In-situ High-Resolution Synchrotron XRD study of Temperature Phase evolution in $(Mg,Co,Ni,Zn)_{1-x}Cu_xO$ high entropy system

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The incorporation of Cu in the High Entropy System $(Mg,Co,Ni,Zn)_{1-x}Cu_xO$ severely influences the Rock-Salt (RS) structural stability of the prototypical compound (Mg,Co,Ni,Cu,Zn)O (HEO-5) [1,2]. This study investigates the high-temperature evolution of this system across eight different Cu percentages, above and below the known Cu solubility limit of 28%. The starting specimens, stabilised in a highly defective RS structure upon quenching, are a single-phase rock-salt (RS) structure for Cu percentages below 28%. On these specimens, we performed in-situ high-resolution X-ray diffraction (HR-XRD) at the ID22 beamline of the ESRF by heating them up to 900°C with a heating rate of 10°C/min. A pattern was recorded every 20°C (2 min).
While preliminary experiments suggested the possibility of obtaining a pure RS phase at 900°C even for a Cu content above the solubility limit (28%), this systematic study revealed the presence of a single-phase system only for compositions within the known solubility limit. The study also showed the presence of non-trivial peak broadening due to the heavily distorted RS matrix, especially for temperatures lower than 700°C, and a composition-dependent demixing staring at about 300°C and disappearing above 850°C. To handle this massive and complex dataset and successfully model the complex microstructural broadening, we implemented a dynamic sequential Rietveld refinement strategy using Topas V.7 [3]. We grouped the patterns into temperature ranges, allowing the model to enable and disable secondary phases according to the emerging segregation products for each temperature.
Through this approach, we identified the segregation pathway for each composition, providing a crucial insight into the structural and thermodynamic limits of the HEO-5 system. This establishes a robust framework for processing large synchrotron datasets together with the ability to map complex phase-boundaries in heavily distorted and multi-component oxides.

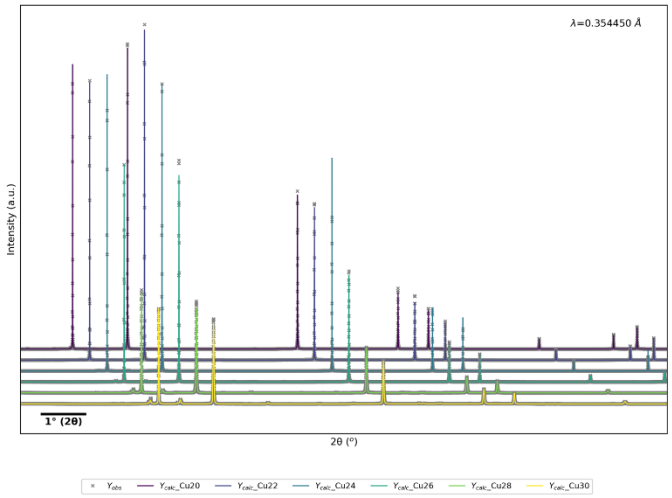


Figure 1. *In-situ HR-XRD data (900< T (°C) <920, λ = 0.354450 Å) and corresponding sequential Rietveld refinements for $(Mg,Co,Ni,Zn)_{1-x}Cu_xO$ (Cu20–Cu30). Profiles are offset for clarity; the scale bar denotes 1° (2θ).*

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