# Nano-scale imaging and spectroscopy of interfaces in (Co,Cu,Mg,Ni,Zn)O high entropy oxides

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In recent years, the entropy-driven formation of multicomponent single-phase structures has extended from the metal to the ceramics and particularly, oxides research communities [1]. Since high entropy oxides (HEOs) greatly expand the available compositional space and possess promising functional and mechanical properties, they are strong candidates for solid electrolytes in batteries, fuel cells/electrolyzers, solid-state electrochemical devices, etc. [2-4]. Research on HEOs is still in its very early stages, with fundamental and exploratory studies still required to understand the uniqueness and similarity of these when compared to conventional oxide ceramics.

Previously, it was shown that a phase transformation occurs in (Co,Cu,Mg,Ni,Zn)O HEO when heat treated, forming a multi-phase material with secondary and ternary phases identified as copper-rich tenorite and cobalt-rich spinel [5]. The interfaces created in the multi-phase HEO take many forms, including as grain boundaries, defects, and inter-phase boundaries within grains [5]. It is well-known that microstructural defects, such as grain boundaries in polycrystals and heterointerfaces between phases in multi-phase ceramics, play a significant role in their properties [6]. Therefore, not only the presence of the transformed phases, but also the various types of interfaces present in multi-phase HEOs, are expected to contribute to macroscopic functional properties, such as ionic conductivity and mechanical deformation [7]. However, little is known about the interfaces and atomic-level phase change mechanisms in these complex concentrated materials. Additionally, there are challenges in performing high spatial resolution interface characterization in the electron microscope, such as the complex spectral quantification procedure for multicomponent systems, difficulties in probing overlapping areas, and electron beam damage. Therefore, learning about HEOs by overcoming these challenges, can expand our knowledge about the nature of interfaces and the mechanisms of phase transformation, leading to optimal materials synthesis and design in the future.

This paper presents observations of the local atomic structure, composition, defect chemistry, and electronic structure of grain boundaries and heterointerfaces in single- and multi-phase HEOs. A 300-kV double spherical aberration-corrected scanning transmission electron microscope (AC-STEM) equipped with dual large-angle energy dispersive X-ray spectroscopy (EDXS) detectors, Gatan GIF Quantum, and K2 direct electron detector (JEOL Grand ARM) were used to record spatially resolved electron energy-loss spectroscopy (EELS) and EDXS data. Core-loss EELS edges and near-edge fine structures were used to quantify the local concentration of cations, oxygen vacancies, and oxidation states of cations (i.e., $Co^{3+}$, $Cu^{3+}$). This information sheds light on the role of interfaces in these complex systems, which can be correlated to potentially promising macroscopic functional properties.
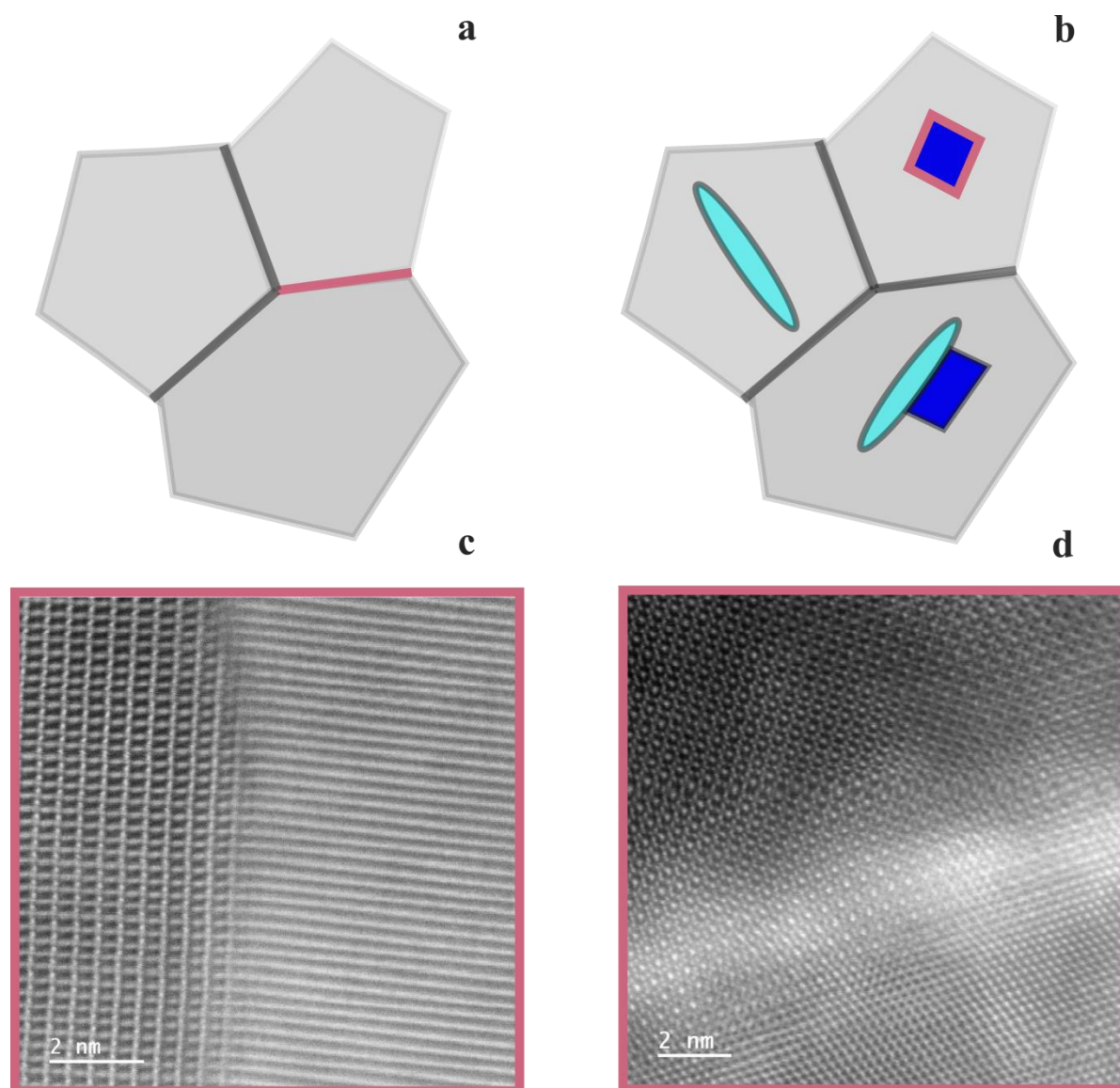
**Figure 1.** Figure 1: a, b) Schematic depicting the interfaces of interest in single- and multi-phase high entropy oxides include grain boundaries (a) and heterointerfaces between matrix, secondary and ternary phases (b). c, d) Preliminary aberration-corrected scanning transmission electron microscopy high-angle annular dark field (HAADF) images of a grain boundary (colored with pink in a), and a heterointerface between high entropy oxide matrix and secondary phase (pink in b).
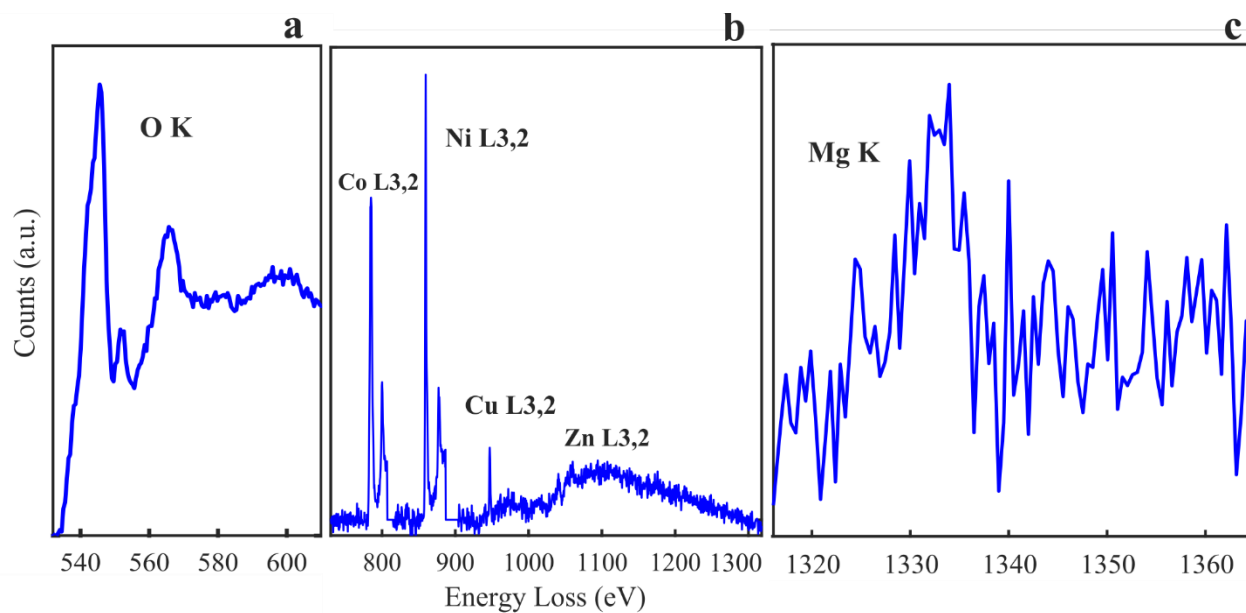
**Figure 2.** Figure 2. Electron energy-loss spectroscopy core-loss data (background subtracted) from high entropy oxide matrix showing oxygen K edge (a), Co, Ni, Cu and Zn L23 edges (b), and Mg K edge (c).

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