

Enhanced dielectric properties of Sr^{2+} and Zr^{4+} doped BaTiO_3 colossal permittivity metamaterials

Qingyang Tang¹, Zhicheng Shi^{1,*}, Shuimiao Xia¹, Xiaohan Bie¹, Yujie Yang¹, Dedong Bian^{2,**}, Daofeng Xu², and Runhua Fan³

¹ School of Materials Science and Engineering, Ocean University of China, Qingdao 266100, PR China

² Shandong Tongfang Luying Electronic Co., Ltd, Linyi 276300, PR China

³ Institute of Marine Materials Science and Engineering, Shanghai Maritime University, Shanghai 201306, PR China

Received: 16 October 2023 / Accepted: 30 April 2024

Abstract. BaTiO_3 , as one of the most important functional materials of perovskite structure, is widely used in the electronic industry. However, the dielectric permittivity of BaTiO_3 remains relatively low, which greatly limits its practical application in metamaterials with colossal dielectric permittivity. In this work, $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ composite ceramics are fabricated via the solid sintering method. Surprisingly, the dielectric properties of $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ composite ceramic materials are strongly dependent on the occupancy of Sr^{2+} and Zr^{4+} at the A-sites and B-sites, respectively. Consequently, via adjusting the doping amount of SrTiO_3 and BaZrO_3 , a greatly enhanced dielectric permittivity of 28287 (65 °C, 1 kHz), along with a high breakdown strength of 84.47 kV/cm is achieved in $(\text{Ba}_{99}\text{Sr}_1)(\text{Ti}_{99}\text{Zr}_1)\text{O}_3$ composite ceramics, which are 2144% and 13 % higher than those of $(\text{Ba}_{99}\text{Sr}_1)(\text{Ti}_{99}\text{Zr}_1)\text{O}_3$ composite ceramics, respectively. Moreover, the reasons for the significant increase in dielectric permittivity are identified through finite element simulations, and the breakdown mechanism of composite ceramic materials is explored. This work provides a facile approach to constructing high dielectric permittivity composite ceramics, the $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ composite ceramics have broad application prospects in electronics and electrostatic energy storage capacitors.

Keywords: Metamaterial / dielectric property / breakdown strength / barium titanate / simulation

1 Introduction

Metamaterials are artificially designed unique composite materials with extraordinary physical properties that distinguish them from traditional materials [1–4]. Metamaterials can be classified into left-handed materials, zero-refractive-index materials, colossal permittivity materials, and graded refractive-index materials based on the distinct electromagnetic characteristics of their equivalent media and the magnitude of their permittivity and permeability values [5–7]. Colossal permittivity materials, which have attracted considerable attention in recent years, are a new type of functional materials with extremely high permittivity (usually greater than 10000), significantly surpassing the permittivity of conventional dielectric materials. Recent works have demonstrated that colossal permittivity materials exhibit analogous properties to metamaterials in certain aspects, including negative temperature coefficient

of capacitance and negative dielectric constant dispersion [8–10]. Therefore, colossal permittivity materials can be regarded as a special type of metamaterials. Ferroelectric ceramic materials, with their inherently high permittivity, are considered potential candidates for the preparation of colossal permittivity metamaterials.

As the core component of capacitors, ferroelectric materials have captured considerable interest because of their better thermal reliability and mechanical properties in miniaturized electronic components [11,12]. Among various ferroelectrics materials, BaTiO_3 , suffers from high polarization hysteresis and low electric field tolerance, restricting its development in the electronic industry [13,14]. Therefore, numerous efforts have been made to enhance the dielectric properties of BaTiO_3 in recent decades.

With the deepening of research on BaTiO_3 ceramics, researchers have also found that preparing BaTiO_3 ceramics with high dielectric permittivity and low dielectric loss is possible [15]. For example, the physical properties of the BaTiO_3 surface can be changed by heat treatment, plasma treatment or microwave treatment to increase its dielectric permittivity [16]. Moreover, the

* e-mail: zcshi@ouc.edu.cn

** e-mail: 13562940122@126.com

dielectric properties of BaTiO₃ can be enhanced by combining with carbon nanotubes or metal oxides [17]. However, the above two methods may bring some negative effects while increasing the dielectric permittivity of BaTiO₃. For example, they may introduce new interface effects and affect the ceramic manufacturing process [18]. Therefore, it is necessary to explore new methods to improve the dielectric permittivity of BaTiO₃ ceramics and consider how to overcome these negative effects to achieve a comprehensive improvement of the dielectric properties of BaTiO₃ ceramics.

In recent years, studies have shown that the electrical properties of BaTiO₃ ceramics can be effectively improved by changing the chemical composition of BaTiO₃ by doping method [13]. SrTiO₃ has been widely studied because of its low Curie temperature ($T_C = -250^\circ\text{C}$) and good temperature stability [19]. However, the low dielectric permittivity (~ 300) of SrTiO₃ at room temperature makes it unable to meet the development of miniaturization in electronic components [20]. Generally, SrTiO₃ is used as a filler in BaTiO₃ to enhance the dielectric permittivity of BaTiO₃ [21]. In addition, Zr⁴⁺ has better chemical stability than Ti⁴⁺, which is usually used to enhance the lattice stability of BaTiO₃ [22]. Such as $(1-x)\text{BaTi}_{0.95}\text{Zr}_{0.05}\text{O}_{3-x}\text{PbTiO}_3$ ($x = 0-1$) ceramics, the partial substitution of Ti⁴⁺ by Zr⁴⁺ in the B-site is a crucial factor for the formation of stable solid solutions even though the electronegativity of the Ba²⁺ and Pb²⁺ ions in the A-site are quite different [23].

In this work, we demonstrate that significantly improved dielectric permittivity and enhanced breakdown strength can be concomitantly achieved in $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ composite ceramics through a facile doping method. By introducing SrTiO₃ and BaZrO₃, which have the same perovskite structure as BaTiO₃, into BaTiO₃ to fabricate a series of $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ composite ceramics and solve the problem of incompatibility between different crystal phases in composite ceramics. We have conducted a detailed analysis of the microstructure, dielectric properties, and electrical insulation properties of the $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ composite ceramics. In addition, the mechanism of the excellent improvement of dielectric permittivity and breakdown strength is studied by finite element simulation.

2 Experimental details

2.1 Materials

The poly(vinyl alcohol) (PVA) particles with an average molecular weight M_w of 80000 were purchased from Sinopharm Chemical Reagent Co., Ltd (China). The BaTiO₃ (BT), SrTiO₃ (ST) and ZrTiO₃ (ZT) powders were provided by Shandong Tongfang Luying Electronic Co., Ltd (China). All the raw materials were used without any treatment.

2.2 Preparation of materials

$(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ (BSTZ) ceramics were fabricated by using the solid sintering method. Firstly, 10 g of PVA particles were added to 90 g of deionized water in a

beaker and stirred at 80°C for 4 h. Secondly, BT, ST and ZT powders were weighed according to the composition of $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ (abbreviated as x-y, where x-y is 1-1, 5-5, 10-10 and 20-20), and ball milled for 24 h in deionized water with zirconia balls. Thirdly, the composite ceramic powders were mixed with 10 wt% solutions of PVA and then pressed into white discs under a pressure of 30 MPa. Finally, the temperature was increased from 25°C to 200°C at a heating rate of $1^\circ\text{C}/\text{min}$, and the heat was maintained for 30 min to remove moisture. Then, the temperature was raised to 400°C at a heating rate of $2^\circ\text{C}/\text{min}$, and the heat was maintained for 30 min to remove the PVA solution. In addition, the temperature was raised to 1150°C at a heating rate of $1^\circ\text{C}/\text{min}$ and held for 2 h for sintering. The $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ composite ceramics were successfully prepared after the samples were cooled to room temperature.

2.3 Characterization of materials

The crystal structures were studied by using X-ray diffraction (D8 Advance, Bruker Corporation, Germany). Observation of micromorphology of sintered samples by scanning electron microscope (Gemini SEM 300, ZEISS, Germany). The frequency dependence of the dielectric properties was tested in the range of 100 Hz to 1 MHz via LCR analyzer (E4980A, Agilent Technologies, USA). The temperature dependence of the dielectric properties was measured in the range of -25°C to 125°C via capacitance Meter (4278A, Hewlett-Packard, USA) with a Temperature (& Humidity) Chamber (PL-2SPH, ESPEC, China) at 1 kHz. The breakdown strength measurements were measured by using a breakdown strength tester (Treck 610C PolyK Technologies, USA) amplifier at room temperature.

2.4 The finite element simulation models

The simulation was performed by Comsol to analyze the polarization distribution of 5-5 composite ceramics and 10-10 composite ceramics with a thickness of $5\ \mu\text{m}$ and the external potential was 25 V. To observe the breakdown paths, the phase field was introduced to characterize the evolution of the damage phase in dielectric, where $s(x, t)$ corresponds to the damage level. When $s=0$, $f(s)=0$, indicating that the material is broken down, and when $s=1$, $f(s)=1$, indicating that the material is intact. Therefore, the dielectric permittivity (ε) can be expressed by the following equation:

$$\varepsilon(s) = \frac{\varepsilon_0}{\eta + f(s)} \quad (1)$$

where $f(s) = 4s^3 - 3s^4$, $\eta = 0.001$. The following formula can be obtained by combining the linear dynamic equation:

$$\frac{1}{m} \frac{\partial s}{\partial t} = \frac{\varepsilon'(s)}{2} \nabla \phi \cdot \nabla \phi + W_C f'(s) + \frac{\Gamma}{2} \nabla^2 s \quad (2)$$

where m represents the speed of breakdown propagation, and W_C represents the critical electrostatic energy density. Then, the time and electric field are normalized, and the

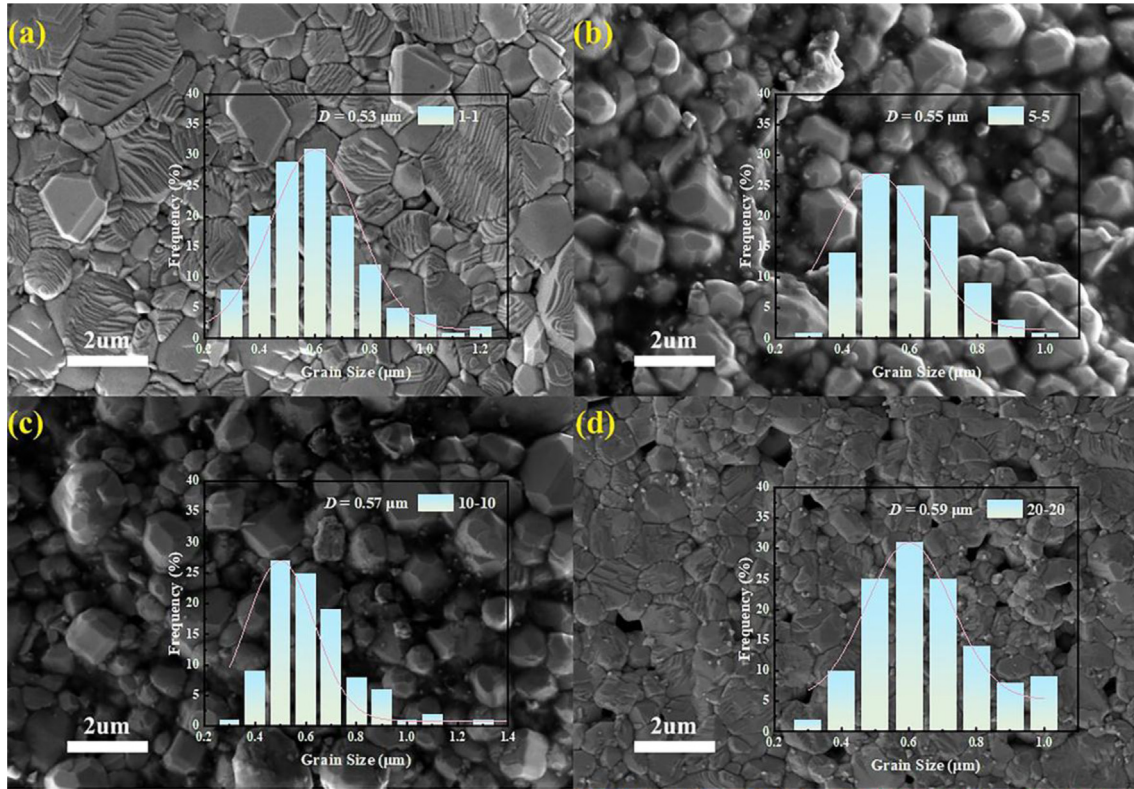


Fig. 1. SEM images and grain size distribution of (a) $(\text{Ba}_{99}\text{Sr}_1)(\text{Ti}_{99}\text{Zr}_1)\text{O}_3$, (b) $(\text{Ba}_{95}\text{Sr}_5)(\text{Ti}_{95}\text{Zr}_5)\text{O}_3$, (c) $(\text{Ba}_{90}\text{Sr}_{10})(\text{Ti}_{90}\text{Zr}_{10})\text{O}_3$, (d) $(\text{Ba}_{80}\text{Sr}_{20})(\text{Ti}_{80}\text{Zr}_{20})\text{O}_3$.

governing equation in dimensionless form is finally obtained, as shown in the following equation:

$$\frac{\partial}{\partial \bar{x}_1} = \left[\frac{1}{\eta + f(s)} \frac{\partial \bar{\varphi}}{\partial \bar{x}_1} \right] = 0 \quad (3)$$

$$\frac{\partial_s}{\partial_t} = -\frac{f'(s)}{2[\eta + f(s)]^2} \frac{\partial \bar{\varphi}}{\partial \bar{x}_1} \frac{\partial \bar{\varphi}}{\partial \bar{x}_1} + f'(s) + \frac{1}{2} \frac{\partial^2 s}{\partial \bar{x}_1 \partial \bar{x}_1} \quad (4)$$

where t , Γ and φ , represent the time, breakdown energy and electric potential, respectively [24–27].

3 Results and discussion

3.1 Material characterizations

The SEM images of BSTZ composite ceramics are shown in Figure 1. A dense and homogeneous microstructure and clear grain boundaries can be seen in Figure 1. Only a few cracks and pores can be observed in the 20-20 composite ceramics. The average grain sizes of 1-1, 5-5, 10-10 and 20-20 are 530, 550, 570 and 590 nm, respectively. This result indicates that the grain size of the BSTZ composite ceramics increased as the addition of ST and BZ increased.

The XRD patterns of BSTZ composite ceramics sintered at 1150 °C are shown in Figure 2a. All the diffraction peaks are well indexed as PDF # 75-0460, indicating that the BSTZ ceramics have a pure perovskite structure without any secondary phases [28]. In addition, all

the prepared composite ceramics have a diffraction peak of BT, indicating that the addition of ST and BZ does not cause changes in the perovskite structure of BT. This is because SrTiO_3 has the same crystal structure as BaTiO_3 and may form a continued solid solution. Similarly, BaZrO_3 also has a typical perovskite structure and does not destroy the perovskite structure of BaTiO_3 . However, there are slight shifts in the peak positions of the BSTZ composite ceramics prepared by the traditional solid-state sintering method, as shown in Figure 2b. According to Bragg's equation,

$$2d \sin \theta = n\lambda \quad (5)$$

where d is the lattice spacing, θ is the diffraction angle, and λ is the X-ray wavelength. We know that the partial substitution of Ba^{2+} (1.61 Å) by Sr^{2+} (1.44 Å) causes lattice contraction, resulting in a shift of the diffraction peak towards higher angles [29]. On the other hand, the diffraction peaks always shift to lower angles because of the partial substitution of Ti^{4+} (0.605 Å) by Zr^{4+} (0.87 Å) [30].

3.2 Dielectric properties of materials

The dielectric properties of BSTZ ceramics as a function of frequency and temperature are shown in Figure 3. It is indicated in Figure 3a that the dielectric permittivity tends to decrease at high frequencies. The decrease in dielectric permittivity is because at high frequencies, the alternating current electric field changes too quickly to affect the orientation of dipoles, resulting in Debye relaxation [31,32]

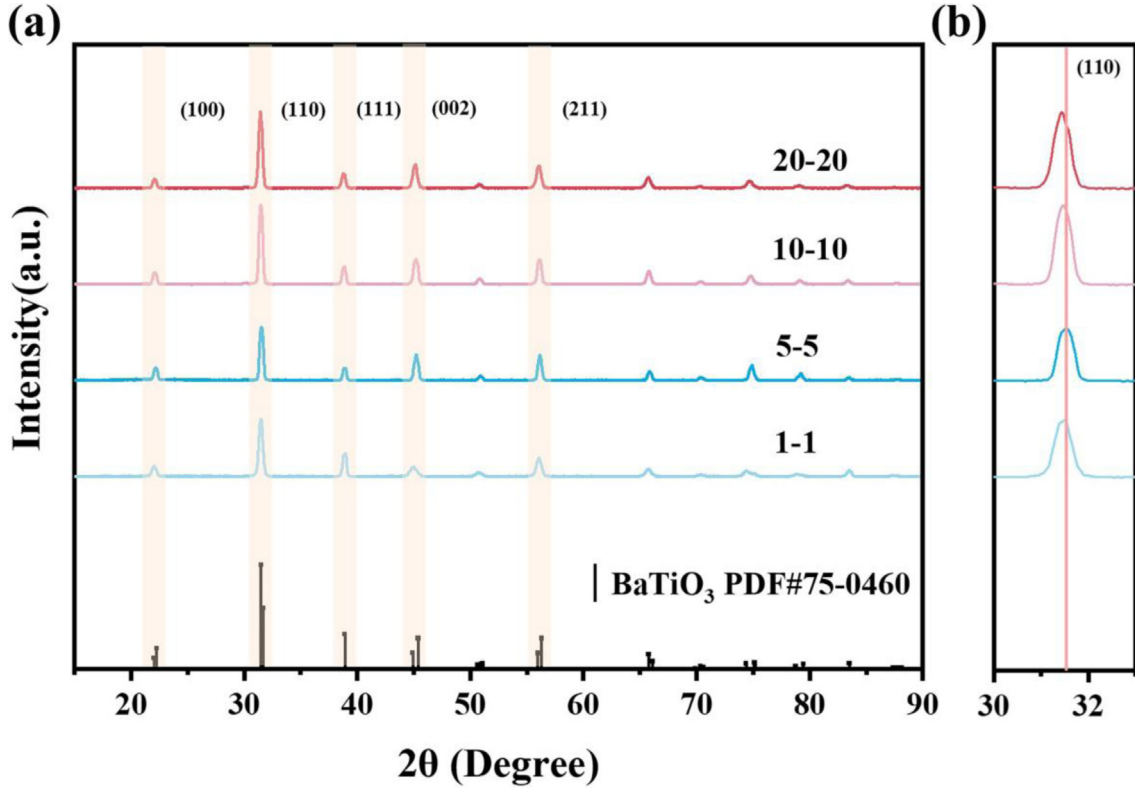


Fig. 2. XRD patterns of $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ ceramics in the range of (a) $10\text{--}90^\circ$ and (b) $30\text{--}33^\circ$.

As shown in Figure 3c, the dielectric permittivity of 10-10 composite ceramics reaches an astonishing value of 28287 at 65°C and 1 kHz. The reasons for this ultrahigh dielectric permittivity are twofold. On the one hand, the T_C of BT will decrease along with the content of ST increases [19]. In addition, the tetragonality will be reduced by the replacement of Zr^{4+} at the B site, hence decreasing the T_C with increasing dielectric permittivity [33]. However, we can find in Figure 3a that the dielectric permittivity of 20-20 composite ceramics is lower than 10-10 composite ceramics. This is owing to the fact that the T_C of 20-20 composite ceramics being lower than 10-10 composite ceramics with the increased added amount, as shown in Figure 3c. Meanwhile, the test temperature of Figure 3a is room temperature, which is close to the T_C of 10-10 composite ceramics. When the testing temperature approaches the T_C , the dielectric permittivity of the composite ceramics will increase significantly. Hence, we can observe that the dielectric permittivity of 10-10 composite ceramics is higher than 20-20 composite ceramics.

The dielectric loss represents the heat dissipation during the process of dipole orientation under an alternating current electric field [34]. Usually, the dielectric loss includes frequency-independent Ohmic conduction loss and frequency-dependent dipole relaxation loss [35]. At low frequencies, the dielectric loss is mainly due to ohmic conduction loss, while at high frequencies, it is mainly due to dipole relaxation. We can see from Figure 3b that the dielectric loss of BSTZ composite ceramics is lower than 0.05, indicating that the BSTZ composite ceramics have an extremely low ohmic conduction loss. The ultralow ohmic

conduction loss means that the resistance and conductivity of the material are lower when the current flows through it, and the efficiency of converting electrical energy into heat energy is also lower [36–40]. Therefore, the BSTZ composite ceramics have excellent electric insulation properties.

3.3 Electric insulation properties of materials

The breakdown strength (E_b) and leakage current densities are shown in Figure 4. The dielectric breakdown strength of the BSTZ composite ceramics is characterized by the two-parameter Weibull distribution. The Weibull distribution is expressed by the following formula:

$$P(E) = 1 - \exp\left[-\left(\frac{E}{\alpha}\right)^\beta\right] \quad (6)$$

where $P(E)$ represents the cumulative probability of electrical failure, E stands for the experimentally tested dielectric breakdown strength, α is the characteristic dielectric breakdown strength at the $P(E)$ of 63.2%, β is the shape parameter which evaluates the dispersion of the data, and a higher value of β indicates a higher data reliability [41–45].

The E_b increases significantly from 75.03 kV/cm for ceramics with a composition of 1-1 to 88.39 kV/cm for the composite ceramics with a composition of 20-20 illustrated in Figure 4a. The remarkable enhancement of E_b can be attributed to the following two aspects. On the one hand, the grain size will decrease due to the replacement of Sr^{2+} at the A-site, resulting in enhanced E_b [20]. On the other

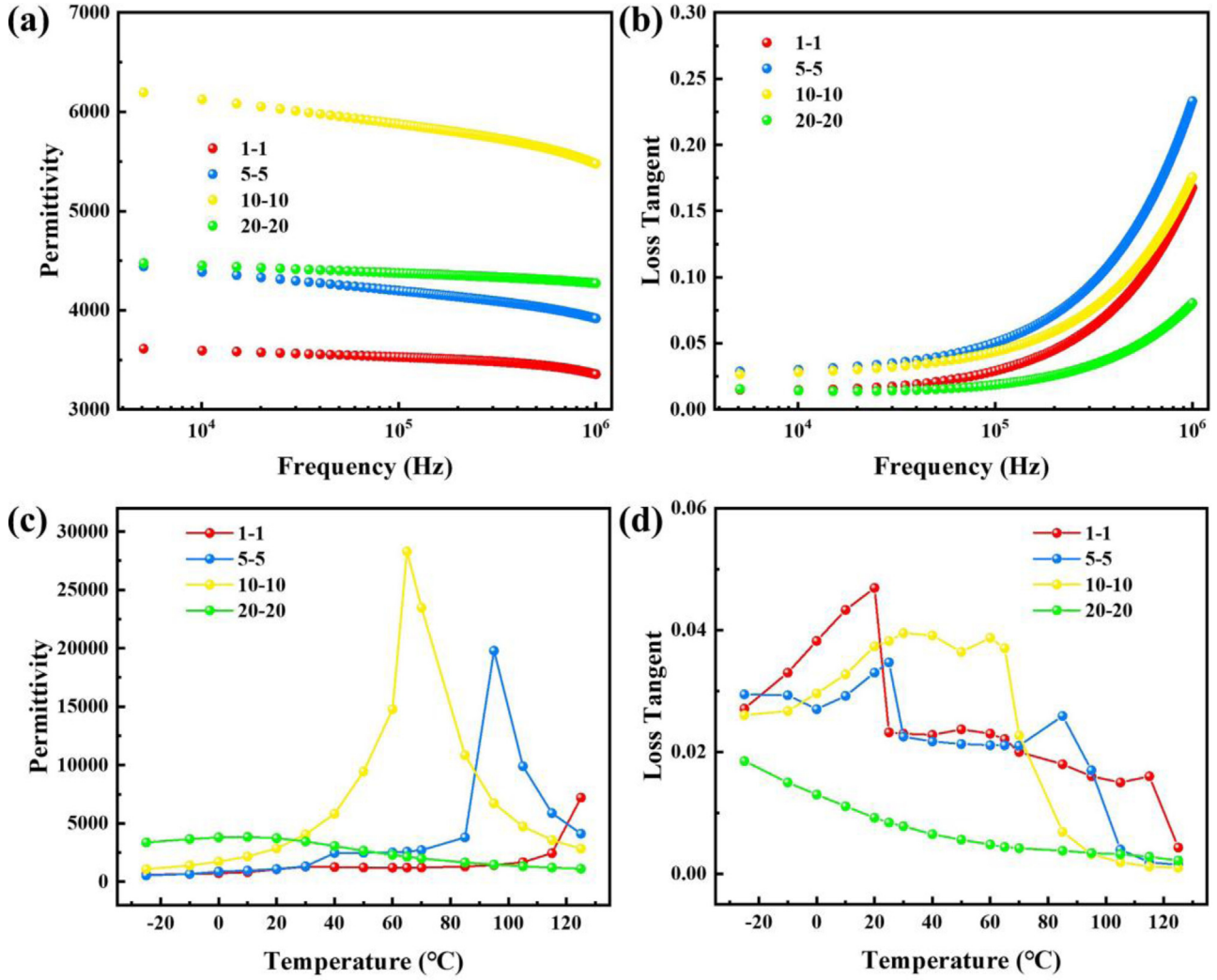


Fig. 3. Frequency dependences of (a) permittivity and (b) loss tangent. Temperature dependences of (c) permittivity and (d) loss tangent of $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ ceramics.

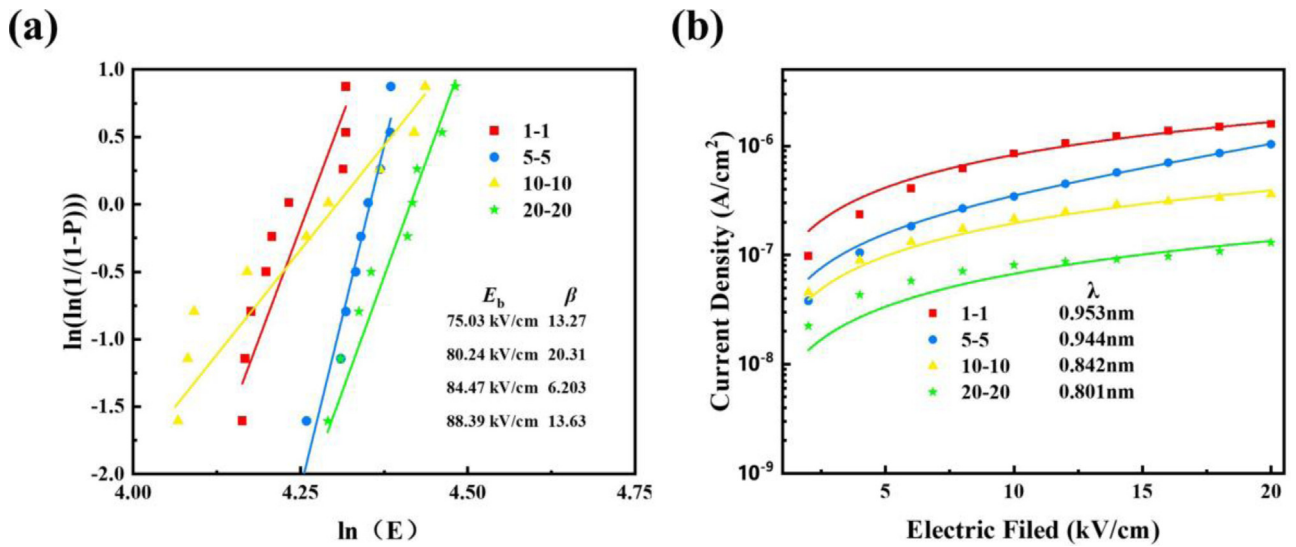


Fig. 4. (a) Weibull distribution of breakdown strength, (b) Leakage current densities of $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ ceramics.

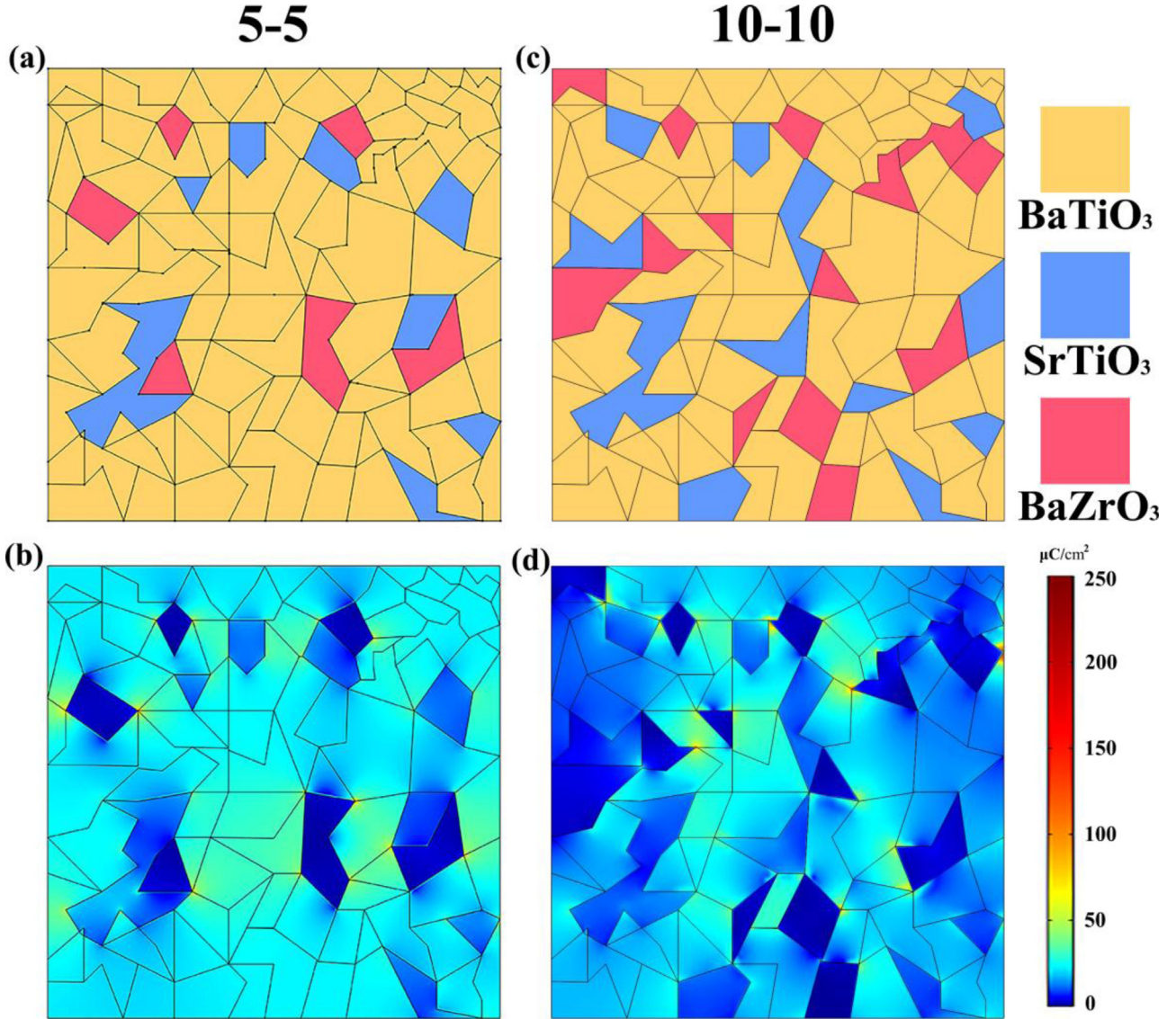


Fig. 5. (a) The simulation model and (b) polarization distribution in $(\text{Ba}_{95}\text{Sr}_5)(\text{Ti}_{95}\text{Zr}_5)\text{O}_3$ ceramics. (c) The simulation model and (d) polarization distribution in $(\text{Ba}_{90}\text{Sr}_{10})(\text{Ti}_{90}\text{Zr}_{10})\text{O}_3$ ceramics.

hand, Zr dopants are more chemically stable than Ti, and therefore, can limit electronic migration between Ti^{3+} and Ti^{4+} ions under stronger electric fields, improving the E_b [22]. In addition, the leakage current densities of BSTZ composite ceramics are shown in Figure 4b. We fit the data via the hopping conduction equations

$$J(E, T) = 2ne\lambda \times \exp\left(-\frac{W_a}{K_B T}\right) \times \sinh\left(\frac{e\lambda E}{2K_B T}\right) \quad (7)$$

where J stands for the dielectric leakage current, E represents the external electric field, T is the thermodynamic temperature, e is the charge on the carriers, λ is the hopping distance and K_B is the Boltzmann constant. Therefore, the above equation can be simplified to the following equation:

$$J(E) = A \times \sinh(B \times E) \quad (8)$$

where A and B are two lumped parameters [46,47]. It is easy to see from Figures 4a and 4b that the dielectric leakage current of BSTZ composite ceramics reduces with the decrease of dielectric breakdown strength. Meanwhile, the hopping distance is decreased with the increased doping amount. Shorter hopping distance means that the trap density in the composite ceramics is higher, and more carriers can be trapped, preventing the formation of breakdown paths, and thus improving the breakdown strength of the composite ceramics.

3.4 Analysis of finite element simulation

The finite element simulation of polarization distribution and dielectric breakdown path of BSTZ composite ceramics are illustrated in Figure 5. The distribution of SrTiO_3 and BaZrO_3 in BaTiO_3 of 5-5 and 10-10 composite ceramics are exhibited in Figures 5a and 5c, respectively. Figures 5b

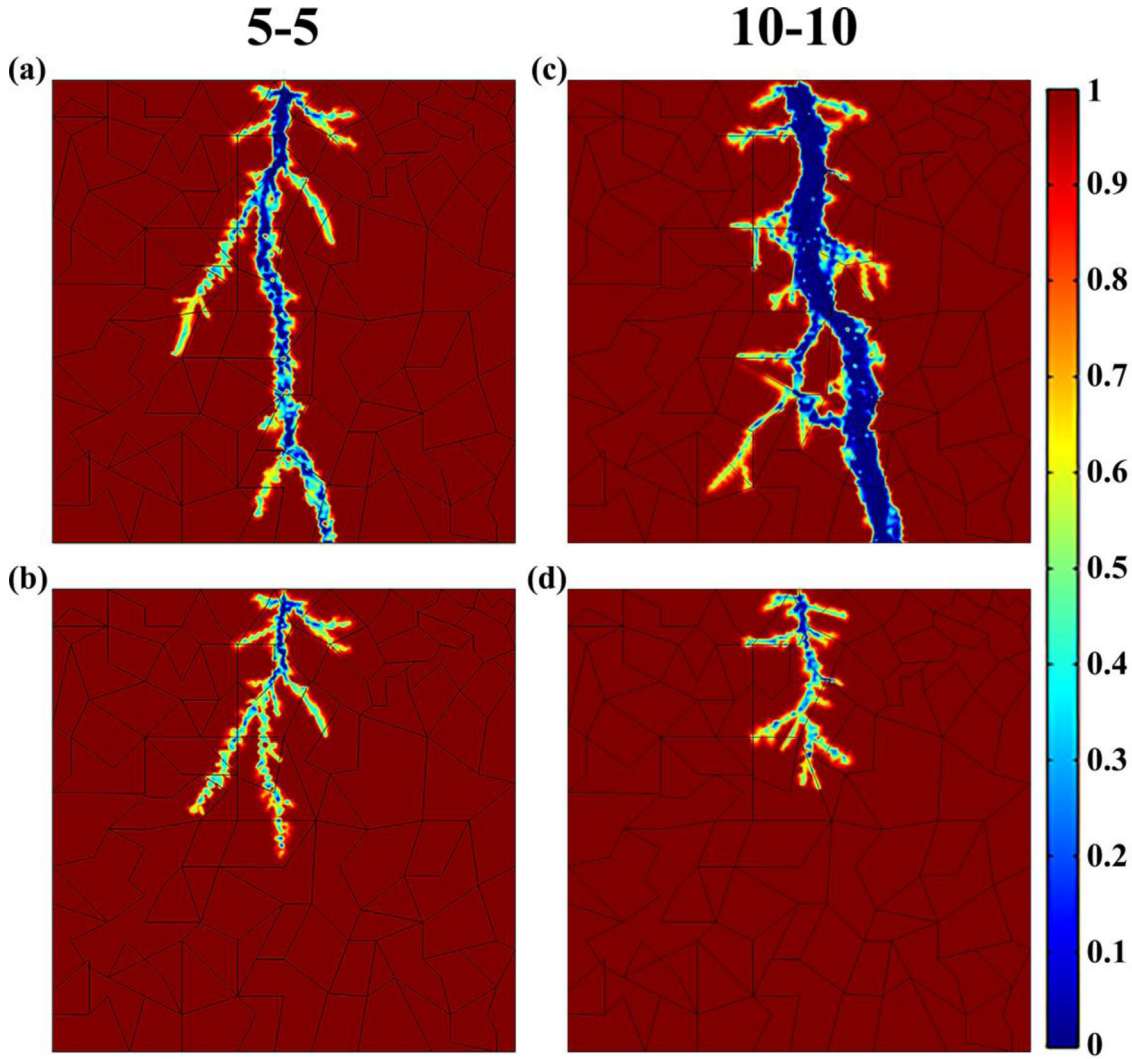


Fig. 6. (a) The simulation of breakdown path, (b) the breakdown path at 0.011s of $(\text{Ba}_{95}\text{Sr}_5)(\text{Ti}_{95}\text{Zr}_5)\text{O}_3$ ceramics. (c) The simulation of breakdown path, (d) the breakdown path at 0.011s of $(\text{Ba}_{90}\text{Sr}_{10})(\text{Ti}_{90}\text{Zr}_{10})\text{O}_3$ ceramics.

and 5d show the finite element simulations of polarization distribution for the two kinds of composite ceramics at the same external potential. It is clearly shown in Figures 5b and 5d that the region with a larger dielectric permittivity generates stronger polarization [48]. Because the dielectric permittivity of SrTiO_3 ($\epsilon = 240$), BaZrO_3 ($\epsilon = 45$) and BaTiO_3 ($\epsilon = 3376$) are significantly different, it will lead to strong Maxwell-Wagner interfacial polarization at the interface where they contact each other under an external electric potential [13,49–51]. Therefore, the Maxwell-Wagner interfacial polarization at the interface of the composite ceramics is enhanced with increasing doping of SrTiO_3 and BaZrO_3 , resulting in a significant increase in the dielectric permittivity. Figures 6a and 6c reveal the dielectric breakdown path of BSTZ composite ceramics, and Figures 6b and 6d illustrate the dielectric breakdown path at 0.011s. The introduction of SrTiO_3 and BaZrO_3 into BaTiO_3 changes the direction of the dielectric breakdown path in composite ceramics to a more circuitous one, playing a role in hindering the propagation of the

breakdown path [52–54]. Therefore, the breakdown path becomes more tortuous as the amount of SrTiO_3 and BaZrO_3 added to the composite ceramics increases. This conclusion is completely consistent with the simulation results in Figures 6b and 6d.

4 Conclusions

In summary, $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ ceramics have been successfully fabricated via the solid sintering method. The effects of Sr^{2+} and Zr^{4+} on the dielectric properties of BaTiO_3 ceramics are thoroughly investigated. Experimental results and the finite element simulation suggest that the enhanced dielectric permittivity and breakdown strength are attributable to the replacement of Sr^{2+} and Zr^{4+} at the A-sites and B-sites. Ultimately, ultrahigh dielectric permittivity of 28287 and breakdown strength of 84.47 kV/cm are concurrently attained in $(\text{Ba}_{90}\text{Sr}_{10})(\text{Ti}_{90}\text{Zr}_{10})\text{O}_3$ composite ceramics, which are increased by

2144% and 13% compared to that of $(\text{Ba}_{99}\text{Sr}_1)(\text{Ti}_{99}\text{Zr}_1)\text{O}_3$ composite ceramics, respectively. Therefore, $(\text{Ba}_{100-x}\text{Sr}_x)(\text{Ti}_{100-y}\text{Zr}_y)\text{O}_3$ ceramics are considered as promising materials for colossal permittivity metamaterial.

Funding

This work was supported by the Fundamental Research Funds for the Central Universities (202241004), Project of Taishan Scholars (tsqn202306090), Shandong Natural Science Foundation for Outstanding Young Scholars (ZR2021YQ39), National Natural Science Foundation of China (51773187).

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability statement

This article has no associated data generated and/or analyzed / Data associated with this article cannot be disclosed due to legal/ethical/other reason.

Author contribution statement

Writing – Original Draft Preparation, Qingyang Tang; Software, Qingyang Tang; Funding Acquisition, Zhicheng Shi; Writing – Review & Editing, Qingyang Tang, Shuimiao Xia and Zhicheng Shi; Formal Analysis, Xiaohan Bie and Yujie Yang; Resources, Dedong Bian and Daofeng Xu; Methodology, Runhua Fan.

References

- G. Fan, K. Sun, Q. Hou, Z. Wang, Y. Liu, R. Fan, Epsilon-negative media from the viewpoint of materials science, *EPJ Appl. Metamat.* **8**, 11 (2021)
- Z. Zhang, Y. Zhao, G. Fan, W. Zhang, Y. Liu, J. Liu, R. Fan, Paper-based flexible metamaterial for microwave applications, *EPJ Appl. Metamat.* **8**, 6 (2021)
- J. You, C. Wang, L. Ma, S. Yin, Safe energy-storage mechanical metamaterials via architecture design, *EPJ Appl. Metamat.* **10**, 1 (2023)
- T. Terao, Numerical methods for design of metamaterial photonic crystals and random metamaterials, *EPJ Appl. Metamat.* **9**, 1 (2022)
- J.B. Pendry, A.J. Holden, W.J. Stewart, I. Youngs, Extremely low frequency plasmons in metallic mesostructures, *Phys. Rev. Lett.* **76**, 4773 (1996)
- J.B. Pendry, A.J. Holden, D.J. Robbins, W.J. Stewart, Magnetism from conductors and enhanced nonlinear phenomena, *IEEE Trans. Microw. Theory. Tech.* **47**, 2075 (1999)
- G. Fan, Z. Wang, H. Ren, Y. Liu, R. Fan, Dielectric dispersion of copper/rutile cermets: Dielectric resonance, relaxation, and plasma oscillation, *Scr. Mater.* **190**, 1 (2021)
- I. Luk'yanchuk, A. Sené, V.M. Vinokur, Electrodynamics of ferroelectric films with negative capacitance, *Phys. Rev. B* **98**, 024107 (2018)
- G. Fan, Z. Wang, K. Sun, Y. Liu, R. Fan, Doped ceramics of indium oxides for negative permittivity materials in MHz-kHz frequency regions, *J. Mater. Sci. Technol.* **61**, 125 (2021)
- P. Xie, Z. Zhang, K. Liu, L. Qian, F. Dang, Y. Liu, R. Fan, X. Wang, S. Dou, C/SiO₂ meta-composite: Overcoming the λ/a relationship limitation in metamaterials, *Carbon* **125**, 1 (2017)
- J. Du, Y. Zhao, Y. Wang, J. Ai, Y. Li, X. Hao, Enhanced energy-storage density in silver niobate ceramics by Yb³⁺ doping at A-site, *Mater. Lett.* **333**, 133524 (2023)
- B. Hu, K. Sun, J. Wang, J. Xu, B. Liu, J. Zhang, Y. Yang, B. Du, High dielectric performance of (Nb⁵⁺, Lu³⁺) co-doped TiO₂ ceramics in a broad temperature range, *Mater. Lett.* **271**, 127838 (2020)
- Q. Tang, Z. Shi, M. Han, Q. He, D. Dastan, Y. Liu, R. Fan, Layered SrTiO₃/BaTiO₃ composites with significantly enhanced dielectric permittivity and low loss, *Ceram. Int.* **49**, 23326 (2023)
- Y. Chen, R. Li, Y. Zhang, Y. Long, N. Liu, H. Xia, X. Luo, B. Meng, Preparation and dielectric properties of lead-free perovskite-structured high-entropy ceramics of (La_{0.25}Sr_{0.25}Ba_{0.25}Na_{0.25})(Ti_{0.5}Me_{0.5})O_{3-δ} (Me=Sn, Zr, Hf) via doping at both A and B sites, *Ceram. Int.* **49**, 1038 (2022)
- H. Luo, S. Tang, Z. Sun, Y. Zhang, Y. Yao, H. Zheng, J. Yang, Y. Ren, M. Tang, H. Huang, H. Liu, M. Hinterstein, J. Chen, Perovskite/metal (Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃/Ag) lead-free composite ceramics featuring enhanced depolarization temperature, *Acta Mater.* **254**, 119024 (2023)
- M. Alkathy, R. Gayam, B. Hazra, K. Raju, Effect of sintering on structural and physical properties of nickel and lithium co-substituted barium titanate ceramics, *Ceram. Int.* **43**, 7937 (2017)
- T. Sebastian, A. Michalek, M. Hedayati, T. Lusiola, F. Clemens, Enhancing dielectric properties of barium titanate macrofibers, *J. Eur. Ceram. Soc.* **39**, 3176 (2019)
- Y. Ning, Y. Pu, C. Wu, J. Zhang, X. Zhang, Y. Shang, Achieving high energy storage performance below 200 kV/cm in BaTiO₃-based medium-entropy ceramics, *Ceram. Int.* **49**, 20326 (2023)
- J. Wu, G. Zhao, C. Pan, K. Tao, J. Yang, X. Zhu, P. Tong, L. Yin, W. Song, Y. Sun, Lattice disorder effect on the structural, ferroelectric and electrocaloric properties of (Ba, Sr, Ca)TiO₃ ceramics, *J. Alloys Compd.* **915**, 165433 (2022)
- Y. Wang, Z.-Y. Shen, Y.-M. Li, Z.-M. Wang, W.-Q. Luo, Y. Hong, Optimization of energy storage density and efficiency in Ba_xSr_{1-x}TiO₃ (x≤0.4) paraelectric ceramics, *Ceram. Int.* **41**, 8252 (2015)
- Z. Li, D.-X. Li, Z.-Y. Shen, X. Zeng, F. Song, W. Luo, X. Wang, Z. Wang, Y. Li, Remarkably enhanced dielectric stability and energy storage properties in BNT-BST relaxor ceramics by A-site defect engineering for pulsed power applications, *J. Adv. Ceram.* **11**, 283 (2022)
- Q. Yuan, M. Chen, S. Zhan, Y. Li, Y. Lin, H. Yang, Ceramic-based dielectrics for electrostatic energy storage applications: Fundamental aspects, recent progress, and remaining challenges, *Chem. Eng. J.* **446**, 136315 (2022)
- M.V. Talanov, A.A. Bush, V.P. Sirotinkin, V.I. Kozlov, Structural origin of strongly diffused ferroelectric phase transition in Ba(Ti, Zr)O₃-based ceramics, *Acta Mater.* **227**, 117734 (2022)

24. X. Li, Z. Shi, M. Han, Q. Tang, P. Xie, R. Fan, All-polymeric multilayer para/ferroelectric dielectric films utilizing a gradient structure toward concurrent high discharge efficiency and energy density, *Mater. Today Energy* **29**, 101119 (2022)
25. Z.M. Cai, X.H. Wang, B.C. Luo, W. Hong, L.W. Wu, L.T. Li, Dielectric response and breakdown behavior of polymer-ceramic nanocomposites: the effect of nanoparticle distribution, *Compos. Sci. Technol.* **145**, 105 (2017)
26. W. Hong, K.C. Pitike, Modeling breakdown-resistant composite dielectrics, *Procedia IUTAM* **12**, 73 (2015)
27. K. Pitike, W. Hong, Phase-field model for dielectric breakdown in solids, *J. Appl. Phys.* **115**, 044101 (2014)
28. L.-M. Wang, Q.-X. Liu, D. Zhou, Dielectric and energy storage properties of the $(1-x)\text{BaTiO}_3-x\text{Bi}(\text{Li}_{1/3}\text{Hf}_{2/3})\text{O}_3$ ($0.08 \leq x \leq 0.14$) ceramics, *Mater. Lett.* **283**, 128823 (2021)
29. Z. Zhao, X. Liang, T. Zhang, K. Hu, S. Li, Y. Zhang, Effects of cerium doping on dielectric properties and defect mechanism of barium strontium titanate glass-ceramics, *J. Eur. Ceram. Soc.* **40**, 712 (2020)
30. O.M. Hemeda, B.I. Salem, H. Abdelfatah, G. Abdelsatar, M. Shihab, Dielectric and ferroelectric properties of barium zirconate titanate ceramics prepared by ceramic method, *Physica B* **574**, 411680 (2019)
31. P.S. Padhi, S.K. Rai, H. Srivastava, R.S. Ajimsha, A.K. Srivastava, P. Misra, Maxwell-Wagner relaxation-driven high dielectric constant in $\text{Al}_2\text{O}_3/\text{TiO}_2$ nanolaminates grown by pulsed laser deposition, *ACS Appl. Mater. Inter.* **14**, 12873 (2022)
32. I. Jalafi, A. Bendahhou, K. Chourti, F. Chaou, E. Hassan Yahakoub, S.E.L. Barkany, M. Abou-Salama, High permittivity and low dielectric loss of the $(\text{Ca}_{0.9}\text{Sr}_{0.1})_{1-x}\text{La}_{2x/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *Ceram. Int.* **49**, 10213 (2022)
33. K.M. Sangwan, N. Ahlawat, R.S. Kundu, S. Rani, S. Rani, Structural, dielectric and ferroelectric properties of substituted BaZrTiO_3 lead-free ceramics, *AIP Conf. Proc.* **2115**, 030027 (2019)
34. D. Ji, S. Song, Y. Lyu, W. Ren, L. Li, B. Yang, M. Zhang, Novel Fabrication of Basalt Nanosheets with Ultrahigh Aspect Ratios Toward Enhanced Mechanical and Dielectric Properties of Aramid Nanofiber-Based Composite Nanopapers, *Adv. Sci.* **2302**, 371 (2023)
35. X. Hu, H. Zhang, D. Wu, D. Yin, N. Zhu, K. Guo, C. Lu, PVDF-based matrix with covalent bonded BaTiO_3 nanowires enabled ultrahigh energy density and dielectric properties, *Chem. Eng. J.* **451**, 1385 (2023)
36. J. Yan, H. Huang, J. Tong, W. Li, X. Liu, H. Zhang, H. Huang, W. Zhou, Recent progress on the modification of high nickel content NCM: Coating, doping, and single crystallization, *Interdiscip. Mater.* **1**, 330 (2022)
37. B. Zhang, L. Ren, Y. Wang, X. Xu, Y. Du, S. Dou, Gallium-based liquid metals for lithium-ion batteries, *Interdiscip. Mater.* **1**, 354 (2022)
38. X. Wang, Z. Gu, E.H. Ang, X. Zhao, X. Wu, Y. Liu, Prospects for managing end-of-life lithium-ion batteries: present and future, *Interdiscip. Mater.* **1**, 417 (2022)
39. G. Wang, Y. Liang, H. Liu, C. Wang, D. Li, L. Fan, Scalable, thin asymmetric composite solid electrolyte for high-performance all-solid-state lithium metal batteries, *Interdiscip. Mater.* **1**, 434 (2022)
40. F. Wang, X. Liao, H. Wang, Y. Zhao, J. Mao, D.G. Truhlar, Bioinspired mechanically interlocking holey graphene@ SiO_2 anode, *Interdiscip. Mater.* **1**, 517 (2022)
41. S. Xia, Z. Shi, K. Sun, P. Yin, D. Dastan, Y. Liu, H. Cui, R. Fan, Achieving remarkable energy storage enhancement in polymer dielectrics via constructing an ultrathin Coulomb blockade layer of gold nanoparticles, *Mater. Horiz.* **10**, 2476 (2023)
42. P. Wang, D. Jing Li, L. Pang, W. Liu, J. Su, C. Singh, S. Trukhanov, A. Trukhanov, Significantly enhanced electrostatic energy storage performance of $\text{P}(\text{VDF-HFP})/\text{BaTiO}_3\text{-Bi}(\text{Li}_{0.5}\text{Nb}_{0.5})\text{O}_3$ nanocomposites, *Nano Energy* **78**, 105247 (2020)
43. C. Yin, T. Zhang, B. Zhang, C. Zhang, Q. Chi, High energy storage performance for flexible PbZrO_3 thin films by seed layer engineering, *Ceram. Int.* **48**, 23840 (2022)
44. C. Yin, T. Zhang, Z. Shi, C. Zhang, Y. Feng, Q. Chi, High energy storage performance of all-inorganic flexible antiferroelectric-insulator multilayered thin films, *ACS Appl. Mater. Interfaces* **14**, 28997 (2022)
45. H. Du, Z. Shi, Q. Hou, S. Xia, P. Yin, D. Dastan, H. Cui, R. Fan, Gold sputtering at the interfaces: an easily operated strategy for enhancing the energy storage capability of laminated polymer dielectrics, *ACS Appl. Mater. Inter.* **15**, 17103 (2023)
46. H. Li, D. Ai, L. Ren, B. Yao, Z. Han, Z. Shen, J. Wang, L. Chen, Q. Wang, Scalable polymer nanocomposites with record high-temperature capacitive performance enabled by rationally designed nanostructured inorganic fillers, *Adv. Mater.* **31**, 1900875 (2019)
47. H. Li, D. Ai, L. Ren, B. Yao, Z. Han, Z. Shen, J. Wang, L. Chen, Q. Wang, High-temperature high-energy-density dielectric polymer nanocomposites utilizing inorganic core-shell nanostructured nanofillers, *Adv. Energy Mater.* **11**, 2101297 (2021)
48. L. Guan, L. Weng, Q. Li, X. Zhang, Z. Wu, Y. Ma, Design and preparation of ultra-thin 2D Ag-NiMOF ferroelectric nanoplatelets for PVDF based dielectric composites, *Mater. Des.* **197**, 109241 (2021)
49. P. Pulphol, N. Vittayakorn, W. Vittayakorn, T. Kolodiazhyi, Dielectric relaxation behavior of BaZrO_3 ceramics at low temperature, *Ceram. Int.* **46**, 24488 (2023)
50. P.S. Padhi, S.K. Rai, H. Srivastava, R.S. Ajimsha, A.K. Srivastava, P. Misra, Maxwell-Wagner relaxation-driven high dielectric constant in $\text{Al}_2\text{O}_3/\text{TiO}_2$ nanolaminates grown by pulsed laser deposition, *ACS Appl. Mater. Inter.* **14**, 12873 (2022)
51. I. Jalafi, A. Bendahhou, K. Chourti, F. Chaou, E. Hassan Yahakoub, S.E.L. Barkany, M. Abou-Salama, High permittivity and low dielectric loss of the $(\text{Ca}_{0.9}\text{Sr}_{0.1})_{1-x}\text{La}_{2x/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *Ceram. Int.* **49**, 10213 (2022)
52. B. Luo, Z. Shen, Z. Cai, E. Tian, Y. Yao, B. Li, A. Kursumovic, J. Driscoll, L. Li, L. Chen, X. Wang, Superhierarchical inorganic/organic nanocomposites exhibiting simultaneous ultrahigh dielectric energy density and high efficiency, *Adv. Funct. Mater.* **31**, 2007994 (2021)

53. Y. Jiang, Z. Luo, Y. Huang, M. Shen, H. Huang, S. Jiang, Y. He, Q. Zhang, Simultaneously increased discharged energy density and efficiency in bilayer-structured nanocomposites with AgNbO₃ lead-free antiferroelectric nanofillers, *J. Mater. Chem. A*. **10**, 18950 (2023)
54. S. Sun, Z. Shi, L. Sun, L. Liang, D. Dastan, B. He, H. Wang, M. Huang, R. Fan, Achieving concurrent high energy density and efficiency in all-polymer layered paraelectric/ferroelectric composites via introducing a moderate layer, *ACS Appl. Mater. Inter.* **13**, 27522 (2021)

Cite this article as: Qingyang Tang, Zhicheng Shi, Shuimiao Xia, Xiaohan Bie, Yujie Yang, Dedong Bian, Daofeng Xu, Runhua Fan, Enhanced dielectric properties of Sr²⁺ and Zr⁴⁺ doped BaTiO₃ colossal permittivity metamaterials, *EPJ Appl. Metamat.* **11**, 13 (2024)