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Research Article

# Major Applications of Advanced Nano Multiferroic Magneto-Electric Materials in Devices: Synthesis and Characterization

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## Abstract

This paper discusses the literature review on various aspects of ferromagnetic and ferroelectric materials and their composites. Due to the technical significance of linking individual components of these multiferroic composites, the inquiry has been given much emphasis. These materials are known as direct magneto-electric coupling and are capable of electrically tuning magnetization or vice-versa. In the current case, the multiferroic field shifted more towards the application portion than its simple physics. These goals take into account the invention of innovative nanoscale materials with efficient electrical and magnetic binding at room temperature0.0. A forum for potential developments can be provided by multiferroic with strong room temperature magnto-electric (ME) coupling. The properties of PbTiO3-Ni0.5Co0.5Fe2O4 composites and their ball-milled samples have been addressed. XRD and SEM micrographs also verified the phase formation and grain size of composites. For milled samples, the average grain size was less than 100 nm. The pristine composite (PT-NCF) XRD pattern exhibits increased peak strength corresponding to the PT period. It is found that with milling length, the amplitude of XRD peaks decreases and peak width increases. A wide difference in transition temperature, Tc, was reported during dielectric measurements due to the reduction in grain size and existence of the ferromagnetic phase. In addition, for the higher milling period study, the lower Tc value is registered. At room temperature, the P-E loops of all the composites of varying particle sizes appeared to be lossy in design. In comparison, as the grain size reduces, the region of the P-E loop rises. In comparison with the ferroelectric (PT) stage, the percentage of the ferromagnetic (NCF) step is weak, but the magnetization values obtained for all the composites were still significantly strong. In this post, recent developments in multiferroic magntoelectric nanostructures clarify.

***KEYWORD:*** Advanced, nano, multiferroic, magneto-electric materials, devices, applications

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## I. INTRODUCTION

Multiferroic materials are those of which magnetic and ferroelectric order coexistence is in a single phase for magnetic field control and vice versa. "The coexistence of magnetic and ferroelectric order is the coupling order measurement known as magneto-electric (ME) coupling. The magneto-electric (ME) effect on separate materials will separate two types of single phase and composite materials. These multiferroic magneto-electric materials are suitable as multifunctional devices in sensors, memories, transducers and data storage technologies.Our everyday life is surrounded by all types of gadgets, such as smart phones, computers, etc., built on developments produced in magnetic and semiconducting materials-centered technologies. Since magnetic materials are used in transformers, generators, appliances and memory systems, etc., the advantage of applied material technology is directly linked to magnetism. William Gilbert extensively studied modern-day magnetism in 1600, and Orsted clarified the connection between electricity and magnetism in 1819. In 1921, Valasek[1] made the discovery of ferroelectricity, while Fox and Scott[2] clarified the magnetic order generated by ferroelectricity and vice versa. Ferroelectric materials show broad spontaneous polarisation and find applications such as non-volatile RAMs, transducers and condensers. It can be assumed that in contemporary science & technology, ferroelectric and ferromagnetic materials play an important role and act as a medium for novel multifunctional applications. In the past few decades, a variety of nano-multiferroic magneto-electric composite materials have been documented in the field of science. At the same time, the multiferroic has a minimum of two ferroic order parameters (ferroelasticity, ferroelectricity, ferromagnetism) in the same step. Due to electrical, magnetic and piezoelectric properties, multiferroic materials are the first choice of multifunctional materials. These multiferroic materials may be used in transduction electronic gadgets, different sensing and other significant applications relevant to memory.

## Objective

- To synthesis of some single-phase compounds and composites with nano-range ferroelectric and ferromagnetic phases and their major applications

## II. LITERATURE REVIEW

In the literature review section we explored the different aspects of ferromagnetic and ferroelectric materials and their composites major applications were discussed as follows:

- Multiferroic materials

Although ferromagnetism and ferroelectricity vary from a theoretical point of view, their combination results in multiferroic materials in the same process. The fundamentals of multifunctional devices have been found to co-exist in a single compound of powerful co-relation forms, magnetism and ferroelectricity. As some potential co-existing order parameters turn out to be mutually exclusive[3-5], the simultaneous presence of these two order parameters in a single compound is challenging. In addition, the simultaneous occurrence of electric and magnetic dipoles does not guarantee a good coupling between them. In recent years, more than one ferrous order (i.e. magnetism, ferroelectricity, ferroelasticity) co-existing concurrently has been found in the number of compounds [6-8].

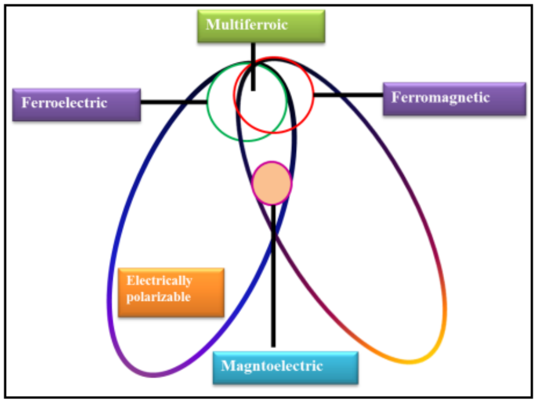


**Figure 1: Multiferroic/magneto-electric materials schematic representation**

- Multiferroicity process

There are many groups of multiferroic materials[4, 5] dependent on the multiferroicity exhibition process, out of which four forms are discussed.

Mechanism of Lone-pair

As seen in Figure 2, the lone-pair system relies on spatial asymmetry and unbonded valence electron across the host /core ion. The electrons cause a ferroelectricity-generating electric dipole. Ferroelectricity in BiFeO3 is responsible for the mechanism of a lone pair. Only BiFeO3 is a single-phase multiferroic substance at room temperature in the community of lone pair structures, has heavy electrical polarisation and prominent magneto electrical coupling [6-8]. In hybridization, cation Bi3+ and valance electron in the S orbital are omitted but cause a local electric dipole and create a spontaneous polarisation below the transition/Curie temperature.

## Mechanism of Charge Ordering

The process of charge ordering will occur only when valence electrons are not evenly distributed in the crystal structure around their host ion and giving rise to periodic superstructure. The Fe atoms form a superlattice arrangement with a series of Fe2+ and Fe3+ions[9] resulting in electrical polarisation and hence ferroelectricity[10, 11] has been documented in the case of LuFe2O4. This compound was the first of its multiferroicity ordering charge form. As an important and fascinating principle of multiferroicity, the charge ordering has emerged.

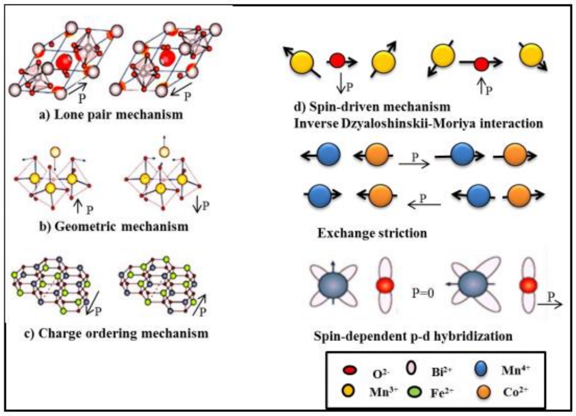


**Figure 2: Various multi-ferroicity pathways.**
(a) BiFeO3 lone pair mechanism (b) Hexagonal geometric mechanism (c) LuFe2O3 charge ordering mechanism produces alternate layers of 1:2 and 2:1 Fe2+/Fe3+ ratios and creates random polarisation b/w two layers (D) spin guided mechanism

## Mechanism of Geometrics

The consequence of space filling and geometric limitations are the product of structural instability in a material. The substance h-LuFeO3 has been documented to exhibit a large magnetic moment at room temperature[12], however the magneto electrical coupling in this material has yet to be verified. In the case of BaNiF4[13], spontaneous polarization[14] is produced by asymmetry between Ba2+ and Fions, resulting in a poor ferromagnetic moment, reversed in the direction of polarisation. Similarly, ferroelectricity is caused by hexaferrite magnetite (ABO3) since MnO5 slanting creates a thick packet and oxygen ions move closer to such A ion and create an electric dipole.

## Mechanism powered by spin

By magnetic order, the inversion symmetry can split. Spin and charge interfere with each other and this interaction will change the non-centrosymmetry from magnetic to electrical lattice, resulting in a polar state being formed. The magnetically field-induced inappropriate ferroelectric materials are responsible for a critical change away from ferroelectrics to the materials in which magnetic order causes electric polarisation. Several routes for multiferroicity formation have been addressed and several have been discussed in reviews[15]. An antisymmetric exchange relation between two spins is the Dzyaloshinskii-Moriya (DM) interaction (spin-orbit magnetic moments). Another widely debated process is the inverse Dzyaloshinskii-moriya (DM) relationship [16]. A non-centric spin structure drives and is provided by displacement of charge of charge[17, 18] in DM interaction). On both the DM and inverse DM interaction, the spin orbit interaction has importance. The resulting polarisation in the inverse DM interaction is deduced by spin configuration from the antisymmetric exchange as a product of neighbouring Sij spins, i.e. The co-relation between magnetic and electrical polarisation is Si-Sj and provides the co-relation between magnetic and electric polarization.

## Comparison between the main processes

In terms of the resulting polarisation, these four pathways can be contrasted. For computer implementations in BiFeO3, the lone pair function describes multiferroicity. Whereas at room temperature, a variety of spin-driven multiferroic materials exhibit heavy coupling[19, 20]. The polarisation values of the multiferroic content can be improved at room temperature by chemical doping and strain and pressure impact regulation, etc. Ferromagnetism and ferroelectricity are considered to classify applications in engines, actuators, etc.[21]. Multiferroic products have multifunctional properties and are used in mobile system processing for memory applications. Therefore, multiferroic magnetization tailored to electric fields has drawn a lot of interest in the construction of specialised devices with quicker and more features. There is a lot of work to look for new multiferroic compounds. Magnetites such as BiMnO3, TbMnO3,[22] are well-known multiferroic products, but heavy magneto electric (ME) coupling is only observed at cryogenic temperatures in these compounds. In addition, ME coupling is seen in the case of TbMnO3 as it forms a spin-frustrated device. While a mechanism for ME coupling is given by the spiral spin order, but only at low temperatures. ME-coupling materials are needed at room temperature for realistic applications.

## Magneto electronic materials description

Magnetoelectricity is a multiple property having a diverse behaviour in magneto-restrictive and piezoelectric materials. Magneto electromagnetic (ME) structures are exposed to electric polarisation in a magnetic field (meh: p= alpha) and vice versa, i.e. electric field magnetization (mee; m= alpha), which can be divided into two forms (1) single phase and (2) composite[23]. Compounds that are not necessarily multiferroic but fall in the group of multiferroic materials where polarisation (magnetization) is linearly caused by an applied magnetic (electric) field may be searched for in order to provide stable magneto electric (ME) coupling at high temperatures. Materials such as hexaferrites of type Y and Z are observed to exhibit field-mediated ferroelectricity (polarisation) and heavy ME coupling[24] For example, hexaferrites such as Ba2Mg2Fe12O22 (BMFO) are documented to have induced higher temperature ferroelectricity (polarisation) but are able to display ferroelectricity in the absence of a magnetic field or may be reported as zero magnetic fields[25]. On the other side, ME mediated room temperature field coupling observed as (Ba, Sr)3Co2Fe24O41[25] for Z-type hexaferrites can serve as starting materials for multifunctional devices. A weak magnetic field is necessary for these materials to cause polarisation and hence room temperature ME coupling.

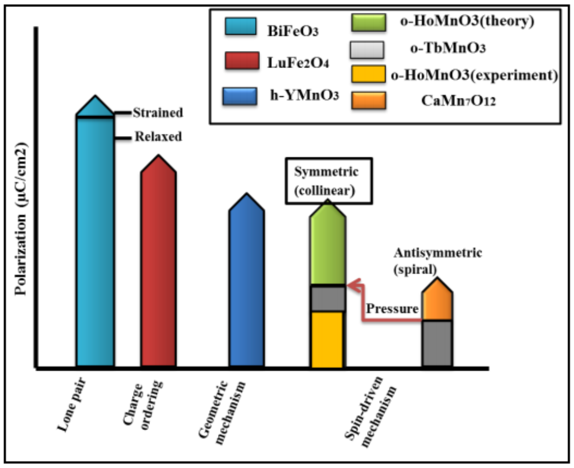


**Figure 3: Comparison of various forms of processes such as electronic lone pair charge ordering, geometry and spin-driven ferroelectric symmetry, demonstrated by DM interaction with various examples**

## Electrical single phase magneto

Magneto electrical devices, which are single-phase materials, are chemically homogeneous and isotropic in design. Co-existence of electrical dipoles and magnetic moments of long-range order is compulsory in single phase products. Due to the coupling of polar and magnetic sublattics in a single step, ME compounds are desirable under such restrictions. Due to poor permeability at room temperature and thus limiting uses, most of these materials demonstrate weak magneto electric coupling. BiFeO3 is a single phase magneto electric compound with strong ferroelectric properties but rather poor ferromagnetic properties above room temperature[26]. In addition, ferroelectricity and a considerable volume of polarisation occur in single phase magneto electrical materials at temperatures greater than the magnetic transition temperature. Multiferroic materials are referred to as type-I multiferroics as mentioned before and have charecterstics such as lone pair, geometric impact and charge ordering etc.

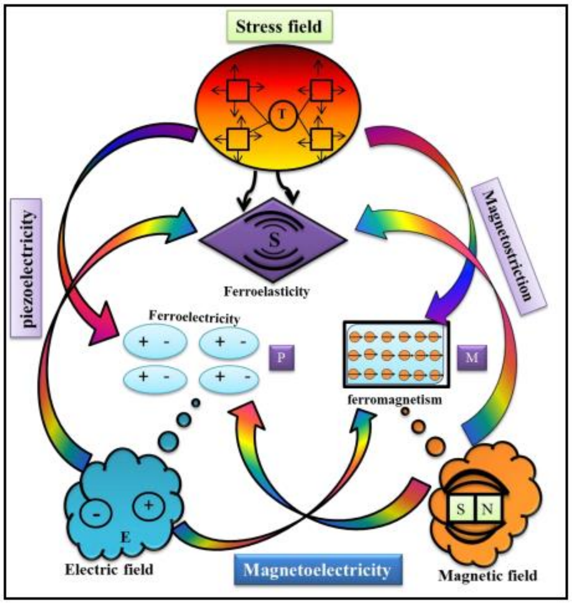


**Figure 4: Magnetic-electric-elastic binding schematic diagram for multiferroic products. Here, magnetization is M, polarisation is P and strain is S.**

- Composite Electric Magneto

Unlike single-phase multiferroic materials, the emphasis nowadays is on composite materials that are capable of providing a broad ME effect[27]. The synthesis or coexistence of these products consists of two distinct kinds of materials[28]. I.e., piezoelectric ferromagnetic magnetostrictive and ferroelectric. In magneto-restrictive materials, the tension caused by the magnetic field is transmitted to material II via the boundaries between materials I, thus turning it into a voltage due to the piezoelectric effect. Magneto electrical coupling in composite materials can be 108 times larger than multiferroic single-phase materials[29] and occurs by numerous pathways described in the following segment.

## Coupling induced by Strain

The strain induced coupling can be explained in two ways, as seen in Figure 4. The ME effect is detected when the magnetostrictive effect in the magnetic phase is combined along with the piezoelectric effect in the piezoelectric phase. Another system for engineering multiferroic thin films is the epitaxial pressure. By choosing the right substrate, a large variety of tensile and comperessive strains can be achieved. As a ferroelectric material is used, the piezoelectric material serves as a substrate to create a strain that can be tuned reversibly with an external voltage. In some cases, atomic alloying and strain can result in the formation of otherwise unstable multiferroic phases in the crystal lattice of the substrate[30].

The connection between ferroelectric and ferromagnetic properties was recently found to be due to the strain in the case of BiFeO3 [30, 31]. In non-ferroic products, the strain can also cause ferrous order. When the density and distribution of vacancies in the materials are regulated by the pressure, a higher degree of freedom for the alteration of material properties is possible[32]. The strain can be transmitted through magnetorestrictive and magneto electric coupling through an interface between ferromagnetic domains and ferroelectric domains[33]. The temperature control and anisotropy of interfacial magnetism found in CoFe-BaTiO3[34] was expected to be regulated by the electric field. It is understood that a significant number of bulk ME composites have a stress-mediated magneto-electric effect at or above room temperature.

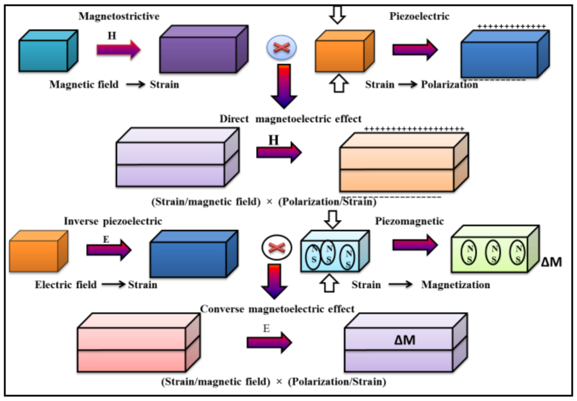


**Figure 5: Strain-mediated magneto-electric effect in a magnetic and ferroelectric layer composite structure.**

(a) Direct effect of magnetoelectric (ME) (b) Converse effect of magnetoelectric (ME).

### Coupling/Interfaces mediated by Charge

It was observed that multiferroic states occur between two components at the interface. Properties may differ at an interface due to confinement influence, low local symmetry, local anisotropy, and gradients of pressure. In fact, it has been observed that the interface between ferromagnetic materials such as Fe, Co and BaTiO3 may be multiferroic and that multiferroicity is retained across the interface within different monolayers[35]. As a consequence, an electric field will rearrange the magnetization axis at the interface, and thus the position along the axis remains unknown in the absence of a magnetic field. The investigation of domain walls is another way to validate multiferroicity at the interface.

### Coupling/ realms and domain walls mediated by Exchange Bias

Domains, both for ferroelectric and ferromagnetic compounds, are the expanded area of atomic parameters of standardised alingment. Typically, multiferroic materials consist of several domains and domain walls are called the interface or barrier between domains. Domain and domain walls are very necessary for different properties such as corecivity, resistance, etc. to be regulated. The magneto electric coupling (ME) originates in the case of multiferroic materials owing to the coupling between identity of ferroelectric and magnetic domains, i.e. the coupling does not originate in the domain but in domain walls.

Advanced functionalities are typically based on complex domain structure[36], symmetry analysis[36] and experimental outcome analysis. For the study of ferroelectric domains, optical methods were used while ferromagnetic domains were imaged utilising the magneto-optical faraday effect[37]. The technique of scanning electron microscopy offers greater domain resolution at the nanoscale and is very useful in studying the dynamic nature of the mutiferrioc domain of BiFeO3 thin films[38]. The emphasis has changed recently from domains to domain walls[39]. Charging or spin phenomena are almost identical to those that exist at heterointerfaces on the domain walls,[40] and may arise. The domain wall has the benefit of being relocated, generated and erased after development.

- Electric binding influence of Magneto by magnetic substance

The magnetism induces ferroelectricity in type-II single phase magneto electrical materials and there is good coupling between them. These show tiny electric polarisation values that occur instead of magnetism at lower temperatures, i.e. ferroelectricity. Any variables describing this kind of existence are explained below.

### Collinear magnets

A collinear magnet is a magnetic state in which, as seen in Figure 1.17, magnetic moments are organised or coupled parallel or antiparallel to their closest atoms and create a paraelectric step due to moment alignment along the X-axis (horizontally). One dimensional up-up-down-down spins are produced in these forms of materials owing to exchange constraints. The distortion generated by up-down and up-down bonds is distinct, which motivates the creation of electric dipoles, such as the rare earth magnetite, CaCoMnO3[41].

### Magnets of the spiral

Spiral or non-collinear magnets are those in which the configuration of the magnetic order is not collinear, but the magnetic moment orientation order is around the y-axis (vertically). The ferroelectric process is therefore caused by cyclodial spin arrangements. Latest theoretical and experimental findings of rare earth magnetites suggest that the spiral spin structure is ferroelectric. The magneto electric coupling was formed by this magnetically induced ferroelectricity and thus exhibits the magneto electric effect. The system becomes ferroelectric in a spiral magnet as the magnetic order is induced and, as with the TbMnO3 arrangement, the inversion symmetry is broken due to this magnetic order. The cycloidal shape, for example, transforms into polar form due to DM interaction[42], which plays an important role in the spiral magnet magnet's magnetoelectric effect.

- Major Applications

The nanostructure of multiferroic magneto electric composites has been documented by Yao Wang, et al.[43] and the application-based impact has been compared in bulk (micro) and nano structure materials. The ME impact on the composites of the nanostructure was observed and the growth of the nanostructure, configuration, atomic arrangement and interfaces were also clarified. Furthermore, Wang et.al explained the behaviour of multiferroic single-phase and determined the coefficient of ME coupling. In the sense of structure, synthesising and successfully describing various properties such as magnetic, microwave properties, magneto electric multiferroic and dielectric at room temperature, different forms of Hexagonal ferrites were examined. A comprehensive study was also provided of the properties of Hexagonal ferrites at nanoscale and its application such as wave frequencies, antennas, activators and switches and sensors of magnetic fields, transducers and transformers, electromagnetic absorber and RAM etc. The nano size effect on magneto electric coupling in multiferroic heterostructures was investigated by X.Lu and H.Li[44] and it was found that size and surface impact the stability of magnetoelectric coupling. Centered on the constitutive principle and thermodynamic model, the size impact on the magneto electric coefficient of BaTiO3/CoFe2O4 was studied.

Zhang et al. [45] examined the influence of bulk (in micron range) composites {(1-x) BaTiO3- x Ni0.5Zn0.5Fe2O4} of various formulations and observed the optimal outcome for x=0.8. All the composites were found to have strong dielectric constants and strong ferromagnetic properties. It was observed that the composite with x= 0.8 had a high permeability of ~36.06 and a low magnetic loss of 1.12 ?? 104 J/m3 ideal for electronic devices. Velhal et al.[46] documented the impact of cobalt ferrite substituted by nickel and addressed its structural, dielectric and magnetic properties.

Hu, Jiamian & Nan et al. (2015)[47] investigated the vigorous research efforts of multiferroic magnetoelectric nanostructures with mixed magnetization and electric polarisation through their interfaces during the past decade. To greatly increase the efficiency of many devices such as memories, tunable radio-frequency/microwave devices, and magnetic sensors, such interface-based magnetoelectric coupling can be exploited. They presented a variety of new or emerging innovations in this article and address their limitations. To improve system efficiency, they explain how the use of magnetoelectric nanostructures will resolve these limitations. They also face problems that need to be overcome in seeking realistic magnetoelectric system applications.

In recent years, Yuxin Cheng et al. (2018)[48] have explored magnetoelectric (ME) materials and related devices which have drawn growing research interest. They show a strong ME coupling effect at room temperature, and it is possible to gain electric field magnetization control or magnetic field ferroelectric polarisation control. In order to improve ultra-fast, low-power, and miniaturised electronics, the ME coupling effect brings new features. Recent developments indicate that ME material efficiency is further enhanced and the materials are being used to build many different forms of electronics, such as high-speed memory, radio frequency resonator, lightweight ME antenna, and weak magnetic field sensor. In this study, we provide an analysis of both the prospects and obstacles for the implementation of ME materials and technology in cutting-edge developments in these areas, with focus on them.

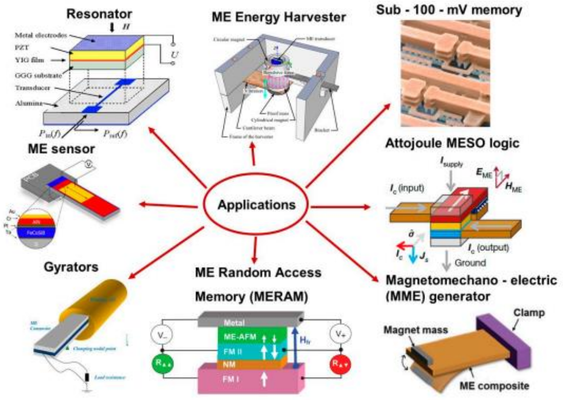


Figure 6. Different uses of composites for magnetoelectric (ME)

Dhiren K. Pradhan et al., (2020)[49] examined multiferroic (MF)-magnetoelectric (ME) composites combining magnetic and ferroelectric components, showing higher operating temperatures (above room temperature) and higher ME coupling (several magnitude orders) relative to single-phase multiferroic materials. The regulation of room temperature and the switching of magnetic properties by an electric field and electrical properties through a magnetic field has inspired research to achieve ultra-low power and multifunctional electronic nano (micro) devices. Any of the leading applications for magnetoelectric composites are reviewed here, and Figure 6 addresses the processes and existence of ME coupling in artificial composite systems. There are also shown ways to improve the ME coupling and other physical properties. Finally, the main unanswered questions and potential developments in this region are emphasised, where recent breakthroughs could have a major effect on the translation of research findings into functional system implementations that can be easily regulated both magnetically and electrically.

## III.MATERIALS AND METHOD

With improved methods for the production of nanocomposites, nanotechnology has enormous potential for future use. Advances in traditional composite synthesis methods have increased control over nanocomposite scale, form and other characteristics. A variety of strategies have been used for nanocomposite synthesis, such as silver coating for ball milling, sol-gel, solid state, hydrothermal and co-precipitation, etc. This segment includes different descriptions of the laboratory techniques used to synthesise and classify multiferroic nanocomposites and magnetoelectric materials.

- Materials

Lead oxide (PbO), Titanium dioxide (TiO2), Anhydrous nickel nitrate Ni(NO3), Cobalt nitrate {Co(NO3)2}, Ferric nitrate {Fe(NO3)3} and Citric acid were procured from Himedia India.

- Synthesis methods

The hexaferrites of multiferroic nanocomposites & Z-type can be synthesised by the technique of solid-state reaction and sol-gel. Raw material with various constituents is taken as oxides and carbonates in a stoichiometry ratio in the solid state reaction process to create the required composite. In the sol-gel technique, on the other side, the starting ingredients are nitrates. The form of solid state and the method of sol gel are seen systematically in (Figure 7)

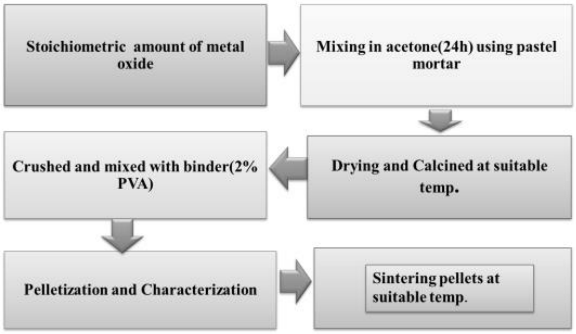


**Figure 7: The flowchart of the synthesis steps was accompanied by the process of solid state reaction.**

- Lead titanate particle synthesis

A solid state reaction method was used to synthesise $PbTiO_3$, for which $TiO_2$ was weighted in the necessary ratio and mixed for 3 hrs through ball milling. The powder was shot at 1100°C for 2hrs after careful mixing. The same method was used for lead titanate synthesis and the calcination of $PbTiO_3$ powder was carried out for 2 hours at $900^{o}$C.

- Nickel-cobalt ferrite nanoparticles' synthesis

Nickel-cobalt ferrite nanoparticles may be synthesised through different methods, such as the precursor form of coprecipitation, hydrothermal and citrate. Citrate precursor technique or sol-gel technique has been used to synthesise nickel-cobalt ferrite nanoparticles in existing science. In this phase, nickel nitrate hexahydrate {$Ni(NO_3)_2•6H_2O$}, Cobalt nitrate hexahydrate {$Co(NO_3)_2 .6H_2O$}, nonhydrate ferric nitrate {$Fe (NO_3)_3$} and anhydrous citric acid are dissolved in deionized water in the molar ratio of 0.5:0.5:2. The solution pH is retained below 9.0 by dissolving the solution with aqueous ammonia. The solution was held for two hours under constant stirring at 80-90°C and ammonia solution was applied drop-wise to preserve the degree of pH. The temperature of the solution was then increased under constant stirring at 100 °C to create a viscous gel. This gel has been burned to create a structure of dendrite that is crushed in a pastel mortar. The nitrate precursor was shot for 2 hours at 1100 °C and the nickel cobalt ferrite nanoparticle powder ($Ni_{0.5}Co_{0.5}Fe_2O_4$) was collected.

- Characterization Techniques

Using X-ray diffractometer(Rigaku), Scanning electron microscope (SEM)(su8010, Hitachi) and field emission scanning electron microscope (FESEM), TGA and DSC(SDT Q600), the dielectric properties are calculated by different characterization techniques to research the structural, dielectric, ferroelectric, ferromagnetic & magneto electric properties of proposed magneto electric nanocomposites, The dielectric properties are measured by impedence analyser (Waynker), vibrating sample magnetometre (VSM) and P-E loop for polarization in ferroelectric materials

## IV. RESULTS AND DISCUSSIONS

Absolute $PbTiO_3$ (PT) and $Ni_{0.5}Co_{0.5}Fe_2O_4$ (NCF) XRD sequence synthesised at 900 and 1100 ° C from Figure 8. For the PT process, no impurity peak appears visible, the NCF phase appears to crystallise in a cubic inverse spinal form (JCPS card no.74-2081)[50]. Rietveld refinement of pure $PbTiO_3$ was carried out in order to evaluate the lattice parameters of $PbTiO_3$ by taking the tetragonal structure as seen in Figure 9. As computed from these refined parameters, the c/a ratio is 1.064 ($a = 3.9002$ Å; $c = 4.151$ Å), which is pretty nearly the same as previously reported [50]. Therefore, in the present case, the tetragonality that is a critical point for the ferroelectric process appears to have been obtained. Analyzing the impact of particle size on the physical properties of the composite is the central problem under review. Therefore, strongly homogeneous composites were produced by combining PT-NCF in a planetary ball-mill. The particle size differs by increasing the milling time and composites are then sintered for 2 h at 850°C to acquire thick samples. At this point, it is of utmost importance to mention that the PT stage used to prepare the composites was already calcinated before ball-milling at 900 °C and NCF at 1100 °C, followed by sintering for 2 h at 850 °C. It has been commonly established that ceramics sintered for longer durations at high temperatures accompanied by natural cooling have a greater grain size relative to low-temperature synthesis techniques. Patankar et. al. [51] in their CuFe2O4-Ba0.8Pb0.2TiO3 research, found out that the lower sintering temperature and shorter holding time tend to reduce Pb deficiency due to its Ba0.8Pb0.2TiO3 instability. Therefore, both the grain size and Pb deficiency may be sustained by the technique followed above, i.e. low sintering temperature and less keeping time (T< 900 °C; 2 h).

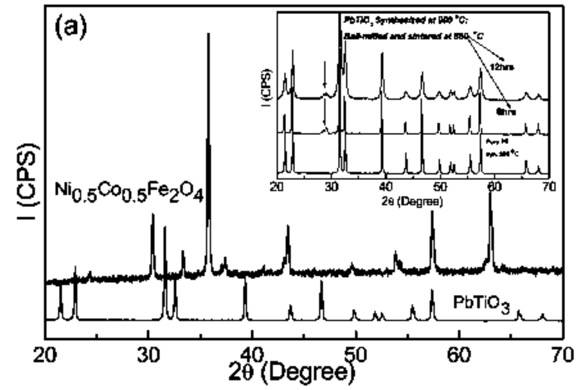


**Figure 8: PbTiO3, NiCoFe2O4 X-ray diffraction pattern; LHS displays a comparable PbTiO3 XRD pattern synthesised at 900 °C and PT ball-milled sample sintered at 850 °C.**

The XRD pattern of composites under review as seen in figure 10. Interestingly, the non-ball-milling composite, i.e. PT-NCF0 displays elevated peak strength at 2 = 21.4, 22.72, 43.7 and 46.49 ° (marked as *) referring to the PT process, while this function is missing from the majority of the samples in the XRD patterns. By comparing PT-NCF0, 1, 2 & 3, it is observed that as the milling time rises, the amplitude of XRD peaks decreases and peak widths increase. The observation that as the crystallite size decreases, the FWHM or peak diameter rises and the pressure decreases is a well-established fact.

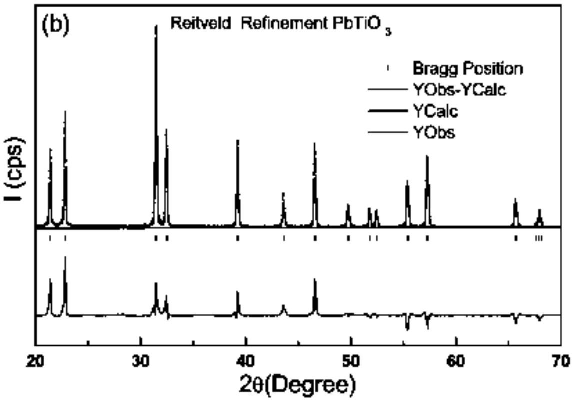


**Figure 9: Pure PbTiO3 Rietveld refinement trend**

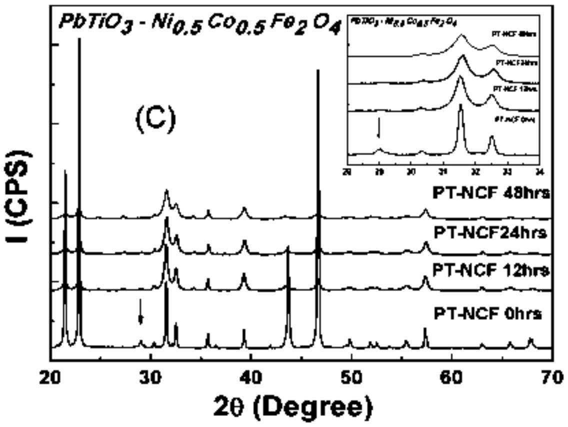


**Figure 10: Ball milled (0h 12h, 24h and 48h) PT-NCF composite X-ray diffraction pattern; inset reveals expanded view of 2 x = 28 ° - 34 °**

As determined by the Scherrer method of PTNCF0, PT-NCF1, PT-NCF2, and PT-NCF3, the average crystallite scale of the PT process is 54, 19, 18 and 11 nm, respectively. Similarly, there are 45, 43, 42 and 41 nm for the NCF process. It is also pointed out here that Scherrer's equations do not assess the consistency of particle size. Around Ishikawa et. An significant fact in this regard has been stated by al.[52, 53] that, according to these authors, the c/a ratio decreases with particle size and may be associated with the change in transition temperature (discussed later). The c/a ratio of the PT phase (as in the PT-NCF composite) with milling is not addressed in depth in the present case, but it is found from Rietveld refinements that the c/a ratio in these composites stays exactly the same for the PT phase.

- Structural analysis

Scanning Electron Microscopy was used to research the surface morphologies of the PT-NCF composites (SEM). From the surface profile of PT-NCF0 {Figure 11 (a & b)}, it is readily apparent that a homogeneous composite consists of two distinct phases co-existing with a clear and larger grain, whereas the other is at the same magnification without clear grain boundaries. It was found that there were smaller grain sizes with no specific grain borders in the ballmilled samples. In other terms, compared with other composites, the average grain size of the composite PT-NCF0 is high, i.e. For PT-NCF1, for PT-NCF2, for PT-NCF3

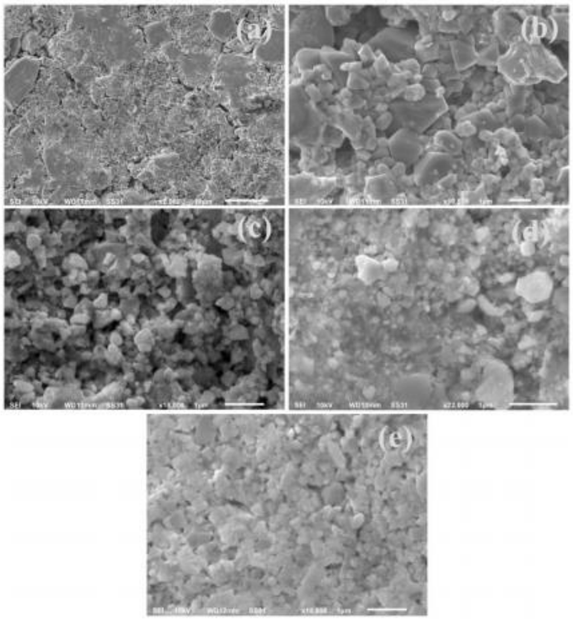


**Figure 11: SEM micrograph of the composites (a)-(b) PT-NCF0, (c) PT-NCF1, (d) PT-NCF2, and (e) PT-NCF3**

TGA and DSC analysis The thermal activity of PT-NCF composites studied using TGA/DSC from room temperature to 800 °C is shown in Figure 12. In the absence of a magnetic field, an exothermic peak of approximately 510 °C is observed in the PT-NCF0 composite DSC curve due to the transition in cobalt ferrite phase from ferromagnetic to paramagnetic (Curie point). The same was explicitly confirmed in the TGA/DSC tests conducted in the presence of magnetic fields (Fig 12b). Peaks related to minor weight loss was observed at 310 °C in the case of ball milled samples and the corresponding peaks are also available in DSC curves.

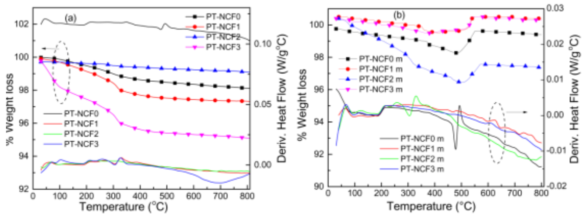
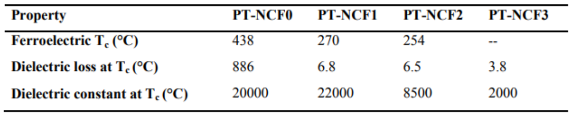


**Figure 12: TGA and DSC hybrid plots of PT-NCF (a) without a magnet and (b) with a magnet (Ball-milling 0, 12, 24 and 48 h).**

- Studies of Dielectrics

Figure 13 indicates the difference of dielectric constant and dielectric loss with temperature. The difference in dielectric properties can be understood by taking into account three factors: (a) reduction in ferroelectric phase particle scale, (b) composite formation at 80:20 ratios and (c) sintering of lead composites at 850 °C after calcination at 900 °C for 2 hours.

Table 1. Transition temperature values, dielectric constant and PT-NCFF dielectric losses.



| Property | PT-NCF0 | PT-NCF1 | PT-NCF2 | PT-NCF3 |
|---|---|---|---|---|
| **Ferroelectric $T_c$ (°C)** | 438 | 270 | 254 | -- |
| **Dielectric loss at $T_c$ (°C)** | 886 | 6.8 | 6.5 | 3.8 |
| **Dielectric constant at $T_c$ (°C)** | 20000 | 22000 | 8500 | 2000 |

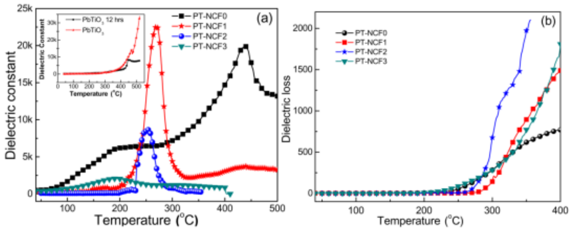


**Figure 13: (a) Variation of dielectric constant while inset indicates variation of pure PbTiO3 dielectric constant (PT 0 h) and sintered PbTiO3 milled at 850 °C for 12 h and (b) shift in temperature dielectric loss behaviour.**

As seen in the table, the change in Tc between the PT-NCF2 and PT-NCF0 tests, as observed in the present case, is more than 100°C. The 48 hour milled composite sample displays a diffused plateau in Figure 13. These results can be described by taking into account three factors: (a) reduction in ferroelectric phase particle scale, (b) composite shape at 80:20 ratios and (c) sintering of lead composites at 850 °C following calcination at 900 °C for 2 hours at 900 °C.

- P-E loop studies

Figure 14 displays the P-E (Polarization vs. Electric field) loops of all the composites collected at room temperature of varying grain size/ milling length. There is no observation of the usual sigmoid form and loops appear lossy in design. The region of the circle grows as the size of the particle decreases. For enhanced/optimized dielectric and ferroelectric properties, a size greater than the critical size is needed for BaTiO3.

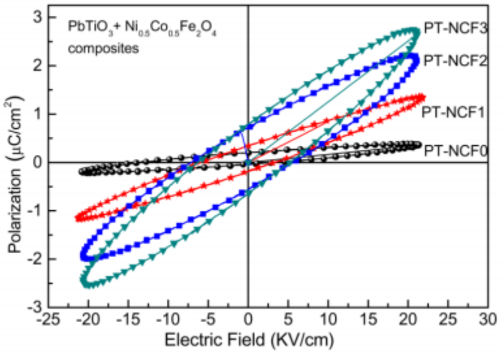


**Figure 14 Hysteresis loops of ferroelectric (P-E) for PT-NCF composites at room temperature.**

Magnetization versus magnetic field M-H curves as seen in Figure 15 for VSM measurements. The samples were put in a varying magnetic field of up to10 KOe. Although the percentage of the NCF process is minimal relative to that of the PT phase, acceptable values of magnetisation are nevertheless obtained in all composites[54]. The saturation magnetization values, i.e. For PT-NCF0, PT-NCF1, PT-NCF2 and PTNCF3 composites, Ms=10.55, 11.48, 12.61 and 9.48 emu/g, respectively, retentivity stays exactly the same for all samples except PT-NCF2. In comparison, the repressive fields for PT-NCF 0, 12, 24 and 48 h, Hc= 618, 532, 732 and 918 Oe, respectively.

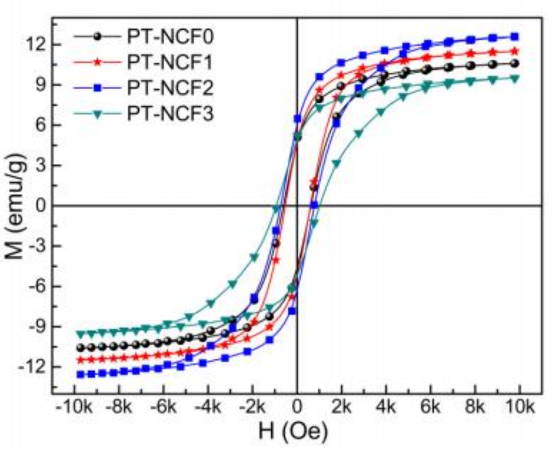


**Figure 15 M-H composite PbTiO3-Ni0.5Co0.5Fe2O4 plots**

- Measurements for ME coupling measurements

The calculation of the magnetoelectric (ME) coupling of the composites PT-NCF0, PT-NCF1, PT-NCF2 and PT-NCF3 was carried out by I measuring the coefficient of magnetoelectric coupling (a) which measures the voltage induced in the sample under the influence of a static magnetic field, superimposed by a small ac field and indirectly by (ii) measuring the shift in the P-E curves with and without a magnetic field. No important ME coupling indication was obtained using the former approach, so the effects of the indirect ME impact method were plotted and are seen in Figure 16 (a). Figure 16(a) explicitly indicates that the P-E loop of PT-NCF0 was unaffected by 2 Tesla magnetic fields. For all other composites, however, differences in the P-E loops were noted. For multiple samples, differences in polarisation have been plotted for further study and are seen in Figure 15 (b). Although the absolute improvement is minimal, it is very obvious from these plots, but the strength of ME coupling seems to increase in composite under tests with reduction in particle size.

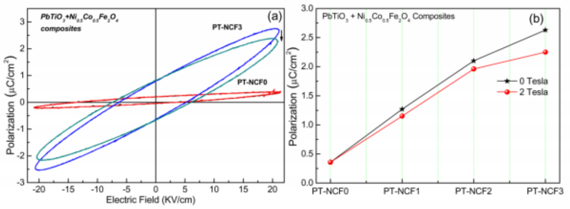


**Figure 16:(a) P-E loop with (H= 2Tesla) and without magnetic field of ball-milled PT-NCF 0hrs & 48hrs (b) Polarization difference of all PT-NCF nanocomposites with (H= 2Tesla) and without magnetic field**

## V. CONCLUSION

In tailoring the electrical, optical and electronic properties of materials, nanostructured structures are useful. It is evident that nanostructured materials will have an increasing impact on electronics, as electronics' increasingly smaller dimensional drive demands higher functionality, higher memory density, and higher speed. The analysis of nanoscale systems focused on modern operating concepts is motivated by the expectation of using results obtained with an additional tenfold reduction in dimension. By systematic nanoscale structure variance, beneficial modulation of the properties of materials may be accomplished. For possible electronic circuits, quantum effect systems or single electron devices are of considerable potential use. In changing electron transport, for instance, one class of devices works on the interruption effect characteristic of wave phenomena. These instruments appear to be microwave analogues or optical devices such as waveguides, interferometers, or modulators. To retain the step of the electron wave, both of these instruments depend on the removal of scattering. This includes strongly organised crystals to be paired with customised electronic and magnetic properties, low temperatures and limited measurements.

Ferroelectric, ferromagnetic materials and soft ferrites & hexagonal ferrite form Z are listed in this article. A quick overview of the nano multiferroic materials and their process, i.e. lone pair, charge ordering and spin-driven, and the comparison of this mechanism is also clarified. In addition, magneto electrical materials and their classification are addressed and defined as magneto electrical coupling mechanisms such as strain mediated coupling, charge mediated coupling/interfaces, effect with domains and domain walls, magneto electrical coupling effect by magnetic material.

The PbTiO3-Ni0.5Co0.5Fe2O4 multiferroic composite was prepared using traditional methods. The phases of the composite samples were ball-milled for various durations in order to minimise the particle size of the product (12, 24 & 48 h). In X-ray diffraction patterns and SEM pictures, the impact of size reduction was clearly noticeable. Due to the reduction in grain size, existence of ferromagnetic phase and instability of Pb, Tc was observed during dielectric measurements of ball-milled samples due to a wide difference in the transition temperature. The explanation for such activity could be linked to the size of the particles and the ferroelectric phase presence. The power of the ME coupling was also found to be weak for implementation purposes. In short, it is advisable to have an ideal grain size of PbTiO3 proper NCF phase ratio and with homogeneous mixing for the synthesis of PT-NCF composites, so that the phases will pair well by mechanical contact, resulting in tight ME coupling at room temperature for potential applications.

## REFERENCES

1. Valasek J., Piezo-Electric and Allied Phenomena in Rochelle Salt, Phy. Rev., vol. 15, pp. 475–481, 1921.
2. Fox D. L. and J. F. Scott, Ferroelectrically induced ferromagnetism, J. Phys. C Solid State Phys., vol. 10, no. 11, p. L329, 1977.
3. Shuvaev A.M., Mukhin A.A., and A. Pimenov, Magnetic and magnetoelectric excitations in multiferroic manganites, J. Phys. Condens. Matter, vol. 23, no. 11, p. 113201, 2011.
4. Bousquet E. and A. Cano, Non-collinear magnetism in multiferroic perovskites, J. Phys. Condens. Matter, vol. 28, no. 12, p. 123001, 2016.

5. Barone P. and S. Picozzi, Mechanisms and origin of multiferroicity, Comptes Rendus Phys., vol. 16, no. 2, pp. 143–152, 2015.
6. Wang J., Neaton J.B., H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V Waghmare, and others, Epitaxial BiFeO3 multiferroic thin film heterostructures, Science (80-)., vol. 299, no. 5613, pp.1719–1722, 2003.
7. Johnson R.D. and Radaelli P. G., Diffraction studies of multiferroics, Annu.Rev. Mater. Res., vol. 44, pp. 269–298, 2014.
8. Fedulov S. A., Determining the Curie Point of BiFeO3 Ferroelectric, in Soviet Physics Doklady, 1962, vol. 6, p. 729.
9. Ikeda N., Ohsumi H., K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and others, Ferroelectricity from iron valence ordering in the charge-frustrated system LuFe2O4, Nature, vol. 436, no. 7054, p. 1136, 2005.
10. Van Den Brink J. and D.I. Khomskii, Multiferroicity due to charge ordering, J. Phys. Condens. Matter, vol. 20, no. 43, p. 434217, 2008.
11. de de Groot J., T. Mueller, R. A. Rosenberg, D. J. Keavney, Z. Islam, J.-W. Kim, and M. Angst, Charge order in LuFe 2 O 4: an unlikely route to ferroelectricity, Phys. Rev. Lett., vol. 108, no. 18, p. 187601, 2012
12. Wang W., J. Zhao, W. Wang, Z. Gai, N. Balke, M. Chi, H. N. Lee, W. Tian, L. Zhu, X. Cheng, and others, Room-temperature multiferroic hexagonal LuFeO 3 films, Phys. Rev. Lett., vol. 110, no. 23, p. 237601, 2013.
13. Ederer C. and N. A. Spaldin, Electric-field-switchable magnets: the case of BaNiF 4, Phys. Rev. B, vol. 74, no. 2, p. 20401, 2006.
14. Eibschütz M., H. J. Guggenheim, S. H. Wemple, I. Camlibel, and M. DiDomenico Jr, Ferroelectricity in BaM2+ F4, Phys. Lett. A, vol. 29, no. 7, pp. 409–410, 1969
15. Tokura Y., S. Seki, and N. Nagaosa, Multiferroics of spin origin, Reports Prog. Phys., vol. 77, no. 7, p. 76501, 2014
16. Dzyaloshinsky I., A thermodynamic theory of weak ferromagnetism of antiferromagnetics, J. Phys. Chem. Solids, vol. 4, no. 4, pp. 241–255, 1958.
17. Mostovoy M., Ferroelectricity in spiral magnets, Phys. Rev. Lett., vol. 96, no. 6, p. 67601, 2006.
18. Katsura H., N. Nagaosa, and A. V Balatsky, Spin current and magnetoelectric effect in noncollinear magnets, Phys. Rev. Lett., vol. 95, no. 5, p. 57205, 2005.
19. Aoyama T., K. Yamauchi, A. Iyama, S. Picozzi, K. Shimizu, and T. Kimura, Giant spin-driven ferroelectric polarization in TbMnO 3 under high pressure, Nat. Commun., vol. 5, p. 4927, 2014.
20. Rocquefelte X., K. Schwarz, P. Blaha, S. Kumar, and J. den Brink, Roomtemperature spin-spiral multiferroicity in high-pressure cupric oxide, Nat. Commun., vol. 4, p. 2511, 2013
21. Shuvaev A.M., A.A. Mukhin, and A. Pimenov, Magnetic and magnetoelectric excitations in multiferroic manganites, J. Phys. Condens. Matter, vol. 23, no. 11, p. 113201, 2011.
22. Dong S. and J.-M. Liu, Recent progress of multiferroic perovskite manganites, Mod. Phys. Lett. B, vol. 26, no. 09, p. 1230004, 2012
23. Nan C.-W., M.I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, Multiferroic magnetoelectric composites: Historical perspective, status, and future directions, J. Appl. Phys., vol. 103, no. 3, p. 1, 2008.
24. Eerenstein W., N. D. Mathur, and J. F. Scott, Multiferroic and magnetoelectric materials, Nature, vol. 442, no. 7104, p. 759, 2006.

25. Okumura K., K. Haruki, T. Ishikura, S. Hirose, and T. Kimura, Multilevel magnetization switching by electric field in c-axis oriented polycrystalline Z-type hexaferrite, Appl. Phys. Lett., vol. 103, no. 3, p. 32906, 2013.
26. Priya S., Islam R., Dong S., and D. Viehland, Recent advancements in magnetoelectric particulate and laminate composites, J. Electroceramics, vol. 19, no. 1, pp. 149–166, 2007.
27. Evans D.M., A. Schilling, A. Kumar, D. Sanchez, N. Ortega, M. Arredondo, R. S. Katiyar, J. M. Gregg, and J. F. Scott, Magnetic switching of ferroelectric domains at room temperature in multiferroic PZTFT, Nat. Commun., vol. 4, p. 1534, 2013.
28. Mandal P., Pitcher M.J., J. Alaria, H. Niu, P. Borisov, P. Stamenov, J. B. Claridge, and M. J. Rosseinsky, Designing switchable polarization and magnetization at room temperature in an oxide, Nature, vol. 525, no. 7569, p. 363, 2015.
29. Kirchhof C., M. Krantz, I. Teliban, R. Jahns, S. Marauska, B. Wagner, R. Knöchel, M. Gerken, D. Meyners, and E. Quandt, Giant magnetoelectric effect in vacuum, Appl. Phys. Lett., vol. 102, no. 23, p. 232905, 2013
30. Sando D., A. Agbelele, D. Rahmedov, J. Liu, P. Rovillain, C. Toulouse, I. C. Infante, A. P. Pyatakov, S. Fusil, E. Jacquet, and others, Crafting the magnonic and spintronic response of BiFeO 3 films by epitaxial strain, Nat. Mater., vol. 12, no. 7, p. 641, 2013.
31. Lee J. H., L. Fang, E. Vlahos, X. Ke, Y. W. Jung, L. F. Kourkoutis, J.-W. Kim, P. J. Ryan, T. Heeg, M. Roeckerath, and others, A strong ferroelectric ferromagnet created by means of spin--lattice coupling, Nature, vol. 466, no. 7309, p. 954, 2010
32. Becher C., L. Maurel, U. Aschauer, M. Lilienblum, C. Magén, D. Meier, E. Langenberg, M. Trassin, J. Blasco, I. P. Krug, and others, Strain-induced coupling of electrical polarization and structural defects in SrMnO 3 films, Nat. Nanotechnol., vol. 10, no. 8, p. 661, 2015.
33. Molegraaf H.J.A., J. Hoffman, C. A. F. Vaz, S. Gariglio, D. Van Der Marel, C. H. Ahn, and J.-M. Triscone, Magnetoelectric effects in complex oxides with competing ground states, Adv. Mater., vol. 21, no. 34, pp. 3470–3474, 2009.
34. Lahtinen T.H.E., Franke, K. J.A. and S. Van Dijken, Electric-field control of magnetic domain wall motion and local magnetization reversal, Sci. Rep., vol. 2, p. 258, 2012.
35. Valencia S., A. Crassous, L. Bocher, V. Garcia, X. Moya, R. O. Cherifi, C. Deranlot, K. Bouzehouane, S. Fusil, A. Zobelli, and others, Interface-induced room-temperature multiferroicity in BaTiO 3, Nat. Mater., vol. 10, no. 10, p. 753, 2011.
36. Fiebig M., T. Lottermoser, D. Fröhlich, A. V Goltsev, and R. V Pisarev, Observation of coupled magnetic and electric domains, Nature, vol. 419, no. 6909, p. 818, 2002
37. Brunskill I.H. and H. Schmid, Polarized light studies of ferromagnetic/ferroelectric/ferroelastic domain patterns in NiCl and NiBr boracite, Ferroelectrics, vol. 36, no. 1, pp. 395–398, 1981
38. Lin S.-Z., X. Wang, Y. Kamiya, G.-W. Chern, F. Fan, D. Fan, B. Casas, Y. Liu, V. Kiryukhin, W. H. Zurek, and others, Topological defects as relics of emergent continuous symmetry and Higgs condensation of disorder in ferroelectrics, Nat. Phys., vol. 10, no. 12, p. 970, 2014.
39. Meier D., Functional domain walls in multiferroics, J. Phys. Condens. Matter, vol. 27, no. 46, p. 463003, 2015.
40. Farokhipoor S., C. Magén, S. Venkatesan, J. Íñiguez, C. J. M. Daumont, D. Rubi, E. Snoeck, M. Mostovoy, C. De Graaf, A. Müller, and others, Artificial chemical and

magnetic structure at the domain walls of an epitaxial oxide, Nature, vol. 515, no. 7527, p. 379, 2014.

41. Sazanovich A., Magnetoelectric properties of ferromagnets/ferroelectrics layered heterostructures, Institute of Physics Polish Academy of Sciences, 2014.
42. Sergienko I. A. and E. Dagotto, Role of the Dzyaloshinskii-Moriya interaction in multiferroic perovskites, Phys. Rev. B, vol. 73, no. 9, p. 94434, 2006.
43. Wang Y., J. Hu, Y. Lin, and C.-W. Nan, Multiferroic magnetoelectric composite nanostructures, NPG Asia Mater., vol. 2, no. 2, p. 61, 2010.
44. Lu X. and H. Li, Size effect on magnetoelectric coupling in multiferroic heterostructures, J. Appl. Phys., vol. 109, no. 7, p. 74112, 2011.
45. Zhang R.-F., Deng C.-Y., L. Ren, Z. Li, and J.-P. Zhou, The Giant Dielectric Constant and High Initial Permeability of BaTiO3-Ni0. 5Zn0. 5Fe2O4 Composite Ceramics, ECS J. Solid State Sci. Technol., vol. 2, no. 9, pp. N165–N168, 2013.
46. Velhal N. B., N. D. Patil, A. R. Shelke, N. G. Deshpande, and V. R. Puri, Structural, dielectric and magnetic properties of nickel substituted cobalt ferrite nanoparticles: Effect of nickel concentration, AIP Adv., vol. 5, no. 9, pp. 97166, 2015.
47. Hu, Jiamian & Nan, Tianxiang & Sun, Nian & Chen, Long-Qing. Multiferroic magnetoelectric nanostructures for novel device applications. MRS Bulletin. Vol.40. pp. 728-735, 2015.
48. Yuxin Cheng, Bin Peng, Zhongqiang Hu, Ziyao Zhou, Ming Liu, Recent development and status of magnetoelectric materials and devices,Physics Letters A, vol. 382, no. 41, pp. 3018-3025, 2018.
49. Dhiren K. Pradhan, Shalini Kumari and Philip D. Rack, Magnetoelectric Composites: Applications, Coupling Mechanisms, and Future Directions. Nanomaterials, vol. 10, pp. 2072, 2020.
50. Lather S., A. Gupta, J. Dalal, V. Verma, R. Tripathi, A. Ohlan, Effect of mechanical milling on structural, dielectric and magnetic properties of BaTiO3–Ni0.5Co0.5Fe2O4 multiferroic nanocomposites, Ceram. Int., vol. 43 pp. 3246-3251, 2017.
51. Patankar K., V. Mathe, R. Mahajan, S. Patil, R.M. Reddy, K. Siva Kumar, Dielectric behaviour and magnetoelectric effect in CuFe2O4-Ba0.8Pb0.2TiO3 composites, Mater. Chem. Phys., vol. 72, 23-29, 2001.
52. Ishikawa K., K. Yoshikawa, N. Okada, Size effect on the ferroelectric phase transition in PbTiO3 ultrafine particles, Phys. Rev. B., vol. 37, pp.5852, 1988.
53. Ishikawa K., T. Nomura, N. Okada, K. Takada, Size effect on the phase transition in PbTiO3 fine particles, Jpn. J. Appl. Phys., vol. 35, pp. 5196, 1996.
54. Baaziz H., A. Tozri, E. Dhahri, E. Hlil, Effect of particle size reduction on the structural, magnetic properties and the spin excitations in ferromagnetic insulator La0.9Sr0.1MnO3 nanoparticles, Ceram. Int., vol.41, pp. 2955-2962, 2015.