to improve the magnetoelectric response in a thin film, we conclude that irrespective of the type of structure one grows, the main challenge in enhancing the direct magnetoelectric response remains the large clamping effect due to substrate stiffness. Since the substrates that are usually used for depositing these thin films or heterostructures are macroscopic in size (~0.3–0.5 mm thickness) as compared to the thickness of film which lies in a range of 10–100 nm (~1000 times smaller), therefore, using substrates of smaller thickness can be an efficient way of enhancing magnetoelectric response in these structures.

2.2 Electric Field Controlled Magnetism

The direction of magnetization in any ferromagnetic material is always controlled by an applied magnetic field. In magnetoelectric multiferroic materials, the magnetization or magnetic anisotropy of a magnetic material can be directly controlled by an applied electric field. The electric field controlled magnetic properties are observed in semiconducting dilute magnetic semiconducting (Ga, Mn) As system [42] and ultra-thin ferromagnetic metal films [43, 44] at temperatures much lower than room temperature. The magnetic properties in a multiferroic magnetoelectric thin film can be controlled by the applied electric field through different phenomena such as charge-driven, exchange bias mediated andstrain mediated magnetoelectric coupling. Let us discuss these in detail.

(a) *Charge-Driven Magnetoelectric Coupling*

In ultra-thin ferromagnetic films deposited as 2–2 type alternate layered heterostructures, the spin-polarized electrons or holes can build up at the interface by an applied electric field, which further changes the magnetization at the interface because of spin-dependent screening of the electric field. Theoretical modeling on surface magnetoelectric effect caused by direct effect of the applied electric field on magnetization of ferromagnetic thin film reveals that measurable change in surface magnetization and surface magnetocrystalline anisotropy can be created by a spin imbalance of the excess charge due to spin-dependent screening [45]. The first principle density functional calculations based on a model of Fe/BTO superlattice [46], explained the magnetoelectric effect produced by electron hybridization between Ti and Fe atoms and not by strain. The ferroelectric instability creates movement of atoms at the interface which modifies the overlap between atomic orbits resulting in the change in magnetization and hence a magnetoelectric effect.

(b) *Exchange-Bias Mediated Magnetoelectric Coupling*

Exchange bias is manifested as a horizontal or vertical shift in the magnetic hysteresis loops along the applied magnetic field axis or magnetization axis, respectively. It results from the exchange coupling between uncompensated spins of antiferromagnetic phase and spins of ferromagnetic layers. The exchange bias phenomenon has been used for controlling the magnetic properties by applied electric field in ferromagnetic thin films. The utilization of exchange bias for magnetoelectric coupling originated from the work on various single phase magnetoelectric multiferroic materials which are antiferromagnetic like Cr_2O_3, $YMnO_3$, and BFO. For example, the exchange bias in multilayer thin film of $Cr_2O_3/(Co/Pt)_3$ can be easily reversed by applied electric field, but it needs thermal cycling [47], on the other hand, in the case of $YMnO_3$/permalloy heterostructures, the exchange bias can be tuned directly by applied electric field [48].

The bilayer of some multiferroic (like BFO) and a ferromagnetic material can be easily used to modulate and control the magnetic properties by an applied electric field even at room temperature [49, 50]. For example, it is observed that the magnetization of the ferromagnetic layer can be tuned by electric field as it changes the ferroelectric polarization and hence the antiferromagnetic ordering through quantum–mechanical exchange coupling. Another possible way to modify the magnetoelectric coupling is by applying an electric field to a material that is both ferroelectric and ferroelastic, the change in electric polarization in such a case produces a mechanical strain which is then transferred to the ferromagnetic layer. The mechanical deformation can change the magnetization of the magnetic layer by possibly changing the preferred orientation of the magnetic domains.

(c) *Strain-Mediated Magnetoelectric Coupling*

As discussed in the previous section, by the converse piezoelectric effect, the shape of a ferroelectric-ferroelastic material can be changed by an applied electric field, this strain produced would be passed on to the magnetic layer thus altering its magnetic anisotropy via magnetostriction. Thus, the electric field controlled magnetization can be achieved in such multiferroic materials through strain-mediated magnetoelectric coupling. In the case of 1–3 type heterostructures, this strain-mediated magnetoelectric coupling is attained by lattice coupling between the ferroic parts of the nanocomposite thin film. In these structures, an applied electric field changes the shape of the piezoelectric matrix, which further modifies the magnetic anisotropy of the ferromagnetic nanopillars embedded in the matrix via magnetostriction [51]. However, most of the reports on electric field control of magnetization involve 2–2 type structures, where a magnetic thin film is deposited on a ferroelectric substrate. The magnetic layer in these structures usually comprises of either metallic films like Fe, Ni, and Ni–Fe alloys, or oxide-based films like Fe_3O_4, CFO, NFO, and LSMO, while the materials like BTO, PZT, PMN–PT, and PZN–PT single crystals or ceramics are used as ferroelectric substrates [52–55]. The magnetoelectric coupling in such structures is manifested by electric field-induced changes in the M–H hysteresis loops.

3 Conclusion

This Chapter discussed the development of multiferroic materials in the form of bulk materials, nanostructures, and thin films. The bulk multiferroic composites are well-studied systems and are ready for applications in magnetoelectric devices as they show large magnetoelectric coupling above room temperature. However, the advancement of multiferroic thin films is still underway and needs to cover up various falls coming in way of designing a good quality thin film ready for application in magnetoelectric devices. Some of the main things to be considered while developing a multiferroic thin film are; control of composition, atomic arrangements, and especially the interface between different ferroic phases, precise control over the domain and the domain wall structures/patterns in multiferroic hetero-films, mechanisms responsible for exchange-bias based and charge-driven magnetoelectric coupling, and size effects.

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