Fabrication and Characterization of Magnetoelectric Ceramics by Tape-Casting Method

A dissertation submitted in fulfilment of the requirements for the degree of

Master of Science

In

Physics

Submitted by

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UNDER THE SUPERVISION OF

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Submitted to:

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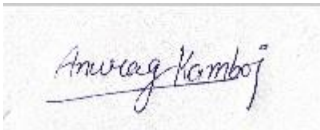
SELF DECLARATION

I hereby declare that the work which is presented in dissertation entitled **"Fabrication and Characterization of Magnetoelectric Ceramics by Tape-Casting Method"** has been done by me for the partial fulfilment of the requirement for the award of degree of **Masters of Science in Physics**, submitted in the **School of Physics and Material Science, Thapar Institute of Engineering & Technology (Deemed to be University), Patiala** is an authentic work of mine carried out under the guidance and supervision of **Dr. Jayant Kolte** (Assistant Professor) during 7 January 2021 to 30 July 2021 and has not been submitted previously in the form of any manuscript or thesis for publication or for the award of any degree, diploma or similar internship report. All the ideas and references has been duly acknowledged.



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CERTIFICATE

This is to certify that the present research work entitled "**Fabrication and Characterization of Magnetoelectric Ceramics by Tape-Casting Method"** being submitted **by Mr. Anurag Kamboj** (Enrollment No – 301904002) in the partial fulfilment of the requirement for the Award of degree of **Masters of Science in Physics**, submitted in the **School of Physics and Material Science, Thapar Institute of Engineering & Technology (Deemed to be University), Patiala** is a record of bonafide research carried out under my supervision during 7 January 2021 to 30 July 2021, School of Physics and Materials Science, Thapar Institute of Science and Technology, Patiala.

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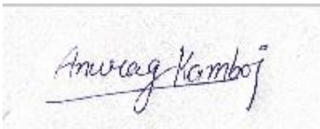

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ABSTRACT

The modern era is the era of new class of materials i.e., the magnetoelectric materials. These magnetoelectric material as they are called, become magnetized in an electric field and electrically polarized in a magnetic field. They are preferred because of their wide range applications. Several lead-based materials possess high magnetoelectric coefficient. but lead being toxic is not preferred. Studies are being conducted on lead free material. BNT, BT and KNN are the suitable candidates for lead free ME composites. BNT base ceramics are excellent due to its good ME properties. BNT with magnetic phase NFO is found as suitable alternate of Pb-based composites. Still no report available on BNT based ME composite film grown by tape casting method and result showed that lead free material in the form of thick/thin films possess high magnetoelectric coefficient as compared to bulk material. Tape casting technique is used to make these films.

Contents

SELF DECLARATION ii
CERTIFICATE iii
ACKNOWLEDGEMENT iv
ABSTRACT v
CHAPTER 1: INTRODUCTION 1
Multiferroic material 1
Magnetoelectric effect 1
Classification of Multiferroic materials 3
Single phase multiferroics materials 4
Multi-phase multiferroics 4
Type of Magnetoelectric (ME) composites 5
Lead-based magnetoelectric 5
Lead free magnetoelectric 5
Toxic effects of lead 5
Application of Magnetoelectric composites 6
CHAPTER 2: TAPE CASTING 8
Production Process 8
Application of Tape casting: 9
CHAPTER 3: LITERATURE SURVEY 11
CONCLUSION 27
References 28

CHAPTER 1: INTRODUCTION

Multiferroic material

In the year 1994, H. Schmid used the word multiferroic to define the materials which have more than one essential ferroic property simultaneously [1]. The different ferroic properties are ferroelectricity, ferromagnetism and ferro- elasticity. Out of these ferroic properties the multiferroic material which are ferromagnetic and ferroelectric are of special interest. As these multiferroic are material with arising properties that lend well to future sensors, filters, phase shifters, electromagnetic interference devices, and tunable transformer and number of applications are investigated for these kinds of materials including in spintronics and as high sensitivity magnetic field sensors. Spintronics is short for spin transport electronics and this could be used for future data storage technology because of its switchable characteristics [2] . In last few these materials are paid much attention not only because of the presence of multiferroic property but also due to the coupling between the multiferroic properties which lead to the phenomenon called Magnetoelectric effect.

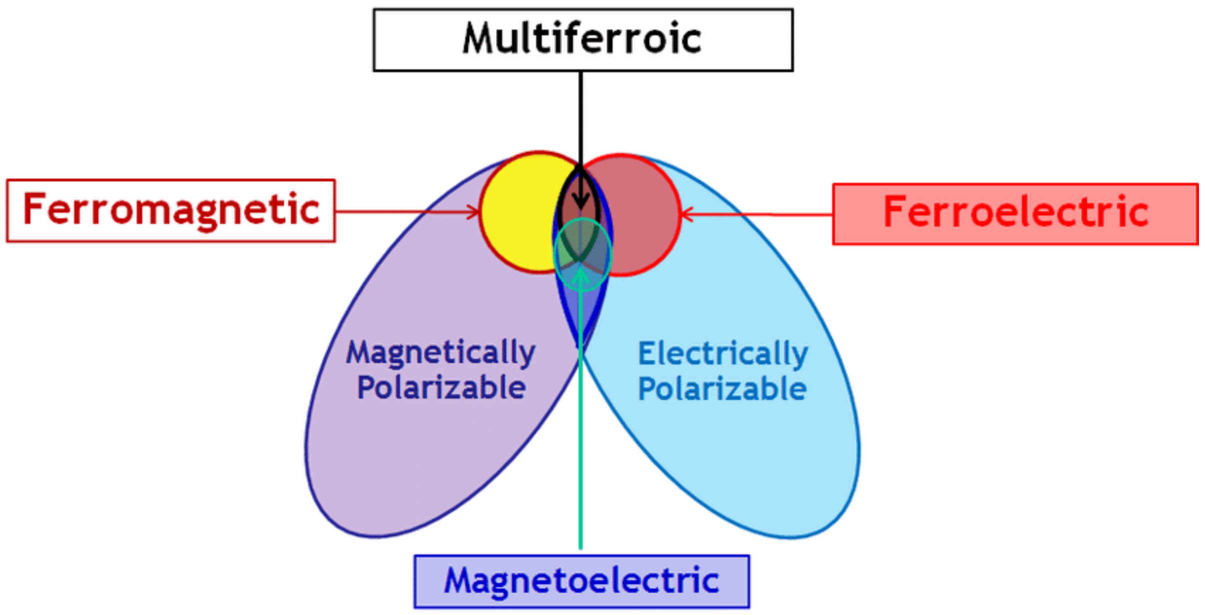

Figure 1. Relationship between multiferroic and magnetoelectric materials.[3]

Magnetoelectric effect

Mechanical deformation caused by mechanical strain can strongly change the band structure of the materials which produce dielectric polarization as a result of phenomenon called Magnetoelectric effect. Magnetoelectric (ME) effect is a phenomenon in which applied electric field induces magnetization or magnetic field generates dielectric polarization [4]. Usually, the coupling works towards the ordering of ferroelectric as well as magnetic properties of the materials. In fact, this magnetoelectric effect is currently regularly utilized in assembling modern devices.ME effect is investigated both by theory and through experiments. The magnetoelectric composites containing magneto-strictive and piezoelectric components bear greater ME effect as compared to that of any normal sign phase ME material by a few significant degrees. ME effect is categorized in two ways direct and converse ME effect.

a) Direct ME effect

In direct ME effect, there occurs a mechanical stress or strain in magneto-strictive phase is delivered when the composite experiences the applied magnetic field. This strain or stress provides a mechanical influence to the piezo-electric phase, which thus delivering a voltage which is piezoelectric and electric field yield proportional to applied magnetic field.

b) Converse ME effect

In the converse ME effect, the piezoelectric phase experiences a mechanical strain which is delivered by the composite applied electric field. There occurs a mechanical stress within the magneto-strictive phase produced by this strain, resulting in change in magnetization.

These ME effect can be conventionally communicated as

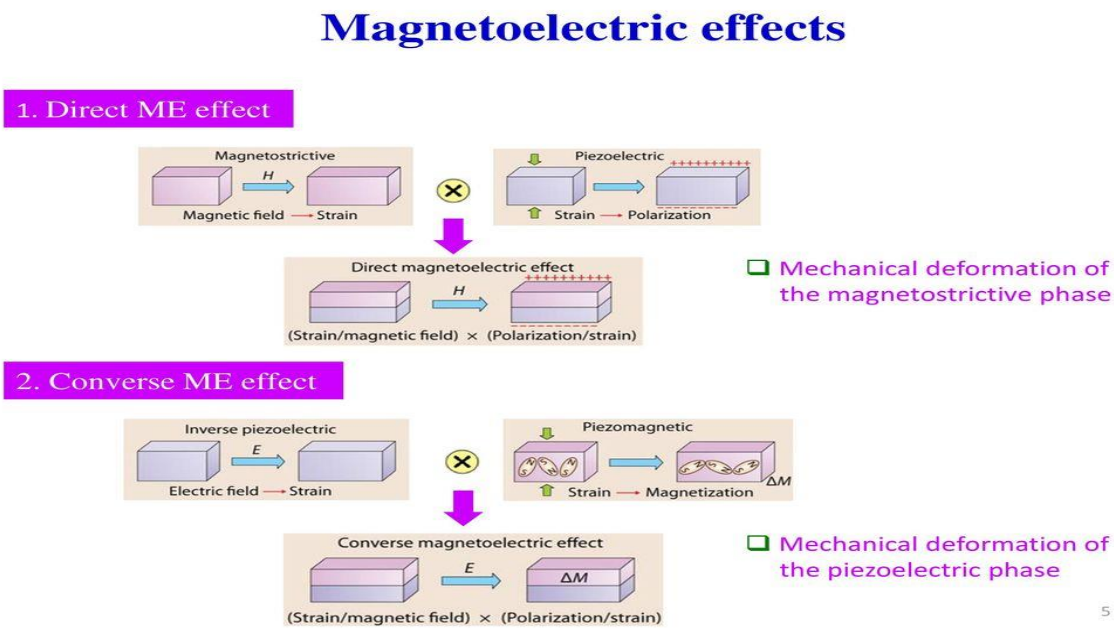

Figure 2. Pictorial representation of 1. Direct ME effect 2. Converse ME effect [5]

Landau in 1935 proposed the theory of magnetic ME effect. He proposed that the free energy, electric field and magnetic field are directly correlated to each other [6]. Fundamentally dielectric polarization is exhibited by the material in the existence of electric field and magnetization is induced by the ferromagnetic material in the existence of the magnetic field. The theory lead to the mathematical representation as well as the behavior of ME material in the existence of electric field (E) and magnetic field (H). In direct ME effect there is change in the polarization (P) W.r.t to applied magnetic field (H).

$$\Delta P=\alpha.H$$

Here the change in the polarization is ΔP. the magnetoelectric coefficient is (α) and (H) is applied magnetic field. Similarly in Converse ME effect there is change in the magnetization (M) w.r.t Change in the electric field (E).

$$\Delta M=\alpha.E$$

There are large number of applications of both the ferroelectric and ferromagnetic material in electric and memory storage industries. There exists a large difference in the technical application of ferromagnetic and ferroelectric material. But as the multiferroic material possess both the ferroelectric and ferromagnetic properties simultaneously in a single phase they can be use in the switches, actuators and new type of electronic storage devices.

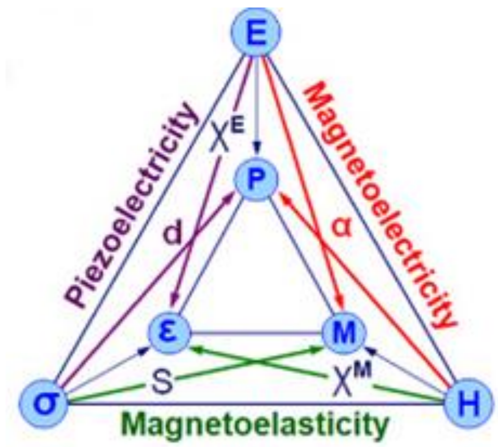

Figure 3. Observation of magnetoelectric effect [7]

Classification of Multiferroic materials

Multiferroic materials are categorized as:

- Single phase multiferroic materials
- Multi-phase multiferroic materials

Single phase multiferroics materials

Over the most recent couple of many years, various single phase ME materials were accounted , where the ME impact emerged because of direct coupling among spin and dipole moment at a atomic level. These materials were called as multiferroics, where the electrical or the inner attractive field are more prominent within the sight of various long–range ordering. These materials shows two of essential ferric characteristics in a single phase. Inappropriately, the usage of these materials towards the application in devices was unsuccessful mainly due to temperatures being low which was much lesser in comparison to room temperature, Curie or Neel temperatures. When the temperature reaches at progress one the magnetoelectric coefficient significantly drops to zero, limits the functional use of such material . Additional inquiries were carried out, especially in the thin films, for the improvement of the multiferroic $BiFeO_3$, which acquires the consideration being ferroelectric, ferro-elastic and ferromagnetic and having improved electric of 1100 K and magnetic ordering temperatures of 650 K. $BiFeO_3$ shows a giant magnetoelectric response of the order of few mV/cm·Oe [8]. But it still remained a very small value towards any everyday usage. Furthermore, to get an access towards the material bearing giant magnetoelectric response under a varied temperature ranges, the multi-phase systems were taken into account Bismuth ferrite (BFO) and rare earth magnetite are well known as single phase multiferroics.

Multi-phase multiferroics

Keeping in view that a variety of single-phase multiferroic materials are studied, not a solitary material has been found to show huge and mechanically helpful magneto-electric coupling at room temperature. Therefore, the focus of the research has been shifted towards the development of the Multi-phase ME composites. Magnetic and electric phase coupling is considerable.

Subsequently the ME coupling coefficient in multiphase material is given by

$$\frac{Mechnical}{Electrical} \times \frac{Magnetic}{Mechanical} = \alpha(E) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Or

$$\frac{Mechnical}{Magnetic} \times \frac{Electric}{Mechanical} = \alpha(E) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Van Suchtelen first gave a thought of the magnetoelectric effect in composites [9]. there are huge number of ME composites got in most recent couple of years that has excellent ME response.

Type of Magnetoelectric (ME) composites

ME composites can be characterized into two composites on the behalf of their constituents

- Lead based Magnetoelectric
- Lead free magnetoelectric

Lead-based magnetoelectric

ME composites that contain lead (Pb) as most immense constituent, that ME composites are known as lead containing magneto-electric. Because of their considerable dielectric coefficient and high piezoelectric coefficient, they are being used in sensors, actuator's etc. Those leads based are suspectable to pollution and health hazards. Hence for the safety of the environment it is ideal issue to investigate the lead free MELs.

Lead free magnetoelectric

Those ME materials that are free from the presence of lead (Pb) in its constitution, well known as Pb-free ME composites.

Table 1: Few examples of lead based and lead-free ME composites[10,11]

Lead based Magneto-electrics	**Lead free Magneto-electrics**
PZT-CFO	NBT-KBT-LB
Ni-PZT	NBT-KBT-BT
LSMO/PMN-PT	CFO-BT
NZFO-PZT	BCZT-CFO
PZT/BaM	BFO-CFO

Toxic effects of lead

The manifestations of lead poisoning are abdominal discomfort, ache in joints and muscle fatigue. The blue line at the dental edge of gum in dental tolerance is due to the deposition of sulfides . Lead harming has been pronounced as profoundly ecological wellbeing danger as a result of its unfavorable impact on scholarly and neurological improvement development.

In adults 30-70% of inhale lead goes into the circulatory system through respiratory track [12]. the significant biochemical properties of lead that lead to its harmful impact in individuals are :

1. Enzymes which are essential for the synthesis of haemoglobin get effected because lead is electropositive nature.
2. Lead connection with nucleic corrosive restricting proteins can influence the hereditary record in D.N.A.

3. The important and initial part of managing of lead harming is expulsion of patient from the wellspring of openness and second by utilizing chelating specialist that structure complex with lead and are removed.

As Pb is harmful for the human being so Pb-free ME composites with ABO_3 type perovskite materials like bismuth sodium niobate (BNT), barium titanate and potassium sodium niobate are broadly studied. Among these BNT is considered as strong candidate for making ME composite with NFO/CFO due to its high piezoelectric coefficient (d_{33}) =234pC/N. Strong polarization and high curie temperature above 320 °C. NFO and CFO are use due to their good magnetostriction coefficient value (i.e., -26 ppm for NFO and -110 for CFO) [13].

Although a number of materials are known to display high magnetoelectric coupling, but they cannot be used in the form of powder directly towards some specific applications. So, keeping the applications in notice, ME multiferroic films have proved to be suitable towards the preparation of integrated magnetic or electric devices. A wide variety of fabrication methods are available for the synthesis of multiferroic thick films, the specific characters and properties of multiferroic thick depend upon synthesis method. A significant issue relating 2 and 3 layered construction is scaling down, since singular layer thickness is a few hundred microns . Thus, the choice of a particular method to synthesis multiferroic thick film is very essential. Nevertheless, the Miniaturization and versatility can likewise be tended to through the use of tape casting skills.

Application of Magnetoelectric composites

A few trademark properties of magnetoelectric composites which are conceivably empowering towards applications. The curve formed between magnetic bias and magnetoelectric coefficient is the major property. In some soft magneto-strictive materials there is existence of High magnetically induced strains. To maximize the induced strain it is necessary to align the magnetization vector towards an easy direction which can be attained by a magnetic bias. Secondly, the magneto electric coefficient present at mechanical resonant frequencies is higher in magnitude in comparison to that present at sub-resonant frequencies. Third major characteristic is the power degeneracy in magnetoelectric composites effects coupling in magnetoelectric materials, which directly effects the efficiency. The final characteristic being, ME composites bears a tunability feature which results in shifting of the resonant frequencies, impedance as well as characteristic output voltage with bias. This load of attributes approves the ME parts towards expected applications in a few memory-based gadgets, attractive sensors, resonators, channels and so forth [14].

The devices bearing memory along with a magnetic or electric write and also read are of major interest thus laying a major focus of ME materials. A gadget dependent on memory in ME composites conceivably will empower a minimal expense as well as effective write/read speeds using lower consumption of power. the capacity of cross-controlling electrical as well as magnetic polarization might act as a key towards switching for its application.

Gyrators

Magnetoelectric composites bearing a loop conveying current bear gyration impact, that changes over current to voltage. The magnetoelectric gyrator is a two-port four-wire gadget . Calculating the parameters like impedance of such device have depicted that the achievement of an ideal gyroscope component when the magnetoelectric susceptibility square is equivalent to result of the permeability as well as permittivity in the magnetoelectric composite . Further, the current-to-voltage conversion, or trans-impedance, introduces as a coefficient of gyration. The magnetoelectric coupling occurring at resonant frequency is way to move toward an optimal magnetoelectric gyrator since power transformation is just apparently upgraded at reverberation: for this situation, the equality of 2ME = μ is around satisfied. A significant component of gyrator is the further developed magnetoelectric coupling in mechanical resonant frequencies.

Sensors

Multiferroics composites Due to its piezo-magnetic switching property it can be very well utilized in sensors as well as in transducer. Material having high ME coupling coefficient shows great sensing as well as transducing properties in such sort of gadgets.

Actuators

Devices producing giant strains are required for making Actuators. For making such a devices multiferroic material with good ME properties are employed. Because of the presence of giant strain inducing properties in these materials in the presence of applied magnetics or electric field.

Medical equipment

Greatest achievement for ME composite is that numerous clinical gears like surgical instruments, wireless capsule endoscopy (WEC) and stimulation of functioning of living cell etc. so forth constituting the ME composites.

Storage devices

Data is stored in the electric form but read in magnetic in most of the memory devices. in order to have such a storage device, ME composite can play a very crucial role because of the presence of switching electric and magnetic property.

CHAPTER 2: TAPE CASTING

Tape casting is a technique, which can be utilized, for example, for the production of flat plates, enormous ceramic parts particularly valuable in the electric and radio field. The tapes can be casted with thicknesses going from a couple of microns to hundred microns

Tape Casting was first presented in 1940's at the time second world war while there has been a basic absence of the of quartermaster substances to make available mica capacitors. Howatt's innovation was conceived out of the pressing need to track down a substitute for mica as a capacitor material. Glenn Howatt is generally viewed as the father of the tape casting since he had the main distribution and patent depicting this process [15]. There had been a few upgrades in ceramics innovation. One of the most recent and generally useful of those innovation has been the development and execution of tape casting for the creation of thin sheets of ceramics materials [16].

Production Process

A tape casting method for a material consists of casting more than one chemical precursors on to a green tap and then drying them.

(i)Ingredient

The most important component for the tape casting method is the powder that the 'tape' is to be consisting of.it is the active component of the final product and the other components such as solvent, surfactants, binders, plasticizers have to be compatible with the powder. Generally, a very fine powder with maximum particle size of 5 micrometers is used. The solvent serves the purpose to distribute different ingredients homogeneously all through the slip to make the uniform blend and also allow the powder to cast, as it liquid in form. Surfactants is a "surface active agent" and is added to actively modifies the molecule surface to give an ideal trademark, for example, lower surface charge, higher surface charge etc. binder is added to provide the network for holding the entire chemical system together for further processing. Furthermore, plasticizers are added which makes the tape, more bendable.

(ii) Slurry manufacturing

These strategies include the scattering of a powdered material into a Solvent, and the addition of dispersants and different materials as discussed above to form a homogeneous slurry using the different methods such as sol-gel method and is transported or stored for further processing's.

(iii)Slurry casting

The casting process is portrayed in the Figure 4. the slurry may be filtered before being applied, to remove imperfect particles. The homogeneous slurry is discharged into the reservoir. The doctors blade act as a knife (with height adjustment) that tape cast the slurry over the peeling belt. The cast slurry is called the green sheet and need furthermore processing like drying and cutting. During the process of casting, it is essential that a perfectly flat surface casting occurs with no streaks. The surface on which the casting is to be done is made from steel, glass, polymer, or coated paper.

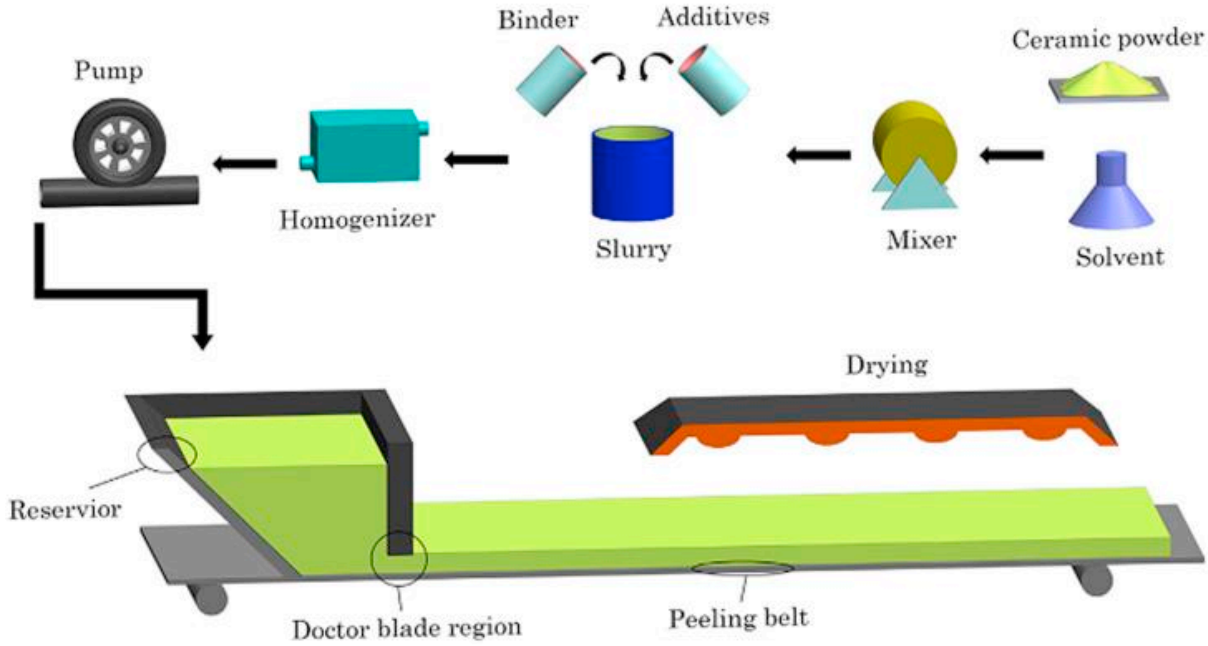

Figure 4. Diagrammatic representation of the concept of tape casting [17].

(iv) Green sheet drying: Further the green tape is heated for a period and at a temperature Sufficient to change the chemical precursor over to their absolute last segment and to anneal and shape the material.

Application of Tape casting:

According to the above conversation the underlying inspiration of the tape casting process was the manufacturing of ceramics sheet for capacitor. However, after almost 60 years, the use of the tape giving has arisen as fabrication instrument inside the ceramic industry. Here we will discuss some of the standard application of the tape casting [17].

(i) **Substrates**: From the couple of years almost the greater part of the substrate materials shaped for the electronic industries were mass-delivered by tape casting technique Substrates are characterized as the "spine" of the electronic circuit. The circuitry is designed on these ceramics insulators (substrate). the surface of substrate has screen printed components on it. the screen-printed act as a carrier as well isolate the components from each other. These components can be conductor, resistors or capacitors etc.

(ii) **Separators for batteries:** the separators in batteries are corrosion resistance and non-conducting material that holds the terminals back from contacting shorting out of the battery. The thickness dimension of the battery separator must have very thin cross-section and have fairly large the other two dimensions. The thin cross-section of separator makes tape casting a suitable method of production.

(iii) **lithium-ion batteries:** The lithium-ion batteries are extremely light weight and are a lot more secure than different batteries that continue them in the compact applications. The capacity of tape casting to make thin film of lithium ions containing polymer onto a transporter like Mylar or other polymeric material aides in the assembling of these batteries.

(iv) **Piezoelectric material:** Tape cast processing of **polycrystalline materials** is widely used for the production of single or multi-layered piezoelectric materials. These materials are ideal for micro-actuator applications

Table 2: contrast of different casting processes [18].

Methods	**Advantages**	**Disadvantages**
Spin coating	➢ It is simple and easy technique. ➢ It is low cost and fast technique	➢ This method has less material efficiency. ➢ Bubbles on the surface of the coated waffer
Electro spinning	➢ Produce very long nano fibres	➢ Uniform porosity cannot be maintained.
Screen printing		➢ Expensive short run

CHAPTER 3: LITERATURE SURVEY

This chapter consists the literature which is related to the dissertation work. Here we introduced diverse multiferroic materials and our major focus is towards Magnetoelectric material. Magnetoelectric material comprises the piezoelectric and magnetostrictive material. We have already discussed certain magnetoelectric materials along with their fundamental behaviors like piezoelectric coefficients and magneto-restrictive coefficients etc. In the recent years a study on the process development and synthesis methods have been conducted to improve the magnetoelectric coefficients of the material. In the previous 5 years there has been a number of research papers published on magnetoelectric materials.

Tape casting creates layering of ceramics which can also be used like single layer or may act as stacked and then covered to multilayered frameworks. Now a days, the majority of the work is committed to improvement of the multifaceted ceramics through tape casting technique. Since it is a somewhat minimal expense strategy for assembling materials with an excellent surface and great control of layer thickness. In recent years roughly 185 research papers (using keyword "Magnetoelectric- refining- tape casting" in web of science) are published each year in which scientists utilized tape casting giving a role as the essential manufacture technique.

In the tape casting process, the major parameters such as mole fraction of the powder and the job of the added substances like solvent, binder, surfactant and plasticizers has been focused towards the advancement of this process. A ceramics slurry comprises various ingredients and every ingredient have distinctive effect and in this powder is the primary fixing ingredient which decide the property of the material.

Srinivasan *et al*., in 2001 reported solid magnetoelectric impact towards the layered composites shaped by ferromagnetic lanthanum manganite and besides piezoelectric lead zirconate titanate. The thick-film structures of (LSMO)-PZT($La_{0.7}Sr_{0.3}MnO_3$) and (LCMO)-PZT($La_{0.7}Ca_{0.3}MnO_3$) were considered. The magnetoelectric (ME) voltage which possessed low-frequency coefficient was assessed in bilayers and multi-facets made through tape casting process. The effect is delicate in LSMO-PZT as compared to LCMO-PZT, and is more fragile in multi-layered contrasted with bilayers. A high value of α_E i.e. 60 mV/cm. Oe stands estimated for transverse magnetoelectric effect also in addition a factor of about 2 to 3 higher in comparison with the longitudinal effect.

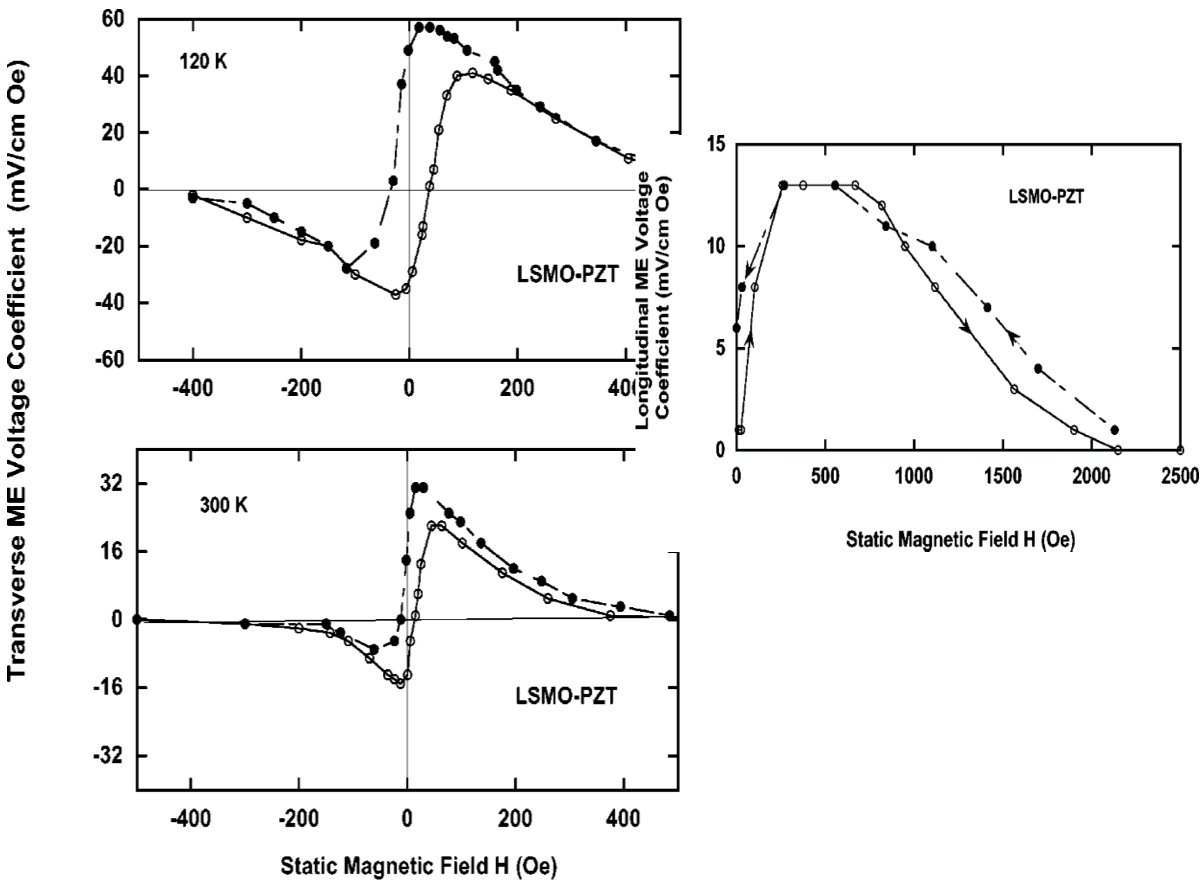

FIG. 5. Transverse magnetoelectric (ME) voltage coefficient α_E as a function of static magnetic field H plane, and Static field dependence of room-temperature longitudinal ME voltage coefficients [19].

For the process of tape casting, the powder was mixed with ethyl alcohol and then, Blown Menhaden fish oil (a dispersant) was ball milled for about 24 hours proceeded by a subsequent ball milling with a plasticizer like butyl benzyl phthalate along with a binder i.e. polyvinyl butyral for nearly 24 hours. The slurries obtained through this process were projected into 20-mm thick films on silicon covered mylar sheets utilizing a tape caster comprising of a couple of fixed sharp edges and a moveable projecting bed. The tapes thus obtained were then dried in air for about 24 h, taken out from the substrate mylar, and then were organized to acquire the ideal structure. A high tension was applied to samples to compact them, and a temperature (400 K), and further warmed at (800–900K) for binder dissipation. The last sintering was done at T_s= (1250–1500 K) for about 1–2 hours. Tests were conducted with an equivalent number of manganite and PZT layers.

Tang *et al*., in 2015 reported a solid self-biased charge magnetoelectric coupling obtained in homogenous two-phase magneto-strictive or piezoelectric laminate stacks. The magnetoelectric stack i.e. Ni/PZT-stack comprises of hard-preparing Nickel foils (Ni) and also a tape-casting multi-layer PZT(Pb(Zr,Ti)O_3) plate bearing high capacitance. Thunderous magnetoelectric couplings were obtained for Ni/PZT-stack along with various thickness proportion of Ni foil was explored exhaustively. Further, exploratory outcomes showed the Ni/PZT-stack with values of n=0.4 has extreme zero- biased resonant magnetoelectric charge coefficients of 47.52 nC/Oe, which is higher than the recently used magnetoelectric laminates. The anticipated self-biased little ME construction might be helpful for multi-functional gadgets, for example, energy reaping i.e., electromagnetic, attractive electric generators as well as magnet field detecting dependent on charge-identification strategy.

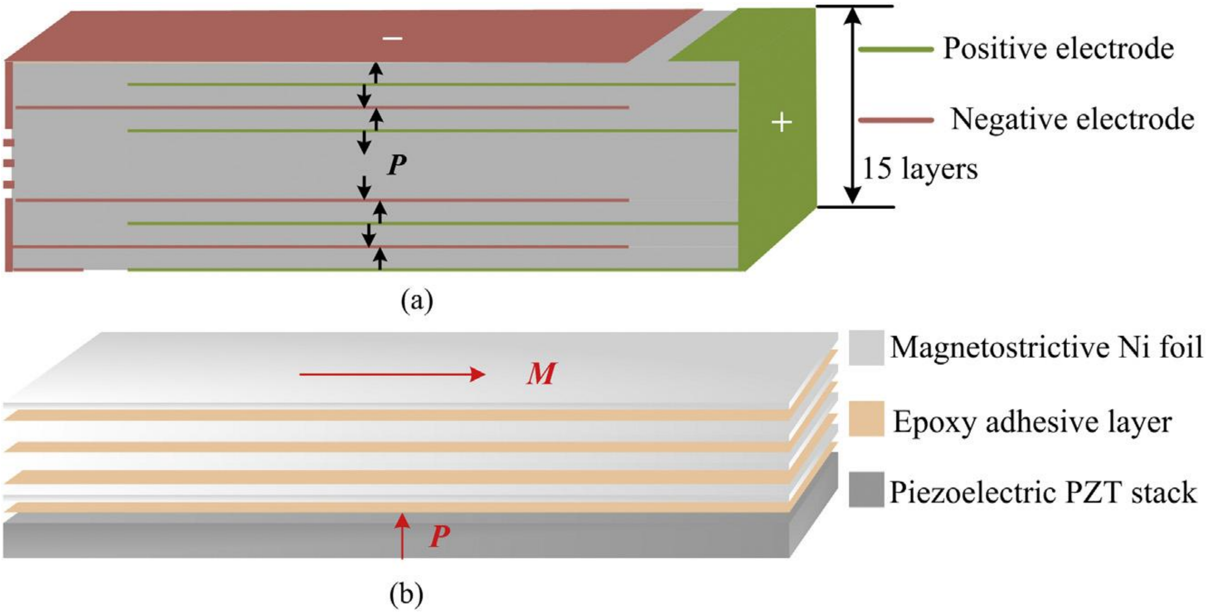

Fig. 6. (a) Schematic illustration of the tape-casting multilayer Pb(Zr,Ti)O3 (PZT) plate with high capacitance, (b) schematic illustration of the ME stack Ni/PZT-stack of multilayer Ni and PZT multilayer stack. The arrows M and P designate the magnetization and polarization directions, respectively [20].

Patil *et al.*, in 2017 have effectively examined the BTO-NFO MELs by thunderous magnetoelectric coupling which was produced through tape-casting technique, that permits large-scale manufacturing of MELs. Huge upgrade towards magnetoelectric voltage coefficient at reverberation frequencies were initiated in the two different varieties of MELs bearing a layer thickness of about t =50 along with 15 mm. A sharp, and a single reverberation top element being noticed for slenderer magnetoelectric laminate with t =15 mm through exceptionally enormous magnetoelectric voltage.

The different slurries of materials like NFO and also BTO powders were made through blending particular powders with ethyl liquor along with polyvinyl butyral cover trailed through ball processing for nearly 24 h. The slurries were then subjected within the green sheets having thickness 15, 50 mm with a tape caster. Then the drying nad cutting of films was carried out into the required shapes. Further covering them under high pressing factor of 100 psi and at a temperature of nearly 60 °C and then sintering them at 1200 to 1300 °C. Thus, they obtained the MELs which bear BTO 25 layers along with 26 layers of NFO for various t values between 15 to 50 mm.

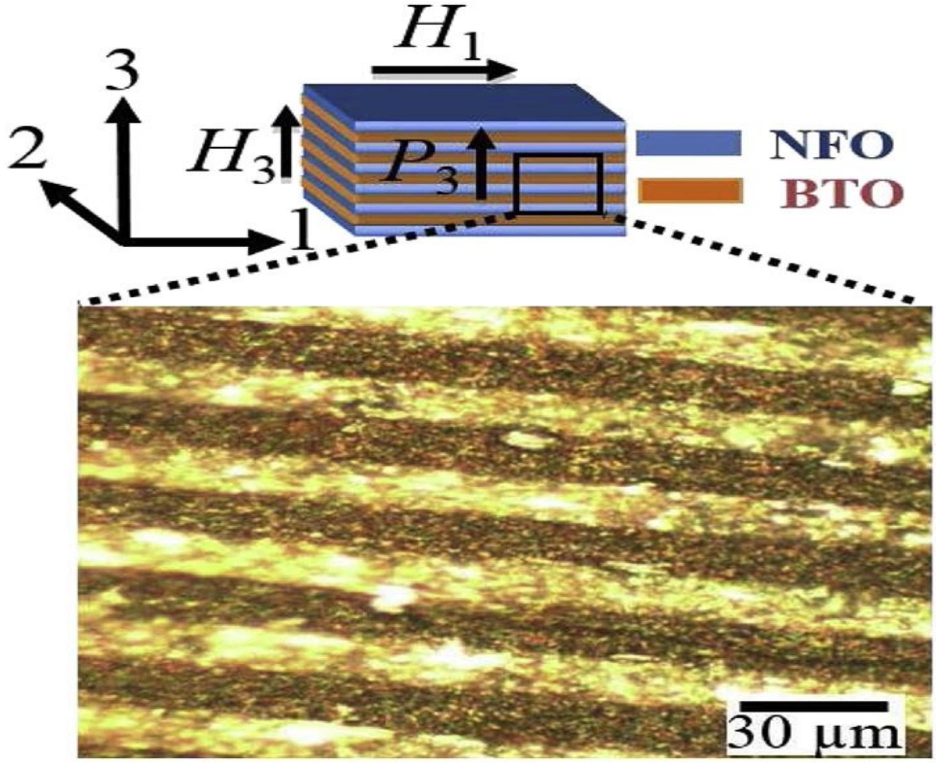

Fig. 7. Schematic structure of the fabricated magnetoelectric laminates (MELs) composed of BaTiO3 (BTO) and NiFe2O4 (NFO) layers (top) and its optical microscope image (bottom) [21].

Schileo *et al.*, in 2017 investigated 2-2 layered multiferroic PZT-CFO multi-layered gadget enveloping three CFO($CoFe_2O_4$) layers bound among four PZT layers (Pb0.99[$Zr_{0.45}Ti_{0.47}(Ni_{1/3}Sb_{2/3})_{0.08}]O_3$) effectively manufactured through tape casting. Box changing sintering temperature and its feasibility to restrict the inter-diffusing of components among CFO and PZT layers forestalling arranging the auxiliary stages, thus consequently holding the ferromagnetic as well as ferroelectric qualities. Besides, concurrence of ferromagnetism along with ferroelectricity in gadget joined along with a suggested communication among the layers empowers critical magneto-electric reaction.

The powdered ($PbCO_3$, TiO_2, NiO, Sb_2O_3, ZrO_2, Co_2O_3 and Fe_2O_3 bearing perfection of 99% were bought from Sigma-Aldrich, UK) precursors were blended and then processed in high-thickness polyethylene bottles having Y_2O_3-settled and ZrO_2 processing media together with solvent propan-2-ol for nearly 24 hours at each step of calcination. Further the calcination of $CoFe_2O_4$ was carried out at 1200°C for about 8 h. Then, the responded powder were used to make the tapes ready, following the procedure: i.e. a suspension was made ready through blending artistic powder 27.6 g together with combination of 5.8 g of a 1:1 ethanol along with methyl ethyl ketone together with 0.346 g of Hypermer KD-1, which is a cationic polymeric surfactant made in HDPE container together with ball processing made overnight along with Y_2O_3-settled zirconia processing. Consequently, a suspension was prepared to separate the eliminated processing media, and then the binder (50% wt i.e 4.62 g wt arrangement made of B-72 paraloid, a thermo-plastic ethylene-methyl acrylate, broken up in Ethanol or MEK) and 1.388 g of butyl benzyl phthalate plasticizer added to frame slurry. Then the slurry was blended utilizing a fast blender at rotations of 2100 rpm for nearly 10 min and then afterwards poured late the specialist cutting edge in little supply. Further the speed of tape 0.7 cm/s was set and then the stature of sharp edge of CFO to 250 µm and PZT 400 µm. Finally, the tapes were dried for 24 h.

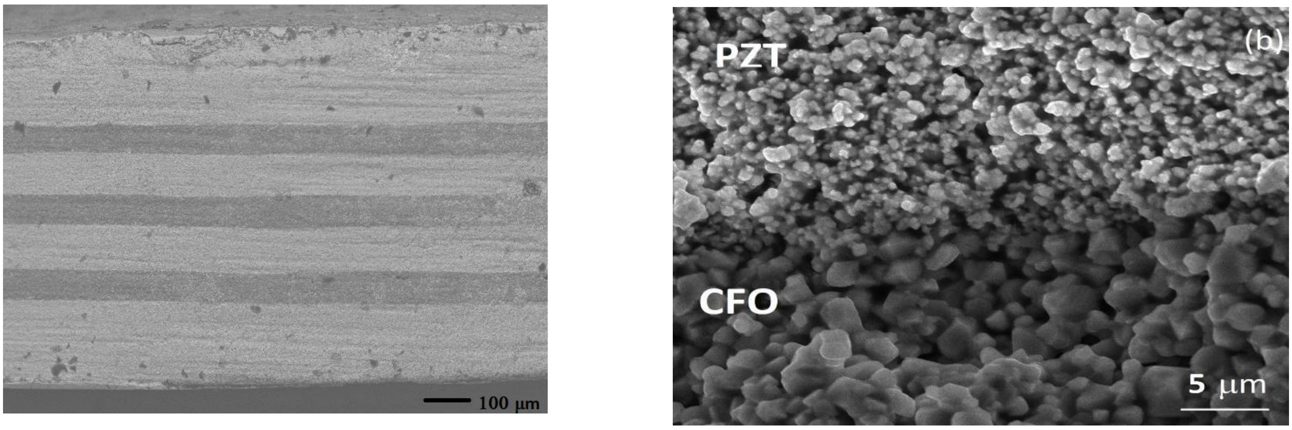

Fig. 8. SEM micrograph of the cross-section for the PZT-CFO composite sintered at 1050°C for 2h and BEI SEM micrograph of the microstructure at the interface between PZT and CFO [22].

Alguer´o *et al.* developed an eco-friendly ceramic multilayer composites by the use water-based tape casting method. Dense ceramic multilayers of magneto strictive $CoFe_{1.75}Mn_{0.25}O_4$ and piezoelectric $(K_{0.5}Na_{0.5})_{0.96}Li_{0.04}Nb_{1-y}Ta_yO_3$ were obtained which processed good bond among the layers and then also high-quality of interfaces, and a complete study on their electrical properties, piezoelectric and magnetoelectric properties was reported and also their functional responses were studied. Likewise, the impacts of multi-layered geometry, categorized through thickness of ceramic layer of several microns and also a huge numbering of layers, also characterization has been done. A characteristic upgrade in functionality for contrast with conventional made layer structures is shown and also the identification of characteristics of strain or stress relaxation across layers. Then a study on the components behind these effects showed that increased magnetoelectric coefficients was related to decrease the piezoelectric thickness of single-layer under the relaxation length characteristic relaxation of material system. Likewise, the phenomena of relaxation controls position of field for greatest reaction, so that it results in multilayering into the unrelaxed ductile stress magneto-strictive layering through high pace of progress of magnetostriction having applied magnetic field subsequently, along with diminished inclination field having greatest reaction.

In this process the powders of KNLNT15 bearing y=0.15 and KNLNT20 y=0.20 were prepared through a reaction of solid-state mixtures stoichiometric of K_2CO_3, Li_2CO_3, Na_2CO_3, Nb_2O_5 and Ta_2O_5. Further, two sequential thermal treatments were given at 750 °C and 800 °C for about 5 h, proceeded by an intermediate ball milling for around 24 hours in the presence of isopropyl alcohol along with Y_2O_3-stabilized grinding zirconia media in order to increase the chemical homogeneity.

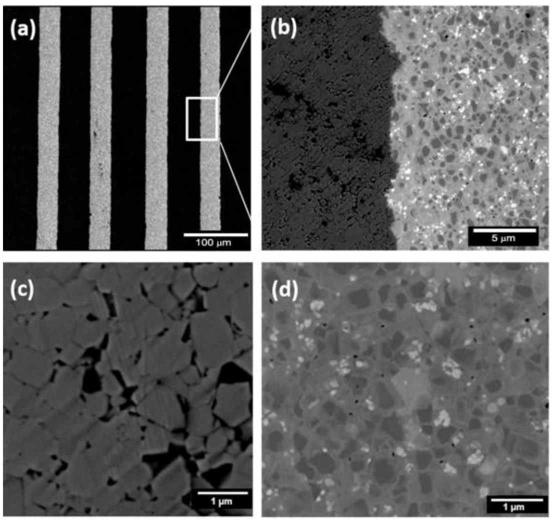

Figure 9: SEM images of a CFM25/KNLNT20 multilayer structure: (a) overall view, (b) interface, (c) ceramic microstructure of the CFM25 component, and (d) of the KNLNT20

Yang *et.al.* used the method of tape casting for the preparation of magnetoelectric materials $Li_{0.058}(Na_{0.535}K_{0.48})_{0.942}NbO_3$ (LKNN)/$Co_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O_4$ (CZFM). Various characteristic studies were conducted for the verification of these materials and the SEM (scanning electron microscopy) pictures of these multilayered composites indicated that two phases of CZFM and

LKNN coexisted. In addition, these multilayer composites also showed good electrical and magneto-electric properties. The ferroelectric properties, dielectric constant and piezoelectric constant of the multilayer composites weaken with increase of thickness t_C of CZFM layer. In this work the transverse coefficient that is maximum attained α_{E31} is 322.3 mV cm^{-1} Oe^{-1}, that is found at $t_C/L = 0.5$. Additionally, the piezoelectric coefficient as well as the polarization saturation decreases with the increase in the magnitude of magneto-electric coefficient along with an increase of tc/L value.

The powders of LKNN and CZFM were made by solid-state approach. The calcined powder of LKNN and CZFM (with Li_2CO_3 0.3 % by wt. included like sintering aid helps for lowering sintering temperature) were optional ball-milled, separated, dried, and afterward blended with organic substances to make the slurry for the tape casting. To prepare slurry, ethyl alcohol and butanone as well as dispersant i.e. olein were ball-milled at rotation of 500 rpm for about 4 h. Further, binder like polyvinyl butyral as well as polyethylene glycol, and the plasticizer like dibutyl phthalate, and LKNN/CZFM powders underwent ball milling at rotation of 250 rpm for about 4 h. At last, the subsequent slurries were casted on Mylar substrates.

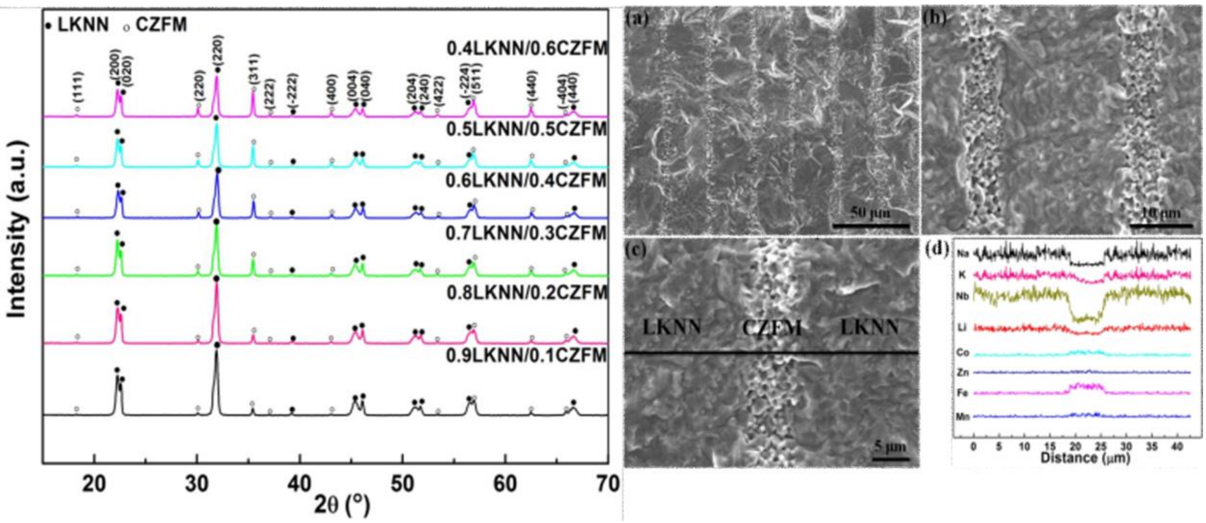

FIG. 10: X-ray diffraction patterns and SEM images of the multilayer LKNN/CZFM composite at $t_C/L=0.1$ [24].

Li *et. al.* with the help of tape casting technique prepared polymer-based magnetoelectric composites. The sandwich prepared of PVDFBTO/ PVDF-SCMO/PVDF-BTO organized composites have strong unpredictable control over voltage for polarization as well as magneto restrictive assets. The SEM image indicated the sandwich structure of these materials. It is interesting that the polarization of sandwich organized composite film varies on applying different poling fields, which possibly begun from the electron orbital multiplication of Co incited by the charges bound to the interface.

To prepare the PVDFBTO/PVDF-SCMO/PVDF-BTO multi-facet composites first, PVDF (0.5 g) and modified dopamine BTO particles bearing a filler content of 60% were dispersed in 6ml DMF and the mixture was blended at the speed of 850 rpm for about 24 h and after that to get the consistent suspension the mixture is ultrasonicated 2 h, the formation of SCMO suspension is identical to that of BTO. To manufacture the organized composite film of sandwiched PVDF-BTO/PVDF-SCMO/PVDF-BTO, the primary layer BTO-PVDF composite film was made by the process of tape casting technique on the substrate made up of glass. Subsequently there drying for a few minutes under a temperature of 160 °C, the second layer SCMO v/s PVDF composite was casted on the main layer, in the wake of drying the last layer of composite BTO-PVDF was projected on the subsequent layer. The pre-arranged composite film was positioned into vacuum stove at 100 °C for 12 h for solvent dissipation, from that point ahead, the film was warmed at 200 °C for 8 min and afterward is placed in ice-water immediately, then, at that point to pull off from the substrate.

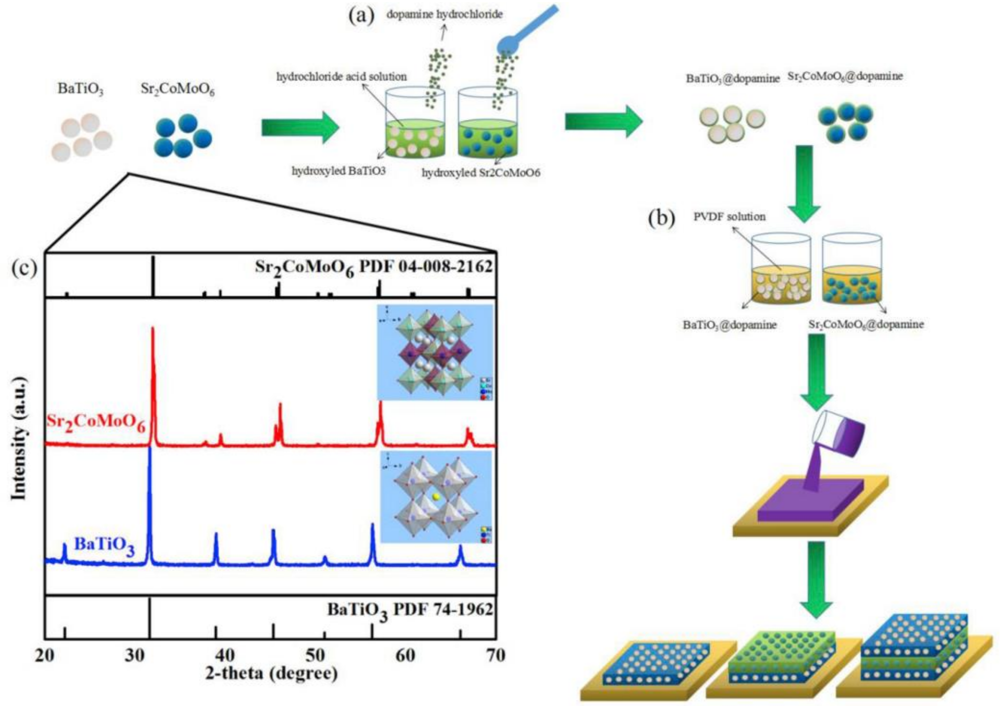

Fig. 11. Schematic illustration for the preparation of layer-by-layer casting for the sandwich PVDF-BTO/PVDF-SCMO/PVDF-BTO composite film. (a) Dopamine functionalization of BTO and SCMO particles. (b) Preparation of PVDF-BTO/PVDF-SCMO/PVDF-BTO sandwich-structured composite. (c) XRD patterns of BTO and SCMO powders and perspective view of the crystal structure of BTO and SCMO [24].

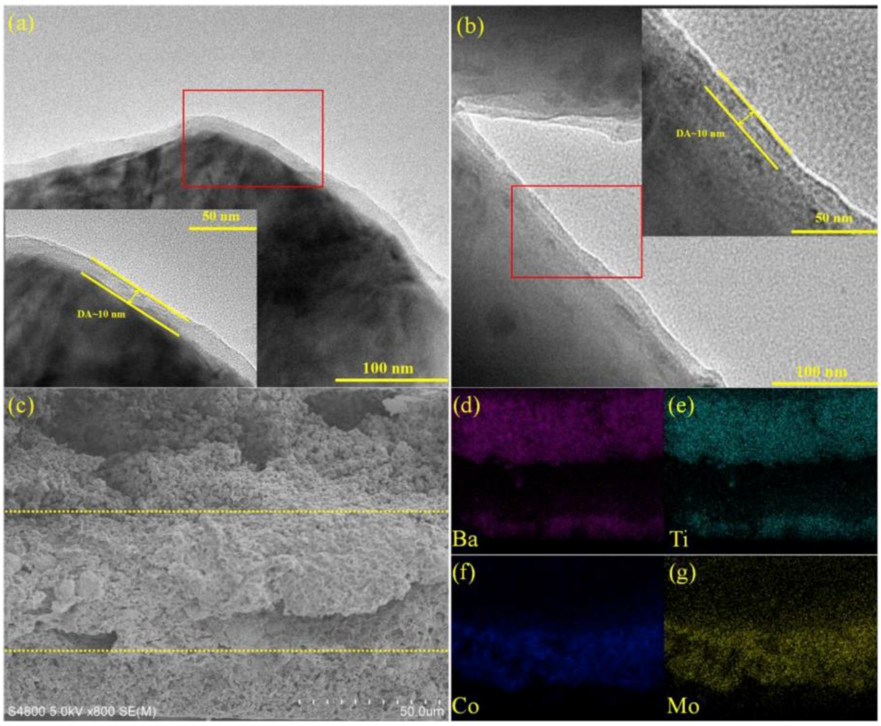

Fig.12. TEM images of (a) BTO@PDA and (a) SCMO@PDA nano powders, the inset is the large view. (c)–(g) SEM image and EDS mapping analysis of the sandwich structured PVDF-BTO/PVDF-SCMO/PVDF-BTO composite film [24].

Rao et. Al. reported a direct co-sintering method for fabrication of magnetoelectric composite of multilayer piezoelectric PSLZT and magnetostrictive NZFO layer. For this purpose, they have synthesized $Pb_{0.95}Sr_{0.025}La_{0.025}(Zr_{0.55}, Ti_{0.45})O_3$ PSPZT which was modified by $(Ni_{0.7}Zn_{0.3})Fe_2O_4$ (NZFO) and Sr, La by solid oxide route. Aquas slurry of PSLZT and NZFO as separate phase was ready by utilizing water as a solvent, poly vinyl alcohol as binder including glycerol as plasticizer. Formation of rhombohedral and tetragonal perovskites phases was confirmed by XRD. Also, this study established the formation of pure individual phases which are necessary to fabricate the composite. Next, thick layers around 100μm layer thickness of PZT were fabricated by tape-casting methods and laminated them together by using Ag- Pd electrodes printed with separate piezoceramic layers. After that these NZFO-PSLZT overlaid composites were effectively co - sintered at 950-1050oC. Also, co sintering of NZFO with six layer was also effectively tried under same conditions. SEM technique was employed for analyzing the interface of these co-sintered multilayer which showed the existence of less inter diffusion between these dense thick films of prepared composites. PFM analysis suggests that PSLZT layer shows homogeneous properties proved by the image that co -sintering of NZFO layer didn't affect these homogeneous properties of PSLZT. Capacitance spectrum and dielectric analysis also supports better bonding at interface of layered composite PSLZT-NZFO rather than PSLZT.

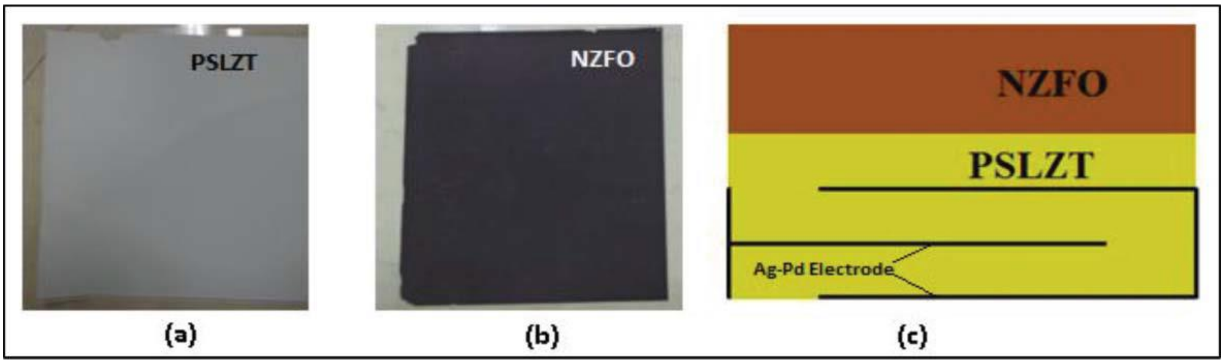

Figure 13. (a) PSLZT tape, (b) NZFO tape, and (c) schematic diagram of PSLZT-NZFO layer composite [25].

Premkumar S and V. L. Mathe jointly studied the impact of co-sintering time on magnetoelectric behavior of Sr, La on fabricated NZFO layered PSLZT by the tape casting technique. For this study they have synthesized powdered separate phases of $Pb_{(1-x-3y/2)}Sr_x La_y(Zr_z, Ti_{(1-z)})O_3$ PSLZT and $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ (NZFO) via solid-state reaction, using 16% PVA (binder) and 14% DI water (solvent) with 70% PSLZT by ball milling method. which was further casted into green tape to prepare dried tape of thickness of 110-115 µm. Co sintering with four-layer NZFO were introduced to laminate PSLZT by using Pt interelectrode. SEM analysis was employed to proven the co sintered, warpage-free as well as delamination-free layered composites of thick film structures. Likewise, SEM investigation uncovered that thickness of composite reductions with expansion in co-sintered time and microcracks were seen in composites when co-sintered for 10 h. After that ferroelectric performance of composites co-sintered were investigated at different temperature between 1-10h which revealed the presence of higher polarization at composite sintered at 6h. The impedance spectrum exposed the presence of resonance and antiresonance behavior at 2h and 6h composite co-sintering denoted bending modes and damped antiresonance at 10h due to generated microcracks. Also, composite sintering for 6h having extreme magnetoelectric coefficient of 230mV/cm Oe with self-biased magnetoelectric property at bending mode, ME value of 6V/cmOe attained.

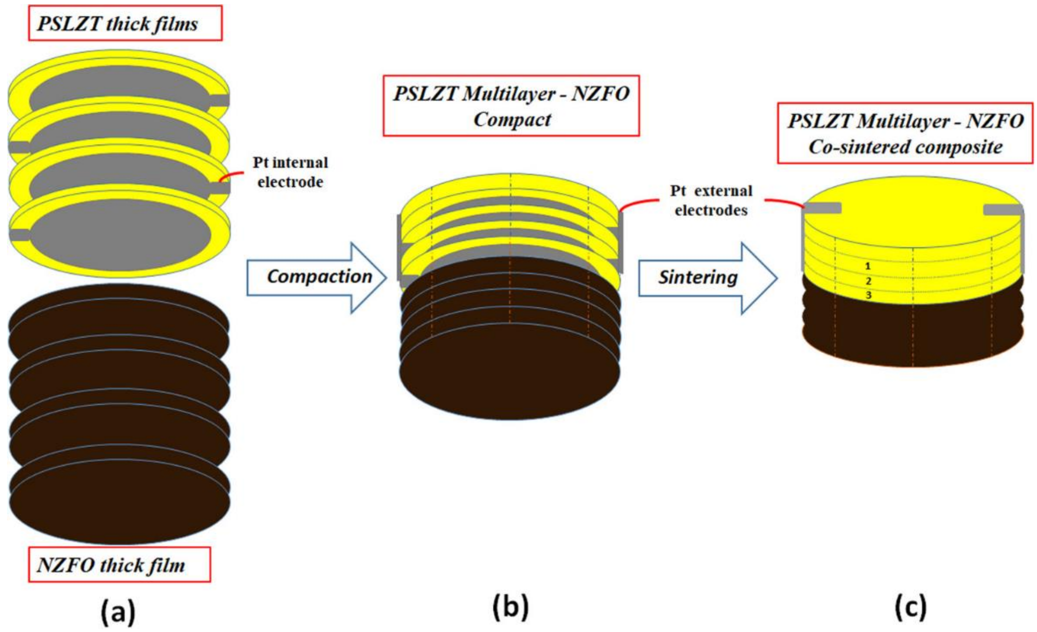

FIG. 14. Schematic representation of(a) circularly blanked thick films of NZFO (bottom) and PSLZT with platinum electrodes, (b) compaction and PSLZT multilayer–NZFO magnetoelectric composite, and (c) PSLZT multilayer–NZFO magnetoelectric composite structure after co-sintering with top electrodes taken out from PSLZT layers [26].

Mathe's group studied about the ferroelectric and piezoelectric behavior on NZFO layered PSLZT. For this study, initially by solid state reaction method $Pb_{(1-x-3y/2)}Sr_x\ La_y(Zr_z,Ti_{(1-z)})O_3$ where x= 0.06, y= 0.03, z= 0.56 (PSLZT) and $(Ni_{0.6}Zn_{0.4})Fe_2O_4$ (NZFO) powders were made ready and later tape casting technique was used for its fabrication and further laminated with three layered by using Pt electrodes and for 2h it was co-sintered at 1060 ^oC to obtain thick layered composites. To Analyze the microstructure and interface of these synthesized layered composite scanning electron microscopy was employed. Next, individual piezoelectric multilayer and magnetoelectric composites were introduced to reveal the ferroelectric behavior. For this purpose, MFM and PFM techniques were employed to recognize the ferroelectric domains and magnetic domains on upper layers of PSLZT and NZFO composites. Remanent polarization value 50.6 $\mu C/cm^2$ and 55 $\mu C/cm^2$ and capacitance worth of 31.5nF and 28.9nF for PSLZT and PSLZT-NZFO composite separately. Also, Piezoelectric coefficient found 980-1030 pC/N and 1050-1150 pC/N for PSLZT and PSLZT- NZFO separately. These layered PSLZT composites have lots of applications in miniaturized sensors and energy harvesting purposes.

Literature Survey on Materials

From reports since 1960's enormous ME coupling coefficient is significant for arising applications like electromagnetic energy harvesters, magnetoelectric generators etc. In recent few years studies have been conducted on the layered ME composites with various connectivity scheme (i.e., 0-3, 2-2 and 1-3 type). 0-3 particulate nanocomposite film with magnetic particle (0) embedded in ferroelectric film matrix(3) [1]. In 2-2 type horizontal heterostructure with suitable ferroelectric (2) and ferromagnetic (2) layers. In 1-3 type is vertical heterostructure with one phase nanopillars (1) embedded in another phase (3). Among all the most commonly adopted scheme is the symmetric 2-2 ME laminates in which the piezoelectric and magneto-strictive layers are stacked alternatively. we have successfully studied that tape casting helps in the mass production of the 2-2 types MELs grown by the tape-casting method, these MELs show much larger voltage coefficient then that of natural multiferroic and bulk composites. These ME layered structures are in demand because of their superior ME properties.

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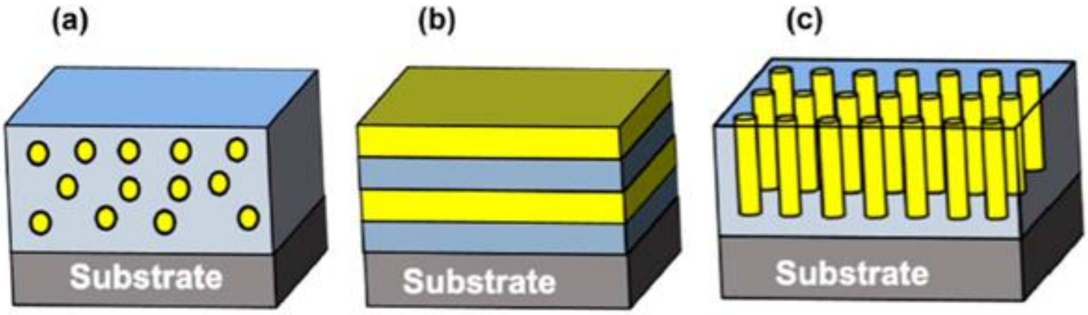

FIG. 15. Schematic of (a)0-3, (b)2-2 and (c)1-3 composite structure

It is well evident that material possessing large surface area are having high ME coupling. As we have seen that the surface area of the 2-2 type composite is large as compared to that of 1-3 and 0-3 type composites. Hence the value of ME coefficient is getting more in 2-2 type ME composites as shown in the Figure 16.

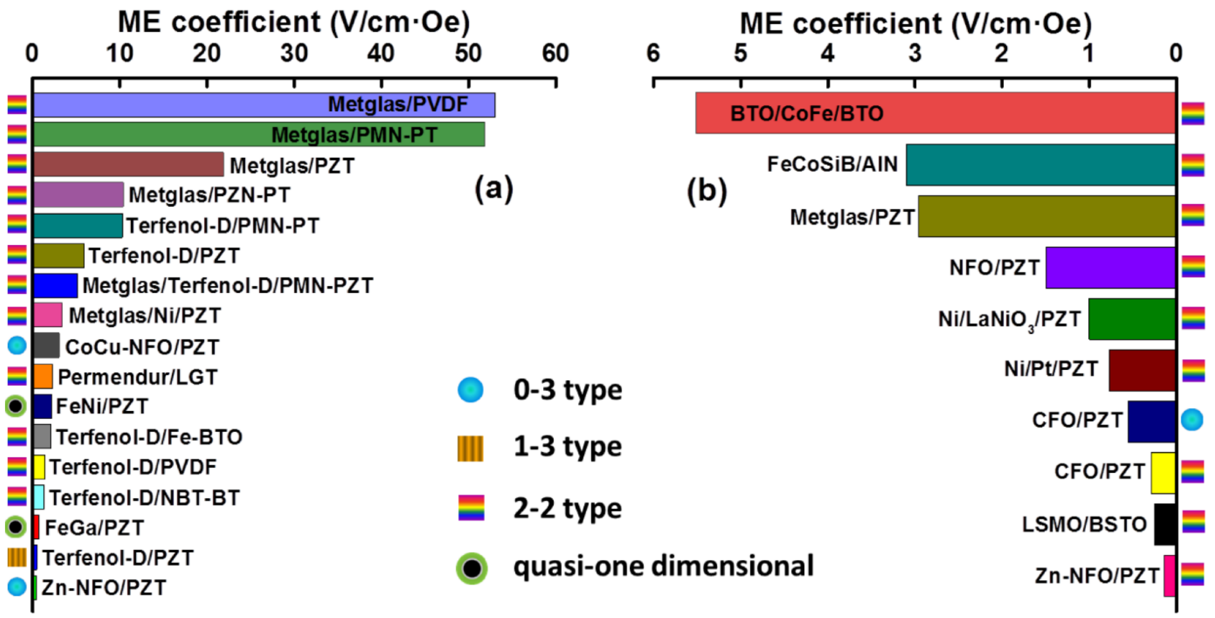

FIG. 16. Magnetoelectric coupling in different schemes [27].

though 2-2 type ME composites are preferred widely. but which lead free composite will give high ME coupling coefficient value. For this, lead free perovskite material. such as $Bi_{0.5}Na_{0.5}Tio_3$(BNT), $BaTiO_3$(BT), $K_{0.5}Na_{0.5}NbO_3$(KNN) based ceramics are used because of their good piezoelectric properties (disordered ABO_3 type structure give polarity. hence, these materials are synthesized and characterized. but of these lead-free promising candidates which particular material will give better ME coupling. for this it is important to know on which parameter ME coupling depend.

As ME coupling is given by equation (a)

$$\frac{Mechnical}{Magnetic} \times \frac{Electric}{Mechanical} = \alpha(E) \; .....(a)$$

ME coefficient is also expressed in the form as

$$\alpha(E) = m\left(\frac{dS}{dH}\right) \times (1-m)\,(g_{33} \times c_{33})$$

Where, m represents the volume fraction of the ferrite. $\frac{dS}{dH}$ represent the change in the strain per unit magnetic field of ferrite in composites. g_{33} represents piezoelectric voltage constant, and c_{33} represent the stiffness of ferroelectric matrix into composite

Value of g_{33} is given in the term of piezoelectric coefficient and dielectric constant as

$$g_{33} = d_{33}/\varepsilon_r \;\; ......(b)$$

As α depend on g_{33} (in equation b). Hence ME coefficient is directly affected by piezoelectric coefficient of material and dielectric constant of material. From here it is clear we should use those material for which piezoelectric coefficient is more as compared to dielectric constant. Particle size plays important role in deciding the ME coupling coefficient of the material. Particle size is different for different synthesis method. It is observed that the change in the synthesis method led to change in the ME coupling coefficient value.

Table 3: Piezoelectric coefficient for different BNT, KNN and BT based ceramics with respect to synthesis method and composite type are given in the table. (ME coefficient value lower than 30 and 10 is ignored in case of BNT and BT based ceramics respectively)

S.No	**Composites**	**d_{33} (pc/n)**	**References**
1	$(Na_{0.5}Bi_{0.5})$ TiO_3-$BaTiO_3$-(K0.5Na0.5) NbO3		[28]
2	x%-Nb: NBT-6BT, x = 0.12, 0.23, and 0.48	2	[29]
3	(100−x) NBT−xKBT (x=5, 8, 12, 15)	238	[30]
4	$0.94(Na_{1/2}Bi_{1/2})$ TiO_3–$0.06BaTiO_3$ lead-free ceramics by doping series SrTiO3	205	[31]
5	$(Na_{0.5}Bi_{0.5})$ TiO_3–$(K_{0.5}Bi_{0.5})$ TiO_3–$BaTiO_3$ (NBT–KBT–BT)	213	[32]
6	NBT-6 %BT with 0.1 %Mn	570	[33]
7	$0.95(Na_{0.5}Bi_{0.5})TiO_3$-$0.05BaTiO_3$	360	[34]
8	$0.94(Na_{0.5}Bi_{0.5}TiO_3)$–$0.06BaTiO_3$	206	[35]
9	$0.93(Na_{0.5}Bi_{0.5}TiO_3)$-$0.07BaTiO_3$	322	[36]
10	$0.94Na_{0.5}Bi_{0.5}TiO_3$–$0.06BaTiO_3$	260	[37]
11	$0.93(Na_{0.5}Bi_{0.5}TiO_3)$-$0.07BaTiO_3$ (NBT-BT)	322	[38]

12	(1 x)(Na,Bi)TiO_3–x$BaTiO_3$ (NBT–BT) ON Mgo substrate	221	[39]
13	95$Na_{1/2}Bi_{1/2}TiO_3$ 5$BaTiO_3$ (NBT–5BT)	207	[40]
14	$Na_{0.5}Bi_{0.5}TiO_3$-5.2%$BaTiO_3$ (NBT-5.2%BT)	400	[41]
15	0.94$Na_{0.5}Bi_{0.5}TiO_3$–0.06$BaTiO_3$ (NBT–6BT)	299	[42]

Table 3: Comparison of Piezoelectric coefficient, Remanent polarization and Curie temperature of KNN, BNT and BT respectively[43].

Ceramics	KNN ($K_{0.5}Na_{0.5}NbO_3$)	BNT ($Bi_{0.5}Na_{0.5}TiO_3$)	BT($BaTiO_3$)
Piezoelectric coefficient (d_{33})	71 pC/N	95 pC/N	95 pC/N
Remanent polarization (P_r)	11.76 $\mu C/cm^2$	38 $\mu C/cm^2$	10.42$\mu C/cm^2$
Curie temperature (T_c)	370 °C	320 °C	120 °C

It is important to choose a good magnetic material with high magnetostrictive property.

Table 4: the magnet- restrictive coefficient of different ferrites [13].

S. No.	Material	λ (ppm)
1	$MnFe_2O_4$	-5
2	Fe_3O_4	40
3	$CoFe_2O_4$	-110
4	$MgFe_2O_4$	-6
5	$Li_{0.5}Fe_2O_4$	-8

6	$NiFe_2O_4$	-26
7	$CuFe_2O_4$	-9
8	YFe_5O_{12}	-2
9	$SmFe_5O_{12}$	3.3
10	$DyFe_5O_{12}$	1.46
11	$EuFe_5O_{12}$	9.48

It is observed that $CoFe_2O_4$, Fe_3O_4 and $NiFe_2O_4$ show good value of magneto restriction (λ) and these ferrites are mostly used for ME coupling. But for $CoFe_2O_4$ and Fe_3O_4 λ is achieved at high magnetic field (around 300 Oe) there for $NiFe_2O_4$ and $NiFe_2O_4$ based ferrites are used as magneto restrictive material for making ME composites due to high magnetostriction coefficient.

CONCLUSION

From the literature review it is analyzed that maximum work of materials is carried out in thick/thin films. It is found that, the ME properties found in bulk composites are not as good as obtained in films. It is that ME properties can be changed by changing the synthesis process and composition. To investigate the ME characteristics, tape casting method is widely used. Most of work has been done on lead-based composites. BNT, BT and KNN are the suitable candidates for lead free ME composites. BNT base ceramics are excellent due to its good ME properties. BNT with magnetic phase NFO is found as suitable alternate of Pb-based composites. Still no report available on BNT based ME composite film grown by tape casting method. So, our goal is to fabricate BNT, NFO composite films by tape casting technique. In future tape casting technique can used to study different material.

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