COMMENTARY

Addressing a novel paradigm toward high energy storage

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Improved energy storage density of dielectric capacitors are highly desired to remove limitations on their applications in super-high-power electronics and systems. Previous strategies to improve the energy storage density and efficiency of relaxor films typically take the avenue of suppressing the domain size by the introduction of chemical heterogeneity. This takes advantage of a suppressed P_r. However, it would decrease the domain volume fraction, which ultimately leads to weakened polarization ability (i.e., P_m). This partly explains that the breakthrough of energy storage density beyond 200 J cm^{-3} in relaxor ferroelectrics films are challenging. In thepioneering work reported by Professor Li et. al., a new paradigm of constructing isolated polar slush led to a maintained superior P_m but a greatly suppressed P_r, resulting in outstanding energy storage density. This isolation strategy also reinforces enhanced breakdown strength of the films, contributing to its outstanding performances.

Electrostatic capacitor based on dielectric materials is a crucial component for electronic devices, with ultrahigh power density (up to 10^8 W kg^{-1}) and high reliability. This facilitates its great potential in super-high-power electronics and systems, such as hybrid electric vehicles, medical defibrillators, spacecraft, satellites, and electrical weapon systems. In particular, films with smaller dimensions could possibly meet the continuous advancement of miniaturized electronics. Nevertheless, the relatively low energy storage density of dielectric capacitors, approximately an order of magnitude less than that of batteries, fuel cells, and electrochemical capacitors, lays limitations on their practical applications. After decades of intensive research, perovskite oxide films, more than ever, seem destined for a great future, with the energy-storage density achieving beyond 200 J cm^{-3} as recently reported. Documented in Science, the groundbreaking research conducted by Li's group explored a novel mechanism to achieve enhanced energy storage performance in $Bi(Mg_{0.5}Ti_{0.5})O_3$-(Sr, Bi)TiO_3 systems.[1]

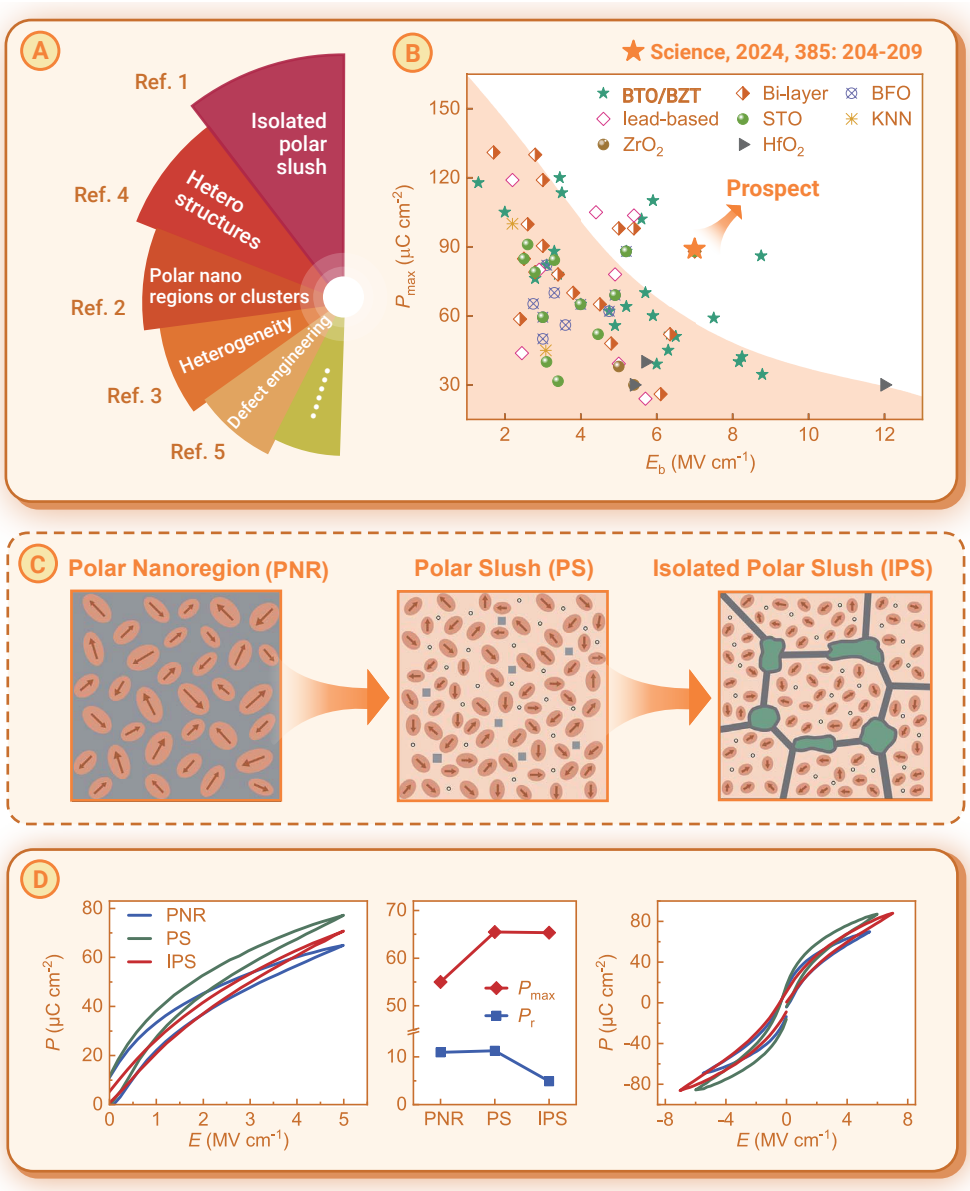

Figure 1. Design route of achieving high energy storage density (A) Documented strategies for achieving large ΔP or high E_b to enhance energy storage density;[1-5] (B) The trade-off relationship between P_m and E_b. The abbreviations BTO, BZT, BFO, STO, and KNN denote for $BaTiO_3$, Ba(Zr, Ti)O_3, $BiFeO_3$, (Bi,Na)TiO_3, and (K,Na)NbO_3, respectively; (C) The schematic of incorporating isolated polar-slush strategy; (D) The documented *P-E* loops of the current study involving three different types of films.

The recoverable energy-storage density, U_e, and the energy-storage efficiency, η, of a dielectric material can be respectively described by:

$$U_e = \int_{P_r}^{P_m} EdP$$

$$\eta = \int_{P_r}^{P_m} EdP \Big/ \int_{0}^{P_m} EdP$$

where P_m and P_r respectively denote the maximum and remnant polarizations, respectively. E is the applied electric field on the material. Therefore, there are two critical ways toward achieving large energy storage density: engineer a large reversible polarization ($\Delta P = P_m - P_r$) and a high breakdown field (E_b). Therein, the as small P_r is crucial for enhancing the energy storage efficiency.

In the family of dielectric materials, ferroelectrics exhibit excellent P_m and serve as an ideal foundation for achieving high energy storage. Previous strategies to optimize both their exceptional P_m and reduced P_r have focused on introducing chemical heterogeneity (Figure 1A). This promotes the formation of polar nano-regions (PNRs), which are nanoscale polar domains (5-10 nm in size) embedded within a nonpolar matrix, leading to weakened local polarizations. It facilitates the relaxor characteristic of the ferroelectric and

subsequently enhanced the energy storage density and efficiency. This strategy has been proven effective in further increasing both the ΔP and E_b by a reduction of the domain size to 2-5 nm of the PNRs, and lead to an enhancement of U_e and η to 112 J cm^{-3} and 80%, respectively Moreover, a further reduction of the domain size to 1-2 nm enables an energy storage density and efficiency of 152 J cm^{-3} and 77% in Sm-doped $BiFeO_3$-$BaTiO_3$ film, respectively.[2] It is worth noting that along this avenue, with reduction of the polar domain size, the domain volume fraction would unavoidably decrease, for instance, in the aforementioned Sm-doped $BiFeO_3$-$BaTiO_3$ film, a domain volume fraction of only 15% is observed. This would result in the suppression of P_r, but also simultaneously lead to a reduction in the P_m.

Therefore, P_m and E_b are typically inversely correlated with each other in a number of relaxor ferroelectric systems studied so far (Figure 1B). This is primarily due to the increased electrostatic energy near the surface, attributed to the larger P_m, which accelerates the breakdown of the film. Additionally, ways that benefit polarization saturation, such as large grain growth during film crystallization, are typically detrimental to their resistivity. Therefore, previous studies have focused on reducing grain size and increasing insulating components, like grain boundaries, to suppress conductivity in the material.

In the current work reported by Li et. al., the PNR strategy is reinforced by transforming polar domains embedded in nonpolar matrix into slush-like polar domains embedded in polar matrix (referred to as polar clusters) (Figure 1C). This strategy is demonstrated in relaxor ferroelectric $Bi(Mg_{0.5}Ti_{0.5})O_3$–(Bi, Sr)TiO_3 –extra Ti 25%. The nonpolar phase within relaxor films is suppressed to create a slush-like polar state, featuring adequate domain volume fraction while maintaining the polar cluster size at only several unit cells to nanometers. Forming isolated polar slushes, the P_m surpasses 70 μC cm^{-2}, while the P_r is also greatly reduced to approximately 5 μC cm^{-2} (Figure 1D), enabling the improvements of U_e and η. The highest recorded U_e and η in Li's report achieved 202 J cm^{-3} and 79%.

The proposed partitioning polar-slush strategy also enables the construction of highly insulating networks to isolate the slush-like polarization, which meanwhile benefits the enhancement of E_b. It relies on the proportion increase of amorphous component in a material, a concept drew on polymer ferroelectrics which normally shows prominent breakdown strength. The work by Li presents the construction of isolating polar slush by adding an excess of Ti (e.g., 25%), which not only enables a high P_m, but also a superior electrical breakdown in materials with relatively simple chemical compositions. As a result, for a binary solid solution, this approach shifts the trade-off between P_m and E_b to the top-right corner, yielding unprecedented energy storage performance. This method is applicable to simpler compositions, offering an alternative to the recently proposed configurational entropy enhancement strategy, which aims to suppress resistivity and improve the breakdown field.[3] Unlike the entropy-based approach, which typically requires highly complex cation species, this method maintains simplicity in composition.

In addition, the reliability and stability of the documented energy-storage performance are exceptional. At a moderate electric field of 2.5 MV cm^{-1}, accelerated charge–discharge testing showed a variation in U_e of ~ 7% and in η of ~ 1% over 1 × 10^7 cycles, which is an order of magnitude better than films with only PNRs, without the polar slush strategy. The thermal stability is also impressive, with only a minor change in U_e and η (within 5%) across a temperature range of 25 to 225°C. These characteristics are critical for practical dielectric capacitor applications.

Most importantly, this work explores large-scale fabrication using the chemical solution deposition technique, which is well-suited for the 4-inch Si industry standard. The films demonstrate excellent uniformity in terms of thicknesses, U_e, and η, facilitating the seamless integration of the studied micro-capacitors for potential on-chip energy storage in the semiconductor industry. This is crucial for various applications, including distributed power systems, electric firing systems, hybrid electric vehicles, laser and radar technologies.

REFERENCES

1. Shu, L., Shi, X., Zhang, X., et al. (2024). Partitioning polar-slush strategy in relaxors leads to large energy-storage capability. Science **385**: 204–209. DOI: 10.1126/science.adn8721.
2. Pan, H., Lan, S., Xu, S., et al. (2021). Ultrahigh energy storage in superparaelectric relaxor ferroelectrics. Science **374**: 100–104. DOI: 10.1126/science.abi7687.
3. Yang, B., Zhang, Q., Huang, H., et al. (2023). Engineering relaxors by entropy for high energy storage performance. Nat. Energy **8**: 956–964. DOI: 10.1038/s41560-023-01300-0.
4. Cheema, S.S., Shanker, N., Hsu, S.-L., et al. (2024). Giant energy storage and power density negative capacitance superlattices. Nature **629**: 803. DOI: 10.1038/s41586-024-07365-5.
5. Kim, J., Saremi, S., Acharya, M., et al. (2020). Ultrahigh capacitive energy density in ion-bombarded relaxor ferroelectric films. Science **369**: 91–94. DOI: 10.1126/science.abb0631.

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AUTHOR CONTRIBUTIONS

L.L wrote the manuscript with input from J.Z. and Y.W., Y.W. supervised the project.

DECLARATION OF INTERESTS

The authors declare no competing interests.