Original Research Article

Classification, preparation process and its equipment and applications of piezoelectric ceramic

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ABSTRACT

The so-called piezoelectric ceramics are piezoelectric polycrystals, a functional ceramic material capable of converting mechanical energy and electric energy from each other. 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 materials are also one of the many 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

Piezoelectric ceramics (piezoelectric ceramics): A piezoelectric effect of the ceramic is known as piezoelectric ceramics due to the polarization treatment of ferroelectric ceramics spontaneous polarization random orientation, so there is no piezoelectricity. Polarization is carried out by spontaneous polarization in the direction of polarization. After the removal of the electric field, ceramic body still retains a certain total residual polarization, so the ceramic body with piezoelectricity as a piezoelectric ceramic. In the high temperature gradient field of high temperature orientation of the crystallization of non-ferroelectric glass ceramic also has piezoelectricity. Common types are:

1.1. Barium titanate ceramics

Barium titanate ceramics is a typical perovskite structure of ferroelectric ceramics. It is usually barium carbonate and titanium dioxide as the main raw material, pre-synthesized and then sintered at high temperatures.

1.2. Lead titanate ceramics

Lead titanate ceramics are ferroelectric ceramics with perovskite structure. 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 obtained.

1.4. Lead zirconate ceramic

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

Ternary system ceramics are usually in the perovskite structure of lead zirconate titanate (PbZrO3-PbTiO3) binary system and then add a third (chemical formula ABO3 type) compounds and the formation of ternary solid solution. The addition of the third component, their common feature is the incorporation of PbZrO3-PbTiO3 in the formation of solid solution does not change the entire lattice of the perovskite structure.

1.6. Niobate system ceramics (niobate system piezoelectric ceramics)

Niobium-based piezoelectric ceramics are ferroelectric ceramics with oxygen octahedral structures. Various niobate ceramics have perovskite type {such as KnbO3}, tungsten bronze type {such as lead niobate PbNb2O6}, pyrochlore type {Such as Cd2Nb2O7} and other structures. Their Curie temperature is high, the dielectric constant is small and the speed of sound is large especially the mechanical quality factor QM of lead niobate is very low, suitable for ultrasonic testing.

1.7. Electro-optical (transparent ferroelectric) ceramics {electro-optic (transparent ferroelectric) ceramics}

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

1.8. Ferroelectric ceramic thin film (ferroelectric ceramic thin films)

Ferroelectric ceramic film is a ferroelectric polycrystalline film, can have piezoelectric and pyroelectric properties and linear or secondary electro-optical effect and nonlinear optical effects and other characteristics. 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 molecular beam epitaxy, magnetron sputtering, chemical vapor deposition and sol-gel (SolGel). The film substrate and the crystallization temperature have an important effect on the orientation of the film grains.

1.9. Piezoelectric composites (piezoelectric composites)

Piezoelectric composites are generally made of piezoelectric ceramics and high molecular polymer {or other materials}. 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, the internal structure of each component and its symmetry in the spatial configuration can be greatly adjusted Some physical properties of composites. According to the actual needs of the design of piezoelectric composite materials, manufacturing the best performance of the piezoelectric transducer. Such as zirconium titanate lead piezoelectric ceramic and polymer polymer 1-3 composites, the isostatic piezoelectric strain constant dh {= d33 + 2d31} than the zirconium titanate lead piezoelectric ceramic dh value is much larger, And its capacitance also has a larger decline.

2. Piezoelectric principle of piezoelectric ceramics

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

2.1. The internal structure of piezoelectric ceramics

(1) Piezoelectric ceramics by a small grain of irregular ‘mosaic’ made, as shown in Figure 1
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Figure 1. SEM image of BSPT piezoelectric ceramic samples

(2) Each small grain is microscopic by atoms or ions are regularly arranged into a lattice, can be

Figure 2. seen as a small single crystal.

(3) Each small grain also has a ferroelectric domain organization, as shown in Figure 3.

Figure 3. Electron microscopic photograph of the domain in PZT ceramics

(4) Overall, the crystal grains and grain lattice direction is not necessarily the same, arranged in a chaotic and irregular, as shown in Figure 4. This structure, we call it 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.

![Figure 5. Schematic diagram of spontaneous polarization in BT](image)

It can be seen from the figure that the positive and negative charge centers coincide with the c-axis, and the positive and negative charge centers do not coincide with each other due to Ti4+ along the c-axis. C-axis of the electrode.

This electrode is not generated by the external electric field, but the crystal within the resulting, so become spontaneous polarization, the phase change temperature TC called Curie temperature.

Piezoelectric ceramics in the spontaneous polarization of the region known as the domain (or 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 coincides with the direction of the electric field is increasing, and vice versa, the whole crystal is changed from multi-domain to single domain, spontaneous The direction of polarization is consistent with the direction of the electric field.

Piezoelectric ceramic polarization process, is in the ceramic chip electrode with a high enough DC electric field, forcing the domain to turn, even if the spontaneous polarization for directional arrangement, as shown.

2.4. Piezoelectric effect

(1) Positive piezoelectric effect

If a pressure F parallel to the direction of polarization is applied to the ceramic sheet, as shown in Fig. The tiles are compressed, the polarization intensity becomes smaller, the release of the original adsorption of free charge, the discharge phenomenon. When F removed, the tiles back to the original state, the polarization intensity becomes larger, but also adsorption some free charge, charging phenomenon. This effect by the mechanical power of electricity, or by the mechanical energy into electricity phenomenon, known as the positive piezoelectric effect.

(2) Inverse piezoelectric effect

An electric field identical to the direction of polarization is applied to the ceramic sheet, as shown in Fig. Polarization strength increases, tiles occur elongation deformation. Otherwise it happens to shorten the deformation.
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This change from electricity to mechanical movement, or from electrical energy into mechanical energy phenomenon, known as the reverse piezoelectric effect.

3. Preparation of piezoelectric materials

Piezoelectric ceramic materials must be polarized before they have piezoelectric properties. Polarization of the material before the ferroelectric domain in the direction of the same direction of the same probability, the external power is 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, so that the material has piezoelectricity. Some piezoelectric materials are ferroelectric, ferroelectricity refers to the T <Tc, the piezoelectric ceramic not only spontaneous polarization and spontaneous polarization direction can also due to external electric field and steering. General polarization electric field is 3 ~ 5kV / mm, temperature 100 ~ 150 °C, time 5 ~ 20min. These three are the main factors that affect the polarization effect. Better performance of piezoelectric ceramics, such as lead zirconate titanate ceramics, the electromechanical coupling coefficient can be as high as 0.313 ~ 0.694.

To obtain a good performance of piezoelectric ceramics, you must master its production process. Changes in process conditions, the impact on the piezoelectric properties of a great. Therefore, we must understand the inherent law of piezoelectric ceramics, the design of a reasonable production process, and strictly control its operation process.

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 l-3 type grow linearly with the volume content of the ceramic phase. O-3 type is between Series 2-2 and 1-3. 3-l type and 3-2 type.

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 is reduced and the piezoelectric constant is increased, so that the merit of the composite is increased, and when the aspect ratio is small. This 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 is also 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. Have shown that IIIJ: Colloidal processes are prepared. A composite material can withstand higher polarized electric fields. So the piezoelectric properties of the composite material has been improved. Our study also shows that the same composition ratio of PZT / PVDF 0 - 3 complex material, relative to the rolling film method. The composite materials prepared by hot pressing have higher dielectric constant and piezoelectric constant.

3.1.5 Polarization process

Polarization of the electric field is too high and will lead to breakdown of the sample. The polarization is too high, the composite material will be deformed, the temperature is too low, the polarization process is slow. It should be said that the longer the better the polarization, but the time is too long, too time consuming. So the artificial polarization is in the appropriate electric field, temperature and time under the conditions of the. The results show that the piezoelectric properties of the polarized composite materials of the piezoelectric ceramic are better than that of the post - perforation polarization and post - filling polarization for the samples prepared by the punch - fill method.

3.2. Polarization:

Ordinary thermal polarization: the sample to be polarized into the silicone oil heated to 120 ~ 140 and then applied at both ends of the sample a direct current electric field, so that the domain as far as possible along the direction of the
external electric field. 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, so that the sample cannot reach the bubble and polarization. For samples with high conductivity, it is easy to add a voltage that does not even damage 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 ~ 20 above the Curie point, and then add the 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 temperature is then cooled as soon as possible to about 100 ° C, while increasing the electric field to about 300 V / mm. Remove the sample by removing the external electric field below 100.

3.3. PZT preparation example

3.3.1 PZT powder preparation steps

(ZrXTi1-X) 03, and then the PZT powder was synthesized by the chemical wet method. The reaction equation PbO + (ZrXTi1-X) was synthesized by the method of B-type pyrolysis. ) 03 Pb (ZrXTi1-X) 03. 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 (ZrTi04) Solid Solution) Tetrabutyl titanate, zirconium oxychloride and citric acid were 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 was 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-X02 and Nb-containing (ZrXTi1-X) 02 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 the samples 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 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, showing 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 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 rise to the polarization voltage of 2.5 kV / mm and the polarization temperature of 120-140, 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. 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, εr = 1397, d33 = 389 pc / N, KP = O. 647.

[(1-x) LF4-xBCW] lead-free piezoelectric ceramics prepared by conventional solid-phase method (1-x) Li0.04Na0.052K0.44Nb0.086Ta0.10Sb0.04O3-xBaCu0.5W0.503 [The effects of different BCW doping (x = 0%, 0.1%, 0.2%, 0.5%, 1%, 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≥1%, the sample is transformed from tetragonal to orthorhombic phase. T0-t and Tc 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 d33, plane electromechanical coupling coefficient, dielectric loss tanδ and dielectric constant εr decrease with the increase of BCW content Mechanical quality factor Qm 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 [(K0.5Na0.5NbO3-K0) 1Na0.4Bi0.5TiO3] -xLiNbO3, 0≤x≤ 0.04] 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 extensive. 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 instances, 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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