7.1 Thesis conclusion

The research work carried out throughout the thesis concludes the following:

- Multicomponent metal oxides have inherently much higher molecular weights and mass absorption coefficients than their metallic alloys counterpart. This essentially increases the inelastic component of scattering during x-ray diffraction (XRD) experiments and raises the Compton modified background level. It has been demonstrated in the case of equimolar quinary (CoCuMgNiZn) ESO (Chapter 4) where a prominent reversal of intensity is observed between the two most intense peaks of an average cubic rocksalt phase. Moreover, sintered and quenched equimolar ternary (CoMgNi) MCO reveals a prominent spinel 220 peak, which is present in the sintered pellet but it is found to be absent in its crushed powder (Chapter 5). Hence the commonplace practice of characterizing such complex chemistry metal oxides in its powder form, established in literature (owing to the brittle nature of the sintered pellets), may be interpreted with caution.
- Cubic rocksalt and cubic spinel phases have highly correlated crystal structure. Both the phases are FCC derivative structures with anions decorating the close-packed lattice. However, in the rocksalt phase, the cations fill out all the four octahedral voids and forms six-fold coordination polyhedras with neighbouring anions while in the spinel phase, cations in their +2 oxidation states fill out half of the octahedral voids whereas remaining cations in their +3 oxidation states occupy one-eighth of the tetrahedral voids. Hence geometric frustration in the lattice (high entropy composition) coupled with external stimulus (temperature, pressure) can bring about interconversion between rocksalt and spinel phases through diffusional reconstructive transformation. It has been shown in Chapters 3, 4 and 5 where local spinel domains inside major rocksalt phase and local rocksalt domains inside major spinel phase are found to coexist, sharing

definite orientation relationship with coherent/semi-coherent interphase interfaces between them.

- Processing parameters like sintering temperature, holding time and subsequent ageing heat treatment play a crucial role in phase formation and its stability. It has been demonstrated in Chapters 3, 4 and 5 that prolonged exposure to high temperatures not only forces non-isostructural phases to combine with the major phase but also possible rearrangement in crystal structure with successive in-plane and out-of-plane rotations. Such arrangement ensures maximum randomness along individual atom-columns (high entropy effect) while also relieving the lattice strain (enthalpic penalty) at the same time. This observation also explains the randomly mixed column chemistry frequently encountered in ESOs/HEOs using high-resolution fine-probe techniques like STEM-XEDS and APT.
- Both the rocksalt forming (CoCuMgNiZn)-ESO (Chapter 4) and spinel forming (CoCrFeMnNi)-HEO (Chapter 5) tends to form nano interweaved modulated microstructure. However, in the former scenario 200-type planes (rocksalt) take part in the process of structural modulation whereas 220-type of planes (spinel) becomes operative in the later. The structurally modulated domains may or may not be associated with chemical modulation. Although the fundamental reason behind such observation remains unanswered at the moment, however, it perhaps explains the oriented growth of spinel 220 type reflection in otherwise phase-pure rocksalt structure of ternary (CoMgNi)-oxide (Chapter 5).
- Iron (II,III) oxide (predominantly in the +3 state) forms an ordered hexagonal phase (hR10; R -3 c prototype) with planar defect-structure in presence of larger ionic radii Ca^{+2} cations and exsolves out of the major rocksalt phase in (CaCoFeMgNi)-oxide (Chapter 3). However, in the presence of similar cationic radii Mn^{+3}, it helps to stabilize

the average cubic spinel structure (cF56; F d -3 m prototype) in (CoFeMgMnNi)-oxide (Chapter 5). Therefore, the same cation in presence of different species is amenable to hop along local minima in the energy landscape and change its coordination environment, in order to stabilize a particular kind of ordered/disordered structure (Chapters 3 and 5). This observation further brings out the enthalpic penalties in highly concentrated compositions and the importance of fluctuation in oxidation states, coordination environment and consequently ionic radii.

- Ternary phase-pure (CoMgNi)-oxide with average rocksalt structure relieves its lattice strain by forming a helical domain structure with small amount of correlated spinel phase formation (Chapter 5). However, quinary phase-pure (CoCuMgNiZn)-ESO with global average rocksalt crystal structure and single-phase (Co(Cr/Mg)FeMnNi)-HEO with global average spinel crystal structure tends to form tweed microstructure with structural modulation. It also hints at non-random distribution of multiple cations and therefore to the presence of short-range order (SRO) domains. The tweeds may act as template for subsequent phase separation to form self-assembled microstructure over large length scales. Further geometric frustration due to disproportionate differences in ionic sizes, leads to chemical segregation along with structural modulation and/or formation of planar fault dominated defect microstructure.
- Equimolar quaternary (CoMgMnNi)-oxide outperforms its quinary HEO counterparts as electrocatalyst for OER activity having a two-phase rocksalt plus spinel structure. This observation leads to the importance of phase-fractions, related crystal structures and their reversible interconversion during oxidation and reduction cycles, bringing out excellent match with a recent model proposed in literature (Chapter 6).

7.2 Scope for further research

Since no scientific research is truly exhaustive, the scope of further research along the lines of this thesis may be summarized as follows:

- Employing high-energy ball-milling on sintered and quenched pellets of MCOs/HEOs/ESOs to refine the particle size and promote inter-mixing of phases. The refinement of crystallite size is bound to enhance the OER activities manifold as established in literature, whereas the effect of forced inter-mixing after sintering can be studied for the first time.
- Exploring domain chemistry and fine structure of such materials through XPS and STEM-EELS spectroscopic techniques and 4D-STEM datasets respectively. Since transition metal oxides are amenable to switch their oxidation states, such experiments may shed further insights regarding phase formation and microstructural evolution. Furthermore, TEM in-situ experiments inside a gas-cell with regulated oxidizing/reducing environment are bound to provide with novel atomistic mechanisms of structural phase transformation.

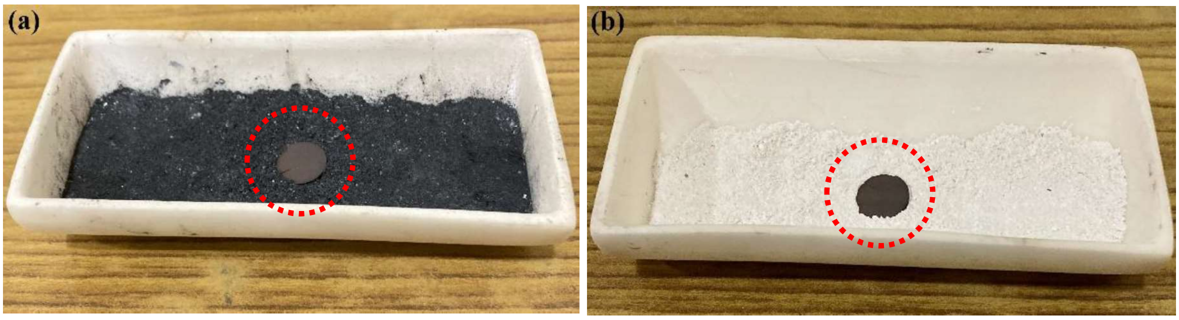

Figure 7.1: Sintered and quenched pellet of equimolar ternary (CoMgNi)-oxide placed on an alumina tray filled with a mixture of alumina and graphite powder (a) before ageing treatment and (b) after ageing treatment. The obvious change in colour of the powder bed and not the pellet, may easily be discerned.

- Enhancing phase separation events through prolonged holding time at low to intermediate temperatures (to overcome kinetic barrier) in order to navigate the energy landscape of the material systems and its manifestation on microstructural evolution.
- Exploration of MCOs/HEOs/ESOs as possible candidates for effective carbon capture, either from environment or industries. In an accidental trial of ageing a sintered pellet placed on a mixture of graphite and alumina powder inside an alumina crucible, it has been seen that the greyish white mixture turns clear white after ageing treatment. The brownish sintered pellet showed no change in colour nor XRD signature when compared to the same composition pellet after ageing without the graphite plus alumina bed.