Excellent Energy Storage Performance in NaNbO_3 -Based Relaxor Antiferroelectric Ceramics Under a Low Electric Field

Xuxin Cheng

Zhaoqing University

Pengyuan Fan (✉ pyfan@hust.edu.cn)

Huazhong University of Science and Technology - Main Campus: Huazhong University of Science and Technology <https://orcid.org/0000-0001-6192-7828>

Xiaoming Chen

Zhaoqing University

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Abstract

NaNbO₃-based antiferroelectric (AFE) ceramics have the prominent advantages of stable performance and low cost. However, its energy storage property is often remarkably limited by the hysteresis of the antiferroelectric to ferroelectric phase transformation. In this work, 0.88Na(Nb_{1-x}Ta_x)O₃-0.12Bi_{0.2}Sr_{0.7}TiO₃ ($x = 0-0.075$) antiferroelectric ceramics were synthesized using a conventional mixed oxide route. Ta⁵⁺ were completely dissolved into the lattice of 0.88NaNbO₃-0.12Bi_{0.2}Sr_{0.7}TiO₃ to form a pure perovskite structure. With increased Ta content, the AFE orthogonal P phase was replaced by AFE orthogonal R phase progressively. Meanwhile, the dielectric constant curve showed relaxor-like properties. As a result, slender $P-E$ curves with reduced hysteresis loss and decreased residual polarization were achieved. Interestingly, a large recoverable energy storage density ($W_{\text{rec}} \approx 2.16 \text{ J cm}^{-3}$) and high energy storage efficiency ($\eta \approx 80.7\%$) were obtained simultaneously under a low driving electric field of 15 kV mm^{-1} at doping ratio (x) of 0.075. In addition, the 0.88Na(Nb_{0.925}Ta_{0.075})O₃-0.12Bi_{0.2}Sr_{0.7}TiO₃ sample exhibited excellent temperature stability, indicating an ideal candidate in future pulsed power capacitor.

1. Introduction

Dielectric energy storage capacitors have fast charging and discharging rates ($\sim \text{ns}$) and higher power density (exceed 10^8 W kg^{-1}) [1–4]. These capacitors are important components of pulse power electronic systems and are widely used in various fields, such as electromagnetic ejection, electromagnetic gun, electric vehicle, medical defibrillator, smart grid, spacecraft, and satellite [5–8]. The materials used in dielectric energy storage capacitors include organic and ceramic materials. Compared with organic and electromechanical materials, ceramic materials have higher dielectric constant (ϵ_r) and can maintain stable energy storage characteristics at temperatures higher than 200°C [9–11]. At present, the research on energy storage dielectric ceramics focuses on four categories, i.e., linear dielectric (such as TiO₂ and SrTiO₃) [12, 13], normal ferroelectric (FE; such as K_{0.5}Nb_{0.5}O₃, BaTiO₃, and BiFeO₃) [14–16], relaxor ferroelectric (RFE; such as Na_{0.5}Bi_{0.5}TiO₃-based) [17–20], and antiferroelectric (AFE; such as PLZST, AgNbO₃, and NaNbO₃) ceramics [21–32]. FE ceramics have low W_{rec} and η because of high residual polarization (P_r). Linear dielectric ceramics often have low ϵ_r , causing a low W_{rec} . Because the breakdown field strength (E_b) of RFE ceramics is low, it has low W_{rec} . AFE ceramics have high maximum polarization (P_m) due to the existence of AFE–FE phase transition, resulting in high W_{rec} . However, its inherent AFE–FE phase transition causes large hysteresis loop, resulting in large energy loss. A high W_{rec} and η are difficult to obtain simultaneously in AFE ceramics, which has become a key problem restricting its energy storage application [24, 28, 33].

The lead-free AFE material in high-power capacitors is attracting a growing body of research because of its advantages of high energy and high power density. It has become one of the most popular and promising research directions. Compared with PLZST and AgNbO₃-based AFE ceramics, NaNbO₃ (NN)-based AFE ceramics have many advantages, such as nontoxicity, stable performance, and low cost [34–

36]. At room temperature (RT), NN exhibits AFE orthorhombic P phase, and it turns into AFE orthorhombic R phase at about 360°C [37]. However, the AFE P phase in undoped modified NaNbO₃-based ceramics is unstable and easily transformed into the orthorhombic FE phase, resulting in an irreversible AFE–FE phase transition and displaying a square P - E loop similar to that of FE materials [35, 36], thus decreasing its η . The two aspects in the current research on the modification of NaNbO₃-based AFE ceramics are as follows. 1) A stable AFE P phase can be obtained by doping BaZrO₃, CaZrO₃, CaSnO₃, and other perovskite structural materials [34–38], which can stabilize the AFE P phase under RT, realize reversible AFE–FE phase transition, and obtain typical AFE double-hysteresis loop (beam waist type). This phenomenon can improve the W_{rec} and η of materials, which are only 3 J cm⁻³ and 74%, respectively. 2) The stable antiferroelectric R phase under RT can be obtained by introducing 12 mol% Bi_{0.5}Na_{0.5}TiO₃ into NaNbO₃-based AFE phase, It has a thinner hysteresis loop than the antiferroelectric P phase can be obtained under RT. Thus a high W_{rec} of 12.2 J cm⁻³ and a acceptable η of 69% were achieved[38, 39].

Ta has been displayed to be a high-quality dopant in AgNbO₃ for improving the AFE phase stability [26–28]. For example, 15 mol.% Ta doping in AgNbO₃ can enhance E_b by nearly 23 kV mm⁻¹, thus obtaining a large recoverable energy storage density of 4.2 J cm⁻³ and increased η of 69%. Results show that the antiferroelectricity can be enhanced by replacing Nb with Ta due to decreased polarizability of B-site cations in distorted AFE configuration. In addition, the addition of Ta can increase the bulk density and reduce the grain size of AgNbO₃ ceramics, thus remarkably improving the E_b of materials [26]. However, research on Ta doping in NN-based system with stable AFE P phase is lacking. This finding is a good example to show that NN is different from other AFE perovskite systems in nature.

In this paper, a new type of lead-free 0.88Na(Nb_{1-x}Ta_x)O₃–0.12Sr_{0.7}Bi_{0.2}TiO₃ solid solution ceramics is fabricated using a traditional solid-state reaction technique. The relationships of structure with ferroelectric, dielectric and energy storage performance are systematically investigated. The phase transition from the AFE P phase to AFE R phase caused by Ta doping contributes to enhanced energy storage performance. As a result, a large W_{rec} of 2.16 J cm⁻³ and a high η of 80.7% under 15 kV mm⁻¹ are obtained in the 0.88Na(Nb_{0.925}Ta_{0.075})O₃–0.12Bi_{0.2}Sr_{0.7}TiO₃ (NN–BST–0.075Ta) sample. Notably, few reports on lead-free dielectrics can obtain a high η (> 80%) and large W_{rec} (> 2 J cm⁻³) simultaneously under 20 kV mm⁻¹. The NN–BST–0.075Ta sample has a remarkable promise in energy storage dielectric capacitors.

2. Experimental Procedure

A novel 0.88Na(Nb_{1-x}Ta_x)O₃–0.12Bi_{0.2}Sr_{0.7}TiO₃ (NN–BST– x Ta, x = 0, 0.025, 0.050, and 0.075) ceramics were fabricated by a conventional solid phase method by using Nb₂O₅ (> 99.5%), Na₂CO₃ (> 99.5%), Ta₂O₅ (> 99.9%), SrCO₃ (> 99.5%), Bi₂O₃ (> 99.5%), and TiO₂ (> 99.5%) powders. Dry raw powders were weighed using the stoichiometric ratio of NN–BST– x Ta and subjected to wet-milling for 36 h in a teflon jar with isopropanol. Dry mixed powders were calcined at 950°C for 2 h and remixed for 10 h to obtain

NN–BST– x Ta as-calcined powders. The refined powder was uniaxially pressed into disk-shaped samples with a thickness of about 1 mm and a diameter of 10 mm. The disk-shaped samples were sintered at 1160°C for 3 h in an air atmosphere to obtain high density. Discs were bedded in the same composition of as-calcined powders to resist the volatilization loss of sodium and bismuth. Sintered disk-shaped samples were ground and polished to obtain a thickness of 0.1 mm and measure the electrical performance. The silver electrode with diameter of 0.5 mm was coated in the middle of the polished disc surface by using the screen-printing method and heated at 550°C.

Field-emission scanning electron microscope (SEM) was used to examine the surface morphology of samples. The crystal structures of NN–BST– x Ta ceramic samples were performed through X-ray diffraction (XRD). The dielectric constant ε_r –temperature (T) and dielectric loss ($\tan \delta$)–temperature (T) curves were tested by an LCR meter at a heating speed of 120°C h⁻¹. Polarization (P)–electric field (E) curves were characterized using an ferroelectric tester under 10 Hz at various temperatures. All specimens were submerged in silicone oil to prevent surface flash over.

3. Results And Discussion

The XRD analysis of NN–BST– x Ta ceramics were presented Fig. 1(a). All the ceramics reveal perfect perovskite structure. No other impurities are contained. It was suggesting that Ta⁵⁺ are dissolved in the NN–BST ceramic lattice and form a uniform perovskite solid solution. The enlarged XRD diffraction patterns in the range of 31.5°–46.8° (Fig. 1(b)) further present variations in (110) and (200) reflection peaks. The (110) and (200) diffraction peaks are not split, which indicates that NN–BST– x Ta ceramics belong to the pseudo-cubic phase. As x increases from 0 to 0.075, the positions of (110) and (200) diffraction peaks remain unchanged, indicating that the lattice volume has not changed. This phenomenon occurs because the radii of Ta⁵⁺ (0.64 Å, CN = 6) and Nb⁵⁺ (0.64 Å, CN = 6) [26, 40].

The SEM images of NN–BST– x Ta ceramics were exhibited in Figs. 2(a)–(d). As can be seen from the figures, NN–BST– x Ta ceramics are sintered compactly. We used a linear interception method by Nano Measurer software to calculate the average grain size of NN–BST– x Ta. Results are displayed in Figs. 2(e)–2(h). The average grain sizes of NN–BST– x Ta are 1.95, 1.72, 1.63, and 1.34 µm at $x = 0, 0.025, 0.050$, and 0.075 , respectively. The average grain size decreases with the increase of Ta content, which is caused by the low ion mobility of Ta [26, 40]. NN–BST–0.075Ta ceramics have a dense microstructure and small grains that may be responsible for increasing W_{rec} and E_b .

Figure 3 shows the ε_r – T and $\tan \delta$ – T curves of NN–BST– x Ta ceramics at 1, 10, 100, and 1000 kHz frequencies. The dielectric peaks of $x = 0$ and 0.025 components are evident at 160°C, corresponding to the antiferroelectric P to R phase transition temperature ($T_{\text{P-R}}$). In addition, at $x = 0$ – 0.05 , ε_r at RT increases significantly and decreases with further increase in x . It can be noted that the P-R phase transition peak for $x = 0.05$ sample. However, the ε_r at RT is higher than that for samples with $x = 0$ and 0.025 , which shows that the ε_r of $x = 0.05$ sample is affected by the antiferroelectric R phase. In addition,

due to the thermal hysteresis of antiferroelectric P–R phase transition during heating, antiferroelectric P phases are few. When $x = 0.075$, the the large ε_r at RT and disappearing dielectric peak T_{P-R} at RT indicate that the sample should consist of the antiferroelectric R phase. Thw similar result has been found in other NN-based relaxor AFEs [25, 29, 41–43].

Figure 4(a) shows the dielectric performance of undoped NN–BST– x Ta ceramics at the temperature range of -170°C to 100°C . NN–BST–0.075Ta has evident dielectric dispersion and small frequency shift at high temperature. Thus, NN–BST–0.075Ta ceramics has class relaxor characteristics. This relaxor behavior is associated with the different polarizability of perovskite B-site ions. The polarizability of Nb^{5+} ($3.10 \text{ \AA}^3$) is higher than that of Ta^{5+} ($2.82 \text{ \AA}^3$). This phenomenon leads to disordered B-site and random electric field. Therefore, the long-distance driving dipoles are weakened [25, 29]. The ε_r and $\tan \delta$ as functions of frequency are shown in Fig. 4(b). The ε_r and $\tan \delta$ almost remain at the same level at testing frequencies. The dielectric performance shows outstanding frequency stability and is beneficial to the practical application of pulse power transistor. These results are related to the large P and high E_b [44–48].

The unipolar curves of P – E tested under different electric fields under 10 Hz for NN–BST– x Ta ceramics are displayed in Fig. 4. Figures 5(a) and (b) present that $x = 0$ and 0.025 samples have stable antiferroelectricity. P_m increases when the E is more than 12 kV mm^{-1} , indicating that evident AFE–FE phase transition occurs. For $0.025 < x \leq 0.075$ samples, increasing Ta content gradually results in slender P curve. P properties show stable relaxor characteristics, resulting in increased E_b (Figs. 5(c)–5(d)). This result is because the polarizability of Ta^{5+} is lower than that of Nb^{5+} , which leads to decreased sensitivity of B-site cations to the E [26]. In addition, P_m increases with increasing of E , and the E of the AFE–FE phase transition is getting blurry. Above results are consistent with the dielectric performance.

Figures 6(a)–(c) compare the curves of P – E , P_r , P_m , and energy storage properties of NN–BST– x Ta ceramic samples at a low E (15 kV mm^{-1}). NN–BST–0.025Ta and NN–BST have relatively stable antiferroelectric properties and large P_r (25.2 and $19.9 \text{ \mu C cm}^{-2}$, respectively) and P_m (53.4 and $44.1 \text{ \mu C cm}^{-2}$, respectively). With increasing Ta content, P_m decreases gradually, and P_r decreases rapidly. Zhang *et al.* [37] studied the NN– $x\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ (NN– x BNT) system and observed similar results. BNT (24 mol.%) is dissolved in NN, and a kind of antiferroelectric material with relaxor characteristics is obtained. In addition, larger nanodomains (30–50 nm) than PNAs are observed in the material. As mentioned previously, the dopant of the perovskite B-site by Ta results in a local random field, weakening the long-range driving dipole and enhancing the dielectric relaxation. Despite the decreases in P_m , W_{rec} increases when $0.025 \leq x \leq 0.075$ due to the P – E curve becomes slender and long, thereby broadening the integral area and increasing W_{rec} . Such changes in P – E curves caused by the transition from the antiferroelectric P phase to antiferroelectric R phase are helpful to improve the energy storage performance [49–52]. Subsequently, the W_{rec} and η of NN–BST– x Ta ceramics are compared with several representative lead-free ceramics for energy storage reported recently at low E (Fig. 6(d)) [15, 16, 26, 38, 41–43]. Interestingly,

NN–BST–0.075Ta ceramics show a large W_{rec} of 2.16 J cm^{-3} and high η of 80.7% at 15 kV mm^{-1} , which are larger than those of other lead-free ceramics at a relatively low electric field.

Considering its practical application, temperature dependence is one of the important indices in the design of dielectric capacitor. Figure 7 displays the (a) unipolar P – E curves, (b) W_{rec} and η of NN–BST–0.075Ta ceramics as a function of temperature under 15 kV mm^{-1} . The unipolar P – E curve displays an excellent temperature stability, which may be due to the stable R phase coexisting in NN–BST–0.075Ta over a wide range of temperature, as displayed in Fig. 7(a). The W_{rec} and η vary from 1.98 J cm^{-3} and 80.7%, respectively, to 2.2 J cm^{-3} and 85.8%, respectively, at 25°C – 125°C (Fig. 7(b)). The variations in W_{rec} and η are less than 11.1% and 6.3%, respectively. The good temperature stability of NN–BST–0.075Ta indicates its potential as lead-free relaxor AFE material for use in temperature-stable pulse capacitor.

4. Conclusion

A novel Ta-doped NN–BST dielectric ceramics with a pure perovskite phase is successfully synthesized by a traditional solid state reaction route. The effect of Ta^{5+} in the perovskite B-site increases the relaxation of the material, thus improving E_b and decreasing P_r . Dielectric and ferroelectric performances reveal that the NN–BST–0.075Ta ceramics belong to relaxor AFEs. Therefore, a large recoverable W_{rec} of 2.16 J cm^{-3} and η of 80.7% at a low electric field of 15 kV mm^{-1} are achieved in NN–BST–0.075Ta ceramics due to improved relaxation property. NN–BST–0.075Ta ceramics also exhibit excellent energy storage temperature stability. These excellent properties in NN–BST–0.075Ta relaxor AFE ceramics indicate its potential as a candidate in future dielectric capacitors.

Declarations

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Figures

Figure 1

(a) XRD image of NN–BST–xTa ceramics.

Figure 2

SEM images and average grain sizes of NN-BST-xTa ceramics: (a)-(e) $x = 0$, (b)-(f) $x = 0.025$, (c)-(g) $x = 0.050$, and (d)-(h) $x = 0.075$.

Figure 3

The dielectric constant (ϵ_r)-temperature (T) and loss ($\tan \delta$)-temperature (T) curves of NN-BST- x Ta ceramics at the temperature range of 25 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$: (a) $x = 0$, (b) $x = 0.025$, (c) $x = 0.050$, and (d) $x = 0.075$. (e)-(f) Room-temperature ϵ_r of NN-BST- x Ta ceramics with various Ta contents measured at 10 Hz.

Figure 4

(a) The dielectric constant (ϵ_r)-temperature (T) and loss ($\tan \delta$)-temperature (T) curves of NN-BST-0.075Ta ceramics at the temperature range of -170 $^{\circ}\text{C}$ to 100 $^{\circ}\text{C}$. (b) ϵ_r and $\tan \delta$ of NN-BST-0.075Ta ceramics as a function of frequency.

Figure 5

Unipolar P-E curves under different electric fields of NN-BST-xTa samples: (a) $x = 0$, (b) $x = 0.025$, (c) $x = 0.050$, and (d) $x = 0.075$.

Figure 6

(a) Unipolar P-E curves, (b) P_{m} , P_{r} , (c) W_{rec} , and η of NN-BST- x Ta ceramics Under different components tested under 15 kV mm⁻¹ at 10 Hz. (d) Comparison of W_{rec} and η between NN-BST-0.075Ta ceramics and some recently reported lead-free dielectrics under low electric fields.

Figure 7

(a) Unipolar P–E curves and (b) corresponding energy storage performance of NN–BST–0.075Ta ceramics at different temperatures under 15 kV mm^{-1} .