



PARADIGM SHIFT IN FERROELECTRIC RESEARCH A NEED OF THE TIME -A REVIEW

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ABSTRACT:

A century old Ferroelectric materials possess spontaneous polarization, are dielectric, piezoelectric, pyroelectric and also show hysteresis. They are used as memory devices, optical phase conjugate, medical, non-medical sensors, Nano probes & hologram recording more over show a second harmonic generation. Researchers may change the focus from applied research to blue sky research with the phenomenological change in the approach that invite not only inter- disciplinary but also trans- disciplinary . The review urged the researchers to adopt chemical, physical and /or biological methods to fabricate lead free pure, doped KNbO_3 in a Nano range with academic & commercial interests.

Keywords: Nano ferroelectric particles, blue sky research, medical sensors.

INTRODUCTION :

Ferroelectricity is a characteristic of certain materials that possess a spontaneous electric polarization that can be reversed by the application of an external electric field.[1][2]. All ferroelectrics are pyroelectric, with the additional property that their natural electrical polarization is reversible. Ferroelectricity was discovered in 1920 in Rochelle salt by Valasek.[3] Some of the most common structures in which ferroelectric materials crystallize are tetragonal, orthorhombic, monoclinic, tungsten bronze, perovskite, pyrochlore. Ferroelectric materials have become potentially useful for device applications

because of their high dielectric constant, non-linear behaviour, polarization reversal, and domain structure and pyro electric & piezoelectric behaviour in a temperature range where semiconducting materials fail. In addition to being nonlinear, ferroelectric materials demonstrate a spontaneous nonzero polarization even when the applied field E is zero. The distinguishing feature of ferroelectrics is that the spontaneous polarization can be *reversed* by a suitably strong applied electric field in the opposite direction; the polarization is therefore dependent not only on the current electric field but also on its history, yielding a hysteresis loop. Typically, materials demonstrate Ferro electricity only below a certain phase transition temperature, called the Curie temperature (T_c) and are par electric above this temperature: the spontaneous polarization vanishes, and the ferroelectric crystal transforms into the para- electric state. Many ferroelectrics lose their piezoelectric properties above T_c completely, because their para-electric phase has a Centro-symmetric crystal structure.[4] The internal electric dipoles of a ferroelectric material are coupled to the material lattice so anything that changes the lattice will change the strength of the dipoles (in other words, a change in the spontaneous polarization). The change in the spontaneous polarization results in a change in the surface charge. This can cause current flow in the case of a ferroelectric capacitor even without the presence of an external voltage across the capacitor. Two stimuli that will change the lattice dimensions of a material are force and temperature. The generation of a surface charge in response to the application of an external stress to a material is called piezoelectricity. A change in the spontaneous polarization of a material in response to a change in temperature is called pyro electricity. In lead titanate, another key ferroelectric material, although the structure is rather similar to barium titanate the driving force for Ferro electricity is more complex with interactions between the lead and oxygen ions also playing an important role. In an order-disorder ferroelectric, there is a dipole moment in each unit cell, but at high temperatures they are pointing in random directions. Upon lowering the temperature and going through the phase transition, the dipoles order, all pointing in the same direction within a domain. An important ferroelectric material for applications is lead zirconate titanate (PZT), which is part of the solid solution formed between ferroelectric lead titanate and anti-ferroelectric lead zirconate. Different compositions are used for different applications; for memory applications, PZT closer in composition to lead titanate is preferred, whereas piezoelectric applications make use of the diverging piezoelectric coefficients associated with the morphotropic phase boundary that is found close to the 50/50 composition. Ferroelectric crystals often show several transition temperatures and domain structure hysteresis, much as

do ferromagnetic crystals. The nature of the phase transition in some ferroelectric crystals is still not well understood. Other ferroelectric materials used include triglycine sulfate, polyvinylidene fluoride (PVDF) and lithium tantalite.[5] It should be possible to produce materials which combine both ferroelectric and metallic properties simultaneously, at room temperature.[6] According to research published in 2018 in Nature Communications,[7] scientists were able to produce a "two-dimensional" sheet of material which was both "ferroelectric" (had a polar crystal structure) and which conducted electricity. One of the most studied ferroelectric crystals was the BaTiO₃ and later the isomorph KNbO₃ the two have the same set & order of phase transitions as a function of temperature. Huge research work has been carried out with BaTiO₃ to explore so as to replace the autonomy of PZT due to its toxicity. Certain researchers have focused their attention to get away toxicity in the materials and the lead free concept prevailed for some decades. The materials studied were namely sodium potassium niobate (KNN). However the achieved properties could not take over the position of PZT till date. The new generation of functional devices requires lead free thin films since the fact that lead containing components are toxic and hazardous to both human as well as environment. As ferroelectric materials have applications as random access memories (FRAMs), and dynamic random access memories (DRAMs) owing to large remnant polarization and high dielectric constant Therefore, investigation of lead-free ferroelectric thin films and devices was the need for ongoing technological development. Among the numerous lead free materials (K_{0.5} Na_{0.5}) NbO₃ (KNN) is a promising candidate because it has a high Curie temperature and excellent ferroelectric, dielectric as well as piezoelectric properties and has orthorhombic crystal structure at room temperature. In 1999 the ceramic technological innovation was patented by Pacesetter, K.Nilsson et.al. [8] for use of KNN as a biocompatible implant material. Also Wakasa and group [9] in 2011 made KNN films on Si substrate by R.F.magnetron sputtering method & fabricated the cantilever. The first KNN thin film was synthesized by Saito et. al. [10] in 2004 by using Pulsed Laser Deposition (PLD) technique. Thereafter, several finding were available from various groups. Relating to composition and stoichiometry Li and group [11] in 2011 has studied the effect of Na and ratio on the properties of K_{a0.48}Na_{0.52}NbO₃ thin films. It was reported that under the same heat treatment the volatilization amount is different for Na and K. The film shows very good ferroelectric properties only at 17 mol% excess values of Na and 6 mol% excess of K respectively. It was concluded that Na is more prone to volatilization than K. However Chiwon-Kanin 2011 et.al.[12] found a contradictory result reported by Li et.al. It was found that the ferroelectric

hysteresis behavior is better when excess of K in precursor was used. Numerous attempts have been made to suppress volatility and doping with suitable element. In 2009 Mgbemere et al.[13] substituted Li at A site and Sb at B site. It was found that Sb doping with 8 mole % enhances the dielectric properties. Lin and group in 2010 added MnO₂ and found that dielectric permittivity increases by three times, which is due to smaller domain size [14]. Similar observation was made by Wang et al. in 2010[15] that Mn doping reduces leakage current with well saturated polarization loop.

KNN material has been quite appreciated and undertaken by various groups. In their studies KNN was grown in ceramics to be used as on a commercial scale. Grain size, dielectric properties etc. have been characterized.

In 2001 Singh et al.[16] have studied KNN ceramics and found that dielectric constant is a function of concentration of K. It was found that as the K content increases, the grain size decreases, and dielectric constant increases with sudden drop at 0.5, but the reason is not clear. Similar work was carried out by Lingwal and group [17] in 2004. They observed that high density and improved oxygen stoichiometry are responsible for the observed high dielectric constant. Thus far there is no reported work on KNN thin films in our country. Growth of KNN based thin films have been studied by several methods such as RF magnetron sputtering [18], Pulse laser deposition (PLD) [10], aerosol deposition method [19], MOCVD [20], and chemical solution deposition (C.S.D.) [21] and [22]. However, to date, there are few reports on KNN thin film fabrication by C.S.D. and P.L.D. However, there always exists a serious problem in KNN films, especially from the C.S.D. method, which usually exhibit high leakage current, resulting in poor ferroelectric properties. [23] Ferroelectric thin films for electronic applications.[24-27]. In the beginning of its historical development (the Rochelle salt period) Ferro electricity was considered an academic curiosity with no practical applications. There was little theoretical interest due to the quality of the ferroelectric materials (very fragile and water-soluble) existing at that time. The discovery of Ferro electricity in robust ceramic materials (barium titanate) during World War II launched a new era of rapid progress in the field. The structural simplicity of barium titanate stimulated numerous theoretical works, while its physical properties were utilized in many devices. Since that time, ferroelectric response has been found in a wide range of materials, including inorganic, organic, and biological species. According to [28] there are 72 families of ferroelectrics presented in Landolt-Börnstein-Vol.III/36 (LB III/36). Forty-

nine of these families are inorganic crystals (19 families of oxides+ 30 families of crystals other than oxides), and 23 families are organic crystals, liquid crystals, and polymers. The enormously broad range of materials exhibiting Ferro electricity and the variety of their physical properties result in numerous applications of bulk ferroelectrics [29]. Recent advances in nanotechnologies, especially in nano instrumentation (for example, scanning probe microscopy [30]) and materials nanofabrication [31], allowed the direct probing of Ferro electricity at the nanoscale. The new and unexplored world of nano scale ferroelectrics (nanoparticles of different shapes and sizes, nano films, nano patterned structures, etc.) raised fundamental questions and stimulated very active research in both academic and industrial sectors [32]. As a result, a new era of nano scale ferroelectrics was launched. Novel effects, associated with reduced dimensions and found in nano scale ferroelectrics, highlighted exciting possibilities for new applications reviewed recently in [33]. Almost all of the attention for the mentioned review [33] was devoted to the thin film nano scale device structures (which can be easily integrated with a Si chip) with focus on ultrafast switching, electro caloric coolers for computers, phase-array radar, three-dimensional trenched capacitors for dynamic random access memories, room temperature magnetic field detectors, and miniature X-ray and neutron sources.

EXPERIMENTAL METHODS TO GROW FERROELECTRIC NANOPARTICLES :

Methods for fabrication of ferroelectric nanoparticles are numerous and can be classified as physical, chemical, and biological .The primary goal of each method is to control size, shape, morphology, and crystallinity of nanoparticles to produce a desirable effect. There are no critical boundaries amongst these methods however they partially overlap Sometimes , a combination of at least two methods becomes essential to grow ferroelectric good quality particles. A brief survey of these methods are shared for the convenience.

CHEMICAL METHODS: The most widely used chemical methods for the synthesis of ferroelectric nanoparticles are:1) solid-state reaction; 2) sol-gel technique; 3) solvo thermal method; 4) hydrothermal method; and 5) molten salt method. The ultra-fine ferroelectric nano particles of BaTiO₃ (<10 nm) in almost all cases except [34] are synthesized in a cubic phase which is not ferroelectric. The tetragonal phase (with ferroelectric response) is possible for relatively large particles(~50-70 nm).

PHYSICAL METHODS: Dry and wet mechanical grindings are methods of choice for inexpensive nanoparticle preparation. For technological applications, wet grinding is preferable because it allows more options to control the size of the nanoparticles. The ability to produce ferroelectric nanoparticles of very small sizes is a defining characteristic of this physical method.

PHYSICAL-CHEMICAL METHODS

In order to prepare ferroelectric nanoparticles with controllable sizes and shapes a combination of chemical methods with external physical factors (electromagnetic fields or mechanical milling) is needed. Chemical reactions under the presence of an external driver (microwave, ultrasonic, milling, heat, pressure) are able to produce very fine particles (~5-10 nm) with tetragonal structures.

BIOLOGICAL METHODS: Biological methods were proposed as eco-friendly “green” alternatives to existing chemical and physical methods. The biosynthesis of different types of nanoparticles was reviewed recently in a few papers [35, 36, 37, 38]. The biological methods applied to synthesize the nanoparticles of the most widely known ferroelectric BaTiO₃. Fungus (*Fusarium oxysporum*, commonly found in soil) has been shown to synthesize extra cellular ferroelectric nanoparticles of barium titanate (4-5 nm of average size) [39, 40] at room temperature, producing small ferroelectric nanoparticles on a scale that has been previously inaccessible. *Lactobacillus* has been shown to synthesize ferroelectric nanoparticles (with sizes ranging from 20 to 80 nm) from the slush of large barium titanate particles [41]. Baker’s yeast (*Saccharomyces cerevisiae*) has also been attempted as a biosynthesis agent; the barium titanate nanoparticles received were on average ~10nm [42]. Peptide Nano rings provide another interesting biomimetic route to the template-mediated synthesis of BaTiO₃ and SrTiO₃ nanoparticles [43]. Developed in 2006, it was the very first method of obtaining ferroelectric barium titanate nanoparticles at room temperature. This process relies on some physical/chemical steps, just like the majority of other biological methods of ferroelectric nanoparticle production that have been developed to date. These bio-inspired methods show great promise because they produce relatively small ferroelectric nanoparticles at room (or low) temperature compared to conventional physical and chemical methods, many of which require lengthy processes, use of high temperatures, harsh chemicals, etc.[44]

APPLICATIONS OF FERROELECTRIC NANOPARTICLES APPLICATIONS IN MEDICINE AND MEDICAL ENGINEERING [44]

Ferroelectric materials in the Nano range can be used for cell imaging or the detection of malignancies in lung cancer studies, or they can be functionalized to induce cell proliferation. Ferroelectric materials have a non-Centro symmetric crystalline structure, and are thus capable of generating a second harmonic of light [45]. This distinctive feature of ferroelectrics is the basis for a growing number of applications of ferroelectric nanoparticles as imaging/diagnostic agents and Nano probes in optical imaging [46]. Second harmonic generation imaging has been successfully used for detection of osteogenesis imperfecta in biopsies of human skin [47] and lung cancer [48]. To improve contrast, many of the imaging methods rely on imaging probes, such as fluorescent markers or quantum dots [49]. By definition, second harmonic generating Nano probes (such as ferroelectric nanoparticles) are capable of converting two photons of light into one photon of half the incident wavelength [50]. This second-harmonic light can be detected using methods of nonlinear optical microscopy. Nonlinear optical properties of ferroelectric nanomaterial's can be used for optical phase conjugation [51] and nonlinear microscopy [52, 53] – these properties have allowed them to spread to the area of medical sensors. Recent advances in this area include imaging a tail of a living mouse with the aid of barium titanate nanoparticles [54]. The intrinsic large values of the dielectric permittivity's of ferroelectric nanoparticles suggest their use to enhance the dielectric contrast of materials, such as polymers [55 and references within] and biological tissue [56]. These unique properties of ferroelectric nanoparticles lead to their novel use as contrast-enhancing agents for microwave tomography, which is a method of non-invasive assessment and diagnostics of soft tissues (such as detecting malignancies) [56]. Recently, ferroelectric electro spun nanofibers also emerged in various biomedical areas including medical prostheses, tissue engineering, wound dressing, and drug delivery [57, 58, 59].

To conclude, ferroelectric materials found a wide variety of biomedical applications in the last decade – and the list is constantly growing [60]. The ferroelectric material (e.g. barium titanate) used in medical implants has been known to accelerate osteogenesis [61], and the same material in nanoparticle form works both as an SHG probe to detect Osteogenesis Imperfecta [47] and, through microwave tomography, to detect lung cancer [56]. The author had mostly worked KNbO_3 , $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ & PZT crystals [62-74] take

this opportunity to share the fact that BaTiO₃ has been the most studied ferroelectric material in the form of (i)Single crystal (ii)Thin film(iii)Ceramics(iv)Composites(v)Nanoparticals. Now using Physical, Physical-Chemical, Biological and medical applications in mind an isomer of BaTiO₃ namely KNbO₃ seems to be a better alternative to explore it's suitability as candidate for academic, device applications with now focus more towards realistic commercial usage.

CONCLUSION :

At this point of time there seems the need to enhance the pure academic growth of the research on one strand of a double helix & simultaneously the commercial aspect on the other in a spiral path. This is only possible if there is a paradigm shift in Ferroelectric research to grow KNbO₃ Nano materials in particular where the study needs to be undertaken by not only in an interdisciplinary manner but also trans-disciplinary way encouraging applied research to blue sky research.

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