Classification, preparation process and its equipment and applications of piezoelectric ceramic
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ABSTRACT
The so-called piezoelectric ceramic is a piezoelectric polycrystal, a functional ceramic material capable of interconverting mechanical energy and electric energy. It belongs to inorganic nonmetallic materials. So far, the most widely used piezoelectric ceramic materials have both good piezoelectricity and ferroelectricity through the substitution and doping in a wide range to adjust its properties to meet the different needs of zirconium titanium lead (PZT) and its composite materials. Piezoelectric ceramic is also one of the prevailing piezoelectric materials, accounting for about 1/3 of the entire functional ceramic materials. It is mainly used for transducers, sensors, resonators and drives.

Keywords: piezoelectric ceramic piezoelectric principle classification preparation process application

1. Common types of piezoelectric ceramics

A piezoelectric effect of the ceramic refers to a spontaneous random orientation due to the polarization treatment of ferroelectric ceramics. Polarization is carried out in an electric field. After the removal of the electric field, ceramic body retains a certain total residual polarization, so it becomes a piezoelectric ceramic. In the high-temperature gradient field, orientation of the crystallization of non-ferroelectric glass ceramic also has piezoelectricity. Common types are:

1.1. Barium titanate ceramics
Barium titanate ceramic has a typical perovskite structure which shows ferroelectric effects. It is predominately consisted of barium carbonate and titanium dioxide. It is usually pre-synthesized and then sintered at high temperatures.

1.2. Lead titanate ceramics
Lead titanate ceramic is also a ferroelectric ceramic with perovskite structures. It is usually made of lead tetrachloride (or lead oxide) and titanium dioxide, and a small amount of additives in advance and then sintered at high temperatures.

1.3. Binary system ceramic (binary system ceramics)
The binary ceramic is a solid solution formed by two kinds of chemicals of the general chemical type ABO3, wherein A represents a divalent cation ion Pb2+, Ba2+, Mg2+, Ca2+, Sr2+, or a monovalent cation K+ and Na+. B represents tetravalent positive ions Zr4+, Ti4+ or pentavalent Nb5+. The most common binary piezoelectric ceramic is PbZrXTi1-XO3. By adjusting the molar ratio of the two ABO3-type structures and by modifying the elements and additives, a variety of different materials can be synthesized.

1.4. Lead zirconate ceramic
Lead zirconium titanate ceramic is commonly referred to as PZT ceramic, which is currently widely used. It is PbZrO3 and PbTiO3 solid solution with perovskite type structure. When the zirconium and titanium ratio is close to 53/47 or so (that is, near the eutectic phase boundary), it shows the strongest piezoelectric properties.
1.5. **Ternary system ceramic**

Ternary system ceramic usually has the base perovskite structure of lead zirconate titanate (PbZrO$_3$-PbTiO$_3$) binary system. A third compound (chemical formula ABO$_3$ type) is then added to form the ternary solid solution. Note that the incorporation of the third compound must not change the entire lattice of the perovskite structure.

1.6. **Niobate system piezoelectric ceramic**

Niobium-based piezoelectric ceramic is ferroelectric ceramic with oxygen octahedral structures. Various niobate ceramics have perovskite type (e.g. KNbO$_3$), tungsten bronze type (e.g. lead niobate PbNb$_2$O$_6$), pyrochlore type (e.g. Cd$_2$Nb$_2$O$_7$) and other structures. Their Curie temperature is high, the dielectric constant is small and the speed of sound is high. The mechanical quality factor QM of lead niobate in particular, is very low, suitable for ultrasonic testing.

1.7. **Electro-optical (transparent) ferroelectric ceramic**

Usually refers to lanthanum (La) lead zirconate titanate (PZT) ceramic which is referred to as PLZT, in addition to bismuth doped lead zirconate titanate which have electro-optic effect. In the ferroelectric ceramic, the change of the domain state is accompanied by the change of the optical properties, for example, the electronically controlled birefringence (fine crystal) and light scattering features.

1.8. **Ferroelectric ceramic thin film**

Ferroelectric ceramic film is a ferroelectric polycrystalline film, which has (i) piezoelectric and pyroelectric properties; (ii) linear or secondary electro-optical effect, and (iii) nonlinear optical effects. It can be used to manufacture pyroelectric detectors and random read memory to facilitate the miniaturization of devices and microelectronics and optoelectronics integration. At present, the main methods of preparing ferroelectric ceramic films are by molecular beam epitaxy, magnetron sputtering, chemical vapor deposition and sol-gel (SolGel). The film substrate and the crystallization temperature have important effects on the orientation of the film grains.

1.9. **Piezoelectric composites**

Piezoelectric composites are generally made of piezoelectric ceramics and are high molecular polymer. By changing the volume or weight percentage of the components in the composite, the internal structures of the components themselves in the three-dimensional space and its symmetry in the spatial configuration can be greatly adjusted. According to the actual needs of the design of piezoelectric composite materials, we can manufacture the best-performance piezoelectric transducer. Such as zirconium titanate lead piezoelectric ceramic and polymer 1-3 composites, the isostatic piezoelectric strain constant $dh = \{d_{33} + 2d_{31}\}$ is much higher than that of the zirconium titanate lead piezoelectric ceramic, its capacitance also declines a lot.

2. **Piezoelectric principle of piezoelectric ceramics**

Piezoelectric principle is: Piezoelectric ceramic structure in the existence of spontaneous polarization and ferroelectric domain. External role (physical force or electric field) can change its polarization state (including domain state) and therefore to achieve energy conversion and pressure electric effect.

2.1. **The internal structure of piezoelectric ceramics**

- (1) Piezoelectric ceramic made of small grains has the irregular 'mosaic' structure, as shown in Figure 1
- (2) Each small grain is a microscopic-scale crystal and is regularly arranged into a lattice, as shown in Figure 2.
- (3) Each small grain also has a ferroelectric domain organization, as shown in Figure 3.
- (4) Overall, the crystal grains and grain lattice direction are not necessarily the same but arranged in a chaotic way, as shown in Figure 4. This structure is referred to as polycrystalline.
2.2. Generation of spontaneous polarization

Taking BT (BaTiO₃) material from cubic to tetragonal phase as an example, the generation of spontaneous polarization is analyzed, as shown in Figure 5.

![Figure 5. Schematic diagram of spontaneous polarization in BT](image)
It can be seen that the positive and negative charge centers coincide not with each other but with the c-axis due to Ti$^{4+}$ along the c-axis. Therefore c-axis is the electrode, which is not generated by the external electric field, but the crystal within. So when a spontaneous polarization occurs, the phase change temperature is referred to as Curie temperature (CT). Piezoelectric ceramic in the spontaneous polarization of the region is known as the ferroelectric domain.

### 2.3. The movement of the domain under the action of an external electric field

If a sufficiently high DC electric field is applied to a multi-domain crystal, the domain of spontaneous polarization that coincides with the direction of the electric field is increasing, and vice versa. The whole crystal is collapsing from multi-domain to a single domain, in the same direction as the electric field. Piezoelectric ceramic polarization process occurs to the ceramic chip electrode with a high enough DC electric field, forcing the domain to merge, regardless of the spontaneous polarization for directional arrangement, as shown in Figure 6.

![Figure 6. Domain polymerization under a strong electric field.](image)

### 2.4. Piezoelectric effect

1. **Positive piezoelectric effect**
   
   If a pressure parallel to the direction of polarization is applied to the ceramic sheet, the tiles will be compressed, the polarization intensity will become smaller, and the original adsorption of free charge will be released (the so-called discharge phenomenon). When the pressure is removed, the tiles restore the original state, the polarization intensity increases, and the adsorption of free charge reoccurs (the so-called charging phenomenon). This effect, triggered by the mechanical force or electricity, is known as the positive piezoelectric effect.

2. **Inverse piezoelectric effect**
   
   When an electric field parallel to the direction of polarization is applied to the ceramic sheet as shown in Figure 6, the polarization strength increases and tiles deform, either being stretched or compressed. This energy change from electricity to mechanical movement is known as the inverse piezoelectric effect.

### 3. Preparation of piezoelectric materials

Piezoelectric ceramic materials must be polarized before they have piezoelectric properties. Polarization of the ferroelectric domain should be in the same direction and at the same probability; the external power is however, not significant. Polarization in the DC electric field under the action of the ferromagnetic domain can be oriented along the direction of the electric field to bestow the material with piezoelectricity. Some piezoelectric materials are ferroelectric (T < TC); their polarization can be spontaneous or due to external electric field and steering. The general electric polarization condition is 3 to 5 kV/mm, 100 to 150 °C, and 5 to 20 min. These three are the main factors that affect the polarization. For better performance of piezoelectric ceramics, such as lead zirconatetitanate ceramics, the electromechanical coupling coefficient can be as high as 0.313 to 0.694.

To obtain a good performance of piezoelectric ceramics, you must master its production process. Changes in process conditions will greatly impact the piezoelectric properties. Therefore, we must understand the inherent law of piezoelectric ceramics, the design of a reasonable production process, and the strict control.
3.1. Factors Affecting the Performance of Piezoelectric Composites

3.1.1 Connection type

Series 2 type dielectric constant and piezoelectric constant are very small. The dielectric constants of the parallel type 2-2 and 1-3 type grow linearly with the volume content of the ceramic phase. O-3 type is between Series 2-2 and 1-3.

3.1.2 Piezoelectric ceramic units

In general, with the increase in the content of chest porcelain, Qm will increase. This is due to the mechanical loss of the piezoelectric ceramic phase smaller than the polymer. With the increase of the content of ceramic phase, the polarization method of linear increase in acoustic impedance is thermal polarization.

3.1.3 Space size of piezoelectric ceramic phase

In the case of the same composition ratio, with the increase in aspect ratio, the dielectric constant of the composite reduces and the piezoelectric constant increases, so that the merit of the composite increases. When the aspect ratio is small, the increase is significant. When the aspect ratio is greater than 50, the superior value of the composite is very slow. This shows that the aspect ratio determines the upper limit.

3.1.4 Molding process

Different molding processes will affect the microstructure of the composite, thus affecting the performance of complex materials. Kwonthoon Han et al. showed that a composite material could withstand higher polarized electric fields if colloidal processes were prepared. So the piezoelectric properties of the composite material could be improved. Our study also showed that for the same composition ratio of PZT / PVDF 0-3 complex material, those undergoing hot pressing had higher dielectric constant and piezoelectric constant.

3.1.5 Polarization process

If polarization under the electric field is operated at too high temperatures, the composite material will deform. If too low, the polarization process lasts too long. Usually the longer processing gives better polarization, but the cost will increase. So the way to obtain the best performance of artificial polarization is to identify the optimal combination of the electric field intensity, operation temperature and duration. Results showed that the piezoelectric properties of the polarized ceramic by the electric filed are better than those of the ceramic polarized by the post-perforation and post-filling methods.

3.2. Polarization

Regular thermal polarization: the sample to be polarized is placed into the silicone oil and is heated to 120-140 °C. A direct-current electric field is applied to both ends of the sample. The advantage of this method is that the device has a simple polarization effect. However, subject to sample size and electrode construction limitations, after the formation of a black conductive channel breakdown, the sample cannot reach the bubble and polarization. For samples with high conductivity, it is easy to add a voltage without damaging the sample.

The high temperature polarization process is to place the sample between the positive and negative electrodes of the high-pressure polarization device in the electric furnace, heat up to 10 to 20 °C above the Curie point, and then add a weak DC electric field (usually 30 - 40V / Mm); then to a certain rate of cooling to Curie point below, while slowly increasing the electric field to 200 V / mm or so. The furnace is then cooled as soon as it reaches 100 °C, while increasing the electric field to about 300 V / mm. Remove the sample by removing the external electric field below 100 °C.

3.3. PZT preparation example

3.3.1 PZT powder preparation steps

The PZT powder is synthesized by the chemical wet method. The reaction equation PbO + (ZrXTi1-X)O3 is synthesized by the method of B-type pyrolysis. 03 Pb (ZrXTi1-XO3). This method is called wet-dry method because of the chemical wet method used in the B-type precursor, and the synthetic ceramic powder is solid-phase reaction.
(A). Preparation of ZT Precursor (Zirconium Titanate (ZrTiO₄) Solid Solution) Tetrabutyl titanate, zirconium oxychloride and citric acid are sequentially dissolved in ethylene glycol, in which zirconium oxychloride and tetra. Molar ratio of butyl ester is about 9%, and the mass ratio of ethylene glycol to citric acid is 60/40. The mixture is heated to 120 °C to form a gel. Finally, the gel was placed in an oven at 120 °C and aged for 72 hours to obtain a polymer intermediate. During the preparation of the polymer intermediates, all metal ions are introduced in the form of organic reactions and are thoroughly mixed in the gel to ensure uniform distribution of metal ions in the polymer intermediates.

(B). Preparation of precursor powder. Polymer intermediate was heated to 300 °C at a rate of 50 °C / h for 4 h to obtain a crisp, black solid material. The black solid was ground into fine powder and then the black powder was heated to 750 °C at a rate of 100 °C / h for 2 h and cooled to room temperature to give a white powder. The purpose of the first step is to remove the organic components of the polymer intermediates, the second step of the purpose of burning is to remove the carbon in the remaining material. The purpose of the black solid grinding is to increase its specific surface area, so that it is fully and air contact, easy to exclude carbon. Our final precursor powder has ZrXTi₁-XO₂ and Nb-containing (ZrXTi₁-XO₂) without Nb. The composition and phase of the white powder were analyzed by XRD.

(C). PZT solid solution powder synthesis Figure 2.2 is PZT ceramic powder preparation process. The prepared single-phase precursor powder was pulverized in proportion to PbC₀₃ (analytical grade, 99%) powder, and dried at high temperature after drying. The product is milled and dried to obtain PZT powder. Our final ceramic powder is free of Nb and Nb-containing elements. The composition of the powder was analyzed by XRD, and the particle size of the powder was analyzed by laser particle size distribution instrument. Since the method used for the preparation of precursors is chemical wet method, the method of synthesizing PZT powder is solid phase reaction, so the whole method of preparing PZT powder can be called wet-dry method.

(D). The self-made PZT piezoelectric ceramic powder was sieved, granulated and pressed to form (50 MPa-200 MPa), pressed into round beads with a diameter of 20 mm and a thickness of 2 mm. (1000 - 1260) in the high temperature resistance furnace, in the sintering process, the billet with PZT piezoelectric ceramic powder separated from the stack in the crucible to maintain the process of burning PbO partial pressure, So that the round sheet is always in the PbO atmosphere to prevent loss of lead.

Sintering of the sample. In this experiment, the sintering of the powder was carried out without pressure air sintering. Samples were placed flat on the plate, and were separated by ingredients. The sample was completely covered with a filler containing PbO, covered with a ZrO₂ sealed between the crucible and the plate, and a large crucible was placed on the outer surface. The sample was then placed in a box furnace and sintered at a set temperature.

(E). The sample is made of silver and the porcelain is an insulator. It must be coated on the surface of the ceramic element with a layer of high conductivity, combined with a solid metal film as an electrode (usually a silver electrode). The role of the electrode has two aspects: First, the strong metal surface attached to the metal electrode to withstand high-voltage electric field, in order to facilitate the full polarization. Secondly, the ceramic element surface charge and charge. In addition, for the need to test the piezoelectric properties of the sample, the silver is also easy to test the role, because the performance test, the ceramic surface requires a conductive layer. The silver process is to uniformly spread the silver paste on the surface of the sample and bake at 200 to 250 °C, followed by a sintering treatment at 850 °C to adhere the silver layer to the surface of the ceramic product. Be careful not to make silver on the edge of the tiles.

(F). Sample polarization. At a certain temperature, the addition of a direct current field to a ferroelectric ceramic element causes the original arbitrarily oriented ferroelectric domain to be oriented in the direction of the electric field. The purpose of polarization is to make the ferroelectric domains in ferroelectric ceramics polycrystalline under the applied electric field direction along the direction of the electric field orientation, from the isotropic to anisotropic, showing the polarity and the piezoelectric effect. Polarization of the sample has the following steps:
(1) Cleaning the sample is a good silver to carefully wash with alcohol and dry, prohibit hand touch, marked positive.

(2) The plate is placed on the two electrodes of the polarizing device and fixed (note the correspondence between the positive and negative). Make sure that the silver layer of the sample is in good contact with the electrode in the oil bath and that both the sample and its poles are open.

(3) Polarization: Connect the polarized equipment line so that the silicon oil in the polarized manganese is sufficient to cover the sample and the electrode. Turn on the power, preheat the polarized device for 10-15 minutes.

Then it is connected to the heating oil bath power supply, 5-10 minutes to 80 °C or so and then in 5.10 minutes while the temperature rises to the polarization voltage of 2.5 kV/mm and the polarization temperature of 120-140 °C, polarization After 15 minutes, turn off the power, cool to room temperature, remove the sample. Such as the phenomenon of breakdown in the polarization, you must immediately turn off the high-voltage power discharge after the sample, with a new sample to re-carry out.

3.4. Newer research progress

Effect of Nb5+ on Dielectric and Piezoelectric Properties of PZT Piezoelectric Ceramics. In order to further improve its performance, we doped Nb5+, and when Nb5+ was introduced into the molar fraction of 0.02, the introduction of Nb5+ allowed the ceramic material to be sintered at a lower temperature of 1070 °C and the sintered ceramic material The dielectric constant, the piezoelectric coefficient and the mechanical coupling coefficient are improved, \( \varepsilon_r = 1397, d_{33} = 389 \text{pc/N}, K_P = 0.647 \).

\[(1-x)\text{LF}4-x\text{BCW}]\] lead-free piezoelectric ceramics prepared by conventional solid-phase method \((1-x)\text{Li}, 0.04\text{Na}, 0.052\text{K}, 0.44\text{Nb}, 0.86\text{Ta}, 0.10\text{Sb}, 0.04\text{O}3, \text{xBaCu}, 0.5\text{W}, 0.503\) [The effects of different BCW doping \((x = 0\%, 0.1\%, 0.2\%, 0.5\%, 1\%, \text{mole fraction})\) on the microstructure and electrical properties of LF4 ceramics were investigated. The results show that the material is still perovskite structure when BCW is introduced. When \(x\geq1\%), the sample is transformed from tetragonal to orthorhombic phase. \(T_0-t\) and \(T_c\) move to the low temperature region with the increase of BCW incorporation. BCW doping content has a "hard" doping effect on the electrical properties of LF4, and its piezoelectric constant \(d_{33}\), plane electromechanical coupling coefficient, dielectric loss \(\tan \delta\) and dielectric constant \(\varepsilon_r\) decrease with the increase of BCW content Mechanical quality factor \(Q_m\) overall improvement. In addition, BCW incorporation reduces the sintering temperature of the ceramic and increases its density.

The Li + modified KNN-BNKT lead-free piezoelectric ceramics was prepared by liquid phase coating method. Li + doped with KNN-BNKT was used to study the effect of Li + doped on \([(K0.5-\text{Na0.5-NbO}_3-K0) 1\text{Na-0.4Bi-0.5TiO}_3-x\text{LiNbO}_3] [0\leq x\leq0.04] \) ceramic crystal phase, microstructure and piezoelectric, dielectric and other properties.

4. Application of piezoelectric ceramics

Piezoelectric ceramics are mainly used in the manufacture of ultrasonic transducer, underwater acoustic transducer, electroacoustic transducer, ceramic filter, ceramic transformer, ceramic frequency discriminator, high voltage generator, infrared detector, surface acoustic wave device, electro-optical Devices, ignition detonation devices and piezoelectric gyroscopes. The use of piezoelectric ceramics is very broad. Here we give a few cases.

Piezo lighter
Now a gas stove on the use of a new type of electronic lighters, is made of piezoelectric ceramics. As long as the pressure with your fingers about the ignition button, the lighter on the piezoelectric ceramic can produce high voltage, the formation of spark and ignite the gas, you can use for a long time. So the piezoelectric lighter is not only easy to use, safe and reliable, and long life, such as a lead-acid lead ceramic made of lighters can be used more than 100 million times.

High displacement of the new piezoelectric actuator
Since the invention of piezoelectric actuators, especially multi-layer piezoelectric actuators, its application is growing, especially in precision positioning. Now multi-layer piezoelectric actuators in foreign countries have been heavily used...
in automotive fuel injection systems and suspension systems.

**Piezoelectric transformer**

Piezoelectric transformer From the 50's began to develop, but until the 90's into the commercialization, the success of the application. Piezoelectric ceramic transformer small size, light weight, can be made into a flat shape, it is actually no electromagnetic noise, only a limited heat, and conversion efficiency of up to 95%, so 90 years with thin power and high frequency (greater than 2 MHz) switching power supply on the piezoelectric transformer urgent requirements, the development of piezoelectric transformers and re-active. Has been developed into a multi-layer piezoelectric transformer, the maximum power has been more than 50 W, and has been used in a large number of notebook computer LCD backlighting power supply and copiers and fax machines high voltage power supply.

**For the active shock absorption and noise reduction of piezoelectric devices**

Many mechanical structures tend to vibrate, which in turn often cause noise, which is of great importance for vibration and noise reduction control (such as running machinery, submarine shells, aerospace vehicles, and cabin) for motion structures. In particular, large-scale precision aerospace flexible structure, the general quality of light, damping small, in the event of vibration, the decay process is very slow; long-term will affect the structure of the operation of the accuracy, and even lead to structural fatigue, instability and so on. So the study of the vibration of the flexible structure is very necessary. The traditional passive damping and noise reduction method is to change the characteristics of the system by increasing the quality, damping, stiffness, or by redesigning the structure. The piezoelectric material itself has the positive and negative piezoelectric effect, making it the ideal material of the detector and the actuator in the active distribution control of the flexible structure.

**Medical miniature piezoelectric ceramic sensor**

Department of Ceramic Engineering, University of Lorraine, Missouri, USA. Professor Huebner has developed a miniature voltage ceramic sensor that is smaller than human hair and can be used to help doctors detect the accumulation of cholesterol near the heart of a patient, such as the coronary artery, potentially fatal. Insert this very small sensor into the arteries and deliver it to the heart through a fine fiber optic cable to diagnose the location and thickness of a life-threatening block of cholesterol, paving the way for laser clearance in the blood vessel.

**Sound converter**

Sound converter is one of the most common applications. For examples, pickups, microphones, headphones, buzzers, ultrasonic depth sounder, sonar and material ultrasonic flaw detector can use piezoelectric ceramics as sound converter. For instance, children's toys on the buzzer is the current through the piezoelectric ceramic piezoelectric effect of vibration, and issued by the human ear can hear the sound. Piezoelectric ceramics through the electronic circuit control, can produce different frequencies of vibration, which issued a variety of different sounds. Such as electronic music greeting cards, that is, through the piezoelectric effect of mechanical vibration into alternating current signals.

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