

MS44 Crystallography in large scale facilities

MS44-04

Structural Complexity in the RP phase $\text{La}_2\text{CoO}_{4+\delta}$ Explored by Synchrotron X-ray Single-Crystal Diffraction and Neutron Powder Diffraction

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Abstract

Oxides with K_2NiF_4 type structure have been extensively studied those past decades, showing a large variety of physical and transport properties, i.e. spin, charge, orbital ordering and ionic-electronic conductivity [1]. In particular, this latter, highlighted the transition metal oxides ($\text{RE}_2\text{MO}_{4+\delta}$, RE = rare earth rare earth, M = Mn, Co, Ni, Cu), being promising materials compounds for intermediate temperature solid oxide fuel cells and oxygen separation membranes. Among them, thereby $\text{La}_2\text{CoO}_{4+\delta}$ is a special case, due to the higher stability of Co^{3+} with respect to Cu and Ni, allowing to take up more interstitial oxygen quantities, the non-stoichiometric region being $0 \leq \delta \leq 0.25$. This system is also interesting in terms of its chemical reactivity, as $\text{La}_2\text{CoO}_{4.0}$ is able to uptake oxygen spontaneously at room temperature. This kind of oxygen mobility at ambient temperature is extremely surprising, as it involves an unusual high oxygen diffusion coefficient (about $10^{-10} \text{ cm}^2/\text{s}$), making this system a unique case so far [2,3]. On the other hand, rare earth cobaltates are an outstanding example of strongly correlated electron materials, which provide a remarkable opportunity to study interplay between dimensionality, lattice, charge, spin and orbital momentum degrees of freedom.

In this study we relied on large scale facilities in order to investigate structural changes and complexity in $\text{La}_2\text{CoO}_{4+\delta}$. By neutron in situ powder diffraction (D1B @ILL, Grenoble), we followed the structural evolution occurring in the stoichiometric $\text{La}_2\text{CoO}_{4.00}$, under oxidizing atmosphere. By Synchrotron X-ray single crystal thermodiffraction on the beamline ID28 (ESRF, Grenoble) we explore the structural complexity of $\text{La}_2\text{CoO}_{4.25}$. From NPD, we report on the extremely rich phase diagram (Figure 1), from a stoichiometric orthorhombic $Bmab$ phase, passing via an ordered intermediated tetragonal phase ($F4/mmm$), to the oxygen rich orthorhombic ($Fmmm$) phase $\text{La}_2\text{CoO}_{4.25}$ and a more orthorhombic phase. Synchrotron single crystal diffraction highlights a very complex modulated structure, where all the satellites reflections, up to at least the 5th order could be indexed using a propagation vector $q = 0.75a^* + 0.5b^*$ (Figure 2), except some reflection (in green) corresponding to a checkerboard charge ordering. These reflections are also visible in NPD, suggesting a sub-mesoscopic oxygen ordering at room temperature. Surprisingly, the oxygen order persists up to 843K, corresponding to the orthogonal to tetragonal phase transition.

This study highlights the complementarity of the two diffraction techniques, neutrons and synchrotron, for the study of complex structures in which oxygen creates superstructures.

References

- [1] Goodenough, J. B. Reports on Progress in Physics 2004, 67 (11), 1915-1993.
- [2] Girgsdies, F.; Schöllhorn, R. Solid State Communications 1994, 91 (2), 111-112.
- [3] Nemudry, A.; Rudolf, P.; Schöllhorn, R. Solid State Ionics 1998, 109 (3), 213-222.

FIG.1 Phase transition of La₂CoO₄ (powder), f(T).

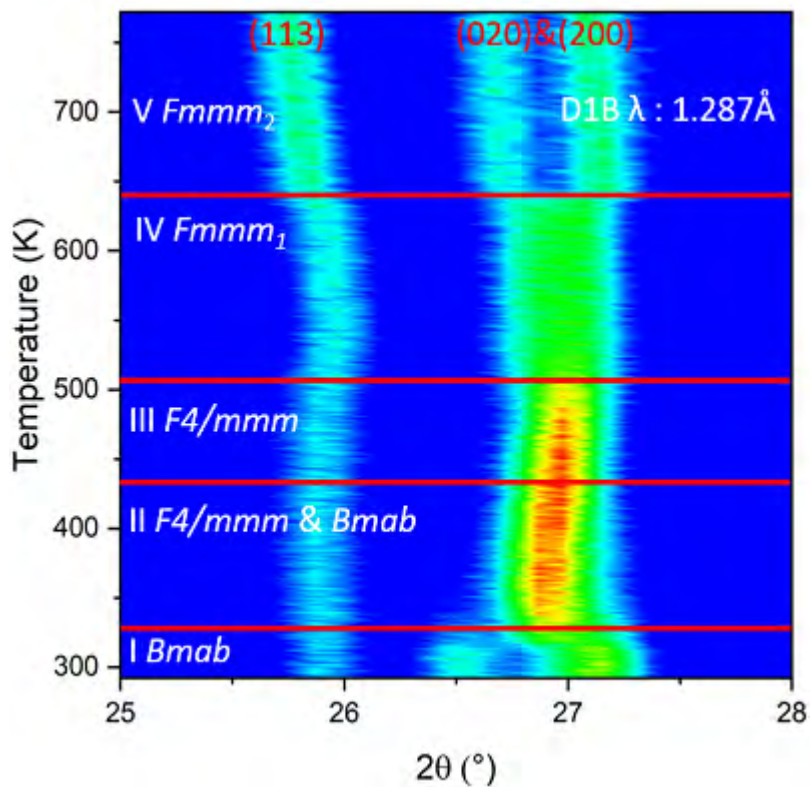


FIG.2 HK4 plane of La₂CoO_{4.25}@RT(single crystal).

