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Preparation Process, Structure and Modification of Alkali Metal Niobate Lead-free Piezoelectric Ceramics

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Abstract: Because lead-based piezoelectric ceramics cause serious lead pollution during the manufacturing process, they also seriously endanger human health. Therefore, the development of environmentally friendly lead-free piezoelectric materials has become a top priority. Lead-free niobate-based piezoelectric ceramics have strong ferroelectricity and high Curie temperature, making them more suitable for making ceramics. For this reason, this article needs to study the preparation process, structure and modification of alkali metal niobate lead-free piezoelectric ceramics in order to improve the environmental protection of the prepared materials and the performance of piezoelectric ceramics. In this paper, experimental methods are mainly used to study the performance change and structure transformation of lead-free piezoelectric ceramics mixed with other metal materials after adding alkali metal niobate. In addition, this article analyzes the changes in the dielectric constant, dielectric loss, and Curie temperature of piezoelectric ceramics by means of comparison. It is found that the sintering temperature is 1100℃, and the ceramic has relatively excellent piezoelectric properties in the experiment.

1. Introduction

Alkali metal elements are abundant in nature and have various properties. They are an important organic chemical raw material and industrial intermediate. With the development of crystal technology, people have conducted a lot of research on alkali metal niobate, mainly using doping methods and solid materials to improve its solubility. Alkali metal niobate crystal is a very special amorphous system. It is a very important and easily soluble in water and chlorine at room temperature, but it cannot be directly used as an organic solvent. It has high specific capacity and excellent mechanical properties.

Lead-free piezoelectric ceramics have the characteristics of high thermal conductivity and good corrosion resistance, so they have become the most widely used new type of material. When working in a pressure vessel, the density of the electrolyte is relatively large and there are more pores, resulting in a continuous increase in the degree of electrical polarization. Lead-free piezoelectric ceramics have high dielectric loss, excellent mechanical strength and corrosion resistance. The lead-free piezoelectric power ratio can effectively improve the structural performance of the crystal film.

In modern industrial production, pollution-free and low energy consumption have become a topic of social concern. Alkali metal niobate lead-free piezoelectric ceramics have received widespread attention and made rapid and practical progress due to their unique and excellent properties. Therefore, there are not few researches on the preparation process, structure and modification of its materials in lead-free piezoelectric ceramics. For example, Yan Bowu said that the alkali metal niobate (K, Na) NbO_3 (KNN) series has become lead-free electrical materials due to its high voltage constant, high electromechanical coupling coefficient, high quality factor and high temperature Curie [1]. Wang Chen said that various ceramic systems such as bismuth layer structure lead-free piezoelectric ceramics and perovskite structure lead-free piezoelectric ceramics have the latest developments in piezoelectric properties and applications [2]. Wang Zhijie believes that piezoelectric ceramics, as a functional ceramic that can convert mechanical energy and electrical energy, have excellent mechanical coupling properties and have gradually become an important part of material technology [3]. Zhang Changsong said that with the introduction of environmentally friendly materials and the requirements of sustainable development, there is an increasing demand for lead-free piezoelectric materials in various fields [4]. Guo Lu reviewed the modification of lead-free piezoelectric ceramic materials from the perspective of doping modification and process optimization [5]. Chen Sen believes that the piezoelectric ceramics produced are all perovskite structures. The introduction of PNN can increase the dielectric properties of the ceramic pressure [6]. Guo Gensheng uses the traditional solid-phase sintering process to produce lead-free piezoelectric ceramics [7]. Li Haitao has successfully prepared lead-free piezoelectric ceramics with higher density and excellent electrical properties at a sintering temperature of 960-980℃ [8]. Dai Zhonghua said that BaTiO3 (BT)-based lead-free piezoelectric ceramics have high relative permittivity, dielectric strength and insulation properties [9]. From the scholars' point of view, the argument presented in this article is an effective attempt to apply alkali metal niobate to the preparation of voltage ceramics.

The innovations examined in this article are as follows: First, a new perspective of reasoning. The purpose of this article is not to study potassium niobate and sodium niobate, but to study alkali metal niobate. The second is new research methods. This article introduces the preparation methods of the materials from beginning to end, and conducts a comparative study. The third is that the research content is novel. In this paper, BNN and KNN matrices are used to form a uniform and stable solid solution, and their influence on the microscopic morphology and electrical properties of KNN-based ceramics is studied. The optimal composition and sintering temperature of the lead-free alkali metal niobate piezoelectric ceramics were investigated, and the area of the near phase boundary of the ternary system was investigated.

2. Preparation of Alkali Metal Niobate Lead-Free Piezoelectric Ceramics

2.1. Lead-free Piezoelectric Ceramic Materials

As an important functional material, piezoelectric ceramic materials are currently widely used in the field of electronic components. It can be used in all aspects of information and data such as piezoelectric transformers, signal sources, and signal conversion [10-11].

(1) Piezoelectric effect

The piezoelectric effect is divided into the positive piezoelectric effect and the inverse piezoelectric effect. The positive piezoelectric effect refers to the electric charges of the same number and opposite sign combined on both ends of the crystal, as shown in Figure 1 (A). The reverse piezoelectric effect refers to the generation of deformation or mechanical stress proportional to the intensity of the electric field, as shown in Figure 1(B) [12-13].

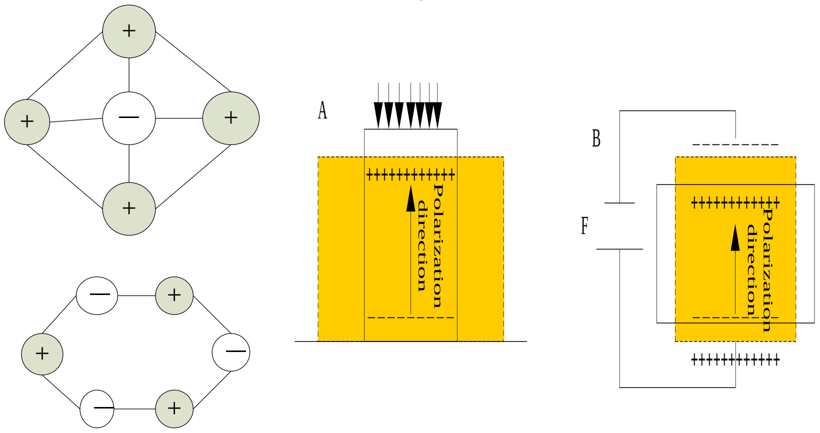

Figure 1. Piezoelectric effect and piezoelectric production

According to geometric principles:

$$\frac{s_x + s_o}{s_y + s_o} = \sqrt{2} \tag{1}$$

In the formula, s_x, s_y and s_o are the ion radii of the x-position ion, the y-position ion and the oxygen ion, respectively. For actual materials, x-position ions, y-position ions and oxygen ions are not exactly tangent, then:

$$\frac{s_x + s_o}{\sqrt{2}(s_y + s_o)} = q \tag{2}$$

In the formula, q is the tolerance factor. The closer q is to 1, the closer the actual perovskite structure is to the ideal cubic perovskite structure, and the more stable the bond formed.

Piezoelectric parameters mainly include: $\varepsilon, \tan\delta, T_c, Q_m, k_p, N_p, d_{33}, P_r, E_e$, which include dielectric constant, dielectric loss, Curie temperature, mechanical quality factor, electromechanical coupling coefficient, etc. The mechanical energy and electrical energy in piezoelectric materials can be coupled and converted, and the strength of energy conversion can be characterized by the electromechanical coupling coefficient, which is defined as:

$$K^2 = \frac{M_x}{M_a M_b} \tag{3}$$

Among them, M_x is interaction energy density, M_a is elastic energy density, and M_b is dielectric energy density.

(2) Testing the bulk density of ceramic samples

The measurement of bulk density is based on the Archimedes principle, weighing the mass of the sample with a precision balance, and measuring the volume with the drainage method. Calculated as follows:

$$\rho = \frac{X_1}{X_3 - X_2} C_1 \tag{4}$$

Among them, X_1 is the mass of the dry sample, X_2 is the apparent mass, X_3 is the mass in the air, and C_1 is the density of the immersion liquid at the test temperature.

2.2. Lead-Free Demand for Piezoelectric Ceramics

The main function of piezoelectric materials is to realize the mutual conversion of mechanical energy and electrical energy. Currently, the most widely used piezoelectric materials are lead-based piezoelectric materials. Traditional lead-based piezoelectric ceramics usually contain more than 70% lead. Lead-containing piezoelectric ceramics have an impact on the environment and they are harmful to people [14-15].

(1) Preparation method of piezoelectric ceramics

The lead-free piezoelectric ceramics produced by the sol-gel process have the following advantages: ceramics have good density and performance; the heat treatment temperature and sintering temperature of the gel are reduced. The solid-phase method is a traditional powder-making method, and the solid-phase method can be divided into mechanical crushing method and solid-phase reaction method according to the characteristics of its processing technology. The hydrothermal method to produce lead-free piezoelectric ceramics has the following advantages: the powder can actually be synthesized at low temperatures, reducing the volatilization of volatiles, and the reaction proceeds in a stoichiometric ratio. It can extract powder directly from the liquid phase [16-17].

The molten salt method improves the fluidity of the liquid phase reaction components, which enables the liquid phase reaction to proceed, and it greatly increases the diffusion rate.

(2) The birth of PZT ceramics

This is a milestone in piezoelectric ceramics, and many new piezoelectric ceramic materials have been developed since then. When these lead-based piezoelectric ceramics are released into nature due to improper management, they will cause serious damage to humans and the ecological environment [18-19].

(3) Principles of making lead-free piezoelectric ceramics

The structure of lead-free piezoelectric ceramics is mainly composed of carbides and inorganic salts. After graphitization, it is placed in a negatively charged conductive sheet; when a voltage is applied, current is generated through these surfaces and converted into electrical energy for transmission to mechanical equipment. Therefore, facts have proved that this material is very environmentally friendly, rich in renewable raw materials, and low in price. Lead-free piezoelectric ceramics are a new type of environmentally friendly material [20-21].

The sintering temperature of lead-free piezoelectric ceramics should be higher than that of lithium batteries to obtain higher output power and good discharge performance under different voltage ratios. In order to improve the capacitance performance and life of the capacitor in the energy storage device, the electrode material and electrolyte concentration should be appropriately selected to determine the final production plan. The manufacturing process of lead-free piezoelectric ceramics should consider environmental factors such as temperature and humidity. Therefore, the processing conditions should be strictly controlled in actual operation to achieve good working conditions.

There is no environmental pollution during use, which means it is safe and effective. The product should have a high level of flame retardancy, sound insulation and low noise. If necessary, the circuit can be improved or new materials can be used. At the same time, it is necessary to ensure that the processing equipment is simple and reliable. It can work stably for a long time, and it will not cause mechanical failure due to improper operation.

Table 1. Basic information on several common compound perovskite compounds

Component	Abbreviation	Tolerance factor q	Crystal structure	T_{max} (℃)	ε_{max}
Pb(Mg1/3Nb2/3)O3	PMN	0.987	PC	-10	17000
Pb(Zn1/3Nb2/3)O3	PZN	0.985	R	139	21000
Pb(Ni1/3Nb2/3)O3	PNN	0.992	PC	-118	4100
Pb(Co1/3Nb2/3)O3	PCN	0.981	M	110	5900
Pb(Fe1/3Nb2/3)O3	PFN	0.976	R	-96	11000
Pb(Mg1/3Ta2/3)O3	PMT	0.985	PC	-170	6000

Table 1 summarizes the relevant information of common composite perovskite-type compounds, εmax indicates the value of the dielectric peak, and Tmax indicates the temperature corresponding to the dielectric peak. Most of these compounds are ferroelectrics with relaxation properties, and the relaxation properties of ferroelectrics are related to the arrangement of B-site ions.

2.3. Progress on Modification of KNN-Based Lead-Free Piezoelectric Ceramics

Alkali metal niobate is a very important inorganic amorphous polymer compound. In nature, it is usually called "gold salt and gold salt". The synthesis of alkali metal niobate is often referred to as sodiumization. It is a class with strong oxidizing and reducing properties, low melting point, good crystallinity, and uniform crystal size, which is used in industry to manufacture electric arc furnaces and high-voltage endless pipe fittings. It can also be used as a new material: for example, it can be used as a high-temperature alloy or corrosion-resistant steel instead of high-strength stainless steel.

Alkali metal niobates are toxic and corrosion resistant. Due to its excellent characteristics, it is considered to be versatile in industry. It can be used as electro-optical and semiconductor shielding materials. In other respects, it can also be applied to electronic devices and magnetic components. In addition, in some cases, alkali metal niobates can also be used as special materials for glass substrates.

Lead-free piezoelectric ceramics based on artificial neural networks have high Curie temperature and good piezoelectric properties. The research of this article mainly focuses on the following two aspects: the regulation and change of the composition and the improvement of the manufacturing process. The manufacturing process of lead-free piezoelectric ceramics is mainly divided into two categories: direct reduction method and chemical treatment. In the direct reduction method, the material must be preheated, rusted and activated before it is carried out in this way, so that the product can be manufactured after reaching a certain temperature. But this method should pay attention to the following points: the raw materials cannot react with the strong oxidizing metal, otherwise it is easy to damage the equipment or cause high temperature fire and high pressure. The heating time should be figured out to ensure the normal operation of the equipment. When making lead-free piezoelectric ceramics, the properties of the material should be modified to ensure that the test results meet the design standards. The properties of the material itself are usually changed by heat treatment or the use of an external electric field.

The main manufacturing processes currently used to improve performance are: sol-gel process, hot pressing and sintering process, hydrothermal process and other manufacturing processes. Features of products made by hot pressing sintering process are : higher density, lower dielectric loss and smaller grain size; features of products made by sol-gel method are: high purity, fine particles, good chemical uniformity, low synthesis temperature and composition, easy to control, simple processing equipment. From the perspective of sustainable development, treatment technology should have environmental coordination characteristics such as low energy consumption and low pollution. Therefore, hydrothermal, electrochemical, and sol-gel methods are used to produce ceramic materials. The sol-gel method is considered to be one of the most widely used wet chemical production processes. It has advantages such as low cost, simple processing equipment, evenly distributed composition, low synthesis temperature and controlled composition. As a low-temperature process, sol-gel can obtain products with high purity, fine particles, and uniform chemical composition. At present, it is widely used in detectors, acoustic impedance coupling materials, dielectric materials and other fields. It is very important to the development of our country's electronics industry.

(1)Modification of ingredients

In order to reduce the sintering temperature of KNN ceramics and improve its sintering performance, sintering aids are often added to KNN ceramics. Sintering aids are substances that can be melted into a liquid phase at high temperatures during the sintering process. As shown in Table 2, adding some low melting point compounds to KNN ceramics can improve the piezoelectric properties of KNN ceramics.

Table 2. KNN ceramic properties after partial addition of a sintering aid

Constitution	d33(pC/N)	Kp	tanδ	εr	Tc
KNN	79	0.35	/	/	419
KNN-1mol%ZnO	113	0.35	/	385	/
KNN-1.8mol%ZnO	115	0.26	/	762	431
KNN-0.70mol%CeO2	126	0.37	0.029	810	/
KNN-0.35mol%KCT	188	0.4	0.002	1290	399
KNN-0.5mol%KCN	178	0.38	/	1190	/

KNN ceramics have an orthorhombic perovskite structure at room temperature. If compounds with other structures are added, the phase structure changes with the content of the added compounds. From a manufacturability point of view, due to the presence of multiple oxides, the lowest eutectic point is lowered, thereby it will decrease the sintering temperature of the ceramic. In addition, since the free energy reduces when plurality of joints are formed, sintering can be promoted.

Preparation process modification

So far, solid phase synthesis is mainly used in the manufacture of lead-free piezoelectric ceramics based on artificial neural networks. In order to fill the problem of difficult to obtain high-density ceramics, researchers use traditional ceramic technology to change the composition of various lead-free piezoelectric ceramic systems, and actively explore their manufacturing processes and methods. Patterned Grain Growth Technology (TGG) is a new process for the production of oriented piezoelectric ceramics. Through observing the morphology and structure of the lead-free piezoelectric ceramics, it can be seen that the pure potassium iron niobate crystal has the best performance when the grain size is 2nm. When adding a certain amount of positive electrode beaker and pure lead-free aluminosilicate piezoelectric ceramics in different volume ratios, it is not difficult to see the presence of inorganic vanadium ions, cobalt oxides and zirconium salts in the crystals.

2.4. Basic Principle of Lead-Free Piezoelectric Ceramics of Alkali Metal Niobate

In practical applications, lead-free piezoelectric ceramics mainly use its mesoscopic mechanical properties to work out. But because there is no metal ion as a medium, it is used directly. Therefore, this material also has a certain degree of limitations. The tension field generated by ceramics under the action of mechanical force is determined by the external and deformation, and changes correspondingly when a certain frequency and voltage are applied externally. These restrictions can change the location of the grain boundaries. The crystal structure changes under the influence of external stress and temperature. Therefore, we can improve the resistance to external environmental influences by controlling piezoelectric ceramics to meet the requirements for adhesion and mechanical properties of substrates with different properties. When crystal structure is crystallized under high temperature conditions, it deforms due to applied load.

The electrical and mesoscopic properties of alkali metal niobate depend on its charge and valence band on the conductor. Among them, due to the ion opposite system, its electric field intensity will change with the applied alternating voltage. Therefore, it can be found that there is a certain degree of interaction between them.

The working principle of piezoelectric lead-acid ceramics is to deform and deform under a certain voltage under the action of external force. Therefore, it not only has the properties (such as conductivity, temperature resistance, etc.) that ordinary materials do not have, but also has super strength and stability. It can also eliminate other defects, such as metal corrosion to the environment and pollution from toxic and harmful gases or dust. Lead-free piezoelectric ceramics is a new type of ultra-light and ultra-light lead-free permanent magnet magnetic resistance technology. Under certain temperature and pressure conditions, the ions containing lead and iron elements are mixed in the eutectic system in an appropriate ratio to form an ordered body with a certain shape, size or pore structure.

Under the action of an electric field, a dielectric interaction occurs between the metal ions and the lead-free piezoelectric electrode. Because lead-free piezoelectric ceramics are a kind of conductive gas, they have the advantages of high power density, good mechanical strength, and good corrosion resistance. At the same time, it can also be used as a charging material for microelectronics.

In the sintering process, the raw materials are first pretreated. Then connecting the processed raw materials or alkali with different voltages. Then put a certain amount of the solution in the oven. Finally, stirring evenly with a magnetic stirrer. The process parameters are: including factors such as load, curing agent concentration and temperature. Structural parameters: mainly the relationship between various variables in the manufacturing process of lead-free piezoelectric ceramics.

In the production process, the piezoelectric medium is usually pretreated first, and then different process parameters are used to control the deformation of the material in a specific area.

At present, the research on the crystal structure of lead-free and metal salt-free piezoelectric ceramics mainly focuses on its manufacturing method, performance test and application. Micro-arc oxidation is one of the emerging technologies that uses high-energy electron excitation energy to dissolve elemental iron alloys in a solution to form nanorod-shaped materials, thereby achieving controllable morphology. The manufacturing methods of lead-free piezoelectric ceramics mainly include mechanical method, solvent evaporation method and thermal mixing method. Liquid phase solidification is added with different content of calcium hydroxide solution in the lead-free synthetic salt. During the reaction process, ion intercalation occurs, which reduces the nucleation rate and the crystal grains become smaller. Factors such as excellent production performance and the ability to meet technical requirements and product quality requirements limit lead-free piezoelectric ceramics.

3. Experimental Method

3.1. Experimental Materials and Specifications

The purity and source of the raw materials used in this experiment are shown in Table 3:

Table 3. Source of Raw Materials and Their Purity

Raw material	Source	Volume	Purity
K2CO3	Sinopharm Chemical Reagent	136.31	≧99.1%
Na2CO3	Sinopharm Chemical Reagent	110.78	≧99.6%
Nb2O5	Sinopharm Chemical Reagent	258.93	≧99.4%
Li2CO3	Sinopharm Chemical Reagent	74.56	≧98.1%
ZnO	Sinopharm Chemical Reagent	126.87	≧98.9%

3.2. Sample Preparation Method

In this experiment, a series of lead-free piezoelectric ceramic samples were prepared by solid-phase synthesis. The preparation process mainly includes the following steps: batching, mixing, pre-sintering, forming, debinding and sintering. The specific process flow is shown in Figure 2:

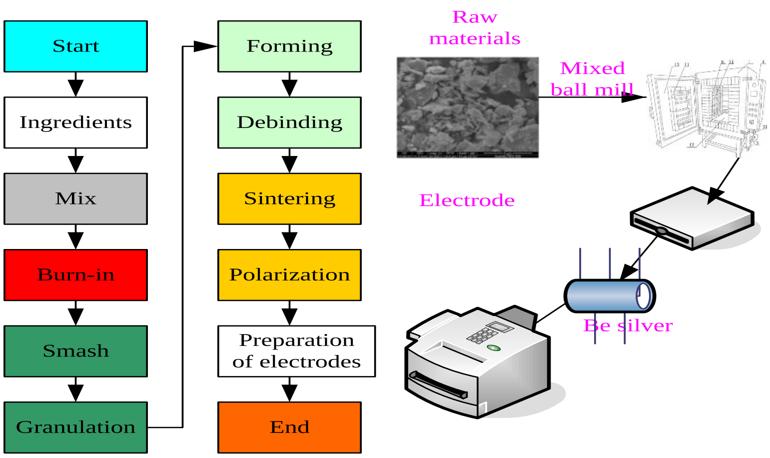

Figure 2. Specific sample preparation process

Batching is the most critical step to ensure the accuracy of ceramic batching. Alkali metal oxides are not easy to store, and are easy to absorb water and degrade during storage. After mixing the ingredients according to the stoichiometric ratio, the medicine should be mixed uniformly. Generally, the ball mill connection has the function of mixing and grinding. The mixing and refining of the uniform powder contributes to the complete solid-phase reaction of the components during the pre-sintering process.

The essence of pre-combustion is the complete chemical reaction of the mixed raw materials at a temperature below the melting point to generate new compounds, volatile substances is removed at the same time in the raw materials. Choosing the best calcination temperature before calcination. During the test, a temperature with increase rate of 10 ℃/min was used to rapidly change from room temperature to 1100 ℃. The DSC/TG curve after mixing BNT is shown in Figure 3. The pre-combustion of BNT raw materials is divided into three stages: the loss of alcohol and moisture at room temperature -110 ℃, and remove the water of crystallization and the reaction step from each component at 110 ℃-650 ℃. The pre-sintering temperature program in the experiment is shown in Figure 3. Starting from room temperature, the heating rate is about 3 ℃/min, and the temperature is kept at 110 ℃ for 1 hour to ensure that the ethanol and water in the raw materials evaporate. Heating and keeping for 3 hours and cooling in an oven.

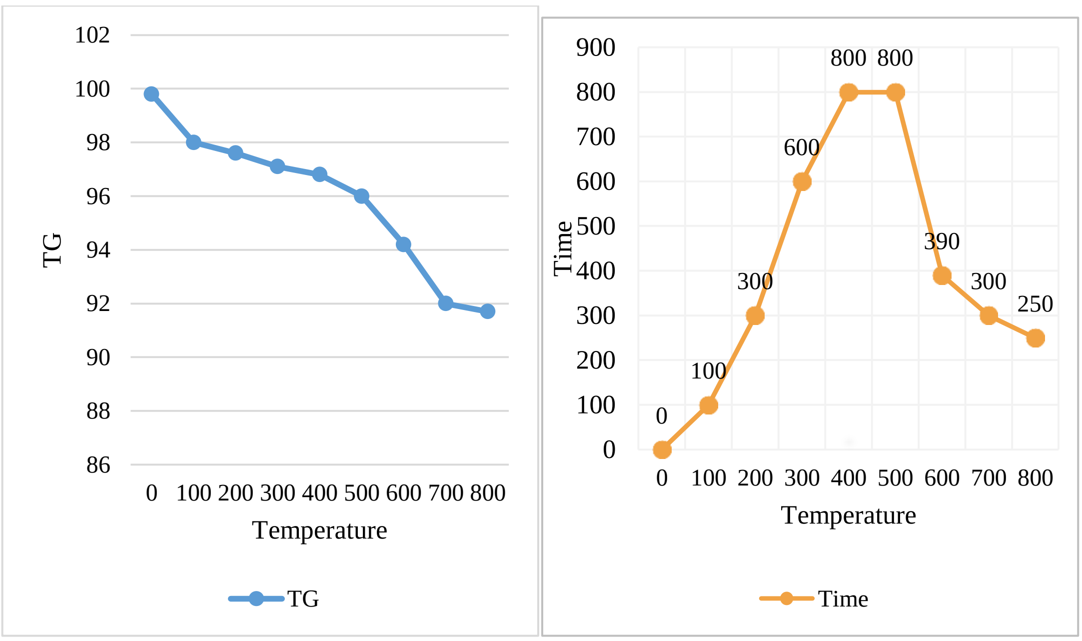

Figure 3. Changes in temperature and time during calcination in the experiment

In the experiment, the dry pressing method was used to prepare the ceramic body during the sample preparation process. Grinding the raw materials with an agate mortar to ensure that the raw materials are fine. Then adding about 5% of PVA binder (8% by weight) for granulation.

In order to produce materials with no delamination in the center, PVA is added to the powder in the molding step to make the powder size uniform and improve the fluidity of the particles. The PVA must be removed from the green body before sintering. This process is called debinding. The temperature rise during degreasing should not be too fast and should not exceed 2 ℃/min. The PVA selected in this study usually begins to decompose at about 240 ℃, and the temperature is maintained at 500 ℃ for 2.5 hours to allow the PVA to be completely discharged from the green body.

Sintering is a process of reducing the volume, increasing the density and increasing the strength of the molded body by moving atoms at a high temperature. The sintering process can be explained by the scattering motion of atoms. The correct sintering temperature makes the ceramic material have a good micro morphology and high density.

3.3. The Electrical Performance Test Method of the Sample

Samples used for electrical performance testing require high-quality electrodes. This experiment uses the silver layer firing process to burn silver, the purpose is to form a dense and highly conductive silver layer on the ceramic surface under high temperature. The silver burning temperature should be lower than the pre-cooking temperature of the ceramic, so as to reduce the influence on the ceramic grain size during silver burning. In this experiment, the sintering temperature of silver is adjusted to about 600 ℃, the heating rate does not exceed 100 ℃/h, and the holding time is 10 minutes, and then it is cooled to room temperature with the furnace. After the upper electrode is completed, it is necessary to repair the edge of the sample and remove the metal layer on the edge to avoid difficulties in the subsequent polarization process. To calculate the dielectric constant, the formula is:

$$\xi_a = \frac{4 \times Z \times s}{\pi \times \xi_0 \times e^2} \tag{5}$$

Z is the dielectric capacitance, e is the diameter of the ceramic disc, and s is the thickness.

The mechanical quality factor R_n indicates the mechanical loss of the ceramic material when it resonates. The calculation formula is:

$$R_n = \frac{g_q^{\ 2}}{2\pi g_t C Z_s (g_q^{\ 2} - g_t^{\ 2})} \tag{6}$$

The electromechanical coupling coefficient L refers to the ratio of the geometric mean value of the interaction energy density to the elastic density and the energy-saving energy density. The calculation formula is:

$$L_q = \sqrt{2.51 \times \frac{g_q - g_t}{g_t}} \tag{7}$$

$$L_s = \frac{1}{\sqrt{\frac{0.405 \times g_t}{g_q - g_t} + 0.81}} \tag{8}$$

Based on 0.8 mol% of bismuth and iron, the basic element Li and sintering aid ZnO were added to prepare piezoelectric ceramics doped with sodium niobate Li and ZnO, and then sintered at different temperatures. The factors on the ceramics are Li content, ZnO content and sintering temperature (K0.496Na0.496) Nb0.992O3-0.008BF. Below this, the lithium content is 4 mol%, 5 mol% and 6 mol%, the copper oxide content is 0.5 mol%, 1 mol% and 2 mol%, and the sintering temperature is 1100 ℃, 1000 ℃ and 900℃ or design 6 experiments. The details are shown in Table 4:

Table 4. Orthogonal experiment data

Test number	Sintering temperature	Li content	ZnO content
T1	1100	0.03	0.004
T2	1100	0.04	0.02
T3	1000	0.05	0.01
T4	1000	0.04	0.005
T5	900	0.06	0.02
T6	900	0.05	0.01

4. Experimental Test Results

4.1. The influence of Sintering Temperature on the Electrical Properties of KNN-LN Ceramics

In the experiments of this article, the electrical properties of KNN-LN ceramics at different sintering temperatures were studied with different temperatures as variables. In this experiment, it is found that most of the ceramics have a coexisting structure of orthogonal and tetragonal phases, indicating that the sintering temperature also has an effect on the piezoelectric properties of KNN-LN ceramics. Small temperature results in large piezoelectric properties. When the sintering temperature is 1060 ℃, the piezoelectric constant d33 of the ceramic is 81pC/N, and the mechanical quality factor Qm is 81. When the sintering temperature is 1080 ℃, d33 reaches the maximum value of 205pC/N, and Qm is the minimum value of 54 at this time. The specific situation is shown in Figure 4:

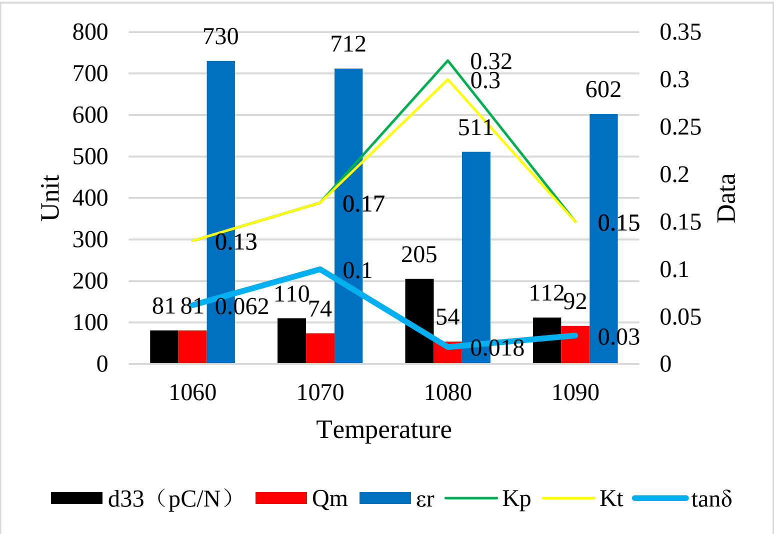

Figure 4. The influence of sintering temperature on the electrical properties of KNN-LN ceramics

In this experiment, the change in piezoelectric properties can be explained by the microscopic morphology of the ceramic. Because the spontaneous stress in the piezoelectric ceramics produces a large internal stress, small crystal grains are easily squeezed by large crystal grains, and it is not easy to form electric domains. However, when the sintering temperature is increased to 1080 ℃, the crystal grains of the ceramic grow and have better uniformity. The growth of crystal grains is beneficial to alleviate internal stress and promote the movement of domain walls. In addition, the binding effect of the grain boundary on the electrical domains is weakened, which has a positive effect on the electrical domains. However, if the sintering temperature is higher than 1080 ℃, the piezoelectric performance of the ceramic is greatly reduced. This may be due to the increased volatilization of alkali metal ions at higher temperatures. The volatilization of alkali metal ions will increase the generation of oxygen vacancies, and the oxygen vacancies play a role in fixing electric domains, thereby it will seriously impair piezoelectric performance.

4.2. KxN1-xN-LN Ceramic Electrical Properties

As shown in Figure 5, when x=0.40, the piezoelectric constant d33 of the ceramic is 230pC/N, and the mechanical quality factor Qm is 32. As x increases, d33 and Qm usually increase first and then decrease. When x = 0.49, the piezoelectric constant of the ceramic reaches its maximum value, d33 is 237 pC/N, and Qm is 24. As x further increases, d33 tends to decrease. The total Qm of the ceramic is kept in a relatively low range. At x = 0.49, Qm reaches the maximum value of 51.

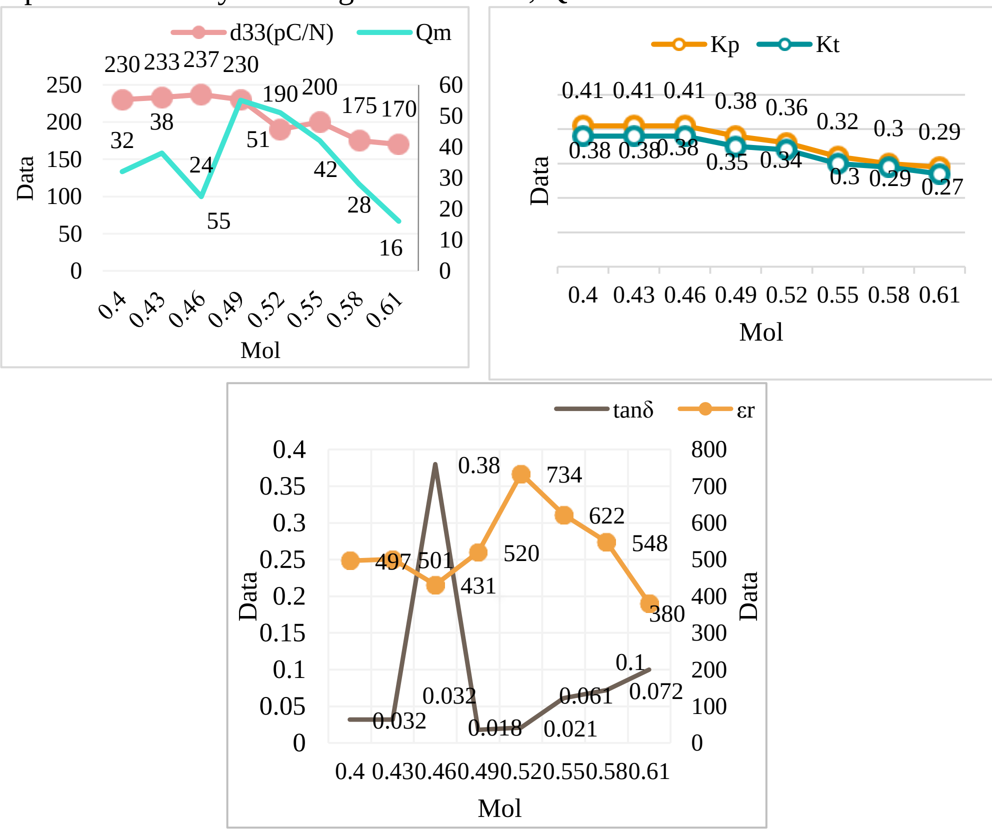

Figure 5. Electrical properties of KxN1-xN-LN ceramics

When x = 0.40, the relative dielectric constant r of the ceramic is 497, and the dielectric loss tanδ is 0.032. As x increases, εr usually increases first and then decreases, while tanδ gradually increases. At x = 0.52, the maximum value is 734. At this time, tanδ is 0.021. The change of K/Na ratio has an important influence on the electrical properties of the ceramics in the system. The best component of ceramic piezoelectric properties is not K/Na=1, but x=0.46, which indicates that a lower K/Na ratio can improve the piezoelectric properties of KxN1-xN-LN ceramics.

4.3. Analysis of Electrical Properties of KNN-xBF Ceramics

The BF-doped piezoelectric sodium potassium niobate ceramics prepared by sintering at 1100 ℃ were tested with quasi-static tester d33, density tester and precision impedance tester Angelon, piezoelectric constant d33, density, and electromechanical coupling coefficient Kp. The dielectric constant εr and the dielectric loss value tanδ are shown in Figure 6.

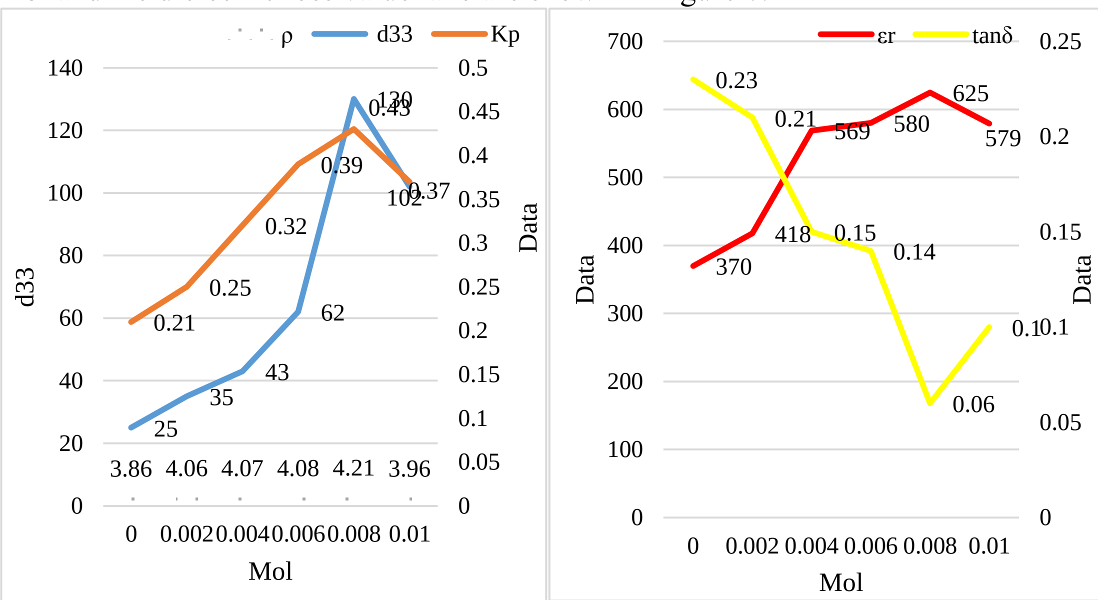

Figure 6. Analysis of the electrical properties of KNN-xBF ceramics

As the content x increases, the overall density first increases and then decreases, and the electromechanical coupling coefficient and piezoelectric constant show the same changing trend. When x is 0.008, as x increases, d33 and Kp increase almost linearly with a certain slope. When x<0.008, the dielectric constant gradually increases. When x = 0.008, the maximum dielectric constant is 625, and the dielectric performance is the best. At this time, the crystal sample is denser and has fewer holes.

5. Conclusion

Using K2CO3, Na2CO3, Nb2O5, Li2CO3, etc. as raw materials, KNN-based piezoelectric ceramic powders are prepared by the sol-gel method, and doped and modified by adding metal modifying elements and ZnO sintering aids to make ceramic materials non-woven for cloth and lead piezoelectric, the following conclusions can be drawn. The sintering temperature is 1100 ℃, the ceramic has relatively excellent piezoelectric properties, and the piezoelectric constant d33 is 306pC/N. Under these sintering temperature conditions, the grain size is larger, and the crystal density is higher and higher. It is a unique orthorhombic perovskite structure. At a sintering temperature of 1080 ℃, ceramics have the best microscopic morphology. The relationship between the composition, temperature, structure and electrical properties of BNBT6-xLN ceramics was analyzed, and a new lead-free piezoelectric ceramic with high voltage electrical response based on BNT was obtained. In the next stage of work, a more in-depth analysis of its fatigue performance and reliability will be conducted. Starting from the powder preparation process, research and development of non-traditional ceramic preparation processes, and the extraction of BNT-B will be conducted.

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Data Availability

Data sharing is not applicable to this article as no new data were created or analysed in this study.

Conflict of Interest

The author states that this article has no conflict of interest.

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