Combined X-ray and Neutron Diffraction investigation of multimetallic and High-Entropy transition-metal Phosphates

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Transition-metal phosphates are extremely attractive for catalytic applications, as the phosphate framework facilitates proton-coupled electron transfers while stabilizing high-valent metal intermediates. The properties could reasonably be enhanced with compositional complexity, as diverse local environments are created. High-entropy phosphates (HEPi) are materials in which five or more cations simultaneously occupy the same crystallographic site, stabilized by high configurational entropy [1]. However, only a limited number of phosphate polymorphs can reasonably be accommodating of multiple cations, and understanding which structures can host multication compositions and what controls their stability remains an important open question.

Tetragonal phosphates (*$I4_1/amd$*) are an intriguing candidate for multi-metal compositions, with chains of edge-sharing MO_6 octahedra connected by PO_4 tetrahedra that allow flexibility on the metal site [2].

In this work we report a series of novel multi-metal and high entropy phosphates, with incremental and combinatorial incorporation of Ni, Co, Mn, Fe and Cr. We will discuss synthetic strategies and polymorphism of the tetragonal structure. The simultaneous crystallographic analysis using powder X-ray diffraction (STOE) and neutron powder diffraction measurements were performed on the PEARL instrument at the TU Delft Reactor Institute allows us to track order-disorder effect and hydrogen-bearing charge compensation. The PEARL data down to cryogenic temperatures unravel the structural stability and magnetism in these structures.

These results provide the first structural insight into multimetal tetragonal HEPi compositions and demonstrate the unique role of neutron diffraction for resolving the effects of the simultaneous incorporation of several metals (structural distortions, magnetic ordering, possible hydroxyl or aqua ligands trapped in the motif).

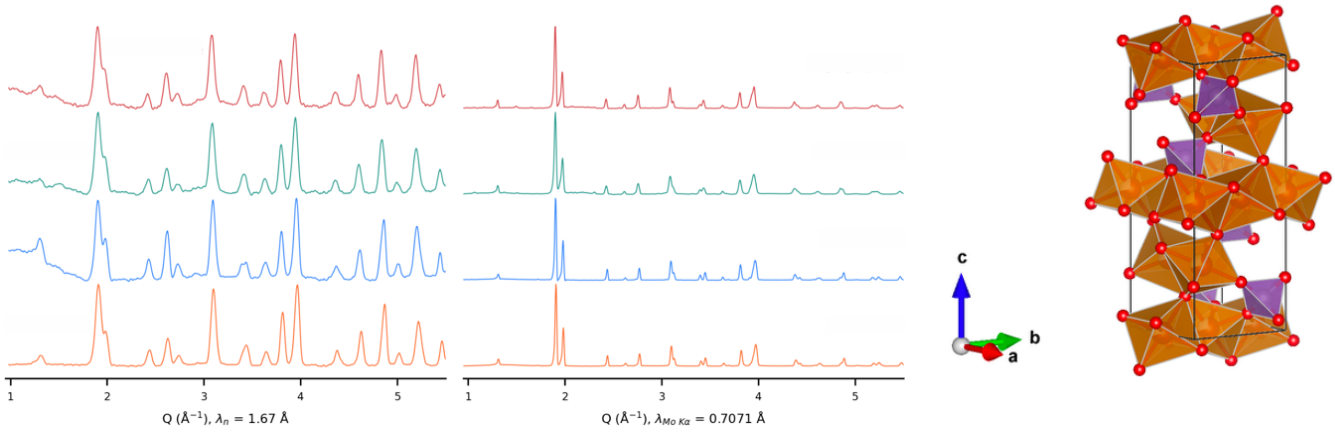


Figure 1. *Powder diffraction patterns from neutron (left) and X-ray (right) diffraction. Patterns are colour-coded by composition: red ($Mn_{1.5}Co_{1.5}Fe_2Cr_2Pi$), green ($Mn_3Fe_2Cr_2Pi$), blue ($Co_3Cr_4Pi$), and orange ($Ni_3Cr_4Pi$). The crystal structure of $I4_1/amd$: orange polyhedra – metal cations, purple tetrahedra – phosphate groups, red spheres – oxygen atoms. ICSD entry: 92292 [3].*

[1] Masquelier et al., Chem. Rev., 113, (2013). https://doi.org/10.1021/cr3001862
[2] T. O. Kozlova et al., Russ. J. Inorg. Chem., 70, (2025). https://doi.org/10.1134/s0036023625602223
[3] Le Fur et al., Solid State Sci., 2, (2000). https://doi.org/10.1016/S1293-2558(00)00102-3