



# Aqueous solution growth at 200 °C and characterizations of pure, 17O- or D-based herbertsmithite $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ single crystals

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Aqueous solution growth at 200°C and characterizations of pure,  $^{17}\text{O}$ - or D-based  
herbertsmithite  $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$  single crystals

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## Abstract

The aqueous solution growth of mm-sized, pure,  $^{17}\text{O}$ - or D-enriched herbertsmithite  $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$  single crystals is presented. A relationship between  $x$  values, antisite disorder amounts and the growth temperature is established. The crystal chemical composition and stability, structural phase and antisite disorder amounts have been characterized by powder X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Electron Probe MicroAnalysis/Wavelength Dispersive Spectroscopy (EPMA/WDS), Inductively Coupled Plasma/Atomic Emission Spectroscopy analysis (ICP/AES), coupled ThermoGravimetric Analysis-Mass Spectrometry (TGA/MS) and magnetic susceptibility measurements. An unambiguous relationship between the  $c$  lattice parameter and the  $x$  value has been found.

## 1. Introduction

Spin liquids represent an exotic class of quantum matter where, despite strong exchange interactions, spins do not order or freeze down to zero temperature [1]. While well established

in one dimension for the Heisenberg spin  $S=1/2$  antiferromagnetic chain, it has been recognized that in higher dimension, frustration is the major ingredient to stabilize such a class of exotic states, which generates a true playground for novel concepts. In two dimensions, this physics is best represented by the now famous example of the Kagome Heisenberg AntiFerromagnetic (KHAF) Hamiltonian. On the Kagome lattice, frustrated triangles share corners and there is a consensus that the threefold combination of such a reduced connectivity, of  $S=1/2$  quantum spins and of frustration leads to a quantum spin liquid (QSL) state with fractional excitations. After 15 years of exploration, herbertsmithite  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  was the first true and now emblematic QSL [2]. Here,  $S=1/2$  spins are organized in perfect, well decoupled, 2D Kagome layers with large nearest neighbor interactions  $J \sim 180$  K dominating any other one by more than a factor of 20. In order to identify and study deeply QSL behavior in  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  experimentally, it is mandatory to have sizeable single crystals. In  $^{17}\text{O}$  nuclear magnetic resonance for instance, the single crystal is the only object which permits to probe selectively, by applying a magnetic field along  $\mathbf{c}$  or  $\mathbf{a}^*$ , the oxygen anion that mediates the antiferromagnetic superexchange between spin-carrying  $\text{Cu}^{2+}$  cations. Single crystals are also essential for inelastic neutron-scattering measurements, to provide crucial information on the nature of correlations and excitations.

In this work, we have investigated the influence of temperature on the growth rate, volume and antisite disorder formation in the single crystals, characterized by powder X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Electron Probe MicroAnalysis/Wavelength Dispersive Spectroscopy (EPMA/WDS), Inductively Coupled Plasma/Atomic Emission Spectroscopy analysis (ICP/AES), coupled ThermoGravimetric Analysis-Mass Spectrometry (TGA/MS) and magnetic susceptibility measurements. The morphology of the crystals was characterized by the Laue method, the thermal expansion of the lattice parameters was determined by temperature-dependent powder XRD and an experimental relationship between the Cu/Zn ratio ( $x$  value in the title formula) and the  $c$  lattice parameter was established.

## 2. Results

### 2.1. Synthesis, thermal stability and crystal growth

$1.479 \times 10^{-2}$  moles of 4N  $\text{ZnCl}_2$  and  $2.967 \times 10^{-3}$  moles of 4N5  $\text{CuO}$  (grinded) powders were first weighed inside a dry glovebox (1 ppm  $\text{H}_2\text{O}$ ). While the latter was poured at the bottom of a cleansed 4-mm thick quartz ampoule, the former was dissolved in exactly 0.25534 moles of

milli-Q water, 30%  $^{17}\text{O}$ -enriched or 99.9% D-enriched water solutions. Since natural O in water and CuO only contains  $3.7 \cdot 10^{-2} \%$   $^{17}\text{O}$   $I_N=5/2$  nuclear spins, we had to use isotope enriched water solutions to perform NMR studies. Deuterium enriched crystals are intended to neutron investigations. The dissolution is exothermic. This latter solution was then poured in the ampoule already containing the CuO powder. The quartz ampoule was then sealed under a low static vacuum (0.7 atm), and slowly heated in an oven at  $120^\circ\text{C}$  (24 h), and finally at  $180^\circ\text{C}$  (48 h). As 1 mL of 30%  $^{17}\text{O}$ -enriched water solution costs 1000 € when we were doing these experiments, we had to fix a special welding assembly with a specifically designed 8-headed ring welding nozzle in order to seal quickly and on a reproducible basis the 4-mm thick quartz tubes. The pale emerald green precipitate that forms at this stage, with no trace of unreacted black CuO, is the expected herbertsmithite phase, however poorly crystallized, as shown by routine powder XRD. The crystal growth was then undertaken in a transparent three independent heating zones furnace, programmed in such a way that the growth temperature at the bottom of the temperature sink between the first two heating zones is  $180^\circ\text{C}$ , and that the growth load temperature is  $195^\circ\text{C}$ . A typical regulation temperatures profile is  $220^\circ\text{C}/220^\circ\text{C}/200^\circ\text{C}$  and the ampoule was slightly tilted ( $\sim 10^\circ$ ) in such a way that the growth load lies at the “bottom”. Six months of growth were necessary to achieve the crystals pictured in Figure 1. We kept the furnaces “transparent”, in order to follow the nucleation and subsequent growth, even if the lack of insulation obliges to consume more heating power. Nucleation in the growth furnace is heterogeneous and multiple, because the growth rate is extremely slow.

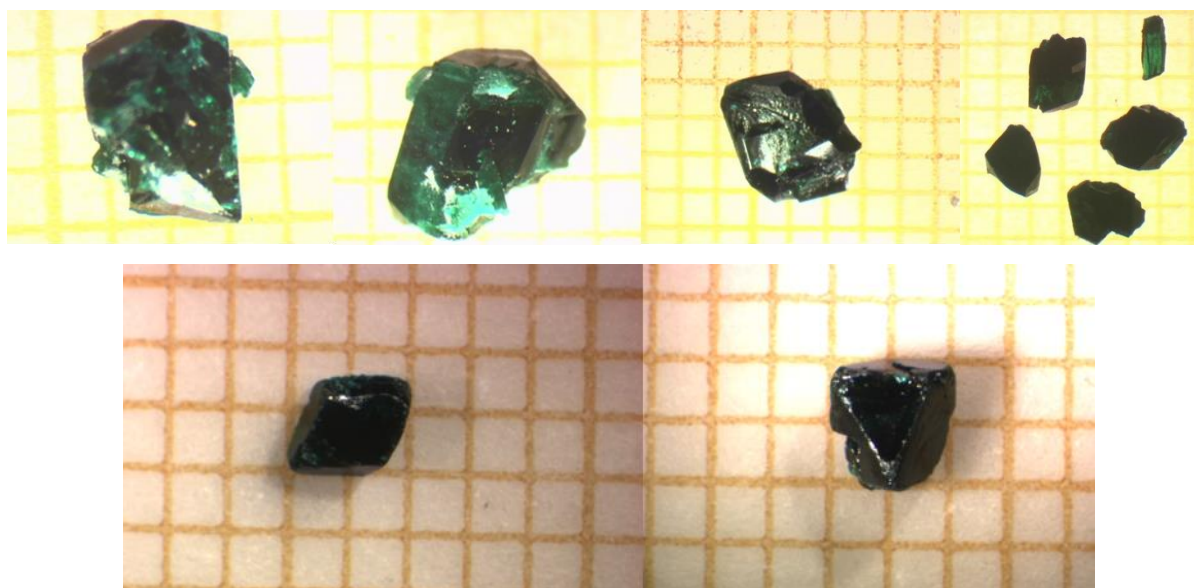
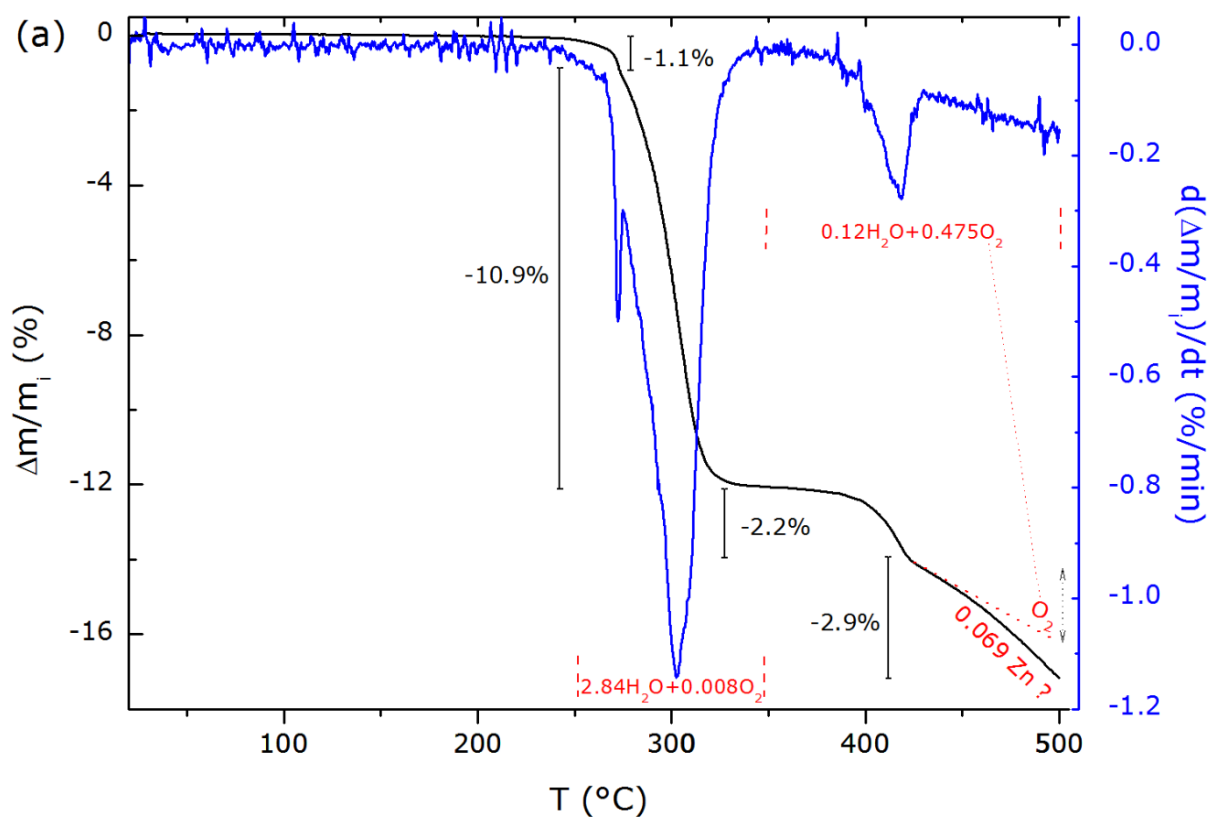


Figure 1:  $\text{ZnCu}_3(\text{OD})_6\text{Cl}_2$  (top) and  $^{17}\text{O}$ -enriched  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  (bottom) single crystals grown in aqueous solution as described in the text. The square grid dimension is 1 mm.

In order to favour the growth of a few crystals at the expense of spurious nucleation, we increased the temperature of the sink between zones 1 and 2, in successive stages from 200 to 255°C. We found that the title formula  $x$  value, which is related to the Cu/Zn ratio by this formula  $x=4/(1+\text{Cu/Zn})$ , depends on the growth temperature. This increase in growth temperature was applied as soon as the first crystallite is seen by naked eye. By doing so, we noticed that the crystals grow  $\sim 3$  times faster, but only  $\sim 3/2$  times bigger. Unfortunately, this growth rate increase goes along with a decrease of the  $x$  value, that is, an increase of the Cu/Zn ratio. When the growth temperature is kept low,  $\sim 180\text{-}185^\circ\text{C}$ ,  $x$  values obtained are typically in the range 0.93-1.04. When this temperature is increased in the  $210\text{-}250^\circ\text{C}$  range, the growth rate increases and two months, instead of six, are sufficient to get 2-3 mm-sized crystals. The  $x$  values obtained are in the range 0.7-0.8, for  $T\sim 255^\circ\text{C}$ . When the solution is kept hot several hours after the charge is consumed, a layer that covers 10% of the total surface with a typical depth 1-5  $\mu\text{m}$  (representing 0.05-0.25% of the crystal's volume) forms with a ratio Cu/Zn=1, as was consistently found by XPS and EPMA/WDS characterizations of selected crystal's surfaces. This formation is likely to be due to Cu depletion in the solution (and the Zn excess), and probably lowers the largest facets growth rate. At temperatures up to  $270^\circ\text{C}$ , gas bubbles formation was observed at the top part of the water solution.

We consequently performed a study of the thermal stability of this phase, by combined quantitative TGA/MS (Figure 2) and semi-quantitative powder XRD measurements of the decomposition product. Figure 2 (a) shows the mass loss and time derivative of a  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  powder upon heating at  $3^\circ\text{C}/\text{min}$  in Ar atmosphere in an alumina crucible, and Figure 2 (b) the number of water and dioxygen molecules lost as a function of temperature, obtained by qualitative and quantitative analysis of the gas phases by mass spectrometry. The mass loss time derivative curve displays three main peaks at  $272.3^\circ\text{C}$ ,  $302.5^\circ\text{C}$  and  $418^\circ\text{C}$ . While the two former peaks correspond mainly to water loss ( $\approx 12\%$ ), the latter is majoritarily due to  $\text{O}_2$  loss ( $\approx 5\%$ ). On Figure 2 (b), the herbertsmithite phase loses first water molecules at temperatures starting from  $255^\circ\text{C}$ , and when all possible water molecules are lost, it is  $\text{O}_2$  that is released ( $T>360^\circ\text{C}$ ). This decomposition process ends up with a complicated mixture. A tentative characterization of the amounts (by decreasing volume %) of the different phases may be given by semi-quantitative analysis of the remaining powder XRD: CuO C2/c, 35.5% ; ZnO P6<sub>3</sub>mc, 26% ; Cu(OH)Cl P2<sub>1</sub>/c, 15% ; CuCl F-43m, 11.5% ;  $\text{ZnCl}_2(\text{H}_2\text{O})_{4/3}$  Pbca, 7% ;  $\text{Cu}_2\text{Cl}(\text{OH})_3$  R-3, 4.5%. No Cl-based nor  $\text{H}_2$  gas is released in the decomposition process. At

temperatures higher than 425°C, the loss could not be identified by mass spectrometry, but it is very likely to be due to Zn ( $P_v(\text{Zn}, 475^\circ\text{C}) = 10^{-3}$  atm). Indeed, if the mass loss would be due to  $\text{O}_2$  gas alone, it would follow a straight line as the one indicated in red dashes (Fig. 2 (a)).



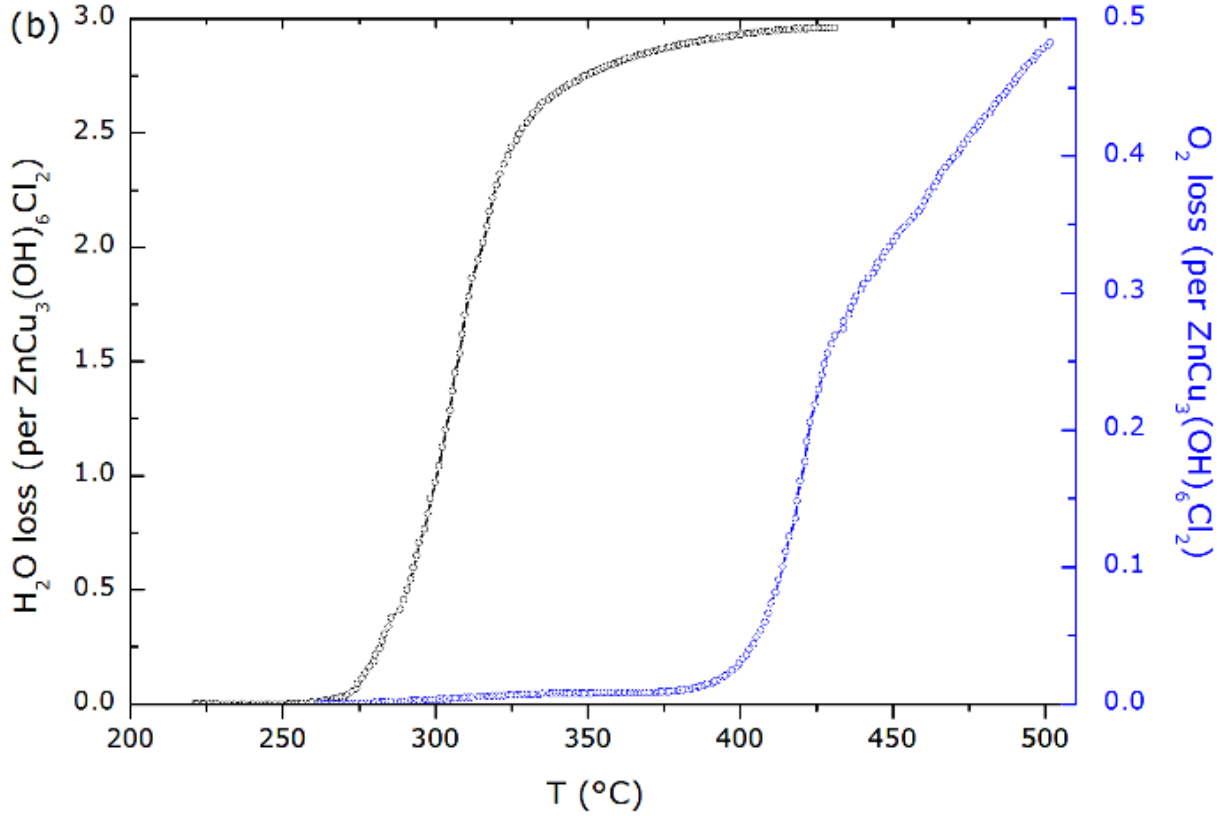


Figure 2: (a) mass loss and time derivative of a  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  powder upon heating in Ar atmosphere in an alumina crucible ; (b) number of water and dioxygen molecules lost as a function of temperature, obtained by qualitative and quantitative analysis of the gas phases by mass spectrometry.

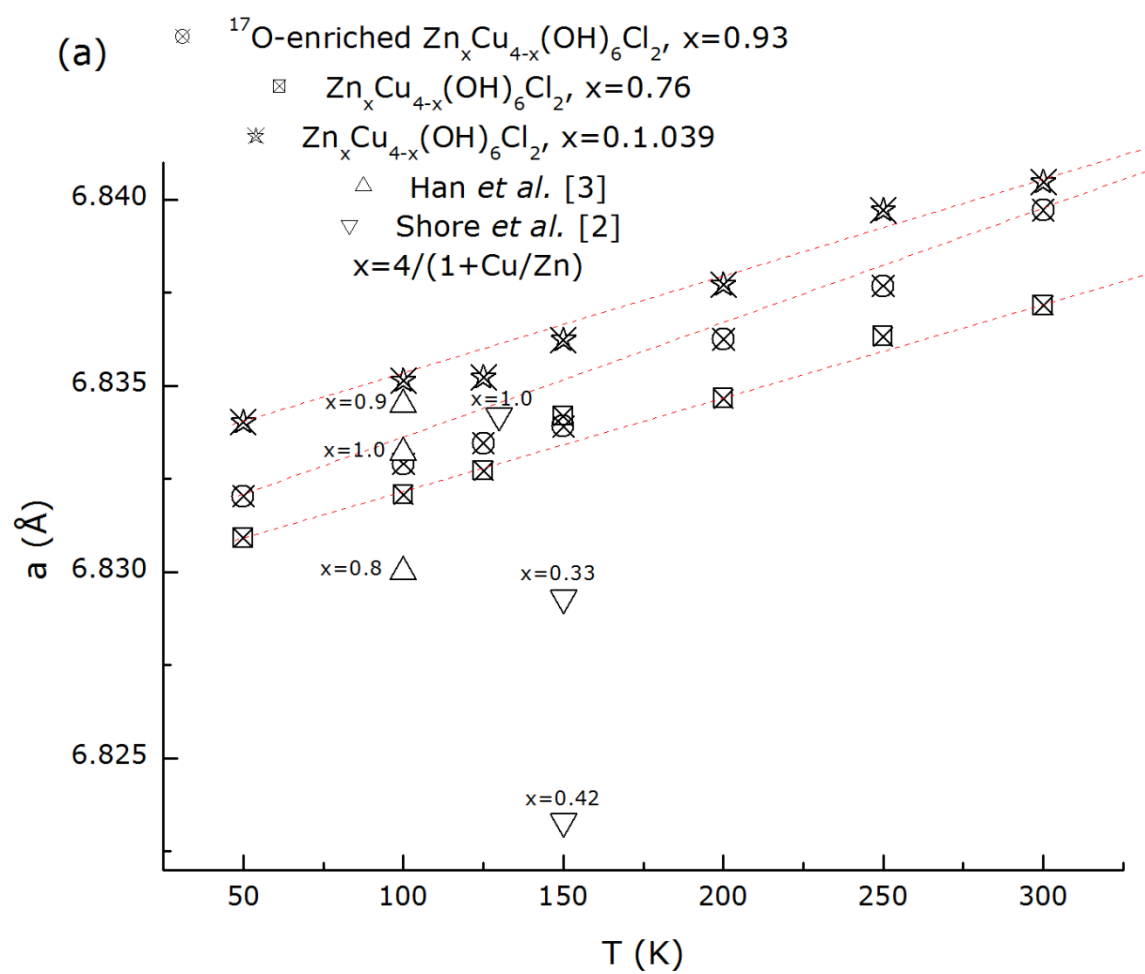
## 2.2. Chemical, structural and magnetic susceptibility characterizations

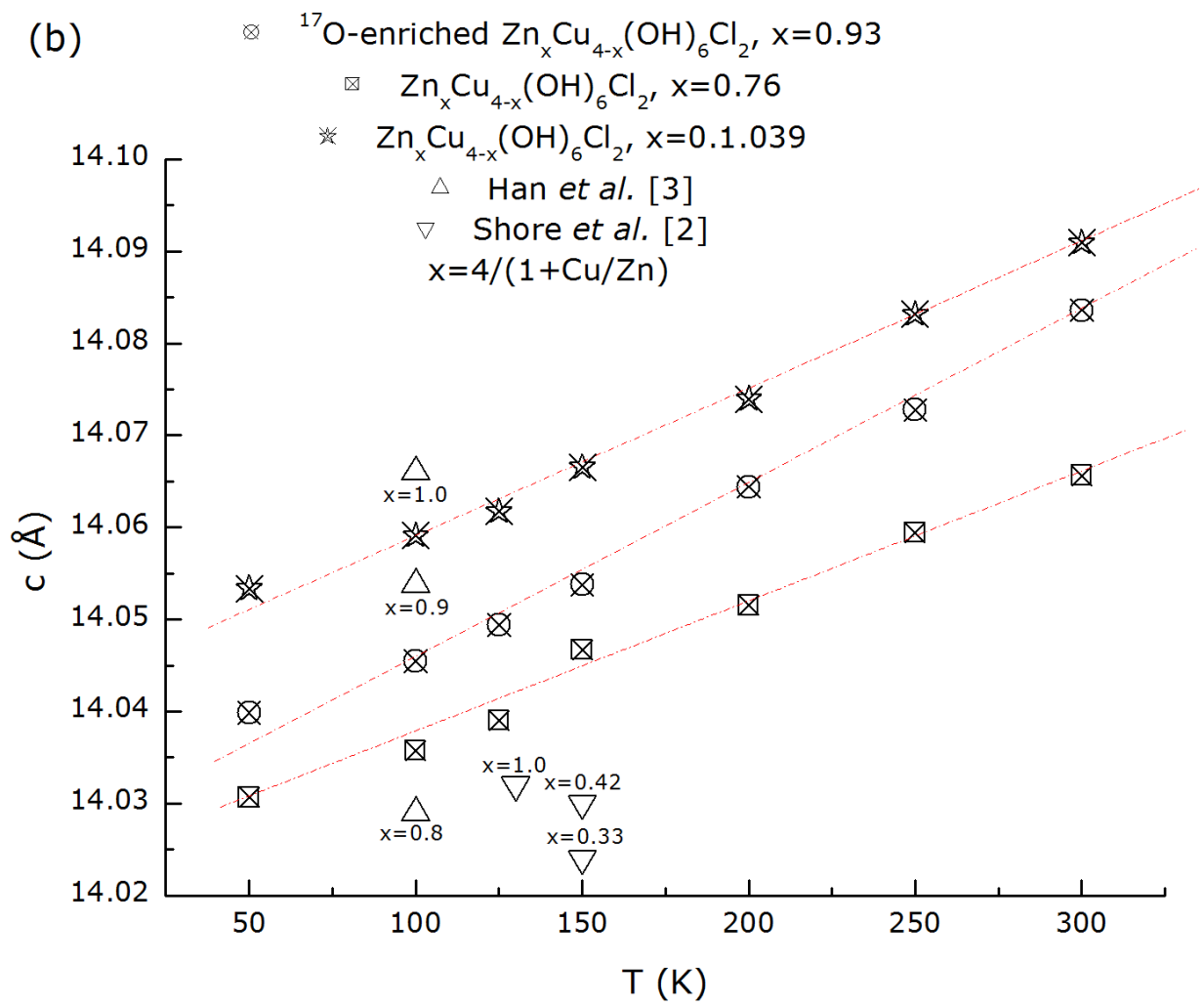
The Cl, Cu and Zn amounts in the as grown crystals were determined by EPMA/WDS analysis. For the herbertsmithite single crystal composition that was the closest to the perfect “ $\text{ZnCu}_3$ ” ratio, it was cross-checked by an ICP/AES measurement. It was necessary to optimize counting times, to prepare fresh standards and to work on powders (by grinding single crystals) to obtain reliable and reproducible data by EPMA/WDS analysis. While the Cl/Cu ratio always remains  $2/3$ , the Cu/Zn one was found to vary, leading to varying average  $x$  values from  $\approx 0.76$  to 1.04 (with  $x = 4/[1 + \text{Cu}/\text{Zn}]$ ). Routine X-ray diffraction performed on powders from the growth load or from crushed single crystals, sieved down to 63 microns, were systematically analyzed by means of Le Bail refinements. No other phase than the rhombohedral one (space group  $R\bar{3}m$ ) was found. The crystals were also found to be highly faceted and the orientation of all the facets was determined by single crystals XRD using a Laue camera in back reflection geometry. Only

(-10-1) or (101) facets were found, which confirms the observations of [4], and can be explained by the fact that it corresponds to the highest lattice spacing possible in this structure (5.455 Å). Herbertsmithite crystal growth occurs near equilibrium, over several months.

Among the many characterizations that we performed, three powders could be selected for both their consistent and reliable Cu/Zn ratio, and the maximum range of x values they span. They were investigated by XRD on different diffractometers. First, a finely tuned “Rietveld” diffractometer was used to extract the reference values of the a and c lattice parameters by LeBail refinement. Then, a “routine” diffractometer, dedicated to quick characterizations, and finally a low temperature diffractometer, were used to allow for comparisons with existing data in the literature (unfortunately available only at low temperatures). In order to quantify the room temperature shifts in a and c lattice parameters between the three diffractometers, we applied exactly the same refinement procedure with datasets recorded on the three different diffractometers. In the data of Han *et al.* [3], there is a consistent relationship between x and the c lattice parameter values at 100 K, and we found the same trend, not only at 100 K but also at room temperature (Figure 3 (b)). The data of Shores *et al.* [2] are more difficult –if not impossible- to understand. In Figure 3 (a), it is seen that for the a lattice parameter value, no such relationship could be unambiguously established. The room temperature c versus x relationship, shown in Figure 3 (c), may be used to estimate the Cu/Zn ratio just by recording a routine XRD pattern on any diffractometer provided it can be calibrated with our reference powders and a systematic refinement procedure. On average over the three samples and between 100 and 300 K, the  $1/c(300\text{ K}) \times dc/dT$  coefficient amounts to  $1.18 \times 10^{-5}\text{ K}^{-1}$ , and the  $1/a(300\text{ K}) \times da/dT$  coefficient to  $4.38 \times 10^{-6}\text{ K}^{-1}$ , which leads to a lattice parameters thermal expansion anisotropy ratio of 2.7.







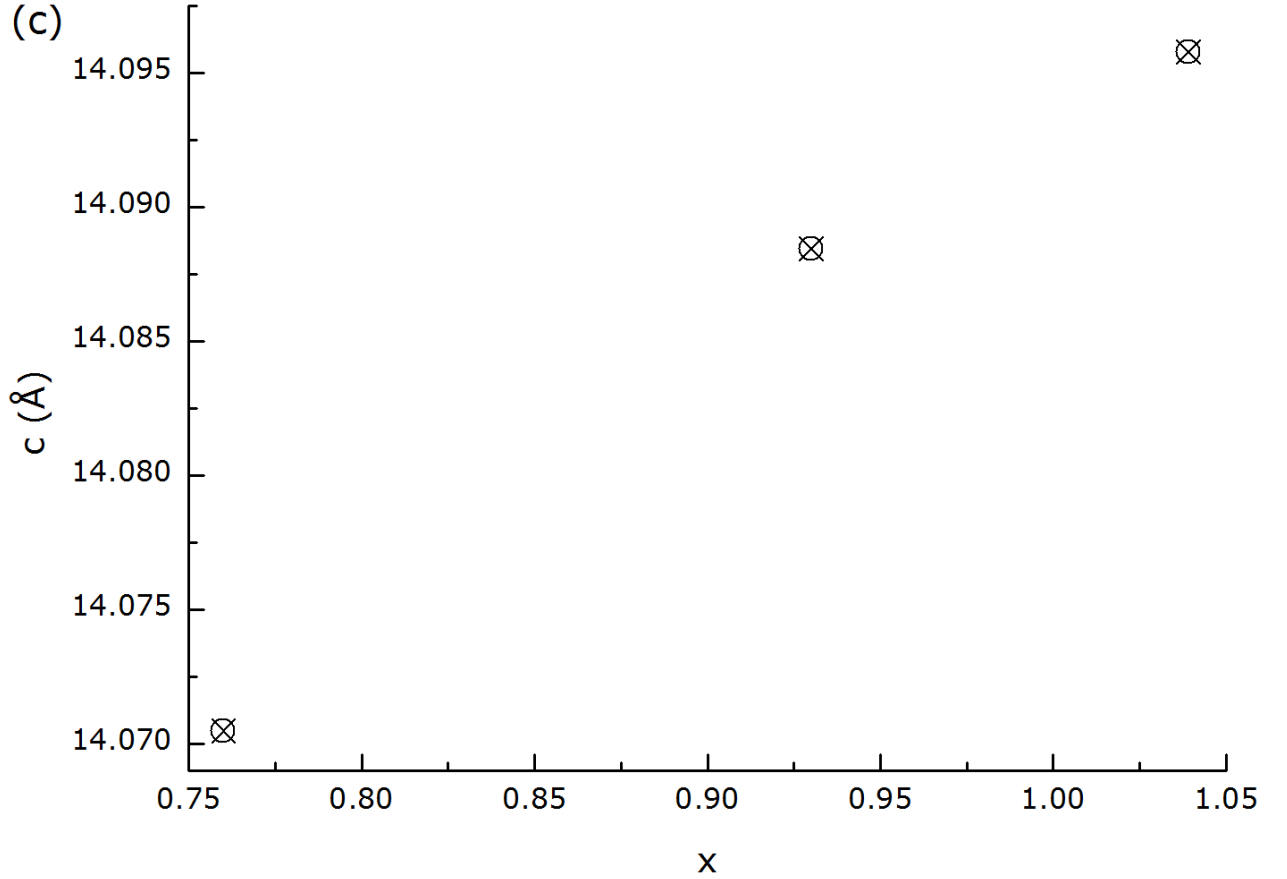


Figure 3: (a) and (b) lattice parameters as a function of temperature measured by powder XRD ; (c) relation between the c lattice parameter and the x value.

Magnetic susceptibility measurements were performed on two reference powders (Figure 4). The high- and low-temperature susceptibilities reveal two different  $\text{Cu}^{2+}$  species. The high-temperature one is due to the  $\text{Cu}^{2+}$  magnetic moments located in the Kagome planes, while the low-temperature one arises from the magnetic moments of the interplane  $\text{Cu}_{\text{Zn}^x}$  point defects. The latter contribution corresponds to quasi-decoupled spins in comparison with those in the kagome planes. It can be fitted using a Curie law with a very small Curie temperature. The Curie constant then enables one to estimate the amount of  $\text{Cu}^{2+}$ 's occupying the interlayer site [4]. The antisite disorder is estimated to be about 8% in the  $x=0.93$  crystal, and 12% in the  $x=0.76$  crystal. So, the lower the x value, or the higher the Cu/Zn ratio, the higher the antisite disorder. The fact that the c-x relationship appears so clearly in Figure 3 (c), and not the a-x one, is due to the crystallographic structure, which is made of planes of corner-sharing perfectly equilateral spin-carrying Jahn-Teller  $\text{Cu}^{2+}$  triangles, well separated from each other by planes containing only isolated nonmagnetic and non Jahn-Teller  $\text{ZnO}_6$  octahedra and  $\text{Cl}^-$  anions, and

to a large extent to the Jahn-Teller effect introduced between the Kagome planes by the  $\text{Cu}_{\text{Zn}}^x$  point disorder.

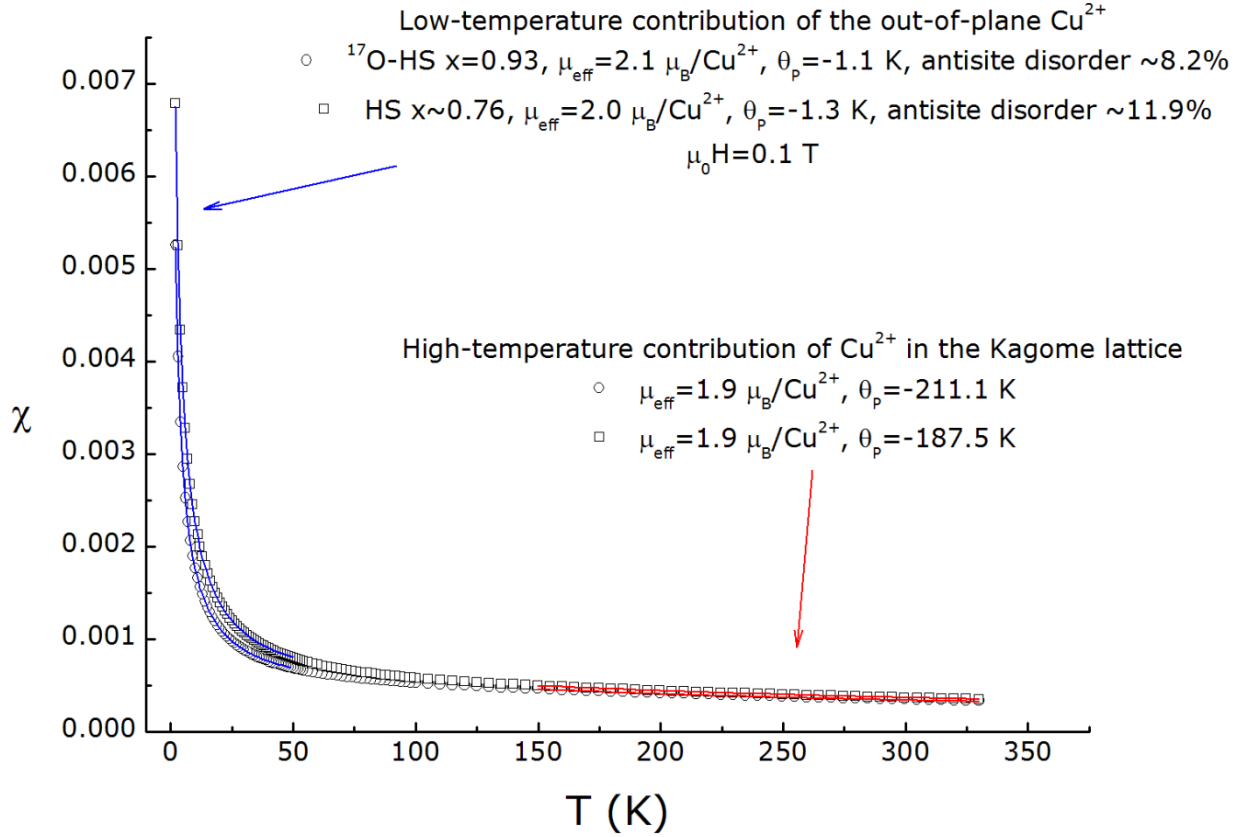


Figure 4: magnetic susceptibility in the MKSA unit system of two  $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$  reference powders.

A more recent  $^{17}\text{O}$  NMR study [5] shows that  $\text{Zn}_{\text{Cu}}^x$  point defects in the Kagome triangles also exist, giving rise to spin dimers and singlet state with an almost null magnetic susceptibility. The solid solution developed formula may be written as  $(\text{Zn}_{x-\delta'}\text{Cu}_{\delta'}) (\text{Cu}_{4-x-\delta}\text{Zn}_{\delta}) (\text{OH})_6\text{Cl}_2$ . In the  $^{17}\text{O}$ -enriched crystal investigated by NMR and pictured in Figure 1, we have  $x=0.93$ ,  $\delta\approx 0.24$  and  $\delta'\approx 0.25$ , so that the formula can be expressed as  $(\text{Zn}_{0.68}\text{Cu}_{0.25}) (\text{Cu}_{2.83}\text{Zn}_{0.24}) (\text{OH})_6\text{Cl}_2$ . Finally, an upper bound for the hyperfine and exchange interactions distributions arising from disorder in this solid solution is  $\Delta A/A \sim \Delta J/J \approx 3.6\%$  [5]. Besides, an upper bound estimate of the  $x=0.93$  composition crystal's mosaïcicity could be performed by applying the magnetic field (and orienting the crystal) along  $c$ :  $2^\circ$ . The weakness of these values reveals that the amount of crystalline disorder is weak and cannot be responsible for the absence of order in this system.

### 3. Conclusions

2 to 3 mm-sized, pure,  $^{17}\text{O}$ - or D-enriched,  $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$  single crystals have been grown in aqueous solution at temperatures around  $200^\circ\text{C}$ , with  $x$  values and antisite disorder amounts varying with the growth temperature. A relationship between the  $c$  lattice parameter and the  $x$  value has been established. The growth rate is very slow ( $<0.3$  mm/month) and all the facets are (101). Increase in growth temperature increases the growth rate ( $\sim 1$  mm/month) and the antisite disorder amount, and decreases the  $x$  value. Typical amounts of point defect disorder at inter-Kagome planes are 8% and 12% for  $x$  values of 0.93 and 0.76, respectively.

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## References

- [1] L. Balents, *Nature*, 464, 199 (2010).
- [2] M. Shores, E. Nytko, B. Barlett and D. Nocera, *J. Am. Chem. Soc.*, 127, 13462 (2005).
- [3] T. H. Han *et al.*, *Phys. Rev. B*, 83 (2011) 100402-1/4.
- [4] A. Zorko *et al.*, *Phys. Rev. Lett.*, 118 (1) (2017), 017202/1-6.
- [5] P. Khuntia *et al.*, *Nature Physics*, *under review*.