Growth and characterization of high quality $La_2CoO_{4.25}$ single crystals

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Hole-doped rare-earth Ruddlesden-Popper cobaltates La_2CoO_4 are strongly correlated electronic oxides with exciting physical and electronic properties originating from the subtle interplay of structural, orbital, charge, and spin degrees of freedom. Hole doping can be either achieved by substituting the trivalent La atoms with bivalent alkaline earth metals or by oxygen doping, yielding $La_2CoO_{4+\delta}$ with $0 \leq \delta \leq 0.25$. While cation substitution requires high synthesis temperatures, resulting into an average distribution of the A-cations, oxygen doping allows to form long-range ordering of the interstitial oxygen atoms [1]. Among the oxygen doped phases, $La_2CoO_{4.25}$ is particularly interesting. Containing an equal amount of Co^{2+}/Co^{3+}, it is the analogous to half-hole doped $La_{1.5}Sr_{0.5}CoO_4$, showing a loosely correlated checkerboard charge ordering [2-3]. Ordering phenomena and their interplay are generally difficult to explore related to weak satellite intensities and thus the availability of high purity single crystals is mandatory. Therefore, we report on the growth and characterization of high quality, centimeter sized $La_2CoO_{4.25}$ single crystals, suitable for neutron scattering experiments [4].

The main problem to overcome for crystal growth was related to the $La_2CoO_{4+\delta}$ incongruent melting and associated difficult nucleation and growth behavior. Instead of separately preparing a pre-enriched CoO seed rod as it is usually the case, a stable melt zone was obtained here using stoichiometric feed and seed rods. In this case, the molten zone regulates itself with the solidification of La_2O_3, thus continuously enriching the quantity of Co in the traveling solvent. The optimized growth parameters allowed obtaining large and homogeneous crystals without significant mosaic spread and stacking faults, as confirmed by diffraction measurements (X-rays and neutrons) as well as scanning electron microscopy coupled with elemental analysis (EDS). Post synthesis annealing at 500°C in oxygen flux yielded phase pure $La_2CoO_{4+\delta}$, showing a complex structure with a 2D modulation vector related to oxygen ordering as revealed by single crystal X-ray and neutron powder diffraction studies. In particular, X-ray single crystal diffraction revealed in addition to the main reflections, a huge amount of satellite reflections. Their intensities are nevertheless significant, suggesting strong structural modulations induced by oxygen ordering, as confirmed by neutron diffraction, but also charge ordering of Co^{2+}/Co^{3+}. Magnetic measurements coupled with neutron elastic scattering experiments show the inset of an antiferromagnetic order at about 36 K, with a complex spin structure, involving a doubling of all orthorhombic axes.

References

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