ESRF	**Experiment title:** Luminescent Copper Clusters Under Pressure	**Experiment number**: **CH-6144**
Beamline: ID15B	**Date of experiment**: from: 06 Nov 2021 to: 09 Nov 2021	**Date of report**: June 30th, 2022
Shifts: 9	**Local contact(s)**: Tomasz Poreba (email: tomasz.poreba@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

PD Dr Simon Grabowsky* University of Bern, Department of Chem. Biochem. Pharm., Bern, CH

Dr Lorraine Andrade Malaspina* University of Bern, Department of Chem. Biochem. Pharm., Bern, CH

Dr Tomasz Poreba* ESRF, Grenoble, FR

Dr Anna Makal* University of Warsaw, Department of Chemistry, Warsaw, PL

Dr Michal Andrzejewski, Paul-Scherrer-Institute, Villigen, CH

Dr Matthias Vogt, Martin-Luther-Universität Halle, Nat. Fak. II, Institut für Chemie, Halle, DE

Prof Dr Jens Beckmann, University of Bremen, Department of Biology and Chemistry, Bremen, DE

Report:

The aim of the experiment was to conduct multiple high-pressure (HP) single-crystal X-ray diffraction (XRD) experiments on the crystals of $[Cu_4(PCP)_3][BF_4]$ (**Cu_4P_3**), a cationic copper cluster. The compound features intense green photoluminescence and electroluminescence at ambient pressure. We aimed to determine the relationship between the distortion of the three-dimensional structure of this copper cluster induced by pressure and its photoluminescence properties, which had been tested in preliminary studies up to 6.5 GPa. Both fresh crystals of a CH_2Cl_2 solvate of **Cu_4P_3** (**solv**) and an isostructural unsolvated single-crystal form (**uns**) were investigated.

For the solvated crystals, a total of four data series for four different single crystals were collected. The first series covered a large single crystal of **Cu_4P_3_solv** placed in a membrane diamond anvil cell (DAC) loaded with He gas as a pressure-transmitting medium (PTM) and pressurized to 0.27 GPa. The aim of this initial experiment was to determine the crystal's uniformity and decide on the optimal exposure time, hence five datasets were collected from five different locations on the crystal. Unit cell parameters (approx.: 22.33Å 18.07Å 20.72Å 90° 105.9° 90°) were confirmed and preliminary structure solution and refinements performed on all five datasets. Based on the data processing and the preliminary refinement statistics (data completeness, R_{int}, R_1, no. of non-positive definite displacement parameters), a single position, yielding the most promising structural model, was selected. The most useful exposure time of 0.5s per frame was also decided on. In the second stage, further twelve data sets were collected at pressures ranging from 0.53 GPa to 6.21 GPa. This series was intended to monitor the crystal behavior and X-ray data quality as the pressure was increased. A significant deterioration in the resolution of the X-ray data and the reflection shapes was observed above 5 GPa and the measurements were terminated.

The next data series covered three single crystals of **Cu_4P_3_solv** placed in a membrane DAC loaded with He gas as a pressure transmitting medium and initially pressurized to 0.19 GPa. The aim of this experiment was to

collect X-ray data to as high a pressure as possible, using three differently oriented single-crystal pieces in order to get a maximum coverage. Data for each of the three single crystals were collected at 15 increasing pressure points in a range from 0.19 GPa to 8.35 GPa. Preliminary analysis showed deterioration of the diffraction data quality for crystals 1 and 2, making them useful for structure determination only to a pressure of about 5.0 GPa. Additional five datasets were collected for the most promising crystal 3 at pressures ranging up to 12.00 GPa, yielding reliable unit-cell parameters and structural data up to 8.8 GPa. Evolution of the unit cell parameters on the most complete dataset from crystal 3 (coded as position 5) showed a slight anomaly at around 5.5-5.8 GPa, indicative of structure reorganization and a possible second order phase transition (Figure 1, left). Photographs documenting the sample's photoluminescence and its red-shift with pressure were taken at each pressure point prior to X-ray data collection.

In the case of the unsolvated **Cu_4P_3_uns** crystal form, four single-crystal pieces were selected after the short screening scans at atmospheric pressure of the initial set of eight samples. The pieces yielding the best X-ray intensities and showing no traces of the solvent in the crystal structure were placed in a membrane DAC loaded with He gas as a PTM and initially pressurized to 0.45 GPa. Diffraction datasets from all four crystals were successfully recorded at 16 pressure points ranging from the initial 0.45 GPa to 10.4 GPa. Of these 64 datasets, the ones collected up to 6.0 GPa were of sufficient quality to yield reliable crystal structures with none or very few restraints. A significant deterioration of the data resolution above 6.0 GPa resulted in data against which refinement of the full **Cu_4P_3** model was no longer possible; however, the unit cell parameters could still be reliably determined. In the case of the unsolvated crystal form, no anomalies were observed during unit cell compression (Figure 1, right).
Again, photographs documenting the sample's photoluminescence and its red-shift with pressure were taken at each pressure point prior to X-ray data collection (Figure 2). The photoluminescence of the unsolvated sample was qualitatively very similar to that of the solvated form.

In addition, a study of the dynamics of X-ray induced radiation damage under pressure was conducted on three crystals of metal-organic compounds containing stable mercury and bismuth phosphines. A single crystal of each compound was placed in a membrane DAC loaded with He gas as a PTM and initially mildly pressurized. A total of five series, containing a dataset per each crystal, was collected at pressures: 1 atm, 0.74 GPa, 1.54 GPa, 3.51 GPa and 1 atm accordingly, with different radiation doses. The experiments showed that radiation damage is not suppressed or mitigated by applying pressure in these compounds.

Cu_4P_3_solv **Cu_4P_3_uns**

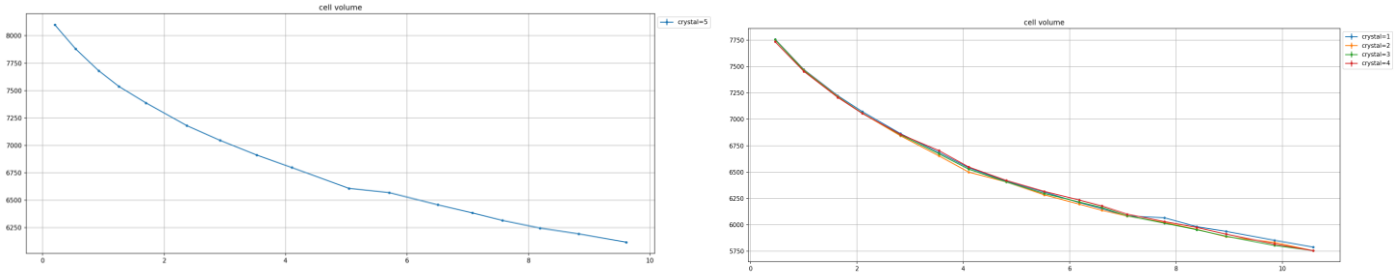

Figure 1. Evolution of the unit cell volume with pressure for the solvated and the unsolvated forms of **Cu_4P_3**.

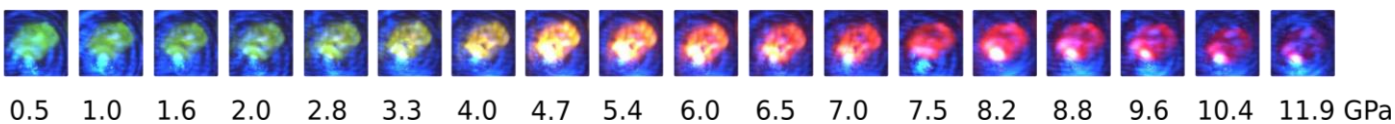

Figure 2. Tracking *in-situ* luminescence evolution on the beamline in the DAC for unsolvated **Cu_4P_3**