



# 1 Introduction

Lead zirconate titanate (PZT) based piezoelectric ceramics are currently the most used for manufacturing actuators, sensors, resonators, transducers and other electromechanical devices due to a combination of excellent piezoelectric properties, wider operating temperature range and a variety of other characteristics [1].

The major component for these piezoelectric ceramics which contributes about 60 wt% is the element lead (Pb). It is a soft element which is classified as a heavy metal and is also toxic. It has been used from as far back as the second century B.C in Rome when lead (II)-acetate  $[(\text{Pb}(\text{CH}_3\text{COO})_2)]$  was used for making wine because of its sweet flavor. Its harmful effects have been known for a long time ago because most of the deaths at the time were traced to it. Children are more susceptible to Pb attacks than adults because their central nervous system is more vulnerable. Lead has the ability to attach itself strongly to sulfhydryl group on proteins and distort the enzymes and structural proteins. It can also cleave to the ribophosphate backbone of transfer Ribonucleic acid (tRNA) catalytically with no evidence of a threshold and mimics or competes with calcium in the body. Some of the consequences of lead poisoning for children include; behavioral disorders, learning difficulties, low intelligence quotient etc. while hypertension and renal failure are some of the consequences of acute lead poisoning. Some of the sources of exposure to lead include leaded dishware, lead workers, electronics, paints, cosmetics etc. Recent studies indicate that there is no threshold for lead but  $10\mu\text{g}/\text{dL}$  is seen to be the acceptable blood levels. The primary way of prevention is the avoidance of contact with leaded materials [2].

Considering all these health problems posed by using lead-containing materials, multinational governments like the European parliament have enacted laws that ban their use for manufacturing many products [3]. Other governments are either considering similar laws or tightening controls on how these toxic materials can be used. In the field of electronic ceramics, concessions which will soon be subject to review were made because

the lead-free ferroelectric replacements still have inferior piezoelectric and electromechanical properties compared to those of lead-based ceramics.

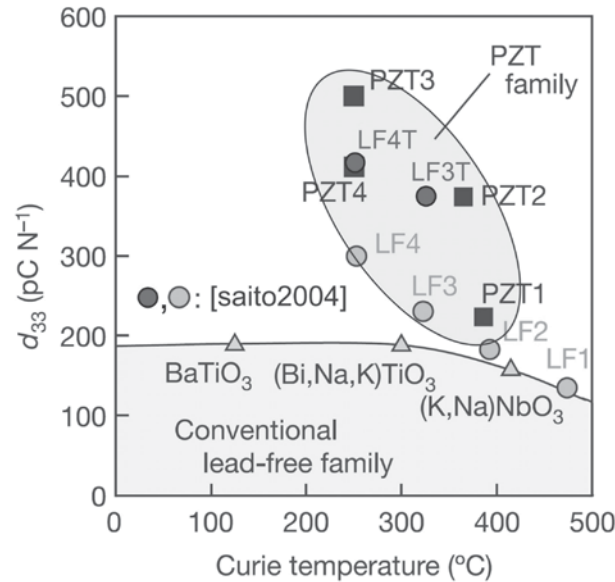


Fig 1.1 Comparison of the piezoelectric charge coefficient  $d_{33}$  at 25 °C among lead-free (LF) ceramics and conventional PZT ceramics as a function of Curie temperature [4].

Research on lead-free piezoelectric ceramics has been on-going for more than 50 years but in the last 10 years, there has been more interest on the subject such that more than 75 % of all published works in the field have been reported in this period. The lead-free piezoelectric ceramics being researched on include  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  based ceramics [5], tungsten bronze ceramics [6], bismuth layered titanates ceramics [7] and  $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$  based ceramics [8].  $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$  abbreviated as KNN which is a solid solution of ferroelectric  $\text{KNbO}_3$  and antiferroelectric  $\text{NaNbO}_3$  appears to be among the most promising because of its comparably high piezoelectric properties, large electromechanical coupling coefficients and high Curie temperature ( $\approx 420$  °C) [8]. The graph in Fig. 1.1 shows a comparison of the piezoelectric charge coefficient ( $d_{33}$ ) values as a function of Curie temperature for lead-free piezoelectric ceramics and selected lead-based piezoelectric ceramics. It is clear that the  $d_{33}$  values close to those containing lead and are even better when the samples are textured. The improvement in the piezoelectric properties of these KNN ceramics is attributed to the introduction of other elements in the form of dopants which leads to phase coexistence and increases the total number of possible polarization

directions. KNN modified with Li, Ta and Sb which was reported by Saito et al. [4] has one of the highest piezoelectric properties for lead-free ceramics. This was initially attributed to the existence of a morphotropic phase boundary (MPB) but later reports have shown that the increase in the piezoelectric activity is closely related to the decrease in the phase transition temperatures. The term “polymorphic phase transition” (PPT) was considered to be more appropriate.

Theoretical materials science has made very big progress in the last couple of years but experimental materials science will continue to be essential for discovering new promising compositions in a couple of years to come. This is because the complexity of material compositions currently being studied requires that more computing infrastructure than presently available is needed [9]. The one at a time approach used in conventional ceramics processing though necessary is a slow method to discover new promising material compositions and so a faster method which applies robotics called “High-throughput experimentation” (HTE) has been introduced. It has been defined as “the use of miniaturization, robotics and parallel techniques to increase the productivity of the research process while the screening/analysis involves using a parallel characterization technique to rapidly assess the properties of the samples produced through this process” [10]. The need to discover new material compositions with better properties while also limiting the amount of raw materials and time used is the driving force for this new process [11]. This process was first used in pharmaceutical research but is now also used for materials research like polymers [11] and catalysts [12]. It has been used for research on thin film-based ceramics [13] and even bulk ceramics [14, 15] where certain properties like the piezoelectric coefficient ( $d_{33}$ ), doping effects, grain size effects are better determined using samples in their bulk form.

Synchrotron radiation has revolutionized X-ray diffraction of crystalline substances. The ability to select wavelengths, as well as moving one of the diffractometer angles makes it possible to exploit anomalous scattering for phase determination. The experimental setup is flexible and can be adjusted to measure substances over a wide range of temperatures. Because new synthesized lead-free ceramics cannot be unambiguously characterized by standardized X-ray diffraction data, synchrotron radiation offers the possibility to analyse the crystal structures of the new materials in detail.



The objective of this research work was to investigate into the structure and properties of KNN-based ceramics. The strategy applied here is to use multiple sites doping to improve the properties of KNN ceramics and it is explained in detail in chapter 3.2. High resolution X-rays were used to determine the structure of modified KNN ceramics.



## 2 Fundamentals

### 2.1 Foreword

The interaction between two different atoms with both positive and negative charges can be used to explain polarization in a dielectric material. Due to this interaction between the opposing charges, an electric dipole moment is established. When an electric field is applied, this dipole moment  $\vec{p}$  will orient with the applied field thereby deforming the electron clouds and this alignment phenomenon is called polarization.

The main polarization mechanisms which can occur within a dielectric material include electronic polarization, ionic polarization, orientation polarization, space charge polarization and domain wall polarization. Electronic polarization is based on the displacement of the negatively charged electron shell against the positively charged core; ionic polarization describes the displacement of the positive and negative sublattices with an applied field; orientational polarization which deals with alignment of permanent dipoles; space charge polarization is caused by accumulation of mobile charges at the interfaces and surfaces of materials; domain wall polarization occurs in ferroelectric materials.

Dielectric ceramic materials are divided into single crystals, thin films, thick films and bulk polycrystalline ceramics. Single crystal concepts are well developed and will be used to describe some piezoelectric concepts but this work is concerned only with bulk polycrystalline ceramics.

Crystals are classified into 32 point groups based on their symmetry. These 32 point groups are subdivisions of 7 basic crystal systems that in ascending order of symmetry include; triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral (trigonal), hexagonal, and cubic. These point groups are divided into two classes which include those with a center of symmetry and those without. There are 21 non-centrosymmetric point groups, 20 (except point group 432) of which exhibit piezoelectricity. Of the 20 point groups, 10 of the crystal classes contain a unique axis where the dipole moment is oriented in the unstrained condition i.e. they exhibit spontaneous polarization.

Crystals whose direction of spontaneous polarization can be reversed by the application of an external electric field are called ferroelectrics. There are basically four different types of ferroelectric ceramics. They include the tungsten–bronze group ( $AB_2O_6$ ), the oxygen octahedral group ( $ABO_3$ ), the pyrochlore group ( $A_2B_2O_7$ ), and the bismuth layer–structure group ( $A_4B_3O_{12}$ ). The main difference between these ceramics lies in the structure of their respective unit cells. The oxygen octahedral group ( $ABO_3$  type) which has the perovskite structure is the most important economically and will be further discussed in this report. The  $ABO_3$  type ferroelectric ceramics are further divided into  $BaTiO_3$ ,  $Pb(Zr_xTi_{1-x})O_3$ ,  $(Bi_{0.5}Na_{0.5})TiO_3$  and  $(K_xNa_{1-x})NbO_3$  family of compositions [16].

## 2.2 Dielectric constant and loss

When an electric field is applied to a dielectric material, partial charge compensation is achieved by polarization. Polarization  $\vec{P}$  is defined as the sum of all dipole moments ( $\vec{p}$ ) per unit volume ( $V$ ) and is represented with equation 2.1

$$\vec{P} = \frac{\sum_i \vec{p}_i}{V} \quad (2.1)$$

When a dielectric material is located between the plates of a capacitor, the capacity of the capacitor  $C$  is increased by a factor  $\epsilon_r$  which is the dielectric constant or relative permittivity of the material. The relationship between the capacitance  $C$  and  $\epsilon_r$  is shown in equation 2.2

$$C = \epsilon_o \epsilon_r \frac{A}{d} \quad (2.2)$$

where  $\epsilon_o$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F/m),  $\epsilon_r$  is the relative permittivity,  $A$  is the surface area of the sample and  $d$  the distance between the electrodes

This increase in the capacitance is due to the polarization of the material due to the applied field  $\vec{E}$ . The higher the field applied, the higher is the distorting force of the dipoles such that the dielectric polarization is proportional to the applied field. The constant of proportionality here is called electric susceptibility  $\chi$  and is a measure of how easily the dielectric material polarizes in response to the electric field. It is related to the polarization in the material with equation 2.3

$$\vec{P} = \chi \epsilon_o \vec{E} \quad (2.3)$$

The total amount of charges stored in a capacitor is a combination of the polarization charge and the charge without a dielectric.

The loss tangent of a dielectric material quantifies its inherent dissipation of electromagnetic energy. When the voltage is alternating, the charge stored in a dielectric material has both real (in phase) and imaginary (out of phase) components as a result of resistive leakage or dielectric absorption [17]. The dielectric loss or dissipation factor ( $\tan \delta$ ) is the ratio of the imaginary component ( $\varepsilon''$ ) to the real component ( $\varepsilon'$ ) in an a.c circuit. Mathematically it is represented with equation 2.4

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (2.4)$$

For polycrystalline ceramics, there are possible contributions of conductivity to the value of the loss tangent. The conduction loss is due to flow of charge through the material while the dielectric loss is due to movement of charges due to changes in polarization direction [18]. When there is a substantial contribution of conduction loss, the loss tangent can be calculated through the relation in equation 2.5

$$\tan \delta = \frac{\sigma}{J\varepsilon'} \quad (2.5)$$

Where  $\sigma$  represents the electrical conductivity and  $J$  represents the angular frequency.

## 2.3 The piezoelectric effect

When some crystals are subjected to stress in certain directions, they develop positive and negative charges at opposite ends. This phenomenon is called piezoelectric effect and was discovered by the Curie brothers in 1880. Some crystals undergo dimensional changes when subjected to an electric field and this phenomenon is called converse piezoelectric effect [19]. This occurrence is a thermodynamic consequence of the piezoelectric effect. Some of the earliest discovered piezoelectric crystals include; quartz, tourmaline and Rochelle salt. A necessary condition for piezoelectricity is the absence of a center of symmetry and from a chemical point of view, chemical bonds between the atoms in the crystal must be heteropolar [20]. A schematic representation of the direct and converse piezoelectric effect is shown in Fig. 2.1. For a single crystal, these polar axis lie in one direction while in a polycrystal, different regions within the material have different polar axes.

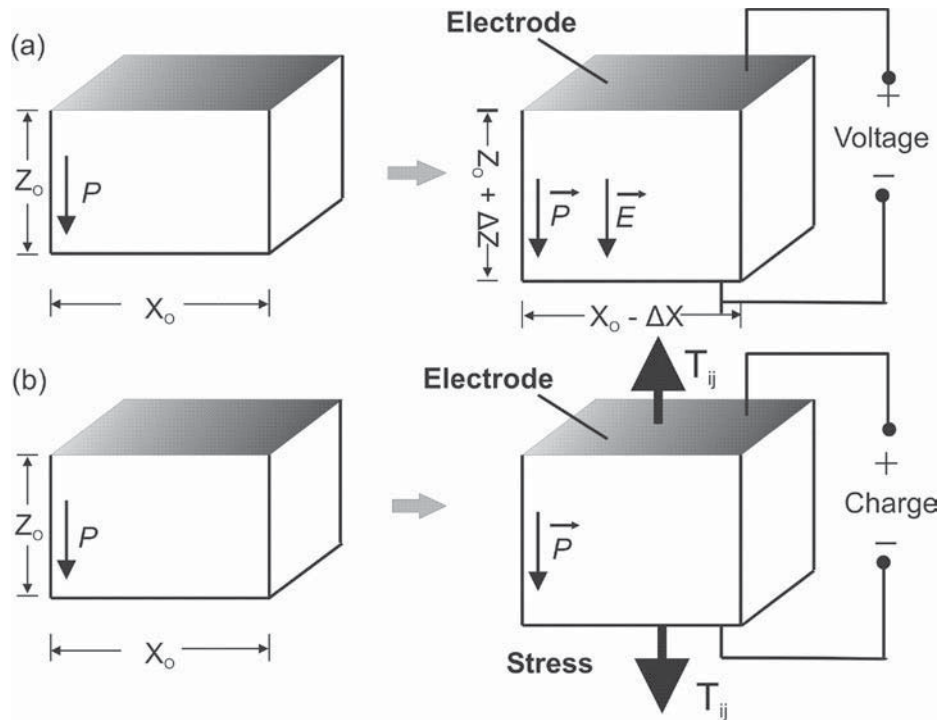


Fig. 2.1 Schematic representations of the direct and inverse piezoelectric effect: (a) an electric field  $\vec{E}$  applied to the material changes its shape; (b) a stress on the material yields to surface charges.

The direct piezoelectric effect can be represented in Tensor notation by equation 2.6.

$$P_i = d_{ijk} T_{jk} \quad (2.6)$$

$$S_{ij} = d_{kij} E_k \quad (2.7)$$

where  $P_i$  is the polarization generated along the  $i$ -axis direction in response to the stress  $T_{jk}$  while  $d_{ijk}$  is the piezoelectric coefficient. The formula for the converse piezoelectric effect is shown in equation 2.7 and describes the induced strain ( $S_{ij}$ ) which is proportional to an applied electric field ( $E_k$ ). The proportionality constant ( $d_{ijk}$ ) is identical in both cases and is called the piezoelectric coefficient with units (C/N or m/V) [17]. The piezoelectric coefficient is a third rank tensor which implies that it has 27 components and therefore complex. To simplify things, the matrix notation is normally used to replace the tensor notation and consequently reduce the number of components to 18.



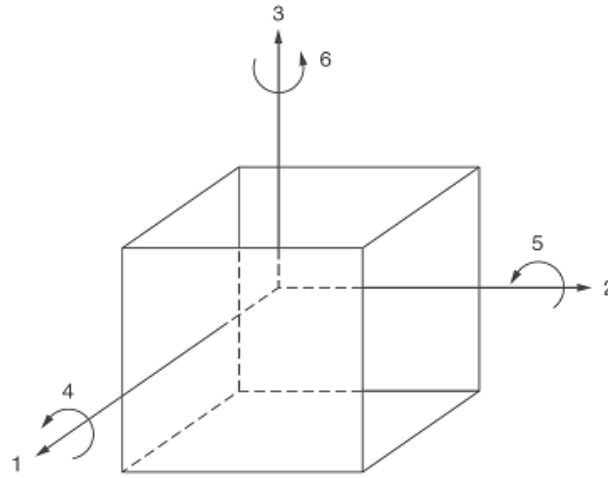


Fig. 2.2 Notation of axis and direction of deformation.

The reference axis for representing the properties of crystals in the  $x$ ,  $y$  and  $z$  component is shown in Fig. 2.2. To simplify the resulting equation, the tensor notation is replaced with the matrix notation as shown in Table 2.1.

Table 2.1 Replacing the tensor notation of crystals with matrix notation

Tensor (ij or jk)	11	22	33	23 or 32	31 or 13	12 or 21
Matrix (i or j)	1	2	3	4	5	6

The conditions used in changing the tensor notation to matrix notation are;

$$d_{ijk} \equiv d_{ij} \text{ if } j = k = 1, 2 \text{ or } 3$$

$$d_{ijk} + d_{ikj} \equiv d_{ij} \text{ if } j = 4, 5, \text{ or } 6$$

Equations 2.6 and 2.7 now become

$$P_i = d_{ij} T_j. \quad (2.8)$$

$$S_j = d_{ij} E_i. \quad (2.9)$$

The convention is that the subscript  $i$  in equations 2.8 and 2.9 indicate the  $z$  axis or 3 which is perpendicular to the plane of the electrodes and the subscript  $j$  the direction of the applied stress or piezoelectrically induced strain [21]. The piezoelectric coefficient ( $d_{33}$ ) is easier to measure in polycrystalline ceramics and will be used mainly in this report.