INDENTATION RESPONSE OF PIEZOELECTRIC MATERIALS

M.Tech. Thesis

By

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UNDER THE GUIDENCE

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INDENTATION RESPONSE OF PIEZOELECTRIC MATERIALS

A THESIS

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requirements for the award of the degree
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PRADEEP ELI

DEPARTMENT OF MECHANICAL ENGINEERING
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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **INDENTATION RESPONSE OF PIEZOELECTRIC MATERIALS** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF MECHANICAL ENGINEERING, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from August 2020 to June 2022 under the supervision of **Dr. Indrasen Singh, Assistant Professor at Indian Institute of Technology Indore**.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

E. Pradeep , 01/06/2022
Signature of the student with date
PRADEEP ELI

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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ABSTRACT

Lead Magnesium Niobate-Lead Titanate (PMN-PT) is a piezo electric material which exhibit ultra-high electromechanical response. The annealing imparts disordered domain orientation as compared to fresh poled ordered domains. The objective of the present work is to understand the effect of annealing temperature on mechanical properties like hardness and toughness and also on the flow of the cracks at a particular indentation load. In view of the above objective Vickers micro-indentation experiments are performed on (001) oriented poled PMN-PT single crystal.

TABLE OF CONTENTS

List of tables

List of figures

Chapter 1

INTRODUCTION

1.1 Basic introduction of piezoelectric materials

Piezoelectric phenomena were found on quartz (SiO_2) crystals by the Curie brothers, Pierre and Jacques in the early 1880s. Since the discovery, it's an ever long lasting research. Valasek discovered the ferroelectric occurrence in Rochelle salt in 1920. Despite being lead based, PZTs has been the dominant group than $BaTiO_3$ in terms of usage and properties for more than 40 years due to their high piezoelectric properties and Curie point temperature, T_c. As the time flies, the relaxor materials (PMN-xPT single crystals, showing perovskite structure ABO_3) came into picture, showing extensive properties in the Morphotropic Phase Boundary (MPB) range. MPB range is still unclear to understand, even after decades of research. Today, piezoelectric materials are widely used in industrial applications, particularly in ultrasonic transducers.

1.1.1 Classification of dielectric materials

A dielectric substance is an insulating material that can be polarized during an applied electric field. Piezoelectric materials belong to the family of dielectric materials. Charge redistribution happens whenever an electric field got applied toward a dielectric material. The bound charge carriers remain in their unit cell and are only aligned in the direction same as the applied electric field. Equation below shows how the size of the displacement (polarization density) increases proportionally with the applied electric field.

$$P = \epsilon_o \epsilon_r E$$

The vacuum and relative dielectric permittivities are represented by ϵ_o and ϵ_r respectively. An applied voltage, V and the capacitance, C, of the material can be used to determine the dielectric permittivity, which

is a measurement of electrical energy stored. The capacitance is calculated using equation below, where A is the surface area while t is the material thickness.

$$C = \epsilon_o \epsilon_r . \frac{A}{t}$$

There is also an electric-field induced strain effect, which is provided by equation, where S represents strain, which is related to polarization by the electrostrictive coefficient, Q.

$$S = Q \times P^2$$

These materials can be classified on the basis of symmetry point groups. These involve materials showing different electro mechanical responses. For better understanding check out the following flow diagram (1.1) and subgroups of dielectrics (1.2).

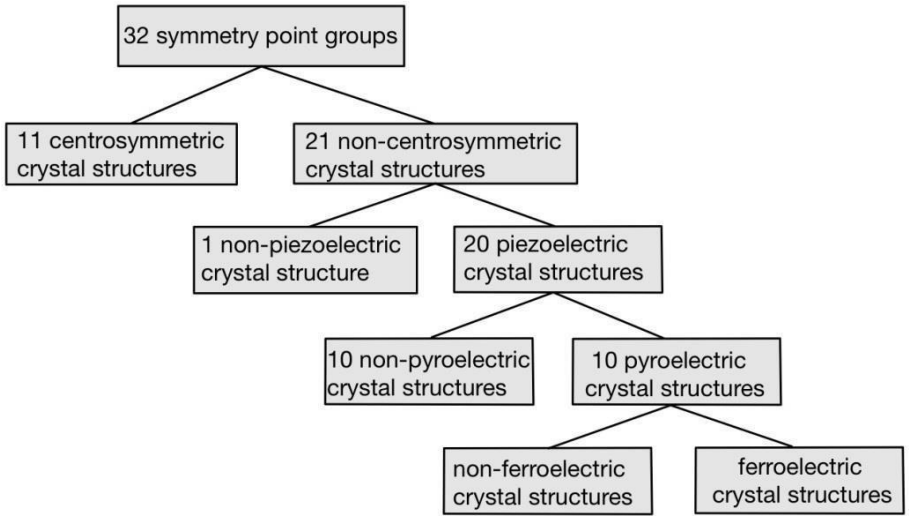

Fig. 1.1: Based on the symmetry system, piezoelectric, pyroelectric, and ferroelectric crystals are classified.

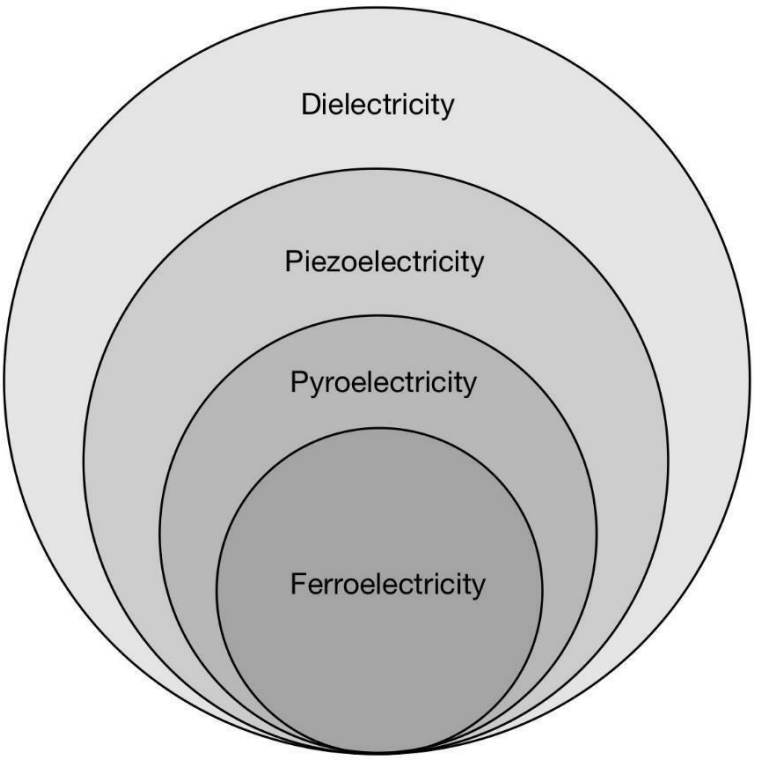

Fig. 1.2: Subgroups of dielectrics

Piezoelectric materials are dielectric materials, and which may or may not possess the spontaneous polarization. All pyroelectric and ferroelectric materials are piezoelectric materials but vice-versa cannot be true.

Pyroelectrics are a type of piezoelectric material that has temperature-dependent spontaneous polarization. The polarization dependence of temperature can be described with the help of pyroelectric coefficient.

Ferroelectric materials are a subset of pyroelectric materials that have two or more spontaneous polarization orientational states that it can be reversed by an external electric field. All ferroelectric materials belong to pyroelectric materials but vice-versa cannot be true.

Consider a crystal of PZT below to understand the terms of being centrosymmetric (left crystal) and non-centrosymmetric (right crystal).

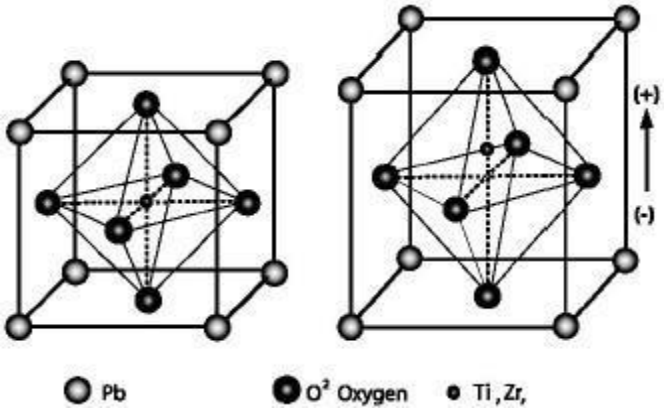

Fig. 1.3: Centrosymmetric and non-centrosymmetric crystals [2]

1.1.2 Piezoelectric effects

Piezoelectric materials contain both polar and non-polar piezoelectric materials. Generally, piezoelectric materials contain two kinds of effects. They are inverse piezoelectric effect and direct piezoelectric effect.

Direct piezoelectric effect involves generation of electric charge, when we apply a force externally. The positively and negatively charge centers of each molecule align before external stress is applied, resulting in an electrically neutral structure. Dipoles are got formed by change in distance between positive and negative centers. This separation is caused by the application of external mechanical stress. The material is polarized, and the phenomenon is known as direct piezoelectric effect. Check out a simple molecular model below for better understanding of direct piezoelectric effect.

$$D = d\,T$$

Where D, d, and T are piezoelectric polarization vector, piezoelectric coefficient and stress applied respectively.

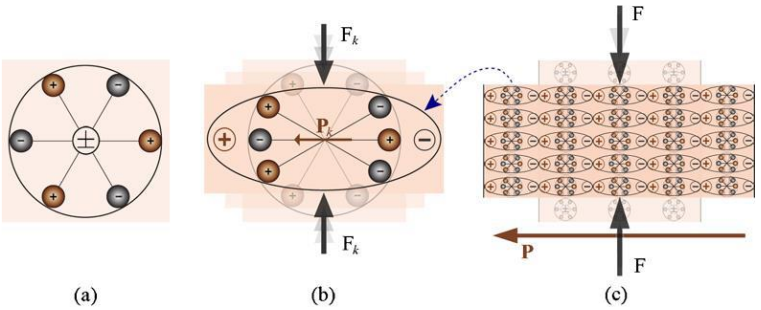

Fig. 1.4: a) Molecule with zero polarization, b) Polarization produced with the help of an external mechanical force, c) In same way, externally force helps in producing polarization on whole beam. [1]

When a voltage is put between the electrodes, some materials display the reverse piezoelectric effect, which causes a mechanical strain in the material. The strain created in this fashion could be utilized to shift a linked mechanical load, for example. For many applications, this way of transforming electrical energy into useable mechanical energy is crucial.

1.2 Ferroelectricity and their related parameters

Ferroelectric materials are the longlasting topic for research ever since they got discovered, and still there is not enough data to understand these materials because of the complex nature of properties or parameters involved with them.

1.2.1 Domains

Ferroelectricity is a property of certain materials that exhibit spontaneous electric polarization and can be reoriented by an electric field. This reorientation of polarization is achieved by change in directions of domains. A ferroelectric crystal is made up of numerous grains, each of which contains domains. These domains contain several number of dipoleswhich are uniform. Polarization vector direction is same as dipole direction. Domains are got separated by a wall called domain wall. These

domains can be observed experimentally by using different equipments like Sanning Elecron Microscope (SEM), Piezoresponse Force Microscope (PFM) and Polarized Laser optical Microscope (PLM).

According to many researches, the crystal functionality in applications is significantly correlated with the domain wall density. The better the piezoelectric capabilities, the higher the domain density in the ferroelectric crystal. Domain engineering is thus a novel way for manipulating the density of domain walls in ferroelectric crystals.

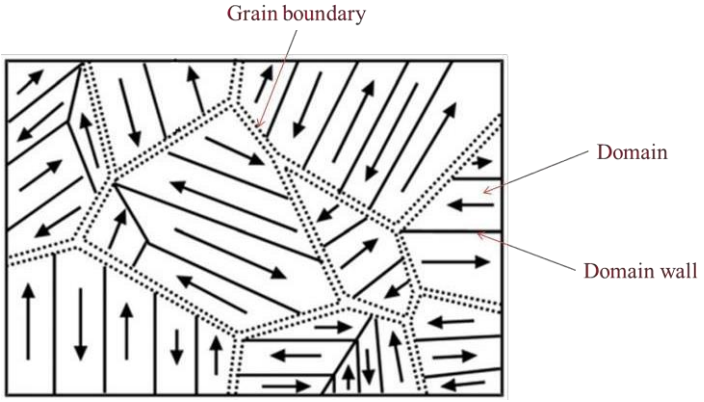

Fig. 1.5: Micro-structure of ferroelectric materials [2]

Sum of dipole moments (p_i) per unit volume (ΔV) is called Polarization intensity, P. This will help us in viewing the dipoles or domains in a vectorial form. This polarization can hcause the material to show electrical response.

$$P = \frac{\sum \vec{p_i}}{\Delta V}$$

There are three main mechanisms of polarization are involved in piezoelectric materials. They are ionic,electronic and orientation polarizations.

Electronic polarization involves the formation of polarization by displacement of negatively charged electron to positively charged nucleus. This kind of polarization occurs in all the available dielectric materials. Whereas ionic polarization occurs only in ionic materials. Ionic

polarization occurs by displacement of cations and anions from away each other. Orientation polarization is known to occur only in certain material that are able to possess permanent dipole moments. Orienetation polarization is straight forward in which by the application of electric field, there isa n orientation of polarization occurs.

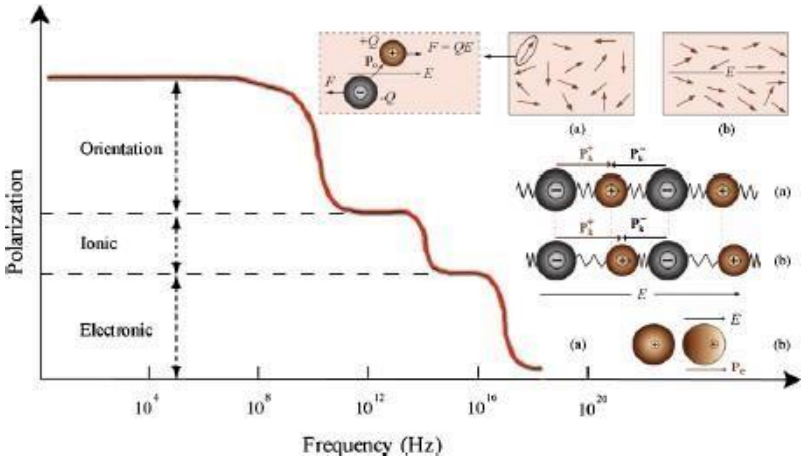

Fig. 1.6: Polarization mechanisms [1]

1.2.2 Poling

After applying large electric fields, the the domain will reorient according to the direction of electric field. These domains will obviously got reoriented on the expense of other domains. As the process goes, all the domains gets aligned with the applied electric field and reaches a saturation polarization. And when the electric field got removed, there is still a polarization available in the material called remanent polarization.

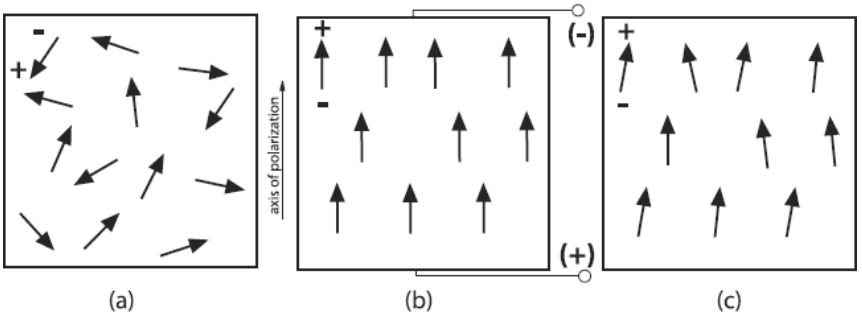

Fig. 1.7: a) prior to poling, domains oriented randomly, b) during poling, c) after poling [2]

If the material posses polarization even without applying electric field, then this polarization is called spontaneous polarization. Generally, rhombohedral symmetry has eight spontaneous polarization directions along <111> directions, tetragonal symmetry has six spontaneous polarization directions along <001> directions, orthorhombic symmetry has twelve spontaneous polarization directions along <011> directions. Consider the figure below for a better view.

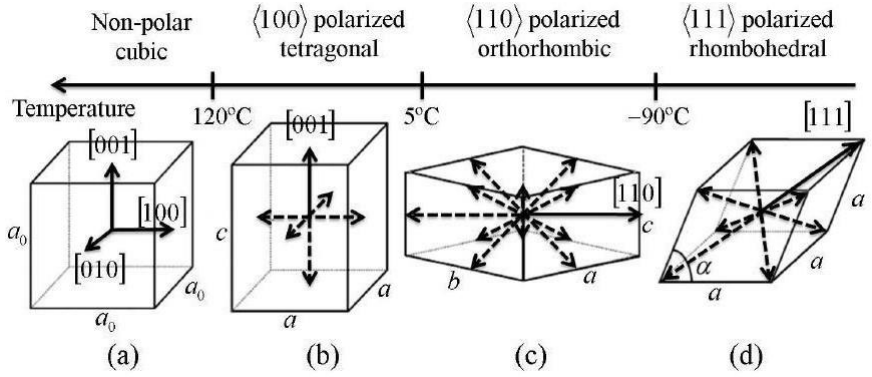

Fig 1.8: Phase transformation in barium titanate [3] (a) Cubic crystal system, (b) Tetragonal system with 6 crystal variants, (c) Orthorhombic system with 12 variants, (d) Rhombohedral system with 8 variants.

Considering the angle between these spontaneous polarizations, we can have different domain walls. For rhombohedral symmetry, the angle between spontaneous polarizations are 70.5°, 109.5° and 180° domain walls. For tetragonal symmetry, the angle between sponataneous polarizations are 90° and 180° domain walls. Poling can induce the spontaneous domains to change accordingly to the direction of electric field applied. Observe the same as shown below.

Crystal phase	Polar directions	Poling direction	Engineered domain configuration	Exist domain walls
Rhombohedral (R)	⟨111⟩	[001]	4R	109°, 71°
		[011]	2R	71°
		[111]	1R	Single domain
Orthorhombic (O)	⟨011⟩	[001]	4O	90°
		[011]	1O	Single domain
		[111]	3O	60°
Tetragonal (T)	⟨001⟩	[001]	1T	Single domain
		[011]	2T	90°
		[111]	3T	90°

Fig. 1.9: Domain engineered by changing poling [4]

1.2.3 Domain engineering

A method needs to be developed for much better electromechanical responses from these materials. Hence a domain change can be done by applying poling in different directions. This method of controlling the domain configuration is called "Domain Engineering". This electric field induction produces domain wall motion and hence domain engineering. This domain engineering can be achieved either by changing the compositions of the crystal or by changing the poling conditions of the crystal. Changing chemical composition involves the development of relaxor ferroelectric materials and doping of the material. Changing poling direction can help us in engineering domain and domain wall configuration.

Crystal	T_c(°C)	T_{RT}(°C)	E_c(kV/cm)	K_{33}^T	d_{33}(pC/N)	k_{33}	Q_m
PMN-0.29PT (Gen I)	135	96	2.3	5400	1700	0.91	150
PMN-PT (MPB) (Gen I)	155	65	2.8	8200	2800	0.95	100
PIN-PMN-PT (Gen II)	191	125	5.0	4400	1500	0.92	180
PIN-PMN-PT (MPB) (Gen II)	197	96	5.5	7200	2700	0.95	120
Mn: PIN-PMN-PT (Gen III)	193	119	6.0	3700	1100	0.90	800
Mn: PMN-PT (Gen II)	203	141	6.3	3400	1100	0.92	1050

Fig. 1.10: Domain engineered by changing chemical composition[5]

1.2.4 Curie Temperature, T_c

At certain point of temperature, above which the ferroelectric material changes to cubic symmetry crystal. That means it has either all centrosymmetric crystals with no dipole moments or overall net polarization becomes zero by cancelling out all polarization vectors. This is also called a paraelectric phase. This point of temperature is called curie point temperature (T_c). Below curie point temperature, these crystals can be in teragonal or rhombohedral or some other minor forms of phases like orthorhombic and monoclinic phases.

1.2.5 Morphotropic Phase Boundary, MPB

Researchers found that, a way to improve piezoelectric capabilities is by changing the crystal composition. In this process, they found a region called Morphotropic Phase Boundary (MPB), in which these materials seems to show high piezoelectric responses. This region is found to separate to crystal symmetries that are rhombohedral and tetragonal. This region can contain extra phases like orthorhombic and monoclinic. Therefore, an intensified research is going on to understand these parameters. The morphotropic phase boundary (MPB) denotes temperature-independent phase transitions caused by changes in composition. The research work on morphotropic phase boundary were started on Lead Zirconate Titanate (PZT) solid solutions. And after successful work on PZT, the relaxor materials like Lead Magnesium Niobate – Lead Titanate (PMN-PT) and Lead Zirconate Niobate – Lead Titanate (PZN-PT) single crystals were used for further improvements. Typically, all these materials show similar phase diagrams. These works

helped in improving the performance of these crystals in applications like the piezoelectric transducers.

At morphotropic phase boundary, we can observe better piezoelectric responses because of coexistence of differenet phases in this region, which is stated by several researchers. Generally, coexistence of two or more phases can be slightly less stable than a mono phase crystal structure. This coexisitence is possible by having different spontaneaous polarizations that can be rotated between possible symmetries. Check out the following phase diagram of PMN-PT solid solution.

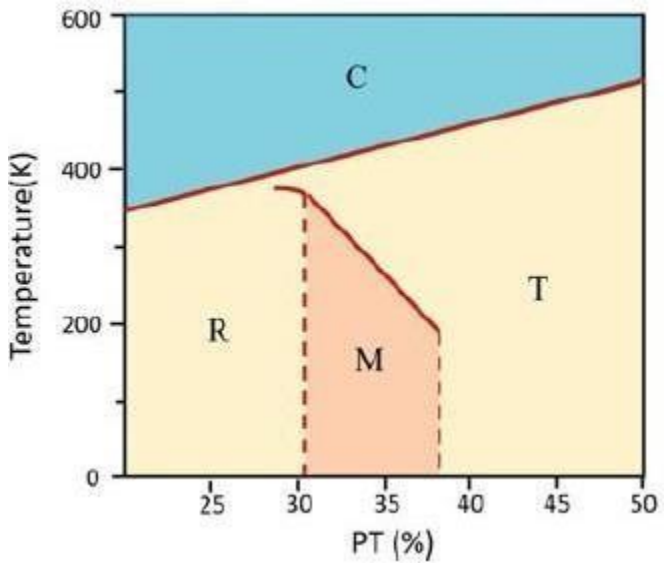

Fig. 1.11: Typical phase diagram of PMN-PT single crystal [6]

For PMN-PT, this region is typically between 30% to 35% of PbTiO_3 and 8% to 15% of PbTiO_3 for PZN-PT single crystals.This shows that morphotropic phase boundary is typically a range rather than a single line, which can be observed from the phase diagram above. Consider a PMN- 0.28PT single crystal, this consists of a rhombohedral symmetry. After applying poling in [001] direction i.e., by applying electric field, we can observe that another phase like orthorhombic is got induced. It is worth to note here that this existence of multiple phases and multiple domains helps in having high piezoelectric coeffiecient, and electromechanical coupling factors.

1.3 Relaxor Ferroelectric single crystals

Relaxor ferroelectric materials were made by sharing B-site of their perovskite structure (we will discuss it in the sub sections) with two atoms. They have a complex domain structure than compared to that of a normal ferrolectric material. In this project, we have used PMN-PT single crystals, which was formed by a relaxor ferroelectric PMN and normal ferroelectric PT. These kind of formation of ferroelectric material can be able to exhibit high values of electromechanical coupling factors about 0.85-0.95 than compared to that normal ferroelectrics which has about 0.6-0.8 only. Electromechanical coupling factor means the ratio between converted electrical energy and supplied mechanical energy. Then better the electromechanical coupling factor, better the usage of these materials in different applications. These materials also known to show the phase transition from ferroelectric to paraelectric at temperature range called curie range but not a temperature point called curie point as in normal ferroelectrics. Lets discuss the structure of a perovskite, hysteresis and butterfly loops, and finally concludes the basic introduction with some applications in which we can use these kind of ferroelectric materials.

1.3.1 Perovskite structure

Perovskite name belongs to a mineral called Calcium Titanate ($CaTIO_3$). These are a group of ferroelectrics that are commonly seen to be studied. Its general chemical formula is $AB^1B^2O_3$ or ABO_3. Where A site is occupied by smaller cations like Ba^{2+}, Ca^{2+}, Na^{+}, Pb^{2+}, etc., at corners of the crystal structure has a coordination number of twelve, while B site is occupied by larger cations like Zr^{4+}, Zn^{2+}, Mg^{2+}, Co^{2+}, Nb^{5+}, Ti^{4+}, etc., at the center of the crystal structure has a coordination number of six, while O oxygen atoms were occupied at the face centers of the crystal structure. In a simple cubic structure, these can be regarded as the arrangement of BO_6 molecules.

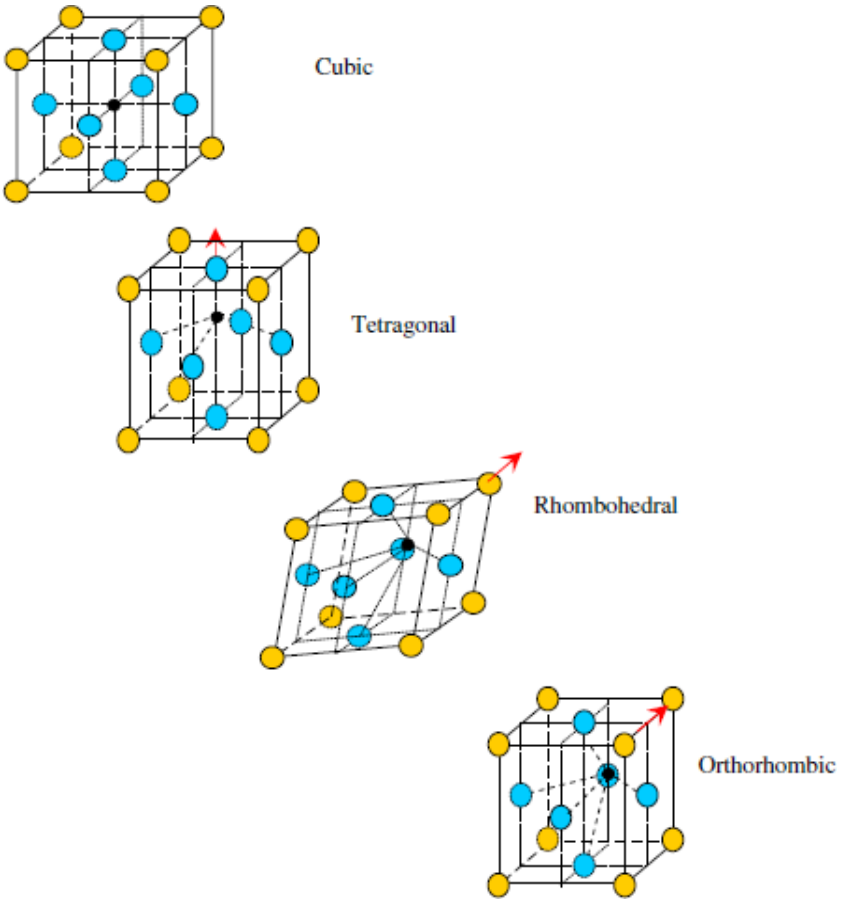

Fig. 1.12: Perovskite structures of different available symmetries in the ferroelectric materials [7]

From the figure above, we can see the different structures for different symmetries. We can change the symmetries by either changing the composition of $PbTiO_3$ in materials like PMN-PT, PZN-PT or by changing the temperature. Polarization vector is directed usually from oxygen to B-site atom. Also observe the spontaneous domains (indicated by red arrows), they are different for each symmetry. These materials tend to bend towards the direction of polarization in general. In morphotropic phase boundary region, we can observe the coexistence of multiple phases within the material and so there will be multiple perovskite structures be available within the material. Point group symmetries helps in defining the possible number of variants or properties of the material. Different classes has different point groups. For example, rhombohedral has 3m, tetragonal has 4mm, orthorhombic has mm2 etc.

1.3.2 P-E and S-E loops

Under the application of electric field (E), there will be polarization direction and magnitude change will occur depending on the direction and magnitude of electric field. The crystals will tend to deform in the direction of polarization. This produces a strain in the body. These polarization and strain changes are not irreversible and do not cause hysteresis but domain wall motion helps in producing the hysteresis. Domain wall motion or sweep helps in producing the change in polarization direction with in that volume. See the figure below, for better visualization of P-E hysteresis loop. Initially, consider a piezoelectric material on which we want to show a hysteresis loop. Increase in electric field makes the randomly oriented domains to get reorient in the direction of applied external field. And the polarization reaches a saturated value called saturation polarization (P_{sat}). Also spontaneous polarization can be calculated by linear interpolation from saturation polarization. At this saturation polarization almost all dipoles are in the direction of applied electric field. When the electric field is removed and becomes zero, there will still be a polarization remained in the material called remanent polarization (P_r). When we turn the electric field in the opposite direction and applies it until the domains align in the new directions and the polarization reaches a zero value, then such electric field we have to apply is called Coercive field (E_c).

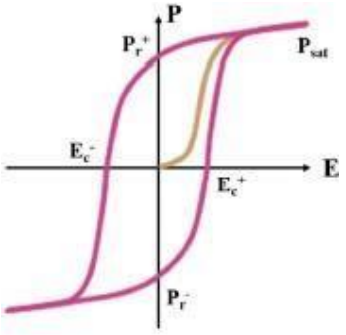

Fig. 1.13: Hysteresis P-E loop [8]

And as we increase the electric field, it reaches a saturation polarization which is almost 180° to domains at first saturation polarization. Reversing electric field now produces domains to reorient to initial saturation polarization forming a hysteresis loop. Besides polarization , strain also gets injected with the external electric field and in the similar way, we can observe the hysteresis loop called butterfly curve. Strain is symmetrical about y axis i.e., 180° change in electric field does not produce any change in strain. Non 180° domain switching (produced either by external stress or electric field) produces internal stress. These internal stresses will later help cracks to grow or to stop (i.e., switching toughening or switching weakening)

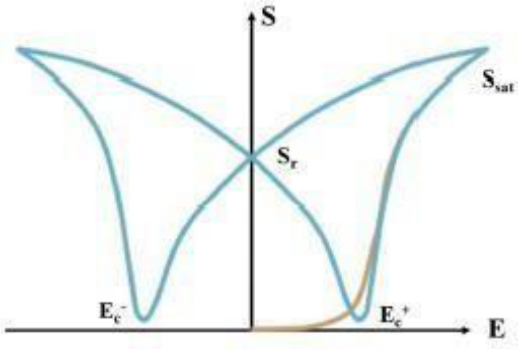

Fig. 1.14: Butterfly S-E curve [8]

1.3.3 Single crystal preparation

Since the discovery of these materials, there were several methods employed to develop the poly crystal materials. Later, researchers found out that these single crytals show high electromechanical properties. In general, it's so hard to manufacture a long single crystal, which results in small, thin sample preparations. Small samples mean it's hard to measure their properties. Several manufacturing methods were used to grow these single crystals of which Bridgman technique is extensively used to prepare single crystals which are a growth from melt type of method. Here are some conventional techniques to manufacture these materials:

1) Growth from Melt: This method is based upon the solidification and crystallization of melted material.

   Ex : Czochralski and **Bridgman** methods

2) Growth from Solution: This method is based upon dissolution of material to be crystallized within a suitable solvent or flux (*PbO*, PbF_2, Bi_2O_3, Li_2O, ….)

   Ex: **Flux – Growth** method

3) Growth from Vapor Phase: This method is based upon fabrication of thin films over substrates.

   Ex: Sublimation method

Crystal growth rate is in the increasing order of: vapor phase, solution and melt. Crystal quality is in the increasing order of: melt, solution and vapor phase. Some of the most used single crystal manufacturing techniques are flux growth and bridgman methods.

In flux growth method, there are two processes. In process 1, PbO, MgO, Nb_2O_5, TiO_2 and B_2O_3 are directly mixed in an alumina mortar with 100ml alcohol. Dried in an oven. 100g of this paste is added to platinum crucible. Placed in small alumina crucible. Then placed in large alumina crucible. And in process 2, Pbo, MgO, Nb_2O_5 mixed and presintered at 950 ℃ for 3h. This paste is grounded and mixed with Pbo, TiO_2 and B_2O_3. 100g of this paste is added to platinum crucible. Placed in

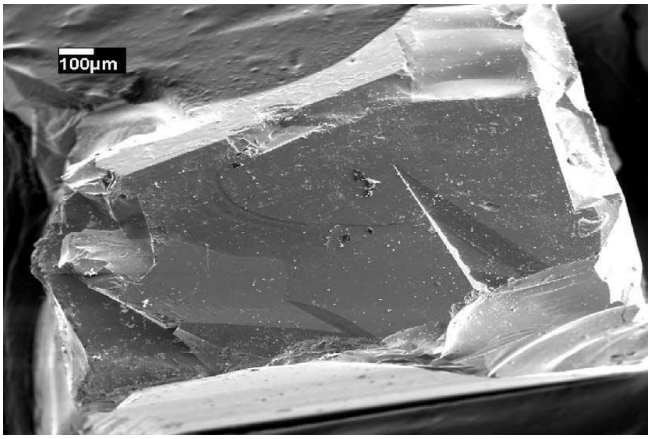

Fig. 1.15: Morphology of PMN-PT single crystal [9]

small alumina crucible and added some PbO, MgO powders sprayed on top. Then placed in large alumna crucible. All this mixing is done in a furnace heated from room temperature to 1150 ℃ in 7h. Maintained at 1150℃ for 4h to reach homogeneity of solution. Cooled at 2℃/h to 850 ℃. Cooled to room temperature at 100℃/h. Now crucible removed from furnace. Weighed and rinsed with boiled 50% nitric acid for over 20h to separate single crystals from residual flux.

In bridgman method, high purity PbO, MgO, Nb_2O_5, TiO_2 were mixed by ball-milling with zirconia balls in ethanol for 5h and dried at 90℃ for 2h. Starting material (sintered PMN-PT ceramic) is placed in a platinum crucible along with seed crystals. This crucible is placed in a furnace with sharp temperature gradient (50-100 ℃/inch). Crucible is pulled through furnace and then seeds promote single crystal growth. Growth runs for 7-14 days. Crystal boule formed with diameter is equals to 4cm, length of boule is greater than 7cm. This boule is cut to several single PMN-PT crystals of different orientations and compositions. Its limitations include, along boule length, missing crystal homogeneity (composition gradient along boule). This causes piezoelectric property variation along boule, Lowers the yield of high-performance material

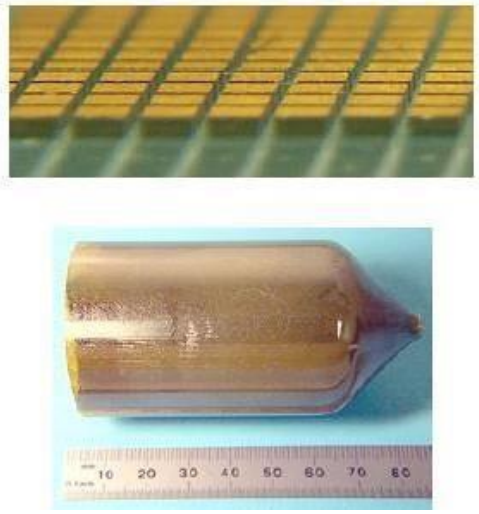

Fig. 1.16: PMN-PT crystal boule grown by Bridgman method [10]

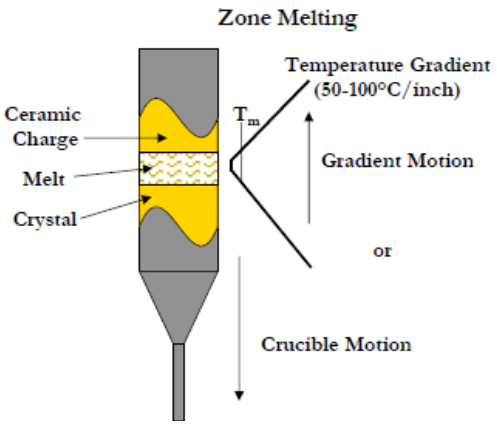

Fig. 1.17: Zone melting method setup [10]

growth per run. These increases cost. This issue can be solved by having different melting zones (Zone melting method). Only difference here is the "only a portion of ceramic starting material is melted at any one time, limiting chemical segregation". This increases composition uniformity. Continuous feeding crystal growth can be used. Able to produce 4-6 boules per month.

1.3.4 Applications

Reasearch on these ferroelectric single crystals were keep going on in the basis of application oriented. PMN-PT single crystals being a ferroelectric show all the properties of piezoelectric, pyroelectric and ferroelectric. These materials were extensively used in the applications having mechanical – electrical energy conversions. The development of advanced piezoelectric devices will benefit from the successful, rapid expansion, high-quality PMN-PT relaxor ferroelectric single crystals. There are numerous successful applications of high piezoelectric performance PMN-PT single crystals currently available, some of which have even evolved into commercial devices. The most common application of piezoelectric material is gas lighter, in which piezoelectric crystal is hit by external force and results in electric spark is generated. Other applications are watch, tennis racquet, actuators, mechanical energy harvesting, substrates, on screen figure print sensors etc. The other applications

including hydro-acoustic transducer, medical ultrasonic imaging, piezoelectric actuator, piezoelectric transformer, heat energy harvesting, infrared detector.

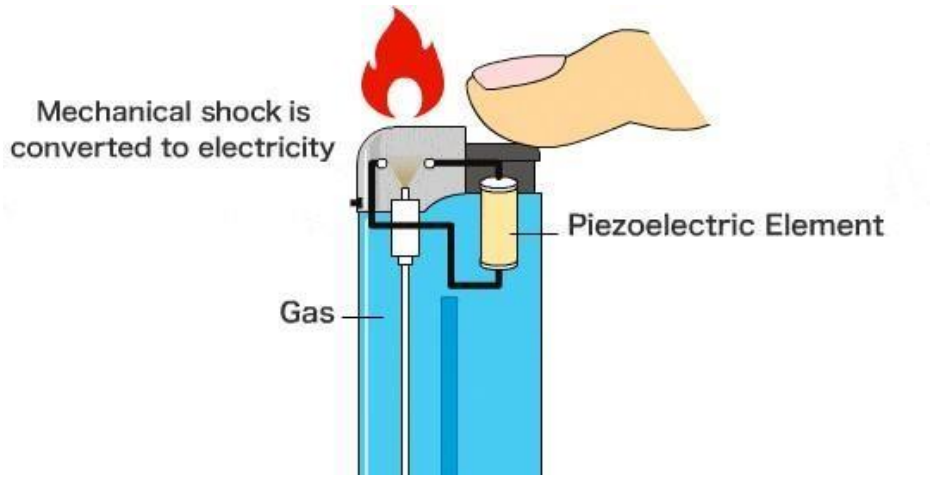

Fig. 1.18: Gas lighter [11]

1.4 Motivation for this work

Now a day's application of piezoelectric materials has suddenly increased in various fields. Mechanical properties and electromechanical response of piezoelectric materials is greatly influenced by its microscopic characteristics. Thus, polarization switching under mechanical loading and thermal loading i.e., annealing is of practical importance.

1.5 Organization of the thesis

This thesis is organized into following chapters:

In chapter 1, introduction to piezoelectricity and its parameters and their applications has been discussed.

In chapter 2, summarizes review of the relevant literature available on microstructure, electromechanical properties of piezoelectric materials.

Objectives and methodology of the present research work are also presented in this chapter.

In chapter 3, presents experimental results, microstructural analysis, and evaluation of the electromechanical properties and observed the domains under different thermal conditions.

In chapter 4, results obtained from the work have been discussed.

In chapter 5, presents conclusions and possible avenues to extend this research work in future.

Chapter 2

Literature Review and Problem Formulation

Since the invention of piezoelectric materials, they have been a very attractive area for various researchers in the field of various applications involving mechanical energy and electrical energy conversion processes. Still they are not still understood well enough, to use them at their peak performances. Let us see some past work, which helped in the experimental and analysis of this research work.

2.1 Past Work on Piezoelectric Materials

Shang and Tan [12] observed butterfly shaped *domain switching under the presence of stress* induced by Vickers microindentation. They have used (010) oriented PMN-0.35PT, which is in morphotropic phase boundary region with tetragonal as the dominant phase. They have observed domains by the use of a Transmission Electron Microscope (TEM) and a cross polarized light.

Song et al. [13] has done microindentation of 200g on PMN-0.35PT single crystal and observed same butterfly shaped domain switching as in [10] but they regarded it as a plastic deformation zone. They observed the domains by using equipment called Scanning Electron Acoustic Microscope (SEAM). The three major responses observed here are plastic deformation underneath the indenter, cracks got extended by increasing loads and newly formed 90° lamellar domains, which helps in relieving the stress and increasing the toughness.

Y. Hosono et al. [14] has done microindentation experiments on PZN-0.09PT which were prepared by solution bridgman method. Under these experiments they have observed that critical fracture toughness value is higher in the direction vertical to the domain wall than compared to the critical fracture toughness value in direction parallel to the domain wall i.e., *domain wall stops the propagation of induced cracks.*

Z. J. Xu et al. [15] performed his research on PMN-0.38PT single crystals and calculated piezoelectric coefficients (d_{33}) along <001>, <110> directions, which showed d_{33} is high along non spontaneous direction <110>. They also observed that applied electric field in non-spontaneous direction has enhanced the piezoelectric coefficients than compared to that in spontaneous direction.

M. Gharbi et al. [16] performed some theoretical calculations on ferroelectric materials to understand the size dependent hardening when subjected to indentation. They find out that the phenomenon of *flexoelectricity* has to be the reason for this Indentation Size Effect (ISE).

Q. Wan et al. [17] performed experiments on (001) poled PMN-0.32PT single crystals under stress and electrical fields. Under electric failed, the material is found to show enhanced induced strain and piezoelectric coefficients at an optimized compressive stress. Under small compressive stress, the material is shown to exhibit shape memory feature i.e., able to repolarization after unloading low loads. As the compressive stress increases, the polarization is rotated through monoclinic states and reaches orthorhombic and tetragonal phases. Orthorhombic being unstable state, it recovers to rhombohedral stat while tetragonal is stable form of phase. The possibility of enhanced electromechanical properties could be due to intermediate states.

W. Zhang et al. [18] done nanoindentation experiments on both [100], [110] oriented PIN-PMN-PT single crystals to understand its mechanical properties. As maximum indentation depth (h_{max}) increases, the plastic residual percentage is found to increase. At each specific h_{max} , the plastic deformation is found to be high for [110] oriented crystal than compared to that of [100] oriented crystal. This

proves that these materials show anisotropic nature in its mechanical characteristics.

G. Singh et al. [19] observed the domains of unpoled (001) oriented PZN-0.09PT single crystal by a Polarized Light Microscopy

(PLM). It was found to have both rhombohedral and tetragonal phases. Dielectric measurements do not show rhombohedral to tetragonal phase transitions so they have used birefringence measurements to know the phase transitions. It was found to have 30 kelvin difference at phase transition between heating and cooling.

J. Xu. et al. [20] prepared both (001) and (111) oriented PZN-0.07PT single crystals and done both micro and nano indentations to understand its mechanical response. They observed that (111) showed better mechanical properties (microhardness (H), residual elastic modulus (E_r), fracture toughness (K_c)) than compared to that of on (001) plane. They have observed anisotropy on both mechanical and piezoelectric properties. K_c is found to be high when crack is perpendicular to domain wall, but it is low, when crack is parallel to domain wall i.e., *domain walls relieves the stress and restrains the crack development*. Piezoelectric responses are high for (001) crystals than (111) crystals. Based on applications, these materials can be selected.

D. Fang et al. [21] used a poled Barium titanate ($BaTiO_3$) single crystal to understand the interaction between domain switching and crack propagation under three point bending loading. They observed the cracks to be propagated in zig-zag motion forming 90° domains in front of the cracks. Using R-curve, they found that the formation of these 90° domains helps in increasing the fracture toughness.

H. F. Yu et al. [22] has done experiments of indentation on (110) oriented PMN-0.33PT single crystal. They have observed the topography by Atomic Force Microscopy (AFM). The stress by indentation, is relieved as plastic deformation underneath the indentor and along the indentor diagonal, as induced micro cracks, as non 180° domain formation. It was observed that 90° domains formation increases fracture toughness and increases piezoelectric properties.

P. Ramesh Babu et al. [23] observed stripe like domains along (110) on (001) oriented Sodium Bismuth Titanate ($Na_{0.5}Bi_{0.5}TiO_3$) single

crystal by using polarized light microscopy at room temperature. As temperature increases beyond Curie temperature (220℃), these stripe-like domains were found to be disappeared. But these striped domains reappeared with polarization reversal above 240℃, marking this as a transition from ferroelectric to ferroelastic.

P. Zeng et al. [24] prepared (001) poled, unpoled single crystals of PZN-0.07PT. After a successful berkovich nanoindentation, they have observed that the critical crack initiation load for negative surface is in between positive surface and unpoled crystals, with positive surface having high critical crack initiation load among all.

M. M. Chaudhri et al. [25] investigated the metals experimentally and understood that pileup affects the hardness values. Pileups also support the indenter load.

Jiang et al. [26], the mechanical reactions of [100 and [110] oriented poled PMN-PT ferroelectric single crystals under indenter loading were the subject of their research. Through a pop-in event, load–displacement curves of protrusions were recorded to indicate the yielding or inelastic performance in [100] and [110] oriented PMN-PT. When a Berkovich indenter was used for mechanical response testing, some other pop-in event was observed at a lower indentation depth than one for the elastic– inelastic transition, which could indicate a pressure-induced phase transition of the PMN-PT single crystals from rhombohedral (R) to tetragonal (T).

R. Le. Bihan [27] used $BaTiO_3$ single crystal to observe the ferroelectric domains at temperatures near curie point. He has observed a, c+ and c- domains. Difference in contrast of a,c domains is due to difference in work function which is due to difference in charge and crystal orientation. c domains tend to disappear after Tc-10 but a domains exist.

X. Li et al. [28] prepared PMN-PT, PIMN-PT single crystals to observe their dielectric and piezoelectric response at phase transitions. These phase transitions can be achieved by temperature change, applied

electric field, applied stress and composition change. Polymorphic phase transitions were found to have less temperature stability than morphotropic phase transitions. Presence of sates during phase transitions was found to be the real reason for the high piezoelectric properties near MPB.

E. Sun and W. Cao [29] showed that remanent polarization decreases with increase in temperature i.e., crystal tending to become paraelectric as we increase the temperature. They have observed (001) poled PMN-0.33PT to have monoclinic phase at room temperature, tetragonal phase at temperature above 62℃. Orthorhombic phase is known to be unstable than compared to other phases like rhombohedral and tetragonal.

Lu et al. [30] used KNN based single crystals and observed that annealing temperature has a negligible effect on crystalline structure but significant effect on domain structure, electrical properties, and surface morphology. At a specific annealed temperature (nearly 700℃) above Curie temperature (around 400℃), these materials tend to show high electrical responses.

K. H. Kim et al. [31] conducted ion milling on PMN-0.3PT and observed the micro domains, which is attributed to stress resulted by amorphization of surface layer. Whereas annealing samples have nano domain structures.

Vaibhav S. Kathavate et al. [32] performed nanoindentation experiments on pristine, partially annealed and fully annealed samples of PMN-PT ceramics and observed that partially annealed samples show high hardness and marginal increase in young's modulus and marginal decrease in piezoelectric coefficient (d_{33}). Fully annealed samples show marginal increase in hardness and zero d_{33}. Annealing effects the domain structure i.e., d_{33} decreases as temperature increases.

2.2 Identified issues from the literature

Some of the observed research gaps or issues from literature review are:

- Very few attempts were made to understand the mechanical properties of these materials.
- Most of the researchers work focused on the electrical responses by different electrical field conditions.
- The variation of hardness with load at a particular annealing state is not well understood.
- The effect of annealing temperature on domain configuration is not well understood.
- It is difficult to understand the role of domain configuration on hardness using single crystal PMN-PT.

2.3 Objectives and Methodology of the Present Research Work

Objectives involved in this research work are:

- To understand what are piezoelectric materials and their working principles.
- To perform the Vickers micro-indentation experiment on PMN-PT single crystals at different annealing temperatures in a direction anti-parallel to poling direction.
- To analyze their mechanical responses like hardness and fracture toughness at different loads and annealing conditions.
- To observe the crack flow on the indentation surface at a particular load and different annealing conditions.

Methodology used to achieve the identified research objectives of the present work is:

- A commercially available (001) oriented poled PMN-0.32PT was obtained from TRS Technologies of size 10 x 10 x 0.5 mm^3.

- X-Ray diffraction is done to observe the microstructure of this material, followed by a d_{33} measurement.
- This sample is cut into four equal sizes by using a slow speed diamond cutting tool.
- Three samples were annealed to a temperature of $0.6T_c$, $0.8T_c$ and $1.2T_c$ where T_c = 145℃ (Curie temperature), followed by d_{33} measurements on all four samples.
- Vickers micro-indentations with loads of 50, 100, 200 and 300 grams with four to six indents at each load were done.
- Observed the cracks on indentation sites by using Optical Microscope.

Chapter 3

Details of Experimentation

The (001) oriented poled PMN-0.32PT ferroelectric single crystals were grown by the improved Bridgman growth method and were commercially available from TCS Ceramics. First, we anneal the samples to different temperatures and then followed by Vickers micro indentation of four different loads and observing the surfaces by optical microscopes. In order to understand all these processes, we need a detail understanding of all these experimental procedures.

3.1 X-Ray Diffraction (XRD) Experiments

A high-resolution Rigaku RINT (SmartLab 2000) X-ray diffractometer is used to detect the x-ray diffraction patterns of the PMN-0.32PT single crystals. These patterns will be helpful in finding the crystal structure and phases of the samples. Cu/K radiation (= 1.54) is used in the XRD tests, which are carried out in the diffraction angle range of 10°–80°. A step size of 10 s and a scan rate of 0.01° are used to get a large number of counts and easily discern the closely spaced peaks. Some reference papers were used to index the peaks and identify the phases that correspond to them. A lot of other information like lattice parameters etc., can be calculated from this XRD analysis.

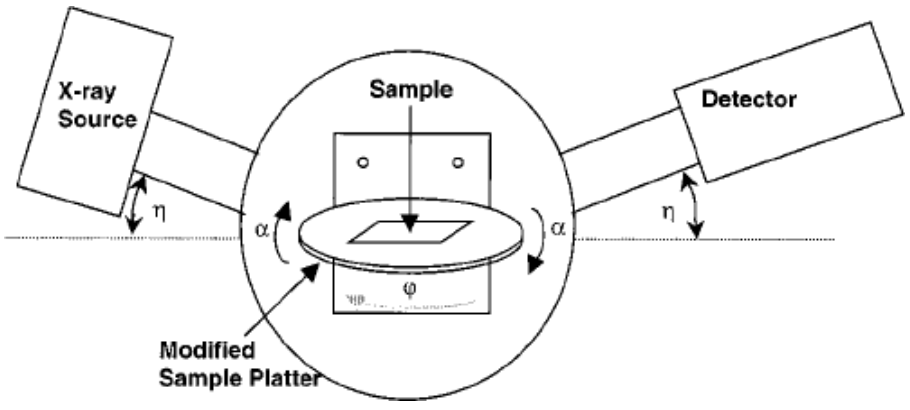

Fig. 3.1: Schematic diagram of an X-Ray Diffractometer [33]

3.2 Microindentation Experiments

To get the micromechanical characteristics, a quasi-static microindentation studies were carried out utilizing a Vickers pyramidal micro indenter. Vickers micro-indentations with loads of 50, 100, 200 and 300 grams with four to six indents at each load were taken. The holding time is for about 10 seconds. An optimum distance between indents is maintained, in order to avoid any interaction of strain fields underneath them or avoid any collisions of cracks between them.

Vickers Hardness (HV) is determined by the ration of indentation force (F) to the contact area (A).

$$HV = \frac{F}{A}$$

$$\text{Where, } A = \frac{d\text{^}2}{2\sin\left(\frac{136}{2}\right)} = \frac{d\text{^}2}{1.8544}$$

d = average indentation diagonal length

$$HV = 1.8544 \times \frac{F}{d\text{^}2} \ (\text{Kgf}/mm^2)$$

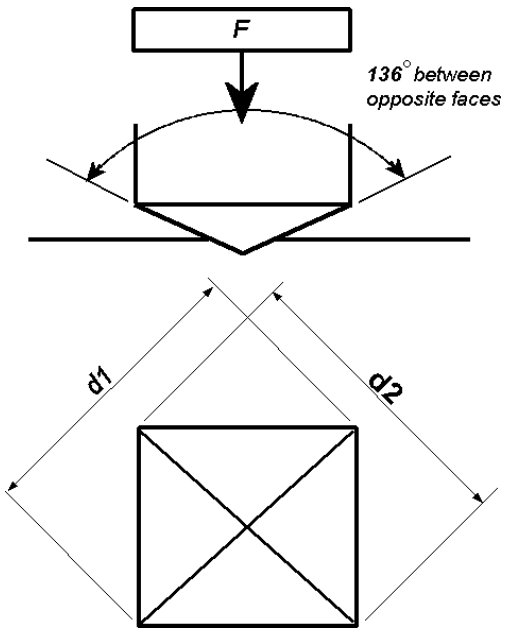

Fig. 3.2: Schematic diagram of a Vickers microindentation [35]

Fracture toughness formula taken from the reference [34] can be calculated as follows:

$$K_{IC} = 0.016 \times \frac{F}{c\text{^}1.5} \times \left[\frac{E}{HV}\right]^{0.5}$$

Where, c = average half crack length

E = young's modulus

Polishing up to 0.25μm diamond paste is done well on all the available samples in order to get the mirror polishing. These samples then cleaned ultrasonically in a RO water. This will help in observing the surface clearly with a better contrast using optical microscope, to get better accurate results. Piezoelectric coupling coefficient, d_{33} values of the samples were measured by using d_{33} meter (APC International ltd.).

Chapter 4

Results and Discussions

This chapter presents the results of our obtained experimental investigations conducted on various PMN-0.32PT single crystals along with their discussions.

4.1 Characterization of crystal structure

The fact that PMN-0.32PT compositions are closer to MPB compositions may explain the chance for the presence of multi-phase coexistence with reference to several researches. Then indexing is done

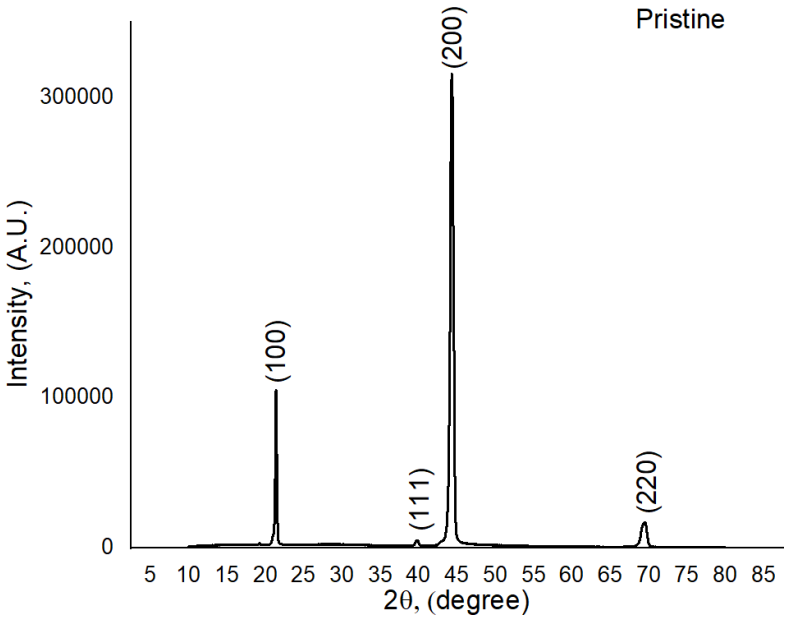

Fig. 4.1: XRD pattern for a pristine sample

Earlier works shown that PMN-0.32PT has a dominant rhombohedral structure. From the above pattern, we can observe that it is a single crystal of PMN-PT.

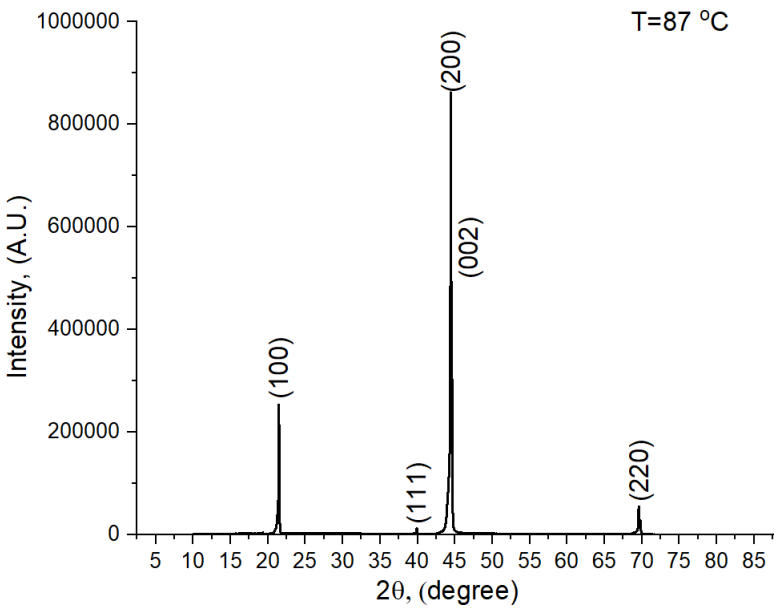

Fig. 4.2: XRD pattern for sample with Annealing temperature = 87℃

The above pattern at annealing temperature of 87℃ shows a peak splitting at 2θ = 44.8°. This shows that it has a tetragonal phase.

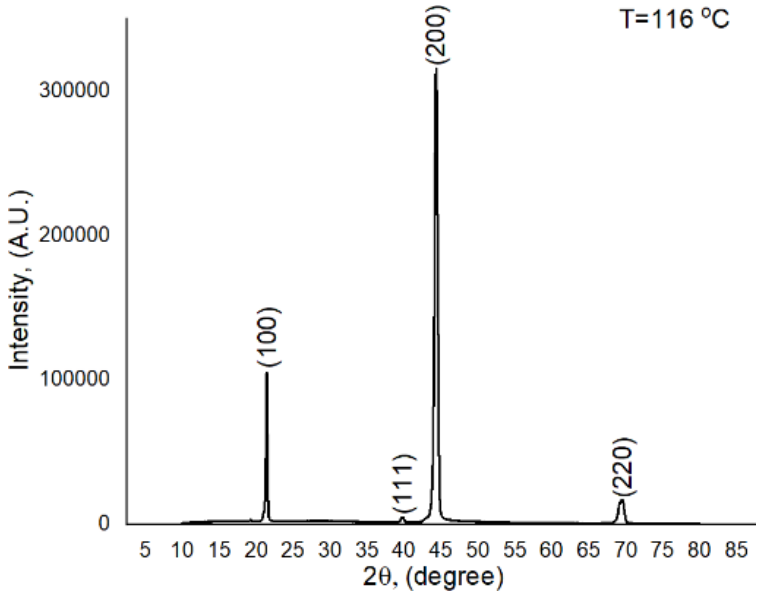

Fig. 4.3: XRD pattern for sample with Annealing temperature = 116℃

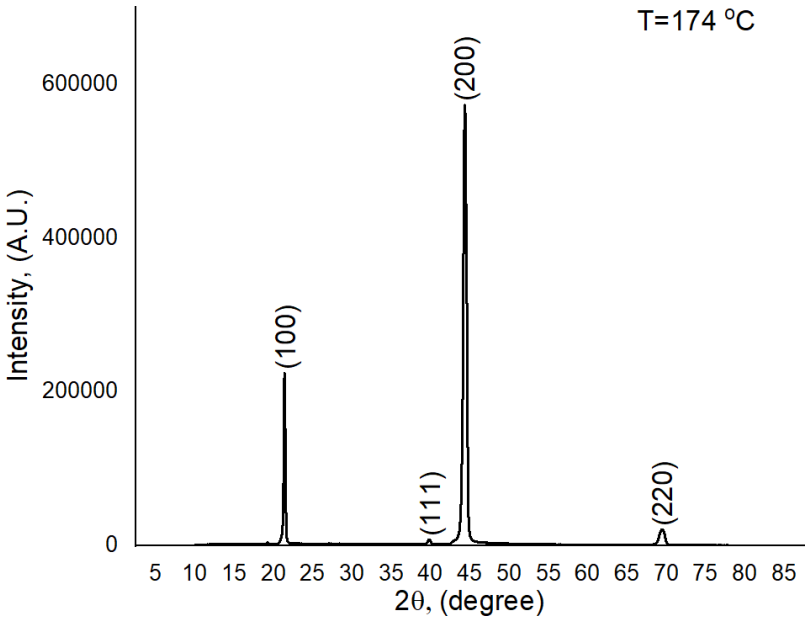

Fig. 4.4: XRD pattern for sample with Annealing temperature = 174℃

The above last two figures show that there can be a possibility that phase got restored back to a dominant rhombohedral phase. There could also be some minor existence of meta stable phases which helps in dominant piezoelectric properties of these materials in morphotropic phase boundary region.

4.2 Characterization of microstructures

Initially before cutting the sample into four equal pieces, the piezoelectric coefficient d_{33} is found to be 1710±20 pC/N. Whereas after cutting and annealing each sample to different temperatures, the piezoelectric coefficient value for pristine was found to be 331±25 pC/N, piezoelectric coefficient value for sample with annealing temperature of 87℃ is 344±12 pC/N, piezoelectric coefficient value for sample with annealing temperature of 116℃ is 344±12 pC/N, piezoelectric coefficient value for sample with annealing temperature of 174℃ is 2±7 pC/N. These values are as shown in the table below,

Sample No.	d_{33} (pC/N)	Temperature (°C)
1	331±25	Pristine
2	344±12	$0.6T_c$=87
3	132±5	$0.8T_c$=116
4	2±7	$1.2T_c$=174

Table 4.1: Variation of d_{33} with different annealing temperatures

This trend of decreasing piezoelectric coefficient value with increasing annealing temperature shows that there is a decrease in overall polarization in these single crystals. Above curie point temperature, the piezoelectric coefficient almost becomes zero showing that net polarization tends to zero which results in having a centrosymmetric crystal structure i.e., a conversion from ferroelectric to paraelectric structure is clear from this observation. The same result can be observed from the polycrystal PMN-PT from the reference [32], showing that domains get effected by changing to different annealing conditions.

4.3 Analysis of load-hardness and load-fracture toughness curves

The load vs hardness curves obtained after microindentation for different annealed samples were shown in the fig. 4.5. Here there is no reverse indentation size effect, which can be due to no surface irregularities were produced during sample preparation. These perfect single crystals were made by TRS Technologies by using the Bridgman method. At a specific annealed condition, there is a specific trend here is

that, hardness keeps on decreasing with increasing loads, but then hardness goes to a constant value after a load of nearly 1.5N. This trend is generally called as normal Indentation Size Effect (ISE). In general, in metals the indentation size effect was found to be by geometrically necessary dislocations. But in piezoelectric materials, it was found that flexoelectric phenomena, domain switching responses were added chances for the possibilities of indentation size effect. Compared to polycrystal materials, these single crystals lack grain boundaries, producing less complicated structure and might help in Besides indentation size effect, we can observe here how harness is varying with respect to load at different annealing conditions. In piezo ceramics its observed that hardness values for sub annealed samples is high because of their high elastic recovery, also could be due to their less porosity, cracks than compared to that of fully annealed and pristine samples. But in these ferroelectric PMN-0.32PT single crystals, the difference in hardness values at different annealing conditions is almost found to be negligible. This can be due to negligible difference in elastic recovery of every sample at different annealed conditions. Also, a minimal porosity and crack formation inside the crystals could be a possible reason for their minimum differences in hardness values. At high temperatures, the lattice strains were tended to produce with in the crystals. Thermal aided relaxation mechanism had a very less effect in changing the hardness values in ferroelectric single crystals.

Still there is a deep understanding of these materials under different loading conditions like thermal, mechanical and electrical is required on the basis of domains and their switching for their better under different applications. We can observe the domains beneath and around the indentation area by using suitable equipments like Polarized optical Light Microscope (PLM) or Piezoresponse Force Microscope (PFM). Hardness can also be affected by change in phase transitions. So, any further study of domains and phase transitions in these single crystals will significantly help in the research of these single crystal materials. Observe the load vs hardness and load vs toughness curves as shown below,

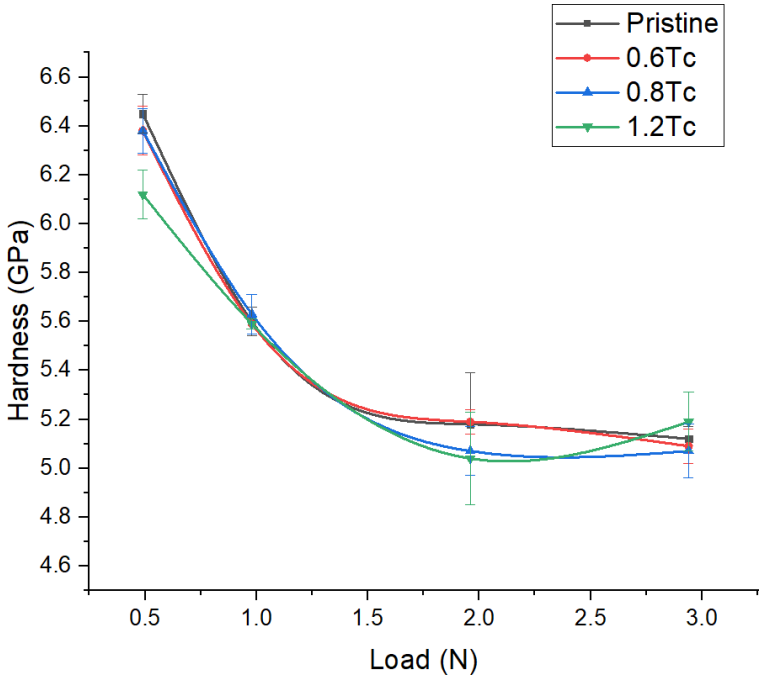

Fig. 4.5: Variation of hardness values with the indentation load of different annealed samples

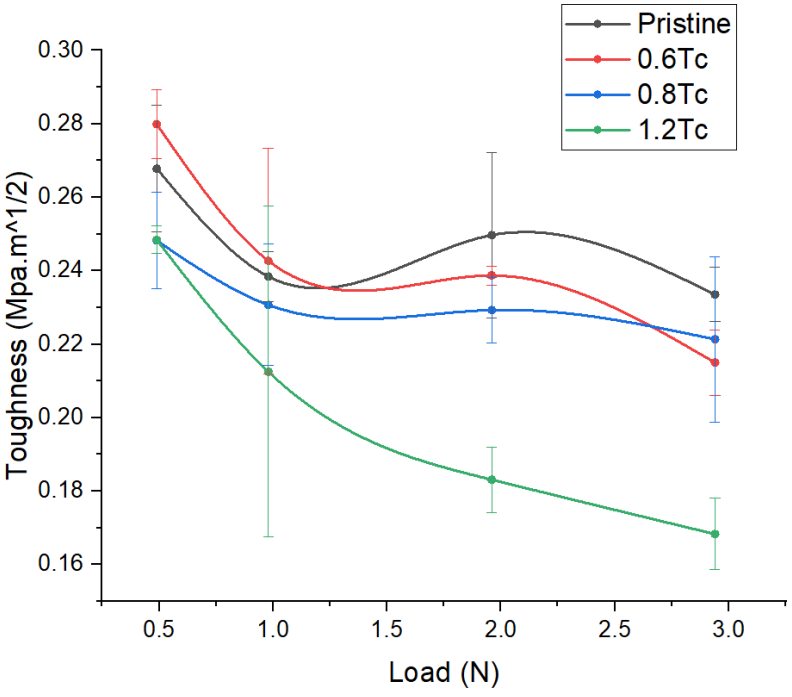

Fig. 4.6: Variation of fracture toughness values with the indentation load of different annealed samples

Fracture toughness is an important property of a structural material that indicates its resistance to cracks and is determined by the amount of work required to fracture it. The above load-fracture toughness curve shows that as the indentation load increases, the toughness values decrease. That is as we increase the amount of load, their ability to resist against the crack propagation reduces. We can also see that the fracture toughness of these single crystals decreases as the annealing temperature rises. Generally, the formation of 90° domain walls improve the toughening ability of the piezoelectric materials which was found out from some experimental results. From the previous research on piezoelectric materials, it is said that as we increase the annealing temperature, the decrease of 90° domain walls occur which results in decrease of toughness of these crystals. There is also a need to observe and understand the crack flow on the indented surface. Optical micrographs at a particular load of 300gms were as shown below for different annealed samples:

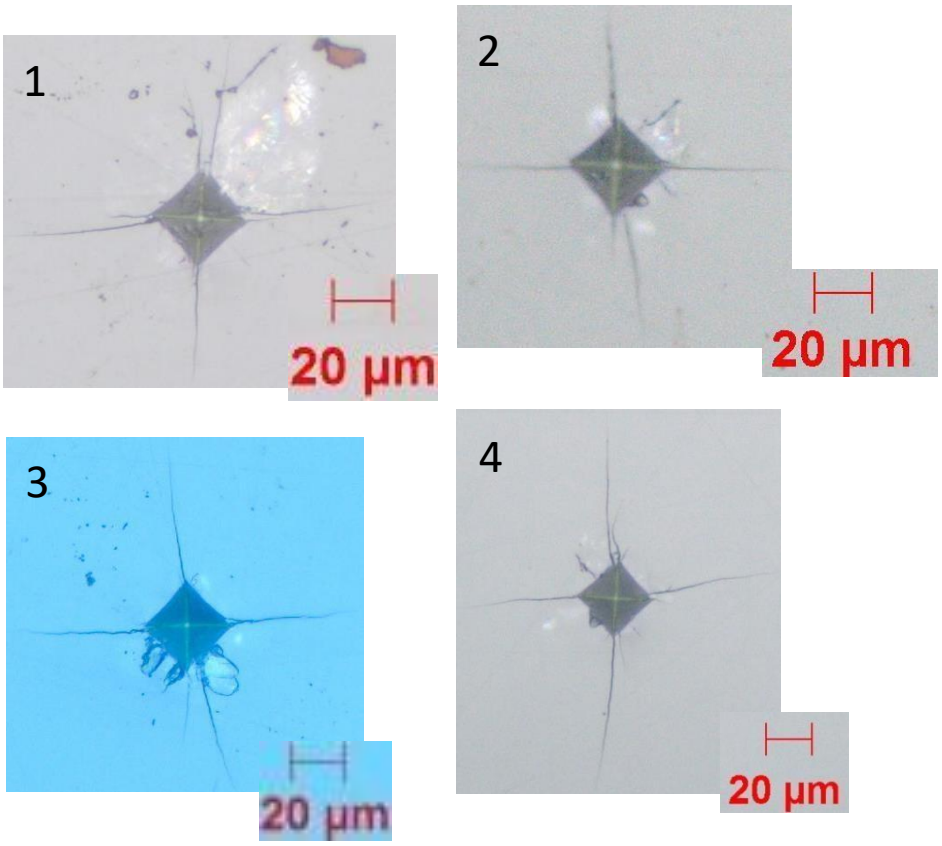

Fig. 4.7: Optical micrographs at a load of 300gm with different annealed samples with (1) pristine, (2) annealed temperature of 87℃, (3) annealed temperature of 116℃, and (4) annealed temperature of 174℃

Sample No.	T (℃)	A1	A2
1	pristine	112.92	121.44
2	87	122.88	128.66
3	116	134.83	126.18
4	174	166.07	143.25

Table 4.2: Variation of crack lengths with different annealing temperatures at a particular load.

Here A1 is the crack length along vertical direction, A2 is the crack length along horizontal direction of the shown indentation surfaces. At a particular load of 300g for all samples, the crack lengths at different annealing temperatures shows a specific trend here. That is the crack lengths increase with the load which we can observe same trend from load-toughness curve. We can conclude here that as the load increases the 90° domain walls tend to move away from the indented region. Further study of cracks can be fully utilized for their applications in electromechanical related technological industries.

Chapter 4

Conclusions and future work

4.1 Conclusions

The present work focusses mostly on the mechanical responses of the ferroelectric single crystal at different annealed conditions. In the process of experimentation, we have observed the response of these materials which were observed in the previous section. Here are the conclusions we can make from this thesis:

- The piezoelectric material and their working principle are well understood.
- The sample preparation for indentation is done.
- The XRD plot confirms the obtained crystal is single crystal and peak splitting shows the phase transition due to annealing.
- Annealing temperature above curie temperature makes the single crystal to go from ferroelectric to paraelectric.
- All annealed single crystals show indentation size effect, which could be due to flexoelectric phenomena, domain switching, dislocations.
- Toughness of the crystal decreases with the increase in annealing temperature. Crack length increase as the load increases.

4.2 Scope for further work

Following are some suggestions for further research:

- Observe the domain structure using Piezoresponse Force Microscopy (PFM) under different annealing conditions in a ferroelectric single crystal and understand their behavior towards all the external conditions that they are facing.

- Better mechanism of domain switching beneath the indenter is still need to be explored.
- Hardness and phase transition relations can be explored. Hardness values can be affected by any pileups which also needs to be explored.

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