# High entropy strategy on thermoelectric materials

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High-entropy materials, which consist of multiple elements occupying a single sublattice in a disordered manner, have emerged as innovative material systems with various promising applications. Many macroscopic physical properties, such as electrical transport and thermal transport, are closely related to the periodic distribution of atoms. In high-entropy compounds, the long-range periodic arrangement of atoms is broken down by the disordered distribution of various elements, which would lead to changes in physical properties. Therefore, the high-entropy idea will open new avenues for designing these functional materials with promising performance and high reliability. This perspective focuses on the high-entropy strategies of thermoelectric materials, discussing how high entropy will alter their properties. The possible routes of designing high-entropy high-performance thermoelectric materials are prospected, which can also provide enlightenment for the development of high-entropy systems in other research fields.
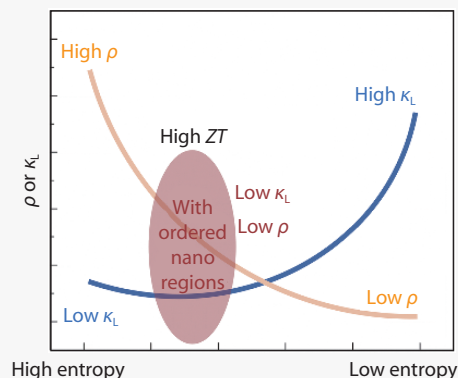
High igh entropy materials are formed by mixing multiple elements in equal or near-equal proportions at a single crystallographic site and are attracting increasing attention due to their versatile properties.[1–6] According to the Gibbs law $\Delta G = \Delta H - T\Delta S$ (where G is the Gibbs free energy, H is the enthalpy, T denotes the absolute temperature, and S is the entropy), a sufficiently high entropy can dominate the change of enthalpy, making $\Delta G < 0$. Therefore, new compounds stabilized by entropy can be obtained.[7–8] Typically, a multi-element material with entropy larger than $1.61R$ (R denotes the molar gas constant, 8.31 J mol^{-1} K^{-1}) can be regarded as a high entropy compound,[9] which distinguishes it from an ordinary multi-element doped material. The idea of high entropy is first applied in metal alloys, which results in high-entropy alloys with exceptional properties such as high strength and high corrosion resistance.[1,10–11] Since then, the concept of high entropy has also been broadened into various other fields such as catalysis,[12–13] dielectrics,[6,14] and thermoelectrics,[15–17] where the materials usually have a complex crystal structure consisting of different sets of sublattice. For those materials with complex crystal structures, multiple elements can populate one single sublattice to engineer the configurational disorder, yielding high-

entropy oxides, tellurides, etc. Typical high-entropy compounds with NaCl (AB) structure and perovskite (ABO$_3$) structure are presented in Figure 1a and 1b, respectively. When only one single sublattice is occupied by multiple elements and the other sublattices remain undisturbed, the configurational entropy can still be high, provided that there are enough alloying species and their ratio is close. Meanwhile, the undisturbed sublattice would also allow for greater lattice distortion, further stabilizing the structure.[3]

The periodicity of the atoms is one of the most important features of crystal structures and the origin of most macroscopic functions such as heat transport.[18] The introduction of multiple elements, if randomly and disorderly occupying one single sublattice, would result in the interruption of the local atom periodicity. In thermoelectric materials, the transport of charged carriers and heat-carrying phonons is highly responsive to atomic periodicity. The performance of thermoelectric materials is characterized by the dimensionless figure of merit, $ZT = S_M{}^2\sigma T/\kappa$, where S_M is Seebeck coefficients (normally S is used to represent the Seebeck coefficient, here the subscript is used to distinguish Seebeck coefficient from the entropy), σ is electrical conductivity, κ is thermal conductivity, and T is the absolute temperature.[19–21] Physical properties are not only attributed to individual constituent elements but also to their mutual interactions. Different elements have different atomic masses and ionic radii, which would also lead to bonds with different strengths. Since the phonon dispersion is closely related to the atomic mass and the bond strength, the interrupted periodicity of these parameters would significantly scatter the phonons.[22–23] As a result, the phonons will be localized, leading to low lattice thermal conductivity, which contributes to enhanced thermoelectric

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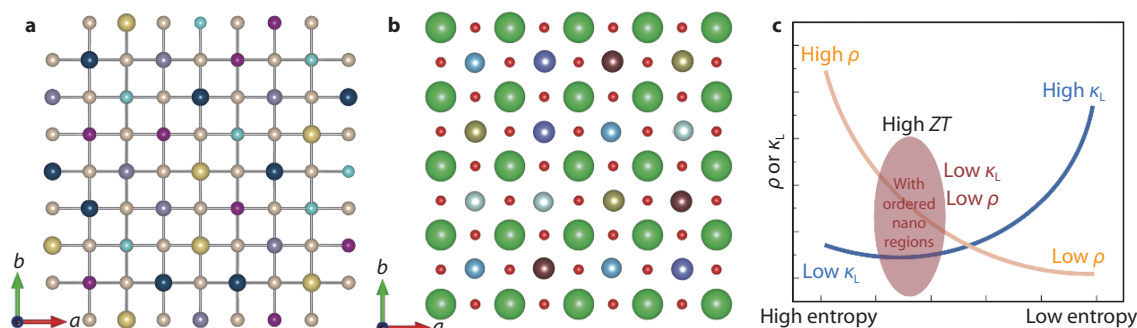
Fig. 1　**a** High-entropy compound with a typical *Fm-3m* structure (AB, sublattice A is engineered with high-entropy). **b** High-entropy perovskite (ABO$_3$, sublattice A is engineered with high entropy). **c** Schematic display of electrical resistivity and lattice thermal conductivity for the compound with different entropies.

properties.[5,15–16,24–27] As for electrical properties, high-entropy compound prefers to hold simple phases with high symmetry, which can provide the most equivalent sites for multiply elements to occupy and maximize the configuration entropy.[28] The high symmetrical structure usually have electronic bands with multivalley features, which will enhance the electronic density-of-states and effective mass, leading to a high Seebeck coefficient.[15,29] Due to the above advantages of high-entropy materials, the potential of high-entropy strategy in thermoelectricity has been firstly demonstrated in Pb(S/Se/Te), Cu$_2$(S/Se/Te), and (Mn/Ge/Sn/Pb)Te.[15,30] Then this idea has been extended to various systems such as SnTe, SnSe, GeTe, and PbSe.[5,16,24,26,29] Particularly, the developed (Pb/Sn)(Se/Te/S) material has a high *ZT* of 1.8 at 900 K, while (Ge/Ag/Sb/Pb)Te exhibits an exceptional *ZT* of 2.7 at 750 K.[5,26]

However, intrinsic limitations remain because the disordered atoms can also interfere with the transport of carriers, which will cause a decrease in electrical conductivity (Figure 1c).[31–32] Therefore, maintaining the electrical conductivity with significantly suppressed thermal conductivity is key to realizing high-performance thermoelectric high-entropy compounds. The opportunity lies in tailoring the precise arrangement patterns of the multiple elements. Multiple elements can be randomly distributed throughout the entire sublattice, completely disrupting the periodicity. However, some of them can also be regularly clustered or arranged over several nanometers to form orderly structured nanofeatures. As described in AgSbTe$_2$ with a cubic structure, where both Ag and Sb occupy the same cation sites, Cd doping can induce orderly structured nano-regions. These ordered nanoregions can facilitate the transport of carriers, leading to increased electrical conductivity and PF.[33] For ordered nanoregions with different arrangements of elements, the valence band maximum (VBM) or conduction band minimum (CBM) may have different energies. Therefore, the ordered nanoregion with the smallest energy difference between its VBM or CBM and that of the matrix would be the most ideal. At the same time, if the size of these nanoregions matches the mean-free path of phonons, they can even reduce the thermal conductivity, contributing to high thermoelectric performance (Figure 1c). Therefore, designing ordered nanoregions is promising to develop high-performance high-entropy thermoelectric materials. Here, it is also important to

consider the amount of ordered nanoregions, as their presence can lead to a decrease in entropy. Thus, careful design of the amount of ordered nanoregions is necessary to maintain the high entropy characteristics of the material.

To design the atomic arrangement of the multiple elements, their arrangement patterns should be detected and analyzed. Several techniques can be applied to capture the feature of local structural configuration as well as element distribution, including total scattering/pair distribution function (PDF), extended X-ray absorption fine structure (EXAFS), scanning transmission electron microscopy (STEM), and atomic probe tomography (APT).[34–36] Then, particular attention should be given to the synthesis process because the diffusion of atoms (which is generally at a low rate in high-entropy materials) and resultant phase structure are sensitive to external conditions such as pressure and temperature, which will lead to a different arrangement of atoms. The atomic arrangement of a high-entropy structure also strongly depends on the selection of elements. Affected by the difference in masses, ionic radii, and electronegativity, atomic interaction varies among different elements. Therefore, such local periodic arrangement of atoms can be stabilized by carefully selecting the constituent elements.[37]

As the performance of high-entropy compound is related to the constituting elements, the selection of elements is important. Here, some principles and methods can be referred to. Firstly, for thermoelectric materials with inherently low carrier mobility, the increase in entropy may not have a significant impact on carrier mobility. This allows for more flexibility in selecting the constituent elements for such materials. Secondly, the valence charge balance should be considered. When introducing an aliovalent element, the deficiency of cations/anions or co-introduction of another aliovalent element is needed to balance the valence charge. It is also important to minimize the covalent radius and/or valence state difference between the substituted and host atoms in high entropy alloys. This can help reduce lattice distortion and alloy scattering, which in turn can minimize the loss of carrier mobility. Thirdly, the sublattice to be engineered with high entropy should be chosen wisely, as different sublattices play different roles in affecting the physical properties. For electrical transport, valence bands (conduction bands), which are responsible for hole (electron) transport, are usually dominated by anions states (cations states). Therefore, engineering

the correct sublattice can alleviate the influence on the transport of holes or electrons.[38] Meanwhile, elements that can optimize carrier concentration and increase the density-of-states effective mass through band engineering are promising candidates. This can help offset the possible reduced carrier mobility. Lastly, advanced computing methods such as machine learning can speed up the search for suitable high-entropy compounds. As the best performance may not be achieved in compositions where multiple elements are mixed exactly in equal mole ratios, it would be tedious and laborious to find the exact composition with the best performance. As demonstrated by the discovery of high-entropy Invar alloys based on machine learning, the integration of machine learning, density-functional theory, and experiments can significantly lessen the experimental time taken to develop high-performance high-entropy compounds.[39]

In conclusion, there is still a lot of room for exploration of high-entropy strategies, from design principles to high-performance novel compounds. We believe that the engineering of the atomic arrangement and a wise selection of constituting elements will advance the development of high-performance thermoelectric materials. Meanwhile, high entropy compounds generally have high stiffness due to the solid-solution strengthening effects, which can also contribute to the stability of devices.

■ CONFLICT OF INTEREST

The authors declare no conflict of interest.

■ AUTHOR CONTRIBUTIONS

Jinfeng Dong: Writing-Original draft. Jing Gao: Writing-Original draft. Qingyu Yan: Writing-Review & Editing, Funding Acquisition. All authors had approved the final version.

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