

DEPARTURE FROM SOLID SOLUTION BEHAVIOUR IN DOUBLE PEROVSKITES

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Mixed ionic electronic conducting oxides (MIEC) serve a plethora of electrochemical applications such as cathodes for solid oxide electrochemical cells and oxygen evolution reaction catalysts for water splitting. These applications rely to a large extent on the MIEC's ability for electron and/or ion transfer across the solid/gas or solid/liquid interface. The efficacy of these reactions being governed by the surface defect chemistry and electronic structure, rational design of the (surface) chemistry presents itself as an auspicious path to tune these properties towards optimal device performance.

The perovskite structures' (ABO_3) unmatched capability to accommodate virtually the whole periodic table of elements in the cation sublattice suggests the ability to tune the electronic and ionic defect structure towards

favorable electrochemical activity by careful engineering of the cation composition.

Many favorable choices of chemistry, however, may lead to a departure from the ideal cubic perovskite structure, be it in the form of a complete decomposition or more subtly by ordering phenomena in either sublattice, impacting defect and electronic structure profoundly and thus presenting a limit to guided design. One boilerplate example is the double perovskite $Pr_xBa_{1-x}CoO_{3-d}$ (PBCO) where A-site as well as vacancy ordering may take place.

In this work, we investigate the whole compositional space of PBCO with X-Ray absorption spectroscopy, Resonant and High Energy Grazing Incident X-Ray diffraction to assay the phase relations and their impact on electronic and defect structure and with that the electrocatalytic activity.

We find a departure from solid solution behavior that, in addition to the anticipated transition from the hexagonal to a cubic polytype, manifests itself in the formation of superstructures along the substitution series pointing to subtle ionic rearrangements. At

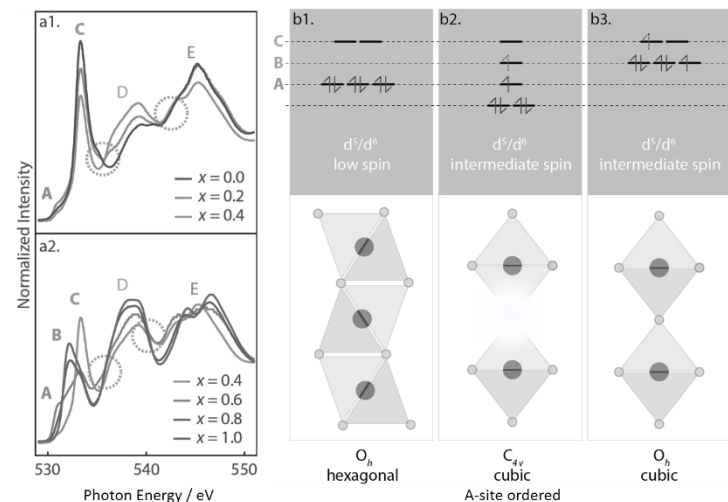


Figure 1 – Oxygen K-Edge X-Ray Absorption spectra (a) showing miniscule effects across the hexagonal-to-cubic transition (a1) and profound electronic rearrangements with A-site ordering (a2). The corresponding structural BO_6 octahedral motifs and the proposed electronic structure is shown in (b).

higher Pr contents we found A-site ordering to form the double perovskite structure $AA'B_2O_{6-d}$, which shows a profound impact on the electronic structure close to the Fermi level of the CoO_6 building block which is generally found to be responsible for electrochemical activity. Surprisingly, aliovalent A-site substitution, as well as the hexagonal to cubic transition, only has a minuscule effect on the electronic structure and the electrocatalytic efficiency, contrary to the A-site ordering showing a considerable one attributed to the rearrangement of the electronic states induced by ordering effects. Additionally, in oriented thin films of the ordered polymorph we found a hugely anisotropic electronic structure at the CoO_6 manifold by means of X-Ray linear dichroism spectroscopy pointing to a further avenue to engineer the density of states at the Fermi level and with that electrocatalytic performance.