High-entropy ceramics: Present status, challenges, and a look forward

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Abstract: High-entropy ceramics (HECs) are solid solutions of inorganic compounds with one or more Wyckoff sites shared by equal or near-equal atomic ratios of multi-principal elements. Although in the infant stage, the emerging of this new family of materials has brought new opportunities for material design and property tailoring. Distinct from metals, the diversity in crystal structure and electronic structure of ceramics provides huge space for properties tuning through band structure engineering and phonon engineering. Aside from strengthening, hardening, and low thermal conductivity that have already been found in high-entropy alloys, new properties like colossal dielectric constant, super ionic conductivity, severe anisotropic thermal expansion coefficient, strong electromagnetic wave absorption, etc., have been discovered in HECs. As a response to the rapid development in this nascent field, this article gives a comprehensive review on the structure features,
theoretical methods for stability and property prediction, processing routes, novel properties, and prospective applications of HECs. The challenges on processing, characterization, and property predictions are also emphasized. Finally, future directions for new material exploration, novel processing, fundamental understanding, in-depth characterization, and database assessments are given.

**Keywords:** high-entropy ceramics (HECs); processing; structure; properties; applications

## 1 Introduction

High-entropy ceramics (HECs) are solid solutions of inorganic compounds with one or more Wyckoff sites shared by equal or near-equal atomic ratios of multi-principal elements.

This concept is inherited from that of high-entropy alloys (HEAs), which are multi-principal element alloys (MPEAs) with equal or near-equal atomic fraction of constituting elements [1,2]. For HEAs, two definitions have been proposed based on the composition and configuration entropy [3]. In light of composition, HEAs are defined as alloys comprising more than five principal elements mixed in an equiatomic or near-equatomic fraction. In light of entropy, HEAs are defined as alloys having configuration entropies larger than 1.5\(R\) (herein \(R\) is the gas constant) when random solid solutions are formed. The difference between HEAs and traditional alloys lies in not only properties but also design strategy. In the traditional alloy design paradigm, one base element such as Fe, Ni, and Ti is used as a principal element and some minor alloy elements are added to enhance properties (the so-called base element concept) [4]. In the HEA design strategy, five or more multi-principal elements are mixed into a single lattice to form a solid solution [5]. In the phase diagrams, the compositions of traditional alloys are generally located at the corners which have limited compositional design space, while those of HEAs are located in the central region; thus the design space has significantly been opened through the combination of multi-principal elements as well as microstructures [6]. The significantly different design philosophy has brought about four core effects for HEAs, as summarized by Yeh [7]: i.e., (1) high-entropy effect, which expands the solution limits between elements and offers the stability for the formation of random solid solutions; (2) sluggish diffusion effect, which retards the growth of second phase nanoparticles; (3) severe lattice distortion, which contributes to strengthening and hardening; (4) cocktail effect, which provides unexpected properties after mixing many elements [8]. The unique combination of these characteristics has led to a great number of new materials with appealing properties such as superb specific strength [9], high strength at elevated temperatures [10], high cryogenic temperature fracture toughness [11,12], good wear and corrosion resistance [13], enhanced magnetocaloric effect [14], superconductivity [15], high hydrogen storage capacity [16], etc.

Inspired by the breakthrough in metal community, the high-entropy concept has been extended to ceramics (HECs), polymers (HEPs), and composites (HECOMPs) [17]. Similar to HEAs, all high-entropy materials (HEMs) are long-range structurally ordered but compositionally disordered. Compare to HEAs, the advent of high-entropy ceramics (HECs) provides more opportunities for tuning properties and overcoming the bottleneck for material applications. On one hand, the crystal structures of ceramics are more diverse in contrast to the simple FCC, BCC, and HCP structures for metals [18]. On the other hand, the diversity of band structure and chemical bonding opens up new avenues for material design and property tuning through band structure engineering and phonon engineering. Due to the countless possibilities in composition design and property tuning paradigms, HECs have been found to exhibit better stability, enhanced mechanical properties, amorphous-like thermal conductivity [19], colossal dielectric constant [20], super ionic conductivity [21], and are promising in structural and functional applications covered from ultrahigh temperature thermal protection and thermal insulation in hypersonic vehicles, thermal/environmental barrier protection of engine materials, high-speed and dry cutting to Li-ion batteries, thermoelectrics, catalysts, electromagnetic wave absorption, and electromagnetic interference shielding [22,23]. Despite of the rapid development, the field of HECs is still in the infant stage for both academic research and practical applications. In addition, the novel design
concept and the unknown mechanism that underpin
the unusual phenomena pose great challenges both
theoretically and experimentally. As a timely response
to this emerging field, this review aims to provide the
ceramic community a comprehensive overview of
current status in compositional design, processing,
properties, and potential applications of HECs. The
theoretical and experimental challenges posed by this
new material design paradigm will also be introduced.
And future directions will be given to guide the
academic studies and technical breakthrough in this
emerging field.

It is worth mentioning that there are several review
papers that have already been published concerning
HECs [24–26]. To make a difference from these early
papers, this review is organized as follows. Section 2
discusses the electronic and crystal structure features,
existing material systems, and methods for stability
prediction. In Section 3, synthesis and densification
methods are summarized. In Section 4, properties of
HECs are overviewed and methods for tuning properties
are proposed. In Section 5, present and prospective
applications are introduced. In Section 6, future
directions are suggested, and finally conclusions are
given in Section 7.

2 Structure features and material systems

2.1 Crystal structure features

2.1.1 Crystal structure

For HEAs and HECs, the crystal structures are generally
determined by the crystal structures of individual
constituents. In HEAs, since most elements prefer a
BCC or FCC structure, it is not surprising that most
HEAs are in simple BCC or FCC structure [4]. Several
criteria have been proposed to predict the structure of
HEAs, such as valence electron concentration (VEC)
[27] and atomic-level strain energy [28]. The situations
in HECs are quite different, since the crystal structures
of HECs are diverse instead of the simple BCC and
FCC structures. Rost et al. [29] have proposed a
rationale for the selection of individual constituents,
i.e., no uniform crystal structure exhibited in the
ensemble of binary compound, electronegativity or
cation coordination, and existence of pairs that do not
exhibit extensive solubility. Based on these criteria,
series of novel HECs with diversity and complex
structures emerged [30–33]. Besides, HECs with
constituents disobeying the rationale proposed by Rost
et al. have also been reported [34–38], which has
expanded the library of entropy-stabilized ceramics.
Up to now, no matured conclusions have been drawn
on the relationship between the structure of HECs and
single-component systems yet. However, the diversity
in crystal structures of HECs has provided an
orthogonal strategy to discover new crystalline matters
and untapped opportunities for property engineering
[29].

2.1.2 Atomic distribution

Down to the atomic arrangement, a major difference
between HEAs and HECs is the existence of an
ordered anion/cation sub-lattice and more uniform
distribution of elements in HECs. For ideal HEAs, all
elements distribute randomly in the structure. While in
real HEAs, regulated by entropy and diffusion barriers,
local vibrations in chemical composition or short-range
order (SRO) exist, as shown in Fig. 2.1 [39]. The
so-called incipient concentration waves decrease the
configuration entropy but provide new deformation
mechanisms and mechanical properties for HEAs. In
HECs, as demonstrated by Rost et al. [29], with the
existence of an ordered sub-lattice, the differentiation
between every cation lattice site is small since each has
the same immediate surroundings. A large number of
quasi-equivalent sites in a crystal with an intermediate
sub-lattice will increase the distribution homogeneousness
and configurational entropy of cations and favor the
formation of single-phase solid solution. The homogeneous
atomic arrangement of HECs has been observed
experimentally by scanning electron microscopy with
energy dispersive X-ray spectroscopic system (SEM–EDS)
for various HECs, and this technique is now considered
as a standard tool to probe distribution homogeneity
[33,35,37]. Delicate techniques to determine element
distribution, such as scanning transmission electron
microscopy (STEM) and atomic probe tomography
(APT), have also been employed, and the atomic scale
homogeneous distribution has been reported and no
significant aggregation has been found in high-entropy
oxides, carbides, borides, etc. [22,40–44]. Nevertheless,
segregation of elements at the grain boundary of triple
point of high-entropy perovskite has been observed
[45], which may significantly influence the mechanical
properties of HECs. Thus, more delicate works are
needed to probe the element distribution, especially
2.1.3 Lattice distortion

Ideally, all atoms locate perfectly in their own atomic sites in solids. However, affected by atomic size, electronegativity, and neighboring atoms, fluctuation from perfect site is observed in HEMs, leading to severe lattice distortion, which is one of the core effects in HEMs [4]. Using fitted extended X-ray absorption fine structure (EXAFS) data, Rost et al. [29,46] quantified the local atomic structure of (Mg₀.₂Ni₀.₂Co₀.₂Cu₀.₂Zn₀.₂)O on an element-by-element basis. The local bond lengths between metal and oxygen were found to vary around each cation, while the interatomic distances of second nearest neighbor (i.e., the cation–cation pair) were uniform. Model fitted experimental data and density functional theory (DFT) calculations demonstrated that the anion sublattice with oxygen ions displaced from ideal positions to accommodate the distortions, while metal atoms distributed randomly on an FCC sublattice with minimal positional disorder. Berardan et al. [47] measured the electron paramagnetic resonance (EPR) signal of copper ion in (MgCoNiZn)₀.₇₄Cu₀.₂₆O lattices, and a distorted signal was yielded, indicating deviation of lattice from ideal rock salt structure. DFT and molecular dynamics calculations on the structure of (MgCoCuNiZn)O system verified that the lattice distortion was derived from the effect of a combination of both Jahn–Teller and/or simple size arguments [48,49]. Dai et al. [50] employed a deep learning potential to predict the structure of high-entropy (Zr₀.₂Hf₀.₂Ti₀.₂Nb₀.₂Ta₀.₂)C ceramic and found that the carbon atoms deviated more significantly from the ideal positions in comparison with transition metal atoms, which was also verified by Ye et al. [41,51] using DFT calculations, as illustrated in Fig. 2.2. Similar result on lattice distortion of high-entropy diborides around the imperfections.
Fig. 2.2 Lattice distortion in high-entropy carbide (TiZrHfNbTa)C. (a, b) the atomic deviations from their ideal position estimated by deep learning potentials, illustrating more significant deviation of carbon from its ideal position. (c) Atomic displacements of the different elements expressed as the fraction of the lattice constant after relaxation, and large displacement of carbon is observed. Reproduced with permission from Ref. [50] for (a, b), © Elsevier 2020; Ref. [51] for (c), © The American Ceramic Society 2018.

was also reported by Dai et al. [52]. In short, lattice distortion is one of the main structure features in high-entropy materials, and it shapes the unique combination of mechanical and thermal properties of HECs, such as low thermal conductivity and hardening.

2.2 Electronic structure and band gap engineering

The electronic structure of a material is decisive to the stability, transport, and optical properties. For HECs, the mixing of more than five principal elements provides huge chemical space for tuning the electronic structure and tailoring the related properties. With the development of calculation techniques, it is more convenient to obtain the electronic structure from theoretical calculations than experiments. Among the available predictive techniques, DFT method is probably the most desirable technique to tackle the electronic structure problem of HECs, since the only required input into the DFT calculations to yield electronic properties is the crystal structure. For HEMs, modeling of the structure is challenging since completely disordered structure requires a supercell that is large enough to include the effect of lattice distortion and eliminate the periodicity errors. Such calculations are computationally very demanding. Therefore, few works on the calculation of electronic structure of HE carbides, borides, and oxides have been conducted. Rák et al. [53] carried out extensive DFT calculations on three high-entropy oxides (HEOs), (MgCoCuNiZn)O, (MgCoCuNiZnLi)O, and (MgCoCuNiZnSc)O [53]. To model the random structure, a 480 atoms rock-salt supercell with a size of 3×4×5 unit cells was constructed. Analysis on the Bader charges and density of states indicated that the addition of Sc to (MgCoCuNiZn)O resulted in the reduction of a majority of Cu cations, and these Cu cations deviated from their ideal lattice sites largely. While addition of Li to (MgCoCuNiZn)O resulted in oxidation of Co, Ni, and Cu atoms with no substantial displacement from their ideal lattice sites. Using the same model, they calculated the density of states of (MgCoCuNiZn)O, and found that the CuO6 octahedra were in both elongated and compressed geometry [48]. The projected DOS of Cu atoms illustrated a splitting of Cu d-states near Fermi level, and the elongated and compressed Cu-centers adopt different electronic ground states with half-filled d1/2-1/2 or d3/2 orbitals, respectively. The displacement of O atoms was responsible for the experimentally observed Jahn–Teller distortion in (MgCoCuNiZn)O.

To reduce the scale and overcome the difficulty of calculations, special quasi-random structures (SQS) are introduced to construct the disordered structure of high-entropy ceramics. The concept of SQS [54,55] is to build a special periodic structure with a small number of atoms per unit cell whose correlation functions for the first few nearest-neighbor shells are as close to those of a target random alloy as possible such that the periodicity errors only exist between more distant neighbors. Using this technique, Ye et al. [41] and Jiang et al. [56] constructed the 2×2×2 SQS supercell of high-entropy carbide (TiZrHfNbTa)C with 64 atoms. The predicted DOS of carbides was preserved, and the presence of a pseudogap at the Fermi level suggested
strong covalent bonding between metal atoms and carbon. Similar results were also reported by Wang et al. [57] in the calculation of electronic structure of (TiZrHfNbTa)B₂ using SQS supercell. Liu et al. [58] constructed an SQS supercell containing 100 atoms for Zn₀.₃Ca₀.₃Sr₀.₄Ba₀.₄ZrO₃. They found that the lattice distortion resulted from high-entropy effect induced chemical bond inhomogeneity, which was reflected by the different binding energy ranges of A–O (A = Zn, Ca, Sr, Ba) and Zr–O bonds. Zn–O and Ca–O bonds are weaker than Sr–O and Ba–O bonds, which is responsible for the lower stiffness and mechanical properties of high-entropy ceramic than their single-component counterparts. Although SQS is efficient in constructing the quasi-random structure and easing the calculation burden, usage of this method should be proceeded with caution. Since in SQS, the interactions between distant neighbors are considered to contribute much less to the system, which may not be the case for ionic crystals where long range interactions may still be important under a given unit cell size constraint. Moreover, the energy of the SQS of some systems might be sensitive to the atomic configurations and the uncertainty in the energy of those systems is too high, especially for anisotropic lattices [59].

Besides theoretical exploration on the electronic structure of HECs, experimental efforts have also been devoted in tuning the band structure by controlling the compositions to tailor the properties of high-entropy oxides. Sarkar et al. [60] prepared high-entropy rare earth oxides (HE-REOs) containing 3–7 rare earth cations (Ce, Gd, La, Nd, Pr, Sm, Y) in equiatomic amounts by nebulized spray pyrolysis. The structure of HE-REOs was identified as fluorite-type structure and transformed to a bixbyite-type structure upon calcination. Band gap measurement with ultraviolet–visible (UV–Vis) absorption spectra revealed narrowing of the gap compared with CeO₂. They speculated that multivalent element Pr was responsible to the band gap narrowing, and thus, enabled HE-REOs to absorb light over the entire visible spectral range. To verify the hypothesis, they further obtained element resolved charge state and electronic structure of (CeLaPrSmY)O₂–δ by X-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS) [61], and the ability of Pr in tuning the bandgap energy of HE-REO by redox reaction was confirmed, as demonstrated in Fig. 2.3.

Bérardan et al. [20] synthesized high-entropy oxide (MgNiCoCuZn)O and colossal dielectric permittivity was found. With the alkaline metal Li introduced, the colossal dielectric constant of HEOs was preserved while the band gap reduced from 1 to 0.6 eV. The lithium content has a large impact on the observed dielectric constants. The less lithium the sample contains, the higher its intrinsic resistance and also the higher its maximum permittivity. These pioneering works have demonstrated the vast potential for the application of HECs as catalyst, energy storage, electric and optical materials by tuning the electronic structure and band gap of HECs, which is achievable simply by choosing suitable additional elements due to their huge chemical and structural space.

In HEAs, the selection of constituents is constrained in metallic elements and the structures are limited to BCC, FCC, and HCP [4]. While for HECs, selection of constituents and crystal structure types is abundant and new types of HECs are still emerging. The crystal structures of two representatives of HECs, i.e., high-entropy carbide and diboride [50,52], are shown in Fig. 2.4. In the recently published reviews, a comprehensive list of the material systems in HECs can be found [24–26,62]. Inspired by the pioneering work of Rost et al. [29], most of the researches focus on the synthesis and property exploring of entropy stabilized oxides. Shortly, oxides with rock salt [21,29, 63–67], fluorite [38,60,68–71], pyrochlore [36,37,
72–75], and spinel [80–83] structures were explored and fascinating properties brought by high-entropy effects have been reported. Gild et al. [34] extended the material systems to ultrahigh temperature ceramics (UHTCs) by fabricating high-entropy borides with AlB2 structure. And soon after, carbides and nitrides in UHTCs category were also synthesized [35,84]. These materials often possess enhanced hardness, ultralow thermal conductivity compared to their binary constituents, which make them suitable for extreme environment applications. Other than materials with simple structures, high-entropy materials with relatively complex and low-symmetry structure are also fabricated recently, such as monosilicates [43,85,86], disilicates [87–89], aluminates [23,90,91], phosphates [92,93], magnetoplumbites [94], monoborides [95–97], hexaborides [98,99], tetraborides [100], silicide carbides [101], and silicides [33,102], which have enriched our knowledge on the HECs, as shown in Table 1.

In ideal HECs, the elements are incorporated into

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**Fig. 2.4** Crystal structure of high-entropy (a) carbide and (b) diboride. Small balls are carbon and boron atoms, and colored big atoms are metal atoms. Reproduced with permission from Ref. [50] for (a), © Elsevier 2020; Ref. [52] for (b), © Elsevier 2021.

**Table 1** High-entropy material systems

| Structure type | Material system | Ref. |
|---------------|----------------|------|
| Rock salt     | (MgCoNiCuZn)_{x,y,z},Ga_{x},Au_{y},O (A = Li, Na, K) | [21] |
|               | (MgCoNiCuZn)O | [26,63–66] |
|               | Li_{1-x}Mn_{x}Ti_{1-x}Nb_{x}O_{1} | [67] |
|               | Hf_{x}Zr_{1-x}Nb_{1/2}Ti_{1/2} | [35] |
| Fluorite      | (Hf_{x}Zr_{1-x}Ce_{1/2}Y_{1/2})O_{2} | [38] |
|               | (Hf_{x}Zr_{1-x}Ce_{1/2}Y_{1/2}M_{2}O_{2})O_{2} (M = Yb, Ca, Gd) | [39] |
|               | (Hf_{x}Zr_{1-x}Ce_{1/2}Y_{1/2}M_{2}O_{2})O_{2} (M = Yb, Gd) | [40] |
|               | (Hf_{x}Zr_{1-x}Ce_{1/2}Y_{1/2}M_{2}O_{2})O_{2} | [41] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [60] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} (x = 0–0.5) | [61] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} (x = 0–0.5) | [62] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [63] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [64] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [65] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [66] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [67] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [68] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [69] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [70] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [71] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [72] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [73] |
|               | (Ce,Gd)_{x}La_{y}Sn_{1/2}Sn_{1/2}O_{2} | [74,75] |

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one sublattice in equimolar ratio. Recently, Wright et al. [103] proposed to extend HECs to compositionally complex ceramics (CCCs) to include medium-entropy and non-equimolar compositions. In CCCs, the mixing configurational entropy is in the range of (1–1.5)kB per cation. Materials with one cation sublattice include 3–4 equimolar cations or non-equimolar cations (3–4 principal plus a few minor cations) can be classified as medium-entropy ceramics (MECs). These CCCs are found to prevail against their high-entropy counterparts in lowing thermal conductivity [73]. Moreover, broadening of HECs to CCCs increases compositional space and provides more degrees of freedom to tune properties [26].

### 2.3 Theoretical methods for stability prediction

Searching for more unknown stable members with unexpected properties is one of the main subjects in the field of HEMs, and this process can be accelerated by theoretical prediction on the stability of possible candidates. Up to now, different simulation techniques
have been used to identify stable HECs. DFT is the most common method in the establishment of different descriptors that help to predict single-phase formation in HECs. As we have stated above, due to the difficulty and scale of the calculation, auxiliary methods are needed in structure construction. Ye et al. [51] used DFT to calculate the mixing enthalpy and configurational entropy of SQS supercells of (TiZrHfNbTa)C. Using the thermodynamical data, they determined the stable temperature of (TiZrHfNbTa)C when the mixing Gibbs free energy was negative, which guided the synthesis of this high-entropy carbide. Sarker et al. [104] used DFT calculations to validate their descriptor, i.e., entropy forming ability (EFA), on the synthesizability of 56 five-metal high-entropy carbides. The calculations on the mixed-phase enthalpy, formation enthalpies of competing binary and ternary ordered structures, and energy spectrum were conducted within the Automatic FLOW framework [105]. Pitike et al. [106] presented a generic method to evaluate the relative feasibility of formation of 56 single-phase multi-component compounds. They adopted a nearest neighbor model (NNM), whose parameters could be easily obtained from two-component oxides, to reduce the computational costs of DFT calculations. They established descriptors related to the enthalpy and configurational entropy obtained from the mixing enthalpies of two-component oxides and used these descriptors to evaluate the stability of candidate HEOs.

Other than DFT, molecular dynamics (MD) and CALPHAD can also be used to explore the stability of HECs. The advantage of MD calculations is the ability to deal with at least thousands of atoms; however, the accuracy of this method depends on the interatomic potentials. Anand et al. [49] explored the stability of (MgCoNiCuZn)O and its derivatives and the competition between enthalpy and entropy of these materials. The Buckingham interatomic potential was used to depict ionic interaction. Nevertheless, usage of MD is still limited due to the lack of high accurate interatomic potentials to capture the chemical complexity for different material systems. Recently, a new paradigm emerges with the development of machine learning and artificial intelligence. In this new paradigm, machine learning methods are adopted to fit interatomic potentials from data sets by DFT calculations. The fitted potentials are called machine learning potentials [50,52]. These potentials show high accuracy comparable to DFT calculations. To the authors’ knowledge, the application of machine learning potentials to the stability of HECs has not been reported yet. CALPHAD describes the Gibbs free energy of a system using a large amount of thermodynamic data, which is obtained from experiments or DFT calculations [107].

In perovskite LaMnO$_{3+y}$ system [108], combining with defect chemistry, CALPHAD was used to investigate the effects of oxygen partial pressure on the thermochemical properties and the correlation between thermochemical properties and defect mixing behavior. Using this approach, mixed ionic–electronic conductive HECs in co-doped systems could be designed.

### 3 Synthesis and densification methods

#### 3.1 Synthesis methods

Besides theoretical impact, the advent of HECs also poses challenges on the synthesis and densification of this new family of materials. In order to obtain random distribution of constituting elements in HECs, various methods including solid state reaction [32,58,85,99,101,109–111], wet chemical route [37,60,63–65,91,93], solidification [112–114], field assisted synthesis [115,116], and epitaxial growth [117] have been used.

Solid state reaction synthesis is the most commonly used method for the preparation of HECs, which is suitable to not only oxides but also silicates, borides, carbides, silicide carbides, and sulfides [32,58,67,80,85,88,95,96,99,101,109–111]. For example, Chen et al. [90] synthesized phase-pure high-entropy (Y$_O$Yb$_{0.2}$Lu$_{0.2}$Eu$_{0.2}$Er$_{0.2}$)Al$_{12}$O$_{3+δ}$ with uniform distribution of constituting elements using Y$_2$O$_3$, Yb$_2$O$_3$, Lu$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, and Al$_2$O$_3$ as starting materials. The whole process is schematically shown in Fig. 3.1(a). The solid-state reaction at 1600 °C can be described in Eq. (3.1).

$$3Y_2O_3 + 3Yb_2O_3 + 3Lu_2O_3 + 3Eu_2O_3 + 3Er_2O_3 + 25Al_2O_3 = 10(Y_{0.2}Yb_{0.2}Lu_{0.2}Eu_{0.2}Er_{0.2})Al_2O_{12} (3.1)$$

During the heating process, (Y$_O$Yb$_{0.2}$Lu$_{0.2}$Eu$_{0.2}$Er$_{0.2}$)Al$_{12}$O$_3$ was identified as an intermediate phase so that the possible stepwise reactions for the synthesis of high-entropy (Y$_O$Yb$_{0.2}$Lu$_{0.2}$Eu$_{0.2}$Er$_{0.2}$)Al$_{12}$O$_3$ can be described following Eq. (3.2) and Eq. (3.3):

$$Y_2O_3 + Yb_2O_3 + Lu_2O_3 + Eu_2O_3 + Er_2O_3 + 5Al_2O_3 = 10(Y_{0.2}Yb_{0.2}Lu_{0.2}Eu_{0.2}Er_{0.2})Al_2O_{3} (3.2)$$
Intriguingly, high-entropy (Y\textsubscript{0.2}Yb\textsubscript{0.2}Lu\textsubscript{0.2}Eu\textsubscript{0.2}Er\textsubscript{0.2})\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} exhibits a low thermal conductivity of 3.81 W·m\textsuperscript{-1}·K\textsuperscript{-1} at 300 K, a close thermal expansion coefficient ((8.54±0.29)×10\textsuperscript{-6} K\textsuperscript{-1} at 673–1273 K) to that of Al\textsubscript{2}O\textsubscript{3}, a slow grain growth rate when annealed at high temperatures. Most importantly, there is no reaction between high-entropy (Y\textsubscript{0.2}Yb\textsubscript{0.2}Lu\textsubscript{0.2}Eu\textsubscript{0.2}Er\textsubscript{0.2})\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} and thermally grown (TG) Al\textsubscript{2}O\textsubscript{3}, indicating the potential for the application of this high-entropy complex oxide as thermal barrier coatings on top of TG-Al\textsubscript{2}O\textsubscript{3}. Using Y\textsubscript{2}O\textsubscript{3}, Yb\textsubscript{2}O\textsubscript{3}, Lu\textsubscript{2}O\textsubscript{3}, Er\textsubscript{2}O\textsubscript{3}, and SiO\textsubscript{2} powders as starting materials, Chen et al. [85] also synthesized high-entropy (Y\textsubscript{0.25}Yb\textsubscript{0.25}Lu\textsubscript{0.25}Er\textsubscript{0.25})\textsubscript{2}SiO\textsubscript{5}. Upon heating,
solid state reaction was completed before 1484 °C according to Eq. (3.4). 
\[
Y_2O_3 + Yb_2O_3 + Lu_2O_3 + Er_2O_3 + 4SiO_2 \\
= 4(Y_{0.25}Yb_{0.25}Lu_{0.25}Er_{0.25})_3SiO_5 
\]
Further heating to 1600 °C, a bulk (Y_{0.25}Yb_{0.25}Lu_{0.25}Er_{0.25})_3SiO_5 of about 88% was obtained. This monosilicate (Y_{0.25}Yb_{0.25}Lu_{0.25}Er_{0.25})_3SiO_5 has strong anisotropic thermal expansion coefficient and is promising as a thermal barrier coating or environmental barrier coating material if the preferred orientation can be controlled. Recently, Sun et al. [88] synthesized γ-type (Gd_{1/6}Yb_{1/6}Dy_{1/6}Yb_{1/6}Y_{1/6}Si_2O_5, through the solid state reaction using RE_2O_3 (RE = Gd, Dy, Tb, Sm, Eu, and Lu), Tb_2O_7, and SiO_2 as starting materials. This new high-entropy disilicate has outstanding phase stability without polymorph transition from room temperature to the melting point (over 1900 °C).

High-entropy borides and carbides can also be synthesized using the solid state reaction method. For example, Tallarita et al. [118] synthesized high-entropy (Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2 powders using elemental Hf, Mo, Ta, Nb, Ti, and B powders as raw materials. The reaction process can described as
\[
0.2Hf + 0.2Mo + 0.2Ta + 0.2Nb + 0.2Ti + (2 + x)B \\
\rightarrow (Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2 
\]
The reaction was conducted by self-propagating high-temperature synthesis and the use of excess of B (x = 0.2) was helpful for the removal of oxide impurities in the raw powders. X-ray diffraction analysis indicated that besides high-entropy (Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2, impurities such as HfO_2, HfB_2, (Ta_{0.5}Ti_{0.5})B_2, and (Hf_{0.5}Ti_{0.5})B_2 could also be detected. High-entropy (Mo_{0.2}Ta_{0.2}Ni_{0.2}Cr_{0.2}W_{0.2})B [95] and (Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Mo_{0.2})B [96] bulk ceramics were also prepared by direct reaction of transition metal powders with B powders through reactive hot-pressing (HP).

Wet chemical routes including co-precipitation, sol–gel, nebulized spray pyrolysis, and flame spray pyrolysis have the advantage of homogeneous mixing of constituting elements at a molecular level in the solutions and thus synthesis of HECs can be conducted at lower temperatures [37,60,63,64,66,91,93,119]. For example, Zhao et al. [91] used a co-precipitation method to synthesize high-entropy (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})_3Al_2O_3 powders. As shown in Fig. 3.1(b), nitrate salts of RE(NO_3)_3·6H_2O (RE = Nd, Sm, Eu, Y, and Yb) in equal molar ratio were mixed and dissolved in distilled water to form a clear solution. Then Al(NO_3)_3 solution was added into the mixed RE(NO_3)_3 solution with stirring. After thoroughly mixing, excess aqueous ammonia was added slowly into the mixed solution with vigorous stirring to obtain gel-like precipitants. The precipitants were then filtered, washed, and finally calcined at 1873 K for 1 h to obtain high-entropy (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})_3Al_2O_3 powders.

Nebulized spray pyrolysis (NSP) is an aerosol-based synthesis technique in which the decompositions of the precursor solution at elevated temperature lead to the formation of the either intermediate or desired phase [120]. This method has been used by Sarkar et al. [31,60] and Witte et al. [78] to the synthesis of rare earth and transition metal based entropy stabilized perovskite-type oxides as well as fluorite structured rare earth oxides. As illustrated in Fig. 3.1(c), to synthesize perovskite type oxides [31], water based solution containing nitrate salts of Gd, La, Nd, Sm, Y, Co, Fe, Mn, and Ni were delivered into the nebulizer, and then the generated mist containing fine droplets of the solution was transported by flowing oxygen into the hot-wall reactor where the particles were formed at 1050 °C and a pressure of 900 mbar. Further solid solution treatment was conducted by calcining at 1200 °C for 2 h in air, which resulted in the formation of high-entropy RECoO_3, RECrO_3, REFeO_3, REMnO_3, RENiO_3, GdTMO_3, LaTMO_3, NdTMO_3, SmTMO_3, YTMO_3, and RETMO_3 (RE = Gd, La, Nd, Sm, Y, Ti = Co, Cr, Fe, Mn, Ni). Sarkar et al. [119] also compared the phase composition and microstructure of nebulized spray pyrolysis (NSP), flame spray pyrolysis (FSP), and reverse co-precipitation (RCP) synthesized (CoMgNiZn)O and (CoCuMgNiZn)O. They found that rock-salt structured high-entropy oxides could directly form after NSP, but for the FSP and RCP produced powders, high-temperature annealing was needed.

The wet chemical route can also be used to synthesize high-entropy carbide and boride ceramics. For example, Du et al. [121] synthesized (Hf_{0.25}Nb_{0.25}Zr_{0.25}Ti_{0.25})C powders by mixing HfCl_4, ZrCl_4, NbCl_5, TiCl_4, and C_2H_6O in butanol (CH_3CH_2OH) with stirring followed by polymerization at 200 °C for 20 h to obtain a polymer precursor. After pyrolyzing at 2200 °C, rock-salt structured (Hf_{0.25}Nb_{0.25}Zr_{0.25}Ti_{0.25})C powders were obtained. Aside from carbides and borides, high-
entropy metal nitride composed of V, Cr, Nb, Mo, Zr, and N was synthesized using a soft urea strategy [122]. Different from the conventional methods, applying an electric field during the solid-state reaction process can significantly reduce the reaction time and allow the synthesis and sintering conducted at low furnace temperature. This flash sintering approach also enables the production of high-density ceramics in a single step by combining a solid state synthesis with densification [123]. Using the reactive flash sintering methods, high-entropy (Mg0.2Ni0.2Co0.5Cu0.2Zn0.2)O has been successfully prepared even at room temperature [124, 125]. Recently, Wang et al. [126] synthesized high-entropy Sr(Ti0.2Y0.2Zr0.2Sn0.5Hf0.2)O3-x using a reactive flash sintering method. Using Y2O3, SnO2, SrO, HfO2, SrTiO3, SrZrO3 powders as starting materials, single-phase perovskite-structured Sr(Ti0.2Y0.2Zr0.2Sn0.5Hf0.2)O3-x was formed at 1000 °C in 1 min, demonstrating the prospective of this ultrafast synthesis and sintering method.

Carbothermal shock (CTS) method provides a novel route to synthesize a diverse array of high-entropy nanoparticles with narrow size distribution and uniformly dispersion. Moreover, the easily tunable processing parameters, rapid and energy-efficient synthetic procedure make CTS promising technology for high-rate and high-volume production of high quality HE nanoparticles. To put it simply, the CTS method employs a rapid heating process in milliseconds through an electrical pulse and a controllable cooling process of metal precursors on oxygenated carbon support. A serial of HEA nanoparticles containing up to ten elements were fabricated using this method. In addition, three strategies (temperature, oxidation, and entropy-driven mixing) were proposed for the efficient synthesis of different HEA and oxide nanoparticles [127,128].

Solidification process is also a promising strategy to synthesize HECs, which involves melting the raw materials, forming homogeneous melt, and cooling. This process has widely been used in the preparation of metallic materials and has been proven to be simple, quick, and cost-effective. Using this method, Zhang et al. [113] successfully synthesized high-entropy amorphous oxide spheres through melting 10La2O3–20TiO2–10Nb2O5–20WO3–20ZrO2 mixture by aerodynamic levitation. Very recently, Guo and Li [114] prepared high-entropy (RETiZrYAl)O (RE = La, Sm, Gd) glass with ultra-high hardness and Young’s modulus.

3.2 Synthesis methods for different forms of HECs

3.2.1 Powders

High-quality HEC powders are starting materials for sintering of bulk materials, thermal/environmental barrier coatings, and also final products for anodes of Li-ion batteries, catalysts, electromagnetic wave absorbers, etc. Depending on the application targets and material systems, a variety of methods including solid-state synthesis, sol–gel or co-precipitation followed by high-temperature calcination, reactive high-energy ball milling, molten salt synthesis, carbothermal reduction, borothermal reduction, boron/carbothermal reduction, etc., can be used. The following are typical examples that have been utilized to synthesize HEC powders. The first example is a room temperature sonochemical-based method for one-pot synthesis of perovskite-structured nanoparticles [115]. Taking the advantage of the acoustic cavitation phenomenon in the ultrasonication process, single-phase BaSr(ZrHfTi)O3, BaSrBi(ZrHfTi)FeO3, and Ru/BaSrBi(ZrHfTi)FeO3 nanoparticles with an average crystallite size of approximately 5.9 nm were crystallized through ultrasonication exposure without calcinations [115]. In the second example, Dong et al. [87] synthesized (Yb0.2Y0.2Lu0.2Sc0.2Gd0.2)2Si2O7 powders using a sol–gel method. In this process, tetraethoxysilane (TEOS) was first dissolved in distilled water and ethanol with molar ratio of 1:4:1. Then, the RE(NO3)3 solution was added into the TEOS solution with stirring until the TEOS was fully hydrolyzed. Subsequently, the solution was heated at 70 °C for 24 h and 120 °C for 24 h to obtain the dry gel. After calcining at 800 °C for 2 h and 1500 °C for 2 h in air, β-type (Yb0.2Y0.2Lu0.2Sc0.2Gd0.2)2Si2O7 powders were obtained.

Solid state synthesis has widely been used for preparing HEC powders. For example, Dabrowa et al. [32] prepared spinel-structured (CoCrFeMnNi)4O4 by vibrational milling the Co3O4, Cr2O3, Fe2O3, MnO, NiO powders and then calcining the powder mixture at 1050 °C for 20 h. Pu et al. [129] prepared (Na0.2Bi0.2Ba0.2Sr0.2Ca0.2)TiO3 by calcining the Na2CO3, Bi2O3, BaCO3, SrCO3, CaCO3, and TiO2 powder mixture at 1050 °C. Chen et al. [101] synthesized high-entropy rare earth silicide carbides (Tm0.2Y0.2Pr0.2Gd0.2Dy0.2)2Si2C2 and (Tm0.2Y0.2Pr0.2Gd0.2Tb0.2)2Si2C2 powders at 1600 °C with dwell time of 1 h in Ar using rare earth elements and SiC powders as starting materials.
Since the densification of high-entropy ultrahigh temperature ceramics (UHTCs) including transition metal carbides and borides ceramics usually requires higher temperatures, reducing the particle size of the starting powders with higher surface energies is beneficial, which provides a higher driving force for densification. To achieve such a goal, various methods have been used to synthesize ultrafine high-entropy carbide and boride powders. Moskovskikh et al. [130] synthesized high-entropy Hf0.2Ta0.2Ti0.2Nb0.2Zr0.2C and Hf0.2Ta0.2Ti0.2Nb0.2Mo0.2C powders through reactive high-energy ball milling (R-HEBM) of elemental transition metal powders and graphite particles. X-ray diffraction analysis indicated that rock-salt structured high-entropy carbides could be formed after ball milling for 60 min. Another example is that Guan et al. [131] synthesized high-entropy metal boron carbonitride (Ta0.2Nb0.2Zr0.2Hf0.2W0.2)BCN, (Ta0.2Nb0.2Zr0.2Hf0.2Ta0.2)BCN, and (Ta0.2Nb0.2Zr0.2Ti0.2W0.2)BCN powders via mechanical alloying at room temperature. Molten salt method was also used to prepare nanometer sized (Ta0.25Nb0.25Ti0.25V0.25)C powders. Using Ta, Nb, Ti, and V powders as starting materials and KCl as the molten salt medium, high-entropy (Ta0.25Nb0.25Ti0.25V0.25)C with particle sizes of 50–100 nm was synthesized at 1300 °C by Ning et al. [132]. Aside from the foregoing low temperature processes, carbothermal reduction, borothermal reduction, and boro/carbothermal reaction are also beneficial for the synthesis of fine-grained high quality powders. For example, Feng et al. [133] synthesized (Hf60Zr20Ta20Nb18B2)C powders with an average particle size of about 550 nm at 2000 °C using transition-metal oxides and carbon powders as starting materials. Liu et al. [134] synthesized (Hf0.2Zr0.2Ta0.2Nb0.2Ti0.2)B2 with an average particle size of ~310 nm at 1700 °C using a facile borothermal reduction method. Zhang et al. [135] prepared (Hf0.2Zr0.2Ta0.2Nb0.2Ti0.2)B2, (Hf0.2Zr0.2Mo0.2Ta0.2Ti0.2)B2, and (Hf0.2Mo0.2Ta0.2Nb0.2Ti0.2)B2 powders through boro/carbothermal reduction of transition metal oxides at 1600 °C using B4C and graphite powders as reducing agents. Utilizing the ultrafine high-entropy carbides and borides as initial materials, near fully dense bulk carbide and boride HECs with improved mechanical properties have been prepared [130,135–137].

3.2.2 Dense and porous bulks

Although the initial work of Gild et al. [34] implies that densification of high-entropy boride ceramics is difficult and pressure assisted methods such as spark plasma sintering (SPS) and HP are needed for borides and carbides, densification of bulk HECs in other system including oxides, silicates, and sulfides can be achieved using pressureless sintering or a single step process combining synthesis and densification. Generally, for ultrahigh temperature HECs including borides and carbides with strong covalent bonding [138] and low self-diffusion coefficient, SPS, HP, or oscillatory hot pressing (OHP) methods are needed to achieve nearly full density at temperatures over 2000 °C. For example, Gild et al. [34] prepared bulk (Hf0.2Zr0.2Ta0.2Nb0.2Ti0.2)B2, (Hf0.2Zr0.2Ta0.2Mo0.2Ti0.2)B2, (Hf0.2Zr0.2Mo0.2Ta0.2Nb0.2)B2, (Hf0.2Mo0.2Ta0.2Mo0.2Ti0.2)B2, and (Mo0.2Ta0.2Nb0.2Ti0.2)B2 by SPS at 2000 °C and 30 MPa using high-energy ball milled constituting boride mixtures as starting materials. Zhang et al. [139] prepared (Hf0.2Zr0.2Ta0.2C0.2Ti0.2)B2, (Hf0.2Mo0.2Zr0.2Nb0.2B2, and (Hf0.2Mo0.2Ta0.2Nb0.2Ti0.2)B2 by SPS at 2000 °C and 30 MPa using the high-entropy powders synthesized by borothermal reduction method as initial materials. Gu et al. [140] fabricated (Ti0.3Hf0.2Zr0.2Nb0.2Ta0.2)B2 by SPS at 2000–2050 °C and 50 MPa of boro/carbothermal reduction produced powders. Feng et al. [141] prepared dense (Hf0.2Zr0.2Ta0.2Nb0.2)B2 using a two-step SPS process. In the first step, the boro/carbothermal reduction produced powder compact was heated to 1650 °C under mild vacuum (~2 Pa) at 15 MPa load; and in the second step, densification was conducted at 2000–2200 °C under 50 MPa. Monteverde et al. [142] fabricated (Hf0.3Nb0.2Ta0.2Zr0.2B2 by hot-pressing carbo/boro-thermal reduction produced powders at 1927 °C and 50 MPa. It is worth mentioning that the final microstructure and mechanical properties strongly depend on the particle size and impurity content of the raw materials and densification temperature. Small grain size and high purity of raw materials and low sintering temperatures generally result in fine grain size and enhanced mechanical properties [34,135,137,139–141]. For high-entropy carbides, Castle et al. [143] prepared (Hf0.25Ta0.25Zr0.25Ti0.25)C and (Hf0.32Ta0.32Zr0.32Nb0.32)C with a relative density of ~99% by SPS at 2300 °C and 16–40 MPa. Yan et al. [35] prepared (Hf0.2Zr0.2Ti0.2Ta0.2B2 with a relative density of ~93% by SPS at 2000 °C in a vacuum of 2×10−2 Torr under a pressure of 30 MPa. Sarker et al. [104] produced (Hf2ZrTiTaNb)C ceramics with a relative density of ~99% by SPS at 2200 °C. Intriguingly, a combination of in situ synthesis and
pulsed current processing (PCP) resulted in the formation of a new hexagonal phase $B_4(HfMo_2TaTi)C$ from a mixture of $HfC$, $Mo_2C$, $TaC$, $TiC$, and $B_4C$ [144].

For HECs in other systems, although SPS has also frequently been used in many works, near fully dense bulks have been prepared by pressureless sintering [45,110]. In addition, other methods such as solidification [113,114] and reactive flash sintering have been utilized to prepare bulk HECs [124,125]. For examples, bulk $(Mg_{0.2}Ni_{0.2}Co_{0.2}Cu_{0.2}Zn_{0.2})O$ [125] and $(La_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2}Gd_{0.2})_2Zr_2O_7$ [145] have been fabricated by reactive flash sintering at low furnace temperatures, which combines the solid-state reaction and densification in one step. A good example of pressureless sintering is the fabrication of transparent $(Lu_{0.2}Y_{0.395}Gd_{0.2}Yb_{0.2}Tm_{0.005})_2O_3$ [110], which was conducted through vacuum sintering at 1800 °C for 20 h followed by annealing in air at 1000 °C for 13 h, using $La_2O_3$ and $ZrO_2$ as sintering additives. Another example is that bulk $(Ca,Sr,Ba)ZrO_3$ with a relative density of 97.8% was prepared by pressureless sintering of $CaZrO_3$, $SrZrO_3$, and $BaZrO_3$ mixed powder compact at 1550 °C [45]. Although not widely used, the results of these pioneer works are appealing since they demonstrate the potential to fabricate HECs in a simple pressureless sintering method, which is useful in scaling up the sample size and beneficial for manufacturing complex and large size bulk HECs for the practical applications.

Porous ultrahigh temperature ceramics play a pivotal role in ultrahigh temperature insulation. They also find applications in molten metal and corrosive gas filtration, catalyst supports, and electromagnetic wave absorption. However, high thermal conductivity is the main obstacle for ultrahigh temperature insulating application. In order to reduce the thermal conductivity, low thermal conductivity high-entropy carbides and borides were selected as backbone materials and a novel in-situ reaction/partial sintering method was developed to fabricate highly porous bulk materials [146–148]. This process is based on the fact that high-entropy carbides and borides can be synthesized through carbothermal reduction, borothermal reduction, and boro/carbothermal reduction. The reaction released gases can not only increase the porosity but also block...
the large shrinkage, e.g., the volume shrinkage during carbothermal reduction of ZrO$_2$ is about 60%. Thus no pore forming agent is needed and the synthesis/partial sintering of the porous high-entropy carbide and boride ceramics can be finished in a single step. Using this novel method, high porosity (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C$_{22}$, (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_2$ [40], and (Y$_{0.2}$Yb$_{0.2}$Sm$_{0.2}$Nd$_{0.2}$Eu$_{0.2}$)B$_6$ [98] have been prepared. Figure 3.2(a) illustrates the in situ synthesis/partial sintering process for the fabricating of high porosity (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C$_{22}$ [22]. The total reaction for the formation of high-entropy (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C can be described in Eqs. (3.6)–(3.12):

$$2\text{ZrO}_2(s) + 2\text{HfO}_2(s) + 2\text{TiO}_2(s)$$
$$+ \text{Nb}_2\text{O}_5(s) + \text{Ta}_2\text{O}_5(s) + 32\text{C}(s)$$
$$= 10(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{C}(s) + 22\text{CO(g)}$$  \hspace{1cm} (3.6)  

$$\text{ZrO}_2(s) + 3\text{C} = \text{ZrC} + 2\text{CO(g)}$$  \hspace{1cm} (3.7)  

$$\text{HfO}_2(s) + 3\text{C} = \text{HfC} + 2\text{CO(g)}$$  \hspace{1cm} (3.8)  

$$\text{TiO}_2(s) + 3\text{C} = \text{TiC} + 2\text{CO(g)}$$  \hspace{1cm} (3.9)  

$$\text{Nb}_2\text{O}_5(s) + 7\text{C} = 2\text{NbC}(s) + 5\text{CO(g)}$$  \hspace{1cm} (3.10)  

$$\text{Ta}_2\text{O}_5(s) + 7\text{C} = 2\text{TaC}(s) + 5\text{CO(g)}$$  \hspace{1cm} (3.11)  

$$\text{ZrC}(s) + \text{HfC}(s) + \text{TiC}(s) + \text{NbC}(s) + \text{TaC}(s)$$
$$= 5(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{C}$$  \hspace{1cm} (3.12)  

To obtain porous samples with excellent shape stability, the in-situ synthesis/shrinkage process must be precisely controlled such that cracking and collapse can be avoided. Based on the linear shrinkage ($dL/L_0$ with $L_0$ being the height of columnar shaped green bodies at room temperature) and linear shrinkage rate (($1/L_0)dL/dt$) curves together with the corresponding thermogravimetric (TG) and differential thermogravimetric (DTG) curves shown in Fig. 3.2(b), porous (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C with homogeneous microstructure (Fig. 3.2(e)) was prepared through carbothermal reduction at 1500 °C with carefully controlled slow heat rate and partial sintering at 1850 °C. The grain size is 100–500 nm and the pore size is in the range of 0.2–1 μm. The porosity is 80.99% with a compressive strength of 3.45 MPa and low room temperature thermal conductivity of 0.39 W·m$^{-1}$·K$^{-1}$.

Using a similar method, porous (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_2$ with a porosity of 75.7%, grain size of 400–800 nm, pore size of 0.3–1.2 μm (Fig. 3.3(a)), compressive strength of 3.93 MPa, and room temperature thermal conductivity of 0.51 W·m$^{-1}$·K$^{-1}$ was prepared following reaction (3.13) [40]:

$$14\text{ZrO}_2(s) + 14\text{HfO}_2(s) + 14\text{TiO}_2(s)$$
$$+ 7\text{Nb}_2\text{O}_5(s) + 7\text{Ta}_2\text{O}_5(s) + 52\text{B}_4\text{C}(s)$$
$$= 70(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2(s)$$
$$+ 34\text{B}_2\text{O}_3 + 52\text{CO(g)}$$  \hspace{1cm} (3.13)  

Porous (Y$_{0.2}$Yb$_{0.2}$Sm$_{0.2}$Nd$_{0.2}$Eu$_{0.2}$)B$_6$ [98] was also prepared by the in-situ synthesis and simultaneous partial sintering method (reaction (3.14) or (3.15)). It is interesting to note that the microstructure of the porous materials depends on the reaction route, e.g., porous (Y$_{0.2}$Yb$_{0.2}$Sm$_{0.2}$Nd$_{0.2}$Eu$_{0.2}$)B$_6$ produced by borothermal reduction (reaction (3.14)) has larger pore size, as shown in Fig. 3.3(b):

$$\text{Y}_2\text{O}_3(s) + \text{Yb}_2\text{O}_3(s) + \text{Sm}_2\text{O}_3(s)$$
$$+ \text{Nd}_2\text{O}_3(s) + \text{Eu}_2\text{O}_3(s) + 70\text{B}$$
$$= 10(\text{Y}_{0.2}\text{Yb}_{0.2}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{Eu}_{0.2})\text{B}_6(s)$$
$$+ 5\text{B}_2\text{O}_3(\text{g})$$  \hspace{1cm} (3.14)  

$$\text{Y}_2\text{O}_3(s) + \text{Yb}_2\text{O}_3(s) + \text{Sm}_2\text{O}_3(s)$$
$$+ \text{Nd}_2\text{O}_3(s) + \text{Eu}_2\text{O}_3(s) + 15\text{B}_2\text{C}$$
$$= 10(\text{Y}_{0.2}\text{Yb}_{0.2}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{Eu}_{0.2})\text{B}_6(s) + 15\text{CO(g)}$$  \hspace{1cm} (3.15)  

![Fig. 3.3 XRT images of porous (a) (Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_2$ and (b) (Y$_{0.2}$Yb$_{0.2}$Sm$_{0.2}$Nd$_{0.2}$Eu$_{0.2}$)B$_6$. Reproduced with permission from Ref. [98]. © Elsevier 2020.](image-url)
3.2.3 Thin films and thick coatings

Taking the advantages of tunable thermal expansion coefficient, high hardness, slow grain growth rate, and better stability, HEC thin films and coatings show great potential in the field of thermal/environmental barrier coatings (TBC/EBCs) [23,37,71,85,87–90,93,149], hard coatings, oxidation and corrosion resistant coatings [150–157]. TBC/EBCs can be deposited by atmospheric plasma spraying [149], while nitride, carbide, and oxide thin films can be prepared by reactive RF magnetron sputtering or DC sputtering of high-entropy alloys or co-sputtering of pure metal targets [150–157].

Atmospheric plasma spraying (APS) is a conventional technique to prepare thermal barrier coatings (TBC) on superalloy substrates, adapting to yttria stabilized zirconia (YSZ), rare earth zirconate, rare earth phosphate, and other material systems. Recently, Zhou et al. [149] found that APS is also suitable for preparing thermal barrier HEC coating. They deposited a \((\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7/\text{YSZ}\) double-ceramic-layer (DCL) coating on Ni-based superalloy by APS, which exhibited enhanced thermal stability. Thermal cycling tests demonstrated that the \((\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7/\text{YSZ}\) DCL coating exhibited improved thermal stability due to the good sintering resistance and close thermal expansion coefficient of \((\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Gd}_{0.2})_2\text{Zr}_2\text{O}_7/\text{YSZ}\) DCL coating. Besides APS, Dong et al. [87] fabricated a \((\text{Yb}_{0.2}\text{Y}_{0.5}\text{Lu}_{0.3}\text{Sc}_{0.5}\text{Gd}_{0.2})_2\text{Si}_2\text{O}_7\) environmental barrier coating (EBC) on carbon fiber-reinforced silicon carbide composites (C/SiC) by a slurry paste process, in which liquid polysilazane was dissolved in ethanol and mixed with \((\text{Yb}_{0.2}\text{Y}_{0.5}\text{Lu}_{0.3}\text{Sc}_{0.5}\text{Gd}_{0.2})_2\text{Si}_2\text{O}_7\) powders and then \(\text{Ba}_3\text{Si}_2\text{O}_5\) was added as a sintering aid to lower the sintering temperature. After 1250 °C and up to 300 h test in 50% \(\text{H}_2\text{O–50% O}_2\) environment, the \((\text{Yb}_{0.2}\text{Y}_{0.5}\text{Lu}_{0.3}\text{Sc}_{0.5}\text{Gd}_{0.2})_2\text{Si}_2\text{O}_7\) coated C/SiC exhibited significantly reduced weight loss and high residual strength compared to the uncoated C/SiC composite.

Sputtering, including reactive RF magnetron sputtering, DC sputtering, and multi-metal co-sputtering, can be used to make hard and corrosion resistant HE nitride, carbide and oxide films. For example, Chen et al. [150] deposited HE nitride films using Fe–Co–Ni–Cr–Cu–Al–Mn and Fe–Co–Ni–Cr–Cu–Al\(_{0.5}\) alloys as target materials through reactive sputtering and found that the measured hardness of nitride films (11 GPa) was significantly higher than that of alloy films (4 GPa). In addition, \((\text{AlCrTaTiZr})_2\text{N}\) [151,152], \((\text{AlCrTaTiZr})_7\text{Si}_2\text{N}\) [153], \((\text{Al}_{23}\text{Cr}_{18}\text{Nb}_{0.7}\text{Si}_2\text{Ti}_{23})_7\text{N}_{50}\) [154], \((\text{Al}_{23}\text{Cr}_{18}\text{Nb}_{0.7}\text{Si}_2\text{Ti}_{23})_7\text{N}_{50}\) [154], \((\text{TiAlCrSiV})_7\text{N}\) [155], \((\text{CuSiTiY}_{2}\text{Zr})_C\) [158], \((\text{CrNbSiTiZr})_C\) [159], \((\text{AlCrCoCuFeNi} (x=0.5, 1, 2))\) oxide [160], and \((\text{AlCrCoCuFeNi} (x=0.5, 1, 2))\) oxide [161] were also prepared by reactive RF sputtering. The influence of atmosphere components and their ratio, substrate bias voltage and gas flux rate on the microstructure, mechanical and tribological properties of the HE coatings has been investigated to find optimized processing conditions for harder and more corrosion-resistant HE coatings. For example, the highest hardness (29.5 GPa), lowest friction coefficient (0.15), and best wear-corrosion resistance were reached for the \((\text{CuSiTiY}_{2}\text{Zr})_C\) coating with carbon/metal ratio of about 1.3 and \(\text{CH}_4/\text{(CH}_3\text{ and Ar)}\) flow rate as 0.50 [158].

Other methods have also been employed to prepare HE thin films. \((\text{TiZrH}_7\text{V}_7\text{Nb})_7\text{C}\) coatings [162] with hardness of 43–48 GPa and friction coefficient of 0.14–0.16 at the loads 2.2–5.2 N were produced by ion scattering of a TiZrH7V7NbTa alloy target in plasma of compressed vacuum-arc discharge. Thin \((\text{CrNbTaTiW})_7\text{C}\) (30–40 at% C) films with different metal contents were deposited using non-reactive DC magnetron sputtering [163] and corrosion studies revealed that the \((\text{CrNbTaTiW})_7\text{C}\) films exhibited excellent corrosion resistance in 1.0 M HCl, superior to that of a reference hyper-duplex stainless steel. Besides nitrides and carbides, HE boride \((\text{Zr}_{0.23}\text{Ti}_{0.20}\text{Hf}_{0.19}\text{V}_{0.14}\text{Ta}_{0.36})_7\text{B}_7\) thin film with improved hardness (47 GPa) was prepared by physical vapor deposition (PVD) method [164].

4 Properties and tailoring methods

4.1 Phase stability

Thermodynamically, the phase stability of HECs is determined by the Gibbs free energy, which can be defined as

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \]  

(4.1)

where \( \Delta H_{\text{mix}} \) is the mixing enthalpy, \( \Delta S_{\text{mix}} \) is the mixing entropy, which can be expressed as

\[ \Delta S_{\text{conf}} = -R \sum_{i} \left( \sum_{j} c_j \ln c_j \right) \]

(4.2)

where \( R, x_i, n, \) and \( c_j \) are the gas constant, fraction of
the sublattice $i$, number of components, and atomic fraction of components $j$, respectively. Larger entropy favors lower Gibbs free energy and hence phase stability. Rost et al. [29] initially pointed out the critical role of configurational entropy in stabilizing (MgCoCuNiZn)O, in spite of an enthalpic penalty associated with the structure transition of CuO and ZnO from tenorite and wurtzite to rock-salt. This effect is confirmed by the endothermic reaction of (MgCoCuNiZn)O and MD simulation [165], and thus utilized to predict and explain the stability of other high entropy systems, such as oxides, carbides, and borides [38,58,96,98]. Sarker et al. [104] developed an entropy related descriptor called entropy forming ability (EFA) to address the synthesizability of HECs from first-principles calculations, which is defined as

$$EFA = \left( \frac{\sum_{i=1}^{n} g_i (H_i - H_{\text{mix}})^2}{\left( \sum_{i=1}^{n} g_i \right)^{-1}} \right)^{-1}$$

(4.3)

where $n$ is the total number of sampled geometrical configurations and $g_i$ are their degeneracies. $H_{\text{mix}}$ is the mixed-phase enthalpy approximated by averaging the enthalpies $H_i$ of the sampled configurations:

$$H_{\text{mix}} = \frac{\sum_{i=1}^{n} g_i H_i}{\sum_{i=1}^{n} g_i}$$

(4.4)

Large EFA corresponds to large entropy for a given composition. A total of 56 five-metal carbides were generated in their simulations and nine of them were synthesized, while six out of nine were single-phase high-entropy carbides. Combining simulations and experiments, they proposed a potential threshold for 5-metal carbides that could form single phase: EFA larger than 50 (eV/atom)$^{-1}$. In addition, by utilizing large configurational entropy, it is possible to stabilize the unstable phase to ambient conditions and improve the phase stability at high temperatures, as demonstrated in silicides, silicates, phosphates, niobates, and tantalates [33,71,88,92].

Besides configurational entropy, the phase stability of HECs could be affected by the size and charge of the constituent elements. Djenadic et al. [30] found the important role of Ce in the formation of fluorite-structured high-entropy rare earth oxides. The systems without Ce could not form single-phase fluorite. They suggested that the oxidation state (+4) and size ratio of Ce to oxygen atom are the main factors in the stabilization of fluorite structure. Transformation from bixbyite ($Ia3d$) structure to fluorite structure is found in Ce–Gd–Nd–Pr–Sm–O and Ce–Gd–La–Nd–Pr–O systems with the addition of Mo [69]. High oxidation state of Mo (+6) seems to be responsible. Intriguingly, the atomic size difference (δ) is one of the main factors that influence the formation of single phases in HEAs, where the threshold is 6.5% [29]. Nevertheless, in HECs, single phases are still observed in the systems with δ larger than 6.5% [71,76,88]. Jiang et al. [76] proposed that the Goldschmidt tolerance factor ($t$) was a useful parameter in predicting the stability of high-entropy perovskites. They found that the systems with unity tolerance factor tended to form single phase in spite of large size difference. It is also suggested that having unity tolerance factor is a necessary, but not sufficient, condition for forming single phases [76].

Some more interesting phenomena regarding phase stability of HECs are observed. Jiang et al. [76] found precipitation in the high temperature treated Sr- and Ba-based high-entropy perovskites. The dissolution of high-entropy ceramics is opposite to the concept of entropy-stabilization. In a very recent work, Qiu et al. [45] synthesized an entropy stabilized (Ca,Sr,Ba)ZrO$_3$ with tetragonal perovskite structure from orthogonal perovskite structural CaZrO$_3$, SrZrO$_3$, and cubic perovskite structural BaZrO$_3$. The structure of final product is different from those of all raw materials. These intriguing results demonstrate the complexity of phase stability of HECs due to their vast and complex chemical and structure space, which warrants investigations theoretically and experimentally.

### 4.2 Hardness and strength

For HEAs, Yeh et al. [1,3,7] attributed the excess strength to severe lattice distortion, which is one of the four core effects of HEAs. The severe lattice distortion results in pining of dislocations which provides excess strength. Lattice strain arises from the atomic radius difference and elastic modulus mismatch between the constituent elements. According to the model of Toda-Caraballo and Rivera-Diaz-del-castillo [166], solid-solution strengthening effect can be expressed by

$$\Delta_{\text{SS,HEA}} = \left( \sum_{i} B_i^{3/2} x_i \right)^{3/2}$$

(4.5)

where $x_i$ is the atomic fraction, $B_i$ is a hardening parameter.
parameter depending upon atomic radius difference, shear modulus, and Young’s modulus misfit. From Eq. (4.5), a pronounced strengthening and hardening are anticipated [167]. Similar to HEAs, strengthening and hardening have been widely observed in HECs. Csanádi et al. [168] investigated the strength and slip behavior of grains of a high-entropy carbide (HF-Ta2Zr-Nb)C during micropillar compression. Significantly enhanced yield and failure strength were observed. Intriguingly, this high-entropy (HF-Ta2Zr-Nb)C exhibits a hardness of 36 GPa [143], being much higher than the constituting components. Actually, for most current investigated HECs, the measured hardness values are well beyond the values estimated from the rule of mixture. Very recently, superhard high-entropy transition metal monoborides were reported [95,97]. TEM images of (Mo2Ta0.2Ni0.2Cr0.2W0.2)B, which has Vickers of 48.5±4.07 GPa measured at 0.49 N, show a high density of dislocations pinned within the (Mo2Ta0.2Ni0.2Cr0.2W0.2)B grains [95], indicating the severe lattice distortion. This hardening mechanism is supported by the work of Wang et al. [169], who investigated the irradiation damage in (Zr0.25Ta0.25Nb0.25Ti0.25)C. They observed irradiation-induced hardness increase, which was possibly caused by dislocation loops and lattice strain. One of the main important reasons for the severe lattice distortion in (Mo2Ta0.2Ni0.2Cr0.2W0.2)B is that the constituting components have not only atomic radius mismatch but also different type of crystal structures. The significance of this work is that it opens new windows for designing new superhard materials through the formation of solid solutions from constituting components with big atomic mismatch and different crystal structures.

In addition to room temperature strengthening, the flexural strength can be maintained up to 1800 °C for high-entropy carbide (HFZrTiTaNb)C and 1600 °C for medium-entropy carbide (TaZrNb)C [170,171], demonstrating significant high-temperature strengthening. High-temperature strengthening was also demonstrated by recent investigation on the creep behavior of (TaHfZrNb)C [172]. As reported by Han et al. [172], due to the lattice distortion and the good thermodynamic stability of high-entropy (TaHfZrNb)C at elevated temperatures, the measured steady-state creep rates are approximately 10 times lower than those of the corresponding monocarbides. These results are appealing for their application in ultrahigh temperature environment.

In contrast to HEAs, high fracture toughness or low temperature ductility was not observed in HECs. The exceptional ductility and fracture toughness of HEAs are attributed to the extremely low stacking fault energy (SFE) and easy twinning [1,10,173]. Such mechanism may not work for ceramic materials. The available data revealed that the room temperature mechanical properties of HECs are comparable to their constituting components. For example, the four-point flexural strength (421±27 MPa), fracture toughness (3.5±0.3 MPa m1/2), and Young’s modulus (450 GPa) but Vickers hardness (25.0±1.0 GPa at a load of 4.9 N) are close to those of single components [170]. Brittleness index [174] B = H / KIC and damage tolerance index D = KIC · E / σf · H [175] are quantitative measure of brittleness and damage tolerance of ceramics, where H, KIC, E, and σf are Vickers hardness, fracture toughness, Young’s modulus, and flexural strength. High brittleness index or low damage tolerant index is an indication of brittleness. The higher hardness and strength but comparable fracture toughness and Young’s modulus imply that the high-entropy carbide [170] has become more brittle. The very recent work by Sun et al. [176] clearly indicated that high-entropy bixbyite structured oxides RE2O3 (RE = Sm, Eu, Er, Lu, Y, and Yb) had higher brittleness and lower damage tolerance values, implying that they are more brittle than the single component like Y2O3. Needless to say, more works are needed to confirm the brittleness of HECs.

4.3 Thermal conductivity

Lattice distortion and mass disorder are the main features of high-entropy ceramics. Controlled by the scattering process of phonons and electrons, the reduction of thermal conductivity (κ) for these materials is a natural deduction, since these structure features are efficient scattering sources for phonons and electrons. We have summarized the thermal conductivity of several high-entropy material systems [19,35–40, 43,44,58,68,71,73,74,79,86–88,90–93,95,102,130,177–181] and presented the results in Fig. 4.1. For all high-entropy material systems, the diminishment in thermal conductivity is reported. However, few researches have investigated this phenomenon in depth to reveal the mechanism behind the deterioration. Braun et al. [19] investigated the thermal conductivity of (MgCoNiCuZn)O and found that with the addition of sixth cation (Sc, Sb, Sn, Cr, or Ge), 50% reduction

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in thermal conductivity could be achieved. Using a virtual crystal approximation (VCA) model, they attributed the amorphous or glass-like thermal conductivity to disorder in interatomic force constants (IFC) rather than mass and size disorder, which was verified by EXAFS analysis and molecular dynamics simulation. Their results also demonstrated that it was possible to achieve ultralow thermal conductivity to disorder in interatomic force constants (IFC) rather than mass and size disorder, which was verified by EXAFS analysis and molecular dynamics simulation. They found that in their YSZ-like compositionally-complex ceramics to achieve lower thermal conductivity than the ideal mixing parameter was a more effective descriptor to forecast configurational entropies. They found that size disorder was significant in reducing the thermal conductivity. Although the thermal conductivity of HE carbides and borides is significantly lower than their monolithic constituents [177,180], it is still too high for thermal insulating. To decrease the thermal conductivity of HE carbides and borides further, Chen et al. [22,40] employed a gas-released in situ reaction followed by high-temperature sintering to fabricate porous HE (Zr$_{0.2}$Hf$_{0.2}$TiO$_{2}$)C and (Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_{2}$. The grain and pore size distribution was uniform and the thermal conductivity of these porous ceramics was only ca 1/20 of the dense high entropy ones, as shown in Fig. 4.1.

Theoretically predicting the lattice thermal conductivity for HECs is appealing due to the ability of modeling to reveal the micro-mechanism of transportation, screen material systems, and tune the thermal property. Lim et al. [183] constructed a cell containing a total of 30,720 atoms and calculated the thermal conductivity of J14 (Mg$_{0.2}$Co$_{0.2}$Ni$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$)O as well as J14 plus Sc, Sn, Cr, or Ge in equal-molar cation proportions by MD. The thermal conductivity was calculated using the Green–Kubo method, and the interatomic potential was modeled using a pair sum of an exponential-6 function and long-range Coulomb interactions.

Fig. 4.1 Summarized thermal conductivity of some typical high-entropy oxides, carbides, and borides.
interactions. They controlled the atomic mass and charge in the interatomic potential to identify the main factor that determines the thermal behavior of these HEOs. They found that phonon scattering from charge disorder was responsible for the lowering of thermal conductivity with the addition of a sixth cation. It is worth noting that the interatomic potentials in classical MD are oversimplified, and the accuracy is not guaranteed. To tackle this problem, Dai et al. [50,52] employed a deep leaning potential to investigate lattice thermal conductivity of HE (Zr0.2Hf0.2Ti0.2Nb0.2Ta0.2)C and (Zr0.3Hf0.2Nb0.2Ta0.2Ti0.2)B2. They found that the predicted lattice thermal conductivity of these two HECs was rather low, which is consistent with experiments.

4.4 Thermal expansion

For the applications of HECs that involve high temperature, thermal expansion is a critical but less investigated property. Intrinsic thermal expansion of a material is related to the lattice energy which is determined by its composition, structure, and bonding. Generally, materials with higher lattice energy exhibit lower thermal expansion coefficients (TECs). The complex composition, distorted lattice, and various bonding in HECs compared with single component systems lead to unexpected behavior of TECs. Experimentally, the average TEC can be probed by a high temperature push-rod dilatometer or an optical dilatometer [71,91,93], while the anisotropic TEC can be obtained from high-temperature powder XRD or high temperature push-rod dilatometer using single crystals [23,85,86,90,91]. Yan et al. [35] measured the thermal expansion of (TiZrHfNbTa)C at 25–300 °C, and the TEC of HE carbides did not show significant deviation from the binary carbides. Zhao et al. [71,93,91] systematically investigated TECs of several high entropy oxides, such as (La0.2Ce0.2Nd0.2Sm0.2Eu0.2)PO4, (Sm1/6Eu1/6Y1/6Tb1/6Lu1/6Er1/6)3(Nb1/2Ta1/2)O7, (Y0.2Yb0.2Er0.2Lu0.2)2(Zr0.3Hf0.5)2O7. They observed an obvious decrease in thermal expansion of HEOs compared to their single component counterparts and proposed that the high entropy effect hindered the oscillation amplitude of constituting atoms by severe lattice distortion and decreased the thermal expansion [71]. Meanwhile, increase in TECs of (Y0.2Nd0.2Sm0.2Eu0.2Er0.2)Al2O3, (Yb0.23Y0.25Lu0.25Er0.25)3SiO5, (Y0.2Yb0.2Lu0.2Eu0.2Er0.2)Al2O3, (Nd0.2Sm0.2Eu0.2Y0.2)4Al2O6 had also been reported [23,85,90,91]. To illustrate the anisotropy in thermal expansion, Zhao et al. [23,91] and Chen et al. [85] used high-temperature powder XRD to explore the structure change of HECs with temperature. Interestingly, the anisotropy of thermal expansion is dependent on the material systems. For (Nd0.2Sm0.2Eu0.2Y0.2)Al2O3 and (Yb0.23Y0.25Lu0.25Er0.25)3SiO5, the anisotropy in TECs increased, while for (Y0.2Nd0.2Sm0.2Eu0.2En0.2)Al2O3, the TECs were more isotropic. In the investigation on anisotropy of TEC for (Nd0.2Sm0.2Eu0.2Y0.2)Al2O3, Zhao et al. [91] employed a simple theory called chemical bonding theory (CBT) to describe their observation quantitatively. They found that bond energies of Al–O bonds were significantly higher than those of RE–O, indicating that the chemical environments around RE atoms determined the expansion behavior of HEOs. The energy changing for different RE–O bonds was anisotropic: the bonds with large energy degradation were almost parallel with ab plane, leading to the increase of anisotropy in bonding strength between ab plane and c direction. Ridley et al. [86] used the same technique to investigate the anisotropic thermal expansion of X2-(ScYDyErYb)SiO4. They found that linear CTE generally followed the rule of mixture (ROM), while the c-axis CTE show larger differences. They attributed this deviation to the rigid Si–O tetrahedron in the structure interacted less with incorporated elements. The thermal expansions of reported HEMs are summarized in Fig. 4.2. These preliminary researches have revealed the complexity of structure response of HECs to temperature due to their
complex composition, lattice, and bonding. However, they also demonstrate the possibility of tailoring the thermal expansion of HECs by composition design.

Composition design requires large-scale screening of different combinations of elements. Theoretical prediction is regarded as an efficient and feasible tool to achieve automatic and low-cost screening process. Calculating the thermal expansion is accessible by DFT and molecular dynamics (MD). Yang et al. [184] constructed SQS supercells with 64 atoms for (TaNbHfTiZr)C and (TaNbHfTiZr)N, and they used Debye-Grüneisen model to estimate the thermal expansion of these two HECs using the Helmholtz free energy calculated from DFT. The room temperature TEC they estimated was much smaller than the experiment data reported by Yan et al. [35]. Possible explanation is that the Helmholtz free energy ($F$) was treated by the Debye-Grüneisen model, which discards the volume-dependence of $F$. Dai et al. [50,52] employed a deep leaning potential, which combined the accuracy of DFT and efficiency of MD, to calculate the properties of (TaNbHfTiZr)C and (TaNbHfTiZr)B2. The lattice parameter and thermal properties of high-entropy carbide agreed well with experiment, with the TEC slightly higher than experiments. While for high-entropy boride, the TECs along $a$ and $c$ directions at room temperature were estimated as 8.55 and 8.39×10$^{-6}$ K$^{-1}$, respectively. Large expansion along $a$ direction is unusual since strong covalent $B - B$ bond net is parallel to the $ab$ plane. Considering the chemical complexity of high-entropy borides, the inaccurately fitted deep learning potential was believed to be responsible for the unexpectedly large thermal expansion along $a$ direction.

Unlike thermal conductivity, the thermal expansion of HECs is far from understood. The effect of different constituents on the linear and anisotropic TECs of HECs and methods to tune the thermal expansion to meet the requirement of their applications are still blurry, and theoretical methods for accurate prediction of TECs in HECs are still awaited.

4.5 Oxidation and CMAS corrosion

4.5.1 Oxidation

Ultrahigh temperature ceramics (UHTCs) are materials of choice for the nose tip and leading edges of hypersonic vehicles. However, easy oxidation under high temperature and oxygen-containing conditions is one of the obstacles for their applications. In order to adapt to the stringent demands of hypersonic vehicles, a new type of high-entropy UHTCs with better oxidation resistance has been developed.

Gild et al. [34] first developed a variety of high-entropy borides (HEBs), which exhibited much better oxidation resistance than the individual borides at 1000–1200 $^\circ$C for 1 h. Following this work, oxidation behaviors of high-entropy carbides (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C [185–188] and (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})N [189,190] were investigated by several research groups. Similar to HEBs, all these high-entropy carbides exhibited better oxidation resistance than the individual transition-metal carbides. However, the oxidation mechanism of high-entropy carbides is debatable. Ye et al. [185,186] pointed out that the oxidation of (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C was mainly controlled by the inward diffusion of oxidant based on the oxidation activation energy. In contrast, Wang et al. [187] observed the formation of Ti-depleted layer and proposed that outward diffusion of TiO was the controlling-step. This mechanism was supported by thermodynamic calculations indicating that TiO was easily formed with large vapor pressure of TiO during high-temperature oxidation and re-oxidation experiments showing that the weight gain curve during re-oxidation followed the original oxidation curve [187]. It is worth noting that the vapor pressure of TiO at high temperatures is even higher than that of SiO, which is often considered as the diffusion species in traditional UHTC–SiC systems [191–193]. Therefore, the outward diffusion of TiO was also observed in the oxidation process of (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C–SiC ceramics, even with the addition of SiC [188]. The removal of TiC from (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C to form (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C could avoid the formation of high vapor-pressure TiO during oxidation process [189]. A dense oxidation layer was observed and no depleted layer was found in the oxidized (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C. In this case, the oxidation controlling step was transformed into oxidant inward diffusion. Wang et al. [190] also studied the oxidation of (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C and confirmed that the oxidation process was controlled by the diffusion of oxygen.

Regardless of whether the controlling process was species outward diffusion or oxidant inward diffusion, the formed oxide layers for (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C and (Hf$\text{$_0.2Zr$$_0.2Ta$$_0.2Nb$$_0.2Ti$$_0.2$})C were not a single phase.
Previous studies showed that Hf/Zr-rich oxide layer formed the outer layer followed by a Ta/Nb-rich oxide inner layer based on the similarity solution principle [186–191]. The formed sequential oxide layer structure during oxidation was mainly attributed to the selective oxidation among the multicomponent cations. As indicated by Backman et al. [194,195], the sequence of binding ability for the five transition metals for oxygen atoms was Hf>Zr>Ti>Ta>Nb. Thus, the Hf/Zr-rich oxide would form first, followed by the Ta/Nb oxide layer. Meanwhile, the metal-species would also diffuse outward into the formed oxide layer during oxidation even though the controlling process was the oxidant inward diffusion [189]. In the multicomponent oxide, the retarded diffusion of these metal-species might result in the slow thickening of the oxide layer, and thus greatly improve the oxidation resistance of the high-entropy carbides or borides.

It is interesting to note that the high-entropy nitride films of (AlCrTaTiZr)–Si–N, (AlCrTaTiZr)N8, and (AlCrTaTiZr)C0.8Si1.2N1.2 have both high hardness and good oxidation resistance [153–155]. These films are promising for applications as hard coatings for cutting tools.

### 4.5.2 CMAS corrosion

High-entropy thermal/environmental barrier coatings (T/EBCs) have been developed in recent years to meet the requirements for next generation turbines [23,37,196,197]. These coatings demonstrated improved thermophysical [23,37,196,197] and mechanical properties [196] as well as excellent high-temperature stability [43,88]. Thus, they can protect substrate materials (superalloys or ceramic matrix composites (CMCs)) from harsh thermal and environmental attacks.

Since the coatings for next generation turbines would work at temperatures higher than 1300 °C, the attack from molten calcia–magnesia–aluminosilicate (CMAS) is of great concern. The interaction behaviors of high-entropy T/EBCs with CMAS are essential to qualify them as potential T/EBCs materials. For EBCs, Dong et al. [87] and Ren et al. [43] developed high-entropy disilicate ((Er0.25Yb0.25Lu0.25)Si2O7) at 1500 °C. It was demonstrated that the high-entropy disilicate still followed the reaction–precipitation mechanism that has been proved in those individual constituents. The high-entropy disilicate dissolved when it came in contact with molten CMAS and the Ca–Si–RE containing apatite precipitated when the elements reached saturation in the molten glass. It should be noted that, compared with the single constituents such as γ-Y2Si2O7, β-Sr2Si2O7, β-Yb2Si2O7, and β-Lu2Si2O7, the resistance of high-entropy disilicate against molten CMAS was significantly improved. These improvements in high-entropy disilicate can be mainly attributed to the slower dissolution rate and enhanced grain boundary stability, which may originate from the sluggish diffusion effect and lattice distortion introduced by the high-entropy disilicate. Regarding the TBCs, Wright et al. [198] recently reported the CMAS resistance of high-entropy fluorites, which can be potentially employed as TBC materials due to their promising thermophysical and mechanical properties [23,37,43,196]. The equimolar high-entropy fluoride also presented reaction and precipitation behavior at all examined temperatures (1200–1500 °C) similar to high-entropy disilicate. They further compared the CMAS corrosion behaviors among high-entropy fluoride ((Hf0.2Zr0.2Ce0.2Y0.2Yb0.2)O2–δ), medium-entropy fluorites ((Hf0.314Zr0.314Ce0.314Y0.029Yb0.025)O2–δ), (Hf0.284Zr0.284Ce0.284Y0.074Yb0.074)O2–δ), and 8YSZ. The medium-entropy fluorites presented more resistance to molten CMAS than 8YSZ, which was evident by the obvious grain boundary infiltration layer in 8YSZ. Moreover, the high-entropy fluoride showed the most significant CMAS resistance at tested temperatures. Notably, there was no grain boundary infiltration layer in the high-entropy fluoride, which was seen in all other samples. The authors concluded that high-entropy fluorites have the highest reactivity rate with molten CMAS to form a dense apatite phase, which was beneficial for arresting grain boundary infiltration. These experimental results showed significant improvement in resistance against molten CMAS in high-entropy T/EBC materials. High-entropy T/EBC materials tend to react with molten CMAS to form dense apatite phase. Moreover, a sluggish diffusion effect in HEMs retarded the atomic diffusion and thereby reduced further corrosion by CMAS. The above results provide a new perspective for the design of T/EBC materials with comprehensive properties by

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high-entropy compositionally complex route.

4.6 Irradiation resistance

Investigations on HEAs revealed that the unique combination of superior mechanical properties, corrosion resistance, irradiation tolerance made them promising for nuclear applications [199–202]. Motivated by the achievement in HEAs, the irradiation effects of high-entropy carbides were also investigated [169,203]. In contrast to ZrC, which is characterized by structural swelling (i.e., lattice parameter expansion) after neutron, proton, and ion irradiation [204], after 120 keV helium ion irradiation at 25 °C, the coalescence of helium bubbles was significantly suppressed in (Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C [203]. Wang et al. [169] further investigated the irradiation damage of (Zr_{0.25}Ta_{0.25}Nb_{0.25}Ti_{0.25})C. Through irradiation of 3 MeV Zr ions to 20 dpa at 25, 300, and 500 °C, the rock-salt structure was maintained without phase transformation or amorphous formation, indicating good phase stability of (Zr_{0.25}Ta_{0.25}Nb_{0.25}Ti_{0.25})C. About ~0.2% lattice expansion was revealed through XRD analysis. The irradiation-induced microstructures were comprised of defect clusters with diameters of several nanometers, without void formation or radiation-induced segregation at grain boundaries. Nanoindentation tests showed irradiation-induced hardness increase, which was attributed to the high density dislocation loops and lattice strain. These results demonstrated that high-entropy carbides exhibit excellent damage tolerance and are promising for applications in generation-IV reactors.

4.7 Electronic and ionic conductivity

Lattice distortion has widely been used to reduce the electrical contribution to the thermal conductivity, thus for highly conductive ceramics like borides and carbides, electron scattering can be exacerbated resulting in reduced electrical conductivity in high-entropy borides and carbides [167]. Although theoretical calculations indicate that metallic conductivity is preserved in (Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B [57] and (Co_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Mn_{0.2})B [96], the experimentally measured electrical conductivity of (Co_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Mn_{0.2})B (0.49±0.04)×10^6 S/m) is much lower than that of CrB (0.3×10^7 S/m), FeB (0.5×10^7 S/m), and ZrB_2 (1.0×10^7 S/m) [96]. For insulating ceramics such as oxides, the multi-component strategy can narrow the band gap [60] and increase defect species, making them semiconducting or mixed conducting. From this angle, the high-entropy concept provides new avenues for new material design through band gap engineering.

One of the breakthroughs of HECs is the high Li-ion conductivity (> 10^{-3} S·cm^{-1}) [21]. (MgCoNiCuZn)_{1−x}Ga_{x}A_{2}O (A = Li, Na, K) with rock-salt structure were fabricated and their electronic and ionic conductivities were systematically investigated. To the best of our knowledge, this is the first research work on the conductivity of HECs. On one hand, the electronic conductivity (σ_e) was investigated by monitoring the current density of the materials which were employed by a 1 V potential step over 2 days with blocking electrodes. According to Eq. (4.6):

$$σ_e = el/((SΔE))$$

where $e$ is the material thickness, $S$ is the active surface, $ΔE$ is the applied voltage, and $I$ is the residual current intensity measured after 2 days, the electronic conductivity of the material was defined as 2×10^{-9} S·cm^{-1}. Therefore, these materials were regarded as electronic insulators. On the other hand, the room temperature Li^+ conductivity of the compounds with Li > 20% was found to exceed the ionic conductivity of LiPON by two orders of magnitude. These new materials are superionic lithium-ion conductors and fast-ionic sodium-ion conductors, with Li^+ conductivity exceeding 10^{-3} S·cm^{-1} and Na^+ conductivity reaching 5×10^{-6} S·cm^{-1} at room temperature. The extremely high ionic conductivity of (MgCoNiCuZn)_{1−x}Ga_{x}A_{2}O (A = Li, Na, K) was ascribed to the formation of abundant oxygen vacancies through a charge compensation mechanism [205]. When a monovalent element (e.g., Li^+ or Na^+) is introduced, the concentration or the ordering of the oxygen vacancies as well as the size of the divalent cations in the compound can be optimized. That is, the insertion of Li-ions into a rock-salt structure opens several diffusion pathways for Li-ions through the crystal lattice, giving rise to the increased conductivity.

4.8 Dielectric properties

In high-entropy ceramics, there are more than one sublattices in which at least one sublattice site is occupied by multi-elements. The sublattice, on the one hand, exhibits long-range periodicity with the distortion that influences the behaviors of electrons, dipoles and band structure. On the other hand, random
distributed multi-elements results in compositional disorder that reduces short range order. The ample type of HECs provide more flexible ways to tailor the composition, defects, disorder/order, band structure, in which dielectric properties are easily tuned.

The colossal dielectric constant, which is one of the important breakthroughs of HECs, was reported by Bérandan et al. [20] in rock-salt structured HEOs. The dielectric constant (the relative permittivity) for (Mg,Co,Ni,Cu,Zn)₀.₂₅Li₀.₇₅O measured at 440 K and 20 Hz with an LCR bridge method was close to 2×10⁵. Large values of dielectric constant were obtained for (Mg,Co,Ni,Cu,Zn)O family irrespective of substitutions as long as the high-entropy oxide phase was formed. For instance, the dielectric constant for high-entropy (Mg,Co,Ni,Cu,Zn)O without any substitution was larger than 1000 while the dielectric loss (tanδ) was lower than 0.01 measured at 313 K and MHz range.

Zhou et al. [206] investigated the dielectric properties of high-entropy perovskite oxides Ba(Zr₀.₂Ti₀.₈Sn₀.₂Hf₀.₈Me₀.₂)O₃ (Me = Nb⁺⁵, Ta⁺⁵) and found that the dielectric constant and dielectric loss slightly decreased with the increasing of frequency from 1 to 1000 kHz. In the temperature from 303 to 473 K, the dielectric constant and dielectric loss possess excellent stability at fixed frequency. The dielectric constant is in a range from 90 to 113 for Ba(Zr₀.₂Ti₀.₈Sn₀.₂Hf₀.₈Ta₀.₂)O₃ and 120 to 140 for Ba(Zr₀.₂Ti₀.₈Sn₀.₂Hf₀.₈Nb₀.₂)O₃ in the frequency from 1 to 1000 kHz. Intriguingly, the dielectric loss (tanδ) is lower than 0.002. The relatively low permittivity was attributed to a minor concentration of titanium in the B-site sub-lattice and small grain size.

The dielectric relaxation of (Na₀.₂B₄₀.₅Ba₀.₃Sn₀.₂Ca₀.₅)TiO₃ was studied by Pu et al. [129]. The dielectric peak was broad and shifted toward higher temperature with increasing frequency. Meanwhile, the dielectric loss increases with increasing frequency, which is similar to those for the relaxation of other ferroelectrics with perovskite structure. The degree of relaxation is 1.72, being close to the ideal relaxation ferroelectrics. Du et al. [207] investigated the dielectric properties of high-entropy Ba(Ti₀.₈Sn₀.₂Zr₀.₁₅Hf₀.₆Nd₀.₁₅Ga₀.₆)O₃ and found that the dielectric constants are on the order of 40–80 up to 1 MHz and the dielectric loss tangents are in the neighborhood of 0.15. The results also revealed the dielectric relaxation behavior of high-entropy perovskite ceramics. Liu et al. [208] investigated dielectric and energy storage properties of flash-sintered high-entropy (Bi₀.₂Na₀.₈K₀.₂Ba₀.₂Ca₀.₅)TiO₃ ceramic. The dielectric characterization reveals the relaxor ferroelectric nature of (Bi₀.₂Na₀.₈K₀.₂Ba₀.₂Ca₀.₅)TiO₃. The discharge energy storage density and efficiency of the as-prepared high-entropy (Bi₀.₂Na₀.₈K₀.₂Ba₀.₂Ca₀.₅)TiO₃ ceramic are 0.684 J/cm³ and 87.5% under the electric field of 129 kV/cm, respectively. Besides high-entropy oxides, high-entropy metal nitride composed of V, Cr, Nb, Mo, Zr, and N was reported to exhibit characteristics of a supercapacitor with a specific capacitance of 78 F/g achieved at a scan rate of 100 mV/s in 1 M KOH [122].

4.9 Magnetic properties

The soft magnetic properties of HEAs aiming to reach high saturation magnetization and low coercivity are widely investigated [209]. Generally speaking, HEAs are good soft magnetic materials due to low concentration of elements with the highest net magnetic moments, which can be operated under alternating current with lower frequency (usually below MHz) due to the nature of conductivity without a band gap. However, HECs are usually semiconductors or insulators with a band gap and possess higher electric resistivity (usually Ω·cm), which can be applied at the higher frequency (above MHz) under alternating current operation. Compared to HEAs, investigations on magnetic properties of HECs are still in their nascent beginning.

Mao et al. [210] found that (CoCrFeMnNi)₂O₄ basically exhibited a ferromagnetic behavior and M–H loops showed a typical magnetic curves at room temperature. The saturation magnetization and coercivity of (CoCrFeMnNi)₂O₄ changed in the range of 4.85–15.98 emu/g and 176.55–21.39 Oe, respectively, depending on the synthesis temperature.

Mao et al. [211] also investigated the magnetic properties of rock-salt structured Co₀.₃Cu₀.₇Mg₀.₂Ni₀.₄Zn₀.₂O powders and found that nanocrystalline Co₀.₃Cu₀.₇Mg₀.₂Ni₀.₄Zn₀.₂O powders exhibited long-range ordered antiferromagnetic behavior below the Néel temperature (T_N = 106 K), which was ascribed to the extreme chemical disorder of Co₀.₃Cu₀.₇Mg₀.₂Ni₀.₄Zn₀.₂O and the significant amount of nonmagnetic ions, compared to the monoxides CoO, NiO, and CuO. The existence of long-range magnetic ordering in rock-salt structured Co₀.₃Cu₀.₇Mg₀.₂Ni₀.₄Zn₀.₂O below 120 K was also confirmed by Jimenez-Segura et al. [212]. Other rock-salt structured HEOs with various chemical substitutions were found to host...
either an antiferromagnetic order or a spin glass state depending on the amount of magnetic ions. Long range antiferromagnetic ordering below $T_N = 113$ K was confirmed by a cusp in DC magnetic susceptibility, magnetic peaks in neutron powder diffraction, and strong magnetic excitations in inelastic neutron scattering [213]. The magnetic properties of rock-salt structured Co$_{0.25}$Cu$_{0.25}$Mg$_{0.25}$Ni$_{0.25}$Zn$_{0.25}$O were also investigated using theoretical methods involving first-principles calculations in combination with Monte Carlo (MC) simulations [214]. It was found that the material possessed a long range antiferromagnetic ground state in consistent with the literature [211–213]. The antiferromagnetic ordering was suppressed by the presence of Mg and Zn, and the material became paramagnetic when the concentration of nonmagnetic cations exceeded 84%. Meisenheimer et al. [215] reported on the magnetic ordering, anisotropy, and ordering temperature in the anisotropy of permalloy/(Mg$_{0.25}$Co$_{0.25}$)/Ni$_{0.25}$Cu$_{0.25}$Zn$_{0.25}$O heterostructures, in which exchange bias thin film heterostructures are composed of a ferromagnetic layer (Py, 3 nm), an antiferromagnetic layer, and an entropy-stabilized oxides layer with 80 nm. The disorder, exchange field and magnetic anisotropy could be tuned by changing the composition of the Mg$_{0.25}$Co$_{0.25}$Ni$_{0.25}$Cu$_{0.25}$Zn$_{0.25}$O. The exchange bias observed at low temperature could reach 10 times that observed in a CoO/Py control sample.

The magnetic properties of perovskite-type high-entropy oxides with the general composition Gd$_{2}$La$_{x}$Nd$_{0.25}$Sm$_{0.25}$Y$_{0.25}$BO$_{3}$, in which B site was respectively Co, Cr, and Fe, was investigated by Witte et al. [216]. The magnetic behavior of perovskite-type HEOs depended sensitively on the nature of the transition metals on the B site. The magnetic properties of different rare-earth (RE) ions on the A site and transition metal (TM) ions on the B-site were presented. Compounds with five intermixed TM elements on the B site and single RE elements on the A site as well as a compound with five different RE elements on the A site, namely Gd$_{2}$La$_{0.25}$Nd$_{0.25}$Sm$_{0.25}$Y$_{0.25}$Co$_{0.25}$Cr$_{0.25}$Fe$_{0.25}$Mn$_{0.25}$Ni$_{0.25}$O$_{3}$, have been investigated [78]. It was observed that antiferromagnetic behavior in the single-phase ABO$_3$ materials was dominant, combined with a small ferromagnetic contribution. A large degree of magnetic frustration was found due to the high degree of disorder and competing ferromagnetic and antiferromagnetic interactions. Vertical exchange bias of about 25% of the remnant magnetization was obtained due to nanoscale magnetic feature. (B$_{0.2}$Sr$_{0.2}$)(Fe$_{2.5}$A$_{1.5}$Mn$_{2}$Ti$_{2}$Ni$_{2.5}$)O$_{19}$ with a magnetoplumbite structure was explored by Vinnik et al. [94], and a paramagnetic behavior near the room temperature was revealed.

5 Prospective applications

The new material design paradigm and countless composition and microstructure combinations have endowed HECs properties that cannot be achieved in traditional materials. The prospective applications of this nascent family of materials cover from structural to functional including ultrahigh temperature thermal protection and thermal insulation of hypersonic vehicles, thermal and environmental barrier coatings for engine components, irradiation resistant materials for nuclear energy, cutting tools, and wear resistant coatings, electromagnetic wave absorption and interference shielding, anodes for rechargeable batteries, catalysts for clean energy and environment, thermoelectrics, supercapacitors, etc., as shown in Fig. 5.1.

5.1 Thermal protection and insulation

HECs exhibit low thermal conductivity and excellent thermal stability and are promising candidates for thermal protection and insulation. Thermal conductivity arises from both electrical and phonon contributions. In electrical insulating materials, thermal conductivity at low temperature is mainly affected by the directional movement of phonons. Therefore, thermal conduction is mainly restricted by various phonon-scattering processes, including phonon-phonon scattering, grain boundary scattering, and defect scattering [217–219]. Due to the huge differences in atomic mass, ionic radius, and interatomic force between multiple elements in HECs, mass and strain fluctuations are induced, resulting in enhanced phonon scattering. Thus, the thermal conductivity of HECs is much lower than their constituting components. For example, the thermal conductivity of a high-entropy (Mo,Nb,Ta,Ti,W)Si$_2$ (6.9 W·m$^{-1}$·K$^{-1}$) is much lower than those of the individual constituent disilicides (19.1–65.0 W·m$^{-1}$·K$^{-1}$) and the rule-of-mixture (RoM) average (40.0 W·m$^{-1}$·K$^{-1}$) of the five disilicides [33]. Moreover, benefiting from the highly disordered interatomic forces, a class of HEOs (Mg,Ni,Cu,Co,Zn,M,O, where $x = 0.167$, and

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M representing for Sc, Sb, Sn, Cr, and Ge, respectively) show the highest ratio of modulus to thermal conductivity [19].

Among HECs, high-entropy ultra-high temperature ceramics (HE UHTCs), especially highly porous HE UHTCs, have attracted much attention in the area of ultra-high temperature thermal protection and insulation, owing to their low thermal conductivity, good thermal stability, and low density [22,35,40]. Recently, a novel strategy towards making ultrahigh temperature ceramics thermal insulating was proposed as shown in Fig. 5.2 [22,40]. Through this novel strategy, highly porous high-entropy carbides and borides ceramics with low thermal conductivity were fabricated. For instance, the porous (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C with a porosity of 80.99% exhibits an ultralow thermal conductivity of 0.39 W·m$^{-1}$·K$^{-1}$ and a low density of 1.79 g·cm$^{-3}$ [22] while the dense (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C ceramic usually possesses a thermal conductivity of about 6.45 W·m$^{-1}$·K$^{-1}$. Similarly, porous HE (Zr$_{0.2}$Hf$_{0.2}$Ti$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)B$_2$ with a porosity of 80% can also be used as thermal protection and insulation material for its high melting point, high strength (3.93 MPa), and ultralow thermal conductivity (0.51 W·m$^{-1}$·K$^{-1}$) [40].

The low thermal conductivities of highly porous HE

Fig. 5.1 Prospective applications of HECs covering from ultrahigh-temperature structural to energy and catalytic functional applications.

Fig. 5.2 Schematic illustration of the strategy towards making ultrahigh temperature ceramics thermal insulating [22,40].
UHTCs can be attributed to their high porosity as well as the reduced thermal conductivity of high-entropy backbone materials, which can significantly reduce the solid thermal conduction. The porous high-entropy ceramics also show good dimensional and phase stability. The linear shrinkage curve of porous HE (Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C during the second round heating process is shown in Fig. 5.3. It can be seen that there is little volume change during the second round heat treatment even up to 1850 °C. No evidence of decomposition or phase transformation was observed in the XRD pattern. SEM images of as-prepared and heat treated porous (Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C show rarely differences in grain size and microstructure, indicating that the porous HE (Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C is thermally stable at least up to 1850 °C in argon atmosphere which is promising for ultrahigh temperature thermal insulation applications.

Other than passive thermal protection and insulation, porous HECs are also promising for applications in active thermal protection. Transpiration cooling is an active and reusable thermal protection method, which has the potential to reduce heat loads on hypersonic vehicles with higher thermal protection efficiency [220–222]. The unique combination of low density, high porosity, and high permeability makes porous HE UHTCs potential for transpiration cooling applications. Recently, porous HE (Y_{0.2}Yb_{0.2}Sm_{0.2}Nd_{0.2}Eu_{0.2})B_6 (HEREB_6) was synthesized by in-situ reaction/partial sintering method using HE (Y_{0.2}Yb_{0.2}Sm_{0.2}Nd_{0.2}Eu_{0.2})B_6 as the backbone material [98]. The permeability of porous HE REB_6 with a porosity of 70.64% and 64.35% are determined to be 2.73×10^{-11} m² and 2.65×10^{-11} m², respectively according to the Darcy equation [223]. A large number of interconnected pores with a large pore diameter of porous HE (Y_{0.2}Yb_{0.2}Sm_{0.2}Nd_{0.2}Eu_{0.2})B_6 was shown in the XRT image in Fig. 3.3(b), corresponding to high permeability. Thus, porous HE (Y_{0.2}Yb_{0.2}Sm_{0.2}Nd_{0.2}Eu_{0.2})B_6 can be used in the field of active thermal protection.

5.2 Thermal/environmental barrier coatings

HECs exhibit superior properties such as high hardness, good water–vapor corrosion resistance, good thermal stability, low thermal conductivity, low grain growth rate, and tunable thermal expansion coefficient [23,37,58,71,85,88–93] and are thus prospective as thermal/environmental barrier coating materials. According to the strategy for engine materials [224], thermal/environmental barrier coatings (T/EBCs) play pivotal roles in protecting superalloys, silicon-based composites, and non-silicon-based composites. Figure 5.4 shows the roadmap of engine materials and the schematic structures for T/EBCs to protect superalloys, SiC/SiC composites and Al_{2}O_{3}/Al_{2}O_{3} composites. To meet the development of engine materials, a serious of high-entropy ceramics including zirconates [37,74,149,196], aluminates [23,90,91], silicates [43,87–89], phosphates [93], niobates, and tantalates [71] were designed and synthesized.

5.2.1 TBCs for nickel-based superalloys

Rare-earth zirconates have been proposed as potential candidate TBC materials for nickel-based alloys because of their relatively high TECs, low thermal conductivity, and good thermal stability. However, the relatively high thermal conductivity and poor sintering resistance are the main drawbacks that limit their practical application. Recently, high-entropy zirconates with cubic pyrochlore structures have been synthesized as candidates of TBC materials [37,74,145,196]. The high-entropy zirconates exhibit lower thermal conductivity than their components due to the enhanced scattering of phonons. Besides low thermal conductivity, matched
thermal expansion coefficient and a slow grain growth rate are also required for T/EB C materials. Since large lattice distortion hindered the atomic movement and effective diffusion of the atoms, HE (La0.2Ce0.2Nd0.2Sm0.2Eu0.2)Zr2O7 exhibits a much slower grain growth rate [37] such that it has prospective applications as a top layer of TBC.

To improve the thermal shock resistance, a double-ceramic-layer (DCL) [149] thermal barrier coating (TBC) with high-entropy rare-earth zirconate (HE-REZ) as the top layer and yttria-stabilized zirconia (YSZ) as the inner layer was designed. The DCL coating exhibited better thermal shock resistance than that of the single component La2Zr2O7 coating, which was attributed to the matched TEC and slower shrinkage rate owing to the sluggish diffusion effect of high-entropy materials.

High entropy (Y0.2Yb0.2Lu0.2Eu0.2Er0.2)Al2O3 ceramic was also considered as a candidate thermal barrier material [90]. Close thermal expansion coefficient ((8.54±0.29)×10−6 K−1 at 673–1273 K) to TG-Al2O3, low thermal conductivity (3.81 W·m−1·K−1 at 300 K), good phase stability, excellent chemical compatibility with TG-Al2O3, and slow grain growth rate (0.038 μm·h−1) endowed it a promising candidate for thermal barrier applications. A very recent work by Zhao et al. [71] revealed that high-entropy (Y1/3Yb1/3Er1/3)TaO7, (Y1/3Yb1/3Er1/3)NbO7, and (Sm1/8Eu1/8Y1/8Yb1/8Lu1/8Er1/8)2(Nb2Ta2)O7 exhibit high Vickers hardness (10.9–12.0 GPa), close thermal expansion coefficients to that of single-principal-component RE3TaO7 and RE3NbO7 (7.9–10.8)×10−6 K−1 at room temperature), good phase stability, and good chemical compatibility with TG-Al2O3 and are suitable as candidate materials for TBC materials.

5.2.2 EBC for SiC/SiC composites

Rare-earth aluminates such as RE4Al2O7 have been considered as T/EB C materials for silicon-based composite substrates [225]. The main restrictions for the practical application of rare-earth aluminates are phase transition at high temperature, relatively low thermal expansion coefficient, and high thermal conductivity. Recently, high-entropy (Nd0.2Sm0.2Eu0.2Y0.2Yb0.2)Al2O3 was designed and synthesized [91], which has a close thermal expansion coefficient (6.96×10−6 K−1 at 300–1473 K) to that of mullite, good phase stability, and low thermal conductivity (1.50 W·m−1·K−1 at room temperature). The thermal expansion increased linearly with the increase of temperature, indicating that there was no abrupt volume change caused by phase transformations. Intriguingly, strong anisotropy in thermal expansion coefficients of HE (Nd0.2Sm0.2Eu0.2Y0.2Yb0.2)Al2O3 was observed [91], which was attributed to different RE atoms arrangement density, i.e., the arrangement of rare earth atoms along the α- and β-axis is much denser than that along the c-axis in the crystal structure of HE (Nd0.2Sm0.2Eu0.2Y0.2Yb0.2)Al2O3.

Besides high-entropy aluminates, the thermophysical and chemical properties of high-entropy silicates, such as HE (Yb0.25Y0.25Lu0.25Er0.25)2SiO5 [85], HE (Yb0.2Y0.2Lu0.2Sc0.2Gd0.2)2SiO7 [87], and HE (Y1/4Ho1/4Er1/4Yb1/4)2SiO5 [43] were also investigated.

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**Fig. 5.4** Roadmap for the development of engine materials, and schematic structures for the corresponding T/EBCs to protect superalloys, SiC/SiC, and Al2O3-Al2O3 composites.
According to these studies, high-entropy silicates displayed excellent phase stability from room temperature to 1300 °C, matching CTE with silicon-based matrix composites, and good corrosion resistance in water–vapor environments, indicating their potential for applications as T/EBC materials for silicon-based composites. Similar to HE (Nd0.2Sm0.8Er0.2)Al2O3, HE (Yb0.25Lu0.75Er0.25)SiO3 also shows a strong anisotropy in thermal expansion. The TECs in the a, b, and c crystallographic directions are (2.57±0.07)×10⁻⁶ K⁻¹, (8.07±0.13)×10⁻⁶ K⁻¹, and (9.98±0.10)×10⁻⁶ K⁻¹, respectively. The strong anisotropy in thermal expansion is favorable in minimizing the coating/substrate mismatch if the preferred orientation of HE (Yb0.25Lu0.75Er0.25)SiO3 is controlled on different substrates [85].

5.2.3 EBC for Al2O3/Al2O3 composites

In general, the key requirements for selecting the EBC materials of Al2O3/Al2O3 composites include good phase stability and absence of decomposition and phase transformation from room temperature to the service temperature, close thermal expansion coefficient and good chemical compatibility with Al2O3, good durability to extreme environments such as high temperature heat flux and H2O/O2 corrosion, and low thermal conductivity. Figure 5.5(a) compares the thermal conductivity and thermal expansion coefficient of recent designed high-entropy ceramics with other candidate EBCs for Al2O3.

HE (Y0.2Nd0.2Sm0.2Er0.2)Al2O3 possesses a high thermal expansion coefficient (9.02×10⁻⁶ K⁻¹) close to that of Al2O3 (~9.0×10⁻⁶ K⁻¹), and simultaneous excellent water vapor corrosion resistance, which makes it a promising candidate EBC material to protect Al2O3/Al2O3 composites from the corrosion of high-temperature water vapor in combustion environments [23]. Additionally, a dense high-entropy garnet reaction layer forms at the interface when HE (Y0.2Nd0.2Sm0.2Er0.2)Al2O3 reacts with Al2O3 at 1500 °C. The dense HE garnet reaction layer can separate the HE (Y0.2Nd0.2Sm0.2Er0.2)Al2O3 layer from the Al2O3 layer and prevents them from further interaction. Thus, analogous to the YSZ/TG Al2O3/Ni-based super alloy TBC and the RE-silicates/TG-SiO2/(SiCp/SiC composites) EBC structures, a tri-layer EBC system REAlO3/RE2Al5O12/(Al2O3/Al2O3 CMCs) was designed by Zhao et al. [23], as illustrated in Fig. 5.5(b) by using the reacting-formed garnet layer as a barrier for penetrating the water vapor from the top HE REAlO3 layer.

High-entropy rare-earth phosphate monazite ceramic (La0.2Ce0.8Nd0.2Sm0.2Eu0.2)PO4 [93] exhibits good chemical compatibility with Al2O3, without reaction with Al2O3 at high temperatures as high as 1600 °C in air. Its thermal expansion coefficient is 8.9×10⁻⁶ K⁻¹ at 300–1000 °C and is close to that of Al2O3. The thermal conductivity of HE (La0.2Ce0.8Nd0.2Sm0.2Eu0.2)PO4 at room temperature is as low as 2.08 W·m⁻¹·K⁻¹, which is about 42% lower than that of LaPO4. Good chemical compatibility, close TEC to Al2O3, and low thermal conductivity indicate that HE (La0.2Ce0.8Nd0.2Sm0.2Eu0.2)PO4 is suitable as a candidate EBC/TBC material or an interphase for Al2O3/Al2O3 composites [93].

In short, low thermal conductivity, tunable thermal expansion coefficient, slow grain growth rate, excellent phase stability, good resistance to corrosion, and compatibility with the substrate make high-entropy

![Image](https://www.springer.com/journal/40145)
ceramics promising candidates for T/EBC applications.

5.3 Hard and wear resistant coatings

Superhard materials find applications in cutting tools and drill bits for precision processing, hard materials’ machining and wear resistant plates, rolls, etc., in harsh working environments [3]. As we have described in Section 3.2.3, the hardness of high-entropy nitride, carbide, and boride films are significantly enhanced so that they have important applications as hard and wear resistant coatings to extend the lifetime of cutting tools and wear parts. Cutting tools for dry cutting and high-speed cutting need longer lifetime, which can be improved by hard high-entropy coatings. High-entropy nitride films such as (AlCrTaTiZr)–Si–N, (Al23Cr20Nb7Si7Ti20)N30, and (Al20Cr20Nb12Si7Ti22)N30 films exhibit not only high hardness (over 34 GPa) but also good oxidation resistance. Cutting tools coated with these nitride films could have good performance and improved lifetime [152–155]. Cutting performance tests [3] demonstrated that high-entropy nitrides coated insert had superior oxidation and wear resistance over TiN and TiAlN coated inserts for high-speed dry cutting of 304 stainless steel work piece.

TiAlCrSiV/(TiAlCrSiV)N double-layer coatings [156] show high hardness and corrosion resistance and can be used as wear and corrosion resistant coatings. High-entropy carbides films such as (CuSiTiYZr)C have high hardness (over 29 GPa), low coefficient of friction (~0.15) and superior corrosion resistance [159] and can be used as wear resistant coatings working in harsh environment. High-entropy (TiZrHfVNBaC) coatings [160] are superhard with low coefficient of friction and can be used as self-lubricating or wear resistant surface coatings. High-entropy (Zr0.23Ti0.20Hf0.19V0.14Ta0.24)B2 with a hardness of 47 GPa can be used as superhard coatings of cutting tools as excavator buckets [163].

5.4 Nuclear energy

Due to the excellent solubility for minor actinide (MA: Np, Am, Cm) elements in rock-salt structured transition metal carbides and nitrides [226], they can be used as inert matrix fuels (IMF) for transmuting transuranium elements for further use as fission fuel and producing clean wastes [227,228]. In addition, carbide and nitride ceramics can be used as structural materials for cladding and TRISO (tri-isotropic) in nuclear reactors by taking advantages of their favorable thermal and mechanical properties. For high-entropy transition metal carbides and nitrides, they keep the rock-salt structure with atomic scattering and lattice strain inside. The atomic scattering, lattice strain, and low heat dissipation may help improve the stability of lattice during irradiation [203] and the sluggish diffusion may improve the oxidation resistance under 1200 °C water vapor atmosphere [229]. The decreased thermal conductivity due to the enhanced phonon scattering [35], however, is a very critical concern for their application as cladding materials. As such, how to balance the irradiation resistance and the thermal conductivity would be an important issue for the development of high-entropy ceramics for possible application as core materials in nuclear reactors. Furthermore, materials with small values of neutron absorption cross-section are important for the application in fission reactors. The concern for high-entropy ceramics developed for fission reactors is the complicated atomic composition with different values of neutron absorption cross section.

Transition metal diboride has the potential to be used as plasma facing material for nuclear fusion reactors on the strength of its high melting point, high thermal conductivity, low sputtering yield, low hydrogen isotope retention, and excellent resistance to helium ions and neutron irradiation, etc. [230,231]. It can be expected that high-entropy boride ceramics would have good irradiation resistance. However, similar to the high-entropy carbide ceramics, the trade-off between the improved irradiation resistance and the decreased thermal conductivity would be a key issue for the researchers. Non-equimolar and medium-entropy composition design would be a possible approach.

On the other hand, immobilization of high-level radioactive waste (HLW) is important for the safe utilization of nuclear energy. The waste forms must withstand the self-radiation of HLW for long time and demonstrate good chemical durability, high thermal and mechanical stabilities and low leaching rate. Based on these criteria, ceramics are considered as good candidates. As HECs are characterized by sluggish diffusion and good irradiation resistance, they should be competitive in the application of immobilization for the HLW.

5.5 Electromagnetic wave (EM) absorption and EM interference shielding

The increasing electromagnetic hazards including
electromagnetic interference and electromagnetic pollution, which were stemmed from massive usage of electromagnetic technology, has triggered widespread concerns. To cope with this challenge, electromagnetic interference shielding and electromagnetic wave absorbing materials with high performance are greatly needed.

It has come to light that materials with sufficiently large permittivity and permeability values will demonstrate a strong attenuation response to incident electromagnetic radiation as such composites made of conductive/magnetic components show enhanced microwave absorption properties [232]. However, the uniform dispersion of different nanometer sized phases and precise control of their compositions and interfaces pose challenges to the conductive/magnetic composites. Thus searching for single-phase materials with both high permittivity and permeability which allow the optimization of EM absorbing in micrometer grain size through dielectric/magnetic loss coupling is appealing. The advent of HECs makes the design of new materials through dielectric/magnetic loss coupling possible. Besides, developing HECs is also an effective way to tailor the dielectric and magnetic losses at GHz frequency range by compositional design, thus realizing better impedance matching and microwave absorption performance.

Chen et al. [101] investigated the electromagnetic wave absorption properties of high-entropy RE$_2$Si$_2$C/Y RE$_2$O$_3$ (RE = Tm, Pr, Gd, Dy, Tb, Y) composites and found that strong EM absorption capability and wide efficient absorption bandwidth could be achieved for these HECs. Zhou et al. [233] investigated the EMW absorption properties of transition metal carbides TMCs (TM = Ti, Zr, Hf, Nb, and Ta) and high-entropy (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C. Intriguingly, they found that the electromagnetic parameters, i.e., complex permittivity and permeability are tunable by forming single-phase solid solution or high-entropy (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Nb$_{0.2}$Ta$_{0.2}$)C, which opens a new window to design single-phase high performance EMW absorbing materials by dielectric/magnetic loss coupling. Zhang et al. [99] designed five high-entropy rare earth hexaborides HE REB$_6$ including (Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$ (HE REB$_6$-1), (Ce$_{0.2}$Er$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$ (HE REB$_6$-2), (Ce$_{0.2}$Y$_{0.2}$Er$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$ (HE REB$_6$-3), (Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$ (HE REB$_6$-4), and (Nd$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$ (HE REB$_6$-5), and five HE REB$_6$/HE REBO$_3$ composites including (Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$/(Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)BO$_3$ (HE REB$_6$/HE REBO$_3$-1), (Ce$_{0.2}$Er$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$/(Ce$_{0.2}$Er$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)BO$_3$ (HE REB$_6$/HE REBO$_3$-2), (Ce$_{0.2}$Y$_{0.2}$Er$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$/(Ce$_{0.2}$Y$_{0.2}$Er$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)BO$_3$ (HE REB$_6$/HE REBO$_3$-3), (Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$/(Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)BO$_3$ (HE REB$_6$/HE REBO$_3$-4), and (Nd$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$/(Nd$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)BO$_3$ (HE REB$_6$/HE REBO$_3$-5) with dielectric and magnetic losses coupling. These powders were fabricated through a facial one-step boron caride reduction method. (Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$ powders with the average particle size of 1.86 μm were found to possess the best EM wave absorption properties among the HE REB$_6$s. The $RL_{\text{min}}$ value of (Ce$_{0.2}$Y$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$ reached $-33.4$ dB at 11.5 GHz with the thickness of 2 mm; meanwhile, the optimized effective absorption bandwidth ($E_{\text{AB}}$) reached 3.9 GHz from 13.6 to 17.5 GHz with the thickness of 1.5 mm.

Moreover, enhanced electromagnetic wave absorption performances were achieved in high-entropy rare earth hexaboride/tetraboride (HE REB$_6$/HE REB$_4$) composite powders [234]. As shown in Figs. 5.6(a) and 5.6(b), the optimal minimum reflection loss ($RL_{\text{min}}$) and effective absorption bandwidth ($E_{\text{AB}}$) of (Y$_{0.2}$Nd$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$/ (Y$_{0.2}$Nd$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_4$ (HE REB$_6$/HE REB$_4$-1) and (Y$_{0.2}$Nd$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_6$/(Y$_{0.2}$Nd$_{0.2}$Sm$_{0.2}$Er$_{0.2}$Yb$_{0.2}$)B$_4$ (HE REB$_6$/HE REB$_4$-2) are $-53.3$ dB (at 1.7 mm), 4.2 GHz (at 1.5 mm), and $-43.5$ dB (1.3 mm), 4.2 GHz (1.5 mm), respectively. Through combining a second phase of high-performance rare-earth tetraborides (HE REB$_4$) with good electrical conductivity and magnetism, the dielectric loss capability was enhanced without sacrificing magnetic loss ability. As a result, HE REB$_6$/HE REB$_4$-1 and HE REB$_6$/HE REB$_4$-2 possess thin thickness, wide effective bandwidth, and strong absorbing capability in Fig. 5.6(c), which indicates good EM wave absorption performance.

HECs also find applications for EMI shielding, especially under oxidation, corrosion, abrasion, and high temperature circumstances. Zhang et al. [96] designed a high-entropy monoboride (Cr$_{0.2}$Mn$_{0.2}$Fe$_{0.2}$Co$_{0.2}$Mo$_{0.2}$)B and found that the combination of good phase stability, high electrical conductivity and unique mechanical properties rendered it possible as an EMI shielding material. Bulk HE (Cr$_{0.2}$Mn$_{0.2}$Fe$_{0.2}$Co$_{0.2}$Mo$_{0.2}$)B with 3.0 mm thickness exhibit good EMI shielding performance, which surpasses 20 dB (99% shielding) in the K-band. The EMI shielding mechanism (Cr$_{0.2}$Mn$_{0.2}$Fe$_{0.2}$Co$_{0.2}$Mo$_{0.2}$)B is reflection-dominated.
due to its high electrical conductivity.

5.6 Rechargeable (Li and non-Li ion) batteries

The superionic conductivity observed in rock-salt structured (MgCoNiCuZn)O stimulated investigations on the use of HECs in Li-ion batteries [66,235,236]. As an anode material, (MgCoNiCuZn)O delivers a high capacity retention and good cycling stability. The high cycling stability is due to the ability to preserve the rock-salt structure throughout the entire redox process because of the entropy stabilization. Further introducing Li and F element to (MgCoNiCuZn)O, it can be utilized as a cathode material [237]. Element F in Li,(MgCoNiCuZn)OF can play a role in suppressing the oxygen loss during charging and discharging, which can increase the cycling stability of the material. Similar to (MgCoNiCuZn)O, Li,(MgCoNiCuZn)OF also shows a rock-salt structure, where Li and F distribute randomly on the cation and anion sublattice, respectively. Li,(MgCoNiCuZn)OF had a working potential of 3.4 V versus Li+/Li, exceeding that of (MgCoNiCuZn)O, i.e., ~1.0 V. The Li,(MgCoNiCuZn)OF also shows a high cycling stability with a stable columbic efficiency due to the entropy stabilization by reducing the performance degradation aroused from the oxygen release.

In addition to the rock-salt structured HECs, HECs in other systems have also been used in Li-ion batteries, such as spinel and perovskite. Wang et al. [238] fabricated spinel-structured (FeCoNiCrMn)₃O₄ through a high-temperature solid-state reaction method and applied it as anode for lithium-ion batteries. The (FeCoNiCrMn)₃O₄ calcined at 900 ºC exerted a high capacity (discharge/charge, 1034/680 mAh·g⁻¹) and good rate capability (182 mAh·g⁻¹ at 2 A·g⁻¹) with a commercial mass loading. The multiple metal elements
with mixed valence states and different cation radius in (FeCoNiCrMn)\textsubscript{3}O\textsubscript{4} resulted in optimized electron configurations, smooth ion diffusion paths, and abundant active storage sites, which leads to its excellent electrochemical performance. Recently, a class of high-entropy perovskite oxide (HEPO) [(Bi,Na)\textsubscript{1/5}(La,Li)\textsubscript{1/5}(Ce,K)\textsubscript{1/5}Ca\textsubscript{1/5}Sr\textsubscript{1/5}]TiO\textsubscript{3} synthesized by a conventional solid-state method has been explored as anode material for lithium-ion batteries [239]. An outstanding reversible capacity of 120.4 mAh·g\textsuperscript{−1} and superior delivering retention of 100% can be obtained at 1000 mA·g\textsuperscript{−1} after 300 cycles. Such an outstanding cycling stability can be ascribed to the entropy-stabilized structure. Overall, the HEC concept could pave the way to develop advanced anode, cathode, and electrolyte materials, which indicates the possibility of fabricating HEC-based Li and non-Li ion batteries.

5.7 Catalysts and water splitting

Catalysis is one of the most important and intricate processes used in the chemical industry. Finding novel catalysts with high activity and selectivity, good stability, long lifetime, as well as low cost, is the continuous pursuit of scientific researchers. In the hunt of catalysts, many problems are encountered, such as the high cost of precious metal catalytic materials, the light absorption and lifetime of semiconductor photocatalytic materials, the poisoning of catalytic active sites, etc. Nowadays, the development of high-entropy metals and ceramics seems to provide a good remedy. With the broken of solid solution limit, various atoms with distinct atomic sizes occupy the lattice sites and form simple solid solutions, resulting in a non-equilibrium state where atoms possess high potential energy. Thus, HEMs are much more active, and the catalysis process is thermodynamically easier to proceed because less energy is needed to activate the reaction (lower than the activation energy barrier $\Delta E$). From dynamics perspective, activity and selectivity can be enhanced by special chemical composition, severe lattice distortion which provides more active sites and intermediates, and sluggish diffusion that can contribute to high stability. Moreover, the cost can of course be controlled by element design, as shown in Fig. 5.7. In this part, HEA/HECs are reviewed according to their usage in specific catalytic reactions, such as ammonia and carbon monoxide oxidation, oxygen and hydrogen evolution, ammonia decomposition, water splitting, and dye degradation.

5.7.1 Water splitting

Photo/electrocatalytic water splitting to produce hydrogen and oxygen is a promising way to produce clean energy in the future. The essential idea of electrocatalysis is relatively simple, i.e., two-electrode systems are employed and the cathode part involves hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR) while the anode part proceeds with oxygen evolution reaction (OER) or oxidation of some chemical fuels. For example, in an alkaline solution, electrochemical oxygen evolution is of a 4-step process, which can be generally written as

$$M^* + OH^- \rightarrow MOH^* + e^- \quad (5.1)$$

$$MOH^* + OH^- \rightarrow MO^* + H_2O + e^- \quad (5.2)$$

$$MO^* + OH^- \rightarrow MOOH^* + e^- \quad (5.3)$$

$$MOOH^* + OH^- \rightarrow M^* + H_2O + O_2 \uparrow + e^- \quad (5.4)$$

where $*$ indicates the active sites for absorbing discharging species, which is OH$^-$ in this case while $M$ represents the metallic elements, such as Fe, Co, Ni, Cr, and Nb.

The main bottleneck of OER is sluggish kinetics due to the high over potential in the four-electron process. Highly dispersed active sites, large active surface area, severe lattice distortion, superb long-term durability, and fast dynamics of HEMs make them excellent OER catalysts. Ding et al. [240] fabricated a high-entropy intermetallic-oxide core−shell nanostructure by using a eutectic HEA FeCoNiCrNb\textsubscript{0.5} as a template. They found that the bulk porous intermetallic-oxide nanostructure shows outstanding OER activity with the
small Tafel slope (27.7 mV·dec⁻¹) reported so far, a much lower overpotential (0.288 V@10 mA·cm⁻²), and excellent durability for 30 h (Figs. 5.8(a) and 5.8(b)). They proposed and verified that the diversity of the valence states of the oxides/hydroxides in HEO layers provides tremendous intermediates (MOH*, MO*, and MOOH*) and hence active sites, which can easily bypass the kinetic barriers. Moreover, the design of intermetallic-oxide core–shell nanostructure in HEMs increases the active surface area and enhances the OER performance.

Aside from HEOs, spinel structured (Co₀₂Mn₀₂Ni₀₂Fe₀₂Zn₀₂) Fe₂O₄ and perovskite fluorides (HEPFs) K₀.₈Na₀.₂(MgMnFeCoNi)F₃ were prepared and acted as OER catalyst for O₂ evolution [241,242], outperforming the commercial materials IrO₂ and the typical perovskite oxide Ba₀.₅Sr₀.₅Co₀.₃Fe₀.₇O₃–d. The researchers found that the disordered occupation of multivalent cations generated severe lattice distortion and thereby facilitated the formation of structurally stable, high-density oxygen vacancies on the exposed surface, and low overpotential which provided numerous catalytic sites on the surface and enhanced the OER performance.

For hydrogen evolution, developing non-precious catalysts as Pt substitutes for electrochemical hydrogen evolution reaction (HER) with superior stability in acidic electrolyte is of critical importance. The elementary diversity and unique structure of HEAs helps to design catalytic materials with non or less precious metal input and superior stability. Combining the catalytic property of Co, Fe, Ni, and the corrosion-resistant ability of Cr and Al, CoCrFeNiAl HEA electrocatalyst was designed and prepared by mechanical alloying and SPS [243]. The abundant metal hydroxide/oxide groups formed after electrochemical activation on HEA and large electrochemical surface area (ECSA) benefiting from highly dispersed active sites and severe lattice distortion characters of HEMs, enabled the CoCrFeNiAl outstanding HER activity in 0.5 M H₂SO₄ solution with an overpotential of 73 mV at the current density of 10 mA·cm⁻² and a Tafel slope of 39.7 mV·dec⁻¹. Also, taking advantage of the stability of HEA, CoCrFeNiAl achieved improved performance after 4000 cycles.

Two-step thermochemical water splitting method is also used to generate hydrogen; the key is to reduce the reaction temperature. (MgCoNiFe)Oₓ (x ≈ 1.2) has been investigated to perform two-step thermochemical water splitting [244]. The H₂ yields of (MgCoNiFe)Oₓ is 1.4±0.5 mL·H₂·g⁻¹ at 1100 °C, whereas ceria and spinel ferrites require > 1300 °C to yield appreciable H₂ (Figs. 5.8(c) and 5.8(d)). Moreover, almost no performance degradation of (MgCoNiFe)Oₓ was found over 10 cycles, indicating that high mixing entropy prevents phase separation. The authors proposed that reducing particle size, adding redox-active species Fe and high melting point elements in HEOs is of great importance.

For photocatalysis, the limitation is the light absorption range and photo generated carrier lifetime. In HEMs, the energy band can be tailored by HE effects, leading to desirable light absorption. Moreover, the fast dynamic and lattice distortion can help separating photo generated carriers, thus enhancing the photocatalytic efficiency. However, currently there is no relevant research reported, which is one of the future directions.

5.7.2 Oxidation

The catalytic oxidation of methane, ammonia, and carbon monoxide compared with traditional flame combustion is capable of stabilizing complete oxidation of fuel at low temperatures, while simultaneously reducing emissions (for example, NOₓ). The search for high conversion rate, low cost, and good stability of catalytic materials has always been a hot research field. A research group led by Hu at the University of Maryland has designed a series of HEAs with five or more elements and investigated their possibility as the catalyst. For ammonia oxidation, HEA nanoparticles (PtPdRhRuCe) were prepared by a novel two-step carbon thermal shock (CTS) process [127]. The results show that 100% conversion of ammonia and > 99% product selectivity have been reached by PtPdRhRuCe nanoparticles with no performance decay over ~30 hours of continuous operation at 700 °C when using less precious metal and under lower reaction activation temperatures, as shown in Figs. 5.8(e) and 5.8(f), owing to the highly homogeneous and none phase separation or elemental segregation nature of HEMs. The ten-element HEAs they designed also showed excellent performance in the process of methanol catalytic oxidation [128]. Besides, (MgCoNiCuZn)O was used for CO oxidation in a fixed-bed reactor at different temperatures [63]. The entropy stabilized (MgCoNiCuZn)O can help disperse the active sites and improve thermal stability (900 °C), resulting in complete
conversion of CO achieved at 305 °C. Thus, highly homogeneous, phase stability, high temperature stability, randomly active site distribution, and low coat make HEMs promising candidates for catalytic oxidation, accompanied by the need for more in-depth mechanism exploration.

5.7.3 Decomposition

The degradation of pollution is of practical significance from the perspective of environmental protection and water-saving. Lv et al. [245] found that the AlCoCrTiZn powder shows excellent performance with dye degraded in 10 min. They proposed that the severe lattice distortion makes atoms possess high potential energy and are thus much more active than those in conventional alloys, leading to a low activation energy barrier, i.e., 30 kJ/mol. Moreover, selecting highly active elements can boost the catalytic properties. Large specific areas and abundant surface active sites of HEMs play an important role in the excellent dye decomposition behavior. For ammonia decomposition, Xie et al. [246] synthesized a serial of CoMoFeNiCu catalysts with robust control over the Co/Mo atomic ratio. They demonstrated that the formation of HEAs can break the miscibility limitation in bimetallic Co–Mo alloys and present good catalytic activity with the improvement factors exceeding 20 times as compared to precious metal Ru, and even more so versus conventional Co–Mo catalysts. This study proposed that well-mixed surface-active sites on the HEA catalysts, tailored surface absorption properties, controllable *NH*\textsubscript{3} binding strength, and phase stability of HEMs are the reasons for the excellent catalytic performance.

5.8 Thermoelectrics

In view of thermoelectricity, higher efficiency of direct-conversional heat and electricity energy is invariably being hunted by researchers. The efficiency is dominated by the dimensionless figure of merit, i.e., the $zT$ value of materials, which is expressed as

$$zT = \frac{\sigma S^2}{\kappa_L + \kappa_e} T$$

where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the absolute temperature, and $\kappa_L$ and $\kappa_e$ are lattice-induced and electron-induced thermal conductivity, respectively. High $\sigma S^2$ (i.e., power factor, PF) and low $\kappa$ (i.e., power factor, PF) and $\kappa_e$ are the key factors for improving $zT$, but unfortunately, carrier-concentration-associated coupling of $\sigma$, $S$, and $\kappa_e$ leads to difficulty of regulating every
single parameter independently. $\kappa_L$, which is induced by lattice vibration and quantified as phonon, is a relatively independent parameter and focused on as the main tactic for enhancing $zT$. However, scattering phonon generally declines transfer of conductive carrier and deteriorates the electronic transport properties, and thus high $\Delta S$ and low $\kappa$ are difficult to be satisfied simultaneously.

Recently, enhancing chaos intentionally, aka high configurational entropy (HCE) engineering [24–26, 209, 247, 248], is emerging as a new route to increase $zT$ in thermoelectric (TE) community. Compared with ordinary TE semiconductors, which have minor amount of element or doping dosage, at least 5 constituents with 5%–35% proportion should be included in high configurational TE materials for high $\Delta S$. HCE strategy exhibits nice pertinence to penetrate the stubborn problem of TE: tightly coupling correlation of $S$, $\sigma$, and $\kappa$. Thus, this section will sum up the validity of high-entropy engineering in improving TE behavior and put forward the prospect of HCE materials in the future.

Liu et al. [44] developed a predictive model of entropy-indicator for discovering possible multicomponent TE materials. Several combinations of materials, such as (Cu/Ag)(In/Ga)Te$_2$–, Cu$_2$(S/Se/Te)$_2$–, and (Mn/Ge/Sn/Pb)Te-based materials, were successfully predicted and experimentally evaluated. Continuous enhancement of configurational entropy, which is touched off by increased solute constituent, causes drastic phonon scattering, so that $\kappa_L$ is depressed to amorphous limit. Furthermore, increased configurational entropy induces higher and more obvious structural symmetry of crystals in intrinsically low symmetrical materials; such behavior increases the electronic density of state (DOS) and effective mass, as it increases the Seebeck coefficient. The reinforced Seebeck coefficient of Cu$_2$(S/Se/Te) (from 20–40 to 70–130 $\mu$V/K at room temperature) illustrates the connection of entropy-increasing and DOS-increasing. Besides, crystal-symmetry-induced reduction of phase transition temperature is observed in middle and low-entropy system. Another high-entropy-oriented model was illustrated by Zhang et al. [111], and traced down a high-entropy sulfide TE ceramic of Cu$_2$SnMgGeZnS$_6$. The single-phase was synthesized and showed clear metallic behavior with high carrier concentration, which caused poor Seebeck coefficient. By introducing extra Sn, the carrier concentration was reduced and Fermi level was dropped down, and thus PF was 800 mW/(m·K)$^2$ at 773 K, which is comparable with other CuS-based TE materials. Also, low thermal conductivity of ~1.03 W/(m·K) was achieved at 773 K due to intrinsically weak bonding of copper and sulfur, ultimately $zT$ of 0.58 was approached at 773 K. Effect of high-entropy seems negligible in CuS-based TE materials owing to essentially low thermal conductivity, especially in pure phase materials.

Roychowdhury et al. [249] synthesized a high-entropy selenide (GeSe)$_{0.5}$(AgBiSe)$_{0.5}$. The introduction of AgBiSe portion transferred GeSe from p-type to n-type and increased the carrier concentration to $3.29 \times 10^{18}$ cm$^{-3}$, which in one order of magnitude larger than that of pristine GeSe ($1.2 \times 10^{17}$ cm$^{-3}$), but the PF of 380 mW/(m·K)$^2$ still has space to be improved. Attributing to drastic scattering of phonons in high-entropy system, the $zT$ of 0.45 was obtained at 677 K.

Hu et al. [250] employed the multi-principal-element alloying (MPEA) with all-scale phonon-scattering to track higher $zT$ of SnTe-based TE material. MPEA is a lower configuration alloy with less component element, unequal molar compositions but the mix entropy is sufficiently high to acquire the core effects of HEMs [247, 250]. Firstly, pristine SnTe co-alloyed with Sn–Ge–Te–Mn subtly modified by MPEA, such tactic made the Seebeck coefficient and carrier concentration increased concurrently, which was attributed to the better band convergence and higher level of solid solution doping, respectively. Hence $zT$ value of 1.07 was achieved in (Sn$_{0.7}$Ge$_{0.3}$Pb$_{0.1}$)$_{0.5}$Mn$_{0.11}$Te, being much higher than that of pristine SnTe ($zT = 0.38$) at 900 K. Subsequently, all-scale phonon scattering was adopted for reducing thermal conductivity comprehensively by tuning the content of Mn. Benefiting from high-entropy effect, higher content of Mn in this matrix was occurred, which yields hierarchical precipitated phases as phonon scattering sources. Atomic-scale point defect and several micro-scale precipitated phases, i.e., GeTe, MnTe, and Ge, respectively, suppress short-wave and long-wave phonons, while local combination of line defect, strain clusters, and dislocation arrays contributing to hinder short-wave, and middle-wave phonons. At 900 K, the strong phonon rampart restrains the $\kappa_L$ to 0.32 W·m$^{-1}$·K$^{-1}$ (total $\kappa = \approx 1.1$ W·m$^{-1}$·K$^{-1}$) and higher $zT$ of 1.27 was achieved in (Sn$_{0.7}$Ge$_{0.3}$Pb$_{0.1}$)$_{0.75}$Mn$_{0.25}$Te. It is worth mentioning that the tangly line defect and strain clusters are firstly discovered in high-entropy TE materials, which is referential for future development. Finally, content of
Sn was finely tuned to improve over-high carrier concentration for more satisfied PF, eventually the optimized $zT$ of 1.42 was obtained in Sn$_{0.555}$Ge$_{0.15}$Pb$_{0.075}$Mn$_{0.023}$Te at 900 K.

Luo et al. [251] synthesized high-entropy SnSe-based materials to search for higher $zT$ values. AgSbSe$_2$ was adopted to introduce cation disorder for restricting $\kappa_L$ and inducing special multi-peak electrical valence band. And then additional Te atom was led in for extra cation and anion, as well as formation of compact dislocation arrays. Such scenario caused amorphous glass-like compact dislocation arrays. Such scenario caused amorphous glass-like $\kappa_L$ of $\approx 0.32$ W·m$^{-1}$·K$^{-1}$. Simultaneously, convergence of band was promoted in the highest entropy sample (AgSnSbSe$_1$$_{1.5}$Te$_{1.5}$), which represented the effect in enhancing electric behavior by entropy production. A peak $zT$ of 1.14 was achieved at 723 K and the average $zT$ of $\approx 1$ was comparable with other SnSe-based materials. Similarly, Tang et al. [252] intensified atomic disordering to restrain $\kappa_L$ of SnTe-based materials and combined MnTe for increasing the amount of transporting valence band to tune electrical performance. For Sn$_{1/3}$Pb$_{1/3}$Ge$_{1/3}$Te, monotonously decreasing of $\kappa_L$ (as low as 0.6 W·m$^{-1}$·K$^{-1}$) with the increasing of the disorder parameter $\Gamma_{\text{total}}$, which expressed the increased entropy restrained phonon transfer, was observed. Additional introduction of suitable MnTe caused the rise of DOS near Fermi level, which indicated a maximized degeneracy of effective valence band due to the maximum of effective mass, hence ameliorating the transport properties. Besides, Mn ion reinforced point scattering for short-wave phonons, further reducing $\kappa_L$, and finally, $zT$ of $\approx 1.8$ was approached at 850 K.

From the route of enhancing transport properties, carrier behavior could be manipulated by artful doping. Qiu et al. [253] reduced phase transition temperature of GeTe-based material by employing a multi-doping method. Just like other HEMs, hierarchical-scale phonon scattering let $\kappa_L$ go down to 0.4 W·m$^{-1}$·K$^{-1}$ and markedly improved $zT$ from 0.03 for pristine GeTe to 0.5 for Ge$_{0.84}$In$_{0.16}$Pb$_{0.05}$Sb$_{0.05}$Te$_{0.97}$L$_{0.03}$ at RT (the latter also showed 2.1 of $zT$ at 800 K). Tang et al. [254] depicted another path of entropy engineering to manipulate TE behavior, wherein Li and Mn dual-doping were actualized in BiCuSeO system. The introduction of light Li increased carrier mobility dramatically via reduced carrier scattering (as high as 7.39 cm$^2$/(V·s)) for enhancing $\sigma$, while different low-spin states of Mn$^{2+}$ and Mn$^{4+}$ ions rise the spin entropy, making improvement of Seebeck coefficient, which exhibited a novel pathway to rise system entropy. Nano-precipitated phases of MnO and point defect from dual-doping make up the multi-scale phonon scattering sources and suppress $\kappa_L$ to 0.51 W·m$^{-1}$·K$^{-1}$, resulting in a $zT$ of 0.9 at 873 K in Bi$_{0.9}$Li$_{0.1}$Cu$_{0.9}$Mn$_{0.1}$SeO.

In summary, recent works unambiguously demonstrated the routes of enhancing the figure of merit, $zT = \frac{\sigma S^2}{\kappa_L + \kappa_e} T$; multi-element component drives short-range disorder, restrains transmission of heat-phonon due to grain and mass field fluctuation and hierarchical scattering, effectively decreasing $\kappa_L$, while shaping band convergence and increasing band effective mass to increase crystal structure symmetry for improving transport properties, liberating the freedom of regulating $\sigma$, $S$, and $\kappa_e$ to some extent.

In the case of regulating thermal conductivity, phonon scattering is augmented cogently, and the main reasons could be concluded as: (1) dense point defects are contained in multicomponent matrix, which induces fierce lattice distortion; (2) drastic fluctuation of mass and strain occurs due to coupling difference between solvent and solute atoms; (3) sluggish diffusion of atom conduces to hierarchical low-dimensional morphology, which contributes to all-scale phonon scattering. Such increasing $\Delta S$ strategy decreases $\kappa_L$ forcefully and suppresses it to the limitation of amorphous, which depicts a mouthwatering tactic in enhancing energy converting efficiency. In the case of regulating transport properties, multi-atom doping expands solubility and tends to form high-symmetry crystal structure, which causes band convergence and larger band effective mass for adjusting transport properties. Besides, special element doping induces artful reinforcement of PF, such as increased carrier mobility by light-element doping and enhanced Seebeck coefficient by spin-entropy. However, while effectively inhibiting the heat-carrier phonons, severely disordered atom distribution also affects carrier mobility, which results in unsatisfied PF for high $zT$ value. Thus, the degradation of carrier mobility should be compensated by excellent heat-barrier capacity and other electrical transport properties, which is still a need for exploring.

Figure 5.9 concludes the temperature-dependent $zT$ values of materials discussed in this section, illustrating that the ranking of properties is based on the matrix materials. It also implies that the enhancement of high
entropy is finite. Hence, despite high configurational entropy engineering directs the pathway of a new generation TE materials, such next generation TE material exhibits vast space for further improving its TE properties. Firstly, high-entropy produces insufficient benefit in those materials with intrinsically low $\kappa_L$ or high symmetry [44,250]. As a conventional 3-dimensional system, it should be generalized to lower-dimension directions for further breakthrough since the striking effect of low-dimensionality was attested in thermoelectricity [255]. Profiting from the relatively mature film/coating layer application of HEMs [25], it is a promising direction to start corresponding TE researches from the two-dimensional TE films, aiming for a more enhanced effect in combination of high entropy and low-dimensional confinement effect. Also, the concept of high entropy could be expanded from homogeneous distribution of microscopic phases to low-dimensional morphology of hierarchical phases, i.e., the nanoscale inclusion and precipitation, which compose the potential barrier/well for further regulation of carrier and phonon. Besides, the entire mechanism of high-entropy effect in thermoelectricity is still not clear; more relevant theories are urgently needed. At last, what kind of practical application can make the best use of such a material with other excellent properties in addition to TE property, is a meaningful question.

5.9 Supercapacitors

Supercapacitors, the largest electric double-layer capacitors in mass production in the world, are electric double-layer capacitors. According to the choice of electrodes, supercapacitors mainly include carbon-based supercapacitors, metal oxide supercapacitors, and polymer supercapacitors. Among them, carbon-based supercapacitors are now the most widely used. Their performance depends to a large extent on the properties of carbon materials, surface area, particle size distribution, electrical conductivity, electrochemical stability, and other properties of the electrode materials. By introducing HEMs into carbon-based electrode materials, it is possible to increase the active sites and active surface area, and improve electrochemical stability, thereby obtaining higher capacity and current density. FeNiCoMnMg HEA-NPs modified super aligned electrospun carbon nanofibers were prepared and characterized [256]. Taking advantage of the stable charge/discharge rate provided by HEA-NPs, the samples exhibited a high capacitance of 203 F·g$^{-1}$, a specific energy density of 21.7 Wh·kg$^{-1}$, and good stability after 2000 cycles, as shown in Fig. 5.10. Other than HEAs, high-entropy nitride (CrMoNbVZr)N was synthesized using a mechanochemical soft urea approach and investigated for use in supercapacitor applications [122]. (CrMoNbVZr)N exhibited specific capacitances of 78 F·g$^{-1}$, owing to the high surface area and unique chemical properties of HEMs. These findings give hints for the HEA, HECs, and related compounds as promising candidates for energy storage applications.

5.10 Microelectronics

With the miniaturization of microelectronics, novel materials are needed to prevent the formation of Cu$_3$Si at the interface between copper and silicon which increases resistance and reduces the efficiency of the devices. High-entropy nitrides are particularly promising as diffusion barriers for microelectronic devices. The severe lattice distortion and high packing density of HE nitrides caused by distinct atom radius will lead to sluggish diffusion and provide an ideal solution for preventing microelectronic devices’ interdiffusion. Currently, most high-entropy nitrides, like amorphous (AlMoNbSiTaTiZr)N [257], nanocrystalline (AlCrTaTiZr)N [258], and (CrHfTiVZr)N thin film [259] have been reported; even if the thickness of HE nitride film was very thin, only about 10 nm, they show good barrier performance. The performance of amorphous (AlMoNbSiTaTiZr)N film was evaluated by constructing a Cu/(AlMoNbSiTaTiZr)N/Si test structure, as shown in Fig. 5.11, and annealed at the
Fig. 5.10 Synthesis of HEA-NPs/ACNFs film and electrochemical characterization. Reproduced with permission from Ref. [256], © Elsevier B.V. 2020.

Fig. 5.11 Characterization of Cu/MHEAN/Si structure. AES depth profiles of (a) as-deposited, (b) 850 °C-annealed, (c) 900 °C-annealed. Transmission electron micrographs of Cu/MHEAN/Si (e) after 800 °C annealing and (f) after 850 °C annealing. Reproduced with permission from Ref. [257], © AIP Publishing 2008.

temperature range from 750 to 900 °C for 30 min. The results show that the amorphous structure of the as-deposited high-entropy nitride still remained and the current nitride can prevent the reaction between Cu and Si around 800 °C before its failure at 900 °C; even small copper diffusion occurred to a distance of 10 nm, as shown in Fig. 5.11(f). The high thermal stability of the amorphous structure was proposed to originate from the multielement effect first. This multielement mixture led to severe lattice distortion and reduced diffusion kinetics. Secondly, due to the size differences between the various kinds of atoms, a higher atomic packing density was expected, thereby less free volume making diffusion more difficult.
5. 11 Biocompatible coatings

Various materials have been explored for biomedical applications, e.g., orthopedy, dentistry, ophthalmology, pharmaceutical drugs, biopharmaceuticals, etc. At present, only 316L stainless steels, titanium, and cobalt-chromium alloys are considered as suitable biomaterials for dental and orthopedic implants. However, their biocompatibility, wear, and corrosion resistance are relatively low. As usual, good biocompatible coating must have the following characters: low elastic modulus, high chemical stability, good wear–corrosion resistance, low friction coefficient, biological compatibility, and good adhesion to the substrate. For HECs, especially high-entropy carbides and nitrides, solution strengthening and lattice distortion can significantly increase their strength, hardness, and other mechanical properties; sluggish diffusion effects endow them good wear–corrosion resistance and high chemical stability, which makes them promising as coating materials for biomedical implants. HE CaMgZnSrYb amorphous alloy [260] can withstand four weeks of animal tests, and new bone tissue formed around the femur, indicating that the HE CaMgZnSrYb can promote the proliferation and differentiation of rat osteoblasts, and accelerate the healing of bone tissue. Braic et al. [261] investigated the biomedical properties of HE (TiZrNbHfTa)N and (TiZrNbHfTa)C coatings. They reported that the HE carbide coating exhibited wear resistance and excellent biocompatibility when tested in simulated body fluids. Cell-viability tests proved that the osteoblast cells were adherent to the (TiZrNbHfTa)N and (TiZrNbHfTa)C coatings, and a very high ratio of live cells (in green) was observed on their surfaces after 72 h of incubation time, as shown in Fig. 5.12. Si-containing coatings can further improve cell attachment and viability, with (HfNbSiTiZr)C being the most biocompatible material until now [262].

6 Future directions

6. 1 Demand driven materials’ design

Knowledge based materials’ design has long been the objective of material research, especially after the announcement of Materials Genome Initiative (MGI) in 2011, which challenges the traditional “try and error” research schema towards a new paradigm that accelerate the discovery, design, and deployment of materials by synergistically combining experiment, theory, and computation in a tightly integrated, high-throughput manner [263]. Due to the increase of computational capability, the high-throughput and machine learning (ML) assisted approaches are playing increasing roles in the design of materials.

Since the advent of HEMs, including HEAs and HECs, efforts have been carried out to design new HEMs to meet the needs in different domains, e.g., energy, transportation, national defense, and aerospace, etc. The distinct multi-principal elements of HEMs in comparison with traditional materials make people believe that new physics and properties can be discovered in HEMs, e.g., overcoming the strength–ductility trade-off [11], colossal dielectric constant [20], lithium superionic conductivity [21], and amorphous-like thermal conductivity [19]. It is not only the high-entropy single phase state but also the medium-entropy state or multi-phase state can provide intriguing properties. Therefore, the development of HEMs is on its way to compositionally complex materials [26,264–267].

For the demand driven design of HEMs, two fundamental aspects need to be addressed, as shown in Fig. 6.1. One is predicting the formation ability of HEMs with respect to composition and processing; while the other is exploring the “composition–structure–property” relations, and developing property prediction
models. Computational modeling can employ density functional theory (DFT) based method, molecular dynamic (MD) simulations, Monte Carlo (MC) simulations, calculation of phase diagrams (CALPHAD), surrogate models from machine learning, simplified models based on physical assumptions, or other methods.

6. 2  Property prediction

6.2.1  Stability prediction

Very few theoretical investigations have been carried out to predict the formation ability of HECs or to evaluate the order–disorder transformation of HECs. Anand et al. [49] employed generic algorithm and MD simulations with traditional force fields to study order–disorder transformation of HECs in Mg–Co–Ni–Cu–Zn–O oxides, which explains well experimental results reported by Rost et al. [29]. A descriptor called entropy forming ability (EFA), which is based on variance of configurational dependent energies, was proposed by Sarker et al. [64] to predict the formation ability of high-entropy carbides. Kaufmann et al. [267] trained a random forest model (a type of ML model) to predict EFA of HE carbides, and checked the generality of the model with correctly predicted and synthesized Cr-containing HE carbides. Similar idea was also adopted by Pitiike et al. [106], who approximated configurational energies of HECs only by considering pairwise interactions, and analyzed the formation ability of rock-salt oxides by considering both the mean and the variance of configurational dependent energies. Similar descriptors as those of Sarker et al. [64] and Pitiike et al. [106] in combination with redox mechanism were also adopted by Lun et al. [67] to predict the formation ability of high-entropy battery cathodes. Zhang et al. [111] developed a data-driven model to choose elements that may exhibit high possibility to form high-entropy sulfides. In comparison to HECs, more studies on predicting the formation ability have been done in HEAs [166, 268–273]. These works provide guidelines to develop predictive models for HECs, for example, approximating configurational energies by only considering pairwise interactions. Though such simplification loses some accuracy, it greatly reduces the computational consumption that needs to explore the vast combination space of elements, which enables people to fast scanning on large compositional space.

6.2.2  Properties prediction

Theoretical investigations on HECs are in their infant stage, and only limited papers have been published [19,48,50–53,57,183,184,274,275]. Among HECs, Mg–Co–Ni–Cu–Zn–O HEOs family is the most theoretically studied. Rák et al. [48,53] evaluated the charge compensation mechanism in three Mg–Co–Ni–Cu–Zn–X–O oxides and Jahn–Teller distortions related to Cu cations in (Mg<sub>0.2</sub>Co<sub>0.2</sub>Ni<sub>0.2</sub>Cu<sub>0.2</sub>Zn<sub>0.2</sub>)O by DFT calculations with special quasi-random structures (SQS) to model the random occupation of cations. Their results are highly consistent with experimental measurements [29,46,47], which provides atomic scale understanding.
of Mg–Co–Ni–Cu–Zn–O oxides. Braun et al. [19] examined the amorphous-like thermal conductivities of Mg–Co–Ni–Cu–Zn–X–O family oxides with virtual crystal approximation (VCA) and MD simulations, which reveals the importance of charge non-uniformity (more strictly, chemical bonding distortion or atomic force disorder) in reducing the thermal conductivity to an extra-low regime. Their findings were further confirmed by Lim et al. [183], who checked the effects of mass and atomic force disorder on thermal conductivity in Mg–Co–Ni–Cu–Zn–X–O oxides by MD simulations. Chen et al. [274] revealed that substitutions of Li or Mn into (Mg0.2Co0.2Ni0.2Cu0.2Zn0.2)O will reduce the compressibility due to the weaker ionic bonding by MD relaxations. In comparison to HEAs, charge compensation between cations, anions, and vacancies and chemical environment selectivity introduce more freedom of local distortions for HECs, which may offer higher probability to discover intriguing physics and properties.

The other set of HECs that has been studied theoretically is high-entropy UHTCs, e.g., carbides and diborides [50–52,57,104,275]. With SQS and DFT calculations, the electronic structures and mechanical properties of (Ta0.2Nb0.2Hf0.2Ti0.2Zr0.2)C and (Hf0.2Zr0.2Ta0.2M0.2Ti0.2)B2 (M = Nb, Mo, Cr) were studied by Wang et al. [57] and Yang et al. [275], respectively. However, the real compositions in their calculations deviate from the proposed mole ratio of cations due to the limited supercell sizes, even though the deviation may not cause significant changes in the properties. In modeling HEMs, the most fundamental complexity faced with is the chemical complexity due to their multi-principal elements in nature. A sufficient large supercell is necessary to characterize the random occupation state of different elements, which is usually beyond the computational limit of DFT based method. By introducing machine learning potentials to bridge DFT calculations and MD simulations, Dai et al. [50,52] predicted lattice distortions and temperature dependent elastic and thermal properties of (Ti0.2Zr0.2Hf0.2Nb0.2Ta0.2)C and (Ti0.2Zr0.2Hf0.2Nb0.2Ta0.2)B2, where the room temperature results agree well with experimental measurements. This new paradigm enables high accurate and high efficient atomistic simulations in systems with high chemical and structural complexities, e.g., HEMs, surface or interfaces. It is hopeful that deep insight into HECs will come forth in further with such powerful methods.

Up to now, most theoretical investigations focus on DFT calculations and MD simulations, and empirical property prediction models derived based on physical assumptions or trained from data with machine learning methods have rarely been proposed for HECs. Though DFT calculations and MD simulations can provide in depth understanding of “composition–structure–property” relations of HECs, empirical models are still essential for property tailoring and material design due to their ability of fast scanning on large compositional and structural space. In principle, the fast scanning ability is quite important because of the huge compositional space of HEMs.

6.3 Innovative and green processing

Up to now, methods used to make HECs are limited, which will hinder the practical applications and further development of this new family of materials. Currently, the most widely used methods for preparing bulk HECs are SPS and HP, and it is challenging to scale up the sample size for testing and practical applications. Due to limited sample size, hardness, Young’s modulus, and thermal conductivity are frequently reported. However, only very limited data are available on room and elevated temperature strength and fracture toughness of HECs [170]. Besides improving the SPS and HP processes, densification methods like pressureless sintering and reactive sintering are useful to scale up the sample size. As we have mentioned in Section 3, pressureless sintering has successfully been used to fabricate transparent (La0.2Y0.395Gd0.2Yb0.005)3O12 [40] and reactive sintering has been used to prepare bulk (Ca,Sr,Ba)ZrO3 [45], suggesting that these methods are applicable to other systems. Especially, most current ceramic processing techniques comprise powder processing, milling, forming, and sintering; integrating these steps into a forming-reactive sintering process is energy-saving and more efforts need to be devoted in this direction.

Aside from dense bulk, porous and fibrous HECs play pivotal roles in ultrahigh-temperature thermal protection and thermal insulation. Highly porous high-entropy (Zr0.2Hf0.2Ti0.2Nb0.2Ta0.2)C [22], (Zr0.2Hf0.2Ta0.2Nb0.2)B2 [40], and (Y0.2Yb0.8Sm0.2Nd0.2Eu0.2)B6 [98] have already been prepared by the in situ reaction/partial sintering process. Since the process uses carbothermal, borothermal, or boro/carbothermal reduction released gases to produce porous high-entropy carbide and boride ceramics, it has the

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advantages of low-cost starting materials, low synthesizing temperatures, and no need of pore forming agents and sintering additives, and partial sintering can be completed immediately after synthesis. It is expected that this process can be applied to prepare other porous HECs. Up to now, there have been no reports concerning the fabrication of HECs fibers. Since HECs exhibit good high-temperature strength [170,171], excellent creep resistance [172], good thermal/environmental stability, and low thermal conductivity [23,37,71,88–93], it is expected that HECs fibers will have better high-temperature strength, good stability, and low thermal conductivity. In light of this, more efforts should be devoted to this direction. For example, electrospinning of HECs precursor followed by calcining is an efficient and simple way to fabricate fibrous HECs for thermal insulating application [276]. In addition, template method which is usually employed to prepare polymer and ceramic nanowires with various microstructure also has the potential for HE nanowires, and owns the advantages of highly structure controllable, high yield, and less energy input.

Flash sintering, which is characterized by low furnace temperature and ultrafast synthesis, has been used to fabricate HECs powders and dense HECs bulk [123–126]. In addition, solid-state reaction and densification can be integrated into one cycle so that it is an energy-saving process. It is expected that this process can be used in other systems during the hunt for new HECs. Besides flash sintering, other field assisted process such as microwave sintering is also promising as a fast and green processing method since the electromagnetic properties of HECs are tunable, which allows the rapid synthesis and densification of HECs.

For HECs powders, which can be used as initial material for fabrication of bulk HECs or as electromagnetic wave absorbing materials, photocatalysts, battery materials, etc., wet chemical methods are highly recommended due to the fact that multi-components can be homogeneously mixed at the molecular level and synthesis reaction can be conducted at low temperatures. Although wet chemical methods have been used to synthesize high-entropy oxides [31,60, 87,115,119], carbides [121], and nitrides [122], more efforts need to be devoted especially for the synthesis of nanometer-sized HECs powders. Thus, in addition to hydrothermal, co-precipitation, sol–gel, and other methods, we propose that microemulsion method with the advantage of low-cost and controllable size, electrolysis for high purity nanoparticles, reaction ball milling, high-temperature combustion method with high efficiency, and rotating-electrodeposition [277] may also be used to prepare HEMs.

In above content, we have proposed existing and possible methods for preparing HE particles and bulks. However, microstructure, surface modification, and interface construction that of great importance for reaching high performance are barely reported. Fabricating HEMs with various micro-nanostructure, like core–shell and York-shell nanoparticles, hollow fibers, and aligned wires is one of the future directions. Core–shell HEA particles, composed of coarse-grained (CG) core and ultrafine-grained (UFG) shell, have been prepared via a controlled mechanical milling and subsequent SPS process [278]. The adjustable core–shell ratio has great influence on the mechanical properties. Besides physical methods, in order to realize the structural design, one can also learn from the aforementioned wet chemical methods. For example, HEA oxides @ HEA core–shell nanoparticles were synthesized by a facile and rapid electrochemical process and show enhanced OER activities [279]. Thus, microstructure design based on HEMs can promote the development of mechanics, electrochemistry, energy, catalysis, and other fields, which needs more investment and efforts.

From the preparation of functional unit like particles and films to microstructure design, then the next steps will come to the manufacture of devices for microelectronic, catalysis, energy power, drug, or gene delivery, etc. The FePt alloy nanopropeller device has been prepared by electron beam evaporation on silica and titanium layers. This nanopropeller could be accurately steered toward specific cells, where transfection and gene delivery are achieved, indicating broad application prospects in the biomedical field, and it is also very instructive for HEM biodevices [280]. Direct writing technology can precisely manipulate a single micro-nanowire, of course high-entropy fibers, and prepare highly ordered inorganic micro-nanowires on a rigid substrate and a flexible substrate efficiently which is a convenient method to make optoelectronic devices [281]. The spin-coated HE precursor combined with subsequent heat treatment can produce multilayer film devices, such as SOFC. Although it is not easy, the preparation of devices is inevitable for further performance improvement and application development.
6.4 Novel characterization methods

The fascinating properties of HECs are dictated by their microstructures and compositional elements. The large structural and compositional complexity of HECs provide great possibility for engineering their properties; however, design and preparation of HECs with desired properties still hinge on the clearly understanding of the composition–structure–property relationships at microscale and nanoscale. In this part, we focus on the advanced methods for the characterization of the phase composition, elemental distribution, lattice distortion, and valence state of the elements in HECs.

6.4.1 Phase composition and elemental distribution

As is known, an ideal HEC should exhibit a long-range ordered and periodic lattice structure but with compositional disorder. Therefore, single phase composition and homogeneous elemental distribution are two main structural features of HECs, which are commonly characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) equipped in scanning electron microscope (SEM), respectively. Another widely used method to verify the single-phase composition of HECs is through analyzing the selected-area electron diffraction (SAED) pattern obtained in transmission electron microscopy (TEM) or the fast Fourier transformations (FFTs) of high-resolution TEM (HRTEM) image. Jin et al. [122] used HRTEM image and its corresponding FFTs to show the single-phase structure and nanocrystalline grains of a high-entropy metal nitride ceramic. By using similar methods, Sarkar et al. [31] illustrated the perfect crystalline and single orthorhombic perovskite structure of (Gd$_{0.2}$La$_{0.2}$Nd$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)(Co$_{0.2}$Cr$_{0.2}$Fe$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$)O$_3$.

Compared to SEM–EDS, scanning TEM (STEM) is one of the state-of-the-art techniques to probe into the elemental distribution of HEMs at atomic scale. Through analyzing the contrast in the atomic-resolution high angle annular dark field (HAADF) image obtained in STEM, Sarkar et al. [31] showed the homogeneity of the elemental distribution at nanoscale in a high-entropy perovskite oxide. For comparison, STEM–EDS is a more thorough method to character the elemental distribution of HEMs. For example, Rost et al. [29] used STEM–EDS mapping to show the atomic-scale distribution of the Mg, Co, Ni, Cu, Zn in (Mg$_{0.2}$Ni$_{0.2}$Co$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$)O thin film (Fig. 6.2(a)), revealing the chemical and structural homogeneity of (Mg$_{0.2}$Ni$_{0.2}$Co$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$)O. Ding et al. [39] also used this method to investigate the atomic-scale elemental distribution in a CrFeCoNiPd alloy (Fig. 6.2(b)), combined with correlated analysis, they found the existence of short-range ordering nanoscale clusters and revealed their important role in improving the yield strength, strain hardening, and tensile ductility.

Electron energy loss spectrometry (EELS) is also a robust method to characterize the elemental distribution in HECs. Sharma et al. [117] illustrated the atomic-scale homogeneous distribution of Cr, Mn, Fe, Co, Ni in B-site position of a single crystal perovskite La(Cr$_{0.2}$Mn$_{0.2}$Fe$_{0.2}$Co$_{0.2}$Ni$_{0.2}$)O$_3$ thin film by using STEM–EELS. Besides, EELS is a complementary technique to EDS in the determination of low atomic number elements which are difficult to detect by conventional EDS method in HECs. Therefore, it can be used to detect the anion elements (such as B and C) or low atomic number cation elements (such as Li) in HECs.

Atom probe tomography (APT) is a method to characterize the elemental distribution of materials at atomic scale in three-dimension (3D). By using APT, Chellali et al. [282] confirmed the homogeneity of elemental distribution in 3D at atomic scale in three different HECs, including rocksalt (Co$_{0.2}$Cu$_{0.2}$Mg$_{0.2}$Ni$_{0.2}$Zn$_{0.2}$)O, fluorite (Ce$_{0.2}$La$_{0.2}$Pr$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)O$_{2–δ}$, and perovskite (Gd$_{0.2}$La$_{0.2}$Nd$_{0.2}$Sm$_{0.2}$Y$_{0.2}$)(Co$_{0.2}$Cr$_{0.2}$Fe$_{0.2}$Mn$_{0.2}$Ni$_{0.2}$)O$_3$ (Fig. 6.2(c)).

6.4.2 Lattice distortion

Besides phase composition and elemental distribution, lattice distortion is also an important atomic scale structural characteristic of HECs. As one of the four main characteristics of HEMs, lattice distortion is of great significance for the low thermal conductivity, enhanced mechanical properties, and high temperature stability of HECs. Through tuning the lattice distortion, the physical properties such as band gap and magnetic properties of HEC could also be tuned.

Currently, the lattice distortion of HECs is usually illustrated by analyzing the extended X-ray absorption fine structure (EXAFS). By using this method, Rost et al. [46] illustrated the existence of severe distortion around the Cu–O polyhedra in Mg$_{0.2}$Ni$_{0.2}$Co$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$O. After related density functional theory (DFT) calculations, they showed that the lattice distortion in Mg$_{0.2}$Ni$_{0.2}$Co$_{0.2}$Cu$_{0.2}$Zn$_{0.2}$O results from the disorder in the oxygen sublattice. Braun et al. [19] used the similar
method to show a large strain induced strong oxygen sublattice distortion in a class of six-cation HEOs (Figs. 6.3(a) and 6.3(b)).

Pair distribution function (PDF) is another indirect method to characterize the lattice distortion in HECs. By analyzing PDF result, Cheng et al. [283] found the slight deviation of bond angles from the ideal values in a fluorite \((\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2–\delta}\), showing the existence of lattice distortion in this HEO (Figs. 6.3(c) and 6.3(d)). They then used a combination of in situ synchrotron radiation X-ray diffraction, Raman spectroscopy, and ultraviolet–visible absorption spectroscopy to illustrate a pressure-induced reversible tuning of lattice distortion and band gap, showing interesting tunable properties of \((\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2–\delta}\) by applying different pressure.

Besides the above-mentioned indirect methods, annular bright field (ABF) imaging in aberration-corrected STEM provides a direct way to observe the lattice distortion in real-space but is rarely applied in the investigation of the lattice distortion of HECs. By using STEM–ABF, both heavy and light atoms can be imaged at the same time. Therefore, the combination of HAADF and ABF techniques is appropriate to visualize the lattice distortion in oxides. For example, Aso et al. [284] observed the oxygen octahedra distorting at the interface between \(\text{SrRuO}_3\) and \(\text{GdScO}_3\) at atomic level, underlying the important role of lattice distortion in the connection between \(\text{SrRuO}_3\) and \(\text{GdScO}_3\) heterointerface.

With the development of state-of-the-art TEM techniques, such as aberration-corrected STEM (AC-STEM), high-speed pixelated electron detector, and monochromated EELS, the direct observation of more detailed structural characteristics of materials is becoming reality. For example, Gao et al. [285] directly observed the local charge density distribution at the \(\text{SrTiO}_3/\text{BiFeO}_3\) interface with sub-ångström resolution by using AC-STEM equipped with an angle-resolved pixelated fast-electron detector, which presents a new way to characterize the local bonding in heterogeneous materials. More recently, Yan et al. [286] reported a direct way to image local phonon spectral density near a single (111) stacking faults in cubic SiC by using atomic resolution and angle-resolved EELS.

Such attractive STEM techniques could also be further applied in the investigation of structural characteristics of HECs. The direct observation of lattice distortion...
distortion, charge distribution, and local phonon spectral density in HECs would provide new perspectives to understand the composition–structure–property relationships at the atomic scale.

6.5 Tuning properties for prospective applications

In Section 5, we have introduced prospective applications of HECs covered from ultrahigh-temperature thermal protection and thermal insulation to catalysts, batteries, and electromagnetic wave absorption. In fact, balanced properties are often required for many applications such that methods for tuning properties through multiphase compositions and microstructure control are awaited.

To demonstrate the importance of multiphase design, two examples are given here. In the first example [179], dual-phase ultrahigh-temperature ceramics consisting of a hexagonal high-entropy boride (HEB) phase and a...
cubic high-entropy carbide (HEC) phase were fabricated through SPS. Both the density and hardness are found to be higher than the single phase samples, indicating better properties than the single phase solid solutions. In the second example [234], high entropy hexaborides/tetraborides (HE REB/HE REB₄) composites with synergistic dielectric and magnetic losses were designed and successfully synthesized through a one-step boron carbide reduction method. (Y₀.₂Nd₀.₄Sm₀.₄Eu₀.₂Er₀.₂)B₆/(Y₀.₂Nd₀.₄Sm₀.₄Eu₀.₂Er₀.₂)B₄ (HE REB/HE REB₄-1) and (Y₀.₂Nd₀.₄Sm₀.₄Er₀.₂Yb₀.₂)B₆/(Y₀.₂Nd₀.₄Sm₀.₄Er₀.₂Yb₀.₂)B₄ (HE REB/HE REB₄-2) exhibit excellent EM wave absorption properties. The optimal minimum reflection loss (RL_{min}) and effective absorption bandwidth (E_{AB}) of HE REB/HE REB₄-1 and HE REB/HE REB₄-2 are −53.3 dB (at 1.7 mm), 4.2 GHz (at 1.5 mm) and −43.5 dB (1.3 mm), 4.2 GHz (1.5 mm), respectively. The authors found that combination of conducting HE REB₄ with magnetism into HE REB₆ as a second phase enhances dielectric and magnetic losses, which lead to enhanced EM wave absorption performance [234]. These results imply that multiphase compositional design is important for tuning the properties of HECs.

For structural applications, low fracture toughness and damage tolerance are the main limitations that must be overcome. Although the available data are very limited, recent work by Sun et al. [176] indicates that high-entropy bixbyite-structured oxides RE₂O₃ (RE = Sm, Eu, Er, Lu, Y, and Yb) are more brittle than the single component Y₂O₃, which needs further attention in the development of HECs. Actually, considering the enhanced hardness and strength instead of fracture toughness, high-entropy carbide (HfZrTiTaNb)C is also brittle albeit its strength can be maintained up to 1800 °C [170]. Thus improving the fracture toughness is the bottleneck that needs to make a breakthrough.

Thermal shock resistance is also a concern for high-temperature applications. Qiu et al. [45] revealed that (Ca,Sr,Ba)ZrO₃ solid solution possesses good corrosion resistance to TiNi alloy melt and is promising for application as a novel crucible material for the vacuum melting of titanium alloys. However, the observed glass-like low thermal conductivity may lead to exacerbated thermal shock resistance, which needs to pay attention. And more works are needed to balance the properties.

As EBC materials for CMCs, decomposition of rare earth disilicate into monosilicate during air plasma spray and mismatch of thermal expansion coefficient are the main reasons for the cracking of the coatings [287]. High-entropy rare earth silicates have been proven to have good thermal stability without phase transformation [88,89]; however, if decomposition can be restricted during air plasma spray needs to be tested. On the other hand, the tunable thermal expansion coefficient has been recognized as one of the main characteristics of HECs [167]. However, strong anisotropy in high-entropy rare earth monosilicate may induce cracking in coating; thus more efforts need to be devoted to either reduce the anisotropy in thermal expansion coefficient or develop a novel method to precisely control the preferred orientation of the rare earth silicate coatings [85].

Generally, the resistance of high-temperature oxidation depends on the formation of dense and protective scales like Al₂O₃ and SiO₂ [288,289]. However, the presence of multicomponents in HECs may lead to the formation of ternary or quaternary compounds instead of protective scales during high-temperature oxidation from the view point of thermodynamic analysis. In addition, preferential oxidation could result in possible destabilization of the solid solutions or formation of other competing phases [194,195,290]. To tackle this problem, careful composition design needs to be conducted to ensure good oxidation resistance of HECs. One good example is that high-entropy nitride films containing Al, Si, and Cr have both high hardness and strength, and the effect of these elements on the oxidation resistance of carbides and borides need to be investigated, which is expected as an important direction for developing oxidation resistant HECs for high and ultrahigh temperature applications.

We must acknowledge that searching for appropriate compositions is an arduous task using the traditional “try and error” research schema because the composition space is huge. Although many properties are unexpected and unpredictable as a result of cocktail effect, a combination of theoretical prediction and experiments is highly recommended.

7 Conclusions

In summary, this article has reviewed recent progress on HECs. We have summarized the structural characteristics, the current explored material systems, www.springer.com/journal/40145
and theoretical approaches for stability and property predictions, followed by processing methods for powders, dense and porous bulks, thin films, and coatings. Then the structural and functional properties and HECs have been reviewed and prospective applications are proposed. Finally, challenges and future directions are emphasized from aspects of theoretical prediction, micro and nanoscale structure characterization, processing and properties tuning for applications. Distinct from metals, the diversity of crystal structure and electronic structure of ceramics allows properties tuning through both band gap engineering and phonon engineering using the HEMs design paradigm. As such, aside from enhanced hardness, strength, and low thermal conductivity that have been observed in HEAs, the new compositional design paradigm has brought new phenomena that have not been observed in HEAs, such as colossal dielectric constant, super ionic conductivity, strong anisotropic thermal expansion coefficient, etc. The fascinating properties of HECs make them promising for applications as ultrahigh-temperature thermal protection and insulating materials, thermal barrier and environmental barrier coatings for superalloys and CMCs, precise and high speed cutting tool materials and wear resistant parts in harsh environments, irradiation resistant materials for nuclear reactors, electromagnetic wave absorption and electromagnetic interference shielding materials, anode materials for Li and non-Li batteries, catalytic materials for clean energy and environment, thermoelectric materials, supercapacitor materials, molten salt resistant crucibles, etc. However, due to the small sample size, the data on fracture toughness, room and high temperature strength, fatigue and creep resistance are very limited. To scale up the sample size, novel and energy saving single-cycle processing routes like reactive pressureless sintering, field assisted sintering and novel forming methods should be developed. In addition, new single phase and multiphase HECs need to be explored. And more efforts should be devoted to fundamental understanding, theoretical prediction, and database establishment.

Author contributions

This article is a result of group effort. Huimin Xiang wrote Sections 3.2.3, 5.7, 5.9, 5.10, 5.11, and 6.3, and she also designed and plotted Figs. 3.1, 3.2(a), 5.1, 5.2, 5.4, and 5.7; Fu-zhi Dai wrote Sections 6.1 and 6.2; Hongjie Wang wrote Sections 5.1 and 5.2; Lei Su wrote Section 6.4; Lei Miaow wrote Section 5.8; Guojun Zhang wrote Sections 4.6 and 5.4; Yiguang Wang wrote Section 4.5; Xiwei Qi wrote Sections 4.8 and 4.9; Lei Yao wrote Sections 4.7 and 5.6; Yanchun Zhou designed the whole structure of the paper and wrote the Abstract, Sections 1, 3.1, 3.2.1, 3.2.2, 4.2, 5.3, 5.5, 6.4, and 7, and he also rewrote and reorganized the whole paper and made the final check.

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