Chapter 1

Introduction

Rapidly evolving technologies have posed a significant challenge in developing innovative, technologically advanced materials with tailored functional properties. One such frontier is the realm of high entropy materials (HEMs), a class of materials that challenges traditional notions of simplicity in chemical composition. Unlike conventional binary or ternary oxides, HEMs introduced a paradigm shift by incorporating multiple elements in nearly equal proportions. This departure from conventional compositional simplicity opens up a rich and relatively unexplored terrain, promising a plethora of unique functional properties such as electrical [1,2], electrochemical [3–5] and catalytic [6–9]. **Figure 1.1** depicts the projected area of application of HEMs. The traditional approach for developing materials has been to add a limited quantity of elements or compounds as alloying or dopant into a base material or to mix component materials to form a composite. Traditionally, enthalpy has been the main thermodynamic knob utilized for material design, while the entropy term was not much explored. However, in 2004, Cantor et al. [10] and Yeh et al. [11] independently introduced a novel alloying strategy that emphasized single-phase solid solution alloys composed of four or more principal elements in near-equimolar ratios with the aim of investigating an unexplored central region of the multicomponent phase diagram. Yeh et al. [11] showed that increasing configurational entropy of mixing (ΔS_{mix}) by incorporating multiple elements in near-equiatomic proportions promotes the formation of a lesser number of phases than predicted by the Gibbs phase rule and even formed single-phase solid solutions in some cases and coined the term “high entropy alloys” (HEAs). While entropy was historically undervalued in material design compared to enthalpy, the concept of HEA [12,13] has demonstrated its importance. This unconventional approach of incorporating a large (five or more) number of constituent elements allowed researchers to explore the “unchartered central regions” of multicomponent phase diagrams, where unique properties can arise from synergistic interactions. Unlike conventional alloys [14,15], HEAs exhibit unique compositions, microstructures, and adaptable properties, garnering significant attention. In recent years, the scope of high-entropy materials (HEMs) has extended beyond metals to include oxides [16–18], borides [18], nitrides [19], carbides [18,20], and sulfides [21]. Although still a relatively new field, research on high-entropy oxides (HEOs) has rapidly expanded to encompass a wide range of crystal structures and compositions. Rost et al. [22]; in 2015, pioneered the idea of using the entropic contribution to the Gibbs free energy to stabilize new single-phase multicomponent oxide. Since then, several HEOs having diverse crystal structures, including rocksalt [16,17,23–25], spinel [26–31], fluorite [32–35], pyrochlore [36], and perovskite [37–44], have been reported.

Rost et al. [22] successfully synthesized a single-phase rocksalt solid solution ($Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$), integrating five distinct elements into the cation sub-lattice, creating the first-ever high-entropy oxide. While both HEAs and HEOs share the term “high entropy”, their fundamental characteristics differ significantly.

While HEAs rely on metallic bonding, HEOs, on the other hand, predominantly exhibit ionic bonding, which introduces unique challenges such as oxidation state and boding constraints for phase stability. This distinction makes the formation of single-phase solid solutions in HEOs remarkably unique, as phase separation is typically observed in heavily doped oxides. For example, systems like NiO-CuO and MgO-ZnO show limited miscibility, resulting in multiple phases when heavily doped. Still, HEOs such as ($Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$) don't follow this trend, achieving phase purity despite containing several immiscible pairs in near-equal proportions [45].

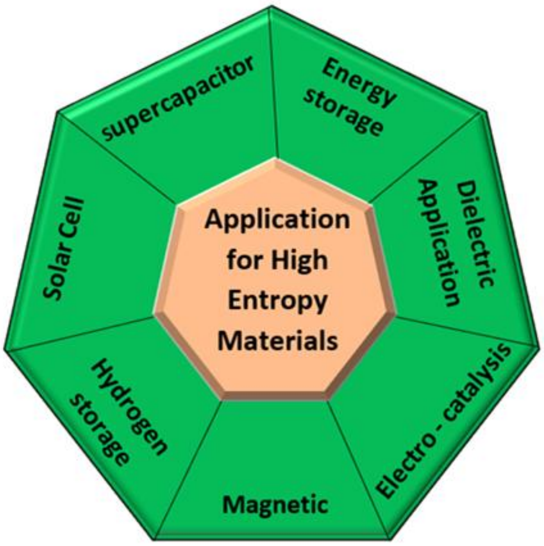

Figure 1.1 A schematic representation of various applications of high entropy oxides.

While high configurational entropy is primarily believed to be the reason for the single-phase formation, several other considerations, such as cation oxidation state and size, are also important [46]. For instance, some HEOs, such as ($Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$), are stabilized predominantly by configurational entropy, while others, such as $(Ce_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}Y_{0.2})O_{2-\delta}$, rely on the oxidation states of specific cations. These varied mechanisms highlight the complexity behind HEO phase stability[47].

1.1 Phase stabilization in HEOs

The configurational entropy of material systems is given by Boltzmann's formulation [46,48] which expresses entropy in terms of the possible number of different configurations:

$$S = k_b \, ln\omega \qquad (1)$$

where S is the entropy, k_b is Boltzmann's constant, and ω is the number of possible configurations for arrangement of elements. In material design, the stability of a solid solution is governed by the change in Gibbs free energy on mixing and given by:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (2)$$

Where ΔG_{mix}, ΔH_{mix}, ΔS_{mix}, and T stand for the free energy of mixing, enthalpy of mixing, entropy of mixing, and temperature, respectively. Increasing the number of components boosts configurational entropy and peaks when components are equimolar. **Figure 1.2** shows the configuration entropy as a function of number of components. Using Stirling's approximation $(\ln(n!) \approx n\ln n - n)$, the configurational entropy of a solution can be expressed as [45]:

$$\Delta S_{config.} = -\mathrm{R}\{(\textstyle\sum_{i=1}^{n} x_i \ln x_i)_{cation} + (\textstyle\sum_{i=1}^{n} y_i \ln y_i)_{anioin}\}. \qquad (3)$$

where R is the universal gas constant, while x_i and y_i represents the mole fraction of each cation and anion, respectively. In HEOs, multiple cations are incorporated; however, the anion remains a single species (i.e. oxygen); therefore, only cations contribute to the configurational entropy. A solid solution phase is stabilized when the configurational entropy and enthalpy of mixing combine to make ΔG_{mix} negative above a critical temperature. Below this temperature, phase separation or intermetallic compound formation may occur. From a thermodynamics point of view [12,45], three key scenarios are possible. In the ideal scenario (rare in reality), the ΔH_{mix} is zero, and the ΔG_{mix} is driven solely by entropy, with $\Delta G_{mix} = -T\Delta S_{mix}$ always negative. In enthalpy-driven stabilization, ΔH_{mix} is negative, which indicates the formation of a solid solution is preferred, making entropy (ΔS_{mix}) less significant. In the third case, which is also known as entropy-driven stabilization, ΔH_{mix} is positive, indicating constituent elements are reluctant to be directly coordinated with each other, and phase stabilization is governed by the $-T\Delta S_{mix}$ term, which should be such that it overcompensates positive ΔH_{mix} and make ΔG_{mix} negative or stabilizing the solution. While early studies on high-entropy alloys (HEAs) suggested that high configurational entropy favors single-phase solid solutions; however, some experiments reveal that entropy alone cannot override competing forces, such as enthalpy, in determining phase stability [49,50]. Temperature also plays a vital role in maintaining single-phase stability.

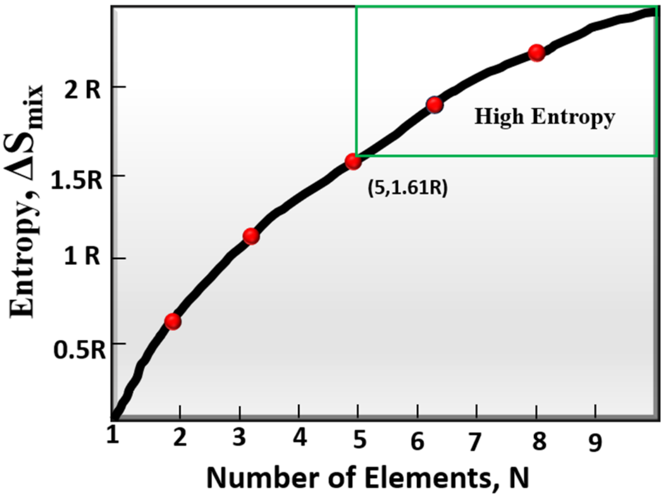

Figure 1.2 Relationship between configurational entropy of mixing (ΔS_{mix}) and the number of constituting elements.

Murty et al. [13,51] categorized HEMs by their magnitude of configurational entropy as

- High Entropy ($\Delta S_{config.} \geq 1.5$ R)
- Medium Entropy (1R $\leq \Delta S_{config.} \leq 1.5$ R)
- Low Entropy ($\Delta S_{config.} <$ 1 R)

This classification has been extended to oxide systems, providing a framework for understanding the diverse behavior of HEOs. Linus Pauling proposed five foundational rules for predicting the possible crystallographic structures of ionic compounds, which also apply to high entropy oxides (HEOs) [45,52]. These rules, ranked by their relative influence, are crucial for understanding the structure formation in HEOs:

1. Each cation is surrounded by a polyhedron of anions, forming a coordination number (CN) determined by the cation-to-anion radii ratio ($\frac{r_c}{r_a}$), as shown in **Table 1.1**. The equilibrium inter-ionic distance corresponds to the sum of their radii $(r_c + r_a)$. For instance, in $CaTiO_3$ perovskite, the Ca^{2+} ions have a CN of 12 ($\frac{r_{Ca}}{r_O} = 1$) forming an FCC sublattice, while Ti^{4+} ions have a CN of 6 (($\frac{r_{Ti}}{r_O} \geq 0.43$)

Table 1.1 Effect of cation and anion radius for specific coordination geometry and polyhedral type around the central atom.

$\left(r_{cation}/r_{anion}\right)$	**CN**	**Polyhedron**
1	12	Cuboctahedral
1-0.732	8	Cubic
0.732-0.414	6	Octahedral
0.414-0.225	4	Square planer
0.225-0.155	3	Triangular
0.155-0	2	Linear

2. There should be charge neutrality of the coordination polyhedral formed by cations and anions. Local charge neutrality is maintained when the total bond strength reaching a specific ion equals its valency. Bond strength is defined as the valency of an ion divided by its CN. For example, in CeO_2, which crystallizes as a fluorite structure, Ce^{4+} has a CN of 8, giving it a bond strength of 4/8=1/2. Consequently, each O^{2-} anion achieves a CN of 4, ensuring local charge neutrality.

3. The coordination polyhedra can share corners, edges, or faces depending upon the need to minimize cation-cation repulsion. Corner-sharing creates the least repulsion, making it the most favorable, followed by edge-sharing, and lastly, face-sharing.
4. Simple structures with fewer crystallographic sites are generally preferred over complex arrangements. In HEOs, this implies that cations with similar sizes and valencies are likely to be distributed randomly over a lattice site. Conversely, increasing dissimilarities among cations promote ordered arrangements and distinct coordination environments.

These rules serve as a foundation for understanding known ionic structures and predicting the features of unknown compositions. For HEOs, specific criteria extend beyond Pauling's rules to account for their unique characteristics. Earlier, it was believed that achieving a single-phase solution lies in maintaining an isovalent composition across the system. However, later studies revealed that the oxidation states of the initial components are not critical for single-phase formation. It was demonstrated that single-phase solid solutions could form in high-entropy oxides (HEOs) under both conditions [53]: (i) when the binary oxides of the components differ in the crystal structure, electronegativity, or cation coordination [53], and (ii) when the binary oxides exhibit limited mutual solubility. At elevated temperatures, equilibrium can be reached through oxygen vacancies, which are preserved upon quenching [2,54]. This discovery significantly broadens the compositional possibilities for HEOs. Aliovalent substitutions, where cations of different oxidation states are incorporated, not only expand the range of potential compositions [55,56] but also open pathways to tailor the properties and applications of these materials.

1.2 Crystal structures of HEO

Since the first report of HEO with rocksalt structure, several different HEOs having several different compositions and crystal structures have been reported [57]. **Figure 1.3** shows a schematic highlighting the timeline of the development of various HEO crystal structures.

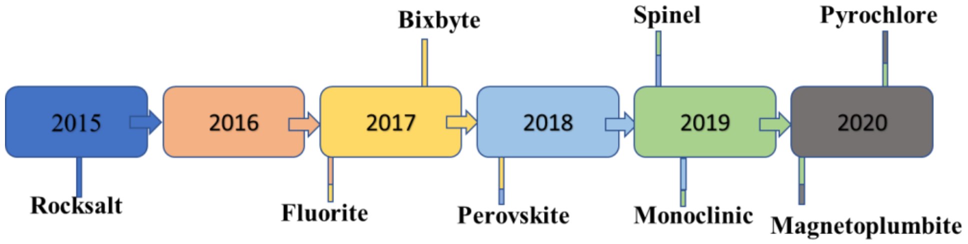

Figure 1.3 A flowchart showing the timeline of development of various crystal structures of high entropy oxides.

Rocksalt HEOs

Rost et al. [22] introduced single-phase ($Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$) HEO with a rocksalt structure in 2015. This structure exhibited a transition from multiphase (rocksalt, wurtzite, tenorite) to a stable single-phase rocksalt structure at elevated temperatures. The stability of this phase was attributed to configurational entropy, which promotes the formation of a homogeneous solid solution. The rocksalt crystal structure features anions forming a face-cantered cubic (FCC) lattice, with all octahedral sites fully occupied by cations. Both anions and cations exhibit a coordination number of 6. Common divalent mono-cationic oxides such as MgO, CoO, NiO, and CaO crystallize in this structure as the cation-to-anion radius ratio

(r_c/r_a) falls in the range of 0.414 - 0.732 [53]. Rocksalt HEOs are well-known for their excellent structural and electronic properties [58,59], making them highly suitable for catalytic[4,60] and electrochemical applications [24,61–63]. These materials are typically synthesized using solid-state reactions and sintering techniques. However, various other methods were also investigated for synthesizing rocksalt HEOs.

Spinel HEOs

In 2018, Dabrowa et al. [64] synthesized the first spinel-structured HEO $(CoCrFeMnNi)_3O_4$. Spinel HEOs are characterized by mixed oxidation states. These materials are particularly useful in applications such as magnetism and energy storage. Spinel-structured HEOs (S-HEO) having general formula $A_2B_2O_4$ in which A site is populated with divalent cations such as Mg, Co, Ni, Zn, etc, and B site with trivalent cations such as Fe, Cr, Al. For the formation of single phase S-HEOs, the temperature should be carefully controlled; otherwise, the spinel phase transforms into a rocksalt structure at higher temperatures (1373-1473 K) [23]. **Figure 1.4** shows various reported crystal structures of high entropy oxides. Ferritic S-HEO shows ferrimagnetic transition at high-temperature whereas chromium-based S-HEO shows low-temperature antiferromagnetic order, at the same time blocking temperature was noticed [29,57]. The presence of blocking temperature implies magnetic domains within the sample are limited and isolated. $(Co_{0.2}Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})_3O_4$, $(Co_{0.2}Mg_{0.2}Mn_{0.2}Cu_{0.2}Ni_{0.2})$ Fe_2O_4, $(Co_{0.2}Mg_{0.2}Fe_{0.2}Cu_{0.2}Ni_{0.2})$ Fe_2O_4 showed field cooled (FC) hysteresis [53,54,65].

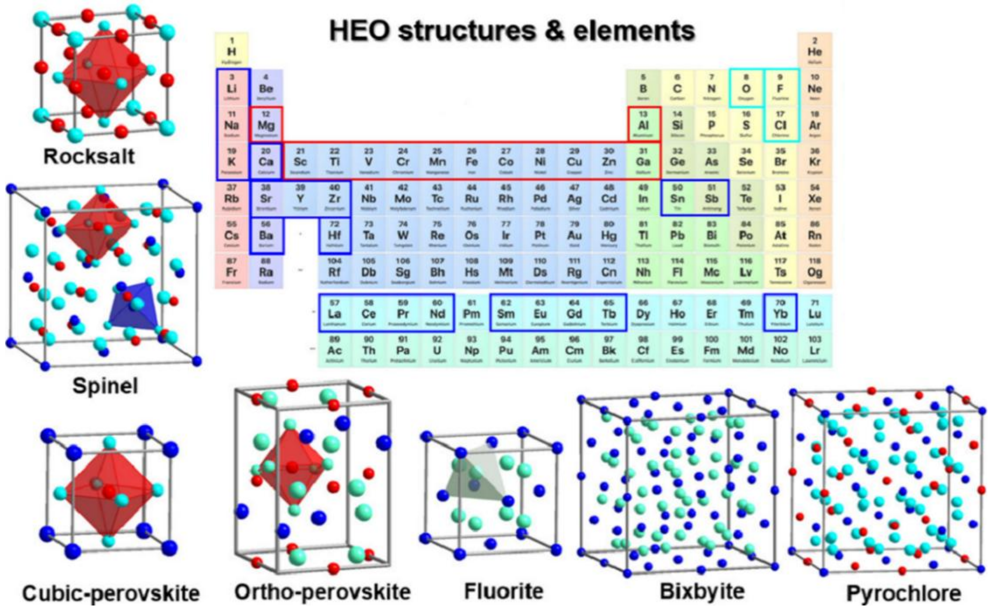

Figure 1.4 Various crystal structures of high entropy oxides [57].

Fluorite HEOs

In 2017, many researchers made an effort to widen the theoretical concept of entropy-driven stabilization to other oxide systems, such as rare earth (RE) and transition metal (TM) oxides with different crystal structures, including cubic fluorite structure [32–34,47]. In addition to the criteria for selecting elements discussed in the earlier section 1.2, some other parameters also become important for achieving phase pure fluorite structure. It is postulated that cerium (Ce) and zirconium (Zr) are crucial elements for any composition to crystallize as a single-phase fluorite structure. Rare-earth (RE) based systems without Ce or Zr have been shown to result in multiple phases, regardless of the number of incorporated elements or synthesis parameters [47]. It has been argued that 4+ oxidation state is thermodynamically feasible for both Ce, and Zr which makes it indispensable for high entropy fluorite phase formation in $(Ce_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}Y_{0.2})O_{2-\delta}$ and $(Zr_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}\ Y_{0.2})\ O_{2-\delta}$. However, a more detailed study is required to explore the stability mechanism in high entropy fluorite structure. Some general combination rules have been proposed for the formation of single-phase high entropy fluorite oxides. $(CeRE)O_{2-\delta}$ and $(HfZrCeM)O_{2-\delta}$ are the two most investigated combinations, where RE stands for rear earth elements such as La, Pr, Sm, Y, etc., and M stands for other metals, whereas δ depends on the valence state of cations [33]. In another general combination, $RE_2TM_2O_7$, single phase high entropy fluorite structure forms when the ratio of ionic radius of the RE cation to that of the TM cation is close to 1.46 [66]. High entropy fluorite structures such as $RE_2(Ce_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Ti_{0.2})O_7$ (RE= Y,Ho,Er,Yb) exhibit high thermal stability, tuneable thermal expansion coefficient, and low thermal conductivity, making it a potential candidate for thermal barrier coatings (TBC) [67].

Perovskite HEOs

HEOs with perovskite structures was first reported in 2018 [68]. Since then, perovskites have been one of the most extensively investigated HEO. These perovskites should have at least two cation sublattices in the form of ABO_3, where A and B display two different types of cation sites. Perovskite structure may exist in cubic, orthorhombic, or hexagonal crystal structures. The ABO_3-type perovskite structure is comprised of 6-fold coordinated B-type cations, 12-fold coordinated A-type cations, and an octahedral oxygen anion. Goldschmidt’s factor (discussed in later section) is important for the prediction of the stability of perovskite structure. However ionic radii and oxidation state are not only the deciding factor but the synergic effect of multiple cations might also have a strong impact on structural parameters and can lead to rather unusual phase compositions in HEOs. For instance $(Gd_{0.2}La_{0.2}Nd_{0.2}Sm_{0.2}Y_{0.2})MnO_3$ has a tolerance factor similar to NdMnO3 and SmMnO3, both of which crystallize into a single phase orthorhombic structure [69]. At ambient temperature, however, the HEO-$(Gd_{0.2}La_{0.2}Nd_{0.2}Sm_{0.2}Y_{0.2})MnO_3$ exhibits a dispersion of eight orthorhombic perovskite phases. These oxides are known for their diverse physical properties, including dielectric and ferroelectric behavior. The perovskite HEOs are utilized in dielectrics, sensors, and solid-state electrolytes [39,70]. These materials were mostly synthesized using wet-chemical routes and solid-state reactions; however, other methods were also investigated for the synthesis of high entropy perovskite oxides [39,53,54,71].

Magnetoplumbite HEOs

In 2019, Vinnik et al.[72] synthesized the first HEO with a magnetoplumbite structure, represented by $Ba(Fe_6Ti_{1.2}Co_{1.2}In_{1.2}Ga_{1.2}Cr_{1.2})O_{19}$. This structure displayed excellent magnetic properties and high thermal stability, making it a strong candidate for magnetic devices and electronic applications. The synthesis of magnetoplumbite-structured HEOs is achieved through high-temperature sintering methods

Monoclinic HEOs

Chen et al.[73] introduced, $(Yb_{0.25}Yi_{0.25}Lu_{0.25}\ Er_{0.25})_2SiO_5$ HEOs with monoclinic structures in 2020. These materials are notable for their exceptional optical properties, which make them suitable for applications in photonics and optical devices.

Pyrochlore HEOs

Researchers discovered HEOs with pyrochlore structures[36] in 2020, those oxides, with their distinctive $A_2B_2O_7$ structure, are a fascinating class of structural and functional ceramics. These materials consist of two types of cations which include A site cations, typically rare-earth (RE) elements with large atomic sizes, which are coordinated with two 8b and six 48f oxygen ions, while B site cations, which are smaller transition metals (TM), are surrounded by six 48f oxygen ions. A unique feature of pyrochlores is the presence of oxygen vacancies at the 8a site, surrounded by four B-type cations, which significantly influence their properties. The general formula for pyrochlore is given as $(RE)_2(TM)_2O_7$. Rare-earth zirconates ($RE_2Zr_2O_7$) a prominent subset of pyrochlores[56], have an ordered fluorite-like structure with two cationic sublattices. These zirconates are gaining attention as promising alternatives to yttria-stabilized zirconia for thermal barrier coatings (TBCs) due to their exceptional elastic modulus and low thermal conductivity.

1.3 Synthesis techniques

The growing interest in high-entropy oxides (HEOs) can be attributed to the ease and flexibility of their synthesis, supported by a variety of processing techniques. These methods allow for the synthesis of HEOs with diverse morphologies and microstructures. For instance, traditional solid-state synthesis methods are commonly used to produce microcrystalline HEOs. In contrast, techniques such as spray pyrolysis[57], solution combustion synthesis (SCS), and sonochemistry enable the production of nanocrystalline HEOs. Bulk HEO pellets with varying microstructural characteristics can be fabricated utilizing processes such as conventional sintering[74], spark plasma sintering [75], and flash sintering[76,77]. These methods allow for precise control over the material's densification and grain size, which in turn influences its structural and functional properties [57]. Epitaxial HEO thin films have also been deposited using Pulse laser deposition (PLD) [78] offering unique opportunities to explore their electrical properties.

1.4 Parameter affecting HEOs formation

In general, the same thermodynamic parameter that governs the phase stability of HEAs also governs HEOs. Here, based on studies that have been published so far, some general guidelines for selecting suitable elements for the formation of single-phase HEOs is discussed. **Figure 1.5** highlights the various factors for the formation of phase pure HEOs.

1.4.1 Enthalpy of mixing

For HEOs, the effect of enthalpy of mixing is relatively identical to that of HEAs, which are considered to be close to zero. The positive ΔH_{mix} of different-structured metal oxides may not be compensated by the high-entropy effect and requires a considerably higher temperature for phase transition and mixing. Whereas large negative ΔH_{mix} values for highly soluble metal oxides are not advantageous for the fabrication of entropy-driven phase stabilized oxides. Rost et el. successfully synthesized an HEO with a single-phase rocksalt crystal structure using the five components having different crystal structures of rocksalt (MgO, CoO, and NiO), tenorite (CuO), and wurtzite (ZnO). Here, tenorite and wurtzite had to assume

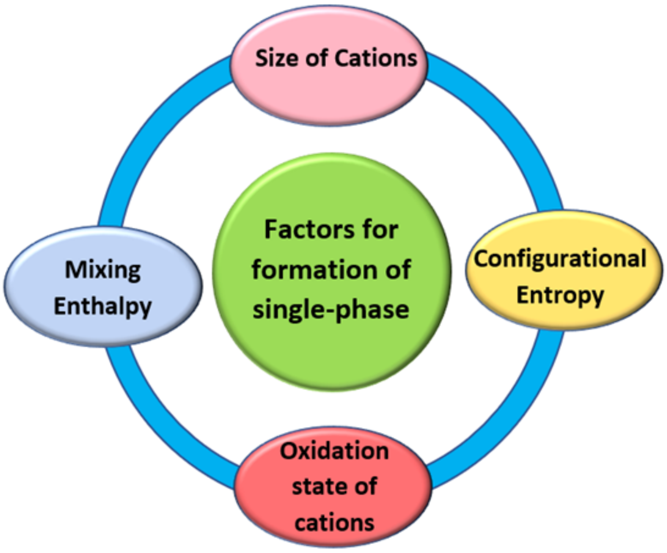

Figure 1.5 Schematic representation of the factors that affects the stabilization of high entropy phase.

to metastable rocksalt phases for the formation of a random solid solution, which has an associated positive enthalpy. The formation of a single-phase rocksalt solid solution, in this case, required entropy-driven stabilization [45]. Therefore, it is postulated that there should be at least one different crystal structure to demonstrate entropy-driven stabilization.

1.4.2 Ionic radius

The ionic radii of the metal cations influence lattice distortion and single-phase HEO fabrication similar to the HEAs. It is important to note that the ionic radius of a cation is not fixed and depends on both its oxidation state and coordination number. A higher oxidation state generally leads to a smaller ionic radius. Similarly, a lower coordination number typically results in a smaller radius. These are critical factors when considering cation substitution in complex oxide systems, as variations in ionic size can lead to lattice distortions, changes in local symmetry, and alterations in the overall structural stability of the material. The coordination number is determined by the ratio of ionic radii of cation and anion. For instance, octahedral coordination is observed when ionic radius ratio is $0.414 \leq \frac{r_c}{r_a} \leq 0.732$. Ionic radii of cations are one of the deciding factors for their site occupancy within the crystal structure. Lattice strain is induced when a cation having larger size than average cation size is substituted into a high entropy oxide. To accommodate this strain and maintain structural stability, the system undergoes geometrical compensation mechanisms which includes oxidation of multivalent cation and creation of oxygen deficit site. Further, for a multi-cationic site such as perovskite (ABO_3 type), Goldschmidt's tolerance factor (t) is a guiding factor for deciding the most stable structure among the possible orthorhombic, tetragonal or cubic symmetry. *t* is a dimensionless number which takes into account sizes of the cations (both A and B) and anion and is given by [37]:

$$\boldsymbol{t} = \frac{\bar{\boldsymbol{r}}_{\boldsymbol{A}}+\boldsymbol{r}_{\boldsymbol{O}}}{\sqrt{2}(\bar{\boldsymbol{r}}_{\boldsymbol{B}}+\boldsymbol{r}_{\boldsymbol{O}})} \qquad (4)$$

where $\bar{r}_A$ and $\bar{r}_B$ stand for the average ionic radii of A and B cations, respectively, while r_O is the radius for oxygen anion. It has been shown that when $t > 1.0$, a hexagonal or tetragonal structure becomes stable, while an orthorhombic or rhombohedral phase forms when $t < 0.9$. On the other hand, a cubic structure is most likely when $0.9 \leq t \leq 1.0$.

1.4.3 Oxidation state

For the single-phase formation in HEOs, the oxidation state of constituent elements plays an important role. In the case of the cubic rocksalt phase, it is assumed that all the cations possess a similar oxidation state of +2 and form MO-type oxides whereas in fluorite, all the cations have an oxidation state of +4 and crystallize in MO_2-type oxides [33,79]. However, later studies showed that the mutual charge compensation mechanism permits cations with different oxidation states to stabilize in single-phase oxides [56,80,81]. In spinel and perovskite-type HEOs, cation with mixed oxygen state interacts [29,30,37].

1.5 Entropy-driven stabilized oxides

Rost et al. pioneered the exploration of entropy-driven phase stabilization by conducting a reversibility test on transition-metal (TM)-based rocksalt high-entropy oxides (HEOs), specifically $(Mg_{0.2}Co_{0.2}Cu_{0.2}Ni_{0.2}Zn_{0.2})O$. Reversibility is a key characteristic of entropy-driven transitions [22,57]. In their study, a reversible phase transition was observed: a single-phase solid solution formed at high temperatures transitioned into multiple phases (tenorite and wurtzite) at lower temperatures and reverted to the single-phase state upon reheating. Thermodynamically, this phenomenon can be explained by entropy-driven phase transition. At high temperatures, the entropy-dominated single-phase solid solution is thermodynamically favoured due to a negative $-T\Delta S_{mix}$ contribution to ΔG_{mix}. Conversely at lower temperatures, enthalpy-driven phase segregation becomes dominant, which leads to the breakdown of the single-phase structure. **Figure 1.6** shows the crystal structure of individual binary oxides and enthalpy associated with the structural change from single phase rocksalt high entropy oxides. Interestingly, this reversibility is not exclusive to high-entropy oxides (>5 elements). Similar behavior has been observed in lower entropy oxide systems such as $(Ni_{0.2}Zn_{0.2})O$ and $(Ni_{0.2}Zn_{0.2}Cu_{0.2})O$ [52]. However, medium-entropy oxides (MEOs) and low

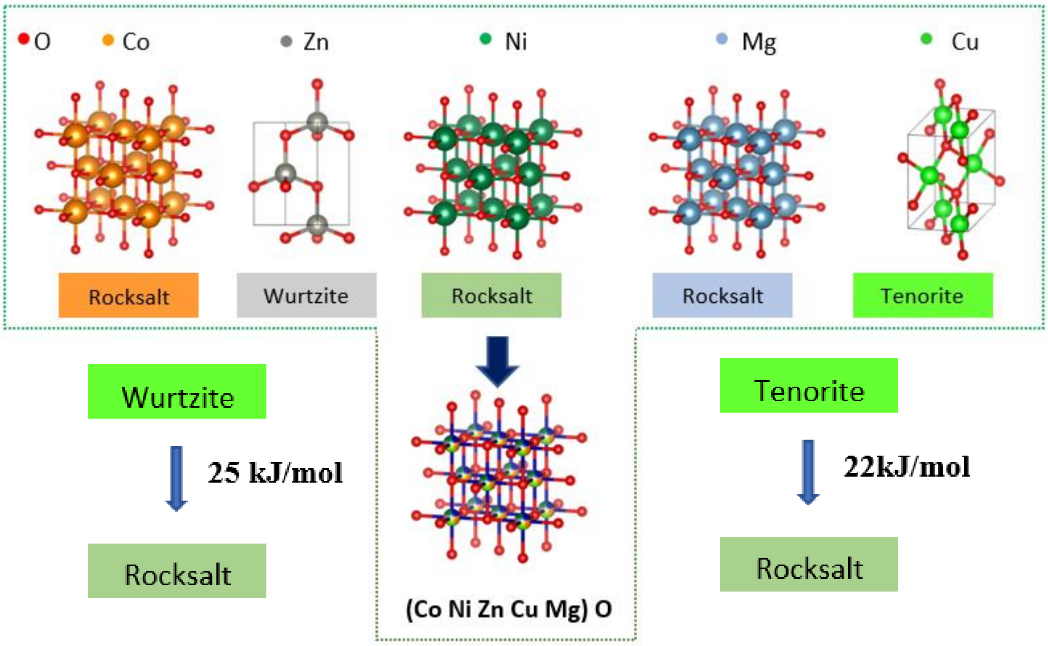

Figure 1.6 Crystal structures of individual binary oxides and enthalpy associated with the structural change to form single-phase rocksalt high entropy oxides.

entropy oxides require significantly higher processing temperatures to achieve single-phase formation, as a higher temperature is needed for the $-T\Delta S_{mix}$ to more than compensate for the positive enthalpy of mixing term (ΔH_{mix}). Given the significant role of entropy in stabilizing these phases, such oxide systems are aptly termed entropy-stabilized oxides (ESOs). This underscores the importance of entropy in phase stabilization and opens avenues for tailoring oxide systems with desired properties through controlled thermal processes.

1.6 Motivation

The pursuit of novel materials with tailored properties has led researchers to explore unconventional compositions and structures. The advent of HEM opened up the exploration of central regions of the multicomponent phase diagrams which remained largely untouched, where potentially unique properties can result from synergistic effects of the components. In contrast to traditional alloys, HEMs feature distinctive compositions, microstructures, and adaptive properties that have earned them a high level of recognition. Research into non-metallic HEMs, such as nitrides and carbides, began as early as 2004. However, the research in HEOs really took off after 2015, when high-entropy oxides (HEOs) synthesis was reported for the first time. HEOs showcased innovative incorporation of five distinct cations (Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) into a cationic sub-lattice of a single-phase rock-salt structure. The versatility of HEOs is rooted in their ability to incorporate multiple oxides into a single-phase structure, despite the immiscibility of certain component pairs (NiO-CuO and MgO-ZnO) in conventional systems. This exceptional behaviour not only broadens their applicability but also presents exciting opportunities for understanding the fundamental principles governing the phase stability.

One of the most compelling aspects of HEOs lie in the variety of synthesis techniques available for their fabrication. Methods such as solid-state reaction, nebulized spray pyrolysis (NSP), flame spray pyrolysis (FSP), co-precipitation hydrothermal, and solution combustion synthesis (SCS) allow researchers to tune material properties by altering processing parameters. Methods such as solid-state fabrication require post-thermal treatment for the fabrication of phase pure rocksalt HEOs whereas NSP and FSP requires expensive instrumentation. SCS on the other hand doesn't require complicated setup and, in some cases, post-thermal treatment (annealing). Moreover, various fuels can be used to tune the combustion rate in SCS. A key challenge in the fabrication of single-phase HEOs is post-thermal treatment, such as high-temperature annealing, to stabilize the desired phase. While effective, these additional steps can be time-consuming, energy-intensive, and potentially limiting for large-scale applications. This challenge opens exciting avenues for innovation to develop approaches in SCS that eliminates the need for post-thermal treatment.

Similar to the valence electron tuning by doping in HEAs [41,82]; the partial substitution either by isovalent and aliovalent element in (Mg,Co,Ni,Cu,Zn)O alters the electronic structure [2,56,81,83]. To accommodate cation having different size and charge, geometrical compatibility and ionic charge balance must be considered, which triggers compensation mechanisms. These compensation mechanisms are often accompanied by defects such as oxygen vacancies and oxidation of multivalent cations. These attributes need to be investigated in depth to understand the phase stability in HEOs. For instance, some article reported phase pure (Mg,Co,Ni,Cu,Zn)O HEO even after large size isovalent and aliovalent substitution such as [63,83,84]. However, in the available literature, discussion on the effect of ionic size and valency mismatch on the stability landscape is limited and needs to be explored in greater detail. At the same time, addition of aliovalent and isovalent cations of varying sizes introduce defects in the lattice which can affect the functional properties. Berardan et al. [2] reported colossal dielectric constant (CDC) in the order of 10^5 for HEOs, without really explaining the reasons for such large dielectric constant. Insight into the role of random distribution of multiple cations of varying sizes, and defects in the polarization mechanisms is scarce. The defect mediated functional properties of HEO systems remain largely unexplored. Further, the scarcity of noble metals in nature poses a significant challenge and thus contributes to the high cost of noble metal catalysts. In response to these challenges, the catalytic potential of transition metal HEOs has garnered attention due the band gap tunability and synergistic effect of the multiple active sites need to be explored.

In order to unlock the potential property tuning, it is important to investigate the effects of isovalent and aliovalent cation addition in (Mg,Co,Ni,Cu,Zn)O and their defect-mediated functional properties.

1.7 Objectives

Based on the earlier discussed literature and motivation of the thesis, followings are the major objectives of the work:

1. To establish the possibility of single-step synthesis of single-phase high entropy oxides via solution combustion synthesis.
2. To study the effect of cation substitution on the structure and electrical properties of HEOs.
3. To study the charge compensation in aliovalent cation substituted HEO and their effect on the catalytic response.

1.8 Organization of thesis

The first chapter provides an overview of the fundamentals of high entropy oxides, thermodynamics of entropy stabilization, crystal structure, synthesis techniques, and properties. This chapter also highlights the motivation for starting the work and main objectives.

The second chapter includes a brief discussion on the history and background of high entropy oxides. It highlights the reported work on high entropy oxides and relevant functional properties.

The third chapter details the experimental and characterization techniques employed throughout this thesis. It describes the processing methods, key parameters, and protocols of synthesis, along with the principal characterization techniques utilized to assess the structure and performance of high entropy oxides.

The fourth chapter discusses the solution combustion synthesis technique for the fabrication of high entropy oxides and the effect of using different fuels in SCS. This chapter also discusses the fine structure of five components (Mg,Co,Ni,Cu,Zn)O HEO.

In chapter five, the effect of lattice strain due to large cation (Ca^{2+}) substitution on the stabilization temperature of (Mg,Co,Ni,Cu,Zn)O HEO is discussed. In addition, local distortion in the lattice due to larger cation substitution is analysed using TEM and EXAFS. The effect of local distortion on the dielectric response is also characterized.

Chapter six discusses the critical role of Ca^{2+} substitution in altering the bandgap and optical properties of (Mg,Co,Ni,Cu,Zn)O, resulting in enhanced visible light photocatalytic activity. This chapter also investigated the dual role of Ca^{2+} in inducing lattice defects which also plays a role in improving the photocatalytic activity.

Chapter seven discusses the synthesis of Li^{1+}, and Na^{1+} incorporated (Fe,Co,Ni,Cu,Zn)O R-HEO. The stability landscape of the HEO as a function of Li and Na addition is also investigated. Synthesized HEOs are evaluated as OER electrocatalysts, and their performance was compared through polarization curves in an alkaline medium (1M KOH).

The eighth chapter presents a comprehensive summary and conclusions of the work. It also highlights the future prospects of the work carried out.