Beyond entropy: diffraction insights into oxygen mobility in doped $BaInO_{2.5}$-derived perovskites

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Barium indium oxide ($BaInO_{2.5}$, BIO) is a prototypical oxygen-deficient perovskite exhibiting high oxide-ion mobility. The ionic transport of BIO has been extensively tuned in literature by modifying the oxygen-vacancy network of its original brownmillerite framework: as chemical substitution stabilises the cubic perovskite structure, the ionic mobility can be moved at lower temperatures and mixed ionic-electronic conductivity can arise. [1]
We have recently harnessed BIO as a flexible testing platform to test the effect of compositional complexity and high-entropy composition on the B-site with a sequential combinatorial doping strategy. Our work highlighted the emergence of cocktail effect in $Ba(InCoFeSnTi)O_{2.5+\delta}$ (*Pm-3m*) overperforming all lower combinations. [2]

In this work, we extend the phase space of the B-site dopants to include Y and Cu, and some 6-dopants compositions, with particular focus on Co-Fe co-doping. We will address the opportunities and challenges of stabilising a single phase-pure cubic phase through compositional complexity. Octahedral Cu (Jahn-Teller active) has the potential to induce local perturbations of the framework and modify vacancy energetics. [3,4]
We thoroughly investigate the three-fold composition-structure-property relationship with a combination of synthetic studies, multi-atmosphere thermogravimetric analysis (TGA) and variable temperature neutron diffraction (2-750 K) across the compositional space.

Our study simultaneously probes the entropy effect on structural stability, the contrast between mobile-oxygen and oxygen-occupancy in the structure, and the impact of compositional complexity on the anisotropic thermal displacement behaviour of the oxygen sublattice.

Our study lays the foundations for an interrelated landscape for highly doped BIO-based perovskites. We aim to unravel the “black box” of the high-entropy approach in these compositionally complex oxides and directly interrogate powder diffraction to address oxygen exchange capabilities.

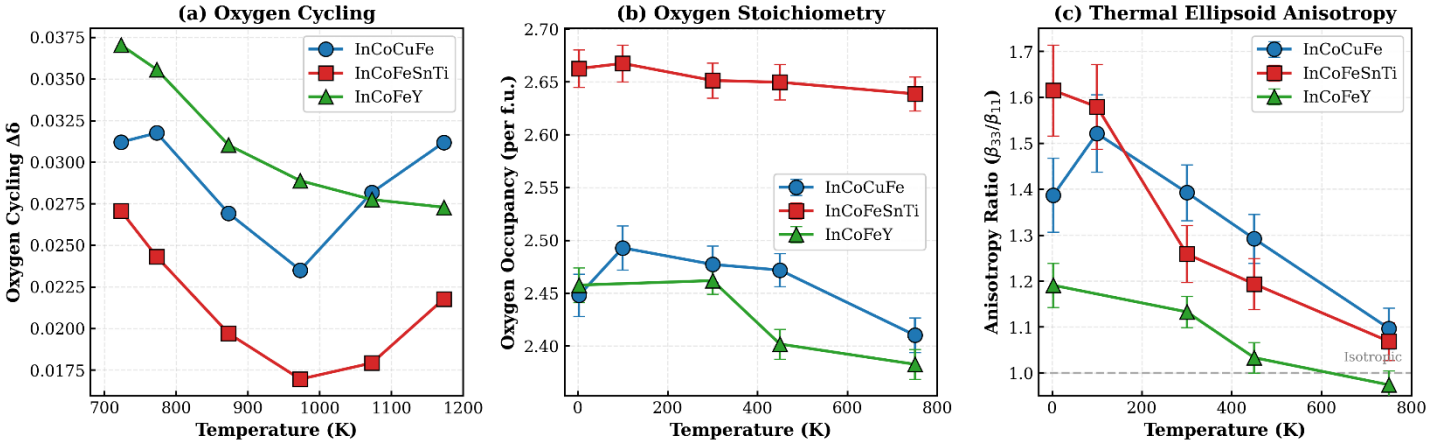


Figure 1. *Example dataset comparing three- and four-dopant compositions within a larger series of sequentially doped materials in this study. Temperature dependence high-temperature oxygen cycling (a), refined oxygen stoichiometry (b) and oxygen thermal anisotropy (c) for $Ba(InCoCuFe)O_{2.5+\delta}$, $Ba(InCoFeY)O_{2.5+\delta}$ and $Ba(InCoFeSnTi)O_{2.5+\delta}$.*

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