ESRF	**Experiment title:** Doping at high pressure of the prototypical high temperature suprconductor oxychloride cuprate Ca2CuO2Cl2	**Experiment number:** HC-3944
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Report:

The cuprate oxychloride $Ca_2CuO_2Cl_2$ is an oxometallate with planar coordination that can be doped with sodium ($Ca_{2-x}Na_xCuO_2Cl_2$) [1, 2] and vacacies ($Ca_{2-x}CuO_2Cl_2$) [3].

It is a high-temperature-superconducting cuprate isostructural to $La_{2-x}Sr_xCuO_4$ in its high temperature tetragonal phase (I4/mmm), but with apical oxygen replaced by chlorine ions, and without transition to other crystalline phases. It is the only superconducting cuprate composed of only low Z ions.

We measured *in-situ* diffraction at high-pressure and high-temperature on id27 in a Paris-Edinburgh press equipped with toroidal anvil, to follow the synthesis, and crystallisation process, of $Ca_{2-x}Na_xCuO_2Cl_2$. We identify its temperature domain of crystallisation for a few, selected pressures, and put in relation with the phase change in its precursors: $NaClO_4$ and NaCl.

For this, we performed 3 experiment:

Experiment 1: studying the pressure and temperature phase diagram of NaCl, $NaClO_4$, with a mixture 1:1 of the two.

Experiment 2: Synthesis of Na doped $Ca_2CuO_2Cl_2$ crystals using 1:0.2:0.2 mixture with NaCl, $NaClO_4$. In this experiment, we can not reached the final synthesis condition nor recover a sample, as the capsule exploded during the temperature ramp.

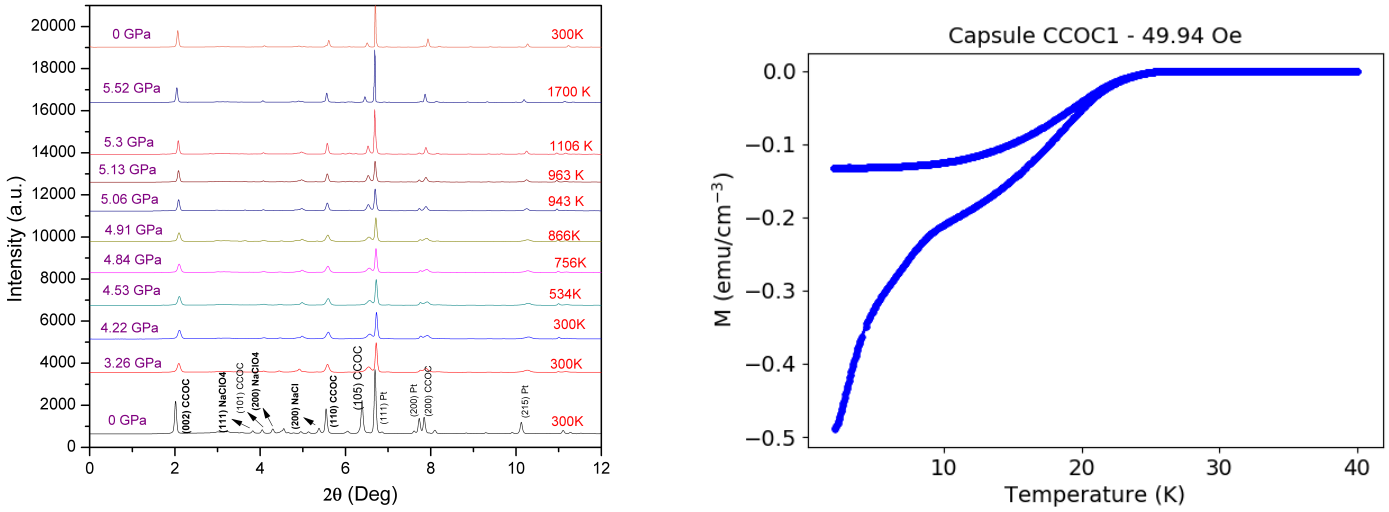

Figure 1: Left panel: In situ high pressure-high temperature XRD patterns of $Ca_2CuO_2Cl_2$: NaCl : $NaClO_4$ powder mixture (1:0.4:0.4 molar ratio respectively) at different temperature and pressure values. Right panel: low temperature magnetisation measurement of the same capsule after the experiment, measured with a VSM-SQUID (MPMS3 Quantum Design ©) at Institut Néel.

Experiment 3: Synthesis of Na doped $Ca_2CuO_2Cl_2$ crystals using a 1:0.4:0.4 mixture with NaCl, $NaClO_4$. This second experiment, shown in Fig. 1 left panel, was successful and we could recover a sample, that was superconducting, with the expected T_c for the condition with reached, as shown in Fig. 1, right panel.

We have then transposed these parameter on a *ex-situ* study, which extended the pressure domain to optimise synthesis at various doping, as well as their the crystal growth, with experiment made in a Conac28 press at Institut Néel, also equipped with toroidal anvil. We could then explore the phase diagram of $Ca_{2-x}Na_xCuO_2Cl_2$ from the maximum of the superconducting dome, down to the underdoped phase in the non-superconducting "spin glass" phase, using a relatively low synthesis temperature of 1000 °C. We could also obtain relatively large single crystals, with a useful surface for experiment of about 0.3 mm^2, for spectroscopy measurements, that we already used for ARPES experiment at SOLEIL and Photon Factory synchrotrons. We are now optimising the crystal growth parameters for each doping condition, as a final part of this study, and plan a paper relating both the *in-situ* and *ex-situ* results, when that latter part will be completed.

References

[1] Z. Hiroi, N. Kobayashi, M. Takano, Nature 371, 139 (1994).

[2] Y. Kohsaka, et al., J. Am. Chem. Soc., 124 12275 (2002).

[3] I. Yamada, et al., Phys. Rev. B 72, 224503 (2005)