High-throughput structural investigation of Cu content-dependent second phase formation in compositionally complex spinel oxide thin film materials libraries

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Compositionally complex oxides (CCO) are of great interest for several applications due to their compositional flexibility and potential for tunable functional properties [1,2]. Nevertheless, their synthesizability and the formation of secondary phases are still objects of research [3,4]. The inclusion of Cu in CCO spinel compositions can result in the formation of secondary Cu phases when the solubility limit of Cu in the spinel lattice is exceeded [5]. With this study, we investigate $(Mn,Fe,Co,Ni,Cu)_3O_4$ spinels and aim identifying limits for Cu dissolution for compositions between 2 and 45 at.% of Cu. Using combinatorial sputter deposition with four sputter sources operating simultaneously, several thin-film samples with well-defined composition gradients were deposited on wafer substrates [6]. Subsequently, these materials libraries (MLs) were mapped in high-throughput by energy-dispersive X-ray spectroscopy (EDX) for their metal contents and by X-ray diffraction (XRD) to get structural information. This approach enables efficient screening of thin films for their phase formation and the correlation of compositional and structural data in a large composition space. The results show that a single-phase spinel forms only up to 18–22 at.% Cu content. Above this, Cu segregates and forms CuO (**Fig. 1**).

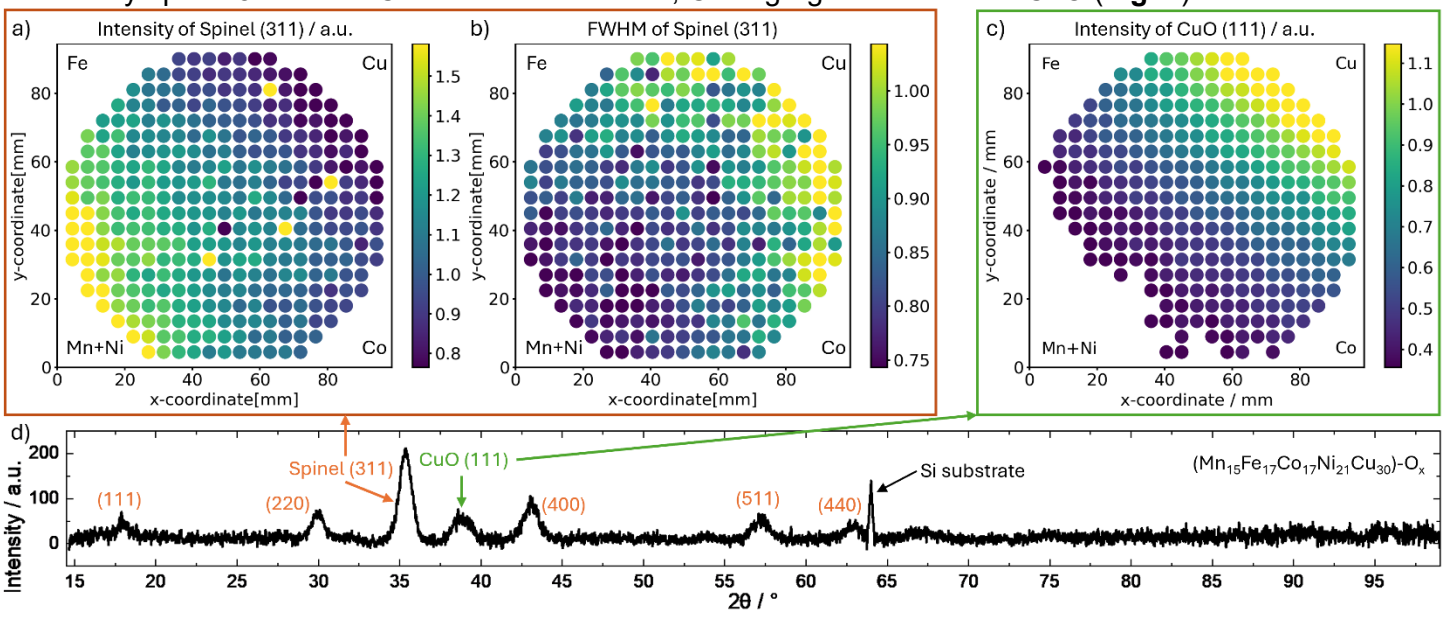


Figure 1. *Property maps of an exemplary thin-film materials library. The element gradient maxima are marked in the corners.* ***a.*** *Maximum peak intensity and* ***b.*** *FWHM of spinel (311) and* ***c.*** *maximum peak intensity of CuO (111).* ***d.*** *Exemplary XRD pattern with spinel and CuO reflections.*

The systematic mapping reveals a continuous diffraction angle shift and peak shape change, with the full width at half maximum (FWHM) of the spinel peaks increasing significantly with the Cu content. These findings provide insights into ion mixability and composition-dependent structural changes in CCOs and demonstrate the efficiency of high-throughput synthesis and mapping for accelerating materials discovery.

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