

A STUDY OF PIEZOELECTRIC CERAMICS MATERIALS TOWARDS MANUFACTURING AND TESTING

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ABSTRACT

Piezoelectricity is the ability of certain crystalline materials to develop an electric charge proportional to a mechanical stress, which is called the direct piezoelectric effect discovered by Curie, brothers in 1880. Soon it was realized that materials showing this phenomenon must also show the converse piezoelectric effect: a geometric strain/deformation proportional to an applied voltage. Typical crystals (e.g., quartz, tourmaline and Rochelle salt) exhibit the piezoelectric effect. Since its discovery the piezoelectricity effect has found many useful applications, such as the production and detection of sound, generation of high voltages and frequency, microbalances, and ultra-fine focusing of optical assemblies. It is also the basis of a number of scientific instrumental techniques with atomic resolution such as the scanning probe microscopy, and everyday uses such as acting as the ignition source for cigarette lighters and pushstart propane barbecues. However, the traditional piezoelectric single crystals suffer from the disadvantages such as weak piezoelectric effect, low mechanical strength, sensitivity to moisture, and very narrow operated temperature range. Compared to the traditional single crystals, electrically poled polycrystalline ferroelectric ceramics, such as barium titanate (BaTiO₃) and lead zirconium titanate (PZT), offer the advantages of large and stable piezoelectric effects, high strength and ease of fabrication in general, especially into complex shapes and large area pieces. Nowadays, they become the dominant piezoelectric materials in the fields of piezoelectric applications such as actuators, sensors, and transducers in intelligent systems and smart structures, dominating the world market today.

KEYWORDS: Piezoelectric ceramic materials; processing; properties and characterization; applications.

INTRODUCTION

Piezoelectricity or pressure electricity is the phenomenon discovered in 1880 by the Curie brothers who were the first to demonstrate the generation of electricity (surface charges) on well prepared crystals of quartz as a result of mechanical pressure. Concerning the amplitudes of piezoelectric ceramic materials and device applications existing already, today we may further expect continuous future development and fascinating new novel application areas. In this chapter, we will present an overview of the state of art in piezoelectric ceramic materials, which covers their processing, properties, characterization,

and applications. We first briefly introduce the history and processing of piezoelectric ceramic materials, then describe the general characteristics of piezoelectric ceramic materials with a focus on the compositions and properties, piezoelectric parameters, and piezoelectric constitutive relationships, followed by the most common characterization methods for piezoelectric properties and ferroelectric domain structures, and finally some potential applications of piezoelectric ceramic materials in actuators, sensors and transducers, are presented, and the personal perspectives towards future trends of

piezoelectric ceramic materials are also given out.

Inversely, when a voltage is applied across a piezoelectric material, it can undergo a mechanical distortion in response. Typical crystals such as quartz, tourmaline, and Rochelle salt, exhibit piezoelectric effect, they have some applications in piezoelectric devices such as sonars. However, the traditional single crystal materials suffer from some disadvantages which limit their use to some extent. For example, they mostly exhibit only a weak piezoelectric effect, usually have low mechanical strength. Some ones are very sensitive to moisture and their operated temperature range is often limited. Compared to the traditional piezoelectric single crystals, piezoelectric ceramics, such as electrically poled barium titanate (BaTiO_3) and lead zirconium titanate (PZT) ceramics, exhibit large piezoelectric effects (high electromechanical coupling). They are mechanically strong, hard, chemically inert and immune to humidity. As a consequence, they become the present primary commercial piezoelectric materials, and hence are widely used as actuators and sensors in intelligent system and smart structures [1,2]. The beginning of the twentieth century gave the birth to most of the classic applications of piezoelectrics, such as quartz sonars, resonators and accelerometers. After the World War II and following the discovery of PZT, the advances made in piezoelectric materials allowed the development of numerous applications based on the tailored piezoelectric properties. High-performance of piezoelectric ceramic materials now open up new possibilities for “energy harvesting,” making use of ambient motion and vibration to generate electricity where batteries or other power sources are impractical or unavailable [3].

REVIEW OF LITERATURE

Piezoelectricity is a property of a group of materials that was discovered in 1880 by Pierre and Jacques Curie during their study of the effects of pressure on the generation of electrical charge by crystals such as quartz, tourmaline, and Rochelle salt. In 1881, the term “piezoelectricity” was first suggested by W. Hankel, and the converse effect was mathematically deduced by Gabriel Lipmann from fundamental thermodynamic principles [4]. The schematic diagram for illustration of direct and converse piezoelectric effects is shown in Figure 1(a) and 1(b), respectively [5]. For the next few decades, piezoelectricity remained something of a laboratory curiosity. More work was done to explore and define the crystal structures that exhibited piezoelectricity. This culminated in 1910 by the publication of Woldemar Voigt's *Lehrbuch der Kristallphysik* (a textbook on crystal physics), which described the 20 natural crystal classes capable of piezoelectricity, and rigorously defined the piezoelectric constants using tensor analysis [6]. However, the complexity of the science of piezoelectricity made it difficult to mature to practical applications until a few years later. In 1917 Paul Langevin and his coworkers developed an ultrasonic submarine detector, which consisted of a transducer made of thin quartz crystals carefully glued between two steel plates, and a hydrophone to detect the returned echo. By emitting a high-frequency chirp from the transducer, and measuring the amount of time it takes to hear an echo from the sound waves bouncing off an object, one can calculate the distance to that object. This success opened up the opportunities for piezoelectric materials in underwater applications and a host of other applications such as ultrasonic transducers, microphones, and accelerometers. In 1935, Busch and Scherrer discovered piezoelectricity in potassium dihydrogen phosphate (KDP) and its isomorph. The KDP family was the first discovered major family of piezoelectrics and

ferroelectrics. From 1940 to 1943, unusual dielectric properties such as an abnormally high dielectric constant were found in BaTiO₃ independently by Wainer and Salmon, Ogawa, and Wul and Golman. After its discovery, compositional modifications of BaTiO₃ led to improvement in temperature stability and high voltage output. Piezoelectric transducers based on BaTiO₃ ceramics became well established in a number of devices. BaTiO₃ ceramics has unusually high dielectric constant due to its ferroelectric (permanent internal dipole moment) nature, thus ushering in a new class of ferroelectrics with the ABO₃ perovskite structure. As shown in Figure 2, the unit cell of BaTiO₃ consists of a corner-linked network of oxygen octahedra with Ti⁴⁺ ions occupying

B sites within the octahedral cage and the Ba²⁺ ions situated in the interstices (A site) created by the linked octahedral [7]. Below the Curie temperature, there is a structural distortion to a lower-symmetry phase accompanied by the shift off-center of the small cation (Ti⁴⁺), as shown in Figure 2(c). Displacement occurs along the c axis in a tetragonal structure, although it should be understood that it can also occur along the orthogonal a or b axes as well. The views of “polarization up” and “polarization down” (representing 180° polarization reversal) show two of the six possible permanent polarization positions. The spontaneous polarization derives largely from the electric dipole moment created by this shift.

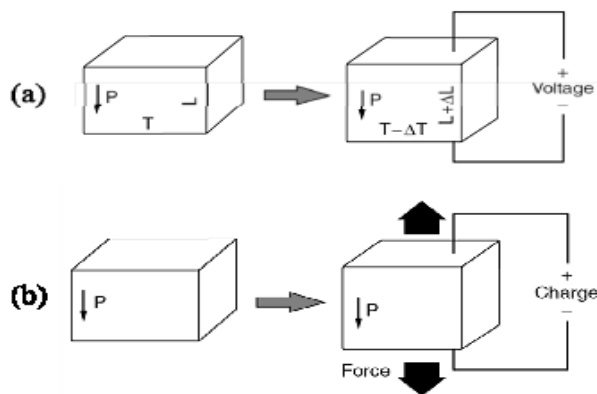


Figure 1. Schematic diagrams of the direct and converse piezoelectric effect

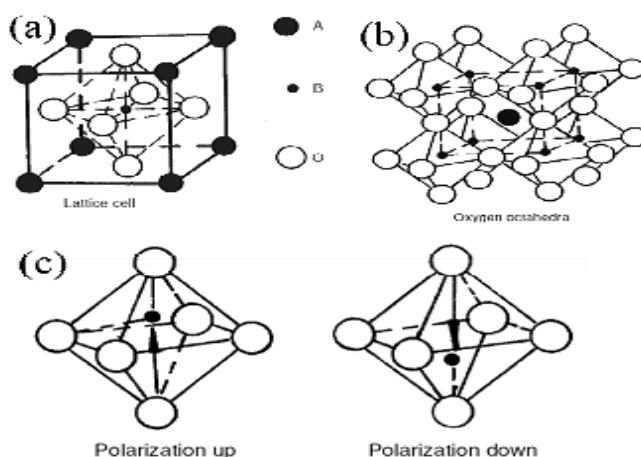


Figure 2. (a) Unit cell of ABO₃ perovskite, (b) oxygen octahedra, and (c) 180° polarization reversal for two of the six possible polarization states produced by displacement of the central cation in the tetragonal plane

PROCESSING OF PIEZOELECTRIC CERAMIC MATERIALS

The fabrication of most bulk piezoelectric ceramics starts with powder preparation. The powders are then pressed to the required shapes and sizes, and the green shapes are in turn processed to mechanically strong and dense ceramics. The more important processes that influence the product characteristics and properties are powder preparation, calcining and sintering. The next steps are machining, electroding and poling (application of a dc field to orient the ferroelectric domains and induce piezoelectricity). The electromechanical properties of piezoelectric ceramics are largely influenced by their processing conditions. First, high purity raw oxide materials are accurately weighed according to their desired ratio and then are mechanically or chemically mixed. During the calcination step, the solid phases react to form the piezoelectric phase. After calcination, the solid mixture is milled to fine particles. Shaping is accomplished by a variety of ceramic processing techniques, including powder compaction, tape casting, slip casting, and extrusion. During the shaping operation, organic materials are typically added to the ceramic powder to improve its flow and binding characteristics. The organic is then removed at a low temperature (500-600° C) burnout step. After organic removal, the ceramic structure is fired to an optimum density at an elevated temperature. Lead containing ceramics such as PbTiO₃, PZT, Pb(Mg_{1/3}Nb_{2/3})O₃ are fired in sealed crucibles in an optimized PbO atmosphere to prevent lead loss above 800° C. Due to the symmetry limitations, the alignment of the ferroelectric domains along the direction of the poled field in poled ceramics is never complete. However, the end result is a ceramic

whose net polarization along the poling axis has sufficiently high piezoelectric properties. For example, depending on the type of crystal structure involved, the degree of poling can be quite high, ranging from 83% for the tetragonal phase to 86% for the rhombohedral phase, and to 91% for the orthorhombic phase. The degree of poling is also increased in ascending order from polycrystalline ferroelectric ceramics, to poled ferroelectric ceramics, to single crystal ferroelectrics and to single-domain single crystals.

CHARACTERIZATION OF FERROELECTRIC DOMAIN STRUCTURE

Ferroelectric domain structures have several important effects on the behavior of piezoelectric ceramics. As a perovskite in ceramic form cools through its Curie point, it contracts isotropically since the orientations of its component crystals are random. However, the individual crystals will have a tendency to assume the anisotropic shapes required by the orientation of their crystal axes. This tendency will be counteracted by the isotropic contraction of the cavities they occupy. Therefore, a complex system of differently orientated domains is formed to minimize the elastic strain energy within the crystals. It is believed that the formation of 90° domains is helpful to minimize both electrostatic and elastic strain energies, whereas the 180° domains only reduce the electrostatic energy. In the tetragonal structure, domains are usually designated as either a domain (with polarization direction perpendicular to the viewing direction) or c domain (with polarization direction parallel to the viewing direction). Considering the crystallographic directions of two neighboring domains, four alternative ways can be derived from two

general domain types, i.e. 90° a-a, 90° a-c, 180° a-a and 180° c-c domains. The two alternatives in each of the two domain types are structurally identical, they only differ by the viewing direction chosen to illustrate the domain configurations. The diagnostic features for identifying the 90° a-a domains are: (a) the domain boundaries lying on the (011) plane appearing edge-on, and (b) diffraction spot splitting along [011] when viewed from [100]. As viewed from [010] direction, the characteristic features of the 90° a-c domains therefore become: (a) the domain boundaries lying on the (011) plane exhibiting asymmetric δ-fringes, and (b) spot splitting along [001] direction. The application of a sufficiently strong field will orient the 180° domains in the field direction, as nearly as the orientation of the crystal axes allows. The field will also have an orientating effect on 90° domains in the tetragonal phase piezoelectric ceramics and on 71° and 109° domains in the rhombohedral phase, but the response will be limited by strain situation within and between the crystals. There will be overall change in the shape of the ceramic body with an expansion

in the field direction and contraction at right angles to it. When the field is removed the strain in some regions will cause the polar orientation to revert to its previous direction, but a substantial part of the reorientation will be permanent. To better understand the piezoelectric properties of piezoelectric ceramics, their ferroelectric domains structures should be clearly classified.

PROPERTIES OF PIEZOELECTRIC CERAMIC MATERIALS

The parameters that are of interest when considering the electromechanical effects of piezoelectric materials, are the piezoelectric coupling factor κ (e.g. κ_{33} , κ_{31} , κ_P and κ_t), mechanical quality factor (Q_m), frequency constant (NI), and piezoelectric coefficients, such as the d and g coefficients which describe the interaction between mechanical and electrical behavior of piezoelectric ceramics. The effective electromechanical coupling coefficient k_{eff} describes the ability of the ceramic transducer to convert one form of energy to another, which is defined by the equation:

$$K_{eff}^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}}$$

Or,

$$K_{eff}^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}}$$

This parameter is a function in equations for electrical/mechanical energy conversion efficiency in actuators, in bandwidth and insertion loss in transducers, and signal processing devices, and in the location and spacing of critical frequencies of resonators. Since the energy conversion is always incomplete, κ^2 is (and thus also κ) is always lower than 1.0. The effective coupling

coefficient k_{eff} is related to the values of f_m and f_n , and can be described as

$$K_{eff}^2 \approx \frac{f_n^2 - f_m^2}{f_n^2}$$

Values for f_m and f_n can be readily measured by using a suitable bridge, which are the frequencies for the minimum and maximum

impedance Z of the circuit as a whole, respectively. The approximations in equation (3) are good provided that the Q_m value for the resonator is high enough, for example greater than 100. The planar coupling coefficient κ_p is related to the parallel and series resonant frequency by

$$\frac{\kappa_p^2}{1 - \kappa_p^2} = f \left(J_0, J_1, \nu \frac{f_p - f_s}{f_s} \right)$$

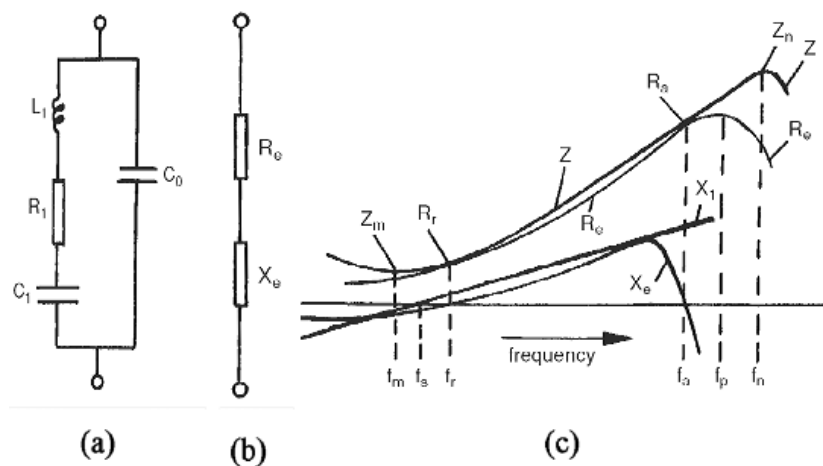
$$Q_m = 2\pi \frac{\text{stored mechanical energy at resonance}}{\text{mechanical dissipated energy per resonant cycle}}$$

The Q_m can be obtained from the following equation:

$$Q_m = \frac{f_p^2}{2\pi f_s |Z_m| (C_0 + C_1) (f_p^2 - f_s^2)}$$

Where $|Z_m|$ is the minimum impedance at resonance, C_0 and C_1 are the capacitance shown in Figure 3(a), respectively. The frequency constant N_l is defined by the following equation

$$N_l = l \times f_r = \frac{1}{2} \sqrt{\frac{Y}{\rho}}$$



Where J_0 and J_1 are Bessel function and ν is Poisson's ratio. κ_{31} can be also calculated from

$$\kappa_{31}^2 = \frac{1 - \nu}{2} k_p^2$$

The mechanical quality factor Q_m , representing the degree of mechanical loss of piezoelectric resonator at resonance, is defined as

Where l is the length of piezoelectric ceramic thin plate, f_r is the resonance frequency in the length direction, Y is the Young's modulus, and ρ is the density. These values of the piezoelectric properties of a material can be derived from the resonance behavior of suitably shaped specimens subjected to a sinusoidally varying electric field. To a first approximation, the behavior of the piezoelectric specimen close to its fundamental resonance can be represented by an equivalent circuit, as shown in Figure 3(a) and Figure 3(b). The frequency response of the circuit is shown in Figure 3(c), in which various characteristic frequencies are identified.

Figure 3. (a) Equivalent circuit for a piezoelectric specimen vibrating close to its fundamental resonance, (b) the equivalent series components of the impedance of (a), and (c) characteristic frequencies of the equivalent circuit, the differences between f_m , f_s and f_r , and between f_a , f_p and f_n are exaggerated

The functions f_r and f_a are the resonant and anti-resonant frequencies when the reactance of the circuit is zero ($X_e=0$); f_s is the frequency at which the series arm has zero reactance ($X_1=0$); f_p is the frequency when the resistive component R_e is maximum; f_m and f_n are respectively the frequencies for the minimum and maximum impedance Z of the circuit as a whole. Piezoelectric vibrators with electrodes covering their two flat faces are used to measure the properties of piezoelectric ceramics. A more common geometry is a thin disc of diameter d electroded over both faces and poled in a direction perpendicular to the faces. In these disk-shaped specimens the resonance is focused on a radial mode excited through the piezoelectric effect across the thickness of the disc. The details about the determination of piezoelectric coefficients can be found in IRE standards on piezoelectric crystals: measurements of piezoelectric ceramics.

CHARACTERIZATION METHODS FOR PIEZOELECTRIC CERAMIC MATERIALS:

Characterization of Piezoelectric Properties: Up to date, different methods have been developed to characterize the piezoelectric properties of piezoelectric ceramic materials. One method is the resonance technique, which involves measuring the characteristic resonance frequencies when a suitably shaped specimen is driven by a sinusoidal electric field. To a first approximation, the behavior of a poled ceramic sample close to its fundamental resonance frequency can be represented by an equivalent circuit, as shown in Figure 3(a). Another one is the direct technique, which is widely used to evaluate the sensor capabilities

of piezoelectric materials at sufficiently low frequencies. Mechanical deformations can be applied in different directions to obtain different components of the piezoelectric tensors. In a simplest case, metal electrodes are placed on the major surfaces of a piezoelectric sample normal to its poling direction. Thus, the charge produced on the electrodes with respect to the mechanical load is proportional to the longitudinal piezoelectric coefficient d_{33} and the force F exerted on the ceramic sample: $Q = d_{33} F$. The charge can be measured by a charge amplifier using an etalon capacitor in the feedback loop.

APPLICATIONS OF PIEZOELECTRIC CERAMIC MATERIALS

Piezoelectric materials can provide coupling between electrical and mechanical energy and thus have been extensively used in a variety of electromechanical devices. Both direct and inverse piezoelectric effects can be used for applications of piezoelectric ceramics. In general, the use of the direct piezoelectric effect can generate a charge or high voltage by applying a compressive stresses; whereas by using the converse piezoelectric effect, small displacements can be generated by applying an electric field to a piece of ceramics. Acoustic and ultrasonic vibrations can be generated by an alternating field tuned at the mechanical resonant frequency of a piezoelectric device and can be detected by amplifying the field generated by vibration incident on the material, which is usually used for ultrasonic transducers. The flexor transducer consists of two piezoelectric ceramic thin plates poled in opposite directions and can be used in gramophone pick-ups and ultrasonic accelerometers. The generation of surface waves enables filters and other devices to be

made for use at frequencies exceeding 1GHz. Applications of piezoelectric materials have now expanded into many fields since the discovery of the effect by the Curie brothers in 1880. Significant progress in applications was made possible after the discovery of PZT ceramic materials. Piezoelectric devices can be divided into four general categories: generators, sensors, actuators, and transducers depending of what type of physical effect used. For all of these basic functionalities, different designs are available.

CONCLUSION

An overview of the state of art in piezoelectric ceramic materials, which includes their processing, properties, characterization, and the potential applications. More than one century after the discovery of piezoelectricity, piezoelectric ceramics have become commercially viable. Among the fabrication process of piezoelectric ceramics, poling process is the most critical step, which is necessary to induce the piezoelectricity in the polycrystalline ferroelectric ceramics. To meet with stringent requirements for specific applications, compositional modifications of piezoelectric ceramics with different doping conditions are possible to adjust the properties to a remarkably wide range of requirements. Characterization of the piezoelectric properties of piezoelectric ceramics is crucial for establishing the relationship between the manufacturing process and ceramic performance, which enables ones to adjust the manufacturing process of the piezoelectric ceramics to produce tailored materials. Insights gained through characterization have led to many new devices and uses. Significant progress has been made in the applications of piezoelectric ceramics since the discovery of PZT ceramics. Various potential applications of piezoelectric ceramic materials in ultrasonic actuators, sensors, transducers, and active vibration controlling, are presented in this chapter, and the personal perspectives towards

future trends of piezoelectric ceramic materials are also presented.

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