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Enhancing reducibility of cobaltate perovskites by A-site solid solution

- New materials and stoichiometry from solid solutions -

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Research in oxygen-deficient perovskite is an important point for solid state ionics considering their ability to reversibly change oxygen stoichiometry by topochemical processes. From a synthetic point of view, low temperature oxidation-reduction of transition metal oxides has already proved to be very effective for achieving novel structures with unexpected oxygen frameworks.

The $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ system is reducible on a very large scale of the solid solution and shows a different structure when x is greater than 0.8; here we focus on the reduced structures when $x < 0.8$. The oxygen stoichiometry of the reduced material has been quantified by thermogravimetric analysis in both oxidizing (O_2) and reducing (H_2) atmospheres. Measurement under oxidizing conditions shows that the oxygen content is close to 2 (*i.e.*, $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_2$), corresponding to an unusual amount of monovalent cobalt up to 50% for $x = 0.5$. Thermal gravimetric analysis under H_2 is in agreement with this stoichiometry. Examination of the effluent gases by mass spectroscopy has excluded the possibility of hydride incorporation into the framework, although some cases of this have been reported in the literature with other cobaltites. Oxidizing the sample at 300°C results in the starting $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$, indicating that this process is reversible.

The structure of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_2$ has been investigated by combined Rietveld refinements of synchrotron X-ray diffraction and neutron diffraction. The solved structure is a tetragonal phase exhibiting oxygen disorder along the cobalt plane, resulting from the mixed tetrahedral/triangular coordination of cobalt.

The possibility of insulating cobaltites systems to induce planar oxygen mobility may bring some new perspective for application in the electrolyte for solid oxide fuel cells working at low temperature.