Lattice disorder and oxygen migration pathways in pyrochlore and defect-fluorite oxides

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Pyrochlore oxides, with the general formula $A_2B_2O_7$, are of considerable interest as catalysts for the oxygen evolution reaction[1-5], where $A_2Ru_2O_{7-\delta}$ pyrochlores have recently emerged as state-of-the-art materials, and as photocatalysts for hydrogen evolution[6-8]. Fundamental to their reactivity is the local-scale vacancy ordering and mobility, which can be tailored through cation substitution[4]. The chemical and structural flexibility of pyrochlore oxides gives them a diverse range of physical and chemical properties leading to technological applications including as fast-ion conductors[9, 10], ferroelectrics[11], magnetism[12], oxide heterostructures[13, 14], and host matrices for the immobilization of actinide-rich nuclear wastes[15].

Atomic-scale disorder plays an important role in the chemical and physical properties of oxide materials. The structural flexibility of pyrochlore-type oxides allows for crystal-chemical engineering of these properties. Compositional modification can push pyrochlore oxides towards a disordered defect-fluorite structure with anion Frenkel pair defects that facilitate oxygen migration. The local structure of the long-range average cubic defect-fluorite was recently claimed to consist of randomly arranged orthorhombic weberite-type domains[16]. In this work we show, using low-temperature neutron total-scattering experiments, that this is not the case for Zr-rich defect-fluorites. By analyzing data from the pyrochlore/defect-fluorite $Y_2Sn_{2-x}Zr_xO_7$ series using a combination of neutron pair distribution function and big-box modelling, we have differentiated and quantified the relationship between anion sub-lattice disorder and Frenkel defects. These details directly influence the energy landscape for oxygen migration and are crucial for simulations and design of new materials with improved properties.

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