

钛酸铋钠基弛豫铁电陶瓷的介电和储能性能

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摘 要: 通过钛酸钡(BaTiO_3 , BT)掺杂改性的钛酸铋钠($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, NBT)基陶瓷体系(NBT-BT)在钙钛矿型铁电材料中表现出优异的介电性能优化特性, 这一特性使其在介电电容器、压电换能器及高密度储能器件等先进电子元器件领域展现出重要的应用价值。然而, 较差的介电温度稳定性限制了其在高温下的应用。本工作采用固相反应法合成了 $(1-x)(0.75\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.25\text{BaTiO}_3)-x\text{BaZrO}_3$ (NBT-BT- $x\text{BZ}$, $x=0, 0.08, 0.14, 0.20$)陶瓷, 研究了固溶 BaZrO_3 (BZ)对结构、介电和储能性能的影响。结果表明, 随着 BZ 含量的增加, 结构从四方相转变为立方相, 在所有成分中都有 1 个宽的介电峰, 这是弥散相变的特征。利用修正的 Curie-Weiss 定律、Vogel-Fulcher 关系和 Lorentz 经验定律分析了相变和弛豫行为, 发现固溶 BZ 显著提高了介电性能的温度稳定性, 并增强了弛豫行为。此外, 放电测量表明, 固溶 BZ 后, 由于其增强的介电常数和弛豫特性, 放电能量密度显著提高, 达到 $1.6 \text{ J}\cdot\text{cm}^{-3}$, 功率密度显著提高到 $52.2 \text{ MW}\cdot\text{cm}^{-3}$ 。上述发现突显了 BZ 固溶 NBT-BT 陶瓷体系在高温介电器件中的潜在应用价值。

关键词: 钛酸铋钠; 储能性能; 弛豫行为; 介电; Vogel-Fulcher 关系

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Introduction

Relaxor ferroelectrics are characterized by high dielectric constants, diffuse phase transitions, and frequency-dependent behavior, thus having some applications in sensors, memory devices, and energy storage system^[1-3]. The dielectric properties of these materials in the phase transition region exhibit a frequency dispersion, which are extensively investigated to clarify the underlying relaxation mechanism^[4-6]. Despite significant progress, the correlation between the physical properties and phase structure of relaxor ferroelectrics remains a challenge.

Among lead-free relaxor ferroelectrics, sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, NBT) has attracted much attention due to its unique crystal structure and

relaxor ferroelectric behavior. The NBT crystallizes in a perovskite (ABO_3) structure, where Na^+ and Bi^{3+} ions randomly occupy the A-site and Ti^{4+} ions occupy the B-site. The relaxor behavior of NBT is attributed to the cationic disorder and the formation of nonpolar nanoregion^[7-9]. Also, the charge inhomogeneity caused by cation disorder is compensated due to the generation of vacancies (*i.e.*, oxygen vacancies form in Na-rich regions), while A-site vacancies aggregate in Bi-rich regions^[7-9]. NBT-based relaxor ferroelectric ceramics show high dielectric constant and polarization, making them suitable for applications in dielectric capacitors, electrostatic energy storage devices, and high-temperature piezoelectric system.

Pure NBT exhibits a frequency-dependent Curie temperature, indicating that its dielectric properties are

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affected by temperature, measurement frequency, and material processing condition. To enhance the dielectric and relaxor properties of NBT, various dopants such as Sr^[10–11], K^[12–13], Li^[14–15] and Bi^[16–17] are incorporated into the NBT structure. These modifications significantly alter the dielectric constant and relaxation behavior, demonstrating the dominant influence of dopants on the material properties^[18]. Among these, the solid solution of BaTiO₃ (BT) with NBT is widely investigated due to its ability to stabilize the perovskite structure and improve dielectric performance. However, the temperature-dependent stability of dielectric properties remains a critical challenge for high-temperature applications.

In this study, (1- x)(0.75Na_{0.5}Bi_{0.5}TiO₃-0.25BaTiO₃)- x BaZrO₃ (NBT-BT- x BZ, x = 0, 0.08, 0.14, and 0.20) ceramics were prepared by a solid-state reaction method. The effect of BaZrO₃ (BZ) addition on the structural, dielectric, and energy storage properties was systematically investigated. In addition, the phase transition and relaxation behavior were also analyzed based on the modified Curie-Weiss law, Vogel-Fulcher relation, and Lorentz-type empirical law.

1 Experimental

1.1 Materials and procedure

(1- x)(0.75Na_{0.5}Bi_{0.5}TiO₃-0.25BaTiO₃)- x BaZrO₃ (x = 0, 0.08, 0.14, 0.20) ceramics (referred to as (1- x)(NBT-BT)- x BZ) were synthesized by a solid phase reaction method (referred to as NBT, NBT-0.08BZ, NBT-0.14BZ, NBT-0.20BZ). The starting materials were powders of high purity Na₂CO₃ (99.8%), Bi₂O₃ (99.9%), TiO₂ (98%), BaCO₃ (99%), and ZrO₂ (99.99%). The powders were weighed according to a stoichiometric ratio (with 1% excess of Na and Bi) and ground with ethanol in a ball mill at 300 r/min for more than 12 h. The weight ratio of raw material to ethanol and zirconium balls was 1:1:2. The dried material was heated at 850 °C for 2 h to promote the formation of NBT-BT-BZ. After further grinding for 12 h, the samples were mixed with a small amount of polyvinyl alcohol (PVA). The samples were then pressed by a uniaxial pressure system to form the samples with the thickness of 1 mm and the diameter of 10 mm. The samples were sintered in air at 1150 °C for 2 h and cooled to room temperature.

1.2 Characterizations

The phase composition of the ceramic samples was determined by a model D8 ADVANCE X-ray diffractometer (XRD, Bruker AXS Ltd., Germany) with Cu target K_{α} rays at X-ray wavelength λ of 1.540 6 Å, 2θ in the range of 10° to 80°, applied voltage of 40 kV, and a current of 500 mA. A silver paste was coated on the two surfaces as electrodes and heat-treated at 700 °C for 10 min. The dielectric properties of the ceramic samples were performed at different frequencies by a model DMS-1000 high-temperature dielectric temperature spectroscopy (BALAB Tech. Co., China) at a ramp rate of 3(°)/min in a temperature range from room temperature to 450 °C. The overdamped (200 Ω) discharge tests for bulk ceramic samples were performed by a model CFD-005 discharge tester (Gogo (GG) Instruments Technology, China).

2 Results and discussions

Figure 1 shows the XRD patterns and SEM images of NBT-BT-BZ ceramic samples. In Fig. 1(a), all the ceramic samples have a perovskite structure without any detectable secondary phase, indicating that zirconium ions can completely enter the lattice and form a solid solution. Based on the locally magnified XRD peaks, the XRD peak shape shifts towards lower angles as a whole as the BZ content increases. This indicates that the overall volume of the crystal cell shows an expansion as Zr ions replace Ti ions, which is related to the ionic radii of Zr and Ti ions. According to the Shannon ion radius data, the radius of Zr ion (*i.e.*, 0.72 Å) is larger than that of Ti ion (*i.e.*, 0.61 Å)^[19]. Therefore, the volume of the crystal cell expands and the XRD peak shifts towards lower angles as the substitution content increases. In addition, the sample with NBT-BT x of 0 shows a tetragonal structure, as evidenced by the apparently double peaks features, such as the two peaks (002)/(200) as $2\theta=45^\circ$. The bifurcation of the two peaks (002)/(200) gradually disappears with increasing the BZ content (see Fig. 1(a),) and the two peaks are merged into a single one, indicating a phase transition from a tetragonal phase to a pseudocubic phase. The SEM images in Fig. 1(c) show that the grain size gradually increases with increasing the BZ content. This indicates that the addition of BZ promotes the grain growth. However, such an increase of

the grain size gradually slows down with the increase of content up to x of 0.20. The limited grain size variation

occurs in the latter two samples. All the samples show a relatively dense morphology.

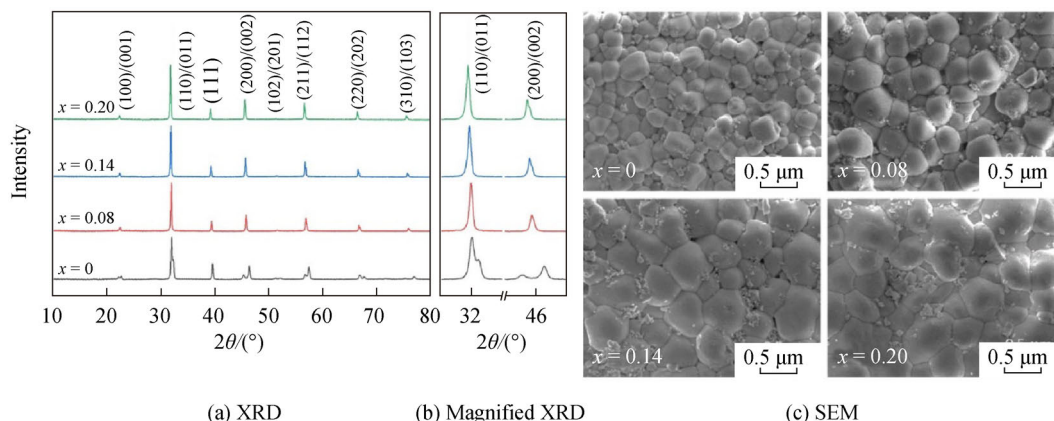


Fig. 1 XRD patterns, locally magnified peaks, and SEM images of NBT–BT– x BZ ($x = 0$ –0.20) ceramics

Fig. 2 shows the temperature dependence of dielectric constant and loss at 100 kHz for NBT–BT–BZ ceramics, the room-temperature dielectric constant (ϵ_0) and dielectric stability as a function of composition x and the temperature-dependent dielectric properties at different frequencies, respectively. In Fig. 2(a), there is only one peak at all the doping concentrations as the temperature increases, corresponding to the transition from a ferroelectric phase to a paraelectric phase. In general, there are two dielectric anomalies in the dielectric temperature spectrum of NBT-based ceramics. The first dielectric anomaly is caused by a phase transition from the ferroelectric phase to the so-called “intermediate phase”^[20]. The second dielectric anomaly corresponding to the maximum value of ϵ_r is located at the Curie temperature (T_m), *i.e.*, it is related to the phase transition between the so-called “intermediate phase” and the paraelectric phase. The dielectric constant ϵ_r decreases with a further increase in temperature, after the temperature exceeds T_m ^[21]. However, the first dielectric anomaly depends on the polarization history and composition of the material. For NBT–0.25BT ceramic sample with x of 0, it is not pooled before dielectric measurement. It is previously reported that the phase transition sequence of BNT– y BT samples with $y < 0.15$ comply with rhombohedral-intermediate phase-cubic, while transforming from tetragonal to cubic directly with the BT content of greater than 0.15. There is no first dielectric anomaly in dielectric temperature spectrum in the NBT–0.25BT ceramic sample. This result is also consistent with the

phase diagram proposed by Picht et al^[22].

In Fig. 2(b), the dielectric constant increases with increasing the BZ content at room temperature, showing the room temperature dielectric constant ϵ_0 , which may be caused by the introduction of Zr ions at the B-site, making it difficult for the ceramic sample to undergo a spontaneous polarization^[23]. During the heating process, only one peak appears, which corresponds to a phase transition from a ferroelectric phase to a paraelectric phase. The Curie temperature of the NBT–0.25BT ceramic samples is 256 °C, which is similar to the reported result^[18]. The Curie temperature decreases gradually with the increase of BZ additive, and the dielectric temperature spectrum flattens out, indicating the enhanced structural and temperature stability of the NBT–BT–BZ ceramics. Fig. 2(b) also shows this effect more intuitively in terms of the rate of change of the permittivity $(\epsilon_m - \epsilon_0)/\epsilon_0$, where ϵ_m corresponds to dielectric constant at T_m . Compared with the nine-fold change of NBT–BT, the change rate of BZ-modified ceramics quickly decreases to about one time or even lower. These can be attributed to the introduction of Zr^{4+} can affect the long-range order of ferroelectrics, leading to an increase in a lattice disorder^[24–25]. The dielectric loss of NBT–BT–BZ ceramic is greater than that of NBT–BT at < 150 °C due to the broadening of the dielectric peak and its shift towards the low-temperature region. However, the peak dielectric loss after solid solution is larger than that before solid solution possibly due to a relaxation caused by solid solution.

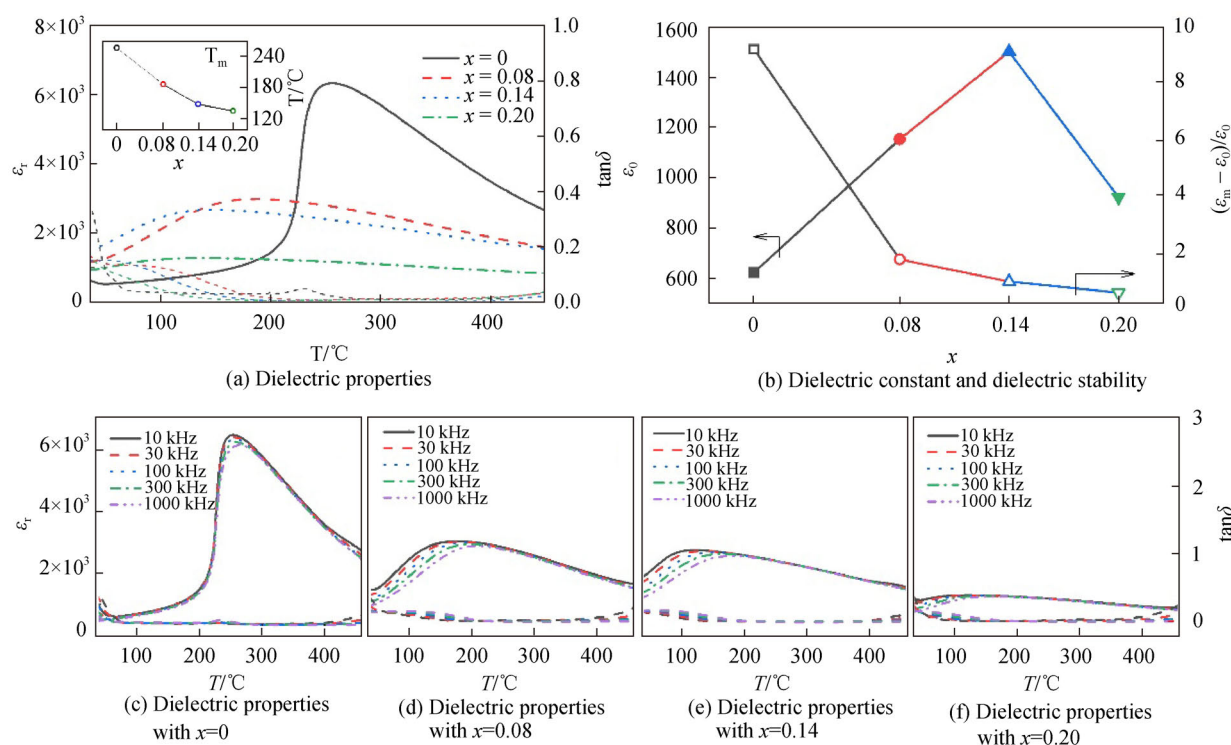


Fig. 2 Temperature dependence of dielectric constant and loss for NBT-BT-BZ ceramics

Fig. 2(c) shows the temperature dependence of the dielectric constant and dielectric loss of all the ceramic samples containing BZ additives at different frequencies. Clearly, the maximum values of all dielectric constants correspond to temperatures that increase with frequency, indicating a dielectric relaxor behavior. A frequency dispersion is accompanied at near the Curie temperature, which can be ascribed to the thermal evolution of the tetragonal polar nanoregions (PNRs) and the mixing effect of the transition from tripartite to tetragonal PNRs^[26]. Besides, the Curie temperature shifts towards lower temperatures with increasing the doping concentration due to the substitution of BZ that can enhance the stochastic localized field, leading to a gradual increase in the dynamics of the PNRs and thus a decrease in the PNRs' size^[27]. The characteristic double dielectric anomalies are commonly observed in NBT-based ceramics, and the dielectric temperature spectrum only exhibits a single-peak. The reason for the dielectric single peak is speculated as follows, there is no polarization, so there will be no depolarization characteristic peak. Furthermore, the possible ferroelectric-relaxor transition temperature depends on the composition and microstructure, either below room

temperature or merging with the Curie temperature to form a characteristic peak^[11,28].

For relaxor ferroelectrics, in order to further investigate the peak dielectric constant and the extent of diffusion of the phase transition, the modified Curie-Weiss law is usually used by

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad (1)$$

where ε_m is the maximum value of the dielectric constant at the transition temperature, C is the Curie constant, γ denotes the degree of dielectric relaxation, and its value varies from 1 to 2. A value of 1 indicates that the ceramics is a typical ferroelectric, and a value of 2 indicates that the ceramics is a fully relaxor ferroelectric. Fig. 3(a) shows the linear relationship between $\lg(1/\varepsilon - 1/\varepsilon_m)$ and $\lg(T - T_m)$. The values of γ for the corresponding components can be obtained from Fig. 3(a), indicating that the Curie-Weiss law can be well fitted to the dielectric constants, and the linear relationship is obtained for all the ceramics. The γ values obtained from the experimental data at 100 kHz are 1.79, 1.83, 1.89, and 1.92 for NBT-BT, NBT-BT-0.08BZ, NBT-BT-0.14BZ, and NBT-BT-0.20BZ, respectively. The γ value increases gradually with the addition of the

BZ contents, which indicates an enhanced relaxation of NBT–BT–BZ ceramics. The stronger relaxation of NBT–BT–BZ ceramics is related to the local consequent electric field variation mainly because of the local

compositional disorder. Also, some localized stresses weaken a long-range ordering of the ferroelectric, thus creating some weakly coupled polar regions, transforming the ceramics into strongly relaxor ferroelectrics^[29].

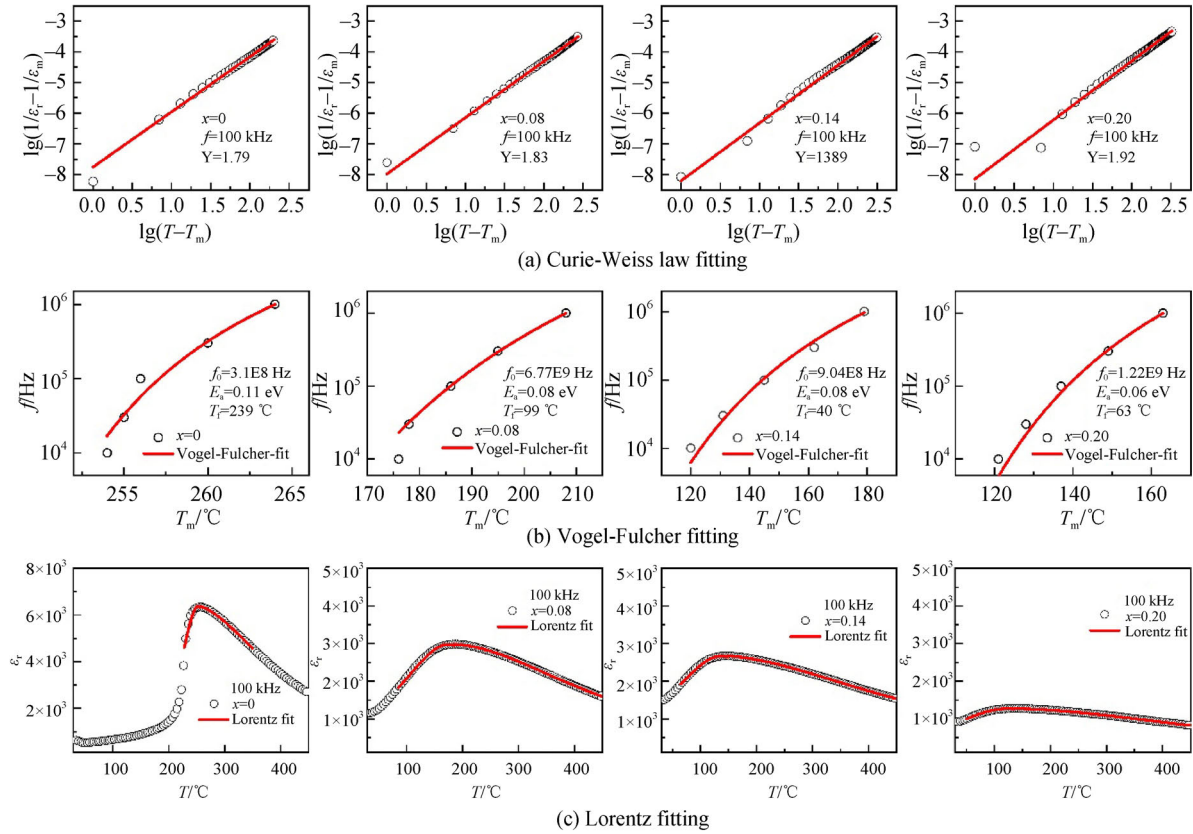


Fig. 3 Modified Curie-Weiss, Vogel-Fulcher and Lorentz-type fitting of NBT–BT–xBZ ($x = 0\text{--}0.20$) ceramics

To analyze the dielectric relaxation properties of relaxor ferroelectrics, the Vogel-Fulcher (V-F) relation is quoted according to the polarization flip-flop frequency, f , which is related to the activation energy, E_a ,

$$f = f_0 \exp \frac{-E_a}{k(T_m - T_f)} \quad (2)$$

where f is the measured frequency, f_0 is the pre-exponential factor (attempt frequency), which means the reciprocal of the minimum relaxation time, E_a is the activation energy, and T_f is the freezing temperature at which the relaxation time spectrum becomes an infinitely wide. Fig. 3(b) shows the V-F fitting of T_m for NBT–BT–BZ ceramics at a frequency of 100 kHz. As is shown, Eq. (2) agrees well with the experimental data for NBT–BT–BZ ceramics. The activation energies of all the ceramics obtained from the fit of x 0, 0.08, 0.14, and 0.20

are 0.11, 0.08, 0.08 eV and 0.06 eV, respectively. It is well known that the dielectric relaxation can be caused by the disorder of nanoscale ions. Therefore, the smaller the activation energy is, the stronger the dispersion will be, which can be used to describe the effect of Zr-containing ions on the dielectric relaxation behavior of NBT–BT–BZ ceramics. The results show that the relaxation of NBT–BT–BZ ceramics increases with the increase of BZ contents. The result obtained from the Vogel-Fulcher fitting is similar to that from the Curie-Weiss law. Therefore, the empirical laws such as the Curie-Weiss law and the Vogel-Fulcher relation can well describe a dielectric relaxation behavior of NBT–BT ceramics with added BZ components.

Lorentz-type empirical relations can be used to express the dielectric constants of relaxor ferroelectrics on both the high and low temperature sides,^[30]

$$\frac{\varepsilon_a}{\varepsilon} = 1 + \frac{(T - T_a)^2}{2\delta_a^2} \quad (3)$$

where T_a ($T_a \neq T_m$), ε_a , and δ_a are parameters, δ_a is frequency independent at sufficiently high frequencies, and it responds to the diffusivity of the dielectric peaks. Fig. 3(c) shows the temperature dependence of dielectric constant at 100 kHz of NBT–BT–xBZ (*i.e.*, $x = 0-0.20$) ceramics fitting by the Lorentz-type law (see Eq. 3). Clearly, the temperature dependence of the dielectric constant on both the low and high temperature sides can be well fitted by a Lorentz-type relationship within a certain temperature interval. Table 1 shows the best fitting parameters. Clearly, there is a large difference in

the parameter δ_a at different temperature ranges ($T < T_m$ and $T > T_m$). This indicates that there are two polarization processes in the material, *i.e.*, in the high temperature region and the low temperature region. However, in both $T < T_m$ and $T > T_m$ regions, the material diffusivity increases with the increase of BZ components. The concentration of oxygen vacancies in BZ-modified NBT–BT ceramics decreases with the increase of Zr contents, possibly leading to a decrease in the degree of diffusion. The Zr substitution induces chemical and structural inhomogeneity and leads to a structural short-range disorder, which is responsible for the increase in the degree of diffusion. This is consistent with the Curie-Weiss fitting results.

Table 1 Curve fitting results by Eq. (3) for NBT–BT ceramics with BZ additives

x	f/kHz	$T_m/^\circ\text{C}$	ε_m	$T_d/^\circ\text{C}$		ε_a		δ_a	
				$T < T_m$	$T > T_m$	$T < T_m$	$T > T_m$	$T < T_m$	$T > T_m$
0	100	256	6340	252	237	6380	6452	28	124
0.08	100	186	2980	175	173	2927	2988	80	208
0.14	100	148	2672	137	115	2668	2695	82	271
0.20	100	137	1269	123	112	1269	1276	99	322

For the enhanced dielectric constant and relaxor properties, a high energy density is desired. The energy storage density of dielectric capacitors can be calculated from hysteresis loops or measured from over damped pulse discharges. Gao *et al.* compared the energy storage densities obtained by these two methods and they found that the former could have higher values^[31]. However, the energy density obtained during the pulse discharge process is more reasonable and reliable rather than that obtained through hysteresis loops since the pulse discharge process is closer to the practical application of

dielectric capacitors. Fig. 4 shows the overdamped ($R = 200 \Omega$) discharge current curves and energy density of NBT–BT–xBZ ($x = 0-0.20$) ceramics as well as the comparison of W_d and P_d of all the ceramics. In Figs. 4(a) and 4(b), the addition of BZ significantly improves the discharge current and energy storage performance^[32]. In Fig. 4(c), a high discharging energy density (W_d) of $1.6 \text{ J}\cdot\text{cm}^{-3}$ with a fast discharging speed ($\tau_{0.9}$) of 75 ns is obtained for the ceramic samples with x of 0.14. This can be attributed to an increased relaxation as the BZ content increases. In addition, a high-power density of $52.2 \text{ MW}\cdot\text{cm}^{-3}$

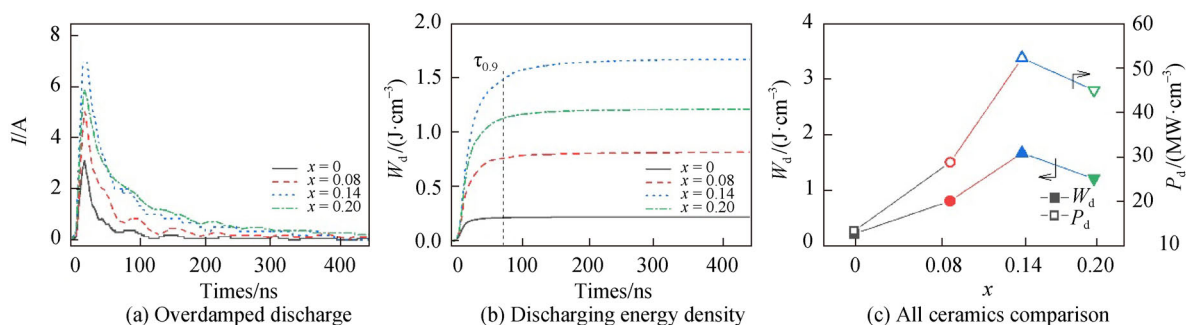


Fig. 4 Overdamped ($R = 200 \Omega$) discharge current curves and energy density of NBT–BT–xBZ ($x = 0-0.20$) ceramics, as well as Comparison of W_d and P_d of all the ceramics

is also obtained for the ceramic sample with x of 0.14 (see Fig. 4 (c)). For the ceramic sample with x of 0.20, although the relaxation is enhanced, the energy storage density is relatively reduced due to the significant reduction of the dielectric constant^[33]. The dielectric constant is generally proportional to the grain size, and the ceramic room temperature dielectric constant gradually increases from 621 as $x = 0$ to 1153 as $x = 0.08$, and then to 1501 as $x = 0.14$ as the BZ content increases. As the content further increases to x of 0.20, the dielectric constant decreases to 921. This is due to no significant increase in grain size and an increase in BZ content without polarization properties, thus decreasing the energy storage density.

3 Conclusions

NBT–BT–BZ ceramics were prepared by a solid-state reaction method. The XRD patterns revealed that a phase transition from a tetragonal phase to a pseudocubic phase occurred as the BZ content increased. The dielectric relaxation behavior of the ceramics could be described by three empirical laws (*i.e.*, modified Curie-Weiss law, Vogel-Fulcher relation and Lorentz-type empirical law). The dielectric relaxation followed the modified Curie-Weiss law and the Vogel-Fulcher relationship. The parameters γ and E_a , which were obtained to evaluate the relaxation behavior, increased at a higher BZ content. Also, the Lorentz-type relationship effectively described the temperature dependence of the dielectric constant on both the low- and high-temperature sides within a specific temperature range for all the ceramics. As a result, the NBT–BT–BZ ceramics exhibited more stable dielectric properties, demonstrating a promising potential for applications in dielectric energy storage.

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Dielectric and Energy Storage Performances of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -Based Relaxor Ferroelectric Ceramics

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Extended Abstract

Introduction Pure NBT exhibits the frequency-dependent Curie temperature, indicating that its dielectric properties are affected by temperature, measurement frequency, and material processing condition. To enhance the dielectric and relaxor properties of NBT, various dopants such as Sr, K, Li and Bi are incorporated into the NBT structure. These modifications significantly alter the dielectric constant and relaxation behavior, demonstrating a dominant influence of dopant on the material properties. Among these, the solid solution of BaTiO_3 (BT) with NBT is widely investigated due to its ability to stabilize the perovskite structure and improve dielectric performance. However, the temperature-dependent stability of dielectric properties remains a critical challenge for high-temperature applications.

In this study, $(1-x)(0.75\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.25\text{BaTiO}_3)-x\text{BaZrO}_3$ (NBT–BT–xBZ, $x = 0, 0.08, 0.14$, and 0.20) ceramics were prepared by a solid-state reaction method. The effect of BaZrO_3 (BZ) addition on the structural, dielectric, and energy storage properties was systematically investigated. In addition, the phase transition and relaxation behaviors were also analyzed based on the modified Curie-Weiss law, Vogel-Fulcher relation, and Lorentz-type empirical law.

Methods The starting materials were powders of high purity Na_2CO_3 , Bi_2O_3 , TiO_2 , BaCO_3 , and ZrO_2 . The powders were weighed according to a stoichiometric ratio (with 1% excess of Na and Bi) and ground with ethanol in a ball mill at 300 r/min for more than 12 h, and the weight ratio of raw material to ethanol and zirconium balls was 1:1:2. The dried material was heat-treated at 850°C for 2 h to promote the formation of NBT–BT–BZ. After further grinding for 12 h, the samples were mixed with a small amount of polyvinyl alcohol (PVA). The samples were sintered in air at 1150°C for 2 h and cooled to room temperature.

The phase composition of the ceramic samples was determined by an model D8 ADVANCE X-ray diffractometer (D8 ADVANCE XRD, Bruker AXS Ltd., Germany) with Cu target $\text{K}\alpha$ rays, at X-ray wavelength λ of $1.5406\text{ \AA}$, 2θ in the range of 10° to 80° , applied voltage of 40 kV, and a current of 500 mA. A silver paste was coated on the two surfaces as electrodes and heat-treated at 700°C for 10 min. The dielectric properties of the ceramic samples were determined at different frequencies by a model DMS-1000 high-temperature dielectric temperature spectroscopy (BALAB Tech. Co., China) with at a ramp rate of $3^\circ/\text{min}$ in a temperature range from room temperature to 450°C . The overdamped ($200\text{ }\Omega$) discharge tests for bulk ceramic samples were performed by a model CFD-005 discharge tester (Gogo (GG) Instruments Technology, China).

Results and discussion The XRD patterns indicate that all the ceramic samples have a perovskite structure without any detectable

secondary phase, proving that zirconium ions can completely enter the lattice and form a solid solution. Based on the locally magnified XRD peaks, the XRD peak shape shifts towards lower angles as a whole as the BZ content increases. This indicates that the overall volume of the crystal cell shows an expansion as the Zr ions replace Ti ions due to different ionic radii of Zr and Ti ions. The SEM images show that the grain size gradually increases with increasing the BZ content. The addition of BZ promotes the grain growth. However, this gradually slows down with the increase of content up to x of 0.20. The limited grain size variation appears in the latter two samples. All the samples show a relatively dense morphology.

The Curie temperature of the NBT–0.25BT ceramic samples is 256 °C, which is similar to the reported results. The Curie temperature decreases gradually with the increase of BZ additive, and the dielectric temperature spectrum flattens out, indicating that the enhanced structural and temperature stability of the NBT–BT–BZ ceramics. The maximum values of all dielectric constants correspond to temperatures that increase with frequency, indicating a dielectric relaxor behavior. A frequency dispersion is accompanied at near the Curie temperature, which can be ascribed to the thermal evolution of the tetragonal polar nanoregions (PNRs) and the mixing effect of the transition from tripartite to tetragonal PNRs.

The γ values obtained from the experimental data at 100 kHz are 1.79, 1.83, 1.89, and 1.92 for NBT–BT, NBT–BT–0.08BZ, NBT–BT–0.14BZ, and NBT–BT–0.20BZ, respectively. The γ value increases gradually with the addition of the BZ content, showing an enhanced relaxation of the NBT–BT–BZ ceramics. The comparison of discharge current curves and energy density of all the ceramics indicate that the addition of BZ significantly improves the discharge current and energy storage performance. A high discharging energy density (W_d) of 1.6 J·cm⁻³ with a fast discharging speed ($\tau_{0.9}$) of 75 ns is obtained for the ceramic samples with x of 0.14. This can be attributed to an increased relaxation as the BZ content increases.

Conclusions NBT–BT–BZ ceramics were prepared by a solid-state reaction method. The XRD patterns revealed a phase transition from a tetragonal phase to a pseudocubic phase as the BZ content increased. The dielectric relaxation behavior of the ceramics could be described by three empirical laws (*i.e.*, modified Curie-Weiss law, Vogel-Fulcher relation and Lorentz-type empirical law). The dielectric relaxation followed the modified Curie-Weiss law and the Vogel-Fulcher relationship. The parameters γ and E_a , which were obtained to evaluate the relaxation behavior, increased at a higher BZ content. The Lorentz-type relationship effectively described the temperature dependence of the dielectric constant on both the low- and high-temperature sides within a specific temperature range for all the ceramics.

Keywords bismuth sodium titanate; energy storage properties; relaxation behavior; dielectric; Vogel-Fulcher relation