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Commentary

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High entropy design: a new pathway to promote the piezoelectricity and dielectric energy storage in perovskite oxides

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Intrinsic polarization is an important property that distinguishes ferroelectric materials from others. Tuning the polarization configuration is crucial for promoting the electric performance, including the piezoelectric and dielectric properties. For example, the traditional strategy of constructing phase boundaries, including morphotropic phase boundaries (MPBs) and polymorphic phase boundaries (PPBs), is usually adopted to tune the polarization configuration with coexisting multiple ferroelectric phases to cause a more flexible polarization configuration than that of a single phase, resulting in higher ferroelectricity or piezoelectricity[1-5]. To enhance the energy storage performance of ferroelectrics, macrodomains with an ordered configuration due to long-range polarization are generally broken by tuning the polarization configuration to nanodomains or polar nanoregions (PNRs)[6-8]. These approaches, however, have limited degrees of freedom in further tuning the polarization configuration and improving electrical performance. "High entropy" is a new materials design strategy developed in the 1980s-1990s, but only recently realized in high-entropy alloys in 2004 by Yeh *et al.*[9], and was gradually extended into the fields of metal carbides and oxides[10,11]. Its excellent high-entropy effect increases the disorder of a system by forming solid solutions of multi-component elements, effectively controlling various properties benefiting from the entropy-

dominated phase stabilization, atomic disorder with lattice distortion, sluggish diffusion kinetics and property synergy from multiple components[12-16]. Recently, Chen's group proposed a high-entropy strategy to successfully promote piezoelectric and energy storage performance in perovskite oxide ceramics by tuning the polarization configuration [*Acta Mater.* 236 (2022) 118115 - high entropy piezoelectrics $Pb(Ni,Sc,In,Ti,Nb)O_3$[17]; *Nat. Commun.* 13 (2022) 3089 - high entropy dielectric $(K,Na,Li,Ba,Bi)(Nb,Sc,Hf,Zr,Ta,Sb)O_3$[18]], opening up new ideas for high-entropy piezoelectrics and high-entropy energy storage materials.

It is well known that different elements have different valence states, ionic radii, electronic configurations, electronegativity and polarizabilities. In recent studies, the high-entropy concept has been tuned to enable various elements, such as Ni^{2+}, Mg^{2+}, Sc^{3+}, Yb^{3+}, In^{3+}, Zr^{4+}, Hf^{4+}, Ti^{4+}, and Nb^{5+}, to simultaneously occupy equivalent lattice sites, such as *B*-sites, in perovskites to enhance the local polarization fluctuation as much as possible, achieving the effect of increasing entropy[17]. After introducing multiple components, as shown in Figure 1A, large-scale transition regions (green color) that are spread out over the whole area demonstrate the high flexibility of this unique polarization configuration. An almost even distribution of polarization angles (θ) over the whole range of 0-45° can be observed in the statistical results [Figure 1B], breaking the constraints of crystallographic symmetry and promoting the polarization rotation under excitation by an electric field[19]. From another perspective, the unique polarization configuration can be considered as coexisting multiple monoclinic phases with different θ values on the atomic scale, which play a bridge-like role between the polarizations of different phases[20], facilitating the flexible rotation between different phases under electric fields. Benefiting from this unique polarization configuration caused by increasing configuration entropy, an ultrahigh piezoelectric coefficient (d_{33}) of ~1210 pC/N can be achieved in the multi-component perovskite ceramics [Figure 1C].

A local diverse polarization configuration can greatly enhance the polarization response rate under electric fields, leading to high W_{rec} and efficiency η in energy storage capacitors[21]. Chen's group introduced the high-entropy concept into KNN-based ceramics and designed "local polymorphic distortion" to tune the local diverse polarization configuration with coexisting rhombohedral - orthorhombic - tetragonal - cubic (R-O-T-C) multiphase nanoclusters [Figure 1D][18]. Notably, the cations (Li^{+}, Ba^{2+}, Bi^{3+}, Sc^{3+}, Hf^{4+}, Zr^{4+}, Ta^{5+}, Sb^{5+}) introduced by the high entropy strategy take into account the substitution on *A*-sites and *B*-sites in perovskites, greatly enhancing the occupancy disorder and perturbation of the polarization. Meanwhile, the cations are also considered as additives used to tailor the phase transition temperatures T_{R-O}, T_{O-T}, and T_{T-C} to construct room-temperature R-O-T-C multiphase nanoclusters coexisting at the local scale. Compared with the dielectrics with single-phase and coexisting two-phase polarization configuration, the high-entropy sample exhibited smaller and more diverse PNRs with weak correlation embedded in the nonpolar cubic phase, providing higher η and delayed polarization saturation under electric fields. In addition, different types of oxygen octahedral distortions exist in different nanophases, which would introduce coexisting multiple randomly-distributed oxygen octahedral tilts, further breaking the local polarization order. As a result, high-entropy designed KNN-based ceramics with local polymorphic distortion achieved breakthroughs in the ultrahigh W_{rec} (≥ 10 J cm^{-3}) and ultrahigh η (≥ 90%) for lead-free ceramics for the first time [Figure 1E]. The results demonstrate that high-entropy design opens a new avenue to enhance electrical performance by tuning the polarization configuration.

The multiple components introduced by high entropy can cause significant local compositional disorder and random fields, resulting in flexible and diverse local polarization configurations in both high-entropy piezoelectrics and high-entropy energy storage dielectrics. It has to be mentioned that the various elements introduced by the high-entropy strategy endow the material with more performance control freedom and

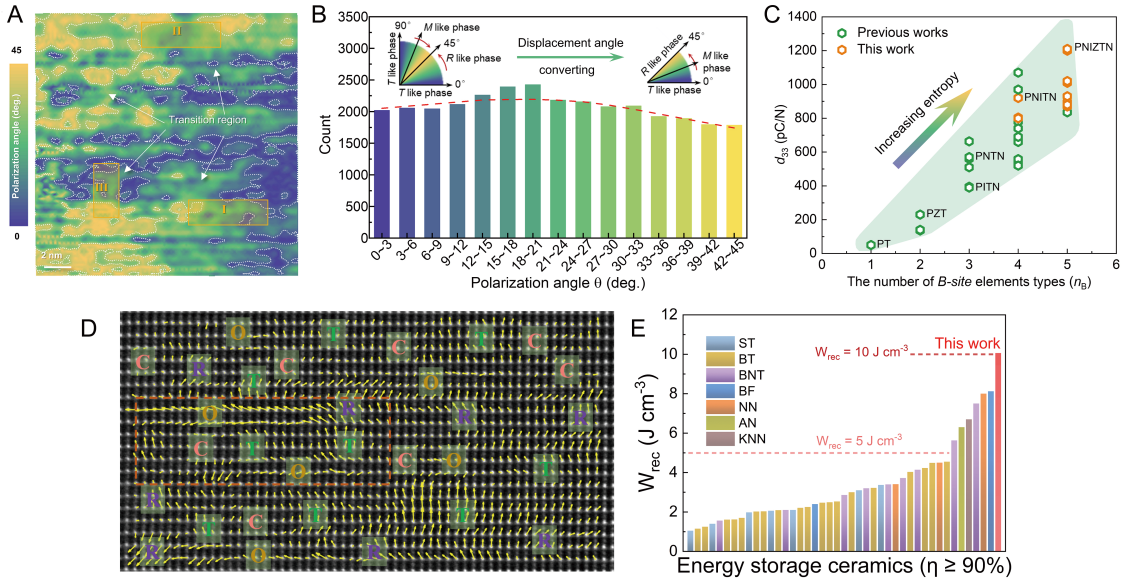

Figure 1. (A) Contour map of the distribution of polarization angles (θ). (B) Statistics of the distribution of θ in the range of 0°-45°, extracted from over 30, 000 polarization vectors. (C) Strong correlation between d_{33} and the number of *B*-site element types (n_B) for a series of PbBO_3-based solid solutions. Reproduced with permission from[17], Copyright 2022, Elsevier. (D) Atomic-resolution high-angle annular dark field - scanning transmission electron microscopy (HAADF STEM) polarization vector image along $[110]_c$. (E) Comparison of the recoverable energy storage density, W_{rec} (efficiency, $\eta \geq 90\%$), of (K,Na)NbO_3 (KNN)-based high-entropy ceramic with other representative lead-free bulk ceramics with $W_{rec} \geq 1$ J cm^{-3}. Reproduced with permission from[18], Copyright 2022, Nature Publishing Group.

control methods, rather than a single ferroelectric/piezoelectric performance improvement. We believe that high-entropy design will become an important way to enhance the electrical properties of perovskite materials, enriching the design of material components thanks to the rapid development of machine learning and materials genome engineering.

DECLARATIONS

Authors' contributions

The author contributed solely to the article.

Availability of data and materials

Not applicable.

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Conflicts of interest

The author declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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