Chapter 8

Conclusions and scope of future research

This chapter summarizes the key findings of this thesis, highlights the main conclusions derived from the study, and outlines potential future directions in this field, suggesting opportunities for refinement and improvement.

8.1 Brief summary and conclusions

This thesis emphasizes the processing of rocksalt high entropy oxides and gives insight into the changes in the stability landscape due to isovalent and aliovalent substitution. The effort is made to investigate the defects introduced due to the substitution of ions varying size and valency. In addition, the defect-mediated functional properties, specifically dielectric and catalytic response, of the rocksalt high entropy oxides are also studied.

Chapter 1 provides an overview of the fundamentals of high entropy oxides, including the thermodynamics of entropy stabilization, crystal structures, various synthesis techniques, and their functional properties. It also outlines the motivation behind initiating this thesis work on high entropy oxides and investigating their functional properties.

Chapter 2 briefly highlights the current state of research in high entropy oxides. The configurational entropy arising from the random distribution of multiple constituent elements plays a critical role in stabilizing these phases, often resulting in exceptional structural stability and intriguing functional properties. In addition to the development of new synthesis techniques, numerous studies have concentrated on exploring novel HEO compositions, their crystal structures, and the fundamental principles governing single-phase stabilization. These efforts aim to understand the role of configurational entropy, ionic size mismatch, and cationic disorder in stabilizing high entropy oxides. Researchers are systematically investigating the relationships between composition, structure, and properties to uncover trends that guide the design of HEOs with desired functionalities.

Chapter 3 outlines the processing and characterization techniques employed in this work. It describes the preparation of the materials, along with the relevant processing parameters. Additionally, the chapter also details structural, optical, electrical, and catalytic characterization techniques, as well as the methods used for data analysis.

Chapter 4 investigates the effect of fuel such as citric acid and glycine in SCS to fabricate high entropy oxides and thus reports low-temperature synthesis of (Mg,Co,Ni,Cu,Zn)O HEO. Using glycine as a fuel has proven to be a more efficient synthesis route for producing single phase five component (MgCo,Ni,Cu,Zn)O HEO compared to citric acid. While the citric acid fuel generates comparable heat, its slower reaction rate does not allow the adiabatic temperature to rise close to the critical temperature and post-annealing (at >850°C) is required to achieve phase purity. In contrast, the glycine combustion reaction rate is much faster, generating intense and rapid heat that enables the formation of a single-phase HEO in a single step during combustion at 185°C, eliminating the need for further thermal treatment and thus reducing energy consumption. However, the reaction is too violent and powders are not uniform.

Chapter 5 presents the simple yet effective mathematical formulation to account for the lattice strain that influences the phase stability of Ca^{2+} added HEO and is validated experimentally. The large ionic size of Ca^{2+} introduces significant strain, creating a high activation energy barrier, making the decomposition of $(Mg,Co,Ni,Cu,Zn)_{1-x}Ca_xO$ into a single phase energetically challenging. It was observed that the solubility limit of Ca^{2+} is somewhere between 0.1 to 0.12 mole fraction. The strain in Ca^{2+} added samples drives the structure to deviate from the ideal rocksalt to a distorted rocksalt structure. The distortion is characterized using XRD, TEM and EXAFS. Further the accommodation of Ca^{2+} combined with oxygen vacancy sites creation and oxidation of multivalent elements being the driving force for enhancing electrical properties. Some important inferences include:

- Dielectric constant and loss at room temperature for $(Mg,Co,Ni,Cu,Zn)_{0.9}Ca_{0.1}O$, and (Mg,Co,Ni,Cu,Zn)O estimated was 3237,1.8 and 2992,1.3 respectively.
- Ac conductivity obtained for $(Mg,Co,Ni,Cu,Zn)_{0.9}Ca_{0.1}O$, and (Mg,Co,Ni,Cu,Zn)O was 1.7×10^{-7} and $5x10^{-8}$ S/cm.
- Impedance spectroscopy suggested IBLC (internal boundary layer capacitance) model for conduction in both the sample.ie. conduction in these oxides system due to semi conducting nature of grain.

Chapter 6 highlights the catalytic properties of Ca added HEO. The distinct electronegativity (χ) and crystal field splitting energy (Δ) of each transition metal (TM) oxide in the five-component high entropy oxide (HEO) contribute to the introduction of multiple 3d states within the native bandgap, effectively narrowing it when compared to the constituting uninary oxides. Additionally, the incorporation of Ca^{2+} further reducing the bandgap. A narrow bandgap enhances absorption across a broader portion of the solar spectrum, improving photocatalytic efficiency. Moreover, to accommodate the large Ca^{2+} ions, Co^{2+} and Ni^{2+} are oxidized to higher valence states and creating vacancies, increasing the covalency of the system. This enhanced covalency lowers the charge transfer energy, enabling these sites to donate electrons more effectively. These sites act as generators of •OH radicals, where dye pollutants are preferentially adsorbed and degraded. Some other observation includes:

- The estimated optical band gap of (Mg,Co,Ni,Cu,Zn)O, $(Mg,Co,Ni,Cu,Zn)_{0.95}Ca_{0.05}O$ and $(Mg,Co,Ni,Cu,Zn)_{0.9}Ca_{0.1}O$ samples are 1.33, 1.25 and 1.18 eV, respectively.
- The results revealed significant dye degradation rates of 40%, 78%, and 97% within 80 minutes for (Mg,Co,Ni,Cu,Zn)O, $(Mg,Co,Ni,Cu,Zn)_{0.95}Ca_{0.05}O$ and $(Mg,Co,Ni,Cu,Zn)_{0.9}Ca_{0.1}O$, respectively, as determined using the Beer-Lambert law.
- The rate constant estimated was about 0.0071, 0.0144, and 0.0445 min^{-1} for (Mg,Co,Ni,Cu,Zn) O, $(Mg,Co,Ni,Cu,Zn)_{0.95}Ca_{0.05}O$ and $(Mg,Co,Ni,Cu,Zn)_{0.9}Ca_{0.1}O$ catalysts, respectively.

Chapter 7 discussed the synthesis of (Fe,Co,Ni,Cu,Zn)O rocksalt high entropy oxides using SCS and incorporated lithium (Li^+) and sodium (Na^+) as sixth elements, maintaining a single-phase rocksalt structure. The addition of Li^+ and Na^+ promoted the formation of oxygen vacancies and the oxidation of multivalent cations, primarily Co^{2+}, thereby enhancing Co/Ni–O covalency and significantly improving catalytic activity. Apart from structural stability landscape this chapter highlights the electrocatalytic oxygen evolution reaction (OER) in 1M KOH.

- Among all the synthesized catalysts, the (Fe,Co,Ni,Cu,Zn,Li)O demonstrated exceptional catalytic efficiency, achieving a remarkably low overpotential of 322 mV at 10 mA/cm² and a Tafel slope of 63 mV/dec. This performance exceeds that of unary oxides like CoO and NiO, highlighting the synergistic benefits of its multi-element composition. These findings underscore the potential of HEOs as a novel platform for optimizing OER performance, paving the way for their use in advanced energy conversion technologies.
- Nyquist plot revealed that the Li^+ added HEO exhibits the lowest charge transfer resistance highlighting its superior catalytic performance.

Overall High entropy oxides represent a transformative approach in materials science, offering a unique platform to tailor structural, electronic, and catalytic properties for diverse applications. With their unparalleled compositional flexibility and the ability to harness synergistic effects among multiple elements, HEOs pave the way for innovative solutions in energy conversion, storage, and environmental remediation, marking a new era in functional materials development.

8.2 Suggestions for future work

The thesis provides a comprehensive understanding of the key parameters influencing the stabilization of rocksalt high entropy oxides (HEOs) and strategies to enhance their functional properties. The primary objective of optimizing HEOs for functionality, with performance comparable or exceeding that of constituent unary oxides, has been largely achieved. By addressing factors such as compositional complexity, lattice strain, defect engineering, and electronic structure tuning, this work highlights the pathways to achieving stability landscape and superior functionality in HEOs. The author believes that performance and versatility of HEOs can be investigated which can unlock additional potential in HEOs. Based on the insights gained, several suggestions for future research directions in this promising field are outlined below:

- Exploring alternative methods beyond solution combustion synthesis to produce nanoparticles with precise control over size, morphology, and composition. Advanced synthesis techniques, such as hydrothermal/solvothermal methods, offer the potential for producing highly crystalline nanoparticles with controlled shapes and surface properties, ideal for catalytic and, electrochemical and electrical applications.
- While the role of configurational entropy dominant in rocksalt HEO however its influence in other HEOs remain ambiguous. Observed phase transition at specific temperature may not solely depends on configurational

entropy other factor such as strain, also play a significant role which should be analyzed in depth.

- High entropy oxides (HEOs) hold immense potential to advance their application by exploring different crystal structures, designing new compositions, and delving into their functional properties.
- Study the role of cation and oxygen vacancies and other point defects to tune the electronic structure, enhance ionic conductivity, or improve catalytic performance.
- Theoretical modeling and computational techniques, including density functional theory (DFT) and machine learning-based approaches, will play a pivotal role in this endeavor. These tools can predict the role of specific elements in enhancing catalytic activity and guide the rational design of compositions by identifying active sites and reaction mechanisms. Furthermore, theoretical studies can provide insights into structure-property relationships, enabling the prediction of stable phases and their functional properties under various conditions.