Research on the Pre-sintering Temperature During the Preparation of (1-x) NBT—xBaTiO₃ Serial Ceramics

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Abstract: According to the formula of (1-x)NBT-xBaTiO₃, this study selects different composition points and measures the volume density and piezoelectric property of the samples at different pre-sintering temperatures, ultimately determining the optimal pre-sintering temperature. Experiments show that for ceramic based on (1-x)NBT-xBaTiO₃, when x<0.06, the optimal pre-sintering temperature should be 900°C; when x≥0.06, it should be 950°C.

1. Introduction
Traditional piezoelectric ceramics has the problem of lead volatilization during preparation, which not only deviates the stoichiometric ratio of the ceramics, but also causes pollution to the environment. Therefore, it is of great practical significance to develop lead-free piezoelectric and ferroelectric ceramics that are compatible with the environment. According to the formula of (1-x)NBT-xBaTiO₃, this study selects different composition points and measures the volume density and piezoelectric property of the samples at different pre-sintering temperatures, ultimately determining the optimal pre-sintering temperature.

2. The determination of pre-sintering temperature

2.1. The effect of pre-sintering
Pre-sintering, also known as pre-synthesis, is an important preparation process of electronic ceramic products by solid-phase synthesis method, a treatment step before the formal sintering. After the high-temperature treatment, the raw materials of the electronic ceramics are undergone the solid-phase reaction, transforming into a sosoloid and synthesizing the principal crystalline phase. During the pre-sintering process, the following main reactions occur:

\[
\frac{1-x}{4} \text{Na}_2\text{CO}_3 + \frac{1-x}{4} \text{Bi}_2\text{O}_3 + x\text{BaCO}_3 + \text{TiO}_2 = (1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - x\text{BaTiO}_3 + \frac{1+3x}{4} \text{CO}_2
\]

Since the optimal pre-sintering temperature for samples with different BaTiO₃ (BT for short) contents may be different, this experiment selects the three composition points of BT2 ((Na1/2Bi1/2)0.98Ba0.02TiO3), BT6 ((Na1/2Bi1/2)0.94Ba0.06TiO3), and BT15 ((Na1/2Bi1/2)0.85Ba0.15TiO3) and determines the rough range of pre-sintering temperature. After that, according to the volume density and piezoelectric property of the samples pre-sintered at different temperatures, the optimal pre-sintering temperature is determined and the formation of the crystal structure of the sample pre-sintered at the optimal temperature is analyzed according to XRD.
2.2. TG-DTA pattern analysis

![Fig. 1 samples' TG-DTA spectrum of BT6](image)

Fig. 1 is the differential thermal pattern of BT6. As illustrated, the DTA curve has an endothermic peak at about 100℃ while the corresponding TG curve has a weight loss, which is primarily attributed to the evaporation of water in the raw material. There is a large weight loss in the 600–680℃ range that is caused by carbonate decomposition, and for the corresponding DTA curve, it has an endothermic process. At about 850℃, there is another endothermic process in the DTA curve, which corresponds to the endothermic reaction in material synthesis. A sharp endothermic peak appears at about 1241.4℃ that corresponds to the melting point of the material, suggesting that liquid phases have begun to appear in large numbers. Therefore, it can be confirmed from the pattern that the pre-sintering temperature should exceed 850℃.

2.3. XRD pattern analysis

In the XRD pattern of Fig.2, BT2 at 850℃ has synthesized the primary crystalline phase of the perovskite structure, but BT6 and BT15 still have the impure phase of Bi12TiO2O, suggesting that the pre-sintering temperature must be increased in the case of the addition of BT. It is mainly due to the higher decomposition temperature of BaCO3 than that of Na2CO3. The decomposition temperature of pure BaCO3 exceeds 1100℃ but it drops down to 900℃ in the presence of TiO2. In the XRD pattern of Fig.3, all the samples at three ratios have synthesized a single perovskite structure at 900℃. From the point of view of the synthetic structure only, setting BT2’s pre-sintering temperature to 850℃ and BT6 and BT15’s to 900℃ has already met the requirements.
2.4. Analysis of volume density and piezoelectric property

Appropriate pre-sintering temperature is the key to prepare quality ceramics with high density. Unduly low pre-sintering temperature leads to insufficient reaction, poorly packed powder particles, and inadequate surface contact, which makes impossible the preparation of ceramics with high density. On the contrary, the unduly high pre-sintering temperature may cause difficulty in powder lot crushing, excessive crystallization of powder particles and the resultant reduction of their activity, which will result in the weakened driving force for sintering and an increased number of pores in ceramics, thereby affecting their density.

As illustrated in Fig.4, the volume density of BT2 reaches the largest at 900°C, and at the moment the piezoelectric property is also the best as shown in Fig.5. BT15 has the optimal volume density and piezoelectric property at 950°C. For BT6, the increase of the pre-sintering temperature from 900°C to 950°C, its volume density nearly remains unchanged, but the piezoelectric property is remarkably improved at 950°C. With the increase of the pre-sintering temperature, the volume density and piezoelectric property of BT15 have maintained a rising trend. Given that excessively high pre-sintering temperature will lead to difficulty in crushing the pre-sintered samples, the pre-sintering temperature is not continually increased herein.
3. Conclusions

In summary, pre-sintering temperature exerts an important influence on the sintering performance, volume density and piezoelectric property of piezoelectric ceramics. Only at the appropriate pre-sintering temperature, can samples achieve the maximum volume density and optimal piezoelectric property. Experiments show that for ceramic based on (1-x)NBT-xBaTiO$_3$, when x<0.06, the optimal pre-sintering temperature should be 900℃; when x≥0.06, it should be 950℃.

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