1

Nanostructured Multiferroics: Current Trends and Future Prospects

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1.1 Single-phase Multiferroics

In ferroics, at least two metastable states can be found. These states are related to the directional arrangement and crystalline limitations of the materials, providing reversible "stored states" that can be switched by external fields. For example, in ferromagnets, an external magnetic field can flip the direction of the material magnetization to align parallel to the field direction. This phenomenon has found several applications nowadays, especially in electronics and information storage devices, both for ferroelectric and ferromagnetic materials [1]. Multiferroics are special class of materials which possess more than one of the primary ferroic properties in the same phase. Multiferroic materials are of great interest in the electronics industry for application as memory storage devices [2, 3], spintronics [4], components [5], and sensors [6]. The perovskite structure is perhaps the most common crystalline structure for multiferroic materials studied so far. Its simplicity is due to its rather straightforward organization and chemical constitution. The general perovskite formula is ABX_3, where A and B are cations and X is an anion, typically oxygen, but also others, like fluorine, are sometimes considered. Materials in which multiple ferroic ordering take place had been already studied, as early as 1960s. Those early studies focused on the synthesis of compounds with extremely complex stoichiometry, such as $(1-x)\text{PbFe}_{0.66}\text{W}_{0.33\text{O}3}-x\text{PbMg}_{0.5}\ \text{W}_{0.5}\text{O}_3$ [7] and nickel iodine boracite, $(\text{Ni}_3\text{B}_2\text{O}_{13}\text{I})$ [8], both of which present too large ionic interactions and crystalline distortions to be able to determine the true origin of their multiferroic behavior. Nevertheless, the methodology was conceptually simple: it aimed to replace d^0B cations, in ferroelectric perovskite oxides, by magnetic d^n cations [9]. To understand magnetic interactions in perovskites, it is important to discuss the Goodenough–Kanamori rule. It was first formulated by Goodenough in 1955, and more rigorous mathematical underpinning was subsequently provided by Kanamori (1959). It is applied to interatomic spin–spin interactions between two atoms that are mediated by virtual electron transfers, for example in the Ni^{2+}–O–Mn^{4+} chain [10, 11].

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Ferroelectricity and ferromagnetism seemed at the beginning to be mutually exclusive in most cases; much effort has gone to overcome this problem the search for single-phase materials, which can allocate two or more ferroic orders, is still of high scientific interest. One way to achieve this goal is to adopt the so-called lone pairs of big stereochemical active atoms such as Bi^{3+} or Pb^{2+} [12–15]. Magnetic and electric ferroic states are mostly independent of each other. Finding a material in which the electric field can affect not only the polarization but also the magnetization ($E_{[P,M]}$) and, in equal manner, a material in which the magnetic field also affects magnetization and polarization ($H_{[M,P]}$), are highly desirable in the industry. Several studies have shown ferroelastic switching in thin films [16–18] to exhibit the potential applicability of these materials in multifunctional heterostructures [19, 20] or artificial multiferroic architectures [21]. Moreover, in materials such as $BiFeO_3$, $PbTiO_3$, and $BaTiO_3$, the ferroelastic domains are known to play an important role in facilitating the coupling between the polarization and the magnetization via the ferroelastic switching [22, 23], an aspect that is highly desirable in nonvolatile memories [24, 25]. Additionally, domain walls have been shown to have a very strong effect on heat flow and phonon scattering, which can dramatically affect device performance [26]. The compounds considered above belong to the class of type I multiferroics, where the charge order and ferroelectricity is of “electric” origin. e.g. $HoMnO_3$ which has an E-type magnetic order [27, 28]. In type II multiferroics, the magnetism causes the ferroelectric polarization, thus, implying a strong magnetoelectric coupling.

There are two mechanisms that govern charge order through magnetic order [29, 30]. The first is the inverse Dzyaloshinskii–Moriya interaction (DMI). This effect is a relativistic correction (spin–orbit interaction) to the superexchange between two TM magnetic ions through the oxygen. It has been observed in RMn_2O_5 compounds, where it induces spiral magnetic order. The second mechanism of magnetically driven ferroelectricity is the exchange striction.

1.2 Multiferroic Study of Pure $BiFeO_3$ Synthesized Using Various Complexing Agents by Sol–Gel Method

Due to long-term technological aspirations in this field, a lot of research work has been reported. The surge of interest in multiferroic materials over the past 15 years has been driven by their fascinating physical properties and huge potential for technological applications. So, there has been the search for a particular material to fulfill the requirement to be a good multiferroic material. Wang et al. [31] worked to enhance polarization and related properties in hetero-epitaxially constrained thin films of the multiferroic $BiFeO_3$ (BFO). The film displays a room-temperature spontaneous polarization (50–60 $\mu C/cm^2$), almost an order of magnitude higher than that of the bulk (6.1 $\mu C/cm^2$). The Curie temperature (T_c) and the Neel temp (T_N) of BFO are 1103 and 673 K, respectively, due to which it acts as a good multiferroic material at RT [14]. Subhash Sharma et al. [32] reported the comparative studies of pure bismuth ferrite prepared by sol–gel method versus conventional solid-state reaction method. This group found that sol–gel method is better compared to solid-state method for preparing pure phase of BFO at low temperatures. The precursors used are $Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, and distilled water. Different complexing agents like citric acid, oxalic acid, glycine, and malonic acid in 1 : 1 M ratio of metal ions were added in stoichiometric solution of above precursors with constant stirring. The grains of BFO samples using different acids are rectangular and the type of structure is rhombohedral [33]. BFO is reported as G-type antiferromagnetic due to local spin ordering of Fe^{3+} at RT. At the same time, there are several reports that show ferromagnetic-like magnetic hysteresis in pure bismuth ferrite. Bismuth ferrite, prepared using citric acid, may be a good candidate for further studies. It can be observed that BFO prepared by sol–gel technique using citric acid as complexing agent shows good ferroelectric properties as compared to other methods, and it exhibits a rhombohedral perovskite structure with less impurity [34].

Dielectric properties of BFO samples, prepared by using various complexing agents and annealed at 600 °C, as a function of frequency have been measured in the range of frequency 10^2–10^6 Hz. It can be observed that the dielectric constant decreases on increasing frequency and becomes independent at higher frequencies. The decrement in ε' is attributed to the dielectric relaxation. The variation of leakage current for applied electric field of BFO for different acids annealed at 600 °C. This gives an idea of leakage current of samples for applied electric field. The leakage current is in the range of 10^{-5}–10^{-10} A/cm^2 for maximum applied field 4000 V/cm. In BFO, oxygen vacancies can be produced by the vaporization of Bi or the presence of lower-valence Fe^{2+} ions, which lead to the formation of a trap level at 0.6 eV below the bottom edge of the conduction band. X-ray diffraction patterns and Fourier transform infrared analysis of various samples show the degree of formation of required phase. Ferroelectric and magnetic study of samples prepared at 600 °C shows their comparative multiferroic properties. Samples show good magnetic and ferroelectric properties at RT, which are the fundamental requirement for any multiferroic material.

1.3 Nanostructured Multiferroics

Bismuth ferrite, BFO, as one of the very few single-phase multiferroics with a simultaneous coexistence of ferroelectric- and antiferromagnetic-order parameters at RT, has attracted considerable attention since its discovery in 1960. Much work has been carried out on the synthesis of pure BFO nanoparticles by numerous methods (e.g. solid-state reactions [35–37], wet chemical synthesis, including sol–gel method with the use of polymeric precursors [38–40], solution combustion methods [41, 42], mechanical activation [43], mechanochemical synthesis [44–46], hydrothermal process [47–49]). Park et al. [50] have also reported an increased magnetization value at the nanoscale, while Mazumder et al. [51] have demonstrated that nanoscale BFO depicts not only high saturation magnetization but also genuine ferromagnetic behavior with finite coercivity at RT. Recently, multiferroic BFO nanoparticles and

La-doped BFO nanoparticles have been synthesized by MSS process in the NaCl [52, 53], NaCl–KCl [54, 55], NaCl–Na_2SO_4 [56], or KNO_3–$NaNO_3$ [57] molten salt. Perejon et al. [58] demonstrated that pure BFO nanoparticles were synthesized via the direct mechanochemical reaction by grinding pure Fe_2O_3 and Bi_2O_3 in an oxygen atmosphere at reaction times even less than 50 minutes. Crystallite size of the BFO nanoparticles from 13 to 20 nm could be tailored by controlling the milling conditions, particularly the milling power. Sol–gel process is a popular processing route for the synthesis of perovskite oxide nanoparticles (e.g. $BaTiO_3$ [59], $PbTiO_3$ [60], $BiFeO_3$ [61, 62]). This process involves the formation of a sol by dissolving the metal oxides, metal–organic, or metal-inorganic salt precursors in a suitable solvent, subsequent drying of the gel, followed by calcination and sintering at high temperature.

The hydrothermal method, involves heating an aqueous suspension of insoluble salts in an autoclave at a moderate temperature and pressure where the crystallization of a desired phase takes place. Solvothermal synthesis is also defined as a hydrothermal reaction that occurs in a nonaqueous solution in the hydrothermal process of BFO nanoparticles, Bi^{3+} and Fe^{3+} ions are first transformed into hydroxide $Fe(OH)_3$ and $Bi(OH)_3$ in the precursor, and then dissolved in the precursor with the presence of alkaline mineralizers (e.g. KOH, NaOH, LiOH). When the ionic concentration in the alkaline solution surpasses the saturation point, the BFO phase begins to nucleate and precipitate from the supersaturated hydrothermal fluid, followed by crystal growth [63, 64].

The term “microwave-hydrothermal process” was coined by Komarneni et al. [65] in the early 1990s, and this process has been used for the rapid synthesis of numerous ceramic oxides, hydroxylated phases, porous materials, and hematite powders [66–68]. It offers many distinct advantages over conventional hydrothermal synthesis, such as cost savings due to rapid kinetics time and energy, rapid internal heating, and synthesis of new materials. The morphologies of the component phases in such vertical composite films containing either magnetic or ferroelectric nanopillars varied markedly with the substrate orientation and phase fractions [69] was inferred from their microscopy observations. Raidongia et al. [70] reported a comprehensive study on core–shell (CFO@ BTO) nanoparticles and nanotubes. Core–shell type nanotubes exhibit a large saturation magnetization and remanent magnetization as compared to the nanoparticles, since the nanotube provides a large interfacial area between two phases. The $NiZnFe_2O_4$@BTO core–shell nanostructures were also extensively studied by Curecheriu et al. [71] and Testino et al. [72]. In the past decades, there was widespread scientific interest in multiferroic nanostructures and thin films, owing to their fascinating multifunctional properties driven by either interface-induced strain (typically in multiferroic thin films) [73–75] or by an intrinsic size effect (in nanostructures), which provides the basis for developing the next-generation electronic devices. The top-down approach involves the construction of small-sized structures from large ones through etching and removal of parts [76, 77]. In this method, lithography usually is applied to produce nanostructures with assistance from energy particles such as photons, ions, or electron beams. Focused ion beam (FIB) milling and electron beam direct writing (EBDW) are popular techniques for fabrication of nanostructures with controlled size and shape.

1.4 Multiferroic Systems of BiFeO$_3$ and BaTiO$_3$ Nanostructures: New Ideas and Insights from Recent Magnetoelectric Advancements

Since BaTiO$_3$ could exist in four different phases depending on the temperature – the paraelectric cubic, ferroelectric tetragonal, orthorhombic, and rhombohedral phases – the resulting displacement gives a polarization of 26 μC/cm^2 along the (0 0 1) direction [78]. The original cubic symmetry is distorted by lengthening of the c lattice constant ($c/a = 1.011$) [79]. The perovskite BiFeO$_3$ with high $T_c \sim 1103$ K and $T_N \sim 643$ K attracts lot of attention because it has simultaneous ferroelectric and antiferromagnetic ordering even at RT. This is because the ferroelectricity in BiFeO$_3$ originates from the 6s^2 lone pair electrons of Bi^{3+} ions due to structural distortion, while the magnetism occurs by Fe–O–Fe superexchange interactions. As an overview, BiFeO$_3$ has a disappointingly low spontaneous polarization and saturation magnetization due to the superimposition of a spiral spin structure of antiferromagnetic order [80]. In this spiral spin structure, the antiferromagnetic axis rotates through the crystal with an incommensurate long wavelength period of 62 nm, which cancels the macroscopic magnetization and also inhibits ME coupling. Hence, for novel electronics of BiFeO$_3$, its magnetic and electric properties must be enhanced. The superexchange between the octahedrally coordinated Fe^{3+} through the O ligand is responsible for the antiferromagnetism, but BiFeO$_3$ has been reported to have a weak ferromagnetic component at RT and is thus canted, with a helical repeat of ∼620 Å [81].

Hund's rule coupling would lead to spins of the TM 3d shell in parallel orientation and this mechanism breaks the strong covalent bonds that are necessary for ferroelectricity [82]. For example, in BiFeO$_3$ and BiMnO$_3$, the ferroelectricity is due to the lone pairs of nonmagnetic Bi, and in YMnO$_3$, it is due to tilting of almost-rigid MnO$_5$ trigonal bipyramids [83]. The structure of the ferroelectric BiFeO$_3$ phase has been resolved experimentally using X-ray and neutron diffraction and found to possess a highly distorted perovskite structure with rhombohedral symmetry and space group R3c [84]. It creates an effective negative pressure that led to a volume expansion [85]. The increase in c/a distortion leads to higher deformation of the TiO$_6$ octahedra [86]. The type of nanomaterials is not well defined in the literature, but it is considered that at least one of its dimensions is below 100 nm [87]. The distribution of nanomaterials is dependent upon its dimensionality; a system having all three dimensions well below 100 nm (critical length) is considered as quantum dots one main difference between ferroelectric nanostructures and bulk materials is the presence of depolarizing field in the former because of the uncompensated charges at the nanostructural surface [88]. The depolarizing field in nanosystems is able to quench spontaneous polarization [89]. An external electric fields and short-circuit boundary conditions are needed to screen the depolarizing field [90, 91]. Modified

Pechini method was also used to prepare $BiFeO_3$ nanoparticles [92, 93]. The rhombohedral distortion in $BiFeO_3$ from cubic structure is reduced by decreasing particle size accompanied by decreasing polarization inferred from atomic displacements. The size-dependent atomic displacement in multiferroic nanostructure reflects the effect of increasing depolarization field with decreasing crystallite size [94].

In small-sized nanostructures, the surface-to-volume ratio becomes so large that it increases again with decreasing particle size. Cao et al. [95] reported a Co-doped $BaTiO_3$ system for which the Co-3d states, ranging from −6 eV to Fermi level, have a strong hybridization with O-2p states. It involves double-exchange mechanism of ferromagnetism. The bonding of the charge carriers mediates the exchange interaction via oxygen vacancy within the local spins to contribute ferromagnetism. Superimposition of ZFC/FC plots around 300 K and a clear separation between FC/ZFC at low temperature, without blocking temperature, indicate that the TM ions in $BaTiO_3$ are not strongly antiferromagnetic [96]. It was predicted that the hybridization between the TM 3d orbitals and the O2p is the origin of observed magnetism [97]. These values of polarization are much larger than those observed in pure $BiFeO_3$ because of the formation of $Bi_2Fe_4O_9$ phase, which causes lower electrical resistivity [98, 99]. The doping of $BaTiO_3$ is located at Fe site and acts as acceptor for improving the electrical properties of BF–BT nanoparticles. For this, the doped $BaTiO_3$ acts as an acceptor to effectively compensate the charge carriers to Fe^{2+}ions at the Fe site and induce lower oxygen vacancy. To modify properties through size quantization such as the suppression of the spin spiral in $BiFeO_3$ and stabilizing phases that are inaccessible through conventional bulk techniques, thin-film growth techniques provide the ability to vary the lattice mismatch between the film and the substrate, so as to introduce epitaxial strain in the thin-film material.

1.5 Effective Properties of Multilayered Nanomultiferroics

The use of multiferroic materials is based on the magnetoelectric (ME) effect. This effect consists in the appearance of an electric field under the action of an external magnetic field and vice versa. In the natural multiferroic Cr_2O_3, the maximum ME coefficient is observed at a temperature of 260 K and amounts to 3.7 pS/m [100]. Unfortunately, this value is insufficient for practical commercial applications. ME coefficients greater by about two orders of magnitude were demonstrated for $TbPO_4$ [101] and HO_2BaNiO_5 [102]. The matrix homogenization method (MHM) presented in this unit provides effective parameters of a layered structure without solution of differential equations in partial derivatives [103–107]. To calculate the parameters, only operations with the matrices entering into the equations are involved. The method can be easily generalized for boundary conditions different from [110]. The effective medium would possess the same anisotropy for monoclinic, orthorhombic, tetragonal, and trigonal systems [111]. The effective structure with initial cubic anisotropy is tetragonal, as a cubic medium is a particular case of the tetragonal one.

Fiber composites are the most common nanostructures and are in use in a variety of systems [112]. Typically, they are modeled by a set of cylinders (inclusions), which are coated with multiple layers of different materials and immersed in a matrix of another material. The presence of an additional parameter – the curvature of the cylindrical layer – gives hope to strengthen the interaction between the electric, magnetic, and elastic fields. That is, by using fiber geometry, one may be able to design nanocomposite multiferroics with larger ME, piezoelectric, and/or piezomagnetic coefficients. Core–shell nanocomposites have been an active research area in the past years because of their promising multifunctional capabilities. These structures demonstrate novel characteristics that are different from their single-component counterpart. Some applications can already be found in bioimaging, cloaking, drug/gene delivery, nanophotonics, optics, and sensors [113–121]. Multilayer nanoshells, or so-called nanomatryoshkas, are a particular and very promising case of core–shell nanomaterials. The classical electromagnetic theory is sufficient to estimate the optical parameters of nanomatryoshkas with core–shell separations larger than a nanometer. Unfortunately, due to the bypass of electron transport between the core and shell through the self-assembled monolayer [122], classical approach fails for the description of nanomatryoshkas with subnanometer-sized gaps. Thus, there is need to employ a quantum approach for the modeling of the small-sized nanomatryoshkas (less than 1 nm). Compared to earlier published works [123–125], this approach does not require usage of special functions like, e.g. spherical or Bessel functions.

The computational scheme is much simpler than the previously existing one, even for the electrostatic problem. It allows finding solutions of more complex problems accounting for the interaction of the fields of different nature [126]. For the determination of the material coefficients of this effective medium in the case of small total thickness, it is recommended to use the MHM, which does not require the solution of a complex system of magneto-electro-elasticity equations. The desired effective characteristics are obtained using only operations with matrices characterizing the properties of single nanolayers. This fact significantly simplifies the calculations and allows multilayer nanosystems to be accurately and easily described.

1.6 Correlation between Grain Size, Transport, and Multiferroic Properties of Ba-doped $BiFeO_3$ Nanoparticles

$BiFeO_3$ is one of the single-phase multiferroic materials with a distorted perovskite structure ABO_3 [127], which shows multiferroic behavior at RT having high ferroelectric Curie temperature ($T_C \sim 1100\,K$) and antiferromagnetic Néel temperature ($T_N \sim 640\,K$) [128], and it continues to be the only compound with coexistence of ferroelectricity and antiferromagnetism at RT [129]. The ferroelectricity and magnetism in $BiFeO_3$ is attributed to the Bi^{3+} $6s^2$ lone pair electrons and partially filled d orbital of Fe^{3+} ion, respectively [130]; thus, the coupling between the ferroelectric and magnetic ordering is usually considered to be rather weak [131]. The impurities, large leakage current, and antiferromagnetic nature are big hurdles in $BiFeO_3$ applications [132], and it is very difficult to obtain a single-phase $BiFeO_3$ by using solid-state reaction at high sintering temperature [51]. Doping at A-site affects the centrosymmetry of FeO_6 octahedra, creates oxygen vacancies, and leads to change in multiferroic properties of $BiFeO_3$. Furthermore, the leakage currents are reduced by Ba^{2+} ion doping [133, 134]. Leakage current due to oxygen vacancies or impurities is the major problem in $BiFeO_3$. It has been observed that doping at A-sites reduces the leakage current in $BiFeO_3$ and enhances the multiferroic properties [135].

The substitution of Bi^{3+} by Ba^{2+} may cause two parallel phenomena with respect to the concentration of oxygen vacancies: (i) the creation of oxygen vacancies to neutralize the charge produced substituting Bi^{3+} by Ba^{2+}, (ii) decrease in concentration of oxygen vacancies by filling the probable vacant volatilized Bi^{3+} sites [136]. The spectra of 630 cm^{-1} are of strong metal oxygen-bending vibration of $M{-}O_4$ [137, 138]; such band vibration is a possibility in impurity phase, since minor impurity phase was seen on substitution in XRD. The magnetic properties of $BiBaFeO_3$ multiferroic nanoparticles depend on particle size because of long-range spin arrangement. The reduction in particle size below the periodicity of cycloidal spin structure will enhance the magnetic properties. However, the weak ferromagnetic founding in $BiBaFeO_3$ multiferroic nanoparticles originated from canting in the Fe^{3+} moments due to tilt of $<FeO_6>$ octahedron and the distortion can suppress the spiral spin structure and increase the weak ferromagnetism. Due to the small particle size, the electron spins fluctuate; this results in decreasing Néel temperature as the fluctuations create disorder. In addition, the reason may be related to the decrease of magnetic exchange interactions with reduction in particle size [92].

The substitution of divalent metal ions Ba^{2+} at trivalent Bi^{3+} sites requires oxygen deficiency for compensating charge, and this may destabilize the system [139]. It is expected to suppress the cycloid spin structure [140]. The small particle sizes observed in the samples of the order of 30 nm are excellent for efficient ferromagnetic properties, due to the magnetic cycloid spin structure of 62 nm in this material [141]. Lattice distortions, oxygen and bismuth vacancies, and defects at the interfaces as well as inside grains are the sources of space charges in $BiFeO_3$ [142]. These space charges are able to follow the applied field at lower frequencies, whereas they cannot find time to undergo relaxation at high-frequency region [143, 144].

1.7 Specific Heat and Magnetocaloric Properties of Some Manganite-Based Multiferroics for Cryo Cooling Applications

Due to the restrictions and disadvantages of the vapor compression technique, the scientific community is looking at new refrigeration technologies, viz. thermoelectric cooling [145], adsorption refrigeration [146], absorption refrigeration [147], thermoacoustic refrigeration, and solid-state magnetic refrigeration. In recent times, the large magnetic entropy change found in perovskite manganites [148] suggests that these materials might be exploited for magnetic refrigeration applications. Apart from this, the rare earth manganites exhibiting multiferroic behavior have attracted attention due to their potential applications in magnetic refrigeration industry [15, 149]. Although research on colossal magnetoresistance and multiferroic manganite materials was initiated almost two decades back, this method was used for the calculation of magnetocaloric effect by using temperature dependence of specific heat data at different magnetic fields [150, 151]. It has been reported that the magnetocaloric effect (MCE) determined by this method has the same accuracy as that from magnetization measurements. Further, the accuracy of this method is better than that of the direct methods. At the transition temperature, an anomaly in the dielectric behavior has also been observed, indicating correlation between these behaviors [152]. Based on the neutron diffraction studies [153], it was reported that the sinusoidal ordering of Mn^{3+} moments transforms into an incommensurate spiral order at this transition, where Mn^{3+} moments are locked. The transformation of sinusoidal to spiral magnetic ordering results in breaking center of symmetry, which, in turn, leads to the polarization in the material. The transition is also observed in dielectric constant data of the present investigation [154], which is attributed to the ferroelectricity. Based on the results of neutron diffraction measurements of $TbMnO_3$ sample, it is reported that the sinusoidal ordering of Mn^{3+} moments transforms into an incommensurate spiral order, which breaks the center of symmetry of the system leading to the spontaneous polarization. In the specific heat studies of present investigation, yet another transition observed at 24, 27, and 18 K is influenced by the magnetic field. At this transition temperature, the commensurate phase becomes low-temperature incommensurate phase. The signature of this magnetic transition can also be seen in dielectric constant behavior of the present investigation [155]. Therefore, this is called second ferroelectric transition (T_{C2}).

Sagar et al. [156] calculated ΔS_M, ΔT_{ad}, and RCP of $EuMnO_3$ at different fields using a simple theoretical approach [157]. Only temperature-dependent magnetization data (M versus T) are needed in this method. It was observed that with increasing field, MCE parameters increase linearly [157]. Several scientific groups also worked on MCE of $GdMnO_3$, $TbMnO_3$, and $DyMnO_3$ samples in their single and polycrystalline forms. Aditya A Wagh et al. [158] investigated MCE properties of $GdMnO_3$ single crystal. They used magnetic and magnetothermal measurements along the three crystallographic axes for the investigation of MCE properties. $DyMnO_3$, which crystallizes in hexagonal form, was also studied by Balli et al. [159]. And calculated ΔS_M along the c-direction and in ab plane at different applied magnetic field variation. In c-direction, when varying the magnetic field from 0 to 2 T, 0 to 5 T, and 0 to 7 T, the maximum variation of the entropy reaches values of 5, 10, and 13 J/kg-K, respectively. Sattibabu et al. [160] also investigated the influence of Er doping on magnetocaloric performance of $YbMnO_3$ sample at different fields. They used two samples with compositional formula $Yb_{0.9}Er_{0.1}MnO_3$ and $Yb_{0.8}Ho_{0.2}MnO_3$ and calculated using heat-capacity data. MCE parameters of this system increase with rise in doping concentration and field, and are comparable with reported values. For the first sample in this series, the ΔS_M values are 1.81, 3.27, 5.45, and 7.26 J/Kg-K at 2, 4, 6 and 8-T fields. Multiferroic manganites with orthorhombic and hexagonal structure show high magnetic entropy and adiabatic temperature changes at below 20 K, which is very useful for liquefaction of gases for cryo cooling applications. The ΔS distribution of the samples is uniform, and it is desirable for an Ericsson-cycle magnetic refrigerator, which is beneficial for the household application of active magnetic refrigerant materials.

1.8 Preparations, Characterization, and Applications of Multiferroic Nanocomposites

Many preparation methods have been adopted in order to produce high-quality materials exhibiting multiferroic properties at room temperature. Salami et al. [161] prepared $(1-x)\mathrm{Bi_2Fe_4O_9}-x\mathrm{CoFe_2O_4}$ $(0.0 \leq x \leq 1.0)$ multiferroic nanocomposites; these nanocomposites have been prepared by wet chemical procedures combining reverse chemical coprecipitation and Pechini-type sol–gel techniques followed by mechanical blending process. The authors have characterized all nanocomposites with XRD and SAED, and the results show that the diffraction patterns were perfectly indexed to the constituent phases present in composite samples. Also, the characteristic peaks in FTIR spectra confirmed formation and purity of all specimens. Many preparation methods have been adopted to produce artificial high-quality materials exhibiting multiferroic properties at RT [162–165]. One interesting approach is to synthesize composite materials with one component being ferroelectric and the second one being ferromagnetic at RT [166–168]. Mitra et al. [169] have combined phases of $\mathrm{GdMnO_3}$ (GMO) and $\mathrm{CoFe_2O_4}$ (CFO) in the nanocomposite state and showed some limitations as multiferroics. The authors have reported high dielectric loss, though magnetic ordering is found at RT, while the $\mathrm{TiO_2}$ matrix hosts the GMO and CFO where the dielectric loss has been remarkably lowered and the dielectric and ferroelectric ordering (below ~13 K) of GMO along with the magnetic phase of CFO are utilized to develop the multiferroic. Mandal et al. [170] investigated ME coupling, dielectric, and electrical properties of $x\mathrm{La_{0.7}Sr_{0.3}MnO_3}$ (LSMO) $-(1-x)$ $\mathrm{Pb(Zr_{0.58}Ti_{0.42})O_3}$ ($x = 0.05$ and 0.1) multiferroic nanocomposites. Duong et al. [171] discussed about the growth of 79% $\mathrm{Bi_2Fe_4O_9}$–21%$\mathrm{Fe_3O_4}$ nanocomposite films on $\mathrm{LaAlO_3}$ substrates using molecular beam epitaxy. X-ray diffraction and field emission scanning electron microscopy confirmed that the nanocomposites consisted of an orthorhombic phase of lamellae $\mathrm{Bi_2Fe_4O_9}$.

Rajesh Babu and Koduri Ramam, [172] reported synthesis, structural, magnetic, and dielectric studies of Ruthenium (Ru)-doped BKFO ($\mathrm{BiKFe_2O_5}$) multiferroic nanocomposite. Ajith et al. [173] prepared and characterized ME multiferroic BCZT–CFO nanocomposites that were synthesized via sol–gel route. XRD measurements and TEM measurements were conducted, and they indicate that the majority of particles formed, have core–shell structure. Tang et al. [174] prepared enhanced ME response for $\mathrm{La_{0.67}Sr_{0.33}MnO_3/PbZr_{0.52}Ti_{0.48}O_3}$ multiferroic bilayer thin film at RT; these nanocomposites have been prepared using pulsed laser deposition method. Vivek Verma et al. [175] proposed improved magnetic properties of

$Bi_{0.9}Pr_{0.1}FeO_3$ in their composites of BPFOx NZFO. For the composites sample BPFO–NZFO 1, the Ms. and Mr. are higher than those measured for the BPFO and continuously increase with the increasing weight percentage of NZFO in composites. Mahalakshmi et al. [176] prepared and characterized the multiferroic composites of $CoFe_2O_4$ and $BaTiO_3$. These nanocomposites have been synthesized by coprecipitation method. Hajlaoui et al. [177] prepared and characterized high-quality $Ba_2NdFeNb_4O_{15}$-based multiferroic nanocomposite films that were grown on Pt/MgO(100) single crystalline substrates. Tuning of ME coupling in multiferroics is of great fundamental and technological importance due to the potential applications of ME effect in advanced devices, such as ME read-head sensors [178, 179], data storages [1, 180, 181], and spintronic devices [12, 107].

Multiferroic nanocomposites can find various applications in magnetic materials covering sensitive H sensors, including biomedical sensing, navigation, magnetoresistance (MR) applications, and many more complex applications in spintronics [182].

1.9 Conclusions

Nanostructured Multiferroic materials offer great prospects at many application levels owing to their unique properties. In this chapter, we have reviewed the various multiferroic materials and preparation, characterizations, and applications. We have also reviewed each chapter through a detailed abstract.

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