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RUIKUN NIU[1*], YANNI MENG[1], HAIQIAO WANG[1]

PREPARATION PROCESS, STRUCTURE, AND MODIFICATION OF ALKALI METAL NIOBATE LEAD-FREE PIEZOELECTRIC CERAMICS

Pb-based piezoelectric ceramics cause serious Pb pollution during manufacturing, Pb-free niobate-based piezoelectric ceramics have strong ferroelectricity and high Curie temperatures, rendering them more suitable for making ceramics. For this reason, this article studies the preparation process, structure, and modification of alkali metal niobate Pb-free piezoelectric ceramics by the solid-state method to improve the environmental protection of the prepared materials and the performance of piezoelectric ceramics. The $0.94(K_{0.5}Na_{0.5})NbO_3$-$0.06LiNbO_3$ lead-free piezoelectric ceramics were prepared, study the performances and structural transformations of Pb-free piezoelectric ceramics mixed with other metal materials after adding alkali metal niobates. In addition, their influence on the microscopic morphology and electrical properties of KNN-based ceramics is studied, the optimal compositions and sintering temperatures of the Pb-free alkali metal niobate piezoelectric ceramics were investigated.

Keywords: Alkali Metal; Niobate Property; Pb-Free Piezoelectric; Ceramic Preparation

1. Introduction

Piezoelectric ceramics, as functional ceramics that can convert mechanical energy into electrical energy, have gradually become an important component of material technology [1].

In modern industrial production, pollution-free and low energy consumption is a topic of social concern. Alkali metal niobate Pb-free piezoelectric ceramics have received widespread attention and made rapid and practical progress due to their unique and excellent properties. Therefore, there has been much research on the preparation process and structure and modification of Pb-free piezoelectric ceramics. For example, alkali metal niobate (K, Na) NbO_3 (KNN) series have become popular Pb-free electrical materials due to their high voltage constants, high electromechanical coupling coefficients, high quality factors, and high Curie temperatures [2-5]. Various ceramic systems, such as Pb-free piezoelectric ceramics with Bi layers and Pb-free piezoelectric ceramics with perovskite structure, are the latest developments in piezoelectric materials [6-8]. With the introduction of environmentally friendly materials and the requirements of sustainable development, there is an increasing demand for Pb-free piezoelectric materials in various fields [4]. Chen Sen believes that the piezoelectric ceramics produced are all perovskite structures. Researchers have previously used traditional solid-phase sintering processes to produce Pb-free piezoelectric ceramics [9-11]. For example, Pb-free piezoelectric ceramics have been successfully prepared with high density and excellent electrical properties using a sintering temperature of 960-980°C [12-15]. $BaTiO_3$ (BT)-based Pb-free piezoelectric ceramics have been produced with high relative permittivity, dielectric strength, and insulation properties [16-18].

By comparison, in this manuscript, using K_2CO_3, Na_2CO_3, Nb_2O_5, and Li_2CO_3 as raw materials, $0.94(K_{0.5}Na_{0.5})NbO_3$-$0.06LiNbO_3$ piezoelectric ceramics were prepared by the solid-state method. These piezoelectric ceramic powders are doped and modified by adding metal modifying elements and ZnO sintering aids to make ceramic materials non-woven for cloth and Pb-free piezoelectrics. This article introduces the preparation methods of the materials from beginning to end and conducts a comparative study. Focus on studying the influence of sintering temperature on the structure and properties of ceramics.

2. Experimental method

2.1. Specification and preparation of experimental materials

The purity and source of the raw materials used in this experiment are as follows: K_2CO_3(≧99.1%), Na_2CO_3(≧99.6%),

[1] JINLING INSTITUTE OF TECHNOLOGY, NANJING, 211169, P.R. CHINA

* Corresponding author: nrk5204@jit.edu.cn

Nb_2O_5(≧99.4%), Li_2CO_3(≧98.1%), and ZnO(≧98.9%), they were all bought from Sinopharm chemical reagents, and used as raw materials.

In this manuscript, $0.94(K_{0.5}Na_{0.5})NbO_3$-$0.06LiNbO_3$ lead-free piezoelectric ceramics were prepared by solid-state synthesis. The preparation process includes batching, mixing, pre-sintering, forming, debinding, and sintering.

Pre-combustion is the complete chemical reaction of the mixed raw materials at a temperature below the melting point to generate new compounds. In this process, volatile substances are removed simultaneously from the raw materials. It is important to choose the optimal calcination temperature before calcination. During the test, a temperature with a ramp rate of 10°C/min was used to heat the sample from room temperature to 1100°C rapidly. The DSC/TG curve after mixing BNT is shown in Fig. 1. The pre-combustion of BNT raw materials is divided into the loss of alcohol and moisture at room temperature to 110°C, the removal of the water of crystallization, and the reaction step from each component at 110°C to 650°C. Starting from room temperature, the heating rate is about 3°C/min, and the temperature is kept at 110°C for 1 hour to ensure that the ethanol and water in the raw materials evaporate. The sample is then heated and kept for 3 hours before it is cooled in an oven.

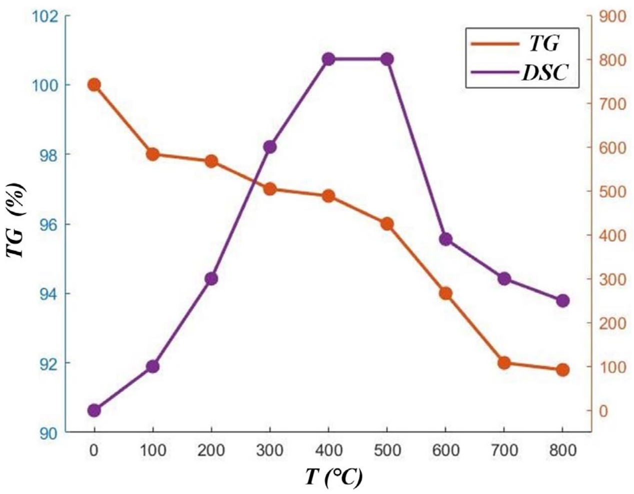


Fig. 1. Changes in Temperature and Time during Calcination in the Experiment

The dry pressing method was used to prepare the ceramic body during the sample preparation process. The raw materials were ground with an agate mortar to ensure that they were obtained as fine powder. Then about 5% of PVA binder (8% by weight) was added for granulation.

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 in a process called debinding. The temperature rise during degreasing should not be too fast and should not exceed 2°C/min. In the sintering process of this experiment, the sample pieces are stacked, and a temperature with a ramp rate of 2°C/min was used to heat the sample from room temperature to 1100°C rapidly. The PVA selected in this study begins to decompose at about 240°C, and the temperature is maintained at 500°C for 2.5 hours to allow the PVA to be completely discharged from the green body.

Based on 0.8 mol% of Bi and Fe, 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 of the ceramics are Li content, ZnO content, and sintering temperature $(K_{0.496}Na_{0.496})Nb_{0.992}O_3$-0.008 BF. Below this, the Li content is 4 mol%, 5 mol% and 6 mol%, the zinc oxide contents are 0.5 mol%, 1 mol%, and 2 mol%, and the sintering temperatures are 1100°C, 1000°C, and 900°C. The details of the six different experiments are shown in TABLE 1.

TABLE 1

Orthogonal Experimental Data

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

2.2. The Electrical Performance Test Method of the Sample

Samples used for electrical performance testing require high-quality electrodes. This experiment uses the Ag layer firing process to burn Ag to form a dense and highly conductive Ag layer on the ceramic surface under high temperatures. The Ag burning temperature should be lower than the pre-cooking temperature of the ceramic to reduce the influence on the ceramic grain size during Ag burning. Here, the sintering temperature of Ag is adjusted to about 600°C, the heating rate does not exceed 100°C/h, and the holding time is 10 minutes. The material is then cooled to room temperature in 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.

3. Experimental test results

3.1. The Influence of Sintering Temperature on the Electrical Properties of KNN-LN Ceramics

The electrical properties of KNN-LN ceramics at different sintering temperatures were studied with different temperatures as variables. Most of the ceramics have a coexisting structure of

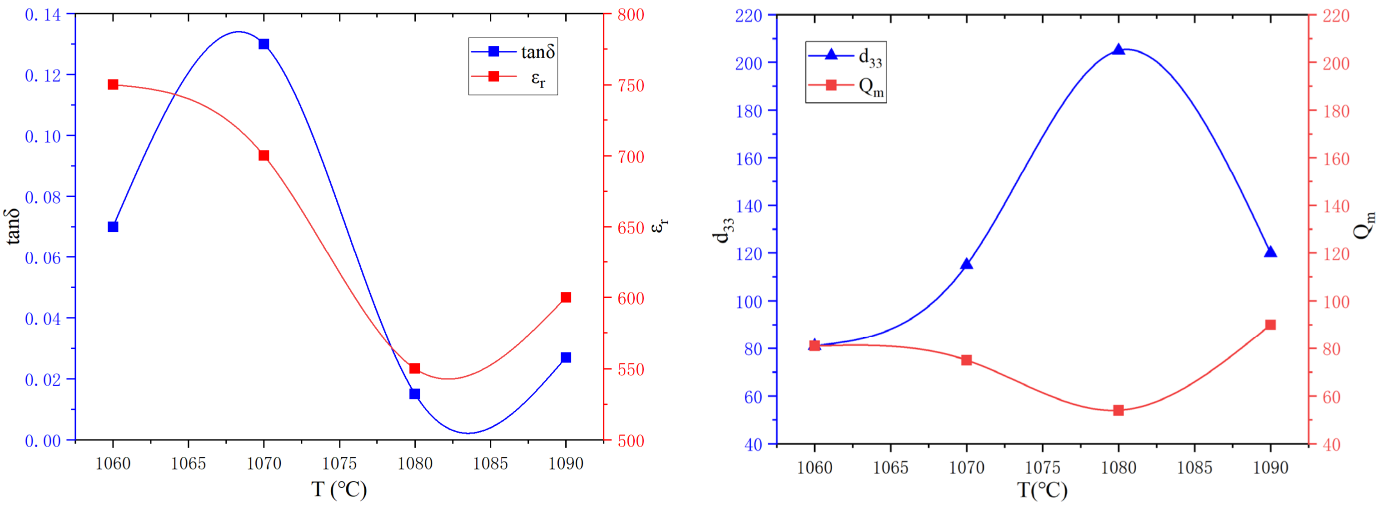


Fig. 2. The Influence of Sintering Temperature on the Electrical Properties of KNN-LN Ceramics

orthogonal and tetragonal phases, indicating that the sintering temperature also has an effect on the piezoelectric properties of the KNN-LN ceramics. Lower temperatures result in larger piezoelectric properties. When the sintering temperature is 1060°C, the piezoelectric constant d_{33} of the ceramic is 81 pC/N, and the mechanical quality factor Q_m is 81. When the sintering temperature is 1080°C, d_{33} reaches the maximum value of 205 pC/N, and Q_m is at its minimum value of 54. This specific situation is shown in Fig. 2 below.

Changes in the microscopic morphology of the ceramic explain the change in piezoelectric properties. 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°C, the crystal grains of the ceramic grow and exhibit enhanced uniformity. The growth of crystal grains is beneficial to alleviate internal stress and promotes 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°C, the piezoelectric performance of the ceramic is greatly reduced. This trend may be due to the increased volatilization of alkali metal ions at higher temperatures. The volatilization of alkali metal ions increases the generation of oxygen vacancies, and the oxygen vacancies play a role in fixing electric domains, thereby seriously impairing piezoelectric performance. The SEM images of the surface of KNN-LN ceramics at different sintering temperatures are shown in Fig. 3.

3.2. Influence of K/Na ratio on electrical performance

As shown in Fig. 4, when $x = 0.40$, the piezoelectric constant d_{33} of the ceramic is 230 pC/N, and the mechanical quality factor Q_m is 32. As x increases, d_{33} and Q_m usually increase first and then decrease. When $x = 0.46$, the piezoelectric constant of the ceramic reaches its maximum value, in which d_{33} is 237 pC/N, and Q_m is 24. As x further increases, d_{33} decreases. The total Q_m of the ceramic is kept in a relatively low range. At $x = 0.49$, Q_m reaches the maximum value of 51.

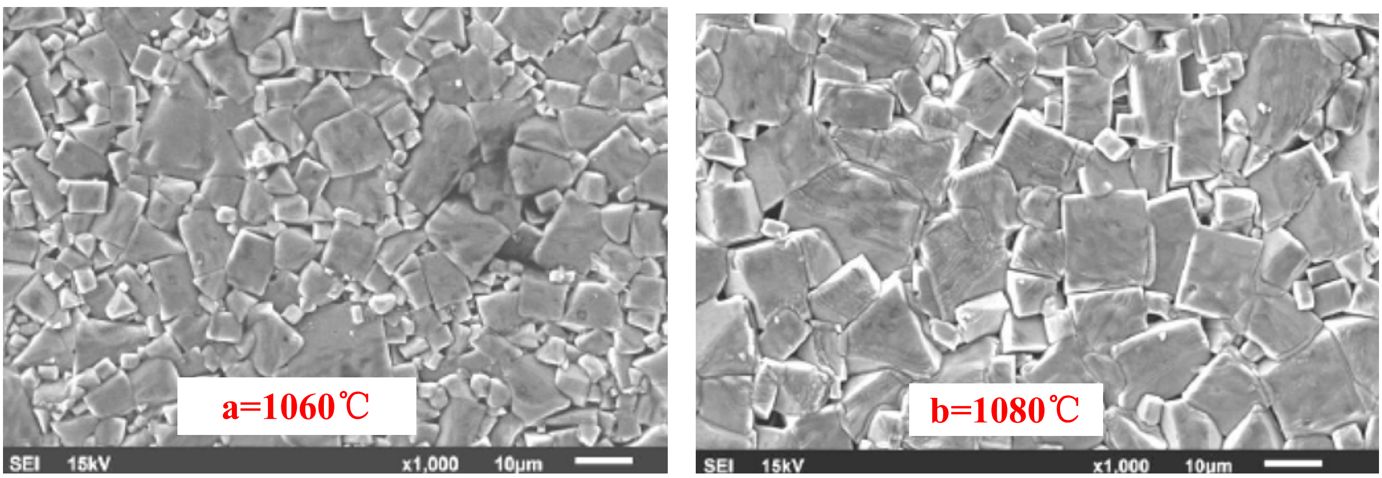
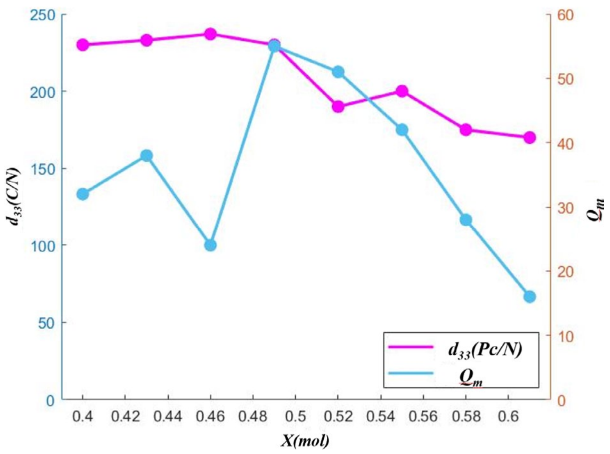
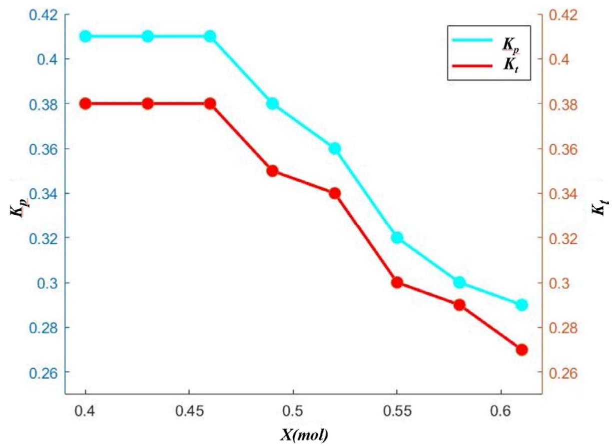


Fig. 3. SEM images of KNN-LN ceramic surface at different sintering temperatures



(a) The relationship between piezoelectric constant and mechanical quality factor



(b) The relationship between dielectric constant and dielectric loss

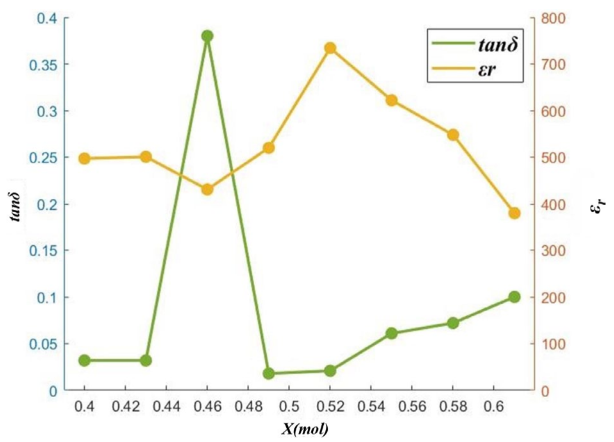


Fig. 4. Electrical Properties of $K_xN_{1-x}N$-LN Ceramics

When $x = 0.40$, the relative dielectric constant εr of the ceramic is 497, and the dielectric loss tanδ is 0.032. As x increases, ε_r increases first and then decreases, while tanδ gradually increases. At $x = 0.52$, the maximum value is 734. At this value, tanδ is 0.021. The change in the K/Na ratio influences the electrical properties of the ceramics. The optimal ratio for the properties of the ceramic piezoelectric is $x = 0.46$, which indicates that a low K/Na ratio can improve the piezoelectric properties of $K_xN_{1-x}N$-LN ceramics. The acceptor ion and oxygen vacancy form a complex with an electric dipole moment, which gradually adjusts its orientation to be parallel to spontaneous polarization, thus forming an internal bias field. Acceptor doping generates an internal bias field, which restricts the motion of the electric domain and reduces the piezoelectric constant and electromechanical coupling coefficient.

3.3. Influence of composition ratio on electrical performance

The BF-doped piezoelectric sodium potassium niobate ceramics prepared by sintering at 1100°C were tested using a quasi-static tester d_{33}, a density tester, a precision impedance tester Angelon, piezoelectric constant d_{33}, and for the electromechanical coupling coefficient K_p. The dielectric constant ε_r and the dielectric loss value tanδ are shown in Fig. 5.

When BF is added, oxygen vacancies are introduced into the ceramic, leading to lattice distortion. These oxygen vacancies gradually diffuse towards the domain walls, creating a "pinning effect" that affects the polarization switching of the electric domains, resulting in a decrease in the number of domain switching during polarization. From this perspective, the ceramic should exhibit hard doping characteristics. At this point, the piezoelectric properties, such as the piezoelectric constant and electromechanical coupling coefficient, should gradually increase, while the dielectric constant increases and the dielectric loss decreases. Therefore, the ceramic exhibits "composite doping" characteristics.

As x increases, the density first increases and then decreases, and the electromechanical coupling coefficient and piezoelectric constant show the same trend. When x is 0.008, as x increases, d_{33} and K_p increase almost linearly. When $x < 0.008$, the dielectric constant gradually increases. When $x = 0.008$, the maximum dielectric constant is 625, and the dielectric performance is optimal. At this value, the crystal sample is denser and has fewer holes. The SEM images of the 1100°C ceramic surface at different BF doses are shown in Fig. 6.

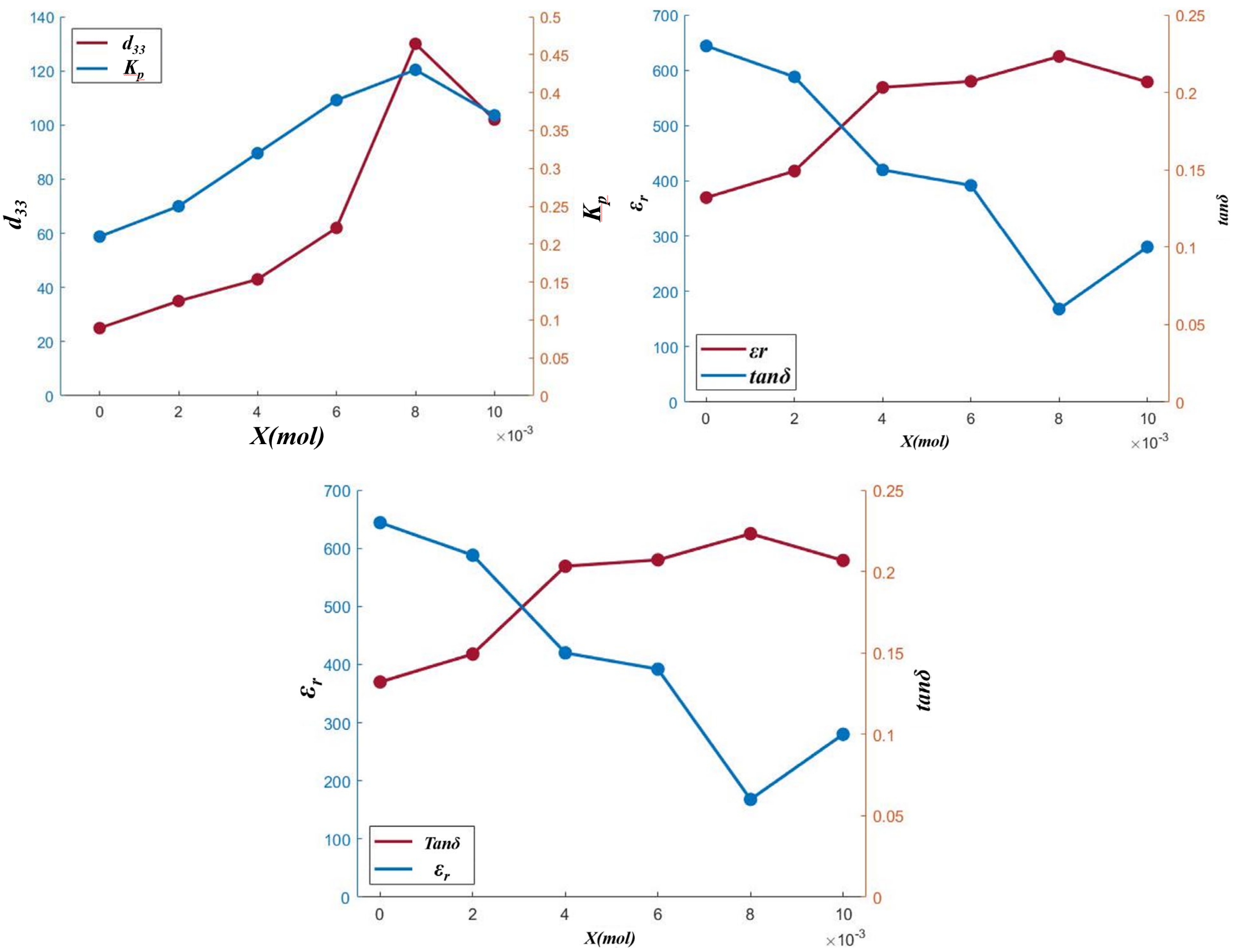


Fig. 5. Analysis of the Electrical Properties of KNN-yBF Ceramics

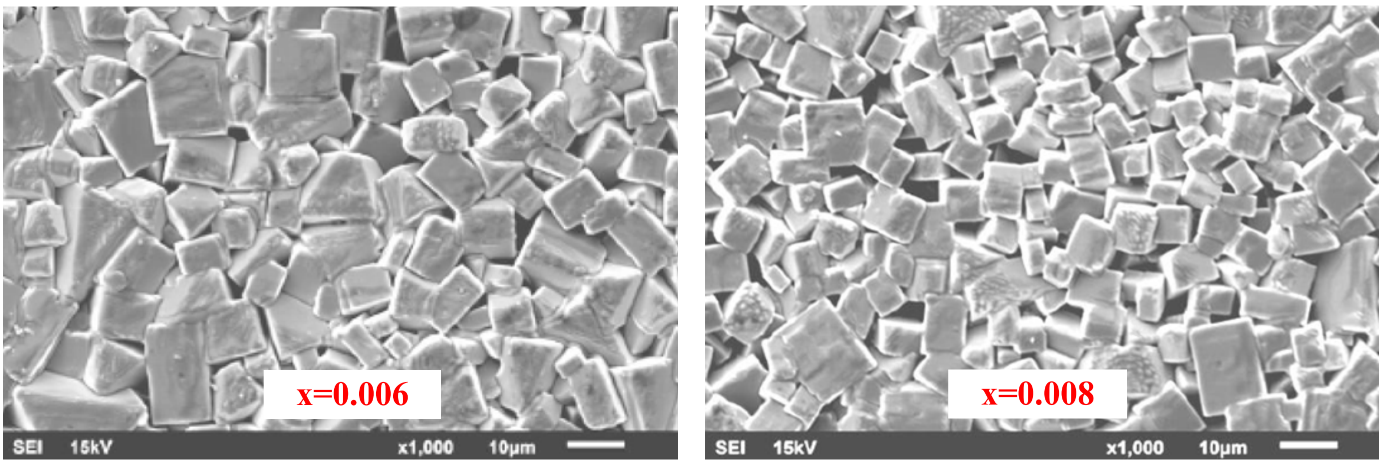


Fig. 6. SEM images of ceramic surfaces at 1100℃ with different BF dosages

4. Conclusions

Using K_2CO_3, Na_2CO_3, Nb_2O_5, and Li_2CO_3 as raw materials, KNN-based piezoelectric ceramic powders were prepared by the solid-state method. These powders are doped and modified by adding metal modifying elements and ZnO sintering aids to make ceramic materials Pb-free piezoelectrics. The following conclusions can be drawn. When the sintering temperature is increased to 1080°C, the crystal grains of the ceramic grow and exhibit enhanced uniformity. However, if the sintering temperature is higher than 1080°C, the piezoelectric performance of the ceramic is greatly reduced. This trend may be due to the increased volatilization of alkali metal ions at higher temperatures. The relationship between the composition, temperature, structure, and electrical properties of piezoelectric ceramics was analyzed, and a new Pb-free piezoelectric ceramic with high voltage electrical response based on BNT was obtained. When $x \geq 0.40$, d_{33} and Q_m usually increase first and then decrease. When $x = 0.46$, the piezoelectric constant of the ceramic reaches its maximum value in which d_{33} is 237 pC/N. When $x = 0.52$, the relative dielectric constant εr of the ceramic is maximum. BF doped sodium potassium niobate piezoelectric ceramics were prepared by sintering at 1100°C. When $x = 0.008$, the maximum dielectric constant is 625, and the dielectric performance is optimal. At this value, the crystal sample is denser and has fewer holes.

In future work, a more in-depth analysis of the material's fatigue performance and reliability will be conducted. Starting from the powder preparation process, research and development of non-traditional ceramic preparation processes along with the extraction of BNT-B will be conducted.

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