Supplemental Information

Detailed information about Rietveld refinement of X-ray powder diffraction pattern of $CaCoO_3$.

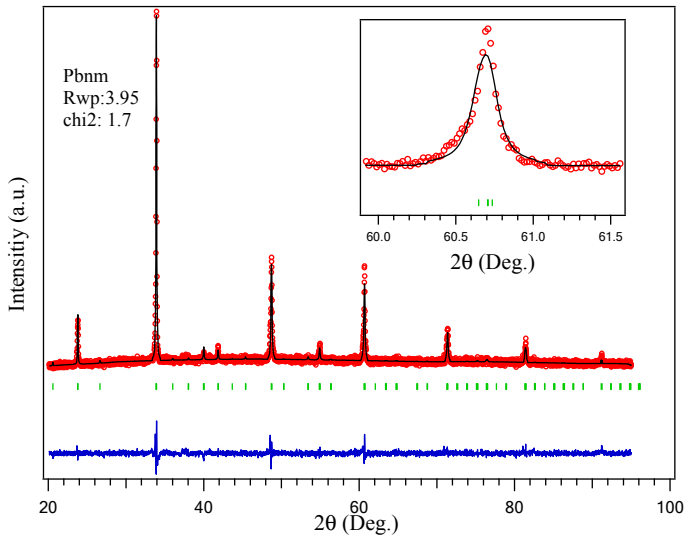

Figure 1. The result of Rietveld refinement with the *Pbnm* structural model. Intensities of simulated peaks are general lower than the observed peaks at high angles, as shown in the insert. Moreover, simulated peaks look broader than the observed peaks due to structural distortions built in the model.

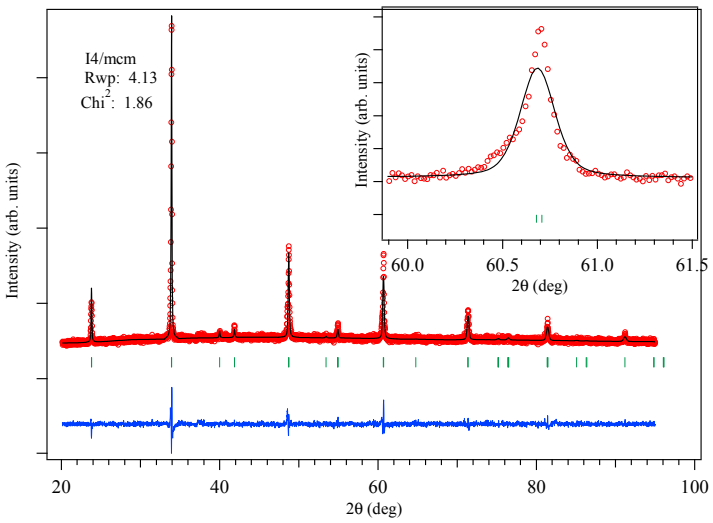

Figure 2. The result of Rietveld refinement with the *I4/mcm* structural model. Intensities of simulated peaks are general lower than the observed peaks at high angles, as shown in the insert. Moreover, simulated peaks look broader than the observed peaks due to structural distortions built in the model.

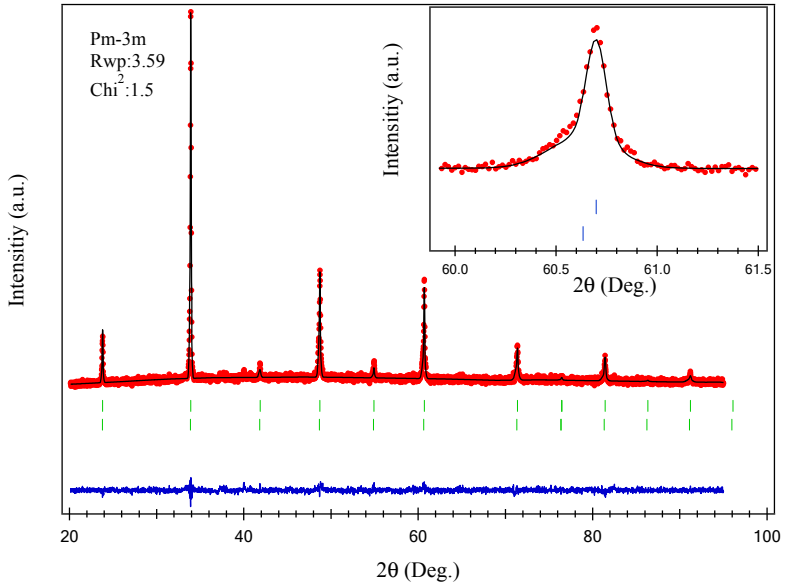

Figure 3. The result of Rietveld refinement with the *Pm-3m* structural model. Intensities of simulated peaks are close to the observed peaks at high angles and the profile matches well too, as shown in the insert. However, we have noticed a small shoulder at the lower angle side of all diffraction peaks, which led us to introduce a second cubic phase with slightly larger lattice parameter in the refinement.