Local Structure of High-Entropy Tungstates

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ABSTRACT

High-entropy oxides (HEOx) are compositionally complex materials in which several cations share the same crystallographic sublattice, producing strong chemical disorder and unusual functional properties [1,2]. Understanding how this chemical disorder is structurally accommodated at the atomic scale is essential for relating the composition to the physical properties. Previous PDF/RMC [3] and EXAFS studies [4,5] have shown the importance of local distortions in HEOx, but systematic composition-dependent investigations remain scarce. So our team initiated a detailed study of the composition – local structure – property relationship thanks to a CSC PhD thesis and CNRS Chimie Emergence project. We are investigating the local structure of high-entropy tungstates with the wolframite-type structure $(M5)WO_4$, where five cations share the M site. Laboratory X-ray diffraction and neutron diffraction @ILL show that the average wolframite structure is retained across the investigated compositions, but individual information on each type of M cation cannot be resolved from this average structure. Therefore, to probe the response of local structure to the chemical disorder, we take advantage of the element selectivity of XAS. HERFD-XAS on FAME-UHD@ESRF was thus employed at low temperatures to probe the W, Ni and Co environments in a series of model $(M5)WO_4$ HEOx.

We will present our first results and conclusions at the Co and W edges. XANES spectra reveal only minor changes in oxidation state and electronic structure among the investigated compositions. In contrast, EXAFS data highlight distinct first-shell structural responses at each cation site. Within the Co-containing HEOx subset, the fitted Co–O bond-length splitting is systematically reduced relative to $CoWO_4$, whereas the W–O one increases. This opposite response indicates that the chemical disorder is accommodated differently around the Co and W sites, despite the preservation of the average crystal structure.

Further EXAFS measurements at additional absorption edges, together with neutron total-scattering PDF/RMC analysis, will be used to determine how these local structural responses depend on the cation chemistry and how they propagate beyond the first coordination shell. Such a combined element-selective and total-scattering approach should provide a route toward establishing the link between the chemical composition, the local structural disorder and the thermal behaviour of high-entropy tungstates.

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