CHAPTER 2

CHARACTERISTICS OF FERROELECTRIC PZT CERAMICS

In this chapter, the general characteristics of ferroelectric PZT ceramics are reviewed. The unique structural and electrical property characteristics near the morphotropic phase boundary of the PZT ceramics are demonstrated. Special attention is paid to the piezoelectric properties of the PZT ceramics. The effects of the microstructure and composition on the piezoelectric properties are also discussed.

2.1. Piezoelectricity

Piezoelectricity is the ability of a material to exhibit spontaneous polarisation when subjected to a mechanical stress. The material will also show the converse effect by undergoing mechanical deformation under the application of an electric field. The direct and converse piezoelectric effects can be expressed in tensor notation as:

$$\mathbf{P_i = d_{ijk}\sigma_{jk}} \quad \text{(direct effect)} \qquad (2.1)$$

$$\mathbf{\varepsilon_{ij} = d_{kij}E_k} \quad \text{(converse effect)} \qquad (2.2)$$

where $\mathbf{P_i}$ is the polarisation generated along the i-axis in response to the applied stress $\boldsymbol{\sigma}_{\mathbf{jk}}$, and $\mathbf{d_{kij}}$ is the piezoelectric coefficient. For the converse effect, $\boldsymbol{\varepsilon}_{\mathbf{ij}}$ is the strain generated in a particular orientation of the crystal on the application of electric field $\mathbf{E_k}$ along the k-axis [Nye, 1990].

The origin of the piezoelectric effect is related to an asymmetry in the unit cell and the resultant generation of electric dipoles due to the mechanical distortion. According to the lattice structure described by the Bravais unit cell of the crystals, the thousands of crystals in Nature can be grouped together into 230 microscopic symmetry types or space groups based on the symmetry elements [Newnham, 1975]. A crystal exhibiting spontaneous polarisation can be visualised to be composed of negative and positive ions. In a certain temperature range, these ions are at their equilibrium positions, at which the free energy of the crystal is a minimum, and the centre of positive charge does not coincide with the centre of negative discharge. For example, Fig. 2.1 shows the crystal structure of barium titanate. Above a certain temperature (which is called Curie point $\mathbf{\Theta_c}$) of 120°C, the prototype crystal structure is cubic, with Ba^{2+} ions at the cube corners, O^{2-} ions at the face centres and Ti^{4+} ion at the body centre, as shown in Fig. 2.1 (a). Below the Curie temperature, the structure is slightly deformed, with Ba^{2+} and Ti^{4+} ions displaced relative to the O^{2-} ions, thereby creating a dipole, as shown in Fig. 2.1 (b). Thus, we may visualise each pair of positive and negative ions as an electric dipole, and the spontaneous polarisation (dipole moment per unit volume) as due to an assembly of these dipoles, which point in the same direction. If the value of the spontaneous polarisation **Ps** depends on the temperature, this is called the pyroelectric effect. Pyroelectric crystals show a **Ps** in a certain temperature range. If the magnitude and direction of **Ps** can be reversed by an external electric field, then such crystals are known as ferroeletrics.

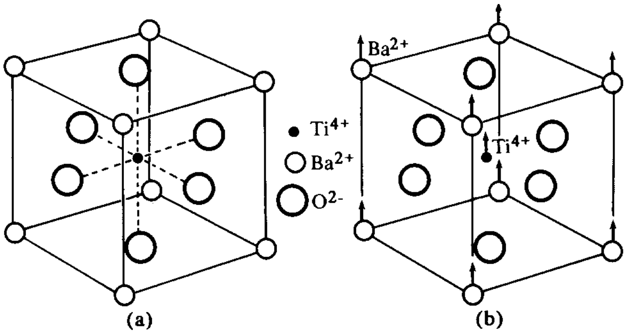


Fig. 2.1. The crystal structure of perovskite barium titanate. (a) Above the Curie temperature the unit cell is cubic; (b) below the Curie temperature the unit cell structure is tetragonal with Ba^{2+} and Ti^{4+} ions displaced relative to the O^{2-} ions [After Xu, 1991].

Ferroelectric crystals possess regions with uniform polarisation called ferroelectric domains. Within a domain, all the electric dipoles are aligned in the same direction. There may be many domains in a crystal separated by boundaries called domain walls. Adjacent domains can have their polarisation vectors in antiparallel directions or at right angles to one another. The boundaries between these domains are, correspondingly, known as 180° or 90° domain walls. A ferroelectric single crystal, when grown, has multiple ferroelectric domains. A single domain can be obtained by domain wall motion made possible by the application of a sufficiently high electric field, the process known as poling. Poling is very important for the application of polycrystalline ferroelectric ceramics. Ferroelectric ceramics do not possess any piezoelectric properties owing to the random orientations of the ferroelectric domains in the ceramics before poling. During poling, a DC electric field is applied on the ferroelectric ceramic sample to force the domains to be oriented or “poled”. While domains cannot be perfectly aligned with the field except when the grain or crystal is coincidentally oriented with its c- or a-axis in the field direction, their polarisation vectors can be aligned to maximise the component resolved in the field direction. After poling, the electric field is removed and a remanent polarisation and remanent strain are maintained in the sample, and the sample exhibits piezoelectricity. A simple illustration of the poling process is shown in Fig. 2.2. But a very strong field could lead to the reversal of the polarisation in the domain, known as domain switching.

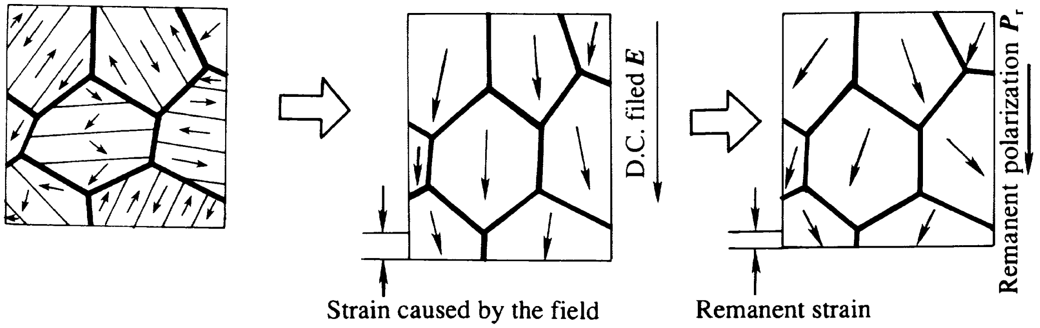


Fig. 2.2. Schematic illustration of the poling process [After Xu, 1991].

A consequence of the resistance to domain switching is that polarisation in a ferroelectric is hysteretic, which is another important characteristic of ferroelectrics; namely, that the polarisation **P** is a double-valued function of the applied electric field **E**, and so is not precisely reversible with field. A ferroelectric hysteresis loop is shown in Fig. 2.3. When a small electric field is applied, only a linear relationship between **P** and **E** is observed because the field is not large enough to switch any domain and the crystal will behave as a normal dielectric material (paraelectric). This case corresponds to the segment OA of the curves in Fig. 2.3. As the electric strength increases, a number of negative domains, which have a polarisation opposite to the direction of the field, will be switched over in the positive direction along the field, and domain orientation begins to take place. This results in a sharply rising **P** with increasing field **E**, and the polarisation will increase rapidly (segment AB) until all the domains are aligned in the positive direction (segment BC). This is a state of saturation in which the crystal is composed of just a single domain. As the field strength decreases, the polarisation will generally decrease but does not return back to zero (at the point D in the Fig. 2.3). When the field is reduced to zero, some of the domains will remain aligned in the positive direction and the crystal will exhibit a remanent polarisation **Pr**. The extrapolation of the linear segment BC of the curve back to the polarisation axis (at the point E) represents the value of the spontaneous polarisation **Ps**. The remanent polarisation **Pr** in a crystal cannot be removed until the applied field in the opposite direction reaches a certain value (at the point F). The strength of the field required to reduce the polarisation **P** to zero is called the coercive field strength **Ec**. Further, increasing the field in the negative direction will cause a complete alignment of the dipoles in this direction and the cycle can be completed by reversing the field direction once again.

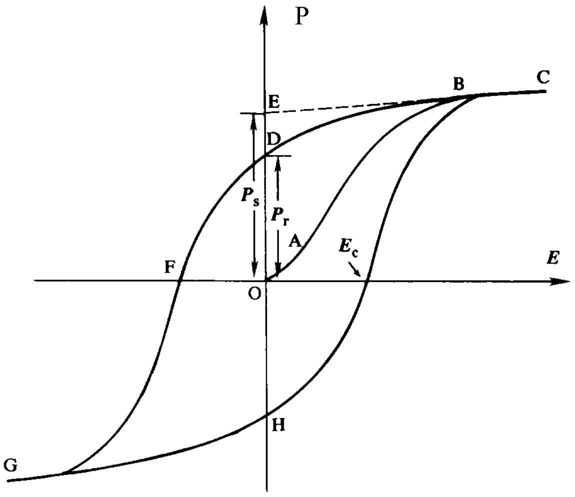


Fig. 2.3. A typical **P**-**E** hysteresis loop in ferroelectrics [After Xu, 1991].

2.2. Piezoelectric PZT System

2.2.1. Perovskite Structure

PZT is a solid solution phase of the $xPbZrO_3$-$(1-x)PbTiO_3$ ($0<x<100$) binary system. Its chemical formula is $Pb(Zr_xTi_{1-x})O_3$. PZT has the perovskite structure with titanium and zirconium atoms occupying A-sites at random, and lead atoms situated at the corners of the unit cell with oxygen atoms located at the surface centres (Fig. 2.4(a)). Both the lead and oxygen ions have radii of about 0.14 nm. Together they make up a face-centred-cubic array, having a lattice parameter of nearly 0.4 nm. Octahedrally co-ordinated titanium or zirconium ions are located at the centre of the unit cell.

2.2.2. Phase Diagram for $PbTiO_3$-$PbZrO_3$ Binary System

The phase diagram of the PZT solid solution is shown in Fig. 2.5, where the T_c-line is the boundary between the cubic paraelectric phase and the ferroelectric phase. A morphotropic phase boundary (MPB) divides the regions of ferroelectric phase into two parts: a tetragonal phase region on the Ti-rich side and a rhombohedral phase region on the Zr-rich size. At room temperature, this boundary is at the point Zr/Ti = 52/48. The lattice parameters of the PZT also change abruptly near the composition corresponding to the MPB (see Fig. 2.6). In the region where Zr/Ti lies between 100/0 and 94/6, the solid solution is an antiferroelectric orthorhombic phase exhibiting no observable piezoelectric effect.

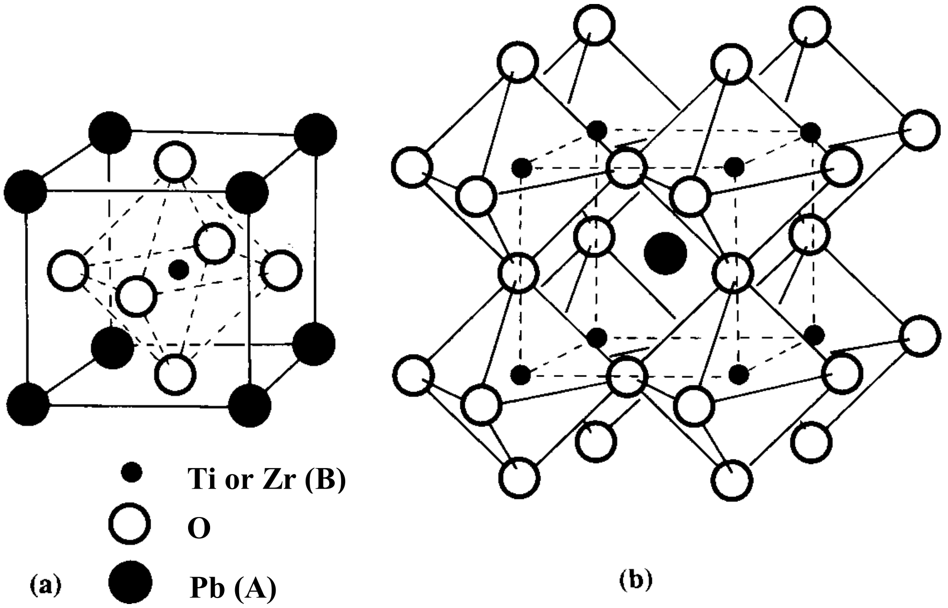


Fig. 2.4. Basic structural unit of perovskite PZT. The basic structural unit is a cube (a). Titanium or zirconium atoms (B) lie at the centre; eight lead atoms (A) occupy the corners and six oxygen atoms (O) are at the surface centres.

Sometimes, the cubic model is replaced with a polyhedral one. The O anions that surround each B cation and are closely bound to it form the points of an octahedron. In such a model, the basic structural unit becomes a group of eight corner-shared octahedrons around an A cation (b). The bulk crystal is a continuous three-dimensional network of such BO_6-octahedra groups [After Xu, 1991].

From the diagram of the PZT solid solution system, the advantages of the system for using as piezoelectric ceramics are evident [Cross, 1995]:

- Above the Curie temperatures the symmetry is cubic, and the structure is perovskite.
- The high Curie temperatures across the whole diagram lead to stable ferroelectric states over wide, usable temperature ranges.
- The MPB separating rhombohedral (8 domain state) and tetragonal (6 domain state) ferroelectric domains is first-order, so there is necessarily a two phase region near this 52/48 Zr/Ti composition.
- In the two phase region, the poling field may draw upon 14 orientation states leading to exceptional ceramic polability (Fig. 2.7) [Newnham, 1997].
- As the MPB is near vertical on the phase diagram, the intrinsic property enhancement in compositions chosen near to the boundary persists over a wide temperature range.

As the result of the unique structure of PZT, both its dielectric and piezoelectric properties show anomalous behaviour near the MPB (Fig. 2.8). There is a maximum in both the relative permittivity and the electromechanical coupling coefficient; the latter is an important parameter describing the piezoelectric properties. This feature makes PZT a practically useful piezoelectric material.

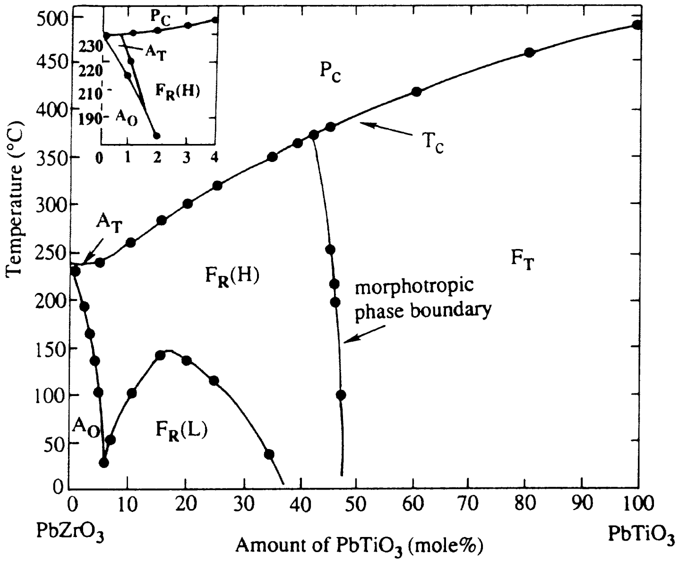


Fig.2.5. Phase diagram of the $PbTiO_3$-$PbZrO_3$ solid solution [After Jaffe *et al.*, 1971].

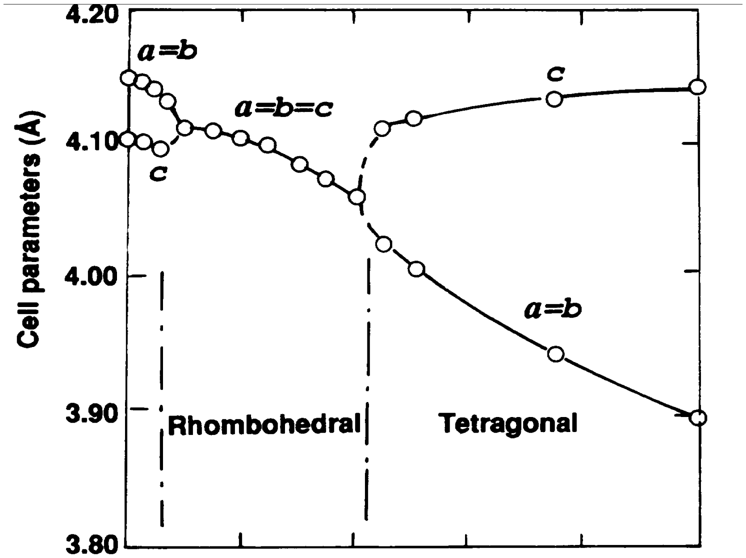


Fig.2.6. Lattice parameter change at room temperature for the $PbTiO_3$-$PbZrO_3$ solid solution [After Shirane *et al.*, 1952].

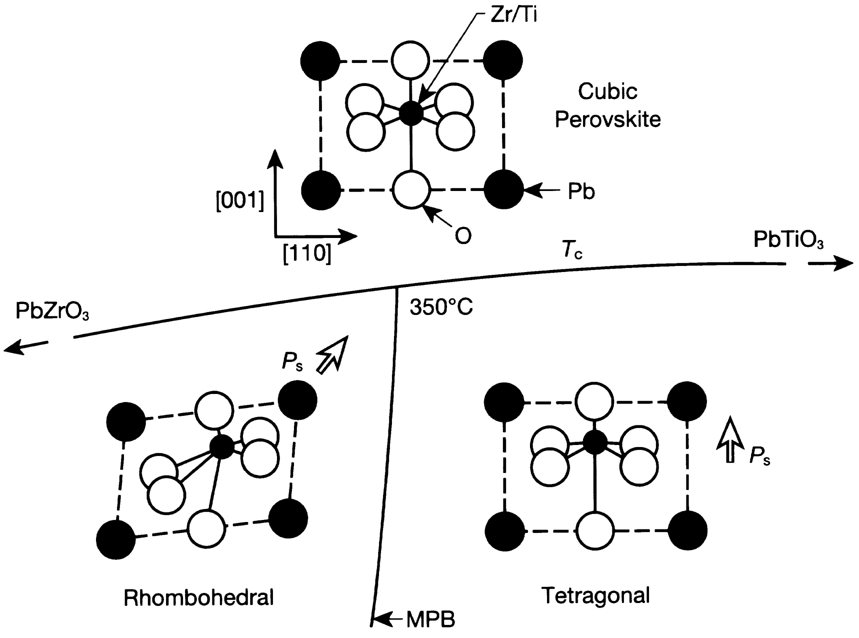


Fig.2.7. A portion of the $PbTiO_3$-$PbZrO_3$ phase diagram showing the structure changes at the Curie temperature (T_c) and the morphotropic phase boundary. Titanium-rich compositions in the PZT system favour a tetragonal modification with sizeable elongation along [001] and a large spontaneous polarisation in the same direction. There are six equivalent polar axes in the tetragonal phase corresponding to [100], $[\bar{1}00]$, [010], $[0\bar{1}0]$, [001], and $[00\bar{1}]$ directions of the cubic paraelectric state. A rhombohedral ferroelectric state is favoured for zirconium-rich compositions. Here the distortion and polarisation are along [111] directions, giving rise to eight possible domain states: [111], $[\bar{1}11]$, $[1\bar{1}1]$, $[11\bar{1}]$, $[1\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}\bar{1}]$. There are fourteen possible poling directions near the MPB over a very wide temperature range, which may in part explain the ceramic piezoelectric behaviour near this boundary [After Newnham, 1997].

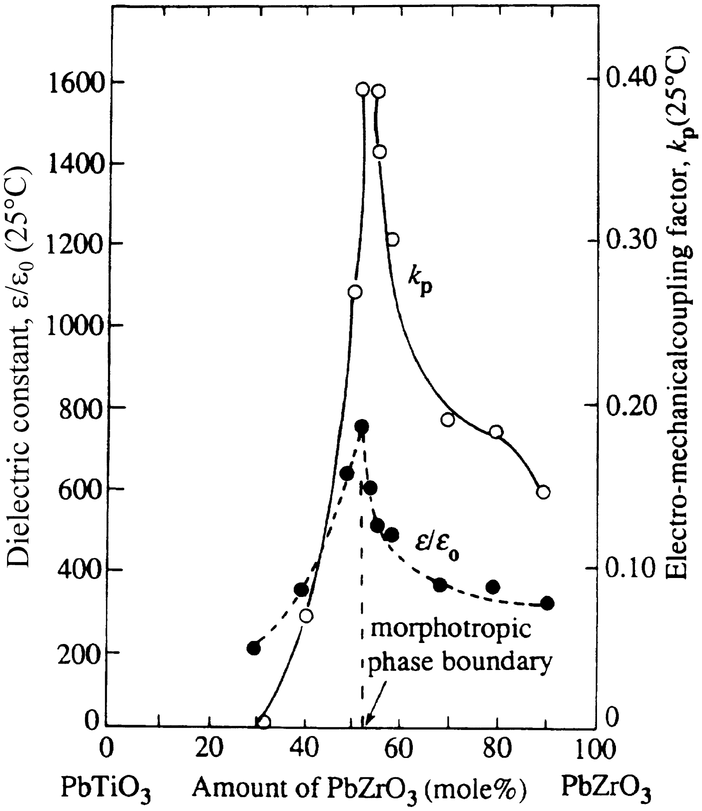
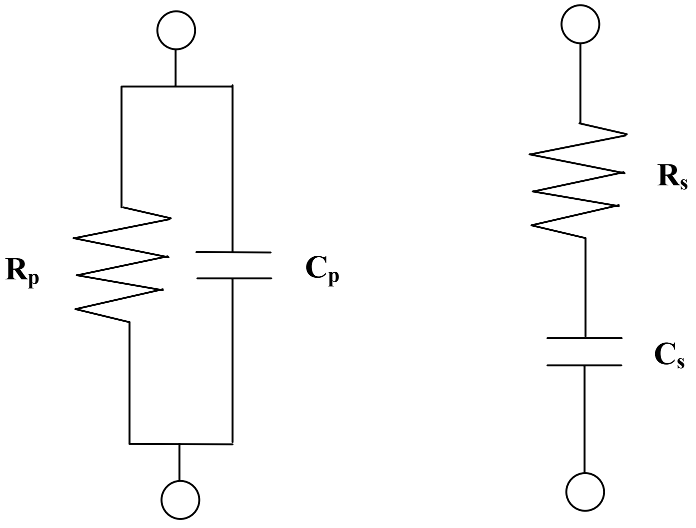


Fig. 2.8. Dielectric and piezoelectric properties of the $PbTiO_3$-$PbZrO_3$ solid solution [After Jaffe *et al.*, 1971].



(a) Parallel (b) Series

Fig. 2.9. Equivalent circuit of a piezoelectric element (non-resonance operation) [After Jones *et al.*, 1996].

2.3. Piezoelectric Properties of PZT Ceramics

2.3.1. Definitions and Measurement of Dielectric and Piezoelectric Properties

2.3.1.1. Dielectric constant and dielectric loss factor

The dielectric constant, or relative permittivity (ε_r) is defined as the ratio of the permittivity of the material to the permittivity of free space. The dielectric loss factor is defined as the tangent of the loss angle (tan δ). The loss factor represents the ratio of resistance of a parallel equivalent circuit of the ceramic element (Fig. 2.9 a). It is a measure of the amount of electrical energy which is lost through conduction when a voltage is applied across the piezoelectric element. The dielectric constant (ε_r) and dielectric loss factor (tan δ) can be measured using a standard impedance bridge or an impedance analyser both of which provide a direct reading. Measurements are generally carried out at 1 kHz to measure the static parameters, away from mechanical resonance, at a low applied electrical field.

The relative permittivity (ε_r) is calculated from the measured values of capacitance and physical dimension of the specimen. The relations are expressed as [Hewlett Packard, 1987]:

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{t \times C}{\varepsilon_0 \times A} \qquad (2.3)$$

where ε_r is the relative permittivity of the piezoelectric material, ε_0 is the relative permittivity of free space (8.854×10^{-12} F/m), t is the distance between electrodes (m), A is the area of the electrodes (m^2) and C is the measured capacitance at 1 kHz (F).

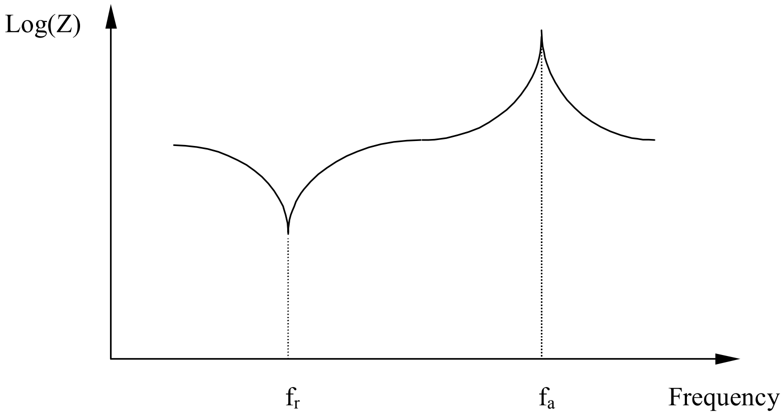


Fig. 2.10. A typical impedance curve of the equivalent circuit for measuring the impedance frequencies.

2.3.1.2. Mechanical quality factor

The most common method of determining the resonance properties of a piezoelectric material involves measuring the impedance (or admittance) of the material as a function of frequency. The impedance of the piezoelectric material passes through a minimum at the resonance frequency (f_r) and a maximum at the anti-resonance frequency (f_a) (Fig. 2. 10). Between f_r and f_a the piezoelectric material behaves inductively; while below f_r and above f_a the piezoelectric material behaves as a capacitor. The mechanical quality factor (Q_m) is defined as the ratio of the reactance to the resistance in the series equivalent circuit representing the piezoelectric resonator (Fig. 2. 9 b). The Q_m can be used to determine the sharpness of the resonance peak. The Q_m is also related to the sharpness of the resonance frequency.

$$Q_m = \frac{1}{2\pi f_r Z_m C}\left(\frac{f_a^2}{f_a^2 - f_r^2}\right) \qquad (2.4)$$

where f_r and f_a are the resonance and antiresonance frequency (Hz), respectively. Z_m is the impedance (Ω) at f_r and C is the static capacitance (F).

2.3.1.3. Piezoelectric coupling coefficient

The piezoelectric coupling coefficient (sometimes referred to as the electromechanical coupling coefficient) is defined as the ratio of the mechanical energy accumulated in response to an electrical input or vice versa. The piezoelectric coupling coefficient can be expressed as [Moulson & Herbert, 1991]:

$$K = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}}$$

or

$$K = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \tag{2.5}$$

Under dynamic DC conditions, as opposed to static DC conditions, the behaviour of the piezoelectric materials is much more complex. It can be characterised in terms of an equivalent electrical circuit which exhibits both parallel and series resonance frequencies. To approximate these frequencies, the frequency of the minimum impedance (f_r) and maximum impedance (f_a) for the material are measured as shown in Fig. 2. 10, since they differ from the actual values by a very small amount (< 0.1%). The planar coupling coefficient K_p for thin disc specimen then can be calculated from [Moulson & Herbert, 1991]:

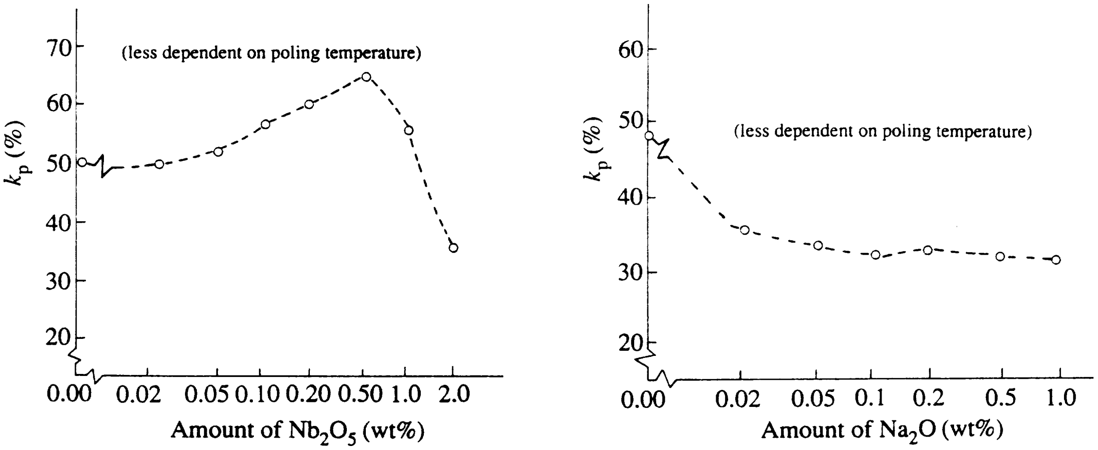
$$K_p = \left(\frac{f_a^2 - f_r^2}{f_a^2} \right)^{1/2} \tag{2.6}$$

2.3.2. Effects of Composition on Piezoelectric Properties

Though the maximum piezoelectric effect was found in the composition of pure PZT at the MPB of Zr/Ti=52/48, in practice, PZT ceramics are often modified to meet the stringent requirements for various applications. For example, for materials used as an underwater sound projector, a high Q_m and a small dielectric loss (tan δ) under high fields are desirable, while for materials used for electroacoustic transformers, a high electromechanical coupling coefficient (K_p) and a high relative permittivity (ε_r) are required. Basically, three types of additives have been employed in the compositional modification of PZT. These typical additives and their effects on the piezoelectric properties of PZT are summarised in Table 2.1.

The first additives used in compositional modification of PZT are the isovalent ones, i.e. Pb^{2+}, Ti^{4+} and Zr^{4+} are replaced partially by other cations with the same chemical valence and similar ionic radii as those of the replaced ions. An example is $Pb_{0.95}Sr_{0.05}Zr_{0.52}Ti_{0.48}O_3$, where 5% of the A-sites have been replaced by Sr^{2+}. The major effect of such isovalent additives is lowering of the Curie point, giving enhanced permittivity.

The second additives are donor type substitutions, known as soft dopants. Ions for soft doping include La^{3+}, Nd^{3+} and other rare earth ions, such as Sb^{3+}, Bi^{3+}, Nb^{5+}, Sb^{5+}, W^{6+} etc. One example is $Pb_{0.97}La_{0.02}Zr_{0.52}Ti_{0.48}O_3$, where 2% of the A-sites have La^{3+} and 1% are vacant. Another example is $Pb_{0.99}Nb_{0.02}(Zr_{0.52}Ti_{0.48})_{0.98}O_3$, where 2% of the B-sites have Nb^{5+} and 1% of the A-sites are vacant. The most outstanding changes caused by soft doping are increases in piezoelectric coupling coefficient (Fig. 2.11 a), relative permittivity and 10^3 increase in resistivity. The changes in characteristics are ascribed to the lead vacancies which occur, and the resulting increase in domain wall mobility. In general, when the ions with larger ionic radii, such as La^{3+}, Nd^{3+}, etc., occupy the A-sites to replace Pb^{2+} ions, extra positive charges are introduced into the lattice due to the fact that the valence of the doping ions is higher than that of Pb^{2+} ions, a Pb vacancy is created in the lattice to maintain electroneutrality. When ions with smaller ionic radii, such as Nb^{5+}, Ta^{5+}, etc., enter into the perovskite lattice, they occupy the B-sites to replace Zr^{4+} or Ti^{4+} ions. Since the doping ions have a higher valence than +4, extra positive charges enter the lattice and again Pb vacancies have to be created to ensure electroneutrality. These Pb vacancies make the transfer of atoms easier than in a perfect lattice; thus domain motions can be caused by a smaller electrical field (or a mechanical stress).



(a) (b)

Fig. 2.11. Variation of the coupling coefficient K_p in the piezoelectric ceramic with (a) soft and (b) hard dopants [After Takahashi, 1970, 1971].

Table 2.1. Typical additives to PZT and their major effects on piezoelectric properties. Ionic radii, in nanometre, are given in parentheses [Berlincourt, 1992 and Xu, 1991].

Additives	**Major Effects**
Isovalent additives Ba^{2+} (0.134) or Sr^{2+} (0.112) for Pb^{2+} (0.132) Sn^{4+} (0.071) for Zr^{4+} (0.068) or Ti^{4+} (0.079)	Lower Curie point Higher permittivity
Soft dopants La^{3+} (0.122), Nd^{3+} (0.115), Sb^{3+} (0.090), Bi^{3+} (0.114) or Th^{4+} (0.110) for Pb^{2+} (0.132) Nb^{5+} (0.069), Ta^{5+} (0.068), Sb^{5+} (0.063) or W^{6+} (0.065) for Ti^{4+} (0.068) or Zr^{4+} (0.079)	Higher permittivity Higher K_p Much lower Q_m Resistivity about 10^3 higher
Hard dopants K^+ (0.133) or Na^+ (0.094) for Pb^{2+} (0.132) Fe^{3+} (0.067), Al^{3+} (0.057), Sc^{3+} (0.083), In^{3+} (0.092) or Cr^{3+} (0.064) for Ti^{4+} (0.068) or Zr^{4+} (0.079)	Lower permittivity Lower dielectric loss Lower K_p Much higher Q_m

The third additives are acceptor type substitutions, or known as hard dopants. Hard doping ions in PZT include K^+ and Na^+, which occupy the A-sites and Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Mg^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+} and Sc^{3+}, etc., which occupy the B-sites in the perovskite structure. Unlike soft doping, hard doping increases the hardness of PZT properties, i.e. lower dielectric constant, lower dielectric loss, higher coercive field, high Q_m, a slightly lower K_p and a lower bulk resistivity. Fig. 2.11 (b) shows that the K_p of PZT (with Zr/Ti = 52/48) is affected by hard doping of Na^+ ions. When hard doping ions with a lower positive valence replace metal ions with a higher positive valence, oxygen vacancies are created in the lattice, on account of the requirements of electroneutrality. For example, when two Pb^{2+} ions are replaced by two K^+ ions, or when two Zr^{4+} or Ti^{4+} ions are replaced by two Fe^{3+} ions, one oxygen vacancy is created. Thus two hard doping ions may cause the creation of one oxygen vacancy, which cannot be removed by sintering the ceramic in an atmosphere of oxygen. Since the perovskite structure is composed of oxygen octahedra, and to maintain the stability of the oxygen octahedron framework, the oxygen vacancy concentration in the perovskite structure must be below a certain limit.

It has been confirmed [Gerson, 1960] that the undoped PZT ceramics possess p-type conductivity (hole-type semiconductor) due to the lead oxide evaporation from the PZT sample during the sintering process, which creates Pb vacancies in the sintered PZT ceramic. Therefore, in a PZT ceramic with hard doping ions, space charge, i.e. both centres of negative charges and hole-carriers, increase dramatically; which cause an internal field $\mathbf{E_s}$ inside the grains of PZT, and this field $\mathbf{E_s}$ may inhibit domain motion. The inhibition of domain motion reduces the dielectric loss (including the energy loss in domain vibration hysteresis), and therefore Q_m is enhanced.

Apart from the above-mentioned additives, there are some other doping ions, such as Ce, Cr and U, they possess variable valence and play the role of both a softener and a hardener. For example, A Cr-doped PZT ceramic has a high Q_m, while its dielectric loss increases and its K_p decreases.

Co-doping, i.e. with two or more metal elements, is also frequently used for better piezoelectric properties. For example, MnO_2-Nb_2O_5 co-doped PZT ceramic is better than that of single doping of Nb^{5+} or Mn^{4+} in terms of its high K_p and Q_m, low permittivity and its excellent temperature stability [Park *et al.*, 1995].

2.3.3. Effects of Microstructure on Piezoelectric Properties

The microstructure of ceramics includes factors such as grain size and/or grain boundaries; density and/or porosity; and homogeneity.

The grain size of PZT ceramics depends on the compositions and sintering conditions. In general, the grain size of PZT ceramics increases with the increasing sintering temperatures and sintering time, from submicron to about 10 μm. Metal oxide dopants will affect the grain growth during sintering process. Some metal oxide may restrain the grain growth in the ceramics. For example, the average grain size will decrease from 5.5 μm in undoped PZT ceramics to 2.7 μm in PZT ceramics doped with 0.3 wt.% Fe_2O_3, while the Q_m increases from 300 to 900 correspondingly [Weston *et al.*, 1969]. It was also shown that, when Fe_2O_3 doping is over 0.8 wt.%, particles containing Fe^{3+} ions would precipitate at grain boundaries, and that properties of the ceramics would deteriorate. Thereby, Fe^{3+} ions can restrain the grain growth, because the solid solution limit of Fe in PZT is about 0.8 wt.% and the remaining Fe^{3+} ions are squeezed out of grains and accumulate at grain boundaries. On the other hand, some dopants (e.g. CeO_2) in PZT ceramics are helpful for grain growth [Xu, 1991].

Consequently, the effect of the grain size on the piezoelectric properties strongly depends on the compositions and sintering conditions. Okazaki et al [1970] reported that for the PZT ceramics with the composition $Pb(Zr_{0.51}Ti_{0.49})O_3$ doped with 0.1 wt.% MnO_2 at a density of 7.70 ~ 7.85 g/cm^3, the piezoelectric properties of the PZT ceramics increase approximately linearly with increasing grain size (see Fig. 2.12). However, Demartin *et al.* [1994] and Ichinose and Kimura [1991] reported that the maximum electrical properties have been obtained at a grain size of 2 to 3 μm for PZT ceramics doped with Nb and partially substituted with $Pb(Sb,Nb)O_3$ respectively.

The deterioration of the piezoelectric properties with decreasing grain size is probably related to fewer domains and less mobile domain walls [Martirena & Burfoot, 1974]. Mishra and Pandey [1995] also pointed out that below a critical size, the formation of ferroelectric domains is not energetically favourable.

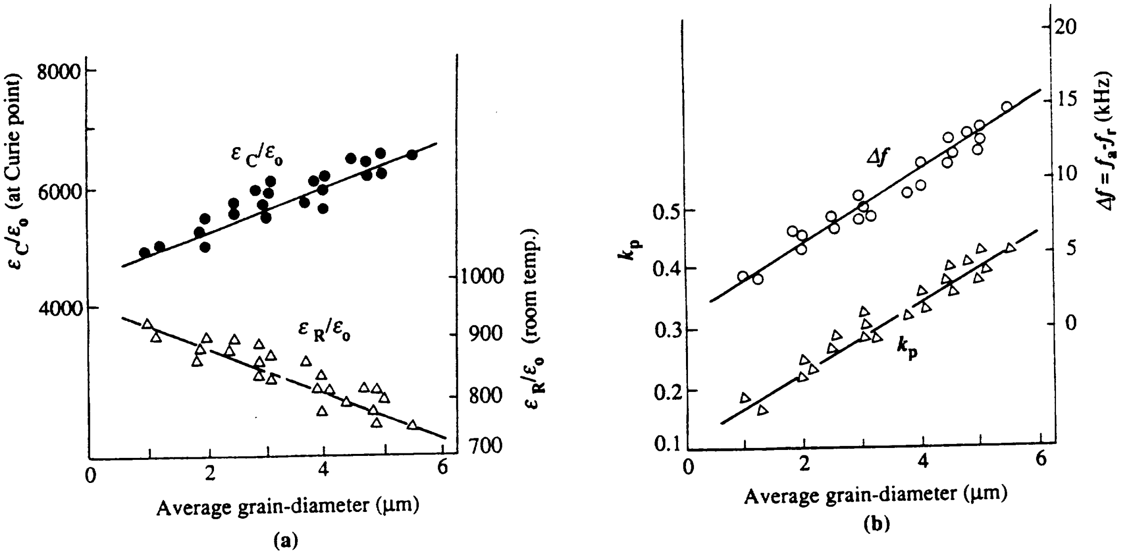
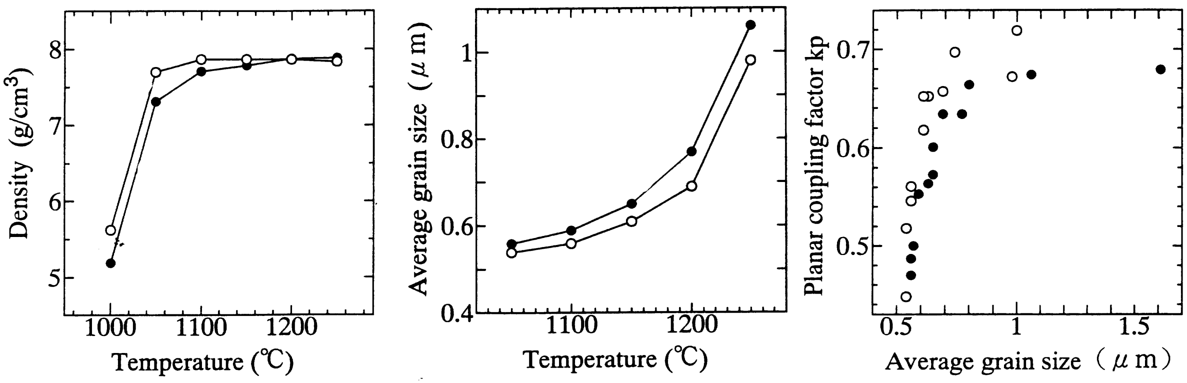


Fig. 2.12. Dependence of dielectric and piezoelectric properties on average grain size in the ceramic $Pb(Zr_{0.51}Ti_{0.49})O_3$ doped with 0.1 wt.% MnO_2 [After Okazaki *et al.*, 1970].

The density and/or porosity which will affect the piezoelectric properties are dependent on the sintering conditions. Sintering in oxygen atmosphere is reported to facilitate the pore-elimination process [Ogawa, 1991]. The PZT ceramics possess higher densities and the grain growth is suppressed with the increase of oxygen partial pressure. Thus the K_p is improved in comparison with that sintered in air (see Fig. 2.13).



(a) (b) (c)

Fig. 2.13. Effects of the sintering atmosphere (• air and o oxygen) on (a) density; (b) grain size; and (c) coupling coefficient K_p in PZT ceramics partially substituted with $Pb(Sb,Nb)O_3$ [After Kudo *et al.*, 1995].

Homogeneity is found to have a more profound effect on the piezoelectric properties regardless of density and grain size. Kim *et al.* [1991] reported that for the same PZT composition processed via different routes, the electrical properties are entirely different. PZT ceramics processed via the conventional mixed-oxide route possessed significantly lower dielectric and piezoelectric properties than those processed via the reactive calcination. This difference reflects inhomogeneity in the PZT ceramics in that the properties, such as ε_r and K_p, are very dependent on the Zr/Ti ratio near the MPB. Also the piezoelectric properties for the latter materials sintered at 1000°C are inferior to those sintered at 1200°C, though having similar densities and grain sizes. The lower values are believed to be related to the crystallinity of materials being less developed. The associated defects thus result in a stiffening out of the extrinsic polarisability (domain wall motion) [Zhang *et al.*, 1983].

It is worth noting that the most striking effects of the grain size, however, are on mechanical rather than electrical properties. Both flexural strength and Vickers hardness increase dramatically with the decrease of grain size [Ichnose & Kimura, 1991], and the fracture toughness is strongly dependent on the grain size [Demartin *et al.*, 1994].