SUPPLEMENTAL

"Zhang-Rice physics and anomalous copper states in A-site ordered perovskites"

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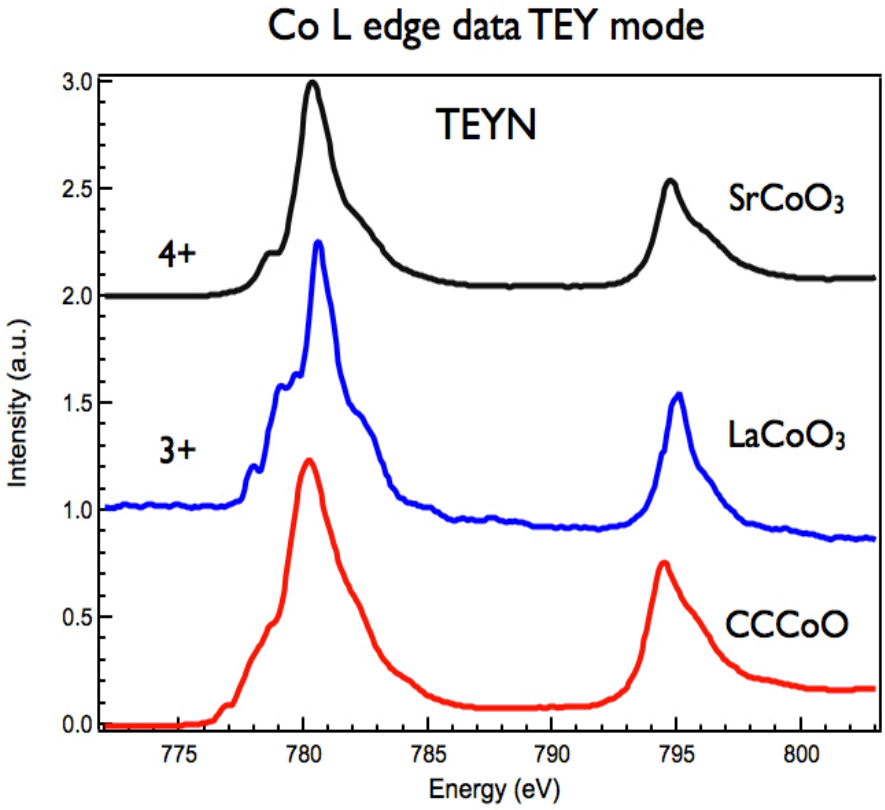
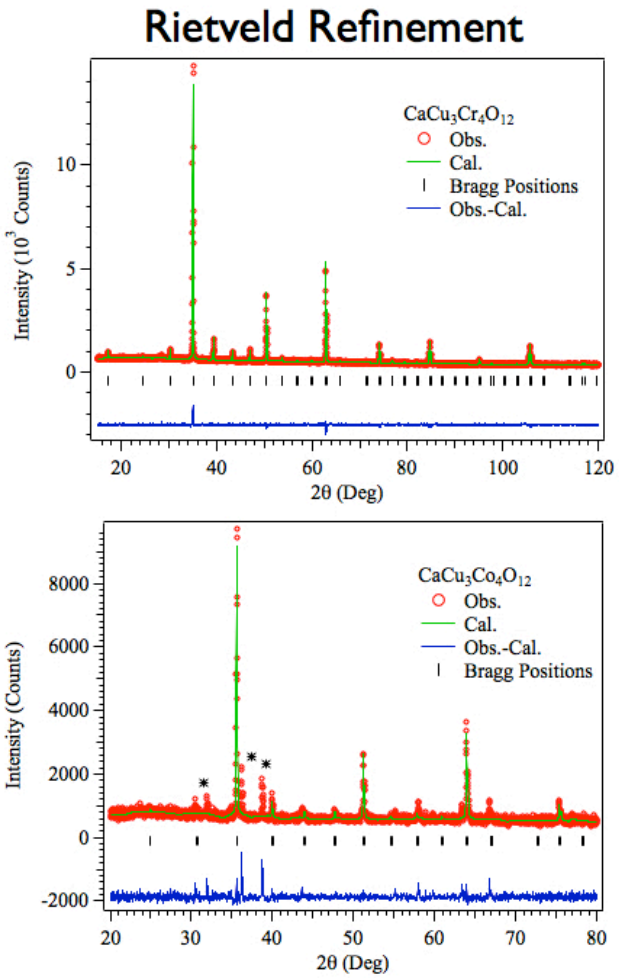
Supplemental Figure S1 shows XAS data for the CCCoO and Co reference samples taken in TEY mode. In good agreement with the main text, the absorption data affirm that the CCCoO sample Co valency is neither pure 3+ nor 4+, but rather a combination of the two (i.e. mixed valency).



Supplemental Figure S1: XAS data for CCCoO and reference samples obtained in TEY mode.

Supplemental Figure S2 shows the Reitveld refinement for the two A-site order perovskites $CaCu_3Cr_4O_{12}$ and $CaCu_3Co_4O_{12}$, showing that the proper crystal structure has been obtained for both samples. A small amount of CuO impurity is present for CCCoO, which is observed as the very small spectral weight impurity peak (<2%) in the Cu L-edge XAS. Such an impurity phase has also been observed as a result of the synthesis process, and reported by Yamada et al [1].



Supplemental Figure S2: Reitveld refinement for CCCrO and CCCoO samples.

References for Supplemental:

[1] Yamada, Ikuya *et al*. Synthesis, Structure, and Physical Properties of A-site Ordered Perovskites $ACu_3Co_4O_{12}$ (A=Ca and Y) *Chem. Mater*. 22, 5328-32 (2010).