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Atomic-resolution scanning transmission electron microscopy study of the valence state transition in $(Pr_{0.85}Y_{0.15})_{0.7}Ca_{0.3}CoO_3$[1] ROBERT KLIE, AHMET GULEC, University of Illinois at Chicago, DANIEL PHELAN, CHRIS LEIGHTON, University of Minnesota — The observation of a first-order magnetic/electronic transition in certain Pr-based perovskite cobaltites, such as $Pr_{0.5}Ca_{0.5}CoO_3$, has attracted significant attention. A simultaneous metal to insulator transition, a sharp drop in the magnetic moment and a change in the electronic structure has been reported to occur below T_{MIT}. It was suggested that the low-temperature phase is stabilized by a shift of the mixed valence Co^{3+}/Co^{4+} toward pure Co^{3+}, enabled by a valence change of Pr^{3+} to Pr^{4+}. We present an atomic-scale study of $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ using atomic-resolution imaging, electron energy-loss spectroscopy and in-situ cooling experiments in a scanning transmission electron microscope. The valence state transition in $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ occurs at a transition temperature $T_{MIT} \sim 135$K for $y = 0.15$ and the in-situ cooling experiments are conducted at 90 K. At room temperature, we find oxygen vacancy ordering associated with a Co valence state ordering and we will demonstrate that the electron transfer occurs from Pr to Co below the transition temperature. The oxygen vacancy ordering disappears as a result of the Co valence state transition. The effects of oxygen mobility, sample homogeneity and the impact on the observed transition will be discussed.

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