

Atomic solvent for tailorable high-entropy ceramics synthesis

Xiaoping Zhou

zhouxiaoping@cqu.edu.cn

Chongqing University <https://orcid.org/0000-0003-1551-6504>

Zheng Luo

Chongqing University <https://orcid.org/0009-0008-3832-6176>

Lunshi Zhou

Stanford University

Junwei Chen

Wuhan University

Dongsheng He

Southern University of Science and Technology

Physical Sciences - Article

Keywords:

Posted Date: March 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-8814062/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: There is **NO** Competing Interest.

Atomic solvent for tailorable high-entropy ceramics synthesis

Zheng Luo¹, Lunshi Zhou², Junwei Chen³, Dongsheng He⁴, Xiaoping Zhou^{1,3*}

¹School of Civil Engineering, Chongqing University, Chongqing 400045, China;

²School of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305, USA;

³School of Civil Engineering, Wuhan University, Wuhan 430072, China;

⁴Core Research Facilities, Southern University of Science and Technology, Shenzhen 518055, China

Abstract

High-entropy ceramics (HECs) exhibit important potential as functional materials due to their tunable compositional variations and unique lattice distortions. However, conventional HECs synthesis requires extreme temperatures, often leading to volatilization of low-melting-point elements and imprecise composition control. Herein, we propose a Galinstan atomic solvent strategy for the synthesis of HECs by rapidly altering the ceramics composition through the liquid metals (LMs) interface and the metal salt solution interface reactions at low temperatures (60°C). LMs is used as a dynamic solvent to increase configurational entropy and produce strong negative configurational entropy, providing a strong thermodynamic driving force for uniformity and phase stability. In-situ liquid-cell transmission electron microscopy observation directly captures the dynamic formation process, showing the elements' absorption and mixed crystal coprecipitation. Thermodynamic theory and density functional theory computations confirm that systems incorporating Galinstan exhibit a 1.61-fold enhancement in the reduction of the Gibbs free energy of mixing. Notably, perovskite, rock-salt, and pyrite crystal structures can be tuned through ion substitution, enabling tailored applications in electrocatalysis, ultra-high temperature insulation, and thermoelectric sensors. Hence, the atomic solvent strategy provides a generalizable platform for designing HECs, enabling the realization of tailored phases optimized for specific applications.

1. Introduction

High-entropy ceramics (HECs) are single-phase materials formed by incorporating five or more elements within a single crystalline lattice¹⁻³. The high configurational entropy arising from atomic-scale

* Corresponding author

Email: zhouxiaoping@cqu.edu.cn. Tel./Fax: +86-23-6512-3511

compositional disorder thermodynamically stabilizes phases otherwise inaccessible under equilibrium conditions^{4,5}. These materials exhibit elemental synergy, tunable composition, and distinctive lattice distortion, offering broad potential for applications in capacitors^{3,6}, aviation components^{7,8}, and energy conversion⁹. Although recent researches suggest that entropy-driven synthesis^{10,11} can produce HECs with huge differences in atomic size, it requires extremely high temperatures to retain the high-entropy state during quenching. This often leads to volatilization of low-melting-point elements, making it difficult to synthesize HECs with controlled crystal structures and precise elemental compositions. Although wet chemical methods^{12,13} can synthesize HECs under mild temperatures, they are primarily suitable for combinations of elements that are miscible, sharing similar atomic radii, oxidation states, and electronegativities. Therefore, developing a mild synthesis strategy with broad elemental compatibility is essential to produce tailored HECs.

The formation of phases in HECs is controlled by the mixing Gibbs free energy: $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, where ΔH_{mix} is the configurational enthalpy, ΔS_{mix} is the configurational entropy, and T is the temperature. Recent synthesis strategies^{10,11,14} use equimolar compositions to emphasize the maximization of entropy but ignore enthalpy contribution. Configurational enthalpy reflects the affinity between elements, and lowering this enthalpy provides another important route to reduce Gibbs free energy. Moreover, during the synthesis process, a liquid phase environment is generally regarded as ideal for the synthesis of HECs. Nanodroplets of liquid metals (LMs) Galinstan (eutectic gallium-indium-tin alloy), and ionic precursor solutions offer an ideal medium for HECs synthesis. Notably, the negative configurational enthalpy between the LMs Galinstan and other metal elements enhances their mutual affinity. This promotes the dynamic incorporation of diverse elements within the liquid phase medium, facilitating the formation of HECs. Hence, LMs Galinstan can serve as an effective atomic solvent for preparing HECs under mild conditions. Its ability to homogenize elements of differing atomic sizes in the liquid phase makes it a promising medium for facilitating HECs synthesis.

In this work, we propose an atomic solvent strategy for synthesizing single-phase HECs under mild conditions to prepare custom-structured HECs with special functionalities. Using LMs Galinstan as a dynamic solvent, this proposed method increases the configurational entropy and endows the structure with negative configurational enthalpy, providing the thermodynamic driving force for the formation of homogeneous phases. In-situ liquid-cell transmission electron microscopy (TEM) observation directly captures the dynamic formation process, showing the elements' absorption and mixed crystal coprecipitation. Thermodynamic theory and density functional theory (DFT) calculations confirm the

mechanism, wherein Galinstan-containing HECs exhibit a 1.61-fold reduction in ΔG_{mix} compared to gallium (Ga)-containing HECs. This proposed method enables the synthesis of diverse HECs with perovskite, rock-salt, and pyrite crystal structures. Perovskite HECs exhibit bifunctional electrocatalytic activity in 1 M KOH, requiring overpotentials of 186 mV for oxygen evolution reaction (OER) and 31 mV for hydrogen evolution reaction (HER) at $10 \text{ mA}\cdot\text{cm}^{-2}$, with Tafel slopes of $39.7 \text{ mV}\cdot\text{dec}^{-1}$ and $89.2 \text{ mV}\cdot\text{dec}^{-1}$. Rock-salt and pyrite HECs demonstrate exceptional potential for high-strength thermal barrier materials and thermoelectric sensing. Hence, this atomic solvent strategy establishes a generalizable platform for designing application-specific HECs with tailored crystal structures.

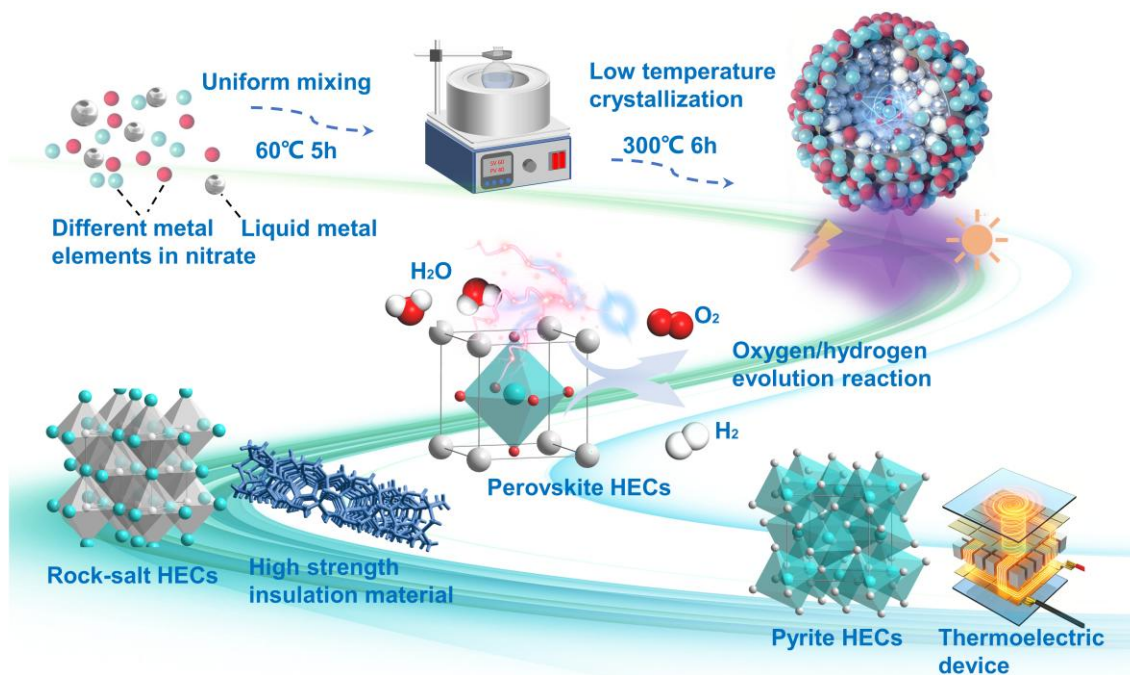


Fig. 1 | Schematic illustration of atomic solvent synthesis strategy for tailorable HECs. The electrocatalysis, high-strength thermal barrier materials, and thermoelectric sensing applications are also exhibited.

2. Results

2.1. Principles of atomic solvent

In this work, the synthesis of functionalized HECs with diverse metallic compositions is achieved using LMs as a reaction medium at 300°C . Fig. 1 shows the atomic solvent strategy for synthesizing HECs by rapid compositional changes at mild temperatures. HECs form by a modified solvothermal self-assembly method at 60°C , followed by calcination at 300°C to yield HECs with high crystallinity. In Step I, the native Ga_2O_3 layer on the LMs surface undergoes hydroxylation in a polar solvent mixture (ethylene

glycol/isopropanol), forming amphoteric Ga–OH groups^{15,16}. Under mildly acidic conditions from NH₄F hydrolysis, these groups deprotonate ($Ga - OH \rightarrow Ga - O^- + H^+(aq)$), imparting a net negative surface charge¹⁵. According to electric double-layer theory^{17,18}, the charged interface electrostatically attracts metal cations (e.g., Fe²⁺, Co²⁺, and Ni²⁺), enriching them at the interface between LMs and polar solvent. This creates localized reaction zones where ion concentrations exceed bulk levels by orders of magnitude, accelerating the subsequent reduction and coprecipitation kinetics.

In Step II, adsorbed metal cations (e.g., Fe²⁺, Co²⁺, Ni²⁺) are reduced to zero valence by borohydride (NaBH₄). Within milliseconds, reduced metal atoms dissolve into LMs nanodroplets, achieving atomic-scale homogeneity among Ga, In, Sn, and incorporated metals (e.g., Fe²⁺, Co²⁺, Ni²⁺) by ultrafast diffusion. This behavior of LMs dissolving metallic elements has been demonstrated in hydrogen-reduction powder metallurgy¹⁹. This forms a thermodynamically stabilized short-range ordered phase. Dissolution is exothermic due to negative configurational enthalpies between reduced metals and LMs, increasing system entropy. The coupled reduction-dissolution process proceeds spontaneously. Liquid phase atomic diffusivity exceeds solid-phase values by >10¹⁰-fold, enabling homogenization within seconds. With five or more principal elements at near-equimolar ratios, configurational entropy (ΔS_{mix}) is maximized. According to the Gibbs free energy equation, $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, a sufficiently high ΔS_{mix} can dominate over a slightly positive ΔH_{mix} , resulting in a negative ΔG_{mix} and thus a thermodynamically stable multi-element phase.

In Step III, fluoride ions (F⁻) from NH₄F and KF diffuse to the metal-enriched precursor interface. F⁻'s high affinity for metals initiates an amorphous fluoride intermediate. A chemical potential gradient at this interface drives crystallization. High configurational entropy suppresses nucleation of simple binary/ternary phases (e.g., KFeF₃, K(FeCo)F₃), favoring entropy-stabilized nuclei that incorporate all elements into a single crystal structure (e.g., perovskite KMF₃, M = Fe, Co, Ni, Mn, Ga, In, Sn). These entropy-stabilized nuclei become the dominant phase. During crystallization, K⁺ ions occupy the top corner site of the perovskite cube, while the transition metals and LMs are randomly distributed at the center sites of the cube. Lattice distortions are compensated by high configurational entropy, preventing phase segregation. Calcination at 300°C yields highly crystalline HECs.

2.2. Phase selection via valence and coordination control

Perovskite, rock-salt, and pyrite HECs are synthesized by an atomic solvent strategy, with each phase defined by the oxidation states of the cations and the coordination of the anions. In the

$\text{K}(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{F}_3$ perovskite fluoride, transition metals and LMs maintain stable oxidation states at the center sites (Fig. 2B), which yields a phase-pure perovskite structure. Its X-ray diffraction (XRD) pattern exhibits a cubic perovskite structure (space group $Pm\bar{3}m$, Powder Diffraction File (PDF) #72-0110, Fig. 2A). The agreement between the experimental XRD pattern and the PDF data confirms complete crystallization upon calcination. A uniform elemental distribution of K, Fe, Co, Ni, Mn, Ga, In, Sn, and F elements in perovskite HECs is confirmed by high-resolution TEM (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) mapping, with an atomic ratio of 24.61 : 6.90 : 7.55 : 7.29 : 6.92 : 6.35 : 2.82 : 1.64 : 35.92 (Fig. 2C, 2D, and Supplementary Fig. 1). Inductively coupled plasma-mass spectrometry (ICP-MS) analysis further confirms that the composition deviates from the target value by less than 0.8% (Supplementary Table 5). Quantitative analysis of the inverse fast Fourier transform (IFFT) and selected-area electron diffraction (SAED) patterns confirms the single-crystalline nature. The measured d-spacing of the (012) plane is 0.15 nm, which is consistent with the XRD-derived value (Fig. 2E–2G). Furthermore, this proposed method also works for HECs containing elements of very different sizes. Although Hume–Rothery rules²⁰ suggest that atoms with radius differences over 15% do not easily form solid solutions, we synthesize perovskite HECs using elements like K (203 pm) and F (64 pm), whose radius differences exceeding 217%. This outcome highlights LMs' unusual ability to dissolve and blend atoms that would not normally mix in solid/liquid-state processes.

In the rock-salt carbide HECs, the combination of early transition metals (Hf, Ta, Nb, Mo) in mixed oxidation states (+2 to +4) with LMs stabilizes a single-phase cubic structure, $(\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Mo}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{C}$, where all cations occupy octahedral sites coordinated by carbon anions (Extended Data Fig. 1B). Its XRD pattern matches the $Fm\bar{3}m$ rock-salt structure (PDF# 38-1364, Extended Data Fig. 1A). Homogeneous elemental distribution is demonstrated by HRTEM and EDS analysis (Extended Data Fig. 1C, 1D, and Supplementary Fig. 2). ICP-MS confirms that the actual composition is within 0.6% of the theoretical value (Supplementary Table 6). Furthermore, electron microscopy images reveal the high crystallinity of the material, and the corresponding SAED pattern verifies its rock-salt crystal structure (Extended Data Fig. 1E–1G).

For pyrite sulfide HECs, the strategy leverages the preference of mixed-valence transition metal ions for octahedral coordination with disulfide (S_2^{2-}) pairs. Many octahedra share edges to form a typical cubic framework (Extended Data Fig. 2B). Synthesize high-entropy sulfides $(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cr}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{S}_2$ is formed in the pyrite structure (space group $Pa\bar{3}$) and matches the reference pattern PDF#83-1455 (Extended Data Fig 2A). ICP-MS chemical analysis shows that the

degree of deviation of the composition from the theoretical target is less than 0.55% (Supplementary Table 7). HRTEM imaging and EDS Mapping confirm the uniform element distribution of the particles at the microstructural level (Extended Data Fig. 2C, 2D, and Supplementary Fig. 3). The HRTEM image shows continuous lattice fringes. The SAED pattern again confirms the structure of single-phase pyrite, and the deviation between the measured interplanar spacing and the X-ray diffraction result is within 0.7% (Extended Data Fig. 2E–2G).

There is a common electronic stabilization mechanism²¹ in X-ray photoelectron spectroscopy (XPS) in HECs. Metals (Fe, Co, Mn, Cr, Ta, Nb) have multiple oxidation states²² to dynamically compensate for charges (Fig. 2H–2O, Extended Data Fig. 1H–1M, Extended Data Fig. 2H–2O, and Supplementary Figs. 4–6). For instance, Fe is present as both Fe^{2+} and Fe^{3+} , and Co as both Co^{2+} and Co^{3+} . This electronic flexibility accommodates extreme compositional complexity without compromising single-phase integrity.

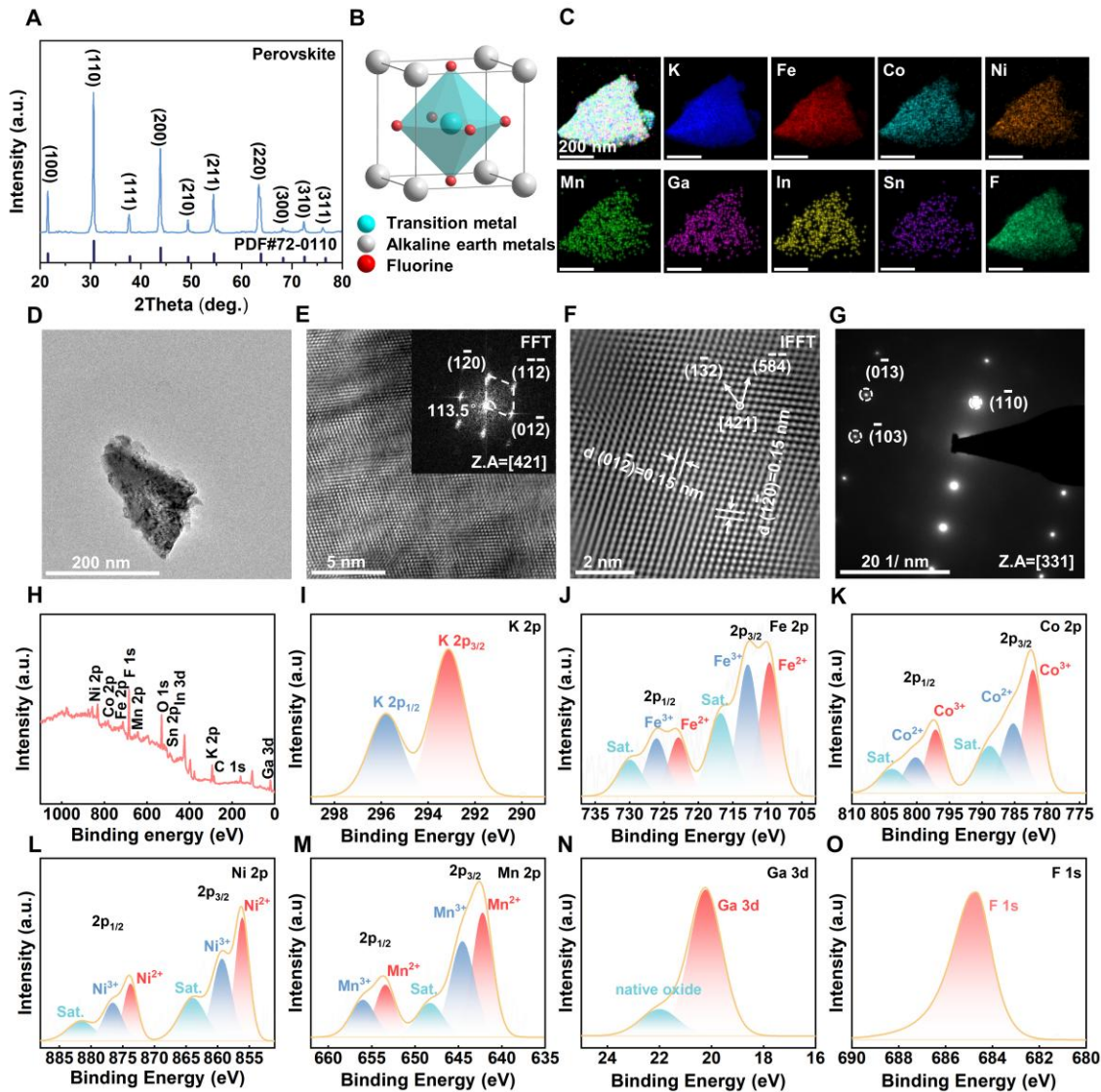


Fig. 2 | Structural and chemical characterization of perovskite HECs. **A**, XRD pattern confirming phase purity (cubic, $Pm\bar{3}m$). **B**, Schematic of the perovskite lattice. **C**, EDS elemental maps showing homogeneous distribution of all constituent elements (K, Fe, Co, Ni, Mn, Ga, In, Sn, and F). **D**, TEM image. **E**, HRTEM image. **F**, IFFT lattice images for perovskite HECs. **G**, SAED pattern along the (331) zone axis. **H**, XPS analysis of perovskite HECs. High-resolution XPS spectra of **(I)** K 2p, **(J)** Fe 2p, **(K)** Co 2p, **(L)** Ni 2p, **(M)** Mn 3p, **(N)** Ga 3d, and **(O)** F 1s.

2.3. In situ TEM dynamics

To elucidate the real-time formation mechanism of HECs via the atomic solvent strategy, we perform in-situ observations using an environmental aberration-corrected transmission electron microscope equipped with a liquid-cell at 60°C. Our designed microfluidic liquid-cell contains the complete reaction mixture (Galinstan nanodroplets, transition metal precursors, and fluoride sources in ethylene glycol/isopropanol

solvent). This setup enables real-time visualization of the transformation from liquid precursors to the $\text{K}(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{F}_3$.

Time-resolved imaging sequences capture dynamic evolution in elemental absorption and mixed crystal coprecipitation (Fig. 3A–3H). At $t = 0$ s, isolated spherical Galinstan nanodroplets (with a diameter of approximately 180 nanometers) are dispersed in a polar solvent mixture, presenting a high-contrast black region relative to the light gray solution background (Fig. 2A). The initial state is consistent with Step I. The high hydroxylation of the natural Ga_2O_3 layer generates amphoteric $\text{Ga}-\text{OH}$ groups. This produces a negatively charged interface, attracting metal cations (Fe^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+}). At $t = 100$ s, the liquid droplet density contrast increases, and aggregation and merging driven by surface tension begin, forming larger aggregates of irregular shape (Fig. 2B). This fusion matches the rapid reduction and dissolution kinetics of Step II. The adsorbed metal cations are reduced by NaBH_4 , and the zero-valent metals enter the Galinstan matrix within milliseconds. The homogenization process in the liquid phase occurs more than 100 times faster than in the solid phase through ultrafast diffusion. Electron energy loss spectroscopy (EELS) analysis at 100 second show that K, Fe, Co, Ni, Mn, Ga, In, and Sn elements' signals are concentrated in the black area (Supplementary Fig. 7). Metal elements are mixed at the atomic level to form precursors of thermally stable short-range ordered solid solutions. At $t = 200$ s, all coalesced liquid droplets start nucleation, and uniform nanoscale precipitates within the droplets are confirmed (Fig. 3C). In Step III, F^- from NH_4F , and KF diffuses to the interface, and amorphous fluoride intermediates begin to form. Chemical potential gradients promote crystallization, high configurational entropy suppresses the nucleation of simple binary/ternary phases (such as KFeF_3), and helps guide the direct generation of high-entropy nuclei. EELS analysis at 200 second show the presence of F in the crystal, an element not detected at 100 s, concurrently with signals from other metal elements (Supplementary Fig. 8). Starting from 300 s, the precipitation grows rapidly, forming a continuous crystal network in the solvent (Fig. 3D–3H). The change in this microstructure indicates a transition from isolated particle growth to a diffusive collective crystallization front.

Atomic-resolution HRTEM is used to verify the crystal structure of HECs. Imaging along the $[421]$ zone axis of the perovskite phase has obvious cubic symmetry (Fig. 3I). The d-spacing is measured by lattice fringes and agrees with the expected value of the $Pm\bar{3}m$ space group. The corresponding fast Fourier transform (FFT) pattern shows sharp diffraction spots in a square grid, confirming the long-range crystal order. Imaging along the $[111]$ zone axis, the rock-salt structure has a hexagonal atomic row arrangement of the face-centered cubic lattice (Figure 3J). Its FFT pattern has higher-order reflections

characteristic of the face-centered cubic lattice along the $[111]$ zone axis, such as (022), (220), and (202). The pyrite phase has a simple cubic symmetry with the $Pa\bar{3}$ space group (Fig. 3K). The FFT pattern has reflections such as (021), (020), and (001), which match the pyrite structure.

Dynamic cation exchange during LMs medium helps crystallization²³ makes metal atoms uniformly at the atomic level. In Fig. 3L, transition, alkaline earth, and post-transition elements are incorporated into the fluoride lattice to construct a dynamic cation exchange environment. Taking metal cation vacancies as exchange points promotes rapid lattice substitution and continuous atomic rearrangement. This vacancy-mediated mechanism²⁴ can achieve uniform element distribution at the atomic scale near room temperature. The resulting high configurational entropy thermodynamically stabilizes these metastable high-entropy phases, thereby circumventing the kinetic barriers inherent to conventional solid-state synthesis.

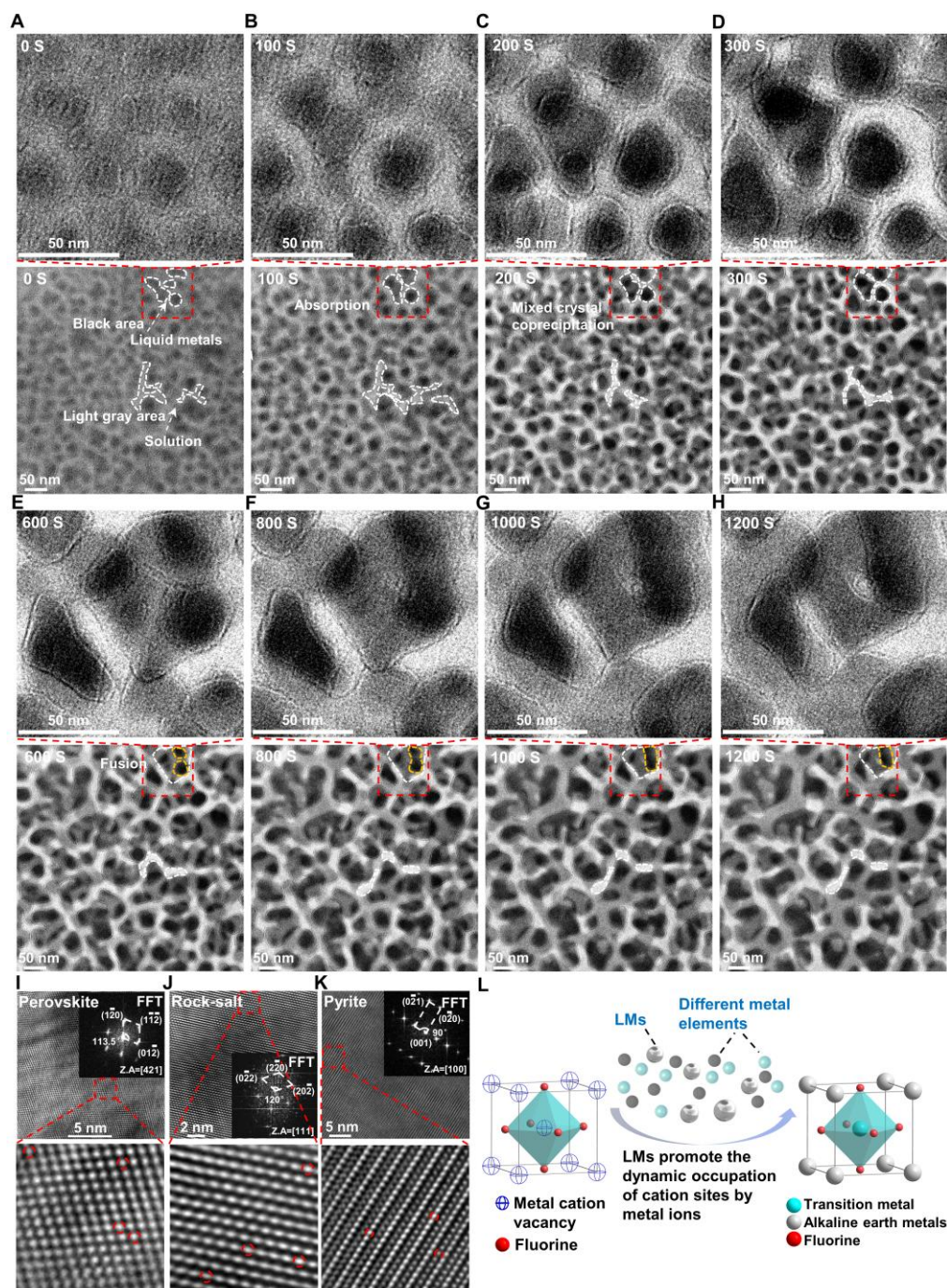


Fig. 3 | Mechanisms of atomic solvent for the formation of HECs shown through in situ liquid-cell TEM at 60 °C. A to H, Sequential in situ TEM images capture the formation of $\text{K}(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{F}_3$ within a liquid environment at 60°C. HRTEM images of (I) perovskite, (J) rock-salt, and (K) pyrite crystal structures. Z.A represents the zone axis. The difference in atomic size within the red dashed circle indicates lattice distortion in HECs. L, Schematic illustration depicting LMs facilitating the adaptive occupation of metal ions at cation sites.

2.4. Mechanism of liquid metals as atomic solvents

The thermodynamic theory for enhanced atomic-level mixing and suppressed phase separation in HECs is governed by fundamental formation parameters. According to the Gibbs free energy equation, $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, thermodynamically stable multi-element phases form when a high ΔS_{mix} combines with a negative ΔH_{mix} to yield a negative ΔG_{mix} . This work demonstrates that LMs, particularly eutectic Galinstan, function as atomic solvents that favorably modulate both parameters, enabling single-phase HECs formation at exceptionally low temperatures.

XRD analysis provides direct experimental evidence for this effect (Extended Data Fig. 3A–3C). Crystalline perovskite fluorides, rock-salt carbides, and pyrite sulfides are obtained by Galinstan-assisted synthesis at temperatures as low as 300°C. Similarly, synthesis using only Ga requires temperatures around 450°C to achieve comparable crystallinity. This difference arises because Galinstan (melting point –19°C) remains liquid at room temperature, whereas pure Ga (melting point 29.8°C²⁵) is solid under room temperature. A single-phase (Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C²⁶ high-entropy carbide can only be obtained via hot pressing at 1800°C when the LMs-free synthesis is employed. HECs containing Galinstan have clear diffraction peaks and match the reference pattern completely. EDS, HRTEM, and SAED also confirm long-range order and atomic-level uniformity (Fig. 2, Extended Data Fig. 1, and Extended Data Fig. 2).

These single-phase structural features are related to the reduction of the thermal barrier. The ΔH_{mix} of three systems is calculated using DFT, and the LMs make the ΔH_{mix} value more negative (Supplementary Table 1). The ΔH_{mix} of K(Fe_{0.2}Co_{0.2}Ni_{0.2}Mn_{0.2}Ga_{0.14}In_{0.04}Sn_{0.02})F₃ containing Galinstan is –4.7 kJ·mol^{–1}. Similarly, the ΔH_{mix} of K(Fe_{0.2}Co_{0.2}Ni_{0.2}Mn_{0.2}Ga_{0.2})F₃ containing Ga is –4.8 kJ·mol^{–1}. Conversely, the ΔH_{mix} of K(Fe_{1/4}Co_{1/4}Ni_{1/4}Mn_{1/4})F₃ without LMs is relatively larger, which is –0.8 kJ·mol^{–1}. This trend is present across all three structural categories, and the ΔH_{mix} of HECs containing Galinstan is up to 500% higher than those without LMs. Besides, the binary interaction energy is used to clarify atomic solvation. The pairwise energy between LMs Ga and other metals²⁷ is more negative than when the other metals exist alone (Table 1). The strong interaction reduces the energy barrier of element integration and promotes atomic-level mixing. The negative ΔH_{mix} values for interactions between Ga, In, Sn, and various metallic elements confirm thermodynamically favorable pairing (Supplementary Tables 2–4), suggesting this synthesis strategy can be extended to other LMs with similar properties.

Table 1 | Binary configurational enthalpies. Experimentally derived or DFT-calculated configurational enthalpies (kJ·mol⁻¹) for element pairs relevant to HECs design. The strongly negative enthalpies between Ga and most metals indicate a high chemical compatibility that drives spontaneous mixing.

	Ga	Fe	Co	Ni	Mn	K	Hf	Ta	Nb	Mo
Fe	-2									
Co	-11	-1								
Ni	-15	-2	0							
Mn	-13	0	-5	-8						
K	12	81	55	45	66					
Hf	-34	-21	-35	-42	-12	92				
Ta	-10	-15	-24	-29	-4	119	3			
Nb	-8	-16	-25	-30	-4	123	4	0		
Mo	-7	-2	-5	-7	5	120	-4	-5	-6	
Cr	-1	-1	-4	-7	2	91	-9	-7	-7	0

Concurrently, LMs' incorporation substantially increases the ΔS_{mix} of the multicomponent systems. The ΔS_{mix} is calculated for equimolar mixtures using the ideal solution model²⁸:

$$\Delta S_{mix} = -R \sum_{i=1}^n x_i \ln x_i \quad (1)$$

where ΔS_{mix} is the configurational entropy of HECs; R denotes the gas constant, usually taken as 8.314; n denotes the number of elements; x_i is the atomic percentage of the i -th component.

The calculated ΔS_{mix} values are 14.71 J/mol·K for HECs containing Galinstan, 13.38 J/mol·K for HECs containing Ga, and 11.53 J/mol·K for HECs without LMs. This ΔS_{mix} enhancement, combined with the favorable enthalpy, yields a significant reduction in the ΔG_{mix} . To further investigate the effect of LMs on ΔG_{mix} , we calculated this energy for three different systems. Extended Data Fig. 3D shows the difference in ΔG_{mix} between perovskite HECs synthesized with and without LMs. A more negative ΔG_{mix} difference indicates that the HECs are easier to form. The results for perovskite, rock salt, and pyrite HECs all demonstrate that samples containing LMs are more readily synthesized than those without LMs (Extended Data Fig. 3D–3F). Furthermore, compared to using Ga, the addition of Galinstan reduces the ΔG_{mix} more significantly, by almost 1.61 times.

Electronic structure analyses further elucidate the role of LMs as atomic solvents. Band structure calculations show that the introduction of Ga/Galinstan makes the band convergence denser and the overlap increases, which indicates stronger orbital hybridization and enhanced electron delocalization (Fig. 4B, 4F, and 4J). Moreover, the HECs containing Galinstan have higher and denser band convergence

than those containing Ga, which is consistent with the thermal calculation results. Moreover, the total density of states shows that the overall electronic topology has no considerable change, confirming that LMs do not induce phase transitions (Fig. 4C, 4G, and 4K). After adding LMs, the peaks in the high-energy region become sharper, and the conduction band becomes flat, which indicates that the bonding between atoms is stronger. Furthermore, in the charge density map, the overlap of electron clouds increases from value d (without LMs) to $1.6d$ (with Ga) and then to $4.1d$ (with Galinstan) (Fig. 4D, 4H, and 4L). The LMs solvent makes the covalent properties stronger, and the interaction between atoms also improved²⁹.

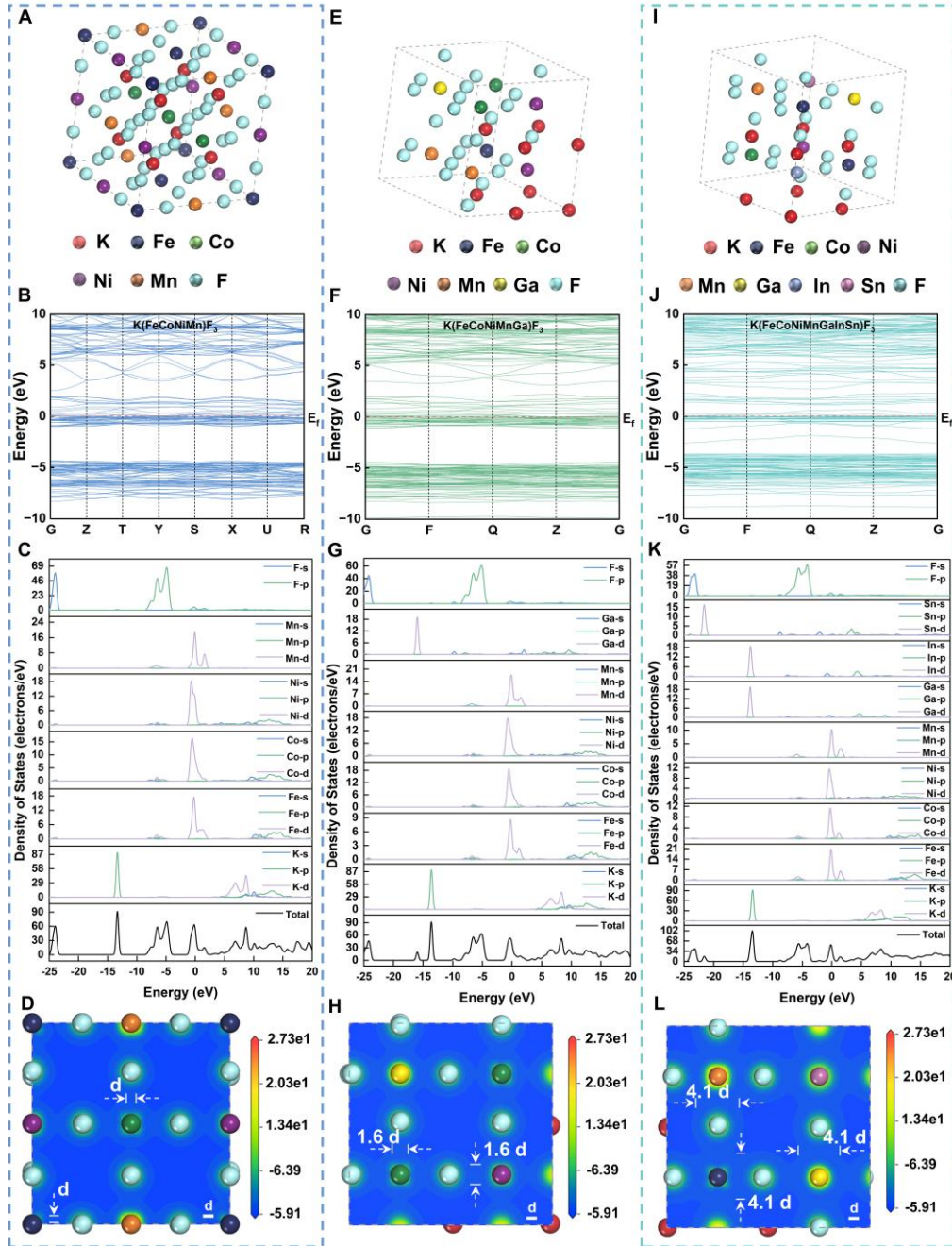


Fig. 4 | Electronic structure evolution mediated by liquid-metal incorporation. (A) The crystal structure, (B) the calculated band structure, (C) the total and partial density of states, and (D) the charge density distribution of the $(\text{Fe}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{Cr}_{1/4})\text{F}_3$ fluoride without LMs. (E) The crystal structure, (F) the calculated band structure, (G) the total and partial density of states, and (H) the charge density distribution of the $(\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Mo}_{0.2}\text{Ga}_{0.2})\text{F}_3$ HECs incorporating Ga. (I) The crystal structure, (J) the calculated band structure, (K) the total and partial density of states, and (L) the charge density distribution of the $\text{K}(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{F}_3$ HECs incorporating Galinstan.

2.5. Application of HECs

2.5.1. Oxygen and Hydrogen Evolution Reaction

Electrocatalytic water splitting to produce renewable hydrogen is the best alternative to non-renewable fuels³⁰. However, the sluggish kinetics of the OER and HER remain a bottleneck in sustainable hydrogen production³¹. High-entropy materials, with their inherent atomic-scale homogeneity, high configurational entropy, and tunable electronic structures, offer a powerful strategy to tailor active sites and enhance catalytic performance³². Based on the well-established activity of Fe, Co, Ni, and Mn in both OER^{32,33} and HER³⁴, these elements are incorporated into the composition of the HECs. Herein, the electrochemical evaluation of $\text{K}(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{F}_3$ (denoted as $\text{K}(\text{FecoNiMnGaInSn})\text{F}_3$), $\text{K}(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.2}\text{Ga}_{0.2})\text{F}_3$ (denoted as $\text{K}(\text{FecoNiMnGa})\text{F}_3$), binary fluorides, and benchmark catalysts in 1 M KOH.

For the OER, linear sweep voltammetry (LSV) shows that perovskite HECs demonstrates superior OER activity compare to the counterparts (KCoF_3 , KNiF_3 , and KFeF_3) and the commercial catalyst IrO_2 (Fig. 5A). At $10 \text{ mA}\cdot\text{cm}^{-2}$, $\text{K}(\text{FecoNiMnGaInSn})\text{F}_3$ only requires an overpotential (η) of 186 mV, substantially lower than $\text{K}(\text{FecoNiMnGa})\text{F}_3$ (252 mV), IrO_2 (281 mV), KCoF_3 (313 mV), KNiF_3 (377 mV), and KFeF_3 (452 mV) (Fig. 5B). Tafel analysis confirms the enhanced catalytic activity of $\text{K}(\text{FecoNiMnGaInSn})\text{F}_3$, evidenced by a low Tafel slope of $39.7 \text{ mV}\cdot\text{dec}^{-1}$ (Fig. 5C), which is markedly lower than values observed for other samples, indicating accelerated reaction kinetics^{35,36}. Moreover, the charge transfer resistance (R_{ct}) of $\text{K}(\text{FecoNiMnGaInSn})\text{F}_3$ measured by electrochemical impedance spectroscopy (EIS) is the lowest, so its interface electron transport efficiency is higher (Fig. 5D). Calculate the electrochemically active surface area (ECSA) of samples using double-layer capacitance (C_{dl}) obtained from cyclic voltammetry (CV) curves (Supplementary Fig. 9) to identify differences in activity. The C_{dl} of $\text{K}(\text{FecoNiMnGaInSn})\text{F}_3$ is 1.78 times that of commercial catalyst IrO_2 . The enhanced C_{dl} performance, which represents a larger ECSA, is helpful for mass transport and interface reaction kinetics in electrocatalysis³⁷. Furthermore, long-term stability is the key to the application of electrocatalysts. $\text{K}(\text{FecoNiMnGaInSn})\text{F}_3$ maintains stable performance over 200 hours at $10 \text{ mA}\cdot\text{cm}^{-2}$ with a minimal potential increase of 5 mV, demonstrating exceptional durability (Fig. 5F). On the contrary, commercial IrO_2 exhibits a substantial potential increase of 206 mV. CV at varied scan rates reveals minimal changes in peak morphology and position, further confirming structural integrity and resistance to degradation during extended cycling (Supplementary Fig. 9).

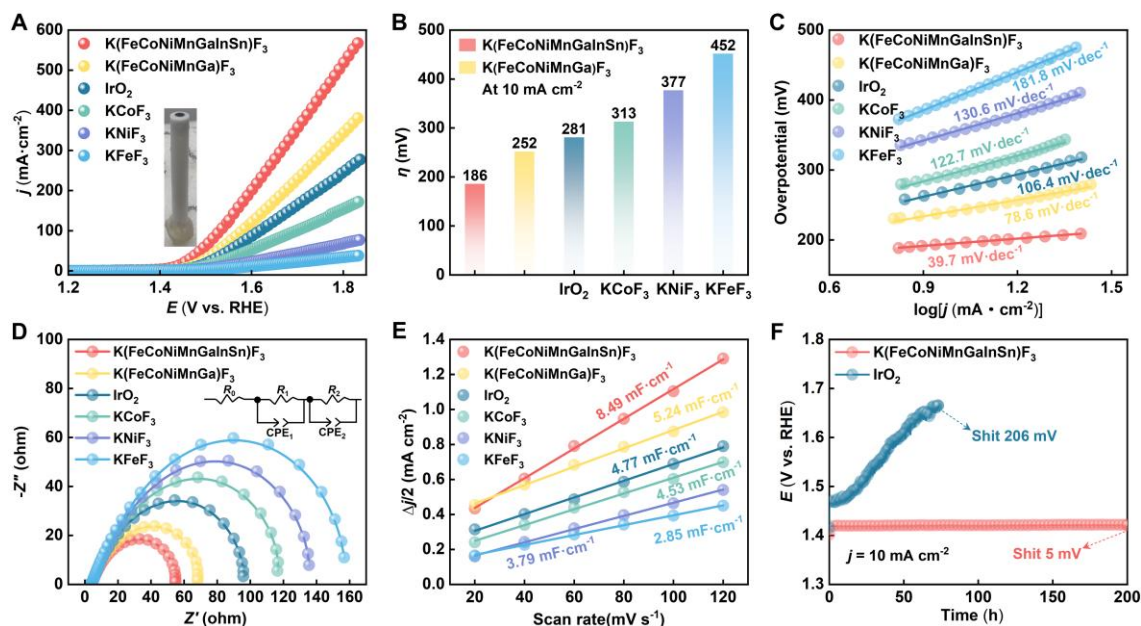


Fig. 5 | Outstanding OER activity and durability of perovskite HECs. A, LSV curves. B, η required to reach 10 mA $\cdot$ cm⁻². C, Corresponding Tafel plots. D, Nyquist plots from EIS for the HECs, commercial RuO₂, and other fluorides. E, C_{dl} values derived from cyclic voltammetry. F, Chronopotentiometric stability test at a fixed current density of 10 mA $\cdot$ cm⁻² comparing the HECs catalyst with commercial RuO₂. Electrocatalytic performance of perovskite HECs in 1 M KOH.

K(FeCoNiMnGaInSn)F₃ also exhibits exceptional HER activity. The LSV curve shows an exceptionally low overpotential of 31 mV at 10 mA $\cdot$ cm⁻², outperforming the K(FeCoNiMnGa)F₃ (54 mV), binary fluorides KCoF₃ (92 mV), KNiF₃ (116 mV) and KFeF₃ (184 mV), as well as the commercial Pt/C (64 mV) (Extended Data Fig. 4A and 4B). LSV analysis shows that K(FeCoNiMnGaInSn)F₃ (89.2 mV $\cdot$ dec⁻¹) exhibits a reduced Tafel slope compared to Pt/C (142.2 mV $\cdot$ dec⁻¹) and binary fluorides catalysts, indicating accelerated reaction kinetics (Extended Data Fig. 4C). In addition, the R_{ct} of K(FeCoNiMnGaInSn) F₃ measured by EIS is the lowest, facilitating rapid electron transfer kinetics (Extended Data Fig. 4D). The C_{dl} of 7.33 mF $\cdot$ cm⁻² indicates a substantial ECSA, contributing to the high catalytic efficiency (Extended Data Fig. 4E). Long-term stability testing demonstrates that K(FeCoNiMnGaInSn)F₃ maintains performance for 50 hours at 100 mA $\cdot$ cm⁻² with a minimal potential drift of 7 mV, while commercial Pt/C exhibits a drift of 343 mV (Extended Data Fig. 4F). CV tests show that the redox reactions in the cycle are consistent, which proves the structural stability of K(FeCoNiMnGaInSn)F₃ under dynamic conditions (Supplementary Fig. 10 and Supplementary Fig. 11).

To explain the mechanism of this special catalytic activity and stability, TEM and XPS analyses are performed on K(FeCoNiMnGaInSn)F₃ after long-term electrolysis. The morphology of

K(FecoNiMnGaInSn)F₃ after electrochemical testing shows that the sample particle edges have a nanosheet structure (Extended Data Fig. 5A). Recent studies show that oxygen vacancy defects are chemically absorbed by H₂O, which then combine with metal elements in the catalyst to form a nanolayer MOOH^{38,39} (MOOH, where M is metals such as K, Fe, Co, Ni, Mn, Ga, In, and Sn). The EDS mapping confirms that all constituent elements (K, Fe, Co, Ni, Mn, Ga, In, Sn, and F) are still evenly distributed after electrocatalysis, indicating a strong ability to resist element segregation, which contributes to the long-term stability of HECs (Extended Data Fig. 5B). XPS testing further explains this high catalytic activity and stability. An overview of XPS spectra reveals characteristic signals of elements such as K, Fe, Co, Ni, Mn, Ga, In, Sn, F, and O (Extended Data Fig. 5C). After the electrocatalytic test, the intensity of the oxygen peak increases, which is associated with the formation of MOOH species observed in TEM analysis. Notably, after the electrocatalytic test, the binding energy of the core level is shifted. The 2p_{3/2} of K moves 0.2 eV to the direction of higher binding energy, the 2p_{3/2} of Fe moves 0.4 eV to the direction of higher binding energy, the 2p_{3/2} of Co moves 0.2 eV to the direction of higher binding energy, and the 2p_{3/2} of Ni moves 0.3 eV to the direction of higher binding energy (Extended Data Fig. 5D–5J, and Supplementary Fig. 12). Besides, the area of Fe³⁺ in the Fe 2p_{3/2} spectrum after testing increased by 4.2%, and the area of Fe²⁺ decreased by 4.2%, which confirms that Fe²⁺ is oxidized to Fe³⁺ (Extended Data Fig. 5E). Similar oxidation situations also occur for other metals, and the proportion of Co³⁺ increased by 5%. The proportion in the Co 2p_{3/2} spectrum is 9%, and the proportion of Ni³⁺ in the Ni 2p_{3/2} spectrum has increased by 4.5%. In conclusion, the synergistic effect of multi-oxidation-state metal cations in perovskite HECs promotes the dynamic generation of catalytically active sites, and thus the electrocatalytic performance of the material is improved.

2.5.2. ultra-high temperature porous ceramic thermal insulator

Porous ultra-high temperature ceramics, with their low bulk density, high surface area, and high melting point, have excellent value in the field of ultra-high temperature insulation, such as scramjet engines and high-temperature solar absorbers⁴⁰. Recent studies show that high entropy materials cause local strain fields due to their unique lattice distortions, leading to phonon scattering and thus reducing thermal conductivity^{41,42}. However, traditional high-entropy materials and commercial porous insulation materials have the disadvantage of low strength. Refractory metals such as Hf, Ta, Nb, and C possess strong chemical bonds⁴³, which contribute to the high Vickers hardness in rock-salt HECs, and their comprehensive strength and thermal insulation properties are superior to those of other materials.

Supplementary Fig. 13 shows scanning electron micrograph (SEM) images of porous rock-salt HECs. All the samples have a pore network with uniform isotropy and interconnected pores. The pore sizes are 45 to 76 μm , 69 to 161 μm , 87 to 206 μm , and 83 to 308 μm , respectively, and the corresponding porosities of the samples are 80.3%, 85.1%, 90.7%, 95.8% respectively. Extended Data Fig. 6A shows an HRTEM image and the corresponding EDS mappings of element distributions of Hf, Ta, Nb, Mo, Ga, In, Sn, and C. The EDS mappings show that the element distribution is uniform, confirming that sintering does not affect rock-salt HECs powder (Experimental details refer to Preparation of porous rock-salt HECs).

Compressive strength and thermal conductivity are the key properties of porous thermal insulators. Inevitably, porosity can affect mechanical strength and thermal conductivity. When the porosity increases from 80.3% to 95.8%, the compressive strength decreases from 40.60 MPa to 0.97 MPa (Extended Data Fig. 6B, blue spheres). Because higher porosity is related to large pores and thin cell walls, the load-bearing capacity and mechanical strength decrease. However, compared with traditional porous materials, when the porosity of rock-salt HECs is 95.8%, the compressive strength is 0.97 MPa, which is 2.5 times stronger than that of Al_2O_3 with similar porosity⁴⁴ (Extended Data Fig. 6B). Similarly, under the same porosity, the compressive strength of rock-salt HECs is higher than that of other porous oxides^{45–47} or carbides^{48–51}. The high strength can be attributed to the higher intrinsic Vickers hardness of the constituent elements in rock-salt HECs compared to other ceramics (Extended Data Fig. 6D, blue column).

At room temperature, thermal conductivity in porous ceramics depends primarily on heat conduction through the solid skeleton. As porosity increases from 80.3% to 95.8%, the solid skeleton fraction decreases, reducing room temperature thermal conductivity from 0.242 to 0.139 $\text{W}/(\text{m}\cdot\text{K})$ (Extended Data Fig. 6F, green column). Notably, the thermal insulation performance of porous rock-salt HECs is superior to traditional carbides^{49–51}, mullite⁴⁶, and oxides^{44,45,47}. For example, the thermal conductivity of rock-salt HECs with a porosity of 85.1% is 0.218 $\text{W}/(\text{m}\cdot\text{K})$, which is much lower than ZrC with a similar porosity of 0.94 $\text{W}/(\text{m}\cdot\text{K})$. Moreover, the thermal conductivity of porous rock-salt HECs increases with temperature, which is consistent with the trend of ZrC⁴⁹ (Extended Data Fig. 6C). The thermal conductivity of rock-salt HECs with 90.7% porosity increases from 0.161 $\text{W}/(\text{m}\cdot\text{K})$ at room temperature to 0.378 $\text{W}/(\text{m}\cdot\text{K})$ at 1500°C. Samples with higher porosity exhibit lower thermal conductivity than less porous counterparts across all measured temperatures. At 300°C, thermal conductivity ranges from 0.327 to 0.568 $\text{W}/(\text{m}\cdot\text{K})$ as porosity increases from 80.3% to 95.8%. Similarly, from room temperature to 300°C, the thermal conductivity of ZrC increases from 0.94 to 1.35 $\text{W}/(\text{m}\cdot\text{K})$ ⁴⁹, a larger relative change than the increase from 0.242 to 0.297 $\text{W}/(\text{m}\cdot\text{K})$ observed in porous rock-salt HECs with 80.3% porosity. These

results demonstrate superior mechanical and thermal properties compared to previously reported carbides^{49–51} and conventional oxides^{44,45,47}.

The low thermal conductivity of porous rock-salt HECs results from synergistic phonon scattering mechanisms operating across multiple length scales. At the microstructural level, the pore network creates numerous interfaces where phonons undergo scattering (Extended Data Fig. 6I). The solid framework serves as the main pathway for heat conduction, facilitating phonon propagation. Each interface at the pore walls induces phonon deflection and facilitates energy dissipation⁵². Such a configuration effectively shortens the phonon mean free path, thereby restricting heat transfer within the solid matrix. Moreover, on an atomic level, rock-salt high-entropy carbides display significant lattice distortions stemming from variations in atomic size and mass among their constituent elements (Extended Data Fig. 6H and 6J). These size discrepancies lead to lattice deformations, creating localized strain fields that scatter phonons⁵³. The mass differences among the atoms modify their vibrational frequencies, enhancing energy dissipation via phonon scattering⁵⁴. This two-tiered mechanism, integrating structural interfaces and lattice irregularities, acts to impede thermal transport throughout the phonon.

2.5.3. Thermoelectric sensor

Thermoelectric sensors are important in energy harvesting applications in industrial process control⁵⁵, wearable electronic devices⁵⁶, and aerospace systems⁵⁷. However, the traditional sensitive components of thermoelectric sensors use unstable, toxic, and inefficient Bi-Te or Pb compounds above 500K^{58,59}. Previous studies show that high-entropy materials have lattice and chemical disorder, which can increase phonon scattering^{41,42}, thereby reducing thermal conductivity and maintaining good electrical performance. This work finds that pyrite high-entropy sulfides ($\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cr}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02}\text{S}_2$) can be used as sensitive components for thermoelectric sensors at high temperatures, with good energy conversion performance.

We prepare a thermal sensor based on the pyrite high-entropy sulfides, which realizes thermoelectric conversion at 825K, and the figure of merit (zT) value reaches 1.89. The sensor structure consists of a ceramic shell, a metal sheet, an n-type semiconductor (pyrite HECs), a p-type semiconductor (Half-Heusler NbCoSn), and electrodes (Extended Data Figure 7A). The bulk pyrite HECs sensing element ($0.5\times0.5\times0.7$ mm) is fabricated using hot pressing at 400°C and 70 MPa (Experimental details refer to Preparation of pyrite HECs thermoelectric devices). The ceramic shells provide mechanical support and

electrical insulation while facilitating heat conduction. The metal sheets conduct heat and electricity between components. Thermoelectric sensors utilize the Seebeck effect, wherein a temperature gradient across junctions between n-type and p-type semiconductors generates a voltage.

The thermoelectric zT of thermoelectric materials is mainly determined by the power factor ($PF = S^2\sigma$) and κ_{total} of the pyrite HECs⁶⁰:

$$zT = \frac{PF}{\kappa_{total}} T \quad (2)$$

where T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity, and κ_{total} is the total thermal conductivity.

We measure electrical conductivity (σ), Seebeck coefficient (S), and total thermal conductivity (κ_{total}) of the pyrite HECs sensor from 300K to 825K to assess thermoelectric performance. Unlike $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$ ⁶¹, which exhibits fluctuating electrical conductivity, the variation trend of pyrite HECs's σ is similar to that of $\text{Ag}_{0.25}\text{Pb}_{0.50}\text{Bi}_{0.25}\text{S}_{0.40}\text{Se}_{0.50}\text{Te}_{0.10}$ ⁶², both of which decrease linearly with increasing temperature (Extended Data Fig. 7B). When the temperature is 725K, the σ of pyrite HECs is $1.83 \text{ S}\cdot\text{cm}^{-1}$, which is 316% and 146% times that of $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$ and $\text{Ag}_{0.25}\text{Pb}_{0.50}\text{Bi}_{0.25}\text{S}_{0.40}\text{Se}_{0.50}\text{Te}_{0.10}$, respectively, indicating pyrite HECs exhibit stable charge transport at high temperatures. Unlike electrical conductivity, the S follows a similar trend to the reference material^{61,62}. The S becomes increasingly negative with temperature, reaching $-244 \mu\text{V}\cdot\text{K}^{-1}$ at 825 K, confirming n-type conduction (Extended Data Fig. 7C). Total thermal conductivity remains low throughout the measurement range, decreasing from $0.55 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 300 K to $0.43 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 825 K (Extended Data Fig. 7D). Compared to $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$, the pyrite HECs shows a 17% reduction in κ_{total} at 825 K. Similarly, the pyrite HECs exhibits κ_{total} 23% lower than $\text{Ag}_{0.25}\text{Pb}_{0.50}\text{Bi}_{0.25}\text{S}_{0.40}\text{Se}_{0.50}\text{Te}_{0.10}$ at 725 K. This reduction results from enhanced phonon scattering due to lattice distortions and atomic-scale heterogeneity^{52,53}.

The above parameters collectively affect the PF and zT of the pyrite HECs. Extended Data Fig. 7E shows the temperature dependence of PF . PF increases with temperature, reaching a maximum value of $9.85 \mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$ at 825 K. The pyrite HECs exhibit PF values more than twice those of reference materials throughout the measured temperature range. Extended Data Fig. 7F shows the temperature dependence of zT values. A zT value of 1.89 is obtained at 825 K. The pyrite HECs exhibit higher zT values than reference materials^{60–64} across the entire measurement range.

The thermoelectric performance of $(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cr}_{0.2}\text{Ga}_{0.14}\text{In}_{0.04}\text{Sn}_{0.02})\text{S}_2$ pyrite HECs arises from its electronic and thermal transport properties. In thermoelectric circuits, the n-type pyrite HECs display a negative Seebeck coefficient due to electron-dominated transport. Under a temperature gradient, electrons migrate toward the cold end, creating a lower electric potential at the cold terminal relative to the hot terminal (Extended Data Fig. 7G). Conversely, the p-type material has a positive Seebeck coefficient because hole-dominated transport. In the case of a temperature gradient, holes diffuse from the high-temperature region to the low-temperature region, and the cold end has a higher potential. This complementary behavior constitutes the basis of the thermoelectric circuit function.

To verify the hypothesis, DFT is used to simulate and calculate the band structures of low-entropy and high-entropy sulfides. Different from low-entropy sulfides, there are multiple conduction band convergences near the Fermi level (E_f) in high-entropy sulfides (Extended Data Fig. 7H, 7I, and Supplementary Fig. 14). Among pyrite HECs, the band convergence is due to enhanced disorder and orbital hybridization. This makes the density of states near the E_f stronger, and the degeneracy of charge carriers increased. The entropy-driven band convergence increases the Seebeck coefficient while maintaining electrical conductivity, thereby improving the PF . In addition, the distortion of the component lattices in pyrite HECs generates fluctuating potentials, and these potentials scatter the heat-carrying phonons^{52,53}. The scattering mechanism leads to a decrease in the lattice thermal conductivity. The total thermal conductivity of this material is as low as $0.43 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 825K, which is 17% lower than that of the reference material $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$ under the same conditions. This phenomenon is consistent with the phonon liquid-electron crystal model^{65–67}.

3. Conclusions

In summary, we propose a LMs Galinstan atomic solvent strategy for synthesizing HECs. This proposed method uses LMs as thermal catalysts and can synthesize single-phase high-entropy fluorides, carbides, and sulfides at 300°C. LMs provide high configurational entropy and negative configurational enthalpy, providing strong thermodynamic driving forces for element mixing and phase stabilization. In-situ liquid-cell TEM directly observes the homogenization process at the nanoscale and finds that LMs contribute to rapid elements' absorption and mixed crystal coprecipitation, forming entropy-stable crystal phases without intermediate phase separation. Thermodynamic theory and DFT calculations confirm the mechanism, wherein Galinstan-containing HECs exhibit a 1.61-fold reduction in ΔG_{mix} compared to Ga-

containing HECs. Besides, the structure of HECs can be tailored by adjusting their elemental composition, enabling the synthesis of perovskite, rock-salt, and pyrite-structured variants. The synthesized perovskite HECs exhibit enhanced OER and HER activities in 1 M KOH electrolyte. Similarly, rock-salt and pyrite HECs show promising properties for thermal barrier materials and thermoelectric sensing, respectively. Hence, the atomic solvent strategy provides a generalizable platform for designing HECs with application-specific optimization.

4. Materials and methods

Materials

The chemical products have analytical grade and were used without further purification. Potassium fluoride, iron nitrate nonahydrate, cobalt nitrate hexahydrate, nickel sulfate hexahydrate, nickel chloride, manganese nitrate tetrahydrate, hafnium dichloride oxide octahydrate, tantalum chloride anhydrous, niobium chloride, molybdenum pentachloride, iron sulfate heptahydrate, cobalt sulfate heptahydrate, nickel sulfate hexahydrate, chromium sulfate, ethylene glycol, isopropanol, sodium citrate, sodium borohydride, ammonium fluoride, glucose, thioacetamide ethanol, silicon carbide, ammonium citrate, gelatin and sodium dodecyl sulfate were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Ga and Galinstan were obtained from Wuhan Tuocai Technology Co., Ltd (Wuhan, China). The water used was ultrapure water.

Preparation of LMs particles

LMs particles were synthesized via ultrasonic processing. Briefly, LMs (0.5 g) was added to ethanol (100 mL) and sonicated at 40°C for 1 hour using an ultrasonic homogenizer (OYA-1012S, Suzhou Eurasia Ultrasonic Equipment Co., Ltd, China; Power 600W, amplitude 80%) to obtain a suspension of LMs microspheres. The resulting suspension was then centrifuged (Avanti J-HC, Beckman Coulter International Trading Co., Ltd, USA) at 8000 rpm for 10 minutes. Finally, the collected product was dried in an oven (PN60, Fulde Instrument Equipment Co., Ltd, Germany) at 60°C for 6 hours, yielding the final LMs particles (Supplementary Fig. 15).

Preparation of perovskite HECs

Perovskite HECs were synthesized via a modified solvothermal self-assembly method followed by calcination. Firstly, a precursor solution was prepared by dissolving stoichiometric amounts of metal salts

(K, Fe, Co, Ni, Mn, and LMs in a molar ratio of 1 : 0.2 : 0.2 : 0.2 : 0.2 : 0.2) in a 20 mL mixed solvent of ethylene glycol and isopropanol (volume ratio 12 : 1). Similarly, an ammonium fluoride solution was prepared in 30 mL of the same mixed solvent, with a molar ratio of fluoride ion to total metal ions set at 3 : 2. A solution containing the reducing agent, sodium borohydride, was prepared in 40 mL of the same mixed solvent with a borohydride to total metal molar ratio of 2 : 1. Secondly, these three solutions were combined and magnetically stirred (IKA myPlate, Aika Instrument Equipment Co., Ltd, Germany) at 200 rpm for 30 minutes under a nitrogen atmosphere, with nitrogen bubbling employed for the first 15 minutes to remove dissolved oxygen. Thirdly, the mixed solution was transferred to a three-neck round-bottom flask and subjected to a solvothermal self-assembly reaction in an oil bath (DF-101S, Shanghai Lichen Instrument Technology Co., Ltd, China) at 60°C for 5 hours under continuous nitrogen flow. After the reaction, the precipitate was collected by centrifugation (Avanti J-HC, Beckman Coulter International Trading Co., Ltd, USA), washed repeatedly three times with ultrapure water and anhydrous ethanol to remove residual organics and free ions, and then dried in an oven at 60°C for 12 hours. Finally, the dried powder was calcined (LD-3-12C, Shandong Leiente Intelligent Technology Co., Ltd, China) at 300°C for 6 hours with a heating rate of 2°C min⁻¹. Rock-salt and pyrite HECs were prepared by similar methods. Rock-salt and pyrite HECs were synthesized using the same method (Supplementary text).

Preparation of porous rock-salt HECs

Pre-synthesized rock-salt HECs powders were used as the starting material. All samples contained 2 wt.% SiC as a sintering aid. Porous samples were prepared by a foam-gelation freeze-casting route. The rock-salt HECs powders and 1 wt.% ammonium citrate (dispersant) were mixed in ultrapure water at solid loadings of 7, 10, 15, and 20 vol.% using a magnetic stirrer (IKA myPlate, Aika Instrument Equipment Co., Ltd, Germany). After stirring for 2 h, 1 wt.% sodium dodecyl sulfate was added under vigorous mechanical agitation to foam the suspension, followed by heating on a hot plate (LY-DB-6, Qingdao Luyang Environmental Protection Technology Co., Ltd, China) to 40°C. Gelatin (5 wt.%) was dissolved into the foam, which was then cast into a mold, frozen in a freezer at -20°C, and lyophilized in a freeze dryer (ZLGJ-18, Zhengzhou Huachen Instrument Co., Ltd, China). The obtained green bodies were pre-sintered in a tube furnace (LD-3-12C, Shandong Leiente Intelligent Technology Co., Ltd, China) at 1500°C for 2 h under flowing argon and finally sintered in a vacuum graphite furnace (EMZM-65-16, Zhengzhou Ermo New Material Technology Co., Ltd, China) at 2000°C for 2 h.

Preparation of pyrite HECs thermoelectric devices

Synthesized pyrite HECs powders were used as the starting material. To fabricate dense pyrite HECs, the powder was first uniaxially pressed in a hydraulic press (YHA8-250T, Dongguan Yihui Hydraulic Machinery Co., Ltd, China) at 50 MPa. Densification was then achieved by hot pressing (A6-3000T, Dongguan Yihui Hydraulic Machinery Co., Ltd, China) at 400°C for 30 min under a uniaxial pressure of 70 MPa in an argon atmosphere, followed by furnace cooling.

Characterization of HECs

We characterized the chemical composition and crystallinity of HECs using X-ray diffraction (Empyrean, PANalytical, Netherlands) and X-ray photoelectron spectroscopy (ESCALAB250Xi, Thermo Fisher Scientific, USA). The range of scan in XRD analysis was from $2\theta = 20^\circ$ to 80° with a scan rate of 2° min^{-1} .

The element contents of HECs were analyzed by inductively coupled plasma mass spectroscopy (NexION 5000, PerkinElmer, USA). The solutions were prepared by digesting the samples in aqua regia, followed by dilution with 2% hydrochloric acid. The resultant solutions were analyzed by ICP-MS.

The microstructure and morphology of HECs were observed by a SEM (SU8600, Hitachi, Japan) and transmission electron microscopes (Talos F200S, Thermo Fisher Scientific, USA). An Oxford Xmax 100TLE windowless X-ray detector was used to collect the energy-dispersive spectra.

In-situ solvothermal self-assembly experiment of precursor

To explain the LMs-enabled atomic solvent mechanism in the liquid phase environment, we used an environmental aberration corrected transmission electron microscope (Titan ETEM G2, Thermo Fisher Scientific, USA) with a silicon nitride liquid cell. Firstly, 0.2 μL of the homogeneous reaction solution was dispensed onto the center of the viewing window of the bottom liquid-cell chip using a micropipette. Secondly, the top chip was aligned and sealed against the bottom chip, forming a hermetic liquid-cell that encapsulated the solution layer. The assembled liquid cell was immediately transferred to the in situ liquid holder. The holder was rapidly inserted into the specimen stage of an environmental transmission electron microscope. Thirdly, the conversion process from precursors to HECs within the liquid environment was recorded in real time using a high-speed, direct electron detection camera. To minimize beam-induced

effects on the dynamic reaction process, a low accelerating voltage (80 kV) and a controlled electron beam current density ($1.6 \times 10^4 \text{ A} \cdot \text{m}^{-2}$) were used.

The electron energy loss spectroscopy of the HECs was acquired using an electron energy loss spectrometer (GIF Continuum ER, Gatan, USA).

Electrochemical OER/HER Measurements of perovskite HECs

All electrochemical measurements were performed using a three-electrode configuration on an Autolab PGSTAT204 workstation (Metrohm, Switzerland) controlled by NOVA 2.1 software. For electrochemical activation, a working electrode was prepared by dispersing 5 mg of the synthesized perovskite HECs in 1 mL of ethanol, drop-casting the ink onto pre-cleaned carbon paper ($1 \text{ cm} \times 1 \text{ cm}$), and drying it. The activation was carried out in a three-electrode system with 1 M KOH electrolyte, using a Pt wire counter electrode and an Ag/AgCl reference electrode. For the preparation of working electrodes used in OER/HER tests, a catalyst ink was formulated by dispersing 2 mg of the perovskite HECs in 1 mL of ethanol containing 20 μL of Nafion solution (5 wt.%). Then, 500 μL of this ink was drop-cast onto pre-cleaned carbon paper ($1 \text{ cm} \times 1 \text{ cm}$) and dried, yielding a catalyst loading of $1 \text{ mg} \cdot \text{cm}^{-2}$. These electrodes served as the working electrodes in subsequent tests. Long-term stability was assessed via chronopotentiometry or chronoamperometry over 200 hours. For HER stability tests, a graphite rod was used instead of a Pt counter electrode to avoid potential Pt dissolution and migration. All measured potentials versus the Ag/AgCl reference electrode were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.098$. The Tafel slopes were calculated from the linear region of the LSV polarization curve according to the equation: $\eta = a + b \times \log j$, where η is the overpotential, a is the constant, b is the Tafel slope, and j is the current density. The EIS was performed at open circuit potential (1.5 V) to evaluate the charge transfer resistance. CV scans in a non-Faradic region estimated the electrochemical double-layer capacitance (C_{dl}) at various scan rates from 20 to 120 $\text{mV} \cdot \text{s}^{-1}$. All experiments were performed at room temperature.

Mechanical and thermal properties testing of rock-salt HECs

The apparent density of both porous and fully dense rock-salt HECs was measured by the Archimedes method, following American Society for Testing and Materials B962 methods. The porosity (P) of the

porous HECs monoliths was calculated as $P = \left(1 - \frac{\rho}{\rho_t}\right) \times 100\%$, where ρ is the measured apparent density of the rock-salt HECs and ρ_t is the theoretical density of the rock-salt HECs. Here, ρ_t was considered as a fully dense hot-pressed bulk with a measured density ($6.52 \text{ g}\cdot\text{cm}^{-3}$) and a relative density of 97.6%. Compressive strength tests were conducted on a universal testing machine (CMT4000, Metes Industrial Systems Co., Ltd, USA) at a loading speed of $0.5 \text{ mm}\cdot\text{min}^{-1}$. For each porosity level, five cylindrical samples (nominal dimensions: $\Phi 20 \text{ mm} \times 20 \text{ mm}$) were tested. Thermal conductivity was measured from room temperature to 1500°C using a commercial analyzer based on the guarded heat-flow method (TC2000, Shanghai Pujian Instrument Co., Ltd, China). For these measurements, samples were prepared as discs with dimensions of $\Phi 50.5 \text{ mm} \times 2.5 \text{ mm}$.

Thermal and electrical performance testing of pyrite HECs

The σ and S were simultaneously measured from room temperature to 923 K using a four-probe method under a helium atmosphere in a Seebeck coefficient tester (HC-RD-1100, Beijing Huace Testing Instrument Co., Ltd, China). The κ_{total} was calculated from the formula $\kappa_{total} = DC_p\rho$, where D is the thermal diffusivity, C_p is the specific heat capacity, and ρ is the sample density. D was measured over the same temperature range (300–923 K) by the thermal conductivity tester (LFA L52, Linsaisi Scientific Instrument Co., Ltd, Germany). The C_p was calculated using the Dulong-Petit law, $C_p = \frac{3nR}{M}$, where n is the number of atoms per formula unit (taken as 3), R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), and M is the molar mass of pyrite HECs ($126 \text{ g}\cdot\text{mol}^{-1}$). The density of the pyrite HECs were estimated from their weight and size. The relative density of the pyrite HECs was 97.2%.

Density functional theory calculations

First-principles DFT calculations using the Materials Studio 20.1 software package to investigate electronic structure and stability. The exchange-correlation interactions were treated within the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional. To model disordered HECs, the special quasirandom structure algorithm was employed. The optimized structures of the perovskite, rock-salt, and pyrite phases are all cubic, with lattice constants of $8.24 \text{ \AA}$, $8.086 \text{ \AA}$, and $8.148 \text{ \AA}$, respectively. A plane-wave energy cutoff of 450 eV was used. The Brillouin zone was sampled with a Γ -centered k-point grid having a spacing of $0.2 \text{ \AA}^{-1}$. The convergence thresholds were set to 10^{-3} eV for

energy and $0.01 \text{ eV}\cdot\text{\AA}^{-1}$ for atomic forces during ionic relaxation. These settings ensured that all configurations were optimized to local energy minima.

Acknowledgements

Funding: The work is supported by the National Natural Science Foundation of China (Nos. 52027814) and National Key Research and Development Program of China (Grant Nos. 2023YFC2907200)

Data and materials availability

All data are available in the main text or the supplementary materials.

Author contributions:

Zheng Luo: Investigation, Visualization, Data curation, Writing – original draft.

Lunshi Zhou: Visualization, Data curation.

Junwei Chen: Investigation , Data curation.

Dongsheng He: Visualization.

Xiaoping Zhou: Conceptualization, Methodology, Investigation, Validation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Competing interests

Authors declare that they have no competing interests.

Supplementary

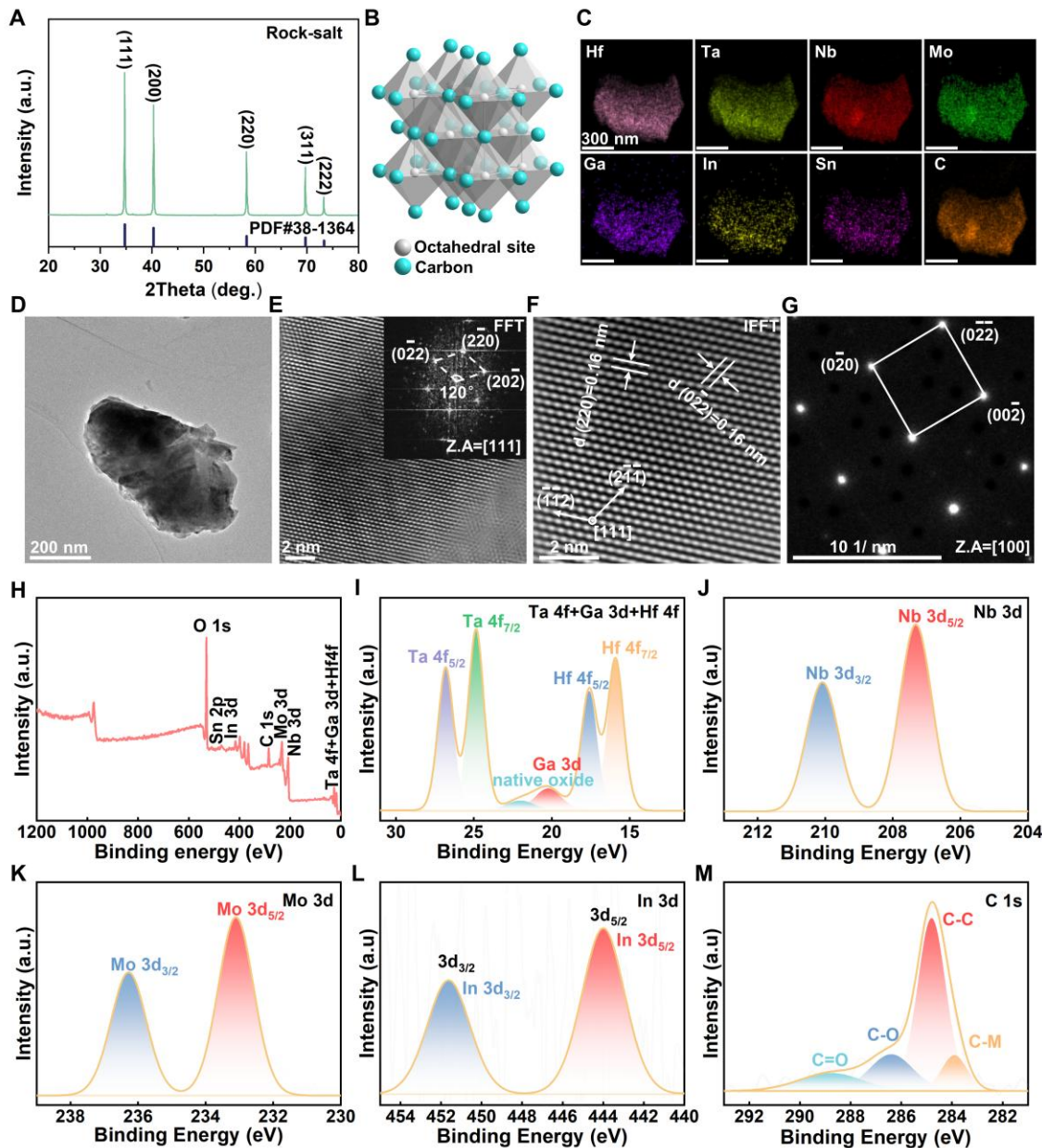
References

1. Divilov, S. *et al.* Disordered enthalpy–entropy descriptor for high-entropy ceramics discovery. *Nature* **625**, 66–73; 10.1038/s41586-023-06786-y (2024).
2. Wang, C. *et al.* High-Entropy Ceramics Enhanced Droplet Electricity Generator for Energy Harvesting and Bacterial Detection. *Adv. Mater.* **36**, 2400505; 10.1002/adma.202400505 (2024).
3. Zhang, M. *et al.* Ultrahigh energy storage in high-entropy ceramic capacitors with polymorphic relaxor phase. *Science* **384**, 185–189; 10.1126/science.adl2931 (2024).

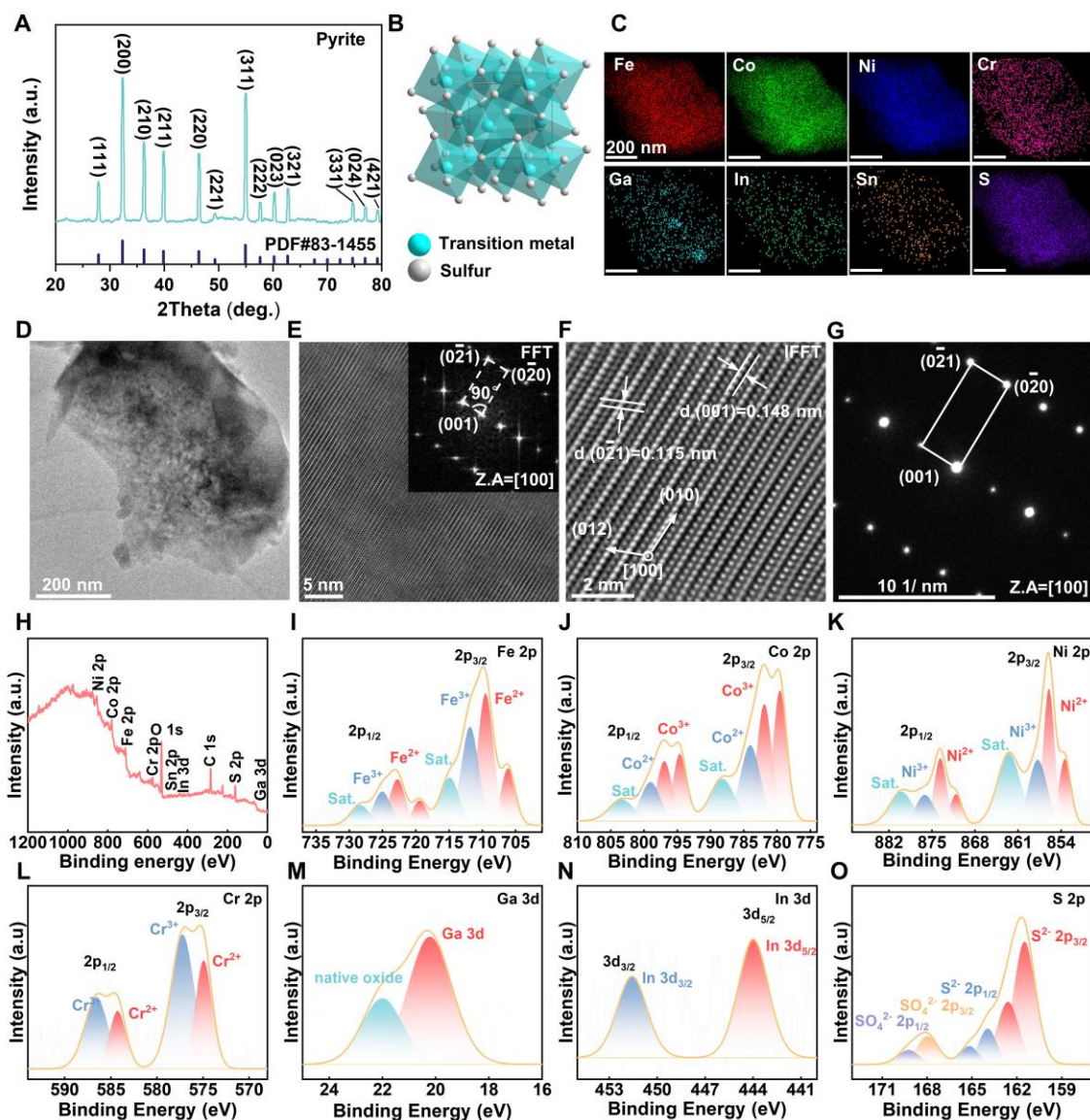
4. Braun, J. L. *et al.* Charge-Induced Disorder Controls the Thermal Conductivity of Entropy-Stabilized Oxides. *Advanced materials (Deerfield Beach, Fla.)* **30**, e1805004; 10.1002/adma.201805004 (2018).
5. Rost, C. M. *et al.* Entropy-stabilized oxides. *Nature communications* **6**, 8485; 10.1038/ncomms9485 (2015).
6. Li, D. *et al.* Atomic-Scale High-Entropy Design for Superior Capacitive Energy Storage Performance in Lead-Free Ceramics. *Adv. Mater.* **37**, 2409639; 10.1002/adma.202409639 (2025).
7. Wen, Z. *et al.* Ultrastrong and High Thermal Insulating Porous High-Entropy Ceramics up to 2000 °C. *Adv. Mater.* **36**, 2311870; 10.1002/adma.202311870 (2024).
8. Bauer, J., Hengsbach, S., Tesari, I., Schwaiger, R. & Kraft, O. High-strength cellular ceramic composites with 3D microarchitecture. *Proceedings of the National Academy of Sciences* **111**, 2453–2458; 10.1073/pnas.1315147111 (2014).
9. Atomic to nanoscale chemical fluctuations: The catalyst for enhanced thermoelectric performance in high-entropy materials.
10. Grubb, S. & Lauritzen, M. Deep sleep drives brain fluid oscillations. *Science (New York, N.Y.)* **366**, 572–573; 10.1126/science.aaz5191 (2019).
11. Sarkar, A. *et al.* High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties. *Advanced materials (Deerfield Beach, Fla.)* **31**, e1806236; 10.1002/adma.201806236 (2019).
12. Sang, W. *et al.* Novel (Sm_{0.2}Lu_{0.2}Yb_{0.2}Y_{0.2}Dy_{0.2})₃TaO₇ high-entropy ceramic for thermal barrier coatings. *Ceramics International* **49**, 9052–9059; 10.1016/j.ceramint.2022.11.061 (2023).
13. Chen, Y.-W., Ruan, J.-J., Ting, J.-M., Su, Y.-H. & Chang, K.-S. Solution-based fabrication of high-entropy Ba(Ti,Hf,Zr,Fe,Sn)O₃ films on fluorine-doped tin oxide substrates and their piezoelectric responses. *Ceramics International* **47**, 11451–11458; 10.1016/j.ceramint.2020.12.272 (2021).
14. Rost, C. M. *et al.* Electron and phonon thermal conductivity in high entropy carbides with variable carbon content. *Acta Materialia* **196**, 231–239; 10.1016/j.actamat.2020.06.005 (2020).
15. Kosmulski, M. Surface Charging and Points of Zero Charge. *Surface Charging and Points of Zero Charge*; 10.1201/9781420051896 (2009).
16. Kosmulski, M. The pH dependent surface charging and points of zero charge. X. Update. *Advances in Colloid and Interface Science* **319**, 102973; 10.1016/j.cis.2023.102973 (2023).
17. Huang, J. & Chen, Y. Editorial Overview Surface electrochemistry (2022) The double layer: A persisting issue with emerging trends. *Current Opinion in Electrochemistry* **35**, 101099; 10.1016/j.coelec.2022.101099 (2022).
18. Schmickler, W. & Santos, E. *Interfacial electrochemistry*. 2nd ed. (Springer, Heidelberg, 2010).
19. Cao, G. *et al.* Liquid metal for high-entropy alloy nanoparticles synthesis. *Nature* **619**, 73–77; 10.1038/s41586-023-06082-9 (2023).
20. Pei, Z., Yin, J., Hawk, J. A., Alman, D. E. & Gao, M. C. Machine-learning informed prediction of high-entropy solid solution formation: Beyond the Hume-Rothery rules. *npj Computational Materials* **6**, 50; 10.1038/s41524-020-0308-7 (2020).
21. Rost, C. M. *et al.* Entropy-stabilized oxides. *Nature communications* **6**, 8485; 10.1038/ncomms9485 (2015).
22. Sarkar, A. *et al.* High entropy oxides for reversible energy storage. *Nature communications* **9**, 3400; 10.1038/s41467-018-05774-5 (2018).
23. Zavabeti, A. *et al.* A liquid metal reaction environment for the room-temperature synthesis of atomically thin metal oxides. *Science* **358**, 332–335; 10.1126/science.aao4249 (2017).
24. Yao, Y. *et al.* Carbothermal shock synthesis of high-entropy-alloy nanoparticles. *Science* **359**, 1489–1494; 10.1126/science.aan5412 (2018).
25. Daeneke, T. *et al.* Liquid metals: fundamentals and applications in chemistry. *Chemical Society reviews* **47**, 4073–4111; 10.1039/c7cs00043j (2018).

26. Ye, B., Wen, T. & Chu, Y. High-temperature oxidation behavior of (Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C high-entropy ceramics in air. *J Am Ceram Soc* **103**, 500–507; 10.1111/jace.16725 (2020).
27. Takeuchi, A. & Inoue, A. Classification of Bulk Metallic Glasses by Atomic Size Difference, Heat of Mixing and Period of Constituent Elements and Its Application to Characterization of the Main Alloying Element. *MATERIALS TRANSACTIONS* **46**, 2817–2829; 10.2320/matertrans.46.2817 (2005).
28. Gu, Y. *et al.* A brief review of high-entropy oxides in solid oxide fuel cell applications. *Materials Science and Engineering: B* **327**, 119260; 10.1016/j.mseb.2026.119260 (2026).
29. Hu, Y. L. *et al.* First-principle calculation investigation of NbMoTaW based refractory high entropy alloys. *Journal of Alloys and Compounds* **827**, 153963; 10.1016/j.jallcom.2020.153963 (2020).
30. Suntivich, J. *et al.* Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries. *Nature Chemistry* **3**, 546–550; 10.1038/nchem.1069 (2011).
31. Liu, J., Zhang, T., Ji, F., Liu, Z. & Wang, Z. High-Performance Perovskite Bifunctional Electrocatalysts for Oxygen Reduction Reaction and Oxygen Evolution Reaction. *ACS Applied Energy Materials* **5**, 8852–8861; 10.1021/acsaem.2c01344 (2022).
32. Wang, T., Chen, H., Yang, Z., Liang, J. & Dai, S. High-Entropy Perovskite Fluorides: A New Platform for Oxygen Evolution Catalysis. *Journal of the American Chemical Society* **142**, 4550–4554; 10.1021/jacs.9b12377 (2020).
33. Friebe, D. *et al.* Identification of Highly Active Fe Sites in (Ni,Fe)OOH for Electrocatalytic Water Splitting. *Journal of the American Chemical Society* **137**, 1305–1313; 10.1021/ja511559d (2015).
34. Qin, F. *et al.* Trimetallic NiFeMo for Overall Electrochemical Water Splitting with a Low Cell Voltage. *ACS Energy Letters* **3**, 546–554; 10.1021/acsenenergylett.7b01335 (2018).
35. Aikens, D. A. Electrochemical methods, fundamentals and applications. *Journal of Chemical Education* **60**, A25; 10.1021/ed060pA25.1 (1983).
36. Man, I. C. *et al.* Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *ChemCatChem* **3**, 1159–1165; 10.1002/cctc.201000397 (2011).
37. Kibsgaard, J., Chen, Z., Reinecke, B. N. & Jaramillo, T. F. Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis. *Nature Materials* **11**, 963–969; 10.1038/nmat3439 (2012).
38. Zhu, K., Shi, F., Zhu, X. & Yang, W. The roles of oxygen vacancies in electrocatalytic oxygen evolution reaction. *Nano Energy* **73**, 104761; 10.1016/j.nanoen.2020.104761 (2020).
39. Chen, F.-Y., Wu, Z.-Y., Adler, Z. & Wang, H. Stability challenges of electrocatalytic oxygen evolution reaction: From mechanistic understanding to reactor design. *Joule* **5**, 1704–1731; 10.1016/j.joule.2021.05.005 (2021).
40. Jain, A., Wang, Y., Guo, H. & Wang, N. Grain size engineered Ba_{0.9}Sr_{0.1}Ti_{0.9}Hf_{0.1}O₃-Na_{0.5}Bi_{0.5}TiO₃ relaxor ceramics with improved energy storage performance. *J Am Ceram Soc* **103**, 6308–6318; 10.1111/jace.17346 (2020).
41. Xiang, H. *et al.* High-entropy ceramics: Present status, challenges, and a look forward. *Journal of Advanced Ceramics* **10**, 385–441; 10.1007/s40145-021-0477-y (2021).
42. Liu, Y. *et al.* Lattice-Distortion-Driven Reduced Lattice Thermal Conductivity in High-Entropy Ceramics. *Advanced science (Weinheim, Baden-Wurttemberg, Germany)* **12**, e2501157; 10.1002/advs.202501157 (2025).
43. Zhou, J. *et al.* High-entropy carbide: A novel class of multicomponent ceramics. *Ceramics International* **44**, 22014–22018; 10.1016/j.ceramint.2018.08.100 (2018).
44. Shimizu, T., Matsuura, K., Furue, H. & Matsuzak, K. Thermal conductivity of high porosity alumina refractory bricks made by a slurry gelation and foaming method. *Journal of the European Ceramic Society* **33**, 3429–3435; 10.1016/j.jeurceramsoc.2013.07.001 (2013).
45. Meng, X. *et al.* Pyrochlore-fluorite dual-phase high-entropy ceramic foams with extremely low thermal conductivity from particle-stabilized suspension. *Scripta Materialia* **194**, 113714; 10.1016/j.scriptamat.2020.113714 (2021).
46. Zhou, L., Li, Z. & Zhu, Y. Porous silica/mullite ceramics prepared by foam-gelcasting using silicon kerf waste as raw material. *Materials Letters* **239**, 67–70; 10.1016/j.matlet.2018.12.066 (2019).

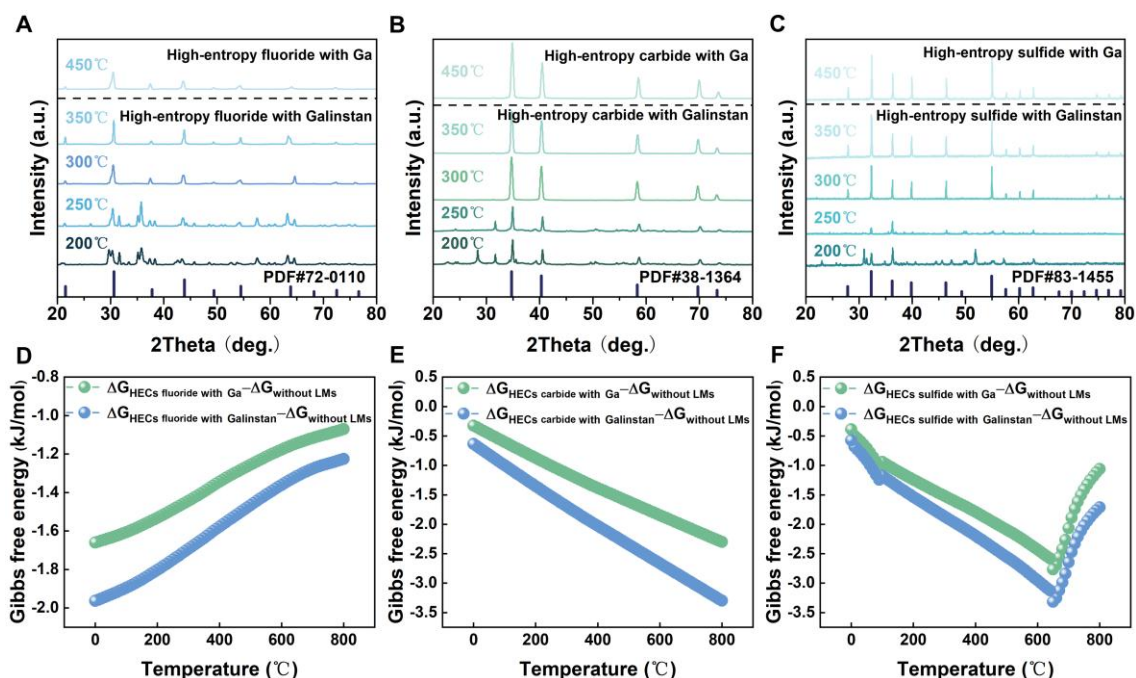
47. Ren, B. *et al.* Preparation of Al₂O₃-Si₃N₄ porous ceramics with a cactus-like architecture for potential filters applications. *Ceramics International* **45**, 6581–6584; 10.1016/j.ceramint.2018.12.046 (2019).
48. Li, F., Liang, M., Ma, X.-F., Huang, X. & Zhang, G.-J. Preparation and characterization of stoichiometric zirconium carbide foams by direct foaming of zirconia sols. *Journal of Porous Materials* **22**, 493–500; 10.1007/s10934-015-9919-7 (2015).
49. Li, F., Kang, Z., Huang, X., Wang, X.-G. & Zhang, G.-J. Preparation of zirconium carbide foam by direct foaming method. *Journal of the European Ceramic Society* **34**, 3513–3520; 10.1016/j.jeurceramsoc.2014.05.029 (2014).
50. Wu, Z. *et al.* Highly porous multicomponent (Hf₁/3Ta₁/3Nb₁/3)C ultra-high temperature ceramic with low thermal conductivity. *Materialia* **18**, 101158; 10.1016/j.mtla.2021.101158 (2021).
51. Chen, H. *et al.* High porosity and low thermal conductivity high entropy (Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C. *Journal of Materials Science & Technology* **35**, 1700–1705; 10.1016/j.jmst.2019.04.006 (2019).
52. Cahill, D. G. *et al.* Nanoscale thermal transport. II. 2003–2012. *Appl. Phys. Rev.* **1**, 11305; 10.1063/1.4832615 (2014).
53. Sarker, P. *et al.* High-entropy high-hardness metal carbides discovered by entropy descriptors. *Nature communications* **9**, 4980; 10.1038/s41467-018-07160-7 (2018).
54. Gild, J. *et al.* High-Entropy Metal Diborides: A New Class of High-Entropy Materials and a New Type of Ultrahigh Temperature Ceramics. *Scientific Reports* **6**, 37946; 10.1038/srep37946 (2016).
55. Di Xiao *et al.* Thermoelectric Generator Design and Characterization for Industrial Pipe Waste Heat Recovery. *Processes* **11**, 1714; 10.3390/pr11061714 (2023).
56. Jia, Y. *et al.* Wearable Thermoelectric Materials and Devices for Self-Powered Electronic Systems. *Adv. Mater.* **33**, 2102990; 10.1002/adma.202102990 (2021).
57. Kilinc, E., Uysal, F., Sari, M. A., Kurt, H. & Celik, E. Sol–Gel Synthesis of Ca_{2.5}Ag_{0.3}Sm_{0.2}Co₄O₉ Semiconducting Materials for Thermoelectric Applications in Aerospace Systems. *Adv. Eng. Mater.* **27**, 2500571; 10.1002/adem.202500571 (2025).
58. Lee, S. *et al.* Oxidation of thermoelectric Bi₂Te₃-based alloys by atomic layer deposition of Ru metal. *Materials Letters* **320**, 132321; 10.1016/j.matlet.2022.132321 (2022).
59. Sun, Y. *et al.* Sb₂Te₃ based alloy with high thermoelectric and mechanical performance for low-temperature energy harvesting. *Nano Energy* **107**, 108176; 10.1016/j.nanoen.2023.108176 (2023).
60. Jiang, B. *et al.* High-entropy-stabilized chalcogenides with high thermoelectric performance. *Science (New York, N.Y.)* **371**, 830–834; 10.1126/science.abe1292 (2021).
61. Dutta, M., Pal, K., Waghmare, U. V. & Biswas, K. Bonding heterogeneity and lone pair induced anharmonicity resulted in ultralow thermal conductivity and promising thermoelectric properties in n-type AgPbBiSe₃. *Chemical science* **10**, 4905–4913; 10.1039/c9sc00485h (2019).
62. Yamashita, A. *et al.* n-Type thermoelectric metal chalcogenide (Ag,Pb,Bi)(S,Se,Te) designed by multi-site-type high-entropy alloying. *Materials Research Letters* **9**, 366–372; 10.1080/21663831.2021.1929533 (2021).
63. Mangelis, P., Vaqueiro, P. & Powell, A. V. Improved Thermoelectric Performance through Double Substitution in Shandite-Type Mixed-Metal Sulfides. *ACS Applied Energy Materials* **3**, 2168–2174; 10.1021/acsaem.9b02272 (2020).
64. Zhang, R.-Z., Gucci, F., Zhu, H., Chen, K. & Reece, M. J. Data-Driven Design of Ecofriendly Thermoelectric High-Entropy Sulfides. *Inorganic Chemistry* **57**, 13027–13033; 10.1021/acs.inorgchem.8b02379 (2018).
65. Berardan, D., Meena, A. K., Franger, S., Herrero, C. & Dragoe, N. Controlled Jahn-Teller distortion in (MgCoNiCuZn)O-based high entropy oxides. *Journal of Alloys and Compounds* **704**, 693–700; 10.1016/j.jallcom.2017.02.070 (2017).
66. Pei, Y. *et al.* Convergence of electronic bands for high performance bulk thermoelectrics. *Nature* **473**, 66–69; 10.1038/nature09996 (2011).
67. Liu, H. *et al.* Copper ion liquid-like thermoelectrics. *Nature Materials* **11**, 422–425; 10.1038/nmat3273 (2012).



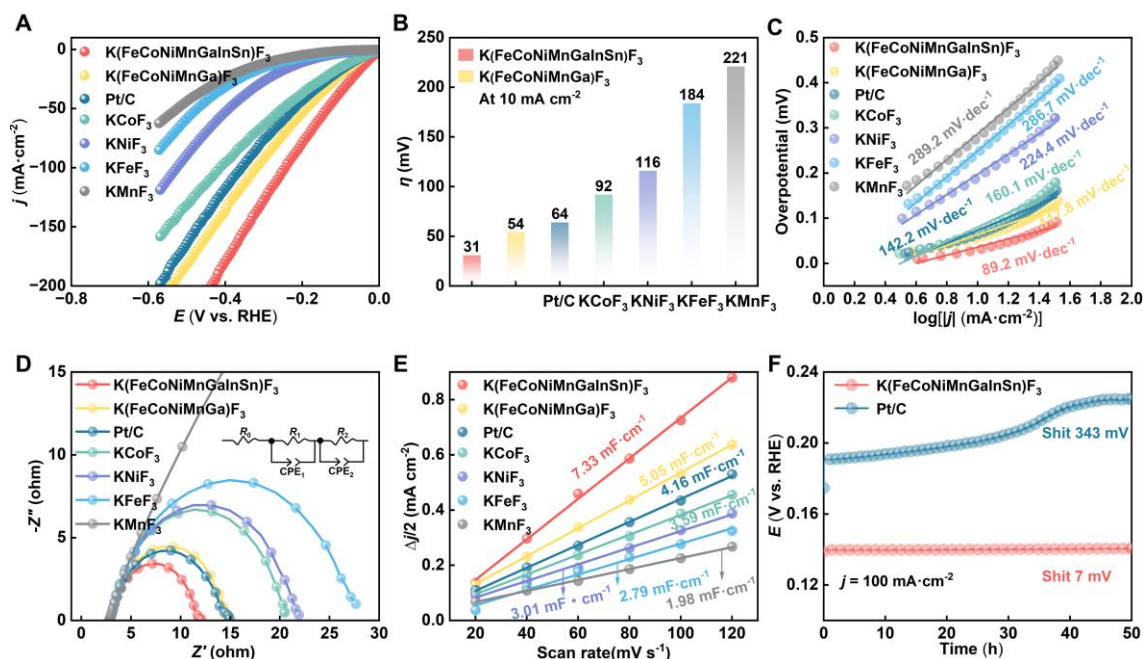
Extended Data Fig. 1 | Structural and chemical characterization of rock-salt HECs. **A**, XRD pattern confirming phase purity (cubic, $Fm\bar{3}m$). **B**, Schematic of the rock-salt lattice. **C**, EDS elemental maps showing homogeneous distribution of all constituent elements (Hf, Ta, Nb, Mo, Ga, In, Sn, and C). **D**, TEM image. **E**, HRTEM image. **F**, IFFT lattice images for rock-salt HECs. **G**, SAED pattern along the (100) zone axis. **H**, XPS analysis of rock-salt HECs. High-resolution XPS spectra of (**I**) Ta 4f, Ga 3d, Hf 4f, (**J**) Nb 3d, (**K**) Mo 3d, (**L**) In 3d, and (**M**) C 1s.



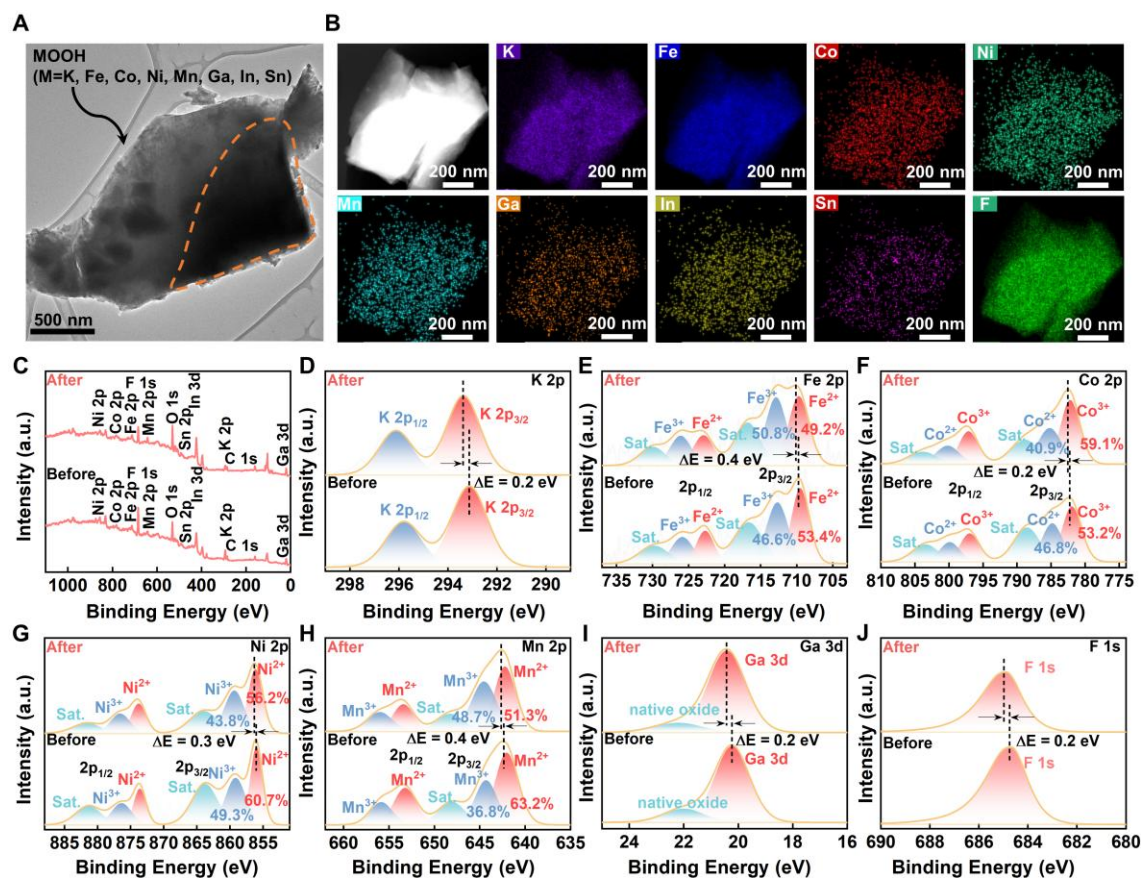
Extended Data Fig. 2 | Structural and chemical characterization of pyrite HECs. **A**, XRD pattern confirming phase purity (cubic, $Pa\bar{3}$). **B**, Schematic of the pyrite lattice. **C**, EDS elemental maps showing homogeneous distribution of all constituent elements (Fe, Co, Ni, Cr, Ga, In, Sn, and S). **D**, TEM image. **E**, HRTEM image. **F**, IFFT lattice images for pyrite HECs. **G**, SAED pattern along the (100) zone axis. **H**, XPS analysis of pyrite HECs. High-resolution XPS spectra of (I) Fe 2p, (J) Co 2p, (K) Ni 2p, (L) Cr 2p, (M) Ga 3d, (N) In 3d, and (O) S 2p.



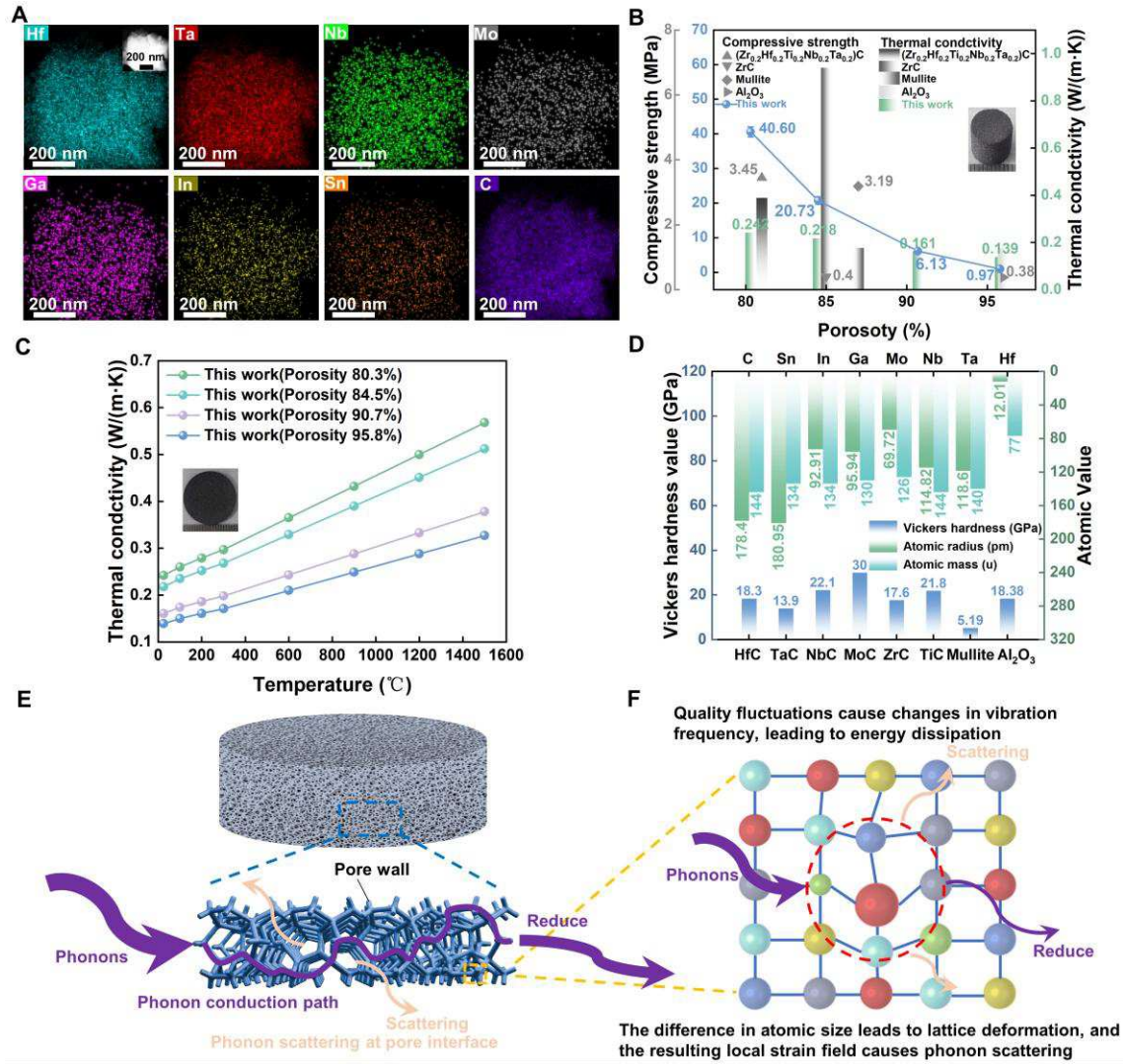
Extended Data Fig. 3 | Structural and thermodynamic impact of LMs in HECs. XRD patterns of (A) perovskite, (B) rock-salt, and (C) pyrite HECs samples. HECs containing Galinstan are calcined at 300°C for 6 hours to obtain a single-phase structure, while HECs containing Ga are calcined at 700°C for 6 hours to obtain a single-phase structure. **D** to **F**, The corresponding change in Gibbs free energy as a function of temperature, calculated as the difference between HECs with and without LMs.



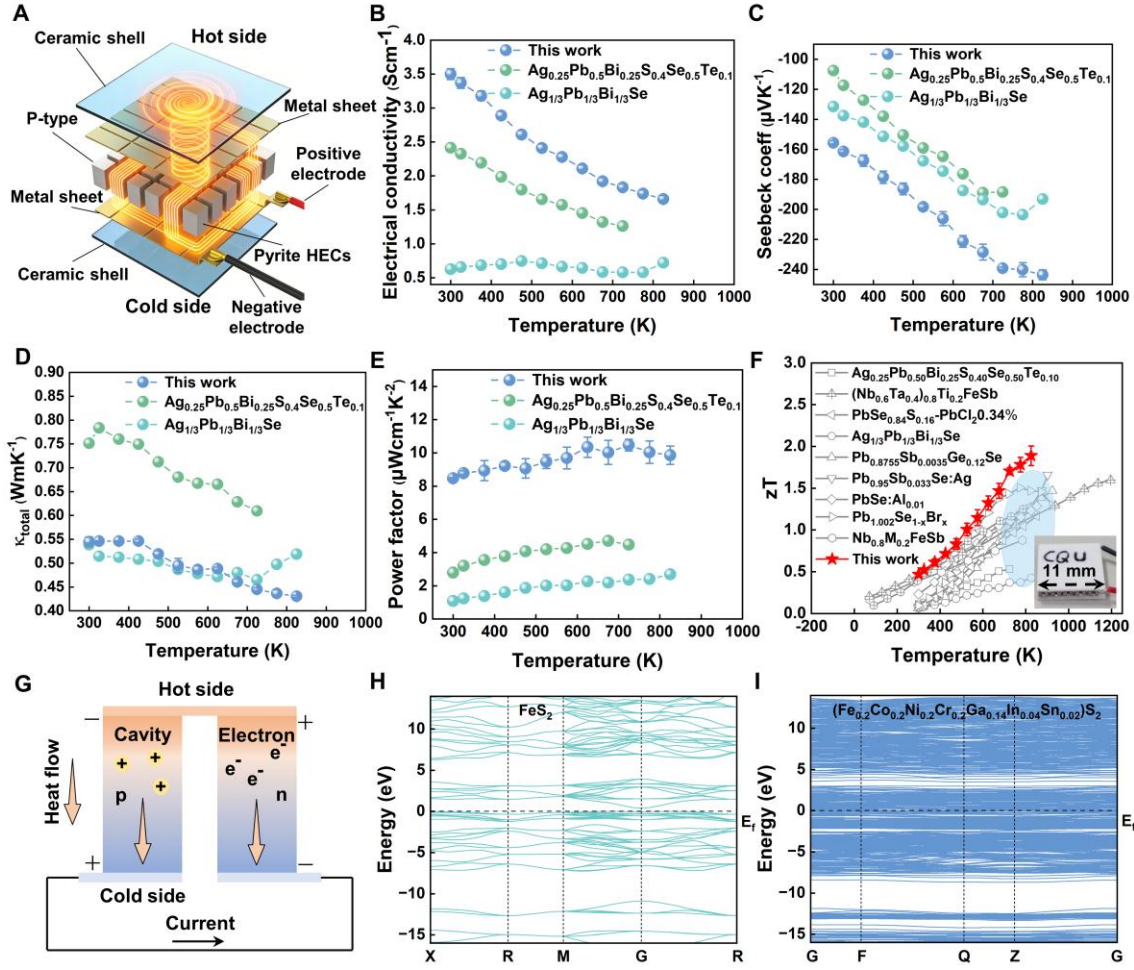
Extended Data Fig. 4 | HER performance of perovskite HECs in 1 M KOH. **A**, Polarization curves from LSV. **B**, η required to achieve a current density of 10 mA cm⁻². **C**, Corresponding Tafel plots. **D**, Nyquist plots from EIS comparing the HECs to commercial Pt/C and other fluorides. **E**, C_{dl} values derived from cyclic voltammetry. **F**, Chronopotentiometric stability test at a fixed current density of 10 mA cm⁻², comparing the HECs catalyst with commercial Pt/C.



Extended Data Fig. 5 | Morphology and chemical composition of perovskite HECs after electrocatalytic testing. **A**, TEM image. **B**, elemental mappings of K, Fe, Co, Ni, Mn, Ga, In, and Sn elements. **C**, XPS analysis of perovskite HECs before and after electrocatalysis. XPS spectra of **(D)** K 2p, **(E)** Fe 2p, **(F)** Co 2p, **(G)** Ni 2p, **(H)** Mn 3p, **(I)** Ga 3d, and **(J)** F 1s.



Extended Data Fig. 6 | Structure and properties of porous high-entropy carbide. **A**, elemental mappings of Hf, Ta, Nb, Mo, Ga, In, Sn, and C elements. **B**, Compressive strength and thermal conductivity of HECs and other thermal insulation materials with different porosities at room temperature. **C**, Temperature-dependent thermal conductivity of HECs with varying porosity. **D**, Vickers hardness, atomic radius, and atomic mass of high-entropy carbide elements. **(E)** Pore interfaces, **(F)** atomic mass and size differences induce phonon scattering, suppressing thermal transport.



Extended Data Fig. 7 | Thermoelectric performance of the high-entropy sulfide. Temperature dependence of the (A) electrical conductivity and (B) Seebeck coefficient, (C) thermal conductivity, and (D) power factor of high-entropy sulfide and other materials. F, zT as a function of temperature for the high-entropy sulfide, alongside reported values for conventional materials. G, Schematic diagrams of charge carrier transport in p-type and n-type thermoelectric semiconductors. The band structures of (H) low-entropy sulfides and (I) high-entropy sulfides.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supplementary.docx](#)
- [SupplementaryVideo1.mov](#)