

# WHAT CAN LEAD-FREE ENERGY STORAGE CERAMICS DO

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Which lead-free bulk ceramics are suitable for electrical energy storage applications? Here, we present an overview on the current state-of-the-art lead-free bulk ceramics for electrical energy storage applications, including  $\text{SrTiO}_3$ ,  $\text{CaTiO}_3$ ,  $\text{BaTiO}_3$ ,  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ,  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ,  $\text{BiFeO}_3$ ,  $\text{AgNbO}_3$  and  $\text{NaNbO}_3$ -based ceramics.

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Does lead-free bulk ceramics have ultrahigh energy storage density? Significantly, the ultrahigh comprehensive performance ( $W_{\text{rec}} \sim 10.06 \text{ J/cm}^3$  with  $\eta \sim 90.8\%$ ) is realized in lead-free bulk ceramics, showing that the bottleneck of ultrahigh energy storage density ( $W_{\text{rec}} \sim 10 \text{ J/cm}^3$ ) with ultrahigh efficiency ( $\eta \sim 90\%$ ) simultaneously in lead-free bulk ceramics has been broken through.

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How to improve energy storage performance of lead-free ceramics? To overcome the inverse correlation between polarization and breakdown strength and to improve the energy storage performance of these lead-free ceramics, strategies such as constructing relaxor features, decreasing grain and domain size, enhancing band gap, designing layered structures, and stabilizing the anti-ferroelectric phase were employed.

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What are the characteristics of lead-free ceramics? Grain size engineered lead-free ceramics with both large energy storage density and ultrahigh mechanical properties High-energy storage performance in lead-free  $(0.8-x)\text{SrTiO}_3-0.2\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$  relaxor ferroelectric ceramics J. Alloy. Compd., 740 (2018), pp. 1180 - 1187

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Why are lead-free ceramics important? Therefore, it is also crucial to improve the energy storage performance of lead-free ceramics along with excellent stability in different environments. The cost of raw materials and the preparation conditions of lead-free ceramics are also important for quantity production.

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Are lead-free anti-ferroelectric ceramics suitable for energy storage applications? At present, the development of lead-free anti-ferroelectric ceramics for energy storage applications is focused on the  $\text{AgNbO}_3$  (AN) and  $\text{NaNbO}_3$  (NN) systems. The energy storage properties of AN and NN-based lead-free ceramics in representative previous reports are summarized in Table 6.

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optimized energy storage density ( $0.47 \text{ J/cm}^3$ ) and efficiency ( $48.67\%$ ), under an applied electric field of  $50 \text{ kV/cm}$ , should be a candidate for solid-state compact pulsed power capacitor materials. Keywords: Sodium bismuth titanate; barium strontium titanate; energy storage ceramics; compact pulsed power. 1. Introduction High-energy



$\text{NaNbO}_3$  (NN)-based materials have attracted widespread attention due to their advanced energy storage performance and eco-friendliness. However, achieving high recoverable energy storage densities ( $W_{\text{rec}}$ ) and efficiency ( $\eta$ ) typically requires ultrahigh electric fields ( $E > 300 \text{ kV/cm}$ ), which can limit practical use this work, we present a synergistic



The newly developed ceramic,  $(1-x) \text{ KNN-xBSZ}$ , exhibited remarkable performance characteristics, including an energy storage density of  $4.13 \text{ J/cm}^3$ , a recoverable energy storage density of  $2.95 \text{ J/cm}^3$  at a low electric field of  $245 \text{ kV/cm}$ , and an energy storage efficiency of  $84\%$ . Additionally, at  $700 \text{ nm}$ , the  $0.875 \text{ KNN-0.125BSZ}$  sample displayed a



The great potential of  $\text{K}_{1/2} \text{Bi}_{1/2} \text{TiO}_3$  (KBT) for dielectric energy storage ceramics is impeded by its low dielectric breakdown strength, thereby limiting its utilization of high polarization. This study develops a novel composition,  $0.83 \text{ KBT-0.095Na}_{1/2} \text{Bi}_{1/2} \text{ZrO}_3\text{-0.075Bi}_{0.85}\text{Nd}_{0.15} \text{FeO}_3$  (KBNBTF) ceramics, demonstrating outstanding energy storage

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$\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  (KNN)-based perovskite ceramics have gained significant attention in capacitor research due to their excellent ferroelectric properties and temperature stability [9], [10] is known that incorporating a second phase into the solid solution has a positive impact on enhancing the degree of ferroelectric relaxation and improving the energy storage ???



Energy storage approaches can be overall divided into chemical energy storage (e.g., batteries, electrochemical capacitors, etc.) and physical energy storage (e.g., dielectric capacitors), which are quite different in energy conversion characteristics. As shown in Fig. 1 (a) and (b), batteries have high energy density. However, owing to the slow movement of charge ???



This study confirms that two-step sintering can also be applied to the preparation of  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based MLCCs and provides a way to improve the energy storage performance of lead-free MLCCs, and benefits to the application of MLCCs as ???

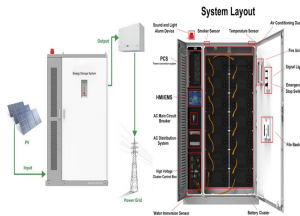


$\text{BaTiO}_3$  ceramics are difficult to withstand high electric fields, so the energy storage density is relatively low, inhabiting their applications for miniaturized and lightweight power electronic devices. To address this issue, we added  $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$  (SBT) into  $\text{BaTiO}_3$  (BT) to destroy the long-range ferroelectric domains.  $\text{Ca}^{2+}$  was introduced into BT-SBT in the ???



Here, we present an overview on the current state-of-the-art lead-free bulk ceramics for electrical energy storage applications, including  $\text{SrTiO}_3$ ,  $\text{CaTiO}_3$ ,  $\text{BaTiO}_3$ ,  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ,  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$

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The structural and electrical complexities inherent in multilayer ceramic structures are due to various factors, including the presence of defects, electrode material compatibility, co-firing processes, and interface challenges [24], [25]. Therefore, preliminary studies of bulk ceramics are crucial for enabling thorough assessments of dielectric energy storage devices, even within ???



Researchers often improve the energy storage performance of  $\text{NaNbO}_3$  ceramics through doping with Bi-based composites. Recent studies have shown that rare-earth elements, such as La and Sm, can



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Chemical modification is an important method for preparing ceramics with excellent energy storage performance. For example, Wang et al. have added  $\text{Sr}_{0.85}\text{Bi}_{0.1}\text{TiO}_3$  and  $\text{NaNbO}_3$  to BNT and obtained  $W_r$  of  $3.08 \text{ J/cm}^3$  and ?? of 81.4% [15]. Hao et al. prepared  $\text{NaNb}???\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{TiO}_3$  ceramics and obtained  $W_r$  of  $2.31 \text{ J/cm}^3$  and ?? of 80.2% ???



The largest amount of energy that ceramic-based capacitors can store is expressed as the energy storage density ( $W$ ) or the energy density of that capacitor. The energy storage density can be calculated from the P-E loops using graphs, by applying the equation below [13] (2)  $W = ?? < P_r$   
 $P_{\text{max}} E_d P$

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In summary, lead-free energy storage ceramic capacitors are still in the laboratory stage of development and have not yet reached the level of industrial application. In addition to the basic research challenges of lead-free ceramics, such as cycle stability, temperature stability, ion defect, grain size, and others, the problems in capacitor



Dielectric ceramics are widely used in advanced high/pulsed power capacitors. Here, the authors propose a high-entropy strategy to design "local polymorphic distortion" in ???



Therefore, numerous efforts have been made to improve the performance of lead-free ceramics for energy storage dielectric capacitors, considering sustainable development [8]. Among



The mainstream dielectric capacitors available for energy storage applications today include ceramics, polymers, ceramic-polymer composites, and thin films [[18], [19], [20]]. Among them, dielectric thin films have an energy storage density of up to  $100 \text{ J/cm}^3$ , which is due to their breakdown field strength typically exceeding  $500 \text{ kV/mm}$ . The ability to achieve such high field ???



Textured lead-based ceramics and lead-free ceramics have better piezoelectric properties than their randomly oriented ceramic counterparts and are comparable, in some cases, Q. Zhang et al., A review on the development of lead-free ferroelectric energy-storage ceramics and multilayer capacitors. J. Mater. Chem. C 8, 16648 (2020)

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Structural, dielectric, ferroelectric, energy storage properties, and electrocaloric effect were studied in lead-free ceramic

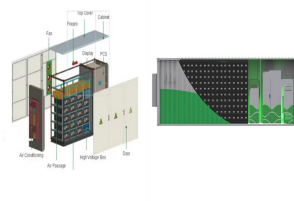
$\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{0.89}\text{Sn}_{0.11}\text{O}_3$  (BCTSn) elaborated by the sol-gel method. Phase purity structure was confirmed from X-ray data using the Rietveld refinement analysis which revealed the coexistence of tetragonal (P4mm) and orthorhombic ???



$(1-x)\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$  [(1-x)BST-xBMZ] relaxor ferroelectric ceramics were prepared by solid-phase reaction. In this work, the phase structure, surface morphology, element content analysis, dielectric property, and energy storage performance of the ceramic were studied. 0.84BST-0.16BMZ and 0.80BST-0.20BMZ have ???



Yang, Z. et al. Grain size engineered lead-free ceramics with both large energy storage density and ultrahigh mechanical properties. Nano Energy 58, 768-777 (2019). Article ADS CAS Google Scholar



This work employs the conventional solid-state reaction method to synthesize  $\text{Ba}_{0.92}\text{La}_{0.08}\text{Ti}_{0.95}\text{Mg}_{0.05}\text{O}_3$  (BLMT5) ceramics. The goal is to investigate how defect dipoles affect the ability of lead-free ferroelectric ceramics made from  $\text{BaTiO}_3$  to store energy. An extensive examination was performed on the crystal structure, dielectric properties, and ???



Recently,  $\text{NaNbO}_3$ -based ceramics have achieved superior energy storage properties by constructing relaxor antiferroelectrics, which integrates the feature of antiferroelectrics (low  $P_r$ ) and relaxor ferroelectrics (high  $W_{rec}$ ). For example, Qi et. al. found that an ultrahigh  $W_{rec}$  of 12.2 J/cm<sup>3</sup> and a satisfied  $\eta$  of 69% can be simultaneously achieved in ???



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But most of BT based ceramics do not possess high energy storage efficiency and high energy storage density, simultaneously. For the practical application, as a lead free dielectric material for energy storage capacitor, not only high energy storage density but also high energy storage efficiency is desirable [28].

## Commercial and Industrial ESS

- Budget-Friendly Solution
- Renewable Energy Integration
- Minimal Design for Flexible Expansion



Recently, lead-free dielectric capacitors have attracted more and more attention for researchers and play an important role in the component of advanced high-power energy storage equipment [[1], [2], [3]]. Especially, the country attaches great importance to the sustainable development strategy and vigorously develops green energy in recent years [4].



Lead is present in most of the high-energy density capacitors, thus limiting their widescale application due to environmental concerns as lead is a toxic heavy metal. The power density of dielectric capacitors is higher than fuel cells, Li-ion batteries, and supercapacitors. However, their lower-energy density hinders their commercialization

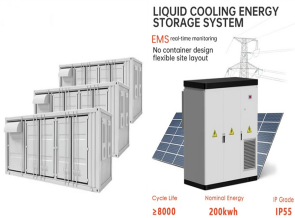


High-entropy (HE) ceramic capacitors are of great significance because of their excellent energy storage efficiency and high power density (P D). However, the contradiction between configurational entropy and polarization in traditional HE systems greatly restrains the increase in energy storage density.



Novel Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> based, lead-free energy storage ceramics with high power and energy density and excellent high-temperature stability. Chem. Eng. J., 383 (2020) Google Scholar High energy-storage performance of lead-free AgNbO<sub>3</sub> antiferroelectric ceramics fabricated via a facile approach. J. Eur. Ceram. Soc., 41 (2021)

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Yang, Z. T. et al. Grain size engineered lead-free ceramics with both large energy storage density and ultrahigh mechanical properties. Nano Energy 58, 768???777 (2019). CAS Google Scholar



One of the long-standing challenges of current lead-free energy storage ceramics for capacitors is how to improve their comprehensive energy storage properties effectively, that is, to achieve a synergistic improvement in the breakdown strength ( $E_b$ ) and the difference between maximum polarization ( $P_{max}$ ) and remnant polarization ( $P_r$ ), making ???



Compared with other lead-free ceramics reported so far, a significant difference is that the high energy density and power density are achieved in 0.9NBT-0.1LT ceramic simultaneously. Energy storage ceramics with a high electric breakdown strength ( $E_b$ ) should possess not only a dense microstructure, but also small and uniform grains inside