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$_3$ 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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