

MS27-04 | SUB-MESOSCALE OXYGEN ORDERING IN NON-STOICHIOMETRIC OXYGEN ION CONDUCTOR $\text{Pr}_2\text{NiO}_{4+\delta}$

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Non-stoichiometric oxides can undergo important variations in the oxygen stoichiometry, enabling to tune physical and chemical properties. Combining neutron diffraction, inelastic neutron scattering and *ab initio* lattice dynamics calculations, we have recently evidenced the importance of lattice dynamics, i.e. soft phonon modes, triggering low temperature oxygen mobility in Brownmillerite type $(\text{Ca}/\text{Sr})\text{Fe}/\text{CoO}_{2.5}$ and Ruddlesden Popper type oxides, e.g. $(\text{Pr}/\text{Nd})_2\text{NiO}_{4+\delta}$. [1-4]. This new concept has technological relevance for the optimization of oxygen membranes and electrolytes in SOFCs.

We report here on single-crystal synchrotron diffraction experiments on non-stoichiometric $\text{Pr}_2\text{NiO}_{4+\delta}$, uncovering unprecedented oxygen ordering up to the sub meso-scale. Complex oxygen ordering is established during a topotactic solid-state reaction already proceeding at ambient temperature, following small oxygen release. The resulting 3D-incommensurate modulated structure is described in terms of modulation vectors and related twin domain structures. Melting of the oxygen ordering around 365°C strongly amplifies the oxygen mobility, evidenced by $^{18}\text{O}/^{16}\text{O}$ oxygen isotope exchange, and associated with phonon softening manifested in a pronounced increase of thermal diffuse scattering. Our results thus strengthen the idea of a phonon assisted oxygen diffusion mechanism, which can be more generally applied to understand cooperative diffusion mechanisms.

[1] Paulus, W., et al., J. Am. Chem. Soc, 2008. 130(47): p. 16080-16085.

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[3] M. Ceretti et al. J. Mater. Chem. A, 3, 42 (2015) p21140-48.

[4] M. Ceretti et al., InorganicChemistry, 2018, 57 (8), pp.4657-4666.