Capturing High Entropy Oxide Formation: Insights from *In Situ* X-ray Scattering and Absorption

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High-entropy oxides (HEOs) are a promising class of functional materials because their compositional complexity offers high tunability of catalytic, magnetic, and electronic properties [1]. In these materials, multiple metal cations share crystallographic sites, which can lead to local disorder and deviations from the average structure [2]. As a result, conventional crystallographic approaches based mainly on traditional X-Ray Diffraction (XRD) can struggle to capture the full structural picture. Techniques sensitive to short-range order, such as Pair Distribution Function (PDF) analysis of total scattering data and X-ray Absorption Spectroscopy (XAS), are valuable tools for probing the local coordination environments of such structures [3]. If employed together, these techniques provide insights into the mechanisms by which these complex materials form.

In this work, we have followed the formation of a $(Co_{0.5}Ni_{0.5})(Cr_{0.33}Mn_{0.33}Fe_{0.33})_2O_4$ spinel HEO. We combine *in situ* X-ray scattering and absorption techniques and collect quasi-simultaneous data while heating a non-crystalline sol-gel precursor to 700 °C. PDF analysis reveals the formation of a nanostructured intermediate around 350 °C whose short-range order already resembles that of a spinel. At higher temperatures, this intermediate gradually crystallises into the final spinel HEO, as observed by XRD.

This structural evolution is accompanied by changes to the electronic structure. X-ray Absorption Near-Edge Structure (XANES) measurements reveal an overall reduction during product formation, and we identify two metals as particularly redox-active species. Once the final spinel has formed, we examine the local ordering of metals into octahedral and tetrahedral sites, as illustrated in Figure 1. By combining XANES and Extended X-ray Absorption Fine Structure (EXAFS), we show that some metals exhibit strong site selectivity, while others display greater flexibility in their local coordination environment. This knowledge about interactions between specific metal cations can help guide the successful synthesis of novel HEO materials.

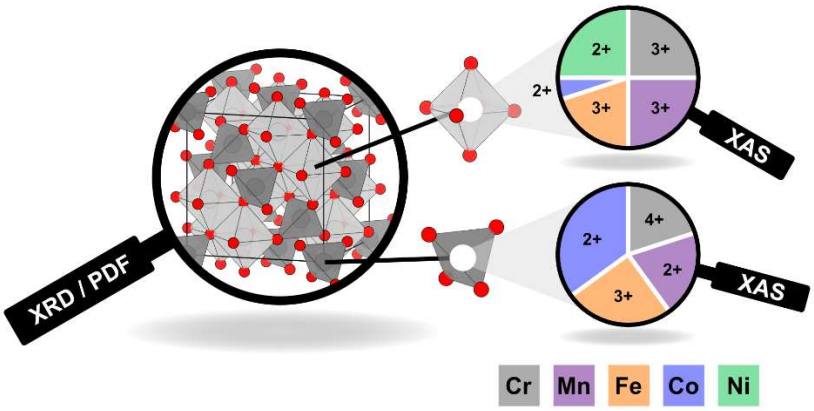


Figure 1. *Schematic of the structural characterisation of a high-entropy spinel. The crystal structure is determined by XRD, with PDF providing insights into the nanostructure in the early stages of synthesis. The distribution of metals in the octahedral and tetrahedral sites is determined by combined XANES and EXAFS analysis.*

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