A first step towards the identification of Herbertsmithite $Zn_xCu_{4-x}(OH)_6Cl_2$ single crystal growth and point defects formation mechanisms

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Getting a crystal the magnetic ground state of which would be a perfect quantum spin liquid (QSL) constitute one of the most exciting endeavors of current materials science, because of both the scientific advancement and quantum technologies development it would trigger. Predicted in the 1970's [1], experimental breakthroughs in this direction have been more recent, since the discovery of such a property in the Herbertsmithite [2], a mineral pseudo-hexagonal solid solution of composition $Zn_xCu_{4-x}(OH)_6Cl_2$. The major current challenge in this system consists in growing such single crystals with a composition as close as possible to the $ZnCu_3(OH)_6Cl_2$ stoichiometry and with an as low as possible antisite disorder amount.

In this work, we have performed aqueous solution growth experiments in three heating zones furnaces under varying conditions of T, pH and initial $ZnCl_2$ concentrations. The obtained crystals' structural, chemical, surface and magnetic properties have been characterized, among many other techniques, by a combination of cutting-edge Laser Induced Breakdown Spectroscopy (LIBS) and synchrotron µ-Laue and µ-X-Ray Fluorescence (XRF) techniques. Indeed, a fully automated and high-frequency LIBS technique, which permits for mapping the Cu and Zn contents inside the crystals, was used to determine the actual x values ($x \approx 0.71$-1.04) in no less than 88 crystals. Combined with Le Bail refinement of associated powder XRD patterns, it led to establish that a correlation exists between the c-lattice parameter and the x value. The coupled µ-Laue/µ-XRF mappings allowed not only for an exhaustive determination of the crystalline facets ubiquitous (101) orientation, but also for a cross-characterization of the surface morphological features such as triangular pile-ups of 3D islands and macrosteps. Thanks to the high spatial resolution and high-speed data taking and manipulation, it was possible to orient -for the first time- 72 macrosteps distributed over 16 crystals, leading to the six possible step structures relevant to crystal growth. Thorough solution thermochemical calculations backed up by *in situ* Raman spectroscopy experiments permitted to identify the hierarchies of Cu- and Zn-based species likely to interact with such steps and terraces structures, and to provide beginnings of explanations for the step bunching and for the most frequently observed Cu_{Zn}^{x} antisite defect. Finally, a systematic analysis of the height-difference correlation functions (HCF) measured by AFM over large terraces and across macrosteps point to the kinetically limiting role of surface diffusion and related noise mechanisms, as exemplified by the observed HCF robust noisy Mullins universality class behaviour.

[1] Anderson, P.W., Materials Research Bulletin, **8 (2)**, pp.153-160 (1973).

[2] Shores, M., Nytko, E., Barlett, B., Nocera, D., J. Am. Chem. Soc.,**127**, pp. 13462-13463 (2005).