

## Probing the local electronic configurations in original tubular thermoelectric cobaltites

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As in all complex oxides, a strong interplay exists in Co-based systems between their lattice, spin, charge, and orbital degrees of freedom; this being a driving force to control their electronic and magnetic interactions. In Co-misfit layers, the CoO<sub>2</sub> hexagonal layers turn out to be at the origin of their metallicity combined with a large thermopower yielding promising thermoelectric (TE) properties. Here, [Bi<sub>2</sub>Sr<sub>2</sub>CoO<sub>6</sub>]<sub>n</sub>[Sr<sub>3</sub>Co<sub>6</sub>O<sub>16-δ</sub>] phase reveals an original 2D tubular structure composed of two sub-lattices interconnected through oxygen-deficient CoO<sub>x</sub> pillars (Fig. a) and b). This complex network has the ability to accommodate a certain structural and chemical flexibility by tuning locally its oxygen stoichiometry and therefore modulates its charge carriers' concentration. Hence, peculiar TE and magnetic properties were achieved with large oxygen stoichiometry changes. However the key-role played by each Co sites on the local electronic structures remains unresolved to date.

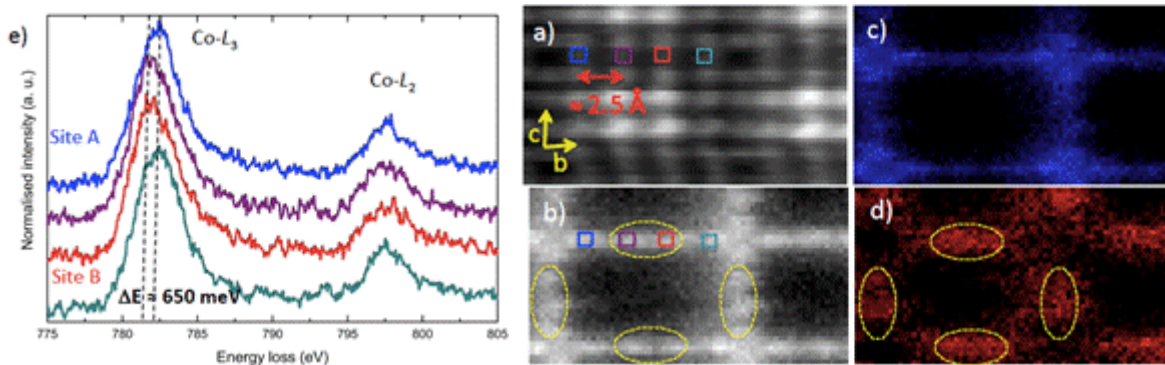


FIG. Local charge modulations in Bi-Sr-Co-O phase a) HAADF intensity and b) Co-L<sub>3</sub> maps, c) higher- and d) lower-energy component maps from vertex component analysis, and e) raw EELS Co-L<sub>2,3</sub> spectra probed at different atomic sites.

Constant and recent advances in electron spectromicroscopy techniques enables us to explore precisely the atomic and electronic structures in these low dimensional oxide systems. Here we used a Cs-corrected STEM - NION UltraSTEM 200 - fitted with EELS with a very high sensitivity optic system for tracking the subtle evolution in the near-edge fine-structures. We probe the effect of electronic charge transfer on individual Co atomic columns (Fig. e). Using advanced post-treatment analysis on non-monochromated data, we map further their two distinct electronic configurations corresponding to the direct visualisation of the Co charge modulation (Fig c) and d).

[1] D. Pelloquin et al., *J. Sol. St. Chem.* 148 (1999) 108.

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