

CHAPTER II

LITERATURE REVIEW

2.1 Dielectric Behavior of Electronic Ceramics

Dielectric materials are electrically insulative, but still susceptible to polarization. Polarization is the alignment of electric dipoles in the presence of an externally applied dielectric field. There are four mechanisms of polarization: electronic, ionic (atomic), dipolar and space charge (diffusion). In the presence of an electric field, dielectric materials can exhibit at least one of these polarization types in particular, while the others are possibly negligible or totally absent [7].

All dielectric materials induce electronic polarization (Fig. 2.1(a)), which results from the distortion of the negatively charged electron cloud, relative to the positive nucleus of an atom. The materials with ionic bonds may have ionic polarization. The result showed in Fig. 2.1(b) was caused by the relative displacement of cations in one direction and anions in the opposite direction. As a result, net dipole moments are induced on this new structure. Only substances with permanent dipole moments may possess an orientation polarization as shown in Fig. 2.1(c). This particular one can be described as the rotation of the permanent dipole moments into an applied electric field direction. Space charge polarization or interfacial polarization is occurred when mobile charge carriers are impeded by physical barrier that inhibited charge migration. The charge piles up at the barrier producing a localized polarization of the materials. Again, polarization is the alignment of either induced atomic (electronic polarization) or induced molecular (ionic polarization) or permanent (orientation polarization) dipole moments or induced charge in space or grain in the direction of an applied electric field. Fig. 2.1 shows the four possible mechanisms of polarization depending on the dielectric materials, and the way of applying the electric field.

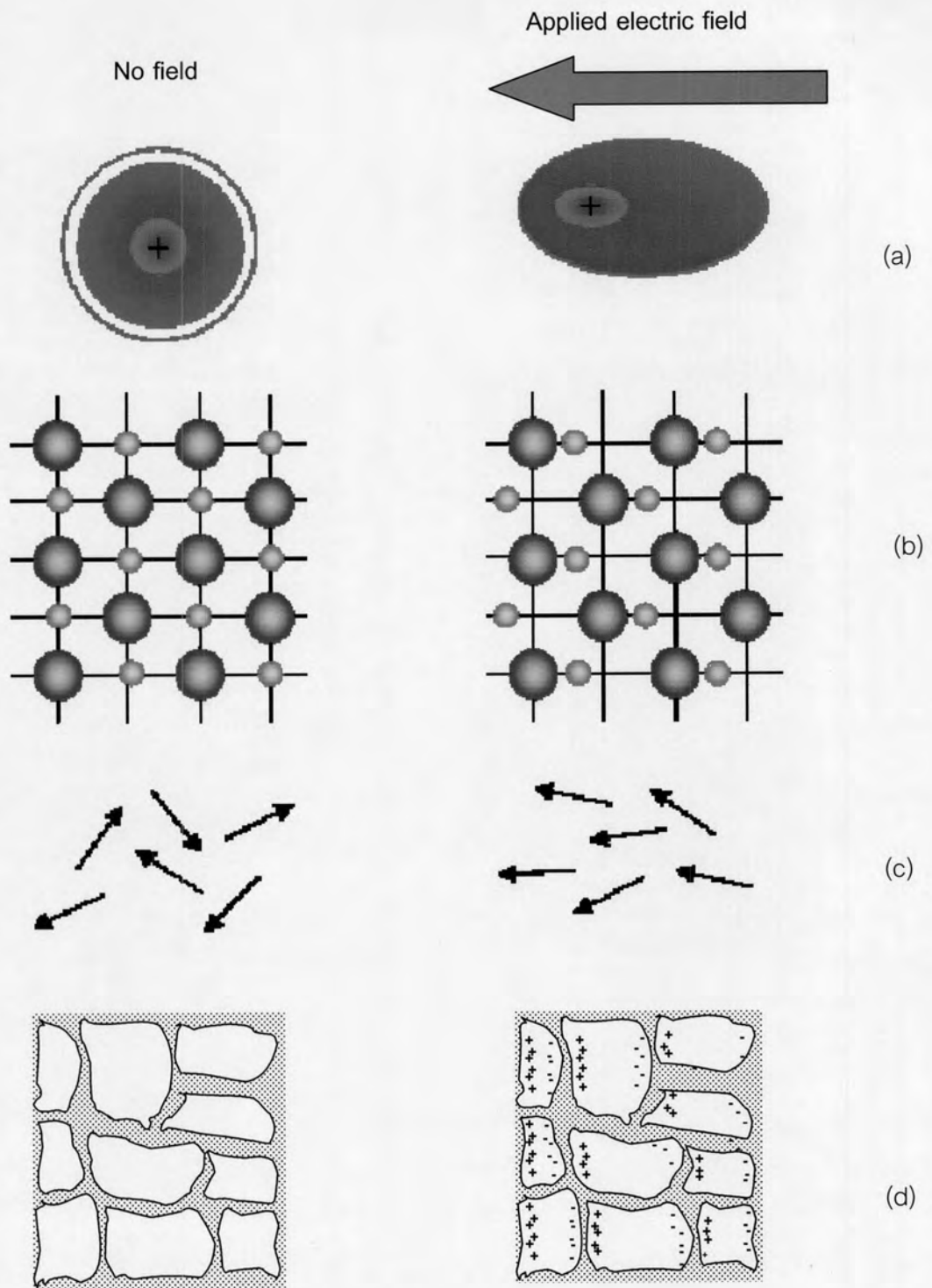


Fig. 2.1 The four mechanisms of polarization. (a) Electronic, (b) Ionic, (c) Dipolar and (d) Space charge [6].

In its most elementary form an electric dipole comprises two equal and opposite points separated by a distance δx . The dipole moment p of the dipole, defined as

$$p = Q\delta x \quad (2.1)$$

when " p " is a vector with its positive sense directed from the negative to the positive charge, and Q is a surface charge density.

A polarized material can be regarded as made up of elementary dipolar prisms, the end faces of which carry surface charge densities of $+\sigma_p$ and $-\sigma_p$ were shown in Fig. 2.2. The dipole moment per unit volume of material is termed the *polarization* P , and, can vary from region to region. From Fig. 2.2 the magnitude of vectors are given by

$$\delta p = \sigma_p \delta A \delta x = \sigma_p \delta V$$

or

$$\frac{\delta p}{\delta V} = P = \sigma_p \quad (2.2)$$

In general, $\sigma_p = n \cdot P$, where n is the unit vector normal to the surface enclosing the polarized material and directed outwards from the material.

Important relationships can be developed by considering the effect of filling the space between the plates of a parallel-plate capacitor with a dielectric material, as shown in Fig. 2.3. From Gauss's theorem, the electric field E , both between and normal to two parallel plates carrying surface charge density σ and separated by a vacuum is

$$E = \frac{\sigma}{\epsilon_0} \quad (2.3)$$

where ϵ_0 is permittivity of free space ($8.854 \times 10^{-12} \text{ Fm}^{-1}$).

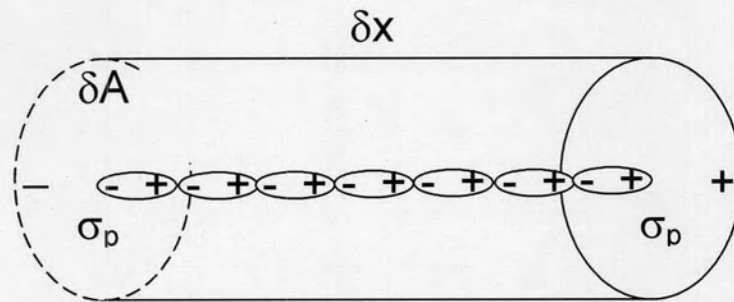
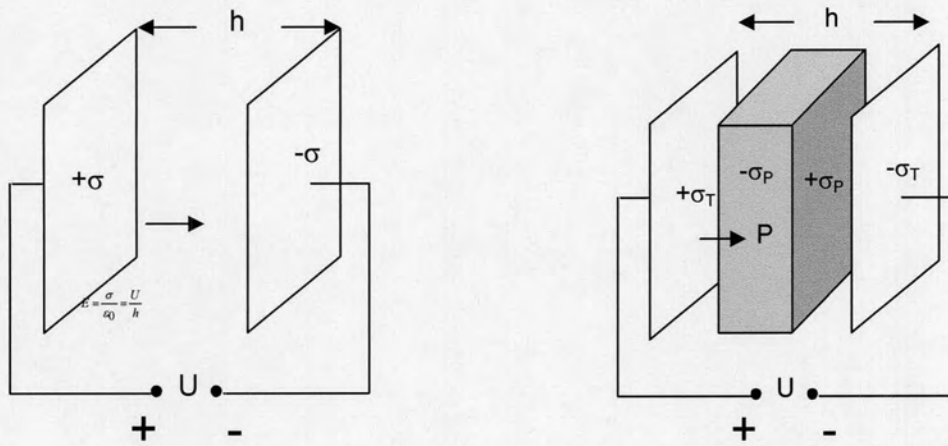


Fig. 2.2 Elementary prism of polarized material [6].



(a)

(b)

Fig. 2.3 The role of the dielectric in capacitor [6].

Since similar voltage is applied in both situation (a) and situation (b), while E still remains the same. However, in (b); the polarization charge density, σ_p appearing on the surfaces of the dielectric compensates part of the total charge density σ_T , carried by the plates. Thus, the effective charge density given rise to E is reduced to $\sigma_T - \sigma_p$, so,

$$E = \frac{\sigma_T - \sigma_p}{\epsilon_0} \quad (2.4)$$

The total charge density σ_T , is equivalent to the magnitude of the dielectric displacement vector D , then,

$$D = \epsilon_0 E + P \quad (2.5)$$

If the dielectric is 'linear', while polarization is proportional to the electric field within the material, which is commonly the case,

$$P = \chi_e \epsilon_0 E \quad (2.6)$$

where the dimensionless constant χ_e is the electric susceptibility. In general χ_e is a second rank tensor. Unless in other cases, they are collinear, in which case χ_e is simply a scalar.

If we follow (2.5) and (2.6), so

$$D = \epsilon_0 E + \chi_e \epsilon_0 E = (1 + \chi_e) \epsilon_0 E \quad (2.7)$$

and, since $D = \sigma_T$,

$$\frac{Q_T}{A} = (1 + \chi_e) \epsilon_0 \frac{U}{h} \quad (2.8)$$

in which Q_T is the total charge on the capacitor plate, and U is an electric potential difference. Therefore the capacitance is

$$C = \frac{Q_T}{U} = (1 + \chi_e) \epsilon_0 \frac{A}{h} \quad (2.9)$$

Since vacuum has zero susceptibility, the capacitance C_0 of an empty parallel-plate capacitor is

$$C_0 = \epsilon_0 \frac{A}{h} \quad (2.10)$$

If the space between the plates is filled with a dielectric of susceptibility χ_e , the capacitance is increased by a factor $1 + \chi_e$

The term permittivity ϵ of the dielectric is defined by

$$\epsilon = \epsilon_0 (1 + \chi_e) \quad (2.11)$$

where

$$\frac{\epsilon}{\epsilon_0} = 1 + \chi_e = \epsilon_r \quad (2.12)$$

and ϵ_r the relative permittivity (or dielectric constant) of the dielectric.

2.2. Piezoelectricity

The piezoelectric effect is the aptitude of certain materials to produce an electric charge, which is proportional to an applied mechanical stress. This is termed the direct piezoelectric effect. By reversing the sign of the stress applied to this material, (from tension to compression) the direction of the electric charge created is reversed as well (Fig. 2.4(a)). The piezoelectric effect is also reversible. When an electric charge is applied, a mechanical

strain is created. This property is called the inverse piezoelectric effect (Fig. 2.4(b)). The piezoelectric effect in a crystal resulted from the creation of electric dipole moments (polarization) and the establishment of an electric field across the specimen by the application of external force. Dipole moments may be induced from three different sources, as explained above.

Within the 32 point groups, only 20 are piezoelectric, possessing a unique polar axis in a non-centrosymmetric unit cell. Among these 20 point groups, only 10 have a switchable polar axis. These 10 can display a spontaneous polarization (Fig.2.5) [7, 8]. The equations that describe a piezoelectric ceramic in regard to its electric and elastic properties are, in their general form, as follow:

$$D = dT + e^T E \quad (2.13)$$

$$S = s^E T + dE \quad (2.14)$$

Where D is the dielectric displacement (consider it equal to polarization), T is the stress, E is the electric field strength, S is the strain, d is a piezoelectric coefficient, s is the material compliance (inverse of stiffness), and e is the dielectric constant. Equation 2.13 describes the direct effect and equation 2.14 the converse effect. Both equations are expressed in matrix form, actually describes as a set of equations that related these properties along the different orientations of the material.

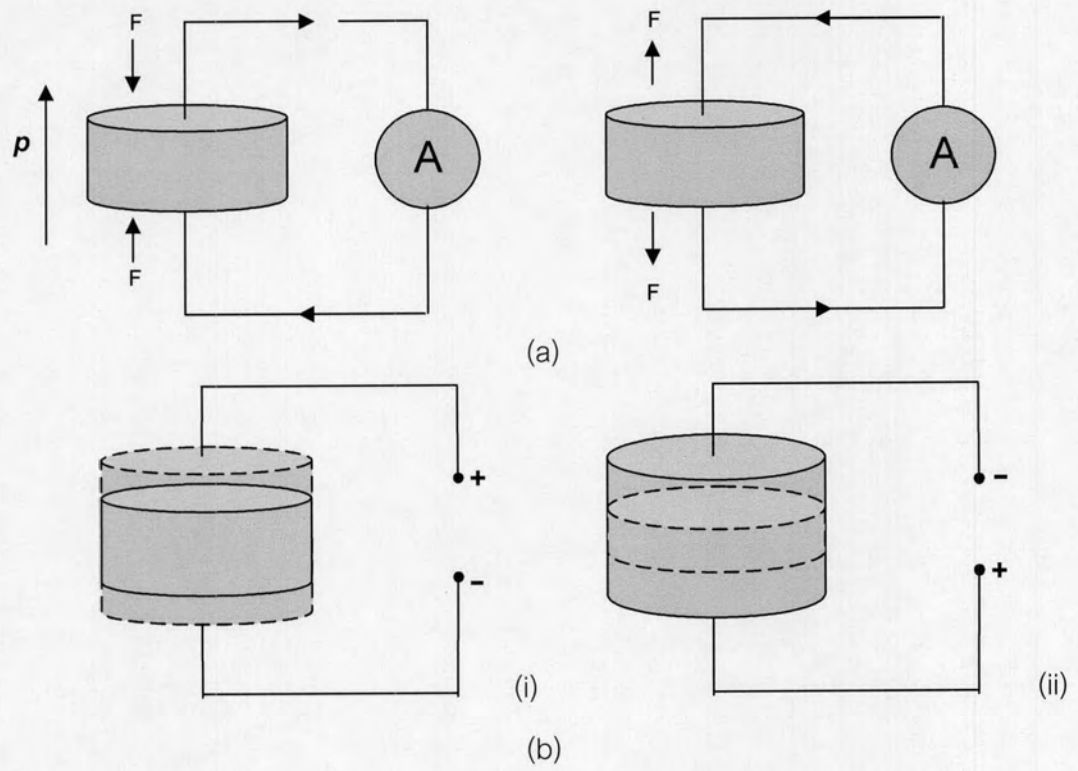


Fig. 2.4 Piezoelectric effects; (a) the direct and (b) the converse effects: (i) contractions; (ii) expansion. The broken lines indicate the original dimensions [6].

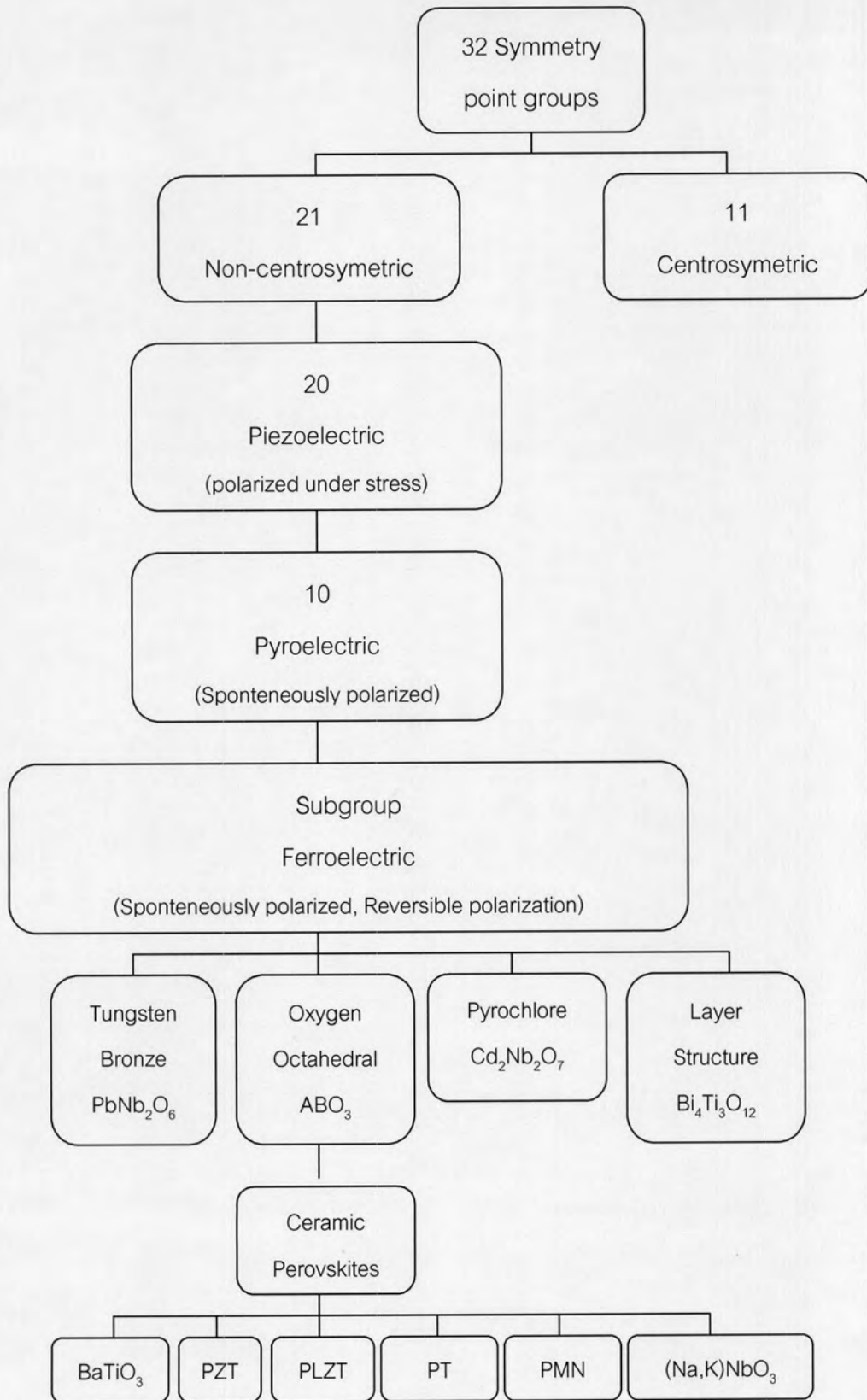


Fig. 2.5 Interrelationship of piezoelectric and subgroups on the basis of internal crystal symmetry [7].

The piezoelectric charge coefficients (d_{33} and d_{31}) and the voltage coefficients (g_{33} , g_{31} and g_{15}) describe the electromechanical parameters of the piezoelectric ceramic materials. For both direct and converse effects, the d coefficient is the proportionality constant between displacement and stress, or strain and electric field, according to the relationships

$$d = \frac{D}{T} = \frac{S}{E} \quad (2.15)$$

where the d coefficient is numerically identical for both effects. High d coefficients are desirable for those materials which are utilized in motional or vibration devices such as sonar and sounders, the g coefficient is related to the d coefficient via the dielectric constant (K). According to

$$g = \frac{d}{K\epsilon_0} = \frac{E}{T} = \frac{S}{D} \quad (2.16)$$

High g coefficients are desirable for materials intended to produce voltages in response to mechanical stress, such as in gas igniters and phonograph pickups, in particular.

2.3. Ferroelectricity

Ferroelectric crystals are the subgroup of the piezoelectric materials. They are distinguishable from piezoelectrics by their aptitude to reverse the spontaneous polarization with the application of an external electric field.

2.3.1 Curie Temperature and Phase Transition

Ferroelectrics undergo a phase transition corresponding to a change in the crystal structures. This phase transition occurs at a particular temperature. And, it is followed by

several electric polarization amplitude and/or orientation modifications. The Curie point T_c , is the temperature from which the ferroelectric crystal undergoes a structural phase transition, from a paraelectric phase at $T > T_c$ (the spontaneous polarization is vanished) to a ferroelectric one at $T < T_c$ (with a spontaneous polarization). The dielectric constant reaches its maximum value at the Curie point. Above T_c , the crystal is paraelectric and does not exhibit any ferroelectricity. The ferroelectric structure is created by a distortion of the paraelectric structure. As a result, the ferroelectric phase always has a lower symmetry than the paraelectric one. At $T < T_c$, the ions move from their equilibrium position (in the paraelectric phase) to create a spontaneous polarization. When a crystal is cooled down belows T_c , the paraelectric-ferroelectric phase transition may be of two types: displacive or order-disorder. Ferroelectrics with a perovskite type structure exhibit a phase transition of the first type, i.e. displacive. Sequential structural phase transitions may occurred in addition to the paraelectric to ferroelectric one. For instance, BaTiO_3 has three ferroelectric phases below 120°C (T_c) and their phase transition temperatures are 0°C and -80°C . Fig. 2.6 represents the atomic displacement occurring at T_c , when the paraelectric-ferroelectric phase transition is happens [9].

2.3.2 Poling of Piezoelectric Ceramics

A ferroelectric material is spatially divided into multiple regions with a uniform polarization. Such regions are called ferroelectric domains. The interface between two domains is called a domain wall. Below Curie temperature, the domain are randomly oriented, no piezoelectric effect is exhibited (Fig. 2.7(a)). A polar direction can be developed by applying a static electric field. The optimum electric field strength can be calculated from 3 or 4 times of coercive field which provide maximum piezoelectricity [9]. Normally, it was exposed into a strong, direct current (DC) electric field at a temperature slightly below the Curie point (Fig. 2.7(b)). Then, the ferroelectric ceramic is polarized or so-called poled. Through this polarizing treatment, domains are almost aligned with the

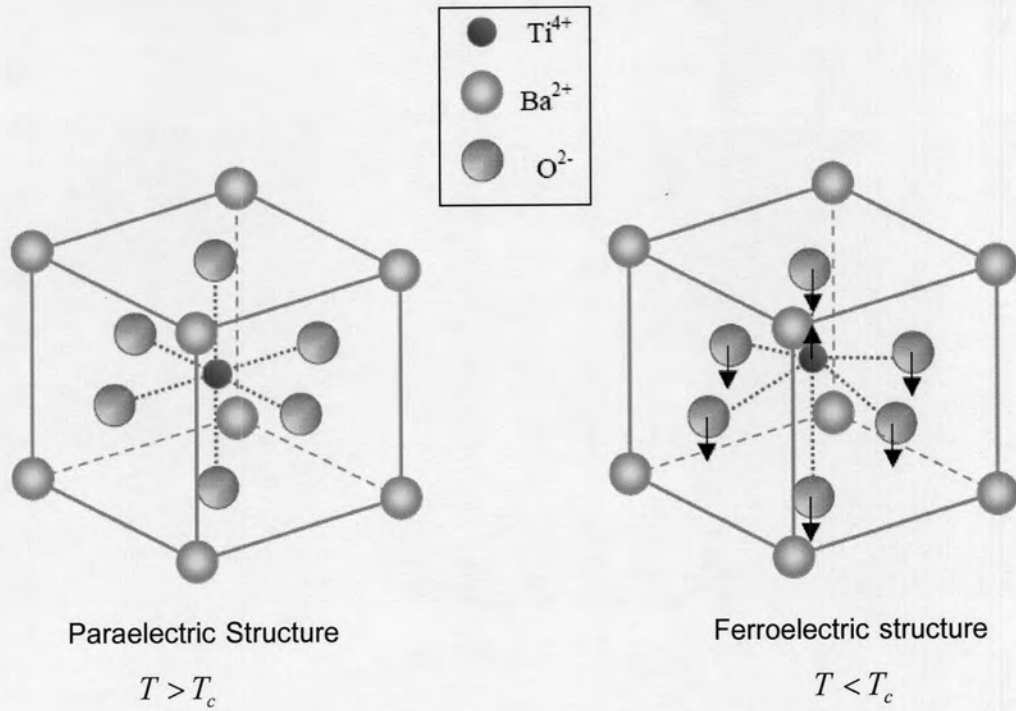


Fig. 2.6 Paraelectric-ferroelectric phase transition in BaTiO_3 occurring at 120°C (T_c) [9]

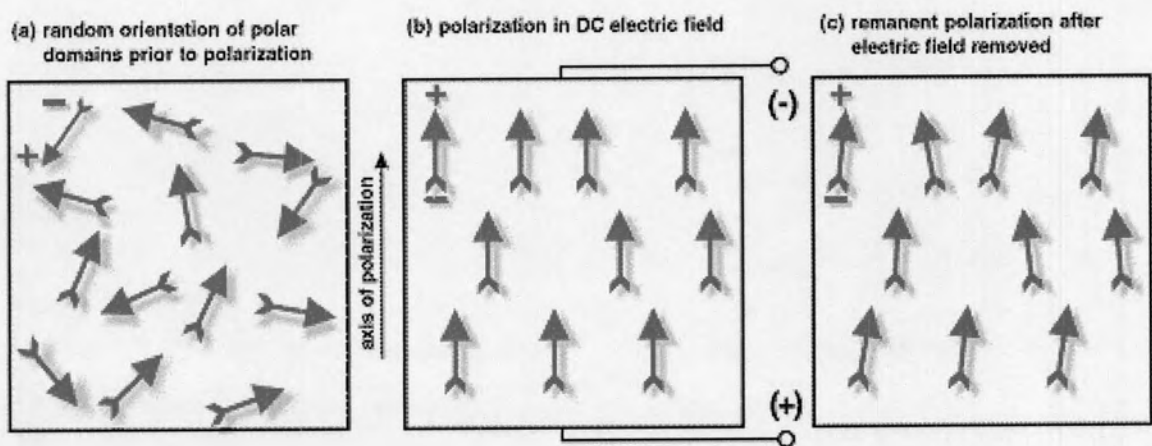


Fig. 2.7 Polarizing (poling) a piezoelectric ceramic [10]

electric field expanded at the expense of domains that are not aligned with the field, and the ceramic lengthens in the direction of the field. When the electric field is removed, most of the dipoles are locked into this configuration of near alignment (Fig. 2.7(b)). This can provide the material with a permanent polarization, called the remanent polarization, and a permanent deformation (elongation) that makes it become anisotropic and different properties, according to the direction in which they are measured.

2.3.3. The Hysteresis Loop of a Ferroelectric

An important characteristic of a ferroelectric is the hysteresis loop (Fig. 2.8). The hysteresis curve created by applying an electric field to a piezoelectric ceramic element until maximum (saturation) polarization, P_s , is attained, reducing the field to zero to determine the remanent polarization, P_r , reversing the field to attain a negative maximum polarization and negative remanent polarization, and again, reversing the field to restore the positive remanent polarization.

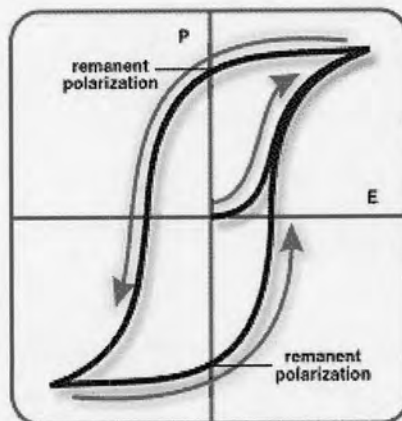


Fig. 2.8 Hysteresis curve for polarization [10]

2.4 Other Piezoelectric Properties

2.4.1 Dielectric Constant (ϵ)

The permittivity, or dielectric constant, ϵ , for a piezoelectric ceramic material is the dielectric displacement per unit electric field. ϵ^T is the permittivity at constant stress; ϵ^S is the permittivity at constant strain. The first subscript to ϵ indicates the direction of the dielectric displacement; the second is the direction of the electric field.

The relative dielectric constant, K , is the ratio of ϵ , the amount of charge that an element constructed from the ceramic material can store, relative to the absolute dielectric constant, ϵ_0 , the charge that can be stored by the same electrodes when separated by a vacuum, at equal voltage ($\epsilon_0 = 8.84 \times 10^{-12}$ F/m).

2.4.2 Dielectric Dissipation Factor

The dielectric dissipation factor (dielectric loss factor), $\tan \delta$, for a ceramic material is tangent of the dielectric loss angle. Such particular factor can be determined by the ratio of effective susceptance in a parallel circuit, measured by using an impedance bridge. Values for $\tan \delta$ are typically determined at the frequency of 1 kHz.

2.4.3 Electromechanical Coupling Factor

The electromechanical coupling factor, k , is an indicator of the effectiveness with which a piezoelectric material converts electrical energy into mechanical energy, or converts mechanical energy into electrical energy. The first subscript to k denotes the directions along with the electrodes are applied; the second denotes the direction along with the mechanical energy is applied.

2.4.4 Frequency Constant

When an unrestrained piezoelectric ceramic element is exposed to a high frequency, it will alternating the electric field, an impedance minimum, the planar or radial resonance frequency, and, coincide with the series resonance frequency, f_s . The relationship between the radial mode resonance frequency constant, N_p and the diameter of the ceramic element, d , is expressed by:

$$N_p = f_s \times d \quad (2.17)$$

At higher resonance, another impedance minimum, the axial resonance frequency, is encountered. The thickness mode frequency constant, N_t , is related to the thickness of the ceramic element, h by:

$$N_t = f_s \times h \quad (2.18)$$

2.5 Applications of Piezoelectric Ceramics

A piezoelectric system can be constructed for virtually any application for which any other type of electromechanical transducer is used. The brief information concerned with these particular applications are summarized in the following subsections [10, 11].

1. Generators

Piezoelectric ceramics can generate sufficient voltages that can create a spark across an electrode gap, and thus can be used as igniters in fuel lighters, gas stoves, welding equipment, and other such appliances in particular. A piezoelectric ignition system is smaller and far less complex than alternative systems using permanent magnets or high voltage transformers and capacitors.

Techniques used to make multilayer capacitors can be adapted to make multilayer piezoelectric ceramics generators. A large surface area per unit volume is made for a high generated charge and relatively low voltage. Such generators are excellent solid state batteries for electronic circuits' applications.

2. Sensors

Sensors convert various physical parameters, such as acceleration or pressure, into electrical signals. In some types of sensors, the physical parameter being monitored acts directly on the piezoelectric ceramic element; in order, an acoustical signal establishes vibrations are, in turn, converted into an electrical signal.

3. Actuators

A piezoelectric actuator converts a voltage or other electrical signal into precisely controlled physical displacement that can be used to finely adjust machine tools, or lenses or mirrors in optical equipments. Alternatively, this displacement can be prevented and enabling a useful force to develop. In addition to position control applications, piezoelectric actuators are used to actuate or control hydraulic valves, to act as small volume pumps or spatial-purpose motors, and several other applications. Energy efficiency losses limit the extent to which electromagnetic motors can be reduced in size. Piezoelectric motors, on the other hand, are unaffected by these constraints since the energy efficiency is size independent. This makes it possible to design piezoelectric motor to size of less than 1 cm^3 . An important additional advantage, in some applications, is the fact that piezoelectric motors do not generate the electromagnetic noise.

4. Transducers

Piezoelectric transducers convert electrical energy into vibration mechanical energy, usually expressed as sound or ultrasound. The mechanical energy, in turn, is used to perform such particular task.

Transducers that generate audible sounds afford significant advantages, relative to comparable electromagnetic devices. They are compact, simple, and highly reliable, and they require minimal energy to produce a high level of sound. These characteristics are suited to the needs of battery-powdered equipment.

Transducers that generate ultrasonic vibrations are use for cleaning, atomizing liquids, drilling or milling ceramics or other difficult materials, welding plastics, medical diagnostics, and for many other purposes. Because the piezoelectric effect is reversible, a transducer can both generate an ultrasound signal and receive a reflected signal. Consequently, systems incorporating either a signal piezoelectric transducer or two transducers are widely used to measure distances and flow rates as well as fluid level sensors by the differentiating between sound transmission in the fluid and in air).

2.6 Bismuth Sodium Titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$)

The Bismuth Sodium Titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$: BNT) system which exhibiting a perovskite structure was found by Smolenskii [1]. The structure of ABO_3 perovskite can be considered in two possible ways. Considered to the first possible structure was where bismuth and sodium cations occupied A-site, the corner of unit cell, while titanium cation situated in the center or B-site and oxygen ions occupied the faced-centered of unit cell. Then, the oxygen octahedral can be formed as showed in Fig. 2.9(a). Another possible formation is concerned as a three dimensional cubic network from 8 corners sharing

between TiO_6 , with bismuth and sodium cations. Hence, the octahedral structure can be formed at cube's center as displayed by Fig. 2.9(b) [9, 12].

The studies of BNT system were of interest by its high Curie temperature around 320 °C, which is in similar temperature range as of the several well-known PZT systems. Moreover, large remanent polarization ($P_r = 38 \mu\text{C}/\text{cm}$) and a high coercive field ($E_c = 73 \text{ kV}/\text{cm}$) [3, 13] were of concern. Nowadays, BNT system is considered as one of the future environmentally benign candidates in piezoelectric and dielectric applications.

It has been found by J.V. Zvirgzds [2] that BNT system has two temperature dependent phase transitions. At 597 °C (870 K), the transition of tetragonal to cubic phase was presented; while at 197 °C (470 K) the rhombohedral to cubic phase transition was occurred. The latter phenomenon was in regard to the changing from ferroelectric to paraelectric state. Table 2.1 summarizes all these particular transitions. As temperature was decreasing, the BNT structure would be changed from cubic to tetragonal and, finally, rhombohedral structure at room temperature. During the transition, coexistence region of each phase was found among each transitional step in particular. Phase transitions are of importance in electronic applications as only non-centrosymmetric space groups can exhibit the ferroelectric properties.

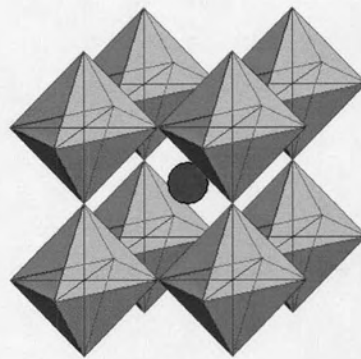
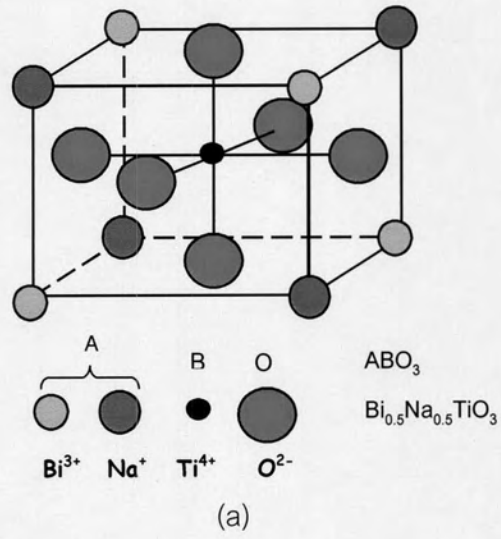


Fig. 2.9 Representation of an ABO₃ perovskite; (a) shown as cubic, (b) shown as cubic network of BNT [6].

Table 2.1 The lattice Parameter of Three Phase Transitions in BNT [2, 14]

Temperature (K)	Symmetry	Parameter (nm)	Volume (nm ³)
870	Cubic	$a_c = 0.39128$	0.05990
670	Tetragonal	$a_t = 0.39004$ $c_t = 0.39057$	0.05942
470	Rhombohedral (psudocubic)	$a_r = 0.38911$ $\alpha = 90^\circ$	0.05891
290	Rhombohedral	$a_r = 0.38848$ $\alpha = 89^\circ 54'$	0.05863

V.P. Avramenko [15] stated that BNT single crystal has a peculiarities temperature behavior in electrical conductivity. Czochralsky method was employed in the preparation of BNT single crystal. The investigation of temperature dependence effect on dielectric permittivity and electrical conductivity were performed at several magnitudes of electrical fields and frequencies. With the increasing of applied electric field, such conductivity was increasing at six to eight orders. This particular phenomenon might probably explain by adopted the hopping model [16]. Basically, the charge movement process was occurred from the electron's hopping from one state to another. Charges movement was then happened and affected the changing in the electric properties.

2.6 Dopant Effects in Bismuth Sodium Titanate

During the past decades, many studies indicated that dopants can affect the structural and related properties of BNT systems. Majority of those interests were in their dielectric and piezoelectric properties. Several modified ones such as A-site and B-site in the BNT systems showed the potential of enhancing some specific and desirable properties.

2.6.1 Barium Doping in Bismuth Sodium Titanate

The effects of barium on the properties of BNT have been characterized by various groups over years. Many studies that involved barium doping also included either A or B-site cations to evaluate the effects of multiple-site doping on several properties [17-23]. Barium titanate (BT) doped BNT provided a morphotropic phase boundary (MPB) between the rhombohedral and tetragonal phase. At MPB, in the amount of 6 to 7 mol% of BT additive presented an anomaly dielectric constant. The MPB compositions exhibited the large, broad dielectric constant peaks. Its broadening was resulted from the MPB behavior, along with increasing disorder created by the substitution of Ba^{2+} ions at A-site of Bi^{3+} and Na^+ ions. Fig. 2.10 shows a phase diagram for a solid solution between BNT and BT with increasing BT mol % [15].

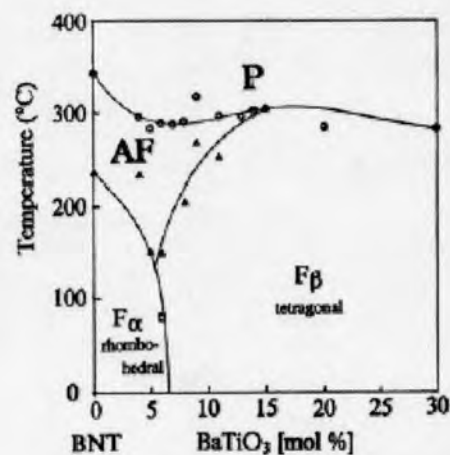


Fig. 2.10 Phase diagram for BNT with increasing mol % BT [19].

Multiple cations doping in BNT system is another way to modify the structure as to obtain the better results than that obtained from single dopant modifications. Sheets et al. simultaneously doped BNT with Ba^{2+} and Zr^{4+} ions in order to stabilize the AFE phase at room temperature. The stability in relative permittivity created the very broadening peak over wide temperature ranges. They also determined the behavior between single crystal samples, then, compared with polycrystalline ones of similar compositions. The larger values of relative permittivity were founded in single crystal samples [18]. Such behavior is highly expected in a dielectric material. In regard to the structure of single crystals, they are free from defects such as cracks, voids and grain boundary effects. Such factors were combined to affect the overall reduction of relative permittivity in the polycrystalline samples.

Li et al. have reported that the doping of 6 mol % Ba and 1 mol % of each La^{3+} , Co^{3+} or Nb^{5+} can be modified the dielectric response compared to BNT doped with 6 mol % Ba only. Each of the dopants was reduced the value of the relative permittivity and several of them could enhance the intermediate phase transition (shoulder). The addition of La^{3+} also produced smaller grain sizes than those of other dopants [20].

Nagata et al. have reported on the properties on the additional of both BaTiO_3 and $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT) into BNT system. The MPB was exhibited at a composition of 85.2% BNT, 2.8% BaTiO_3 and 12% $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$. Fig. 2.11 showed the ternary phase diagram near the MPB for the BNT/BT/BKT system. They have found that the most useful compositions were located near the MPB because they exhibited the anomalous electrical behavior associated with MPB compositions [13, 24].

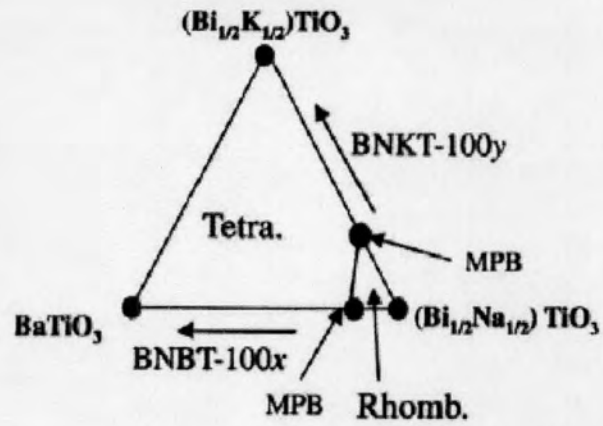


Fig. 2.11 Phase relationship of BNT, BT and BKT near the MPB [13].

2.6.2 Strontium Doping in Bismuth Sodium Titanate

The strontium doping in BNT system has a well defined effect on the dielectric properties of materials. Sr^{2+} ions can be substituted in both Bi^{3+} and Na^+ ions on the A-site of the perovskite structure. As the average valencies of the Bi^{3+} and Na^+ ions are 2+. Fig.2.12 also presented a phase diagram created in 1974 for BNT doped with SrTiO_3 (ST) [3].

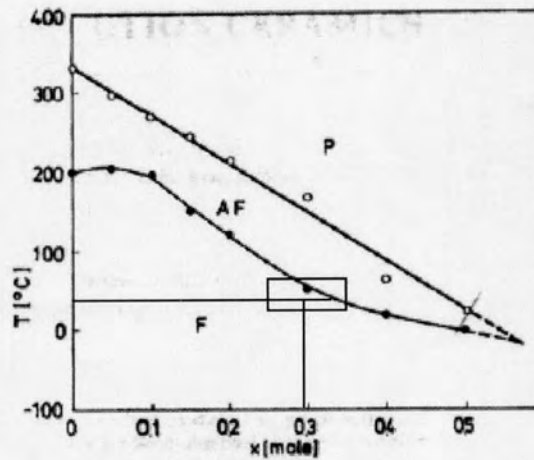


Fig. 2.12 Phase diagram of BNT with increasing strontium doping [3].

It has been reported that SrTiO₃ (ST) doped BNT exhibits the MPB in the range of 26-30 mol % of ST as the phase diagram shown in Fig. 2.12. It was occurred by the tetragonal antiferroelectric region (AFE) between the ferroelectric rhombohedral and paraelectric cubic phases at the up to 50 mol % of ST additives. The compositions with 26-30 mol % ST show the enhancement in dielectric properties with a broaden peak. It has been reported that instead of having the MPB, strontium doped BNT exhibited a very large diffuse phase transition region between 26 mol % ST and 50 mol % ST [21, 26].

2.6.3 Lead Doping in Bismuth Sodium Titanate

Lead compounds have been utilized in the fabrications of electronic ceramic materials for many decades from their good dielectric and piezoelectric properties that they can provide. However, still there were environmental problems persisted with the utilization of lead in the process. Though, the doping of lead Pb²⁺ in the A-site of BNT is a useful one. Because it can supports the increasing of the relative permittivity. Then lead to the enhancement of the response in the intermediate phase transition that occurs near 200°C. Lead-doped BNT compositions have been reported to exhibit the MPB anywhere between 12-18 mol % [27, 28]. Pb²⁺ has also been the modified one on the A-site like other dopants such as K⁺ and La³⁺ ions in the A-site, and B-site with Zr⁴⁺ ions [30-33]. The addition of K⁺ ions to Pb-doped BNT system can affect an extension of the intermediate phase, and an increase in the relative permittivity. Lanthanum addition ones were found to shift all of the phase transitions into the lower temperatures and reduce the relative permittivity. BNT doped with Pb²⁺ and Zr⁴⁺ ions has a more diffuse phase transition, which provides a very broad relative permittivity peak.

2.6.4 Lanthanum Doping in Bismuth Sodium Titanate

Lanthanum (La³⁺) is another interesting dopant in BNT system, because it inhibits grain growth and enhances densification of the sinter ones [34]. In the lanthanum doping

system, the peak broadening has been attributed to increased lattice distortion caused by the strain created when La^{3+} ion replace Bi^{3+} ions on the A-site of the structure [35]. Phases and lattice determination were studied on La-doped BNT samples by Herabut and Safari [4] within the range of lanthanum additive from zero to six mol %. The phase transition between rhombohedral and cubic would occur around the additional of two to five mole %. They have reported that if a proper amount of lanthanum being substituted in the BNT system, and then it could inhibit a phased shifted conductivity as a result from a random displacement of Bi^{3+} and Na^+ ions at high temperatures. This phenomenon can also lead to lower the value of dielectric loss. The two mechanisms that contribute to the solution of such particular problem are to enhance the suppression of the dielectric anomaly and to improve the abnormal dielectric loss with temperature with the random displacement of A-site cations by La ion in BNT system as well as the grain size on domain wall motion.

Moreover, they have reported that the 0.5 at% La substituted at Na^+ site in BNT system $\text{Bi}_{0.5}(\text{Na}_{0.485}\text{La}_{0.005})\text{TiO}_3$ could improve the piezoelectric properties. The replacing of Na^+ with La^{3+} in this formula can reduced the amount of Na^+ ions which predominately influence the loss due to the conductivity at high temperature. Therefore, the piezoelectric coefficient (d_{33}) of this composition was reported around 100 pC/N which is higher than that obtained from PbTiO_3 (56 pC/N) [36].