2020

Energy storage properties of 0.87BaTiO3-0.13Bi(Zn2/3(Nb0.85Ta0.15)1/3)O3 multilayer ceramic capacitors with thin dielectric layers

Hongxian WANG
State Key Lab of New Ceramic and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Peiyao ZHAO
State Key Lab of New Ceramic and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Lingling CHEN
State Key Lab of New Ceramic and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Longtu LI
State Key Lab of New Ceramic and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Xiaohui WANG
State Key Lab of New Ceramic and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Follow this and additional works at: https://dc.tsinghuajournals.com/journal-of-advanced-ceramics

Recommended Citation
Hongxian WANG, Peiyao ZHAO, Lingling CHEN et al. Energy storage properties of 0.87BaTiO3-0.13Bi(Zn2/3(Nb0.85Ta0.15)1/3)O3 multilayer ceramic capacitors with thin dielectric layers. Journal of Advanced Ceramics 2020, 9(3): 292-302.

This Research Article is brought to you for free and open access by Tsinghua University Press: Journals Publishing. It has been accepted for inclusion in Journal of Advanced Ceramics by an authorized editor of Tsinghua University Press: Journals Publishing.
Energy storage properties of 0.87BaTiO$_3$–0.13Bi(Zn$_{2/3}$(Nb$_{0.85}$Ta$_{0.15}$)$_{1/3}$)O$_3$ multilayer ceramic capacitors with thin dielectric layers

Hongxian WANG, Peiyao ZHAO, Lingling CHEN, Longtu LI, Xiaohui WANG*

State Key Lab of New Ceramic and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Received: October 5, 2019; Revised: February 2, 2020; Accepted: February 12, 2020

© The Author(s) 2020.

Abstract: Multilayer ceramic capacitors (MLCCs) for energy storage applications require a large discharge energy density and high discharge/charge efficiency under high electric fields. Here, 0.87BaTiO$_3$–0.13Bi(Zn$_{2/3}$(Nb$_{0.85}$Ta$_{0.15}$)$_{1/3}$)O$_3$ (BTBZNT) MLCCs with double active dielectric layers were fabricated, and the effects of inner electrode and sintering method on the energy storage properties of BTBZNT MLCCs were investigated. By using the pure Pt as inner electrode instead of Ag$_{0.6}$Pd$_{0.4}$ alloys, an alternating current (AC) breakdown strength ($BDS$) enhancement from 1047 to 1500 kV/cm was achieved. By investigating the leakage current behavior of BTBZNT MLCCs, the Pt inner electrode and two-step sintering method (TSS) were confirmed to enhance the Schottky barrier and minimize the leakage current density. With relatively high permittivity, dielectric sublinearity, and ultra-high $BDS$, the Pt TSS BTBZNT MLCCs exhibited a surprisingly discharge energy density ($U_{\text{dis}}$) of 14.08 J/cm$^3$. Moreover, under an operating electric field of 400 kV/cm, the MLCCs also exhibited thermal stability with $U_{\text{dis}}$ variation $\leq \pm 8\%$ over a wide temperature ($t$) range from −50 to 175 °C and cycling reliability with $U_{\text{dis}}$ reduction $< 0.3\%$ after 3000 charge–discharge cycles. These remarkable performances make Pt TSS BTBZNT MLCCs promising for energy storage applications.

Keywords: BaTiO$_3$; multilayer ceramic capacitor (MLCC); leakage current; energy storage

1 Introduction

Multilayer ceramic capacitors (MLCCs) have been widely investigated because of their high power density, fast charge–discharge capability, and long lifetime, compared with lithium-ion batteries, fuel cells, and electrochemical super capacitors [1–3]. They have potential applications in portable electronics, electric vehicles, medical devices, and pulsed power weapons; hence, low-cost and environmentally friendly MLCCs are urgently needed to fulfill these requirements [4,5]. Through the integration of multiple layers of ceramic capacitors, a large amount of energy can be stored and released by the MLCCs. The energy density ($U$) can be calculated by integrating the electric field ($E$) with the polarization ($P$) according to $P$–$E$ hysteresis loops as shown in Eq. (1):

$$U = \int_0^P E \mathrm{d}P$$

(1)

Recently, BaTiO$_3$–BiMeO$_3$ (Me indicates the trivalent or meanly trivalent metallic cations) relaxor ferroelectrics have been of significant research interest [6–10]. Their markedly higher discharge/charge efficiency ($E_{\text{eff}}$)
compared with ferroelectrics, allows for the realization of superior energy storage properties. In previous Ref. [11], 0.87BaTiO3–0.13Bi(Zn0.85Ta0.15)O3 MLCCs with dielectric thickness (D) of 4.8 μm were fabricated using the Ag0.6Pd0.4 (AgPd) inner electrode and two-step sintering method (TSS) [12]. The sub-micron grains (mean grain size, G = 434 nm) of 0.87BaTiO3–0.13Bi(Zn0.85Ta0.15)O3 (BTBZNT) MLCCs are much smaller than the micron grains of reported ceramics for energy storage applications [13–21], and the dielectric layers therefore contained over 10 grains to obtain stable dielectric property. Because of their thin dielectric layers [22–28], remarkable AC breakdown strengthen (BDS) of 1047 kV/cm and a maximum discharge energy density (U_{max}) of 10.1 J/cm³ were achieved.

Such MLCCs with thin dielectric layers are typically subjected to high AC operating electric fields to store and release a large amount of energy, and the possible thermal breakdown may occur when heat generated from the leakage current exceeds the heat lost [29]. The leakage current density (J) of the MLCCs is reported strongly dependent on the thermodynamic temperature (T) and electric field (E), and the Schottky emission model [30] is used to describe these leakage current behaviors, as shown in Eq. (2):

\[
J = \left( \frac{4\pi m^* e^2}{h^3} \right) T^2 \exp \left( \frac{-e\phi_B + \sqrt{e^2 E / 4\pi e_0 e_r kT}}{kT} \right) \tag{2}
\]

where \(e\) is the effective electron mass, \(m^*\) is the effective Richardson constant, \(k\) is the Boltzmann constant, \(h\) is the Plank constant, \(\phi_B\) is the Schottky barrier height, \(e_0\) is the vacuum permittivity, and \(e_r\) is the relative permittivity at optical frequency. In an ideal Schottky barrier [31] (no electrode–dielectric interface states considered), the difference between the metal work function (\(\phi_m\), \(\phi_P = 5.6\ E\)V, \(\phi_{Ni} = 5.1\ E\)V [32], \(\phi_{Pt} = 5.5\ E\)V [33]), \(m = Pt, Ni, Pd, etc.) and the semiconductor affinity (\(\chi\), \(\chi_{BaTiO_3} = 3.9\ E\)V) is the Schottky barrier height of the electrode–dielectric interface [34], as shown in Eq. (3):

\[
\phi_B = \phi_m - \chi \tag{3}
\]

However, the electrode–dielectric counter-diffusion is inevitable during the sintering process, and as-formed interfacial alloys [35–37] of minor work functions (\(\phi_{Ba} = 2.7\ E\)V, \(\phi_{Pt} = 4.3\ E\)V [31]) lower the Schottky barrier height. An effective approach to depress the formation of alloy is using a smart sintering method [38]. By increasing the heating rate from 200 to 3000 °C/h, the interfacial alloy became thinner, and the Schottky barrier height was improved from 1.14 to 1.27 eV [39] in BaTiO3 MLCCs. Therefore, this indicates that by using inner electrodes with large work function and a suitable sintering method, the Schottky barrier of MLCCs can be heightened, and thus, the leakage current density can be minimized.

In this study, BTBZNT MLCCs with thin dielectric layers using different inner electrodes and sintering methods were fabricated. The effects of inner electrode and sintering method on the energy storage property of BTBZNT MLCCs were investigated.

## 2 Material and methods

### 2.1 Powder synthesizing

BTBZNT powders were synthesized via conventional solid-state reactions. Starting powders of BaTiO3 (99.9% purity), Bi2O3 (analytical reagent, AR), ZnO (AR), Nb2O5 (99.99% purity), and Ta2O5 (99.9% purity, Ningxia Orient Tantalum Industry Co., Ltd., China) were first stoichiometrically weighed, and then ball-milled for 24 h in an isopropanol (AR) medium. The well-milled slurry was separated and dried at \(t = 80^{\circ}C\) for 12 h. The obtained powders were calcined at \(t = 900^{\circ}C\) for 4 h. All the powders except for Ta2O5, were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

### 2.2 MLCCs processing

The calcined powders were mixed in a solution with 27 wt% ethyl acetate (AR), 27 wt% ethyl alcohol (AR), and 1 wt% triglycerides as dispersant. The suspension solution was then ball-milled using zirconia balls for 24 h. The organics, including 10 wt% polyvinyl butyral (aerospace grade) as binder, 2 wt% polyethylene glycol (AR) and 2 wt% butyl benzyl phthalate (AR, Aladdin Biochemical Technology Co., Ltd., China) as plasticizer, were added, and the slurry was then ball-milled for an additional 24 h. All the organics except butyl benzyl phthalate were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The well-milled slurry was separated and left to stand for 24 h to remove air. After roll-to-roll tape casting with a test coater (CMD-S1.7/D/4.OH/3-778, Yasui Seiki Corp, Japan), continuous tapes with thickness variation < ±0.2 μm
were formed. The Pt paste (MC-Pt100, GRIKIN Advanced Material Co., Ltd., China) was then screen printed on the green tapes with a size of 2.7 mm × 3.8 mm to serve as the inner electrode with an automated printing machine (NPM-1Y01, Yodogawa NCC Co., Ltd., Japan). Electrode patterned tapes were stacked with a 0.3 mm off-set from each other so that the effective electrode area was 2.7 mm × 3.2 mm. The active dielectric layer quantity and dielectric thickness were controlled using an automated laminating machine (NSM-1Y01, Yodogawa NCC Co., Ltd., Japan). After these processes, the BTBZNT MLCCs with double active dielectric layers (D ≈ 5 μm) were fabricated via the two-step sintering method (TSS, held at \( t = 1185 \, ^\circ\text{C} \) for 1 min and then at \( t = 1015 \, ^\circ\text{C} \) for 3 h) or the one-step sintering method (OSS, held at \( t = 1115 \, ^\circ\text{C} \) for 2 h) in air.

### 2.3 Characterization and testing method

The micro-structure was characterized via scanning electron microscopy (SEM; Supra 40/40vp, Carl Zeiss Corp, Germany) at an operating voltage of 15 kV and high-resolution transmission electron microscopy (HR-TEM; JEM-2010F, JEOL Ltd., Japan) at an operating voltage of 200 kV. The phase structures were detected via X-ray diffraction (XRD; D8 advance-A25, Bruker Co., Ltd., Germany). The temperature dependence of \( \varepsilon_r \) and dielectric loss (tanδ) were measured via an impedance analyzer (HP4278A; Hewlett-Packard, USA) with a temperature controller (Delta Design 9023, Cohu Semiconductor Equipment Group, USA). Hysteresis loops were measured using a ferroelectric measuring system (TF ANALYZER 2000E, aixACCT SystemsGmbH, Germany) at a frequency \( (f) \) of 10 Hz. The \( \varepsilon_r \) versus \( E \) curves were measured using a power device analyzer/curve tracer (Agilent B1505A; Agilent Technologies, USA) with an applied maximum direct current (DC) voltage \( (E = 400 \, \text{kV/cm}) \) and AC bias voltage \( (E = 10 \, \text{kV/cm}) \) at \( f = 10 \, \text{Hz} \). The AC BDS at \( f = 10 \, \text{Hz} \) was measured using a high-voltage tester (YD2670B, Yangzi Electronic Co., Ltd., China). Unless specifically mentioned, all characterization and testing methods were carried out at room temperature (RT, \( t = 25 \, ^\circ\text{C} \)).

### 3 Results and discussion

Figure 1 shows the micro-structure of the Pt BTBZNT MLCCs. The two-step sintering method [40], a universal method for preparing nanocrystalline ceramics, helped to decrease \( G \) of the Pt BTBZNT MLCCs from 346 to 271 nm.

**Fig. 1** SEM images of (a) Pt OSS and (c) Pt TSS BTBZNT MLCCs surface. Grain size distribution of (b) Pt OSS and (d) Pt TSS BTBZNT MLCCs.
Figure 2 shows the XRD patterns of the BTBZNT powders and Pt MLCCs. Perovskite phase structures with no split of the (002) and (200) peaks were detected, implying that all the dopants diffused into BaTiO$_3$ lattices forming a homogenous perovskite solid solution with symmetrical crystalline structure. The broader (002) peak of the Pt TSS MLCCs (full width at half maximum, $2\theta_{FWHM} = 0.142^\circ$) than the Pt OSS MLCCs ($2\theta_{FWHM} = 0.104^\circ$) implied finer grains according to Debye–Scherrer equation, which is consistent with SEM results.

Figure 3 shows the temperature dependence of the $\varepsilon_r$, dielectric loss, and temperature capacitance coefficients of the BTBZNT MLCCs. Because of the existence of PNRs in the grains [11], the BTBZNT MLCCs have a relatively high permittivity ($\varepsilon_r \approx 1200$) and a low dielectric loss ($\tan \delta < 0.5\%$ at $f = 100$ kHz) at RT. Broad Curie peaks can be observed in all MLCCs, and they arise from the random fields created by cation disorder because of the size and charge differences that disrupt the development of long-range polar ordering [41,42]. The Curie temperature ($T_c$) shifts to a higher value with increasing frequency, exhibiting the relaxor phenomenon with a strong diffuse phase transition [43]. The modified Curie–Weiss law [44] is used to describe the diffuse phase transition and is given by Eq. (4):

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = (t - t_m)^\gamma C^\prime$$  \hspace{1cm} (4)

where $\varepsilon_m$ is the maximum $\varepsilon_r$ and $t_m$ is $t$ corresponding to $\varepsilon_m$. $C^\prime$ is the modified Curie–Weiss constant and $\gamma$ is an indicator of the diffuseness degree. By changing the temperature dependence of $\varepsilon_r$ at $f = 1$ kHz into the forms $\ln(1/\varepsilon - 1/\varepsilon_0)$ and $\ln(t - t_m)$, linear regressions with excellent correlations (goodness of fit, $R^2 > 0.999$) could be realized, as shown in Fig. 3 (insets). The large $\gamma > 1.7$ indicates the strong diffuse phase transition in the BTBZNT MLCCs. Because of the broad Curie peaks around RT, the temperature capacitance coefficients (TCCs) between 100 and 1 kHz are maintained at $< \pm 15\%$ in the range of $t = (-55) - 125$ $^\circ$C, which meets the Electronics Industries Association (EIA) X7R specification.

The dielectric nonlinearity, which is the nonlinear reduction of the permittivity with increasing electric field, frequently degrades the energy storage properties of ceramics. The $\varepsilon_r$ versus electric field and electric field capacitance coefficient (ECC) curves of the BTBZNT MLCCs are shown in Fig. 4. The gradual variation in $\varepsilon_r$ with increasing $E$ in the range of $t = (-50) - 150$ $^\circ$C indicates the weak dielectric nonlinearity. The Johnson’s phenomenological expression based on the Devonshire’s phenomenological theory [45] is adopted to evaluate the dielectric nonlinearity, as shown in Eq. (5):

$$\frac{\varepsilon_r(E)}{\varepsilon_r(0)} = \frac{1}{(1 + \alpha\varepsilon_r(0)^3 E^2)^{1/3}}$$  \hspace{1cm} (5)

where $\varepsilon_r(E)$ is the $\varepsilon_r$ at $E$, $\varepsilon_r(0)$ is the $\varepsilon_r$ at $E = 0$ kV/cm, and $\alpha\varepsilon_r(0)^3$ is an indicator of the degree of dielectric nonlinearity. By changing $\varepsilon_r$ versus $E$ curves into the forms $\varepsilon_r(0)/\varepsilon_r(E)$ and $E^2$, linear regressions ($R^2 > 0.996$) were achieved, as shown in Fig. 4. The $\alpha\varepsilon_r(0)^3$ is one order lower than the SrTiO$_3$-surface-modified BaTiO$_3$ relaxor ferroelectrics ($\alpha\varepsilon_r(0)^3 \approx 9 \times 10^{-3}$) [46] with an approximate similar $G$, demonstrating the dielectric sublinearity of the BTBZNT MLCCs. Moreover, a further reduction in $\alpha\varepsilon_r(0)^3$ with increasing temperature significantly benefits the MLCC’s high-temperature energy storage properties, as shown in Fig. 4 (insets).

Because all the MLCCs exhibited similar dielectric property, the effects of inner electrode and sintering method were negligible, considering of the uncertain effective electrode area and dielectric thickness after sintering. Figure 5 shows the complex impedance spectra and three series resistor–capacitance (3RC) equivalent circuit fitting of the BTBZNT MLCCs. By fitting the experimental data with 3RC equivalent circuit [47,48] as shown in Fig. 5, which were assigned to grain, grain-boundary, and electrode–dielectric interface. The Arrhenius relationship is adopted to evaluate the activation energy ($E_a$) of the insulation resistance ($R_{in}$),
Fig. 3  Temperature dependence of the $\varepsilon_r$ and dielectric loss of (a) Pt OSS, (c) Pt TSS, and (e) AgPd TSS BTBZNT MLCC. Insets are the modified Curie–Weiss law fitting. Temperature capacitance coefficient curves of (b) Pt OSS, (d) Pt TSS, and (f) AgPd TSS BTBZNT MLCC.

Fig. 4  $\varepsilon_r$ versus the electric field curves of (a) Pt OSS, (d) Pt TSS, and (g) AgPd TSS BTBZNT MLCC. Electric field capacitance coefficient curves of (b) Pt OSS, (e) Pt TSS, and (h) AgPd TSS BTBZNT MLCC. (c) Johnson’s phenomenological expression fitting of (g) Pt OSS, (h) Pt TSS, and (i) AgPd TSS BTBZNT MLCC. Insets show the temperature dependence of $\alpha \varepsilon(0)^3$. 

www.springer.com/journal/40145
Fig. 5  Complex impedance spectra of experiment data and 3RC equivalent circuit fitting of (a) Pt OSS, (d) Pt TSS, and (g) AgPd TSS BTBZNT MLCC. Insets are magnified complex impedance spectra at higher temperatures. Arrhenius relationship fitting of the activation energy of (d) Pt OSS, (e) Pt TSS, and (f) AgPd TSS BTBZNT MLCC.

as shown in Eq. (6):

$$R_{\text{ins}} = R_0 \exp \left( \frac{E_a}{kT} \right)$$  \hspace{1cm} (6)

where $R_0$ is the characteristic resistance. By changing the Arrhenius relationship into the forms $\ln(R_{\text{ins}})$ and $1000/T$ as shown in Fig. 5. The $E_a$ corresponding to the interface insulation resistance of the Pt TSS BTBZNT MLCC ($E_a = 2.85$ eV) was higher than that of the Pt OSS BTBZNT MLCC ($E_a = 2.26$ eV) and the AgPd TSS BTBZNT MLCC ($E_a = 2.70$ eV). The insulation resistance of grain ($R_g$), grain-boundary ($R_{gb}$), and interface ($R_{int}$) of the BTBZNT MLCCs at various temperatures are listed in Table 1.

To further investigate the conduction mechanisms, current–voltage measurements were performed. Figure 6 shows the leakage current curves and the Schottky thermionic emission model fitting of the BTBZNT MLCCs. Despite the approximate maximum leakage current density ($J_{\text{max}} = 2.15 \mu \text{A/cm}^2$) at $T = 348$ K, the higher $J$ was detected for the AgPd TSS MLCC ($J_{\text{max}} = 44.5 \mu \text{A/cm}^2$) than the Pt OSS MLCC ($J_{\text{max}} = 27.8 \mu \text{A/cm}^2$) and the Pt TSS MLCC ($J_{\text{max}} = 24.2 \mu \text{A/cm}^2$) at $T = 423$ K, implying different $\phi_B$ according to Eq. (1). Leakage current data under $E > 250$ kV/cm were adopted and linear correlations of $\ln(J/T^2)$ and $E^{1/2}$ could be realized, guaranteeing the reliability of the Schottky thermionic emission model fitting results. The $\phi_B$ of the AgPd TSS, Pt OSS, and Pt TSS MLCC, evaluated from the plots of extrapolated values of $\ln(J/T^2)$ for $E \rightarrow 0$ versus $1000/T$ in Fig. 6 (insets), were 0.407, 0.431, and 0.489 eV, respectively.

The higher $\phi_B$ was obtained for the Pt TSS than AgPd TSS MLCC. It can be explained by the difference of the work function between Pt ($\phi_m = 5.6$ eV) and Ag$_{0.6}$Pd$_{0.4}$ alloy ($\phi_m = 4.6$ eV), which was evaluated by

| $T$ (K) | Pt OSS | Pt TSS | AgPd TSS |
|---------|---------|---------|-----------|
|         | $R_g$ (Ω) | $R_{gb}$ (Ω) | $R_{int}$ (Ω) | $R_g$ (Ω) | $R_{gb}$ (Ω) | $R_{int}$ (Ω) | $R_g$ (Ω) | $R_{gb}$ (Ω) | $R_{int}$ (Ω) |
| 748     | 663     | 29,939  | 186,620   | 498       | 22,506     | 81,645     | 780.4      | 1352       | 15,571     |
| 773     | 384     | 19,028  | 65,782    | 307       | 16,793     | 21,819     | 474.9      | 684.2      | 4678       |
| 798     | 215     | 10,987  | 25,487    | 225       | 8998       | 5156       | 297.1      | 425.6      | 1578       |
| 823     | 129     | 6378    | 10,076    | 151       | 5220       | 1271       | 173.2      | 262.5      | 452.1      |
| 848     | 109     | 4684    | 2663      | 97        | 2272       | 507        | 106.7      | 165        | 104        |

$$R_{g} = R_0 \exp \left( \frac{E_a}{kT} \right)$$

$$R_{gb} = R_0 \exp \left( \frac{E_{gb}}{kT} \right)$$

$$R_{int} = R_0 \exp \left( \frac{E_{int}}{kT} \right)$$

Table 1  Comparison between the insulation resistances of the BTBZNT MLCCs
Fig. 6 Leakage current curves of (a) AgPd TSS, (b) Pt OSS and (c) Pt TSS BTBZNT MLCC. Schottky thermionic emission model fitting of (d) AgPd TSS, (e) Pt OSS, and (f) Pt TSS BTBZNT MLCC. Insets show the Schottky barrier height fitting.

the Freeouf empirical model [49] as given by Eq. (7):

$$\phi_{AVG} = \phi_M^x \phi_m^{1-x}$$  \hspace{1cm} (7)

where $\phi_M$ and $\phi_m$ are the work functions of metal M and m, respectively, and $x$ is the concentration of the metal. In addition, a higher $\phi_B$ was also obtained for the Pt TSS than Pt OSS MLCC, indicating that the two-step sintering method suppressed the formation of the interface (the thickness decreased from 35 to 30 nm as shown in Fig. 7), and thus heightened the Schottky barrier.

Figure 8 shows the hysteresis loops and the energy storage property of the BTBZNT MLCCs. The Pt TSS BTBZNT MLCC had an exceptional $E_{max} = 1500$ kV/cm, which was higher than the Pt OSS ($E_{max} = 1301$ kV/cm) and AgPd TSS ($E_{max} = 1047$ kV/cm) BTBZNT MLCC. Thus it was confirmed that using Pt and TSS were effective approaches minimizing the leakage current density, and thus enhancing the breakdown strength.

The Weibull distribution was used to evaluate the AC

Fig. 7 TEM images of the electrode–dielectric interface of (a) Pt OSS and (b) Pt TSS BTBZNT MLCC. Elements line scanning of the electrode–dielectric interface of (c) Pt OSS and (d) Pt TSS BTBZNT MLCC.
BDS data, as given by Eq. (8):

\[ P = 1 - \exp \left[ - \left( \frac{E}{\alpha} \right)^\beta \right] \]  

(8)

where \( P \) is the cumulative probability of failure, \( \alpha \) is a scale parameter characterizing the breakdown strength, \( \beta \) is a shape parameter indicating the dispersion of the data, and \( E \) is the critical electric field above which breakdown occurs. The BDS data are ranked in ascending order and the values of \( P \) are estimated by Eq. (9):

\[ P = \frac{i}{N + 1} \]  

(9)

where \( i \) is the rank and \( N \) is the total number of samples. \( \alpha \) and \( \beta \) are then determined via linear regression of \( \ln[-\ln(1-P)] \) and \( \ln E \), as shown in Fig. 8(d) (inset). The large \( \beta > 8 \) guaranteed the reliability of the Weibull analysis, and \( \alpha \) was in good agreement with the \( E_{\text{max}} \). Despite of lowered \( E_{\text{eff}} \) under increasing \( E \), the \( U_{\text{dis}} \) of the BTBZNT MLCC was compensated by the increasing maximum polarization, showing linear correlations of \( E \) and \( U_{\text{dis}} \) in Fig. 8(d). Because of the enhanced \( E_{\text{max}} \), the \( U_{\text{max}} \) of the TSS BTBZNT MLCC was improved from 10.1 to 14.1 J/cm\(^3\) using Pt instead of AgPd inner electrode.

The Pt TSS BTBZNT MLCC also had an excellent thermal stability and the cycling reliability of over 3000 charge-discharge cycles, as shown in Fig. 9, which were generally superior to the reported energy storage MLCCs [6,9,50–54], as listed in Table 2.

4 Conclusions

BTBZNT double-layer ceramic capacitors with \( D \approx 5 \) μm using the Pt or AgPd inner electrode were successfully fabricated via a one-step or two-step sintering method, and the Schottky thermionic emission was confirmed to dominate the conduction mechanism of the BTBZNT MLCCs. By investigating the leakage current behaviors of the BTBZNT MLCCs, using the Pt and TSS were proved to be effective approaches heightening \( \varphi_B \), minimizing \( J \), and thus enhancing \( BDS \). The Pt TSS BTBZNT MLCC had the remarkable energy property with an \( E_{\text{max}} = 1500 \) kV/cm and a \( U_{\text{max}} = 14.1 \) J/cm\(^3\), and an excellent thermal stability with variation < ±8% at \( t = (-50) - 150 \) °C and \( E = 400 \) kV/cm. The Pt TSS BTBZNT MLCC was generally superior than recently reported energy storage MLCCs, and the improvements in their electric properties further indicate that they have high potential for energy storage applications.

![Fig. 8](image-url) Hysteresis loops of (a) AgPd TSS, (b) Pt OSS, and (c) Pt TSS BTBZNT MLCC. (d) Energy storage property of the BTBZNT MLCCs. Inset shows the Weibull distribution fitting results of AC BDS.
Fig. 9 (a) Hysteresis loop–temperature evolution. (b) Temperature dependence of the discharge energy density and discharge/charge efficiency. (c) Hysteresis loop–cycling evolution. (d) Cycling reliability of the discharge energy density and discharge/charge efficiency of the Pt TSS BTBZNT MLCC.

Table 2 Comparison between the energy storage property and the thermal stability of the reported MLCCs

| MLCC                     | \( U_{\text{max}} \) (J/cm\(^2\)) | \( E_{\text{max}} \) (kV/cm) | \( E_{\text{eff}} \) (%) | Thermal stability of \( U_{\text{max}} \) |
|--------------------------|----------------------------------|-------------------------------|--------------------------|-----------------------------------------------|
| This study               | 14.1                             | 1500                          | 69.7                     | Variation < ±8\% at \( t = (–50) – 150 \) \( ^{\circ}\) C and \( E = 400 \) kV/cm                  |
| 0.7BT–0.3BS [6]          | 6.1                              | 730                           | —                        | —                                             |
| 0.8BT–0.2BZT [9]         | 2.8                              | 330                           | —                        | —                                             |
| 0.62BF–0.3BT–0.08NZZ [50]| 10.5                             | 700                           | 87                       | Variation < ±15\% at \( t = 25 – 150 \) \( ^{\circ}\) C and \( E = 300 \) kV/cm                  |
| 0.75BNF–0.25BT [51]      | 6.74                             | 540                           | 77                       | Variation < ±15\% at \( t = 25 – 150 \) \( ^{\circ}\) C and \( E = 300 \) kV/cm                  |
| NBT–0.45SBT [52]         | 9.5                              | 720                           | 92                       | Variation < ±10\% at \( t = (–60) – 120 \) \( ^{\circ}\) C and \( E = 350 \) kV/cm                  |
| 0.9BT–0.1BLT [53]        | 4.05                             | 466                           | 95.5                     | —                                             |
| PZST-based [54]          | 3.8                              | 300                           | 67.4                     | Variation < ±6\% at \( t = 25 – 200 \) \( ^{\circ}\) C and \( E = 200 \) kV/cm                  |

Acknowledgements

The study was supported by Ministry of Sciences and Technology of China through National Basic Research Program of China (973 Program 2015CB654604), National Natural Science Foundation of China for Creative Research Groups (Grant No. 51221291), National Natural Science Foundation of China (Grant No. 51272123), and CBMI Construction Co., Ltd.

References

[1] Liu C, Li F, Ma L P, et al. Advanced materials for energy storage. *Adv Mater* 2010, 22: 28–62.
[2] Wu LW, Wang XH, Li LT. Lead-free \( \text{BaTiO}_3\)–\( \text{Bi(Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3 \) weakly coupled relaxor ferroelectric materials for energy storage. *RSC Adv* 2016, 6: 14273–14282.
[3] Shen ZB, Wang XH, Luo BC, et al. \( \text{BaTiO}_3\)–\( \text{BiYbO}_3 \) perovskite materials for energy storage applications. *J Mater Chem A* 2015, 3: 18146–18153.
[4] Guo LM, Deng JN, Wang GZ, et al. N, P-doped CoS\(_2\) embedded in TiO\(_2\) nanoporous films for Zn-air batteries. *Adv Funct Mater* 2018, 28: 1804540.
[5] Bi K, Bi MH, Hao YN, et al. Ultrafine core–shell \( \text{BaTiO}_3@\text{SiO}_2 \) structures for nanocomposite capacitors with high energy density. *Nano Energy* 2018, 51: 513–523.
[6] Ogihara H, Randall CA, Troler-McKinstry S. Weakly coupled relaxor behavior of \( \text{BaTiO}_3\)–\( \text{BiScO}_3 \) ceramics. *J
Am Ceram Soc 2009, 92: 110–118.

[7] Choi DH, Baker A, Lanagan M, et al. Structural and dielectric properties in (1-x)BaTiO3-x(Mg0.5Ti0.5)O2 ceramics (0.1 ≤ x ≤ 0.5) and potential for high-voltage multilayer capacitors. J Am Ceram Soc 2013, 96: 2197–2202.

[8] Wang T, Jin L, Li CC, et al. Relaxor ferroelectric BaTiO3–Bi(Mg2/3Nb1/3)O3 ceramics for energy storage application. J Am Ceram Soc 2015, 98: 559–566.

[9] Kumar N, Ionin A, Ansell T, et al. Synthesis, structure and electric properties of a new lead-free ferroelectric solid solution of (1-x)BaTiO3-xBi(Zn2/3Nb1/3)O3. Ceram Int 2015, 41: S57–S62.

[10] Paterson A, Wong HT, Liu ZH, et al. High energy density and fast breakdown strength and energy storage density in lead-free antiferroelectric ceramics via local chemical pressure tailoring. J Mater Chem C 2019, 7: 1551–1560.

[11] Tian Y, Jin L, Zhang HF, et al. High energy density in silver niobate ceramics. J Mater Chem A 2016, 4: 17279–17287.

[12] Zhao PY, Wang XH, Wu LW, et al. High-performance relaxor ferroelectric materials for energy storage applications. Adv Energy Mater 2019, 9: 1803048.

[13] Chen I, Wang XH. Sintering dense nanocrystalline ceramics without final-stage grain growth. Nature 2000, 404: 168–171.

[14] Li S, Nie HC, Wang GS, et al. Significantly enhanced energy storage performance of rare-earth-modified silver niobate lead-free antiferroelectric ceramics via local chemical pressure tailoring. J Mater Chem C 2019, 7: 1551–1560.

[15] Xu Q, Liu LX, Zhang L, et al. Structural and electrical properties of lead-free Bi0.5Na0.5TiO3-based ceramics for energy-storage applications. RSC Adv 2016, 6: 59280–59291.

[16] Li WB, Zhou D, Pang LX. Structure and energy storage properties of Mn-doped (Ba,Sr)TiO3–MgO composite ceramics. J Mater Sci: Mater Electron 2017, 28: 8749–8754.

[17] Li WB, Zhou D, Pang LX, et al. Novel barium titanate based capacitors with high energy density and fast discharge performance. J Mater Chem A 2017, 5: 19607–19612.

[18] Qu BY, Du HL, Yang ZT, et al. Enhanced dielectric breakdown strength and energy storage density in lead-free relaxor ferroelectric ceramics prepared using transition liquid phase sintering. RSC Adv 2016, 6: 34381–34389.

[19] Shao TQ, Du HL, Ma H, et al. Sodium–niobate based lead-free ceramics: Novel electrical energy storage materials. J Mater Chem A 2017, 5: 554–563.

[20] Malec D, Bley V, Talbi F, et al. Contribution to the understanding of the relationship between mechanical and dielectric strengths of Alumina. J Eur Ceram Soc 2010, 30: 3117–3123.

[21] Talbi F, Lalam F, Malec D. Dielectric breakdown characteristics of alumina. In Proceedings of 2010 10th IEEE International Conference on Solid Dielectrics, Potsdam, Germany, 2010: 1–4.

[22] Kim HK, Shi FG. Thickness dependent dielectric strength of a low-permittivity dielectric film. IEEE Trans Dielectr Electr Insul 2001, 8: 248–252.

[23] Chen HD, Udayakumar KR, Li KK, et al. Dielectric breakdown strength in sol–gel derived PZT thick films. Integr Ferroelectr 1997, 15: 89–98.

[24] Chen G, Zhao JW, Li ST, et al. Origin of thickness dependent dc electrical breakdown in dielectrics. Appl Phys Lett 2012, 100: 222904.

[25] Neusel C, Jelitto H, Schmidt D, et al. Thickness–dependence of the breakdown strength: Analysis of the dielectric and mechanical failure. J Eur Ceram Soc 2015, 35: 113–123.

[26] Munz D, Fett T. Ceramics: mechanical properties, failure behaviour, materials selection. Ann Chim-Sci Mat 2000, 25: 75.

[27] Sze SM. PHYSICS OF SEMICONDUCTOR DEVICES. 3rd edn. Hoboken, NJ: USA: John Wiley & Sons, Inc., 2007.

[28] Lüth H. Scattering from Surfaces. Surfaces and Interfaces of Solids. Berlin, Heidelberg: Springer Berlin Heidelberg, 1993: 136–217.

[29] Cann D, Maria JP, Randall CA. Relationship between wetting and electrical contact properties of pure metals and alloys on semiconductor barium titanate ceramics. J Mater Sci 2001, 36: 4969–4976.

[30] Eastman DE. Photovoltaic work functions of transition, rare-earth, and noble metals. Phys Rev B 1970, 2: 1.

[31] Wang YP, Tseng TY. Electronic defect and trap-related current of (Ba0.6Sr0.4)TiO3 thin films. J Appl Phys 1997, 81: 6762–6766.

[32] Yang GY, Dickey EC, Randall CA, et al. Oxygen nonstoichiometry and dielectric evolution of BaTiO3. Part I—improvement of insulation resistance with reoxidation. J Appl Phys 2004, 96: 7492–7499.

[33] Yang GY, Lian GD, Dickey EC, et al. Oxygen nonstoichiometry and dielectric evolution of BaTiO3. Part II—insulation resistance degradation under applied dc bias. J Appl Phys 2004, 96: 7500–7508.

[34] Yang GY, Lee SI, Liu ZJ, et al. Effect of local oxygen activity on Ni–BaTiO3 interfacial reactions. Acta Mater 2006, 54: 3513–3523.

[35] Polotai AV, Yang GY, Dickey EC, et al. Utilization of multiple-stage sintering to control Ni electrode continuity in ultrathin Ni–BaTiO3 multilayer capacitors. J Am Ceram Soc 2009, 92: 110–118.
Soc 2007, 90: 3811–3817.

[39] Polotai AV, Fujii I, Shay DP, et al. Effect of heating rates during sintering on the electrical properties of ultra-thin Ni–BaTiO3 multilayer ceramic capacitors. J Am Ceram Soc 2008, 91: 2540–2544.

[40] Chen I, Wang XH. Sintering dense nanocrystalline ceramics without final-stage grain growth. Nature 2000, 404: 168–171.

[41] Huang X, Hao H, Zhang S, et al. Structure and dielectric properties of BaTiO3–BiYO3 perovskite solid solutions. J Am Ceram Soc 2014, 97: 1797–1801.

[42] Strathdee T, Luisman L, Feteira A, et al. Ferroelectric-to-relaxor crossover in (1–x)BaTiO3–xBiYbO3 (0 ≤ x ≤ 0.08) ceramics. J Am Ceram Soc 2011, 94: 2292–2295.

[43] Nino JC, Lanagan MT, Randall CA, et al. Correlation between infrared phonon modes and dielectric relaxation in Bi2O3–ZnO–Nb2O5 cubic pyrochlore. Appl Phys Lett 2002, 81: 4404–4406.

[44] Uchino K, Nomura S. Critical exponents of the dielectric constants in diffused-phase-transition crystals. Ferroelectrics 1982, 44: 55–61.

[45] Xu Q, Zhang XF, Huang YH, et al. Effect of MgO on structure and nonlinear dielectric properties of Ba0.6Sr0.4TiO3/MgO composite ceramics prepared from superfine powders. J Alloys Compd 2009, 488: 448–453.

[46] Wu LW, Wang XH, Gong HL, et al. Core-satellite BaTiO3@SrTiO3 assemblies for a local compositionally graded relaxor ferroelectric capacitor with enhanced energy storage density and high energy efficiency. J Mater Chem C 2015, 3: 750–758.

[47] Yang GY, Dickey EC, Randall CA, et al. Oxygen nonstoichiometry and dielectric evolution of BaTiO3. Part I—improvement of insulation resistance with reoxidation. J Appl Phys 2004, 96: 7492–7499.

[48] Yang GY, Lian GD, Dickey EC, et al. Oxygen nonstoichiometry and dielectric evolution of BaTiO3. Part II—insulation resistance degradation under applied dc bias. J Appl Phys 2004, 96: 7500–7508.

[49] Freeouf JL. Silicide Scho ttky barriers: An elemental description. Solid State Commun 1980, 33: 1059–1061.

[50] Wang G, Li JL, Zhang X, et al. Ultrahigh energy storage density lead-free multilayers by controlled electrical homogeneity. Energy Environ Sci 2019, 12: 582–588.

[51] Wang DW, Fan ZM, Zhou D, et al. Bismuth ferrite-based lead-free ceramics and multilayers with high recoverable energy density. J Mater Chem A 2018, 6: 4133–4144.

[52] Li JL, Li F, Xu Z, et al. Multilayer lead-free ceramic capacitors with ultrahigh energy density and efficiency. Adv Mater 2018, 30: 1802155.

[53] Li WB, Zhou D, Xu R, et al. BaTiO3–Bi(2Li0.13Ta0.87)O3, lead-free ceramics, and multilayers with high energy storage density and efficiency. ACS Appl Energy Mater 2018, 1: 5016–5023.

[54] Chen LM, Sun NN, Li Y, et al. Multifunctional antiferroelectric MLCC with high-energy-storage properties and large field-induced strain. J Am Ceram Soc 2018, 101: 2313–2320.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

www.springer.com/journal/40145