

Homogenizing energy landscapes and microstructure enabling a linear and stable thermal sensing response in high-entropy niobates

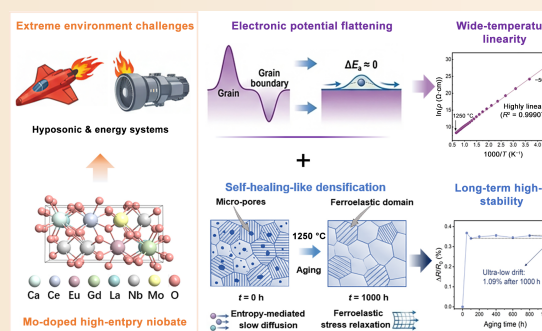
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ABSTRACT: Advanced temperature-sensitive materials play an increasingly important role in modern hypersonic propulsion technology. For such applications, ensuring long-term high-temperature (above 1000 °C) stability is key to enabling integrated structural and functional capabilities. Herein, we develop a Mo-regulated high-entropy ferroelastic niobate strategy for ultrawide-temperature negative-temperature-coefficient thermosensitive ceramics. Density functional theory (DFT) calculations show that the A-site high-entropy facilitates Mo doping in $(\text{Ca}_{0.2}\text{La}_{0.2}\text{Ce}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})\text{NbO}_4$. Consequently, Mo doping broadens the distribution of local atomic configurations, modulates ferroelastic domain structures, and increases atomic-scale displacement disorder. These

structural changes redistribute Hall transport contributions and reduce the mismatch between grain and grain-boundary transport barriers. As a result, the developed ceramics exhibit highly linear Arrhenius behavior ($R^2 = 0.99907$) over an ultrawide temperature range from -50 to 1250 °C, accompanied by a low B -value fluctuation of only 4.44%. High-temperature impedance analysis further confirms closely matched grain and grain-boundary activation energies, with a minimum activation-energy mismatch (ΔE_a) of only 0.009 eV. During aging at 1250 °C, the ceramics exhibit aging-induced postdensification accompanied by an increase in relative density and strain redistribution, resulting in excellent long-term stability with a stabilized-stage resistance drift as low as 1.09% after 1000 h. These findings demonstrate that manipulating entropy-stabilized defects provides a robust pathway to decouple sensitivity from degradation in functional ceramics under thermal stress.

KEYWORDS: high-entropy ceramics; thermosensitive ceramics; thermal stability; lattice distortion; self-healing densification; aging drift; niobate



1 Introduction

The rapid advancement of aerospace propulsion, hypersonic vehicles, and next-generation energy conversion systems has created an urgent demand for thermal sensors capable of operating reliably in extreme environments exceeding 1000 °C [1–3]. In particular, negative temperature coefficient (NTC) thermistors are preferred over thermocouples for their high sensitivity, fast response, and compact integration potential. However, the development of ceramic sensors that maintain both high linearity and long-term stability at such elevated

temperatures remains a formidable challenge. Conventional transition-metal spinel oxides (e.g., Ni–Mn–Co–O) are fundamentally limited by phase decomposition and uncontrolled cation migration above 300 °C, leading to exponential resistance drift [4,5]. Even promising alternatives such as perovskites or fluorites often suffer from functional degradation due to the inevitable thermodynamic drive toward equilibrium at high temperatures [6,7]. Consequently, realizing a sensor material that defies these intrinsic trade-offs requires a paradigm shift from simple composition tuning to the precise engineering of crystal lattice thermodynamics and electronic energy landscapes.

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The failure of functional ceramics in extreme thermal environments is deeply rooted in two coupled microstructural mechanisms. Electrically, the deviation from the Arrhenius law typically arises from the mismatch in activation energies between the bulk crystal (E_g) and the grain boundaries (E_{gb}), together with temperature-dependent changes in carrier concentration, mobility, defect state, and localized hopping pathways [8–10]. Charge carriers must surmount significantly higher potential barriers at grain boundaries, causing a transition in the dominant conduction mechanism and a consequent curvature in the $\ln\rho$ and $1/T$ response. Structurally, and perhaps more critically, long-term instability is driven by defect kinetics [11,12]. For traditional ceramics, high-temperature exposure accelerates Ostwald ripening and pore coarsening as the system minimizes surface energy, leading to irreversible density reduction, microcrack propagation, and significant signal drift [13–16]. Addressing these issues requires a material strategy that can not only homogenize the electrical potential landscape but also kinetically arrest, suppress, or mitigate these structural degradation pathways.

High-entropy oxides (HEOs), stabilized by high configurational entropy (S_{conf}), offer a revolutionary platform to tackle these issues. Beyond the well-known entropy stabilization effect [17–20], the severe lattice distortion induced by the size and mass mismatch of multiple principal cations [21–23] creates a unique “rugged” potential landscape that can act as a tunable filter for carrier transport [24–26]. We hypothesize that such intrinsic disorder can regulate the apparent hopping barriers in both grain interiors and grain-boundary regions, reducing the mismatch between their apparent activation energies and promoting a smoother macroscopic thermosensitive response. Furthermore, the “cocktail effect” of the high-entropy lattice fundamentally alters the doping thermodynamics [27]. The extremely high configurational entropy of the host matrix significantly reduces the Gibbs free energy of the system from a thermodynamic perspective, effectively compensating for the enthalpy penalty typically associated with heteroatom doping [28,29]. Meanwhile, the severe lattice distortion inherently arising from the compositional complexity creates a highly compliant structural environment. This environment accommodates ionic size mismatch through local elastic relaxation, thereby ensuring the stable incorporation of dopant species [30].

Existing high-entropy thermosensitive ceramics, including chromates and aluminates, have demonstrated the benefits of configurational-entropy-assisted stabilization [31–33]. However, many systems still suffer from a limited operating temperature range, inadequate Arrhenius linearity, or an incomplete understanding of the structure–transport relationship. Rare-earth niobates with a monoclinic fergusonite structure are promising candidates for high-temperature thermosensitive applications due to their stable NbO_x -based framework and ferroelastic strain-accommodation capability [34,35]. Nevertheless, a strategy that directly links high-entropy local structure regulation with carrier transport and grain/grain-boundary barrier matching remains lacking. To address this challenge, we designed a series of high-entropy $(\text{Ca}_{0.2}\text{La}_{0.2}\text{Ce}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})\text{Nb}_{1-x}\text{Mo}_x\text{O}_4$ (HEN- x Mo, $x = 0.0, 0.1, 0.2$, and 0.3) ceramics. The A-site combination of Ca^{2+} and multiple rare-earth cations introduces strong compositional disorder and local lattice distortion, while B-site Mo doping regulates the local structural environment and transport barriers. Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging acquired using aberration-corrected STEM, together with cation–cation distance statistics and displacement–strain analysis, reveals that Mo broadens the distribution of local atomic

configurations and increases the average cation-displacement amplitude from 12.02 pm in HEN to 18.16 pm in HEN-0.2Mo. Temperature-dependent Hall measurements reveal compensating changes in Hall mobility and carrier concentration, helping maintain a smooth resistivity response. High-temperature impedance spectroscopy further shows that HEN-0.2Mo has the smallest mismatch between the grain and grain-boundary activation energies, with $E_g = 1.209$ eV, $E_{gb} = 1.218$ eV, and $\Delta E_a \approx 0.009$ eV. The excellent Arrhenius linearity and B -value stability therefore arise from the combined effects of local structural regulation, carrier-transport redistribution, and reduced grain/grain-boundary barrier mismatch rather than a single homogenized conduction pathway. During aging at 1250 °C, HEN-0.2Mo undergoes postdensification accompanied by an increase in relative density and local strain redistribution, resulting in a stabilized-stage resistance drift of only 1.09% after 1000 h. This approach offers a new strategy for designing functional ceramics with high resistance to high-temperature degradation.

2 Experimental

2.1 Synthesis of high-entropy ceramics

The $(\text{Ca}_{0.2}\text{La}_{0.2}\text{Ce}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})\text{Nb}_{1-x}\text{Mo}_x\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.3$) high-entropy ceramics were synthesized via a conventional solid-state reaction method. High-purity powders of CaCO_3 , La_2O_3 , CeO_2 , Eu_2O_3 , Gd_2O_3 , Nb_2O_5 , and MoO_3 ($\geq 99.9\%$; Aladdin, China, or Sinopharm, China) were weighed according to the stoichiometric ratios. The mixtures were ball-milled in anhydrous ethanol for 8 h, dried for 24 h, and subsequently calcined at 1100 °C for 6 h. The calcined powders were remilled to ensure homogeneity and uniaxially pressed into disks ($\phi 10$ mm $\times$ 2.0 mm) at 20 MPa, followed by cold isostatic pressing at 300 MPa for 300 s to enhance green body density. Densification was conducted using a two-step sintering strategy. The samples were first heated to 1400 °C at 3 °C·min^{−1} without an isothermal dwell to activate neck formation and initial densification. They were then immediately cooled to 1280 °C at 2 °C·min^{−1} and held for 12 h. The lower second-step temperature was used to maintain diffusion-assisted pore shrinkage while limiting excessive grain-boundary migration and grain growth during prolonged holding [36,37].

2.2 Structural and microstructural characterization

Phase composition and crystal structure were analyzed by an X-ray diffractometer (XRD; Bruker D8 Advance, Bruker, Germany) with Cu K α radiation. Data were collected using a coupled θ – 2θ continuous position-sensitive device (PSD) scan over the 2θ range of 10°–80°, with a nominal step size of 0.02° and an acquisition time of 0.3 s per step. Owing to the parallel acquisition of the position-sensitive detector, this corresponds to an effective counting time of 57.6 s per angular position. Rietveld refinement was performed using TOPAS software. Polarization-resolved Raman spectra were acquired using a laser-scanning Raman system (Metatest 100, Metatest, China) with a 532 nm excitation laser. The Raman spectra were collected over the range of 200–800 cm^{−1}. During the angle-resolved measurements, the polarization angle of the incident laser was adjusted using a rotating half-wave plate, and the spectra were recorded under parallel and perpendicular polarization configurations. Angle-resolved polarization second-harmonic-generation (SHG) measurements were conducted using the Metatest optical characterization platform with an excitation wavelength of 1064 nm and a pulse width of 6 ps. Microstructural morphology

was characterized using a field-emission scanning electron microscope (FE-SEM; Supra 55 VP, Zeiss, Germany). For atomic-scale analysis, electron-transparent foils were prepared using a focused ion beam (FIB) system (G4 PFIB Hxe, Helios, Germany). Atomic-resolution HAADF images and energy-dispersive X-ray spectroscopy (EDS) elemental maps, collected using an aberration-corrected scanning transmission electron microscope (Talos F200X, FEI, USA) operated at an accelerating voltage of 300 kV, were used to characterize the crystal structure and elemental distribution. Lattice strain maps were derived from HAADF images using geometric phase analysis (GPA). The relative density was measured using an electronic densitometer (MH-300C, MatsuHaku, China) based on Archimedes' principle.

2.3 Electrical transport and stability evaluation

Temperature-dependent impedance spectroscopy was performed using an impedance analyzer (WK6500, Wayne Kerr, UK) over the frequency range of 20 Hz–10 MHz with an alternating current (AC) excitation voltage of 0.5 V. The temperature was increased at a rate of 3 °C·min⁻¹. At each target temperature, the sample was held for 300 s to approach thermal equilibrium before data acquisition, and 100 frequency points were collected for each impedance spectrum. The spectra were fitted using a series combination of two parallel *R*-constant phase element (CPE) elements to deconvolute the grain and grain-boundary contributions. Hall mobility and carrier concentration were measured using a Hall effect measurement system (HMS-7000, ECOPIA, Republic of Korea). Temperature-dependent Hall measurements of HEN-0.2Mo were carried out in AC mode from 400 to 1000 °C at 50 °C intervals under a maximum magnetic field of 0.6 T. For resistance-temperature characteristics and aging tests, platinum paste was applied to the polished surfaces of the ceramic disks and fired to form electrodes, with Pt wires serving as current collectors. Resistance data were automatically logged using a multichannel data acquisition unit (2638A, Fluke, USA). To ensure thermal equilibrium, three resistance readings were averaged at each temperature point (fluctuation within ±0.5 °C). For the long-term aging evaluation, one representative ceramic specimen from each composition was exposed to air at 1250 °C for up to 1000 h. Electrical characterization was performed intermittently at predetermined cumulative aging times. At each time point, the resistance was measured 6 times under identical conditions, and the average value was reported. The corresponding standard deviation reflects the repeatability of the electrical measurement for the same specimen and should not be interpreted as specimen-to-specimen variation.

2.4 Computational details

All calculations were performed using the projector augmented-wave method in the framework of density functional theory (DFT), as implemented in the Vienna *Ab initio* simulation package (VASP) [38]. The electron exchange-correlation interactions were parameterized by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [39,40]. The Brillouin zone was sampled by the Γ -centered *k*-mesh with a resolution of $(2\pi \times 0.04) \text{ \AA}^{-1}$ for geometry optimization and $(2\pi \times 0.03) \text{ \AA}^{-1}$ for single-point calculations. The plane-wave energy cutoff was set to 520 eV, and the convergence tolerances for residual force and energy on each atom during structure relaxation were set to 0.01 eV/Å and 10⁻⁶ eV/atom, respectively. Structural visualization was conducted utilizing VESTA software [41]. The VASPKIT code was used to facilitate the pre- and post-processing of the calculation results [42,43].

3 Results and discussion

As shown in Figs. 1(a) and S1 in the Electronic Supplementary Material (ESM), the formation energy of Mo substituting for Nb in CeNbO₄ was first evaluated. The calculated formation energy yielded a positive value, indicating that the substitution of Nb sites by Mo is energetically unfavorable. To examine the effect of the experimentally designed A-site high-entropy on Mo doping, a (Ca_{0.2}La_{0.2}Ce_{0.2}Eu_{0.2}Gd_{0.2})NbO₄ model containing multiple cations with different ionic radii and chemical characteristics was further considered. Subsequently, a randomly distributed 1 × 1 × 5 supercell of (Ca_{0.2}La_{0.2}Ce_{0.2}Eu_{0.2}Gd_{0.2})NbO₄ was constructed, and the formation energies for Mo occupying 20 distinct Nb sites were systematically calculated. Unlike CeNbO₄, the Mo substitution results in a reduction in the total system energy. The formation energies for all evaluated sites are negative. This indicates that within the high-entropy A-site ligand environment, the incorporation of Mo at Nb sites possesses a thermodynamic advantage. To verify these computational results and investigate the associated structural effects, a series of doped samples were synthesized experimentally. As shown in Fig. 1(b), the diffraction peaks evolve systematically with increasing Mo content. For $x \leq 0.2$, all reflections can be indexed to the monoclinic *C2/c* structure, indicating that the crystal structure remains unchanged after Mo doping. The corresponding Rietveld refinement results (Fig. S2 in the ESM) show good agreement between the experimental and calculated patterns, and the refined structural parameters are shown in Table S1 in the ESM. With increasing Mo content, the diffraction peaks gradually shift toward lower angles, accompanied by a systematic increase in the lattice parameters and unit-cell volume. This trend is consistent with the larger ionic radius of Mo compared with Nb and suggests an average lattice expansion within the monoclinic framework. The compositional complexity arises from the differences in ionic radius, atomic mass, and electronegativity among the constituent elements (Table S2 in the ESM). When the Mo content is further increased to $x = 0.3$, an additional tetragonal (002) reflection appears, indicating the formation of a secondary phase and suggesting that the solid-solution limit has been exceeded.

The local lattice response was further examined by high-resolution transmission electron microscopy (HRTEM). The undoped HEN sample viewed along the [100] zone axis exhibits interplanar spacings of 0.252 and 0.246 nm for the (040) and (002) planes, respectively (Fig. 1(c)). The corresponding fast Fourier transform (FFT) pattern, together with the simulated electron-diffraction pattern and structural projection shown in Figs. 1(d) and 1(e), confirms the monoclinic framework. For HEN-0.2Mo, the corresponding interplanar spacings increase to 0.267 and 0.253 nm (Fig. 1(f)). These local spacing changes are consistent with the structural evolution revealed by XRD refinement. Importantly, the HRTEM results should not be interpreted as evidence of a spatially uniform lattice expansion; instead, they provide local structural evidence that Mo doping modifies the lattice within the retained monoclinic framework.

Low-magnification TEM images of the undoped HEN sample reveal alternating stripe-like ferroelastic twin domains with a characteristic spacing of approximately 3–8 nm (Figs. 1(g) and 1(h)). The corresponding FFT pattern exhibits diffraction-spot splitting, confirming the coexistence of twin-related orientations (Fig. 1(i)). Dislocation arrays are observed near the twin-transition region in the IFFT image (Fig. 1(j)), indicating the presence of incoherent twin boundaries (ICTBs). Moiré fringes are also observed locally (Figs. 1(k)–1(m)), arising from the overlap of lattice regions with slightly different orientations or periodicities.

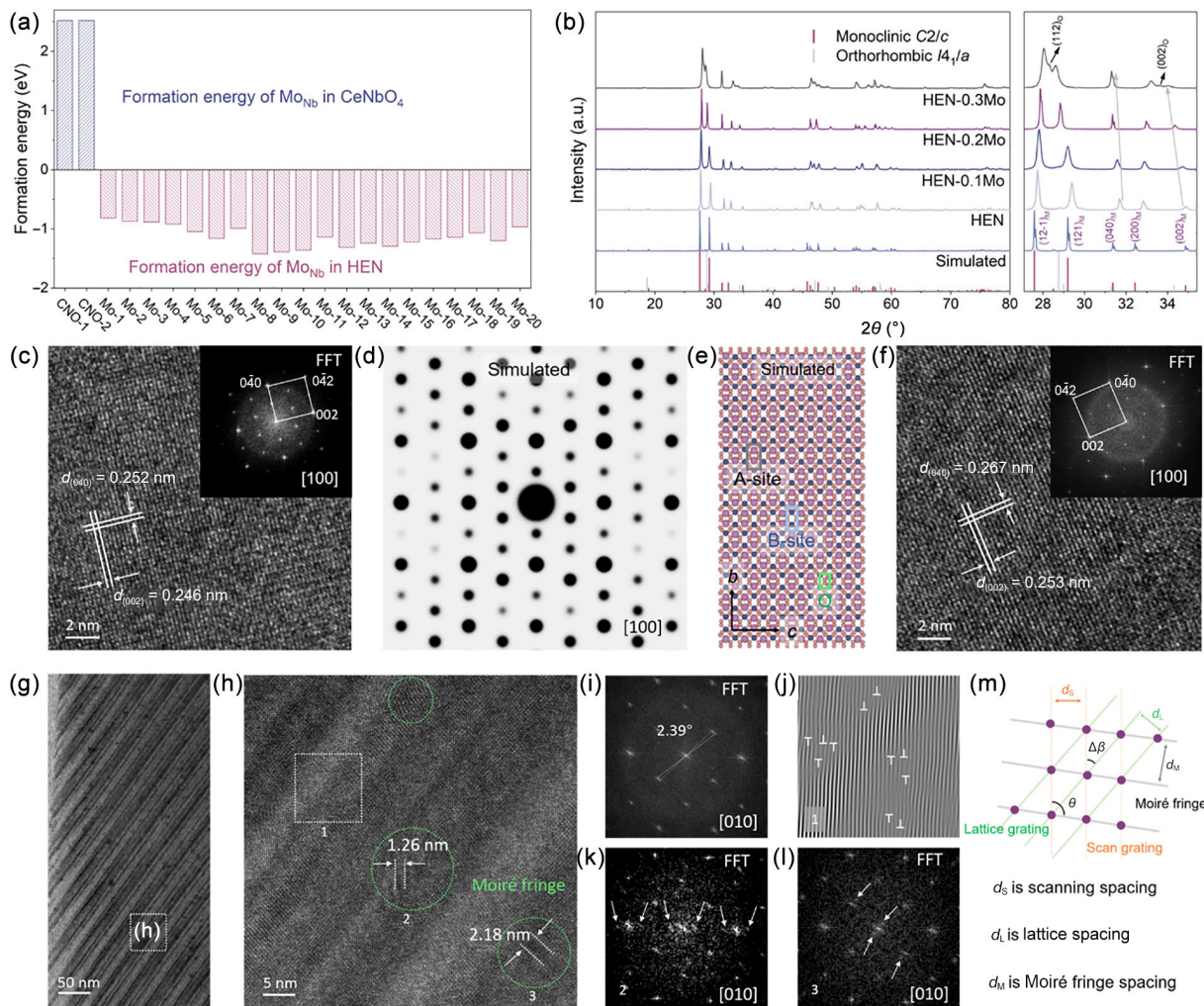


Fig. 1 Structural characterization and microstructural analysis. (a) Calculated formation energy of Mo substitution at Nb sites (Mo_{Nb}) in CeNbO_4 and $(\text{Ca}_{0.2}\text{La}_{0.2}\text{Ce}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})\text{NbO}_4$. (b) XRD patterns of ceramics. The right graph shows an enlarged view of the diffraction pattern in the range of 2θ from 27° to 35° . (c) HRTEM image of the undoped HEN sample; the inset shows the corresponding FFT pattern indexed along the $[100]$ zone axis. (d) Simulated electron diffraction pattern along the $[100]$ zone axis. (e) Atomic structure projected along the a -axis ($[100]$ direction), highlighting the A-site and B-site cation sublattices. (f) HRTEM image of the HEN-0.2Mo sample; the inset shows the corresponding FFT pattern indexed along the $[100]$ zone axis. Interplanar spacings of the (040) and (002) planes are indicated in (c) and (f). (g) Low-magnification TEM image of undoped HEN showing alternating stripe-like ferroelastic twin domains. (h) Enlarged TEM image of the boxed region in (g), highlighting twin contrast and Moiré fringes. (i) FFT pattern of (h) along the $[010]$ zone axis, showing diffraction spot splitting induced by twinning. (j) IFFT image reconstructed from region “1” in (h), revealing dislocation-rich twin transition zones. (k, l) FFT patterns of regions “2” and “3” in (h), corresponding to Moiré fringes arising from overlapping lattice gratings. (m) Schematic illustration of the geometric relationship between the lattice grating, scanning grating, and the resulting Moiré fringe.

Such fringes have been widely used in transmission electron microscopy (TEM) as a qualitative indicator of local lattice distortion, defects, and strain states [44,45]. The geometric relationship between the lattice gratings and the resulting Moiré fringes is illustrated in Fig. 1(m). After Mo doping, the ferroelastic twin domains remain observable, but the characteristic spacing increases to approximately 18–34 nm (Figs. S3(a) and S3(b) in the ESM). The corresponding FFT pattern and GPA maps reveal enhanced local structural modulation and spatially heterogeneous strain distributions (Figs. S3(c)–S3(f) in the ESM). These observations indicate that Mo doping modifies the ferroelastic-domain configuration and the nanoscale strain-accommodation behavior without disrupting the underlying monoclinic framework.

The local structural variations were further quantified by aberration-corrected HAADF-STEM analysis. Figure 2(a) presents a representative atomic-resolution HAADF-STEM image of HEN viewed along the $[010]$ zone axis. Although the average structure

remains monoclinic, noticeable fluctuations in atomic-column positions can already be identified at the local scale, reflecting the intrinsic structural complexity associated with the high-entropy cation configuration. Atomically resolved imaging and FFT analysis along the $[010]$ zone axis (Fig. S4 in the ESM) indicate that all samples maintain a single and highly ordered crystal structure at this scale; meanwhile, the corresponding interplanar spacing shows a gradual upward trend with higher Mo doping content, consistent with previous analytical conclusions. Figure 2(b) provides a schematic of the atomic arrangement in the twin transition region corresponding to the white dashed box in Fig. 2(a). This transition region manifests as a continuous atomic coordination adjustment across the (001) twin plane, rather than an ideal atomic-level abrupt interface. Figure 2(c) presents the cation spacing distribution projected along the c -axis. Since HAADF-STEM imaging is primarily sensitive to heavy elements, the distances obtained reflect the projected spacing between cation columns. Evidently, with increasing Mo doping, the distance

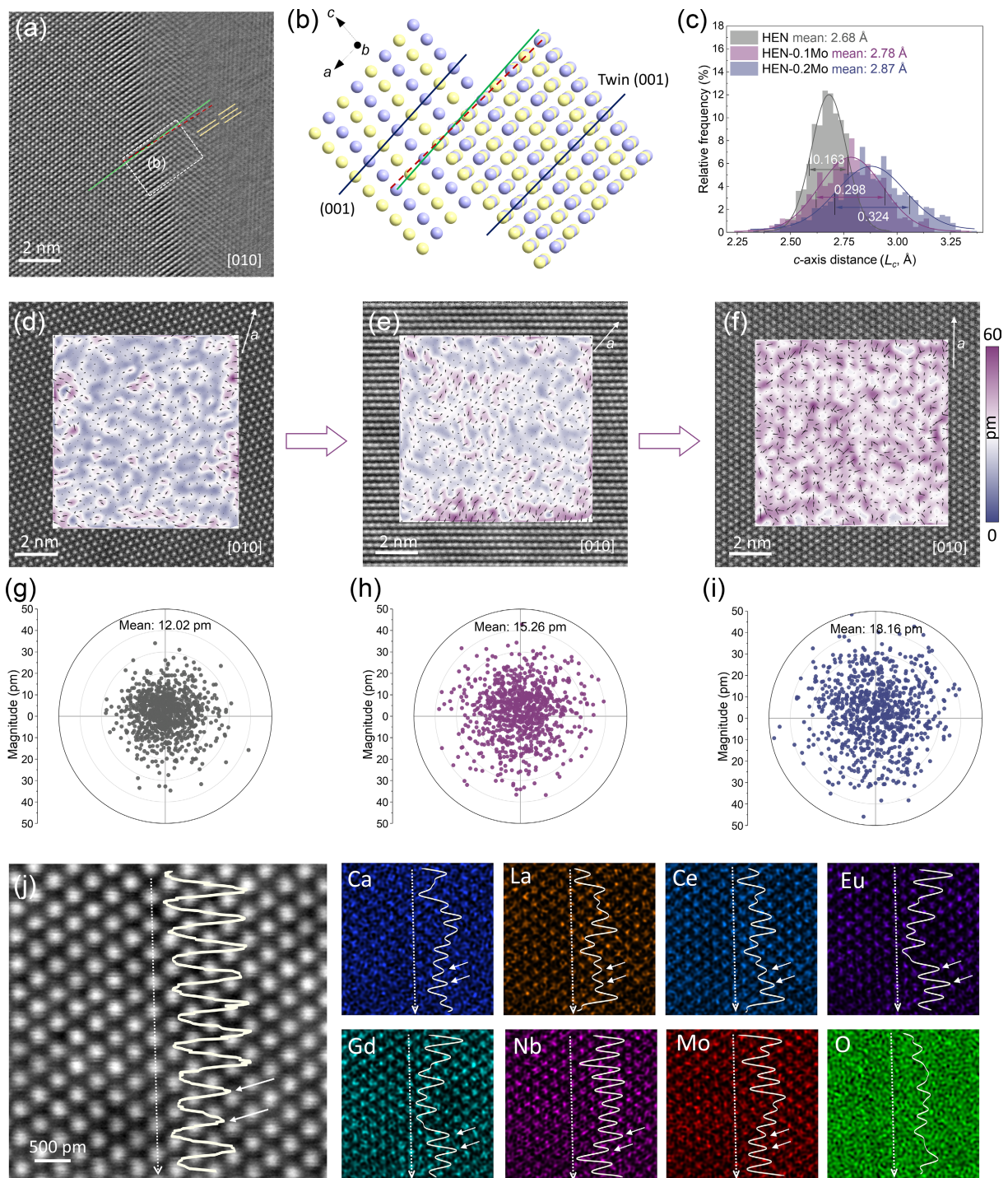


Fig. 2 Atomic-scale lattice distortion and elemental distribution. (a) HAADF-STEM image of HEN viewed along the [010] zone axis, showing atomic-scale features at a twin boundary. The angular mismatch between adjacent twin domains and dislocation features is highlighted. (b) Schematic illustration of the atomic configuration within the twin transition region corresponding to the white dashed box in (a), viewed along the [010] direction. (c) Statistical distributions of cation-cation distances projected along the c axis for HEN, HEN-0.1Mo, and HEN-0.2Mo samples obtained from STEM analysis. (d–f) Atomic displacement maps obtained by DSA from HAADF-STEM images of HEN, HEN-0.1Mo, and HEN-0.2Mo, respectively. Arrows indicate displacement direction and magnitude; color contours represent displacement amplitude. (g–i) Polar plots summarizing the statistical distribution of cation displacement magnitudes extracted from (d–f). (j) Atomic-resolution STEM-EDS elemental maps of HEN-0.2Mo with corresponding line profiles showing intensity fluctuations of individual elements along selected atomic columns.

distribution along the c -axis shifts overall toward larger values; the mean value increases from 2.68 Å for HEN to 2.87 Å for the HEN-0.2Mo sample. This trend aligns with the lattice expansion revealed by TEM observations and Rietveld refinement. In contrast, the average cation spacing along the a -axis does not exhibit a monotonic variation with Mo doping (Fig. S5 in the ESM). However, Gaussian fitting of its distribution reveals that the

full width at half maximum (FWHM) of the bond length distribution gradually increases with Mo doping, indicating a significant enhancement in the degree of local structural dispersion.

Furthermore, we employed displacement separation analysis (DSA) [46] to extract atomic displacement information from high-resolution HAADF-STEM images (Figs. 2(d)–2(f)). The results

reveal nonnegligible cation displacements in all samples, and the displacement directions exhibit a disordered distribution, indicating the presence of nonperiodic local lattice distortions—a typical hallmark of high-entropy lattices. Statistical analysis of the displacement data was performed using polar plots (Figs. 2(g)–2(i)), demonstrating the deviation relationship between experimentally measured atomic positions and corresponding positions in the ideal $C2/c$ monoclinic structure. Quantitative calculations reveal that the average cation displacement amplitudes for the HEN, HEN-0.1Mo, and HEN-0.2Mo samples are 12.02, 15.26, and 18.16 pm, respectively, exhibiting a clear monotonic upward trend. It should be emphasized that although this significantly enhanced lattice distortion macroscopically correlates positively with the increase in the system's configurational entropy (the entropy metric rises from 1.61 to 2.11; see ESM for computational details), its microscopic physical origin is essentially driven by a multivariate strong-coupling mechanism.

With the introduction of Mo, the compositional complexity of the system increases, directly inducing more pronounced local chemical fluctuations (Fig. 2(j)). Multiple mismatches in ionic radius, atomic mass, and electronegativity exist among Mo, the native Nb ions, and the complex A-site species. Such variations in local chemical variables induce highly inhomogeneous local stress fields at the nanoscale [47]. The significant local strain concentrations disclosed by GPA (Figs. S3(d)–S3(f) in the ESM) serve as direct evidence of this conversion from chemical mismatch into a mechanical response. Furthermore, to accommodate and release this inhomogeneous strain energy, the defect structural variables within the material undergo reconstruction, manifested as a substantial increase in the spacing of ICTBs and a rise in the distribution density of nanoscale Moiré fringes. Consequently, the drastic cation displacements measured by DSA are not simply determined by the configurational entropy

value; rather, they represent the ultimate physical manifestation of the synergistic interplay and mutual accumulation among the aforementioned local chemical fluctuations, inhomogeneous strain fields, and defect structure reconfiguration. This complex microscopic interaction effectively breaks the long-range lattice periodicity and induces a deeper level of local structural inhomogeneity at the atomic scale. Crucially, although the average structure of the material maintains the nominal centrosymmetric $C2/c$ space group, significant local atomic displacements and compositional fluctuations effectively break inversion symmetry at the nanoscale. This is consistent with the observed strong SHG signals and polarized Raman anisotropy results (Fig. S6 in the ESM), reconfirming not only the significant internal structural anisotropy of the material but also foreshadowing an anisotropic transport mechanism for carriers at the microscopic scale. These features indicate the formation of local noncentrosymmetric regions within the system; this transition toward effective C_2 symmetry is primarily driven by the configurational entropy effect and may be further reinforced by factors such as local electric fields generated by defects and symmetry breaking at grain boundaries.

To reveal the influence of lattice distortion on electrical transport behavior, Figs. 3(a) and S7 in the ESM present the $\ln\rho$ and $1000/T$ curves for HEN and Mo-doped HEN samples. All samples exhibit a distinct inflection point, clearly dividing the electrical transport process into a low-temperature region and a high-temperature region. In the low-temperature region from -50 to 800°C , the resistivity of the materials gradually increases with increasing Mo doping, while a good linear relationship is maintained between $\ln\rho$ and $1/T$, indicating that the transport process in this temperature range possesses thermally activated characteristics. The aforementioned TEM and STEM results demonstrate that the introduction of Mo significantly enhances local structural distortion, manifesting as a higher density of

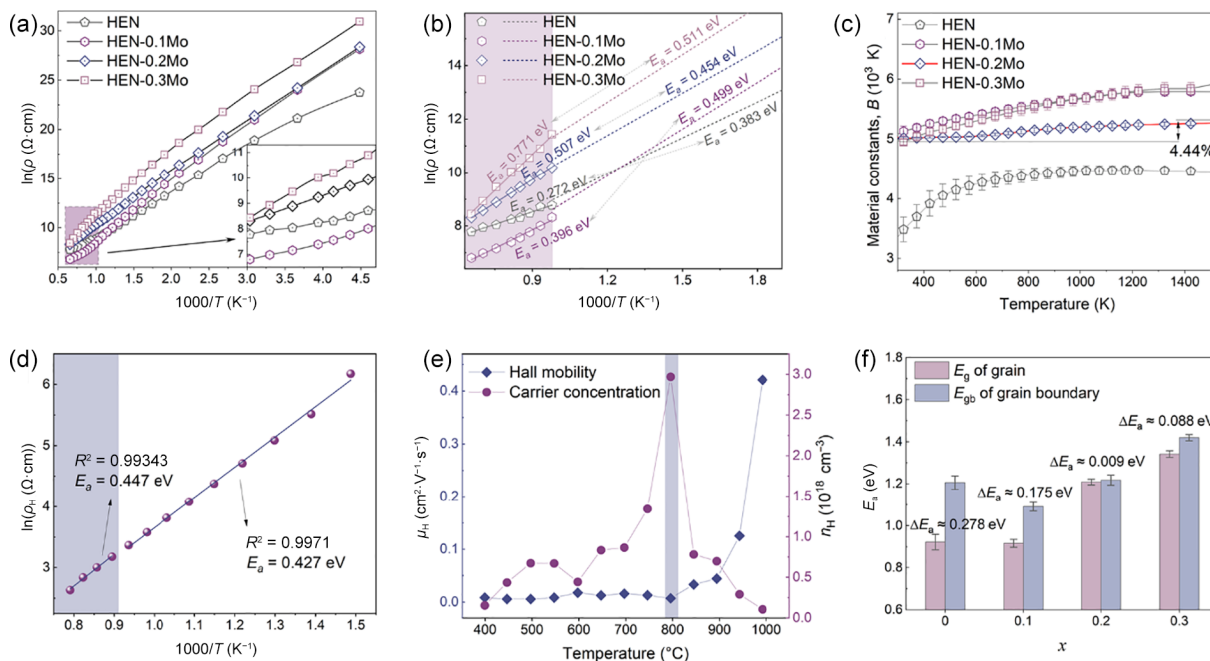


Fig. 3 Electrical transport properties and conduction mechanisms. (a) $\ln\rho$ as a function of $1000/T$ for HEN and Mo-doped HEN samples; the inset shows an enlarged view of the high-temperature region (800–1250 °C). (b) Activation energies extracted from Arrhenius fitting in the low- and high-temperature regions. (c) Temperature dependence of the B -value. (d) Arrhenius plot of ρ_H as a function of $1000/T$, where ρ_H denotes the resistivity measured during the Hall test. The solid lines represent piecewise linear fits in the temperature ranges of 400–800 and 845–1000 °C. (e) Temperature dependence of the Hall mobility (μ_H) and Hall carrier concentration (n_H). (f) Activation energies of the grain and grain-boundary responses extracted from the temperature-dependent impedance fitting results. The values were obtained from Arrhenius fitting of the fitted R_g and R_{gb} .

Moiré fringes and stronger atomic displacement disorder. The enhanced lattice distortion is expected to strengthen the interaction between carriers and the locally heterogeneous lattice environment. This effect may modify the energetic stability of localized carrier states and broaden the distribution of thermally activated hopping barriers, thereby contributing to the observed mobility suppression and resistivity evolution [48,49]. Under conditions of limited thermal energy, it is difficult for carriers to effectively cross the potential barriers caused by local strain fields; thus, their transport process is more easily limited by distortion-related scattering, resulting in increased resistivity in the low-temperature region [50]. The room-temperature Hall results (Fig. S8 in the ESM) show that Mo doping is accompanied by a pronounced suppression of the Hall mobility, whereas the change in the Hall carrier concentration is comparatively moderate. This composition-dependent trend suggests that the increase in resistivity after Mo doping is associated primarily with hindered carrier migration rather than solely with a reduction in the number of electronic carriers.

The inset of Fig. 3(a) displays the relationship between $\ln \rho$ and $1000/T$ in the high-temperature region (800–1250 °C), where the transport behavior differs significantly from that in the low-temperature region. The temperature dependence of resistivity for thermistor ceramics follows the Arrhenius law, where $\ln \rho$ is linearly related to $1000/T$, expressed as Eq. (1) [51]:

$$\rho = \rho_0 \exp(E_a/k_B T) = \rho_0 \exp(B/T) \quad (1)$$

where E_a is the activation energy, ρ_0 is the preexponential factor, k_B is the Boltzmann constant, and T is the absolute temperature. Based on this relationship, the activation energies corresponding to the low-temperature and high-temperature regions were calculated by fitting, with specific values and trends shown in Fig. 3(b). The material constant B can be calculated using Eq. (2) [51]:

$$B = \frac{T_1 T_2}{T_2 - T_1} \ln \frac{\rho_1}{\rho_2} \quad (2)$$

where ρ_1 and ρ_2 are the resistivities at T_1 and T_2 , respectively. We calculated the activation energies and thermistor performance-related parameters for all samples based on Eqs. (1) and (2) (Table S3 in the ESM). It can be observed that the high-temperature activation energy increases monotonically with increasing Mo doping, indicating that the introduction of Mo effectively modulates the energy barrier in the high-temperature region, raising the intrinsic energy threshold required for carrier excitation or migration, while the localized states introduced by doping do not dominate the conduction process at high temperatures. Most notably, the HEN-0.2Mo sample exhibits optimal matching between low- and high-temperature activation energies, with a difference of only 0.047 eV. This continuity in the energy scale effectively suppresses the abrupt change in the conduction mechanism caused by temperature fluctuations, allowing HEN-0.2Mo to exhibit a nearly ideal linear response over the extremely wide temperature range of –50 to 1250 °C. The coefficient of determination (R^2) for the linear fitting of $\ln \rho$ and $1/T$ is as high as 0.99907, and the residual sum of squares (RSS) is only 0.59337, which are significantly superior to those of other doped compositions.

The stability of the B -value is an important indicator of the temperature dependence of the thermosensitive response. As shown in Fig. 3(c), Mo incorporation markedly improves the consistency of the B -value over the investigated temperature range. Compared with the undoped HEN sample, the Mo-doped

samples exhibit smaller B -value variations, among which HEN-0.2Mo shows the lowest fluctuation amplitude of 4.44%. This result indicates that HEN-0.2Mo maintains a relatively stable thermosensitive response over a broad temperature range. Although the TEM results suggest a possible microstructural contribution to the enhanced B -value stability, the underlying mechanism is likely more complex than the effect of any single structural parameter. The TEM observations show that Mo incorporation increases the ferroelastic twin spacing from approximately 3–8 nm for HEN to 18–34 nm for HEN-0.2Mo, indicating a reduced spatial density of ICTBs. Because ICTBs are local interfacial structural discontinuities that can introduce electronically active defect states, carrier traps, and/or potential barriers, a reduced ICTB density is expected to decrease interface-mediated perturbations to carrier transport, thereby yielding a more spatially uniform local transport landscape [52–54].

To further examine how the carrier-transport contributions evolve at elevated temperatures, temperature-dependent Hall measurements were performed on HEN-0.2Mo over the temperature range of approximately 400–1000 °C (Table S4 in the ESM). The Hall coefficient remains positive throughout the investigated temperature range, indicating that the dominant Hall response does not undergo a sign reversal. Meanwhile, the resistivity decreases monotonically with increasing temperature and retains a smooth thermally activated dependence. Piecewise Arrhenius fitting yields activation energies of approximately 0.427 eV in the range of 400–800 °C and 0.447 eV in the range of 845–1000 °C (Fig. 3(d)), corresponding to a small difference of approximately 0.020 eV. Notably, the Hall parameters exhibit a pronounced crossover near 800 °C (Fig. 3(e)). In the lower-temperature region, the decrease in resistivity is accompanied mainly by an increase in the Hall carrier concentration, while the Hall mobility remains relatively low. Above approximately 800 °C, the Hall mobility increases markedly, whereas the Hall carrier concentration decreases. Within an effective Hall description framework, these compensating trends account for the smooth evolution of the macroscopic resistivity despite the temperature-dependent redistribution of the electronic transport contributions.

From a microscopic perspective, the influence of lattice distortion on carrier transport should be understood in terms of the energetic landscape of localized carrier states. Small-polaron formation involves carrier localization accompanied by local lattice relaxation. The energetic stability of such a localized state is governed by the balance between the electronic energy gained through localization and the elastic energy required to distort the surrounding lattice [55]. In the present system, Mo doping introduces chemically heterogeneous B-site-centered environments and enhances the spatial variation of local tensile and compressive strain, as revealed by the GPA results. These local structural fluctuations may alter the relative stability of localized carrier states by modifying the surrounding bond lengths, bond angles, and elastic relaxation energies. The hopping of a localized carrier between neighboring sites requires reorganization of the surrounding lattice. Therefore, the heterogeneous strain field can also modify the relative energies of the initial, transition, and final states, producing a distribution of thermally activated hopping barriers [56]. The increased local strain heterogeneity and cation-displacement amplitudes observed after Mo doping are consistent with the pronounced reduction in carrier mobility obtained from the Hall measurements. However, the GPA analysis does not directly quantify the small polaron formation energy or migration barrier. The present results therefore support a strain-modulated hopping-like transport

picture rather than a quantitative determination of individual small-polaron energetics.

Impedance spectroscopy allows for the separation of characteristic responses from grains, electrical interfaces, and defect-related polarization processes in the frequency domain, providing direct microscopic evidence for the physical origins of the aforementioned Arrhenius behavior, activation energy evolution, and B -value stability. Accordingly, we systematically studied the impedance response characteristics of HEN and Mo-doped HEN samples at different temperatures. As the temperature increases, the diameter of the semicircles in the Nyquist plots for all samples gradually decreases (Figs. S9(a)–S9(d) in the ESM), exhibiting a typical NTC effect. The impedance data were decoupled using an (R -CPE) series equivalent circuit model, successfully separating the electrical responses of the bulk and the grain boundary (Figs. S9(e)–S9(h) in the ESM). To rationalize the assignment of the two arcs, the effective capacitances were calculated from the fitted resistance (R), CPE coefficient (Q), and CPE exponent (n) (Tables S5–S8 in the ESM). The high-frequency arc exhibits effective capacitances on the order of 10^{-12} – 10^{-11} F, which is consistent with a grain or bulk response, whereas the low-frequency arc gives much larger capacitances on the order of 10^{-9} – 10^{-8} F, characteristic of a grain-boundary response [57]. Therefore, the high-frequency and low-frequency arcs are assigned to the grain and grain-boundary responses, respectively. The results indicate that with the introduction of Mo, a significant transition occurs in the dominant resistance contribution of the system. In the undoped HEN sample, the size of the mid-to-low frequency semicircle representing the grain boundary response is significantly larger than that of the high-frequency semicircle representing the grain, indicating that grain boundaries are the main obstacle to charge transport. However, Mo doping induces a reversal of this hierarchical structure, with grain resistance becoming the dominant factor. This transition suggests that due to the intensified lattice distortion and local chemical fluctuations caused by Mo substitution, the carrier hopping barrier within the grains exceeds that of the interface regions. Based on the fitted grain and grain-boundary resistances, Arrhenius relationships were reconstructed (Fig. S9(i) in the ESM), and the corresponding activation energies were calculated (Fig. 3(f)). HEN-0.2Mo exhibits the smallest mismatch between the grain and grain-boundary activation energies, with values of 1.209 and 1.218 eV, respectively, corresponding to $\Delta E_a \approx 0.009$ eV. This reduced mismatch indicates a more balanced apparent transport-barrier landscape between the grain interiors and grain boundaries, which is consistent with the highly linear resistance–temperature response and the reduced B -value fluctuation of HEN-0.2Mo. Therefore, the highly linear Arrhenius response of HEN-0.2Mo should not be attributed solely to the convergence of E_g and E_{gb} . Rather, it is interpreted as the combined result of reduced grain/grain-boundary barrier mismatch, thermally activated hopping-like transport, and the temperature-dependent redistribution of apparent electronic transport contributions revealed by Hall measurements. In contrast, HEN, HEN-0.1Mo, and HEN-0.3Mo show larger differences between the grain and grain-boundary activation energies, indicating a less balanced transport-barrier distribution.

To evaluate the long-term reliability of high-entropy thermistors under severe operating conditions, accelerated aging tests were conducted at 1250 °C for 1000 h. The resistance drift rate was calculated using Eq. (3) [58]:

$$\Delta R/R_0 = (R_0 - R_t)/R_0 \quad (3)$$

where R_0 represents the initial resistance value of the unaged sample, and R_t represents the resistance value of the sample aged for t (h). Figure 4(a) presents the time-dependent evolution of $\Delta R/R_0$ for HEN- x Mo ceramics, derived from the resistance and drift-rate data measured at 1000 °C after aging at 1250 °C, as summarized in Table S9 in the ESM. The curves exhibit two distinct kinetic regimes: an initial sensitization stage during the first 100 h, followed by a stabilization stage. The sensitization phase is primarily governed by metastable relaxation (such as oxygen adsorption/desorption equilibrium) rather than the reorganization of the fundamental lattice structure. Notably, the HEN-0.2Mo sample exhibits an anomalous resistance drift rate surge of up to 36.8% within the first 50 h. However, once it enters the stabilization phase, this composition demonstrates superior stability. Based on this phase, the aging drift rate can be calculated using Eq. (4) [59]:

$$\eta = (\Delta R_1/R_0) - (\Delta R_2/R_0) \quad (4)$$

The calculated η values for HEN, HEN-0.1Mo, HEN-0.2Mo, and HEN-0.3Mo were 11.64%, 5.26%, 1.09%, and 3.49%, respectively, establishing HEN-0.2Mo as the composition with the most stable resistance to thermal aging.

To evaluate the thermosensitive performance of HEN-0.2Mo, a comprehensive comparison is provided in Table S10 in the ESM. The comparison includes conventional spinel, perovskite, perovskite-like, pyrochlore, composite, and high-entropy thermosensitive ceramics. Because the reported aging protocols vary substantially among different studies, the resistance drift rates should be interpreted together with the corresponding aging temperature and duration. Aging tests conducted close to the upper limit of the operating temperature range provide a more stringent assessment of long-term thermal reliability. In this context, HEN-0.2Mo exhibits a competitive combination of a broad operating temperature range from –50 to 1250 °C, high linearity ($R^2 = 0.99907$), and a stabilized-stage resistance drift rate of 1.09% after aging at 1250 °C for 1000 h.

To further evaluate the practical sensing reliability, the stabilized-stage resistance drift was converted into an equivalent drift-induced temperature deviation using the standard NTC β model (Table S11 and Note S4 in the ESM for the derivation). For thermally activated conduction, the effective B -value is related to the activation energy by $B = E_a/k_B$. Using the activation energy of 0.501 eV obtained for HEN-0.2Mo in the high-temperature region, an effective B -value of approximately 5814 K is obtained. Accordingly, the stabilized-stage resistance drift of 1.09% corresponds to equivalent drift-induced temperature deviations of approximately 4.3 °C at 1250 °C, 3.0 °C at 1000 °C, and 2.4 °C at 800 °C. These values describe the calibration offset induced by resistance drift after the initial conditioning stage rather than the total measurement uncertainty of a practical sensing system. The relatively large resistance variation during the initial sensitization stage indicates that preaging conditioning and recalibration are necessary before deployment.

To clarify the microstructural origin of the long-term electrical stability, the surface microstructures, grain-size distributions, and relative densities of HEN- x Mo ceramics were analyzed after aging at 1250 °C for different durations (Figs. S10 and S11 and Table S12 in the ESM). In general, high-temperature aging provides a thermodynamic driving force for reducing interfacial energy through grain-boundary migration, grain coarsening, and possible post-densification [20,23]. Therefore, grain growth is observed in all compositions. However, grain growth alone cannot explain the distinct aging behavior of HEN-0.2Mo. A comparative analysis of

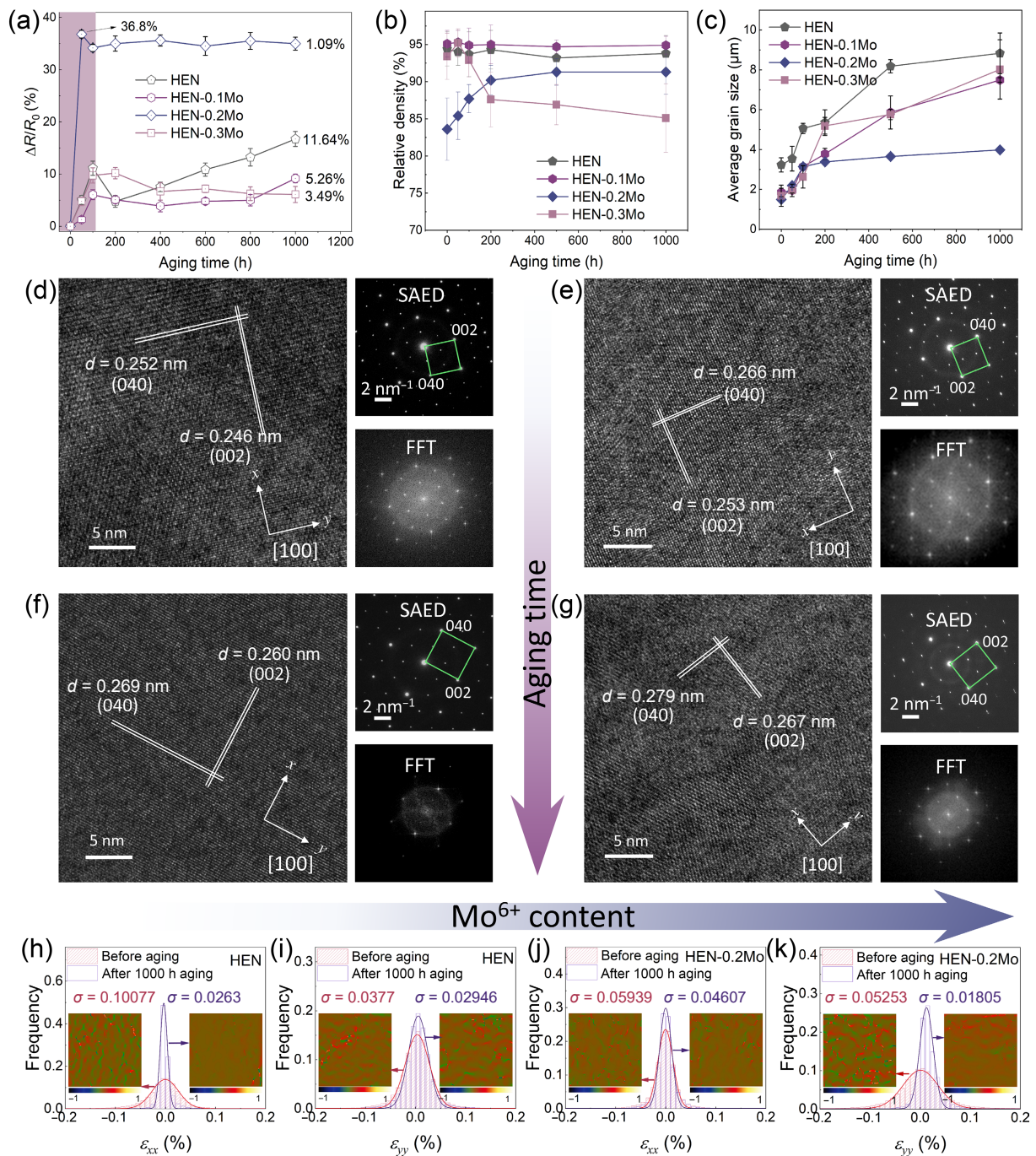


Fig. 4 Long-term thermal stability and microstructural evolution under accelerated aging (1250 °C, 1000 h). (a) Intermittently sampled $\Delta R/R_0$ of representative HEN and Mo-doped specimens. Each curve corresponds to one tested specimen. The markers represent the experimentally acquired aging time points, and the connecting lines are guides to the eye. The shaded region denotes the initial sensitization stage, and the aging drift rates (η) calculated for the subsequent stabilized stage are indicated. Error bars indicate the standard deviations of repeated electrical readings obtained from the same specimen at each aging time point and do not represent specimen-to-specimen variation. (b) Relative densities of HEN-*x*Mo ceramics after aging for different times. (c) Evolution of the average grain size as a function of aging time for HEN-*x*Mo ceramics aged at 1250 °C. HRTEM images viewed along the [100] zone axis for (d) pristine HEN, (e) pristine HEN-0.2Mo, (f) aged HEN, and (g) aged HEN-0.2Mo. Insets show the corresponding SAED patterns (top) and FFT diffractograms (bottom). GPA strain maps and corresponding strain distribution histograms for (h, i) HEN and (j, k) HEN-0.2Mo. (h, j) display the strain field along the *x*-direction (ϵ_{xx}), and (i, k) display the strain field along the *y*-direction (ϵ_{yy}). The red and purple curves in the histograms represent the Gaussian fits for the pristine and aged states, respectively, with σ denoting the RMS strain deviation.

the microstructure and relative density further reveals a composition-dependent aging response among the HEN-*x*Mo ceramics. The unaged HEN-0.2Mo sample shows a relatively low initial relative density of 83.6% (Fig. 4(b)). After aging at 1250 °C, its relative density increases progressively to 85.4%, 87.7%, 90.2%, and 91.3% after aging for 50, 100, 200, and 500 h, respectively, and remains at approximately 91.3% after aging for 1000 h. This time-

dependent density evolution indicates an aging-induced postdensification process in HEN-0.2Mo. Meanwhile, the grain-size statistics show that HEN-0.2Mo exhibits relatively moderate grain growth, with the average grain size increasing from 1.49 to 3.98 μm after aging for 1000 h (Fig. 4(c)). Therefore, the aging response of HEN-0.2Mo is better described as postdensification accompanied by controlled grain growth rather than as abnormal

microstructural coarsening. The initial increase in resistance during the early aging stage may be associated with microstructural rearrangement during postdensification, including grain-boundary relaxation and local transport-barrier evolution. After the density reaches a more stable level, the resistance variation becomes much smaller, leading to a stabilized-stage drift rate of 1.09%. However, this behavior should not be interpreted as a fully proven intrinsic “self-healing” mechanism. Instead, it likely reflects a coupled aging response involving thermally activated postdensification, limited local mass transport, grain-boundary relaxation, and ferroelastic strain accommodation.

To reveal the structural evolution mechanisms during long-term operation at the atomic scale, HRTEM characterization and GPA were performed on HEN and HEN-0.2Mo samples before and after aging (1000 h). HRTEM images taken along the [100] zone axis, along with the corresponding selected area electron diffraction (SAED) patterns and FFT images (Figs. 4(d)–4(g)), confirm that even after prolonged high-temperature aging, the samples maintain high-quality single-crystal integrity without undergoing amorphization. Notably, the aging treatment results in a universal lattice expansion phenomenon. In addition to the intrinsic lattice expansion caused by the introduction of large-sized Mo cations, thermal aging further induces an increase in interplanar spacing. For instance, after aging, the (040) and (002) interplanar spacings of the HEN sample expanded to 0.269 and 0.260 nm, respectively; similarly, the corresponding interplanar spacings of HEN-0.2Mo increased to 0.279 and 0.267 nm, respectively. This volumetric expansion of the unit cell indicates that the aging process effectively released the residual internal compressive stresses “frozen” in the sample during the initial rapid sintering process, driving the lattice toward a more relaxed equilibrium state [60]. We visualized and quantified the strain evolution accompanying this relaxation process using GPA strain distribution maps (ϵ_{xx} and ϵ_{yy}) and root mean square deviation (RMS; σ) (Figs. 4(h)–4(k)) [61,62]. Comparative analysis of the strain histograms shows that the local lattice strain field undergoes significant homogenization after aging. For both HEN and HEN-0.2Mo, the strain distribution curves narrow markedly, reflecting a general decrease in σ values in both axial directions. This attenuation of local strain fluctuations confirms that prolonged heat treatment effectively acts as an annealing process, allowing high-entropy constituent atoms to cross local potential barriers and adjust to energetically more favorable lattice positions. Consequently, this transition from a high-strain metastable state to a homogenized, stress-relaxed configuration greatly reduces the thermodynamic driving force for further structural degradation, thereby providing a solid microstructural basis for the exceptional long-term electrical stability of the HEN-0.2Mo thermistor.

4 Conclusions

In summary, we developed Mo-regulated high-entropy rare-earth niobate thermosensitive ceramics for ultrawide-temperature NTC thermistor applications. The A-site high-entropy promotes Mo doping and preserves the monoclinic framework when x is less than 0.2, while Mo doping further tailors the local structure and transport characteristics of the ferroelastic niobate lattice. Multiscale structural analyses show that Mo doping broadens local cation-distance distributions, increases cation-displacement amplitudes, and reconfigures ferroelastic domains, providing direct atomic-scale evidence of local structural regulation. The optimized HEN-0.2Mo ceramic exhibits highly linear Arrhenius behavior ($R^2 > 0.999$) and a low B -value fluctuation of 4.44% from

–50 to 1250 °C. Temperature-dependent Hall measurements reveal a compensating evolution of Hall mobility and carrier concentration, helping sustain a smooth resistivity response at elevated temperatures. High-temperature impedance analysis further shows that the HEN-0.2Mo ceramic shows a mismatch between grain and grain-boundary activation energies, with $E_g = 1.209$ eV, $E_{gb} = 1.218$ eV, and $\Delta E_a \approx 0.009$ eV. Its stable thermosensitive response therefore arises from the combined effects of local structural heterogeneity, apparent carrier-transport redistribution, and balanced grain/grain-boundary transport barriers, rather than from a single homogenized conduction pathway. During aging at 1250 °C, HEN-0.2Mo undergoes postdensification accompanied by an increase in relative density and local strain redistribution, resulting in a stabilized-stage resistance drift of only 1.09% after 1000 h. These results show that high-entropy thermosensitive ceramics can advance beyond configurational-entropy-driven phase stabilization through the integration of B-site dopant regulation, ferroelastic structural modulation, and transport-barrier matching. This mechanism-based design strategy offers a practical route toward thermally stable NTC ceramics for extreme-temperature sensing.

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Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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