

Study on the Effect of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ on Performance for BNT-BT Ceramics

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Abstract

In this paper, $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3$ ceramics (BNT-BT for short) are used as the matrix, modified by $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$, $(1-x)(0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3)-x(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramics (BNT-BT- x SBT for short), $x=0.1, 0.2, 0.3$ and 0.4 mol, were prepared by a traditional solid state sintering method, and the effect of $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ content on the phase structure, dielectric, ferroelectric and energy-storage properties for BNT-BT- x SBT ceramics was investigated. The results show that BNT-BT- x SBT ceramics have secondary phase because of adding $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$. With the increasing of x , the structure for BNT-BT- x SBT ceramics changes from the coexistence of rhombohedral and tetragonal phase to pseudo-cubic phase at room temperature. ϵ_r sharply increases and $\tan \delta$ slowly increases when x increases. And ferroelectric properties of BNT-BT- x SBT ceramics weaken with the increase of x . BNT-BT- x SBT ceramics with co-occupied in A-site show an enhanced diffusion properties. ϵ_r-T curves have two anomaly dielectric peaks at T_d and T_{\max} . With the increasing of x , T_d and T_{\max} decrease. When $x=0.4$, T_d closed to room temperature, which is used for confirming the pseudo-cubic phase. Compared comprehensively, BNT-BT- x SBT ceramics with $x=0.4$ show pseudo-cubic phase and have an excellent dielectric properties, $\epsilon_r=1723$, $\tan \delta=0.11$, $\epsilon_r > 2000$ (room temperature $< T < 280^\circ\text{C}$). In addition, it displays good energy-storage property, $W_1=0.348\text{J}/\text{cm}^3$, $W_2=0.093\text{J}/\text{cm}^3$, $\eta=78.9\%$ (@52kV/cm).

Keywords

Sodium barium titanate; $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$; dielectric properties; ferroelectric properties.

1. Introduction

Piezoelectric ceramics is polycrystal materials generated by high-temperature sintering solid phase reaction of oxides (titanium oxide, zirconia, lead oxide, etc.), the piezoelectric effect is the basis which piezoelectric ceramics achieve the mutual conversion of mechanical energy and electrical energy[1]. In order to meet the market demand and does not cause environmental problems, the lead-free research of piezoelectric ceramic materials is imperative, and research on this filed is of great practical significance as well[2].

This paper selects a simple binary system BNT-based as the research object, the traditional solid phase method is used to prepare ceramic materials, the phase structure and phase transition property and ferroelectric property which $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ replaces $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ ceramics are studied, and explores the energy storage property of the BNT-based lead-free ceramics.

2. Sample Preparations

The preparation process of piezoelectric ceramics is extremely critical; the synthetic processing will affect the crystal structure of the ceramic materials and the electrical properties of the materials to

some extent, therefore, the technological process must be strictly required. The traditional solid phase synthesis method is used to prepare BNT-based lead-free piezoelectric ceramic in this experiment,. The specific purity of the various raw materials used in the paper is shown in Table 1.

Table 1. Description of raw materials used in BNT-BT-xSBT ceramics and their doping

raw material name	Na ₂ CO ₃	Bi ₂ O ₃	BaCO ₃	SrCO ₃	TiO ₂
molecular weight	105.99	465.97	197.34	147.63	79.87
purity	99%	98.9%	99%	99%	99%

Experimental formula:

$(1-x)(0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3)-x(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramic, which can be abbreviated as BNT-BT-xSBT.

Ingredient calculation: according to the difference of x value, the experiment is divided into four components, x=0.1 mol, x=0.2 mol, x=0.3 mol, x=0.4 mol.

The total mass of the drug that can be added in the nylon grinding mill used in the experiment is about 20g, so the amount of total material is set to 0.1mol, and according to the stoichiometric ratio, the quality of the various types of raw materials required after calculation is shown in Table 2.

Table 2. required quality of each component

component	Na ₂ CO ₃	Bi ₂ O ₃	BaCO ₃	SrCO ₃	TiO ₂
x=0.1	2.2462	10.4360	1.0764	1.0439	8.0677
x=0.2	1.9966	9.8000	0.9568	2.0877	8.0677
x=0.3	1.7470	9.1639	0.8372	3.1316	8.0677
x=0.4	1.4975	8.5279	0.7176	4.1754	8.0677

3. Phase Structure, Dielectric and Ferroelectric Property of BNT-BT-xSBT Ceramics

3.1 Phase Structure of BNT-BT-xSBT Ceramics

The DX-2700X ray diffractometer is adopted in this paper, $(1-x)(0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3)-x(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ ceramic structure with different components (x=0.1, x=0.2, x=0.3 and x=0.4) is tested.

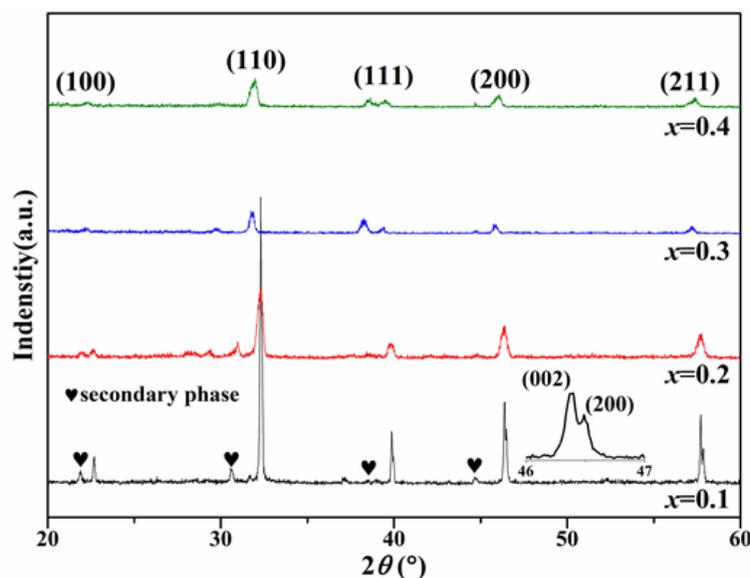


Figure 1. XRD diagram of BNT-BT-xSBT ceramics fired at 1140 °C

Figure 1 is the XRD patterns of each component of the BNT-BT-xSBT ceramics sintered when $T=1140\text{ }^{\circ}\text{C}$, it can be seen from the figure that at the same sintering temperature, although the components are different, the main diffraction peaks are basically consistent, this shows that the main crystalline phase is unchanged; however, there are still some unknown peaks appear, it shows that there is a little impurity phase in the ceramic. The results show that the solid solubility of Sr^{2+} in $(1-x)\text{NBBT-xSBT}$ is limited, and there will be unknown phases after excess.

It can also be seen from the XRD diagram that as x increases, the position of the diffraction peak shifts slightly to low angle, it shows that Sr^{2+} substitution causes cell distortion. $(1-x)(0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-0.06\text{BaTiO}_3)-x(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$, compared with the radius of A ion: $\text{Sr}^{2+}\sim 1.12\text{ \AA}$, $\text{Ba}^{2+}\sim 1.34\text{ \AA}$, $\text{Na}^{+}\sim 0.97\text{ \AA}$, $\text{Bi}^{3+}\sim 0.96\text{ \AA}$, which means that the large radius Sr^{2+} is more likely to replace Na^{+} or Bi^{3+} , which cause cell volume to be larger, so the diffraction peak is gradually shifted to lower angle.

When $x=0.1$, the diffraction angle of BNT-BT-xSBT ceramic around $2\theta\sim 45^{\circ}$ is the separated doublet, (002) and (200), it is the feature which three sides (R) and four sides (T) two phases coexist. As x increases, the doublet gradually becomes a sharp single peak, which is feature of cubic phase. Therefore, with the gradual increase of x , $(1-x)\text{NBBT-xSBT}$ ceramics changed from three-side and four-side coexisting phase to cubic phase.

3.2 Dielectric Temperature Spectra of BNT-BT-xSBT Ceramics

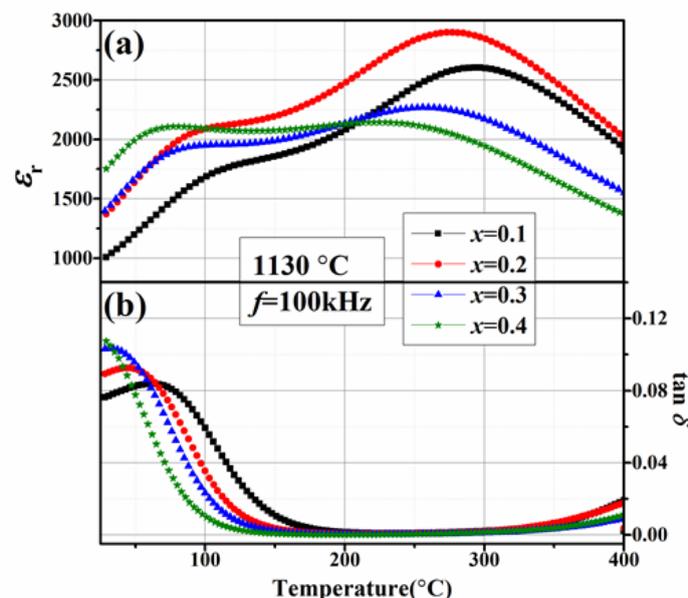


Figure 2. $T=130^{\circ}\text{C}$, change of dielectric constant and dielectric loss of BNT-BT-xSBT ceramics with temperature

Figure 2 shows (a) ϵ_r - T characteristic curve and (b) $\tan \delta$ - T characteristic curve of 1130°C sintered BNT-BT-xSBT ceramics. It can be seen from the $\tan \delta$ - T characteristic curve that the dielectric loss of BNT-BT-xSBT ceramics is higher under low temperature conditions ($T < 100^{\circ}\text{C}$); as the temperature increases, the dielectric loss $\tan \delta$ gradually begins to decrease. After the temperature gradually rises to a higher level ($T > 200^{\circ}\text{C}$), the dielectric loss of each component is nearly the same. Finally, at high temperatures ($T > 350^{\circ}\text{C}$), the loss begins to increase as temperature rises, which is related to the effect of a large amount of space charge at high temperatures.

It can be seen from the ϵ_r - T dielectric temperature characteristic curve that the component dielectric constant of $x=0.4$ is the largest under low temperature conditions, and the components of $x=0.2$ and $x=0.3$ are next and equal, $x=0.1$, the component dielectric constant is the smallest. The dielectric temperature constant of BNT-BT-xSBT ceramics presents similar change rule with the increase of temperature. From room temperature, ϵ_r first increases, rises to a small dielectric step (T_d); then starts

to increase, rises to the dielectric constant to reach the maximum (Tmax) and then decreases. Compared with the curves of different components, it can be seen that as x increases, both Tmax and Td decrease.

In order to more clearly analyze the phase transition characteristics of BNT-BT-xSBT ceramics, the dielectric temperature curves at different frequencies is tested on ceramics, as shown in Figures 3, 4, 5 and 6. It can be seen that the BNT-BT-xSBT ceramic has significant frequency dispersion characteristics; at low temperature Td, the anomalous peak moves toward the high temperature as the frequency increases. This is due to in the BNT-BT-xSBT ceramics; the A is caused by the heterogeneous composition of the various ion complexes.

Generally, the dielectric temperature curve can reflect the phase transition characteristics of the material. The phase transition characteristics of the pure (Na0.5Bi0.5)TiO3 ceramic is combined for analysis. The BNT-BT-xSBT ceramics studied in this paper range from room temperature to the starting point of the dielectric constant platform (corresponding to the low temperature anomalous peak of dielectric loss), in this wide temperature range, the ceramic is a three-side and four-side coexisting phase. Figures 3, 4, 5, and 6 are compared, it can be seen that when x = 0.1, the dielectric constant platform starting point is near 100 °C, it shows that BNT-BT-xSBT ceramic three-side and four-side coexisting phase when x=0.1, this is consistent with the xrd analysis results. With the increase of x, the starting point of the dielectric constant platform moves toward the low temperature direction and gradually approaches the room temperature, so the phase structure gradually changes to cubic phase.

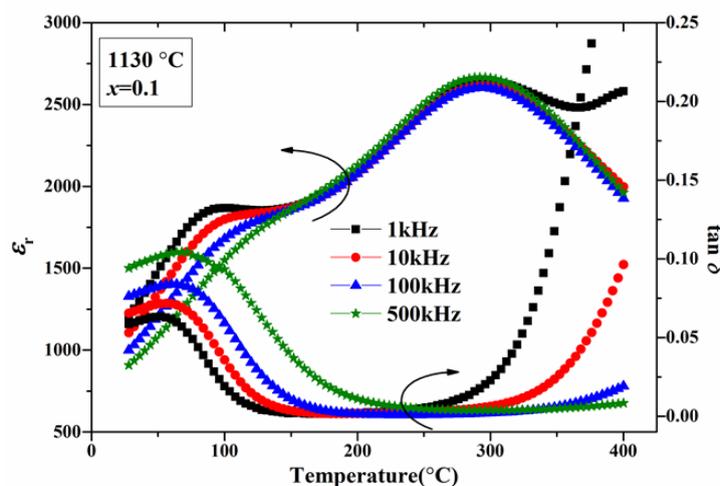


Figure 3. dielectric temperature curve of BNT-BT-xSBT ceramic (x=0.1) at different frequencies

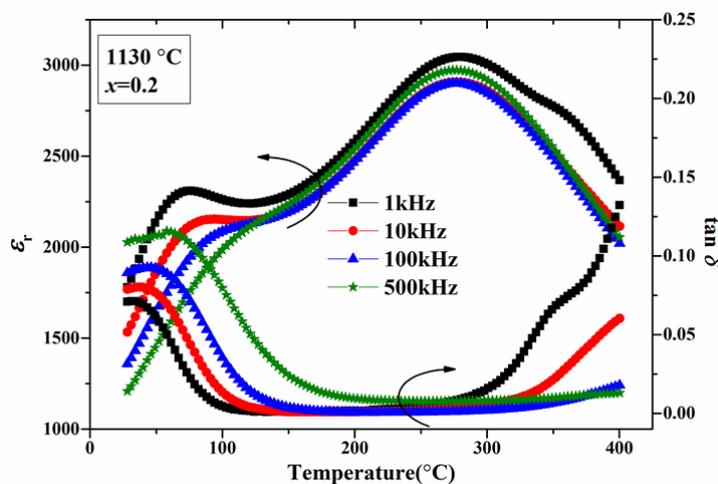


Figure 4. dielectric temperature curve of BNT-BT-xSBT ceramic (x=0.2) at different frequencies

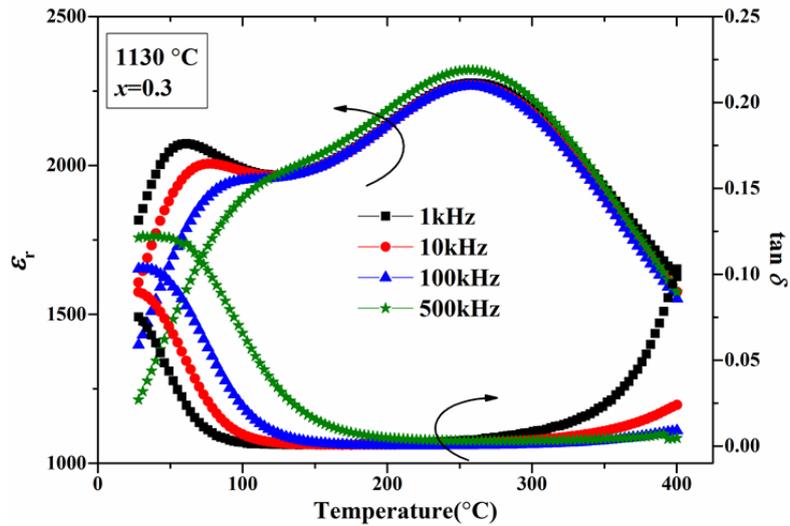


Figure 5. dielectric temperature curve of BNT-BT-xSBT ceramic ($x=0.3$) at different frequencies

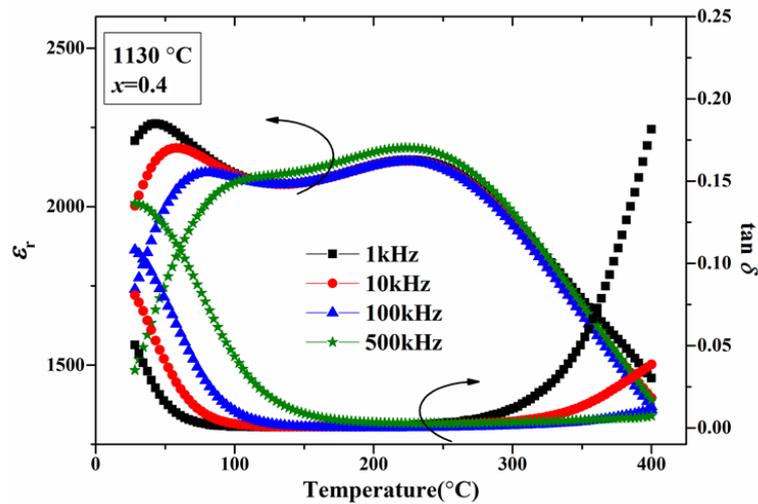


Figure 6. dielectric temperature curve of BNT-BT-xSBT ceramic ($x=0.4$) at different frequencies

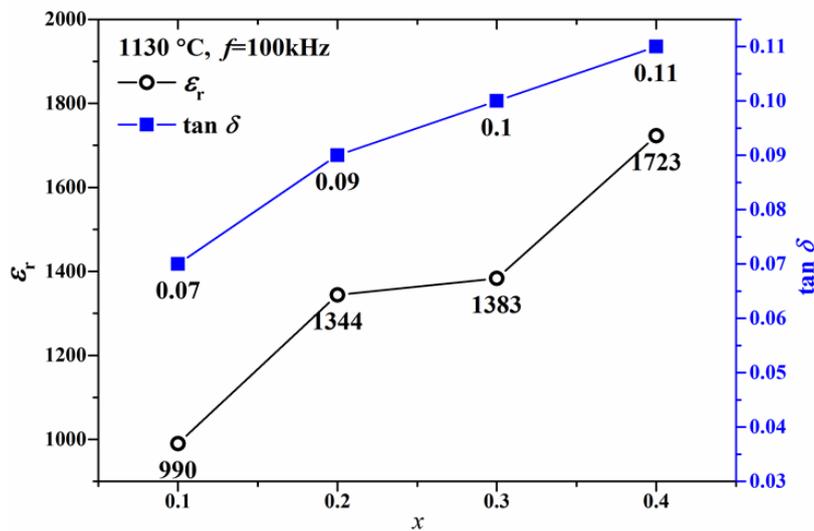


Figure 7. dielectric performance of BNT-BT-xSBT ceramic at 100 kHz when $T=1130\text{ }^\circ\text{C}$

Figure 7 shows the variation of ϵ_r and $\tan \delta$ with component x at 100 kHz when BNT-BT-xSBT ceramics sintered at $1130\text{ }^\circ\text{C}$. When x increases, the dielectric loss $\tan \delta$ of BNT-BT-xSBT ceramics increases slightly from 0.07 to 0.11; the dielectric constant ϵ_r is 990 and increases significantly to 1723. In comparison, when $x=0.4$, the dielectric properties of BNT-BT-xSBT ceramics are better, $\epsilon_r=1723$,

$\tan \delta=0.11$; and when $x=0.4$, the ceramics are in a large temperature range (room temperature $<T < 280 \text{ }^\circ\text{C}$) $\epsilon_r > 2000$.

3.3 Ferroelectric Properties and Energy Storage Characteristics of BNT-BT-xSBT Ceramics

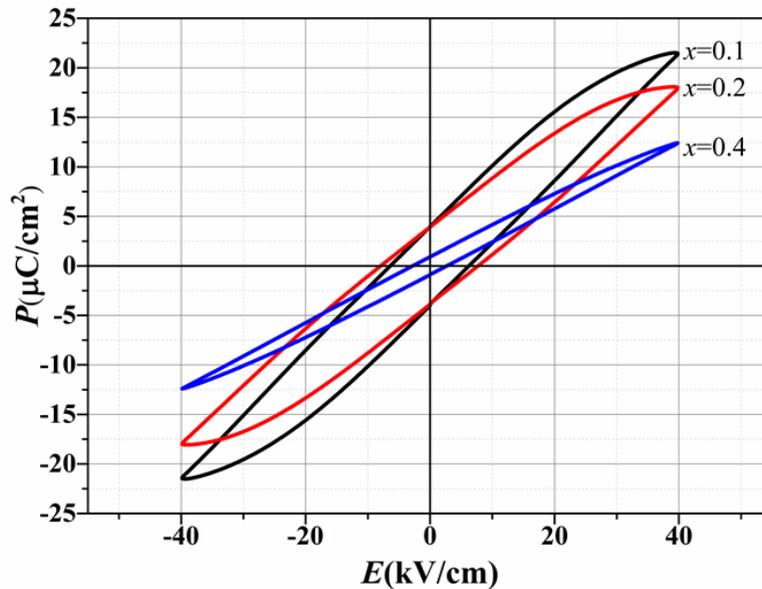


Figure 8. electric hysteresis loop of BNT-BT-xSBT ceramic at 1130 °C ($x=0.1, 0.2$ and 0.4)

Figure 8 shows the electric hysteresis loops measured when BNT-BT-xSBT ceramics, $x = 0.1, 0.2,$ and 0.4 under the same test conditions. Because the thicknesses of the samples are nearly the same, the electric field strength corresponding to the P maximum value in the electric hysteresis loop of each sample is the same. It can be seen that the shape of the electric hysteresis loop is not much different. The BNT-BT-xSBT ceramics of $x=0.1, 0.2,$ and 0.4 have a nonlinear relationship between P and E ; and the PE loops are slender, it shows that the ceramic has weak ferroelectricity; in addition, $x=0.4$ is more flat and longer than $x=0.2$ and $x=0.1$ in ceramics loop, it shows that x increases and ferroelectricity weakens.

The results of xrd and dielectric temperature phase change analysis are further integrated, when x increases, Bx-BT-xSBT ceramics are gradually from three-side and four-side coexisting phase to cubic phases, this proves that the ferroelectric property of BNT-BT-xSBT ceramics are reduced.

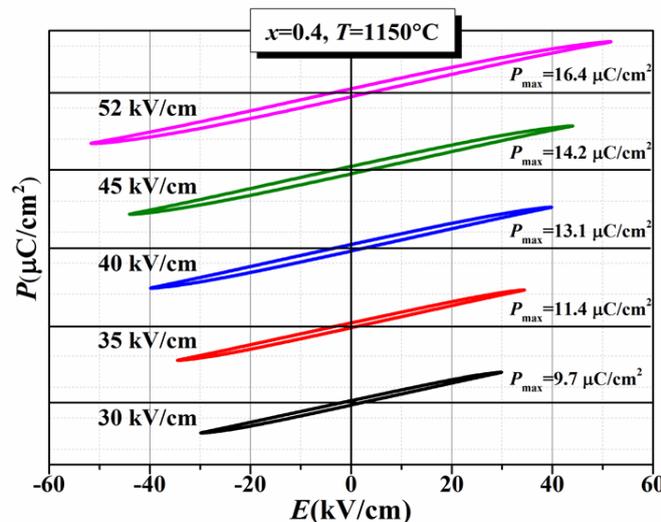


Figure 9. Electric hysteresis loop of BNT-BT-xSBT ceramic in different field strength tests when $x=0.4$

figure 9 shows the electric hysteresis loop of ceramic of $x=0.4$ when at different voltages and fixed test frequency is 1 Hz. It can be seen that as the test voltage increases, the electric hysteresis loop grows significantly and the ferroelectric performance is enhanced. Figure 10 shows that the maximum polarizations P_{max} and P_r change with the test field strength E in the electric hysteresis loop measured in Figure 9. It can be seen that as the test field strength E increases, P_{max} increases significantly, while P_r increases slightly. For the measurement of energy storage characteristics, it is desirable that the material has as large a P_{max} as far as possible, and the smaller the better P_r is.

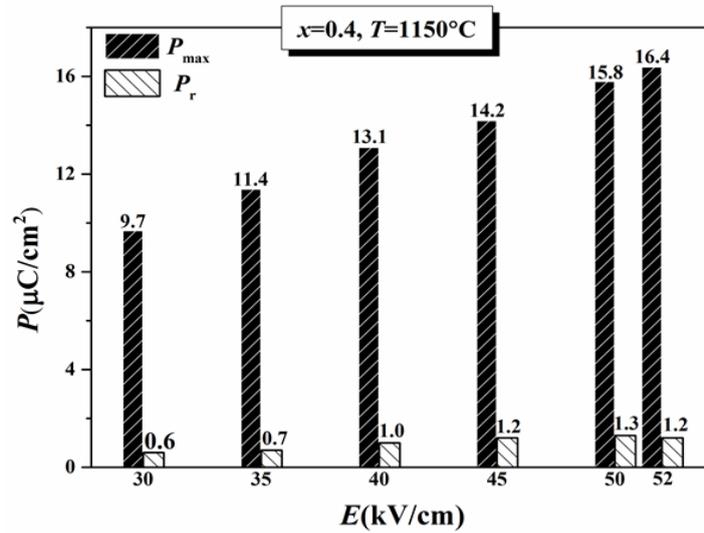


Figure 10. variation of Pmax and Pr of BNT-BT-xSbT ceramics with field strength E when x=0.4

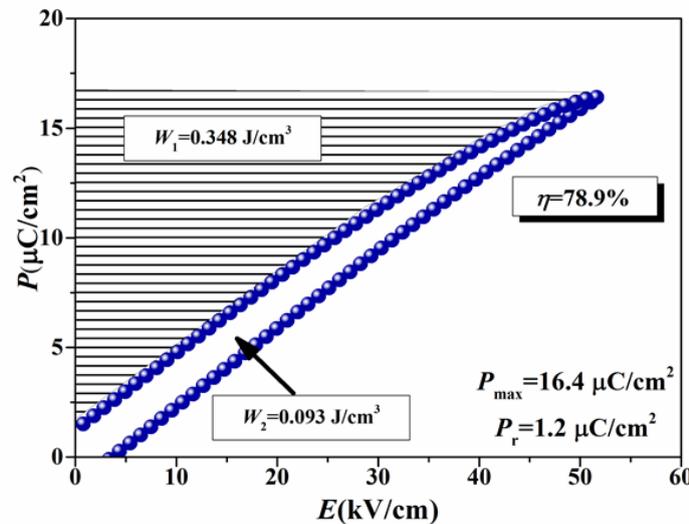


Figure 11. electric hysteresis loop and energy storage characteristics of BNT-BT-xSbT ceramics when x=0.4

Therefore, in allusion to the most excellent electric hysteresis loop ($E=52\text{kV/cm}$, $f=1\text{Hz}$) in Figure 10, the energy storage characteristics of BNT-BT-xSbT ceramics of $x=0.4$ sintered at $1150\text{ }^\circ\text{C}$ are calculated, as shown in the figure 11. The shaded part in the figure represents the energy storage density W_1 , and the calculation method of the energy storage density is shown in formula (1).

$$W_1 = \int_{P_r}^{P_{max}} E dP \tag{1}$$

The area enclosed by the return line in Figure 11 represents the electric hysteresis loss, which is the lost energy W_2 . $\eta = (W_1 / (W_1 + W_2)) \times 100\%$ can represent energy storage efficiency. The calculation results show that the energy storage density of BNT-BT-xSbT ceramics of $x=0.4$ is $W_1=0.348\text{J/cm}^3$, the energy loss is $W_2=0.093\text{J/cm}^3$, and the efficiency $\eta=78.9\%$ (@ 52kV/cm).

4. Conclusion

This paper takes sodium bismuth titanate-based $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ (namely BNT-BT) ceramics as the matrix, and the second component $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ is added to study its impact on phase structure, dielectric properties, ferroelectric properties and energy storage properties of ceramics. $(1-x)(0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-}0.06\text{BaTiO}_3)\text{-}x(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ (namely BNT-BT-xSBT) ceramics is prepared by traditional ceramic solid phase synthesis method ($x=0.1, 0.2, 0.3, \text{ and } 0.4$).

The results show that the introduction of (1) $(\text{Sr}_{0.7}\text{Bi}_{0.2})\text{TiO}_3$ leads to the existence of a small amount of unknown phase inside the ceramic. With the increase of x , BNT-BT-xSBT ceramics gradually changed from the three-side and the four-side coexisting phase to the cubic phase.

(2) BNT-BT-xSBT ceramics in A-site composite occupancy show strong dispersion characteristics. From room temperature, ϵ_r first increases, rise to a small dielectric step (T_d); then starts to increase, rises to the dielectric constant to reach the maximum (T_{\max}) and then decreases. As x increases, both T_{\max} and T_d gradually decrease. When $x=0.1$, $T_d \sim 100^\circ\text{C}$, it shows that the ceramics the three-side and four-side coexistence; when $x=0.4$, the T_d is close to room temperature, and the ceramic is cubic phase structure. This result is consistent with the xrd analysis results.

(3) When x increases, the dielectric loss $\tan \delta$ of BNT-BT-xSBT ceramics is slightly increased from 0.07 to 0.11; the dielectric constant ϵ_r is 990 and significantly increased to 1723. In comparison, when $x=0.4$, the dielectric property of BNT-BT-xSBT ceramics are better, $\epsilon_r=1723$, $\tan \delta=0.11$; and when $x=0.4$, the ceramics has a large $\epsilon_r > 2000$ in a larger temperature range (room temperature $< T < 280^\circ\text{C}$).

(4) BNT-BT-xSBT ceramics have weak ferroelectricity. And as x increases, ferroelectricity decreases, which is also due to changes in phase structure. The BNT-BT-xSBT ceramic of $x=0.4$ has a slender electric hysteresis loop, and it is a ceramic material that can be used for energy storage. When $x=0.4$ is calculated, the storage density of the BNT-BT-xSBT ceramics $W_1 = 0.838 \text{ J/cm}^3$, the energy loss $W_2 = 0.093 \text{ J/cm}^3$, and efficiency $\eta = 78.9\%$ (@52 kV/cm).

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