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## Competitive interplay between long-range oxygen and electronic ordering to promote low-T oxygen mobility in $\text{La}_2\text{CoO}_{4+d}$

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Non-stoichiometric oxides with Ruddlesden-Popper structure type and the chemical formula  $\text{A}_2\text{BO}_4$  (A = rare earth, B = transition metal) can uptake extra O-atoms on interstitial lattice sites (Oint). Due to their high mobility even at room temperature, long-range O-ordering up to the sub-mesoscale is observed in several  $\text{A}_2\text{BO}_{4+d}$  phases, which, together with charge and spin ordering, results into a competitive degree of freedom between structural and electronic ordering. Oxygen ordering thus adds an additional degree of freedom that may affect charge and spin ordering schemes, which is not present in the Sr-doped counterpart  $\text{A}_{2-x}\text{Sr}_x\text{BO}_4$ . In this regard,  $\text{La}_2\text{CoO}_{4+d}$  shows extremely high oxygen diffusion coefficients already at room temperature attaining diffusion coefficients of  $D = 1 \times 10^{-9} \text{ cm}^2\text{s}^{-1}$ . Combining neutron and synchrotron diffraction data, we evidenced for  $\text{La}_2\text{CoO}_{4.25}$  a 3D modulated oxygen ordering setting in below  $600^\circ\text{C}$ , involving translational periodicities of more than  $100 \text{ \AA}$ . Further on, a checkerboard charge ordering between  $\text{Co}^{2+}/\text{Co}^{3+}$  occurs below  $350^\circ\text{C}$ , stabilizing a reconstructive rearrangement of the entire Oint-sublattice, showing a lock-in transition to a formal  $4a \times 4b \times 4c$  ordered Ruddlesden-Popper type unit cell. The strong structural correlations induced by the sub-mesoscopic oxygen ordering are discussed to explain the unusually high oxygen mobility in terms of phonon softening.

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