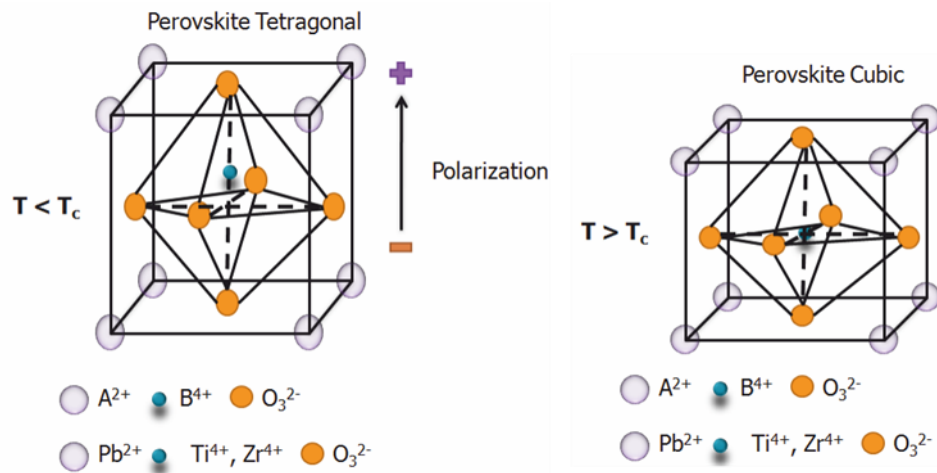


## SYNOPSIS

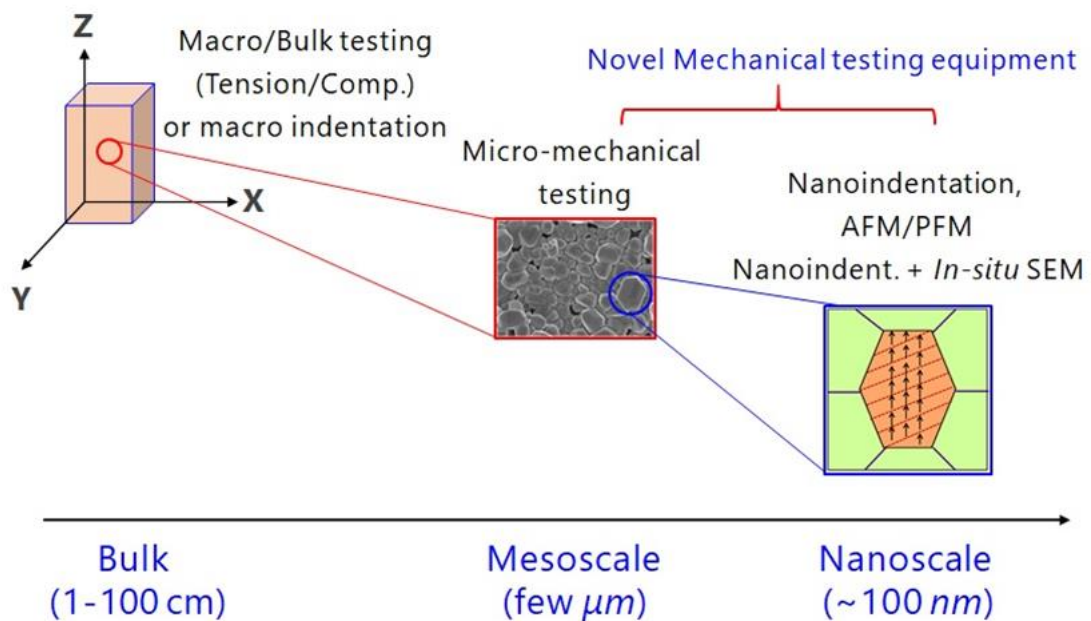
The technology at the driving seat of the 21<sup>st</sup> century is, of course, “*the nanotechnology*”, and the design of nanostructured materials with novel microstructural features for micro-electro-mechanical systems (MEMS) and nano-electro-mechanical systems (NEMS) is going to play a decisive role in the progress of this century. Of the several materials used in MEMS and NEMS, piezoelectric materials are arguably gaining wide attention in applications such as actuators, sensors and energy harvesting due to their inherent polarization and electro-mechanical coupling characteristics. The word “*piezo*” in Greek means “*to press*”, and “*electric*” has a Latin root “*electrum*” implies the flow of electrons. Therefore, piezoelectric materials are a class of materials that exhibit electricity upon external mechanical pressure (or vice versa), which further intermingles the electric and elastic fields. This piezoelectric behaviour is often seen in 20 non-centrosymmetric crystals (out of 32 crystal classes) whose centre of positive and negative charges are spaced apart, thereby creating a dipole effect to exhibit piezoelectricity. However, of the 20 piezoelectric crystals, 10 crystals show reorientation of dipoles upon an external electric field, known as “*ferroelectric crystals/materials*”, while the orientation of dipoles in the remaining 10 crystals can be changed upon an external thermal gradient, often known as “*pyroelectric crystals/materials*”. Therefore, essentially all the ferroelectric and pyroelectric crystals are piezoelectric. However, the converse is not true.

The piezoelectric materials used in actuators mainly contain ceramics of various compounds and exhibit  $ABO_3$  type perovskite structure, with “*A*” atoms occupying the corners of the unit cell, “*O*” atoms at the centre of six faces and “*B*” atoms at the centre of the unit cell. These perovskites exhibit rhombohedral, monoclinic, and tetragonal crystal structure below the Curie temperature ( $T_c$ ) based on their stoichiometric composition with respect to morphotropic phase boundary (MPB), thereby exhibiting the piezoelectric phase, while they possess a cubic symmetry above the  $T_c$  indicating the paraelectric behaviour of the material, shown in Fig.1. Conventional piezoceramics such as lead zirconate titanate (PZT) and barium titanate (BT) have a limited operating temperature range (i.e., 130 to 200 °C). Therefore, self-heating during service due to high frequency electrical and mechanical stresses may induce microstructural incompatibilities in the materials, which further deteriorates the electro-mechanical properties. However, the high-temperature applications of these piezoceramics in fuel injection systems, military impact fuzes, and structural health monitoring demand thermal and electro-mechanical stability. One way to mitigate this

problem is to alter the intrinsic microstructural features that span across  $\mu\text{m}$  sized grains to  $\text{nm}$  sized ferroelectric domains, presented in Fig. 2. Further, the addition of aliovalent acceptor/donor cations are reported to enhance the thermal stability (i.e., increase in  $T_c$ ) of Pb-based and Pb-free piezoceramics.



**Fig. 1** Schematic representation of  $\text{ABO}_3$  type perovskite unit cell of PZT piezoceramics.



**Fig. 2** Representation of microstructural length scales in piezoceramics.

Keeping this in view, polycrystalline systems of  $(\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3)$  (PZT undoped),  $\text{Pb}_{0.98}\text{K}_{0.02}(\text{Zr}_{0.47}\text{Ti}_{0.51}\text{Al}_{0.02})\text{O}_3$  (hard-doped PZT, abbreviated as PZT-H) and  $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Zr}_{0.47}\text{Ti}_{0.51}\text{Nb}_{0.02})\text{O}_3$  (soft-doped PZT, abbreviated as PZT-S),  $0.90(\text{PbMg}_{0.33}\text{Nb}_{0.66}\text{O}_3) - 0.10(\text{PbTiO}_3)$  (PMN-PT), and  $0.94(\text{NaK}_{0.5}\text{Nb}_{0.5}\text{O}_3) - 0.06(\text{NaTaO}_3)$  (NKN-NT- Pb-free) have been systematically investigated to understand the role of intrinsic microstructural length scales on their mechanical and piezoelectric behaviour.

In piezoceramics, the region of directionally aligned dipoles along distinct polarization directions is known as “*ferroelectric domains*”. The previous and recent studies [Mehta and Virkar, 1990, Haertling, 1999 and Wang et al., 2021] have indicated that the ferroelastic effects such as the orientation of the ferroelectric domains and domain wall (DW) motion have a pronounced influence on the piezoelectric and mechanical response of the piezoceramics.

Domain engineering (DE) is a technique used to enhance the electro-mechanical properties of piezoceramics by altering the ferroelectric domain configuration i.e., size, orientation, and interdomain spacing. Several ways of implementing DE technique in piezoceramics are as follows; (i) modifying the crystal structure *via* aliovalent cation doping, (ii) controlling the grain size, (iii) growing the nano-patterns of semiconductor thin films, (iv) altering remnant polarization, (v) imposing mechanical stresses during poling and (vi) controlled thermal annealing. Of all these techniques obtaining the different ferroelectric domain configurations *via* thermal annealing is quite economical and less tedious. However, one of the downsides of thermal annealing is the temperature-induced depolarization in the material. Therefore its use as a DE is limited, despite the applications of piezoceramics at elevated temperatures. Several studies have been highlighted the importance of DE, particularly on single-crystal piezoceramics, as the use of single-crystals rule out the complex interaction between ferroelectric domains and grain boundaries. However, most of the practical applications of piezoelectric materials are based on ceramic polycrystals. Therefore, one of the objectives of the present thesis is to investigate the effects of below- and above- $T_c$  thermal annealing on the ferroelectric domain configurations in polycrystalline piezoceramics. The piezoresponse force microscopy (PFM) is used to probe the differences in local ferroelectric domain configurations in PZT-H, PZT-S and PMN-PT, while piezoelectric charge coefficient,  $d_{33}$  studies are performed to probe the bulk response in other piezoceramics. The implementation of DE technique *via* selective annealing revealed the following observations; (i) distinct peak splitting is observed in X-ray diffraction (XRD) patterns of annealed samples, indicating the change in the ferroelectric domain structure (ii) annealed samples showed a transgranular cracking within the grains, (iii) degree of crystalline disorderness of ferroelectric domains increases with respect to annealing temperature and (iv) the  $d_{33}$ , converse piezoelectric charge coefficient,  $d_{33}^*$  and remanent strain,  $\varepsilon_r$  decreases with an increase in annealing temperature.

Though there have been several studies on understanding the role of domain configurations on electro-mechanical coupling characteristics, limited attention is given to investigate their influence on mechanical properties. During service, piezoceramics often experience variable mechanical loading conditions, particularly at high frequency, and it is important to understand the role of ferroelectric domain configurations on the mechanical behaviour of piezoceramics. Of the several mechanical properties, indentation hardness,  $H$ , a quick estimate of material's resistance to the plastic deformation, is the widely preferred technique due to the following advantages; (i) it requires a small volume of the test specimen and (ii) it is non-destructive (at small indentation loads, as the indentation impressions are confined to the smaller areas). Recent developments in instrumented indentation techniques (IIT) such as nanoindentation allows to obtain indentation load,  $P$  vs. displacement,  $h$  data from which it is possible to determine  $H$  and elastic modulus,  $E$ . During nanoindentation, the fully plastic regime in the material can be achieved even at low  $P$  (from several  $\mu N$  to few  $mN$ ). However, there is no comprehensive understanding of role of microstructural features on the  $H$  of piezoceramics despite the few studies which were focused towards understanding the fracture response (R-curve behaviour) [Mehta and Virkar, 1990 and Webber et al., 2009].

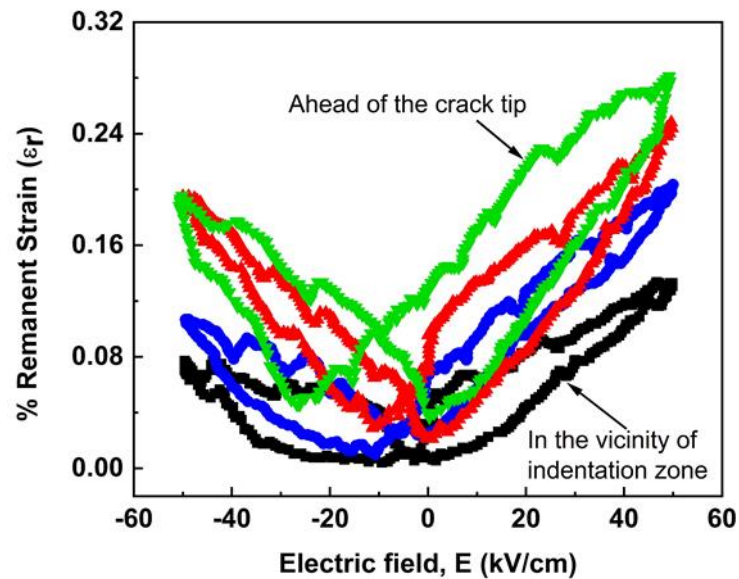
The limited bulk indentation experiments (mostly with the spherical indenters on PZT and BT samples) and nanoindentation simulations have observed that indentation response in piezoceramics is dependent on nature of the material (i.e., poled vs. unpoled), and type of indenter (i.e., electrically conducting vs. insulating) [Ramamurty and co-workers, 1999, 2009 and Cheng and Venkatesh, 2012]. However, these experiments are mostly used for validating the continuum level simulations and ignores the role of microstructural parameters (e.g., ferroelectric domain configurations and DW motion) on  $H$ . It is difficult to probe the mechanical properties with bulk indentation tests as the high indentation loads, often leads to cracking of materials. Therefore, it would be interesting to examine the effect of different ferroelectric domain configurations on  $H$  of the polycrystalline piezoceramics both at micro and nanoscale. The ferroelectric domain configurations are systematically varied by annealing the as poled (AP) piezoceramics at below and above the  $T_c$ , referred to as STD and ATD, respectively. The different ferroelectric domain configurations are characterized directly using piezoresponse force microscopy (PFM), which is also reflected in their  $d_{33}^*$  values. Following this, nano and micro indentation experiments are performed on AP, STD and ATD samples and the nanohardness is determined using Oliver and Pharr method while the microhardness is obtained from Meyer's approach. In PZT (undoped), PZT-H, PZT-S, and NKN-NT samples,  $H$  follows the following trend,  $H_{ATD} > H_{STD} > H_{AP}$ , while in PMN-

PT, it follows the trend as;  $H_{STD} > H_{ATD} > H_{AP}$ . In all the samples, the  $H$  decreases with increasing  $P$ , often known as indentation size effects (ISE). The underlying mechanisms responsible for the enhancement and anomalies in  $H$  and the occurrence of ISE are discussed in detail.

ISE in crystalline materials is attributed to indenter geometry, presence of high plastic strain gradients, nucleation of discrete deformation bands underneath the indenter, the surface free energy of the material, and high dislocation nucleation stresses. However, limited nanoindentation experiments on piezoceramics [Gharbi et al., 2009] have indicated that the presence of ISE in contact stiffness is mainly due to the strain gradient polarization (i.e., flexoelectricity). The ISE is analyzed with the help of analytical, empirical or semi-empirical models which enables to determine the load (or size) dependent and independent  $H$  from the indentation data. The critical analysis of nanoindentation data using classical Meyer's law, Hays-Kendall (H-K) approach, elastic recovery (ER) model, proportion specimen resistance (PSR) model, and modified PSR (MPSR) model lead to the following observations; (i) ISE in  $H$  of all the samples are sensitive to the differences in ferroelectric domain configurations, (ii) all the models show good agreement with the nanoindentation data, and (iii) true (or load independent)  $H$  values obtained from the ER, PSR and MPSR models are comparable to those obtained from nanoindentation experiments (i.e., machine  $H$  values).

During indentation, the material in the vicinity of the impression undergoes a significant amount of deformation, which may alter the ferroelectric domain configurations [Schneider et al., 2005, Park et al., 2007 and Wang et al., 2021]. Further, beyond a critical load, indentation causes cracking at the imprint corners, altering the texture of ferroelectric domains and is expected to influence the crack growth characteristics. To date, there is no clear experimental evidence on the ferroelectric domain configurations in the vicinity of the indentation imprint and near the advancing crack. In the present thesis, ferroelectric domain orientation maps and butterfly curves (remnant strain,  $\epsilon_r$  vs. electric field,  $E$ ) (Fig. 3) are generated in the vicinity of the indentation zone and crack front leads to the following observations; (i) The ferroelectric domains change their texture in the vicinity of the indentation zone, thereby exhibiting indentation-induced domain switching (IIDS), (ii) The ferroelectric domains ahead of the crack tip undergo a considerable change in domain configurations and some of which, based on the location, re-orient back to the initial configurations while some remain inelastic, (iii) The indentation fracture toughness,  $K_{IC}^i$

determined from the indentation imprints showed distinct dependence, albeit small, on the ferroelectric domain configurations.



**Fig. 3** The butterfly loops collected in the vicinity of the indentation zone and crack front.

In summary, the present thesis essentially centered on two parts; (a) altering the intrinsic microstructural features (e.g., ferroelectric domain configurations) of piezoceramics *via* selective annealing and (b) investigating the role of ferroelectric domain configurations on the mechanical and piezoelectric properties at micro and nanoscale.

The organization of the present thesis is as follows;

**CHAPTER 1** presents the introduction of piezoelectric materials, their crystal structure, and related fundamentals responsible for piezoelectric properties. Role of the complex interaction between the intrinsic microstructural features, particularly at lower length scales in the deformation behaviour of piezoelectric materials is difficult to understand and explained as the motivation for the present work. Keeping this in view, all the possible prior literature is presented with a focus on the theories that tailor the piezoelectric and dielectric properties in general and mechanical properties in particular, while specifically emphasizing the mechanical response of the piezoceramics under different structural states. Further, a brief overview of the nanoscale characterization techniques such as nanoindentation and PFM is presented. Finally, possible gaps in previous literature are identified to define the objectives for the present thesis.

**CHAPTER 2** describes the effect of selective annealing (DE technique) on the mechanical properties of PMN-PT and NKN-NT piezoceramics with different ferroelectric domain configurations. The underlying mechanisms of enhancement in mechanical properties in light of crystal structure and ferroelectric behaviour are discussed in detail.

**CHAPTER 3** presents the important results regarding the role of different ferroelectric domain configurations and aliovalent dopants on the mechanical behaviour of PZT (undoped), PZT-H and PZT-S. The toughening mechanisms such as IIDS and domain rearrangement in the vicinity of the indentation site are explained with the help of ferroelectric domain orientation maps. Butterfly curves (remnant strain,  $\epsilon_r$  vs. electric field,  $E$ ) are used to rationalize the results.

**CHAPTER 4** deals with the description of observed ISE in nanoindentation  $H$  of PMN-PT, PZT-H and PZT-S using the mechanistic models. The outcomes of the mechanistic modelling and origins of ISE in  $H$  are further explained in light of the differences in ferroelectric domain configurations.

**CHAPTER 5** presents the conclusions from the present work. The last part of this chapter gives certain directions for the future work from the mechanisms proposed in this study.