ESRF	**Experiment title:** *Machine learning-driven exploratory syntheses in molten salts of copper-based compounds for electrocatalytic reduction of carbon dioxide*	**Experiment number:** MA 5619
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Aim of the proposal

In this proposal, we were aiming at reaching new phases richer in copper which could present high activity and selectivity for the reaction reduction of CO_2. These unreported materials have been identified by using machine learning to predict the formation energy of compounds throughout the Cu-Si-P phase diagram from the data reported for known binary and ternary compounds. To reach this aim, we use a lab-made set-up especially designed to probe *in situ* inorganic molten salts, the reaction media we use to perform these reactions. First, we focused on *in situ* X-ray diffraction to identify reaction intermediates and temperatures of structural transformations in order to drive synthetic efforts in the lab for isolating these new metastable compounds. Second, we addressed several reaction pathways by *in situ* total X-ray scattering to perform sequential Pair Distribution Function analysis.

1. **Set-up**

For the experiment we employed a sample environment setup designed and developed within our group, that is, a capillary vertical oven. This oven has been designed to mimic lab syntheses, including handling of liquid media in an open vessel while flushing inert atmosphere in this vessel (1 mm diameter fused silica capillary). The first shift of the experiment was dedicated to setting up the oven on the beamline and adjusting the geometry of the hutch to reach the *q* range required for XRD experiments. For further description of the *in situ* oven, the reader may refer to the experimental report of the MA-4760 and MA-5188 experiments. The setup was improved compared to these two previous experiments: new heating elements in $Pt_{0.9}Ir_{0.1}$ alloy were used for enhanced thermal stability, and a new temperature

controller was brought by the users with an adequately tuned PID for better temperature control with precision of +/- 1 °C.

2. Selected results on chemical reactions from *in situ* XRD: case of copper silicophosphides

We have studied a range of chemical reactions in molten salts based on copper, silicon and phosphorus, especially in eutectic LiCl/KCl which is yielding *ex situ* in our lab mixtures of copper phosphides, copper silicophosphides and copper silicides. **Figure 1** shows two examples of XRD patterns recorded at one position (plotted as heatmaps) of the crystallization mechanism of predicted $Cu_7Si_6P_7$ (**Figure 1-left**) and Cu_3SiP_6 (**Figure 1-right**). Room temperature reference patterns on top were extracted from the PDF4+ database.
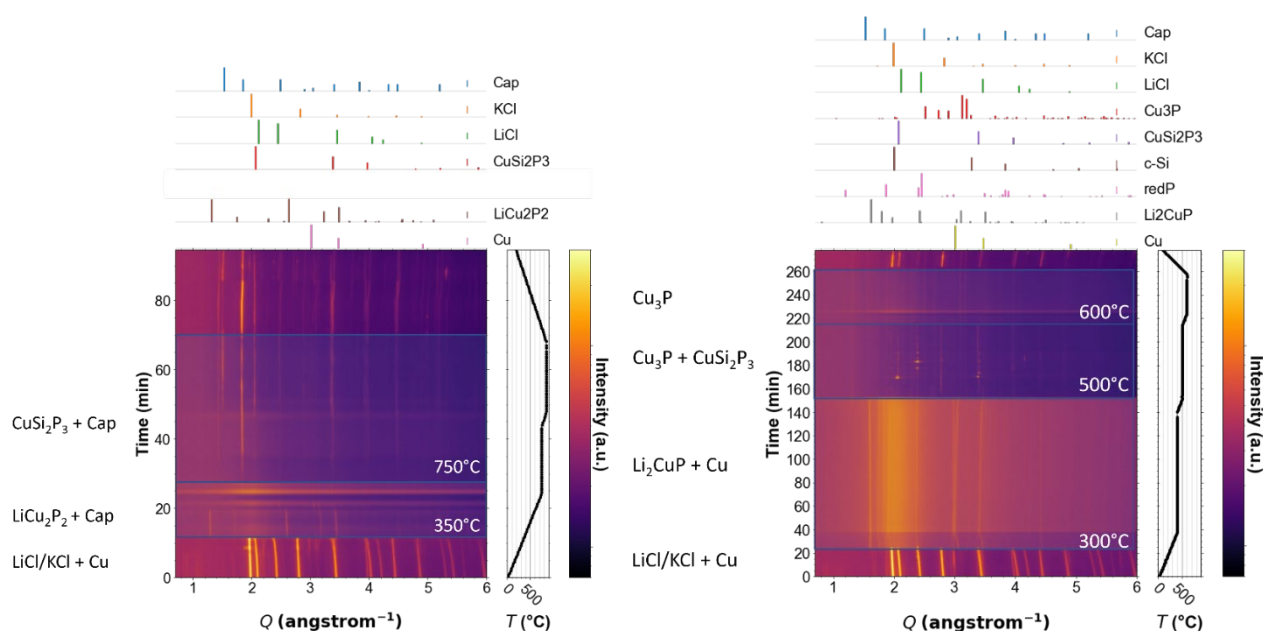

Figure 1. *In situ XRD patterns, with corresponding room temperature reference patterns from the PDF4+ database on the top. The different stages are highlighted in the time y axis, with identification of the main crystalline phases. Monitoring of reactions targeting (left) $Cu_7Si_6P_7$ and (right) Cu_3SiP_6.*

For targeting $Cu_7Si_6P_7$, we have monitored the reaction in LiCl/KCl of commercial copper chloride $CuCl_2$ with red phosphorus, lab-made sodium silicide Na_4Si_4 and sodium hydride as reducing agent. We identify three main stages during the heating up. First, the initial powdered mixture is solid, made mainly of KCl and LiCl, where $CuCl_2$ reduced in $Cu^{(0)}$ is detected by the peak at 3 A^{-1}. When the salt mixture melts at around 350 °C, we observe an abrupt change of the XRD patterns, which we assign to the formation of a lithium copper phosphide intermediate phase $LiCu_2P_2$. The formation of this phase can be easily explained by the reduction of $Cu^{(0)}$ into $[Cu_2P_2]^-$ by the large amount of reducing species (sodium silicide and sodium hydride) in the

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reaction medium. It also indicates the highest reactivity of red phosphorus with copper compared to silicon. As no silicon-based crystalline phase can be detected, we speculate that silicon is present as amorphous silicon or forms solubilized species, like silicon tetrachloride. Finally, we observe the formation of the most stable ternary phase $CuSi_2P_3$ at 750 °C, which was already detected from lab *ex situ* results. This experiment does not evidence the formation of an unknown phase, but provides precious information regarding the reaction of copper in the presence of strongly reducing agent. It also shows that alkali cations from the melt can be inserted provided that sufficient amount of reducing agent is present.

Another example of XRD patterns is shown on the right, which targets the predicted composition Cu_3SiP_6. We monitored the reaction in LiCl/KCl of commercial copper chloride $CuCl_2$ with a lab-made sodium silicide Na_4Si_4, and lithium phosphide Li_3P as phosphorus source. We identify four main stages on the heatmap during the heating up. First, we observe the reduction of $CuCl_2$ into $Cu^{(0)}$ (main peak at 3 A^{-1}) when the powdered mixture is still solid, mainly made of LiCl and KCl. When the salt totally melts, we observe an abrupt change at 300 °C leading to the formation of Li_2CuP where the oxidation state of P is -3 as in Li_3P. The next step is surprising since the most stable ternary phase $CuSi_2P_3$ is formed at much lower temperature than by using red phosphorus (500 °C vs 750 °C). We also notice the formation of a binary copper phosphide Cu_3P at the same time. $CuSi_2P_3$ then decomposes around 600 °C and only Cu_3P is detected. Thanks to this *in situ* experiment, we highlight the impact of the nature of phosphorus sources on the crystallization rate of ternary phases. By using lithium phosphide, an ionic source of phosphorous P^{3-}, the reaction towards ionic phases such as $CuSi_2P_3$ is faster than by using red phosphorus, a source of P^0. We are currently working on understanding how to efficiently optimize the synthesis of new Cu-Si-P compounds for electrocatalysis, for example by looking for less reactive sources of phosphorus.

3. Selected results on chemical reactions from *in situ* XRD: role of p-block elements in the crystallization transformation – case of sulfur

The previous case-study highlights the importance of ionicity in the formation pathways of ternary compounds of copper. To probe further this role we have extended the work to thiophosphides, by replacing silicon by sulfur. The latter should bring more ionicity to the resulting materials. We have addressed a copper-rich thiophosphide in molten salts: Cu_7PS_6, already reported through solid-state reactions. The *ex situ* reactions in our lab yields pure ternary phase. **Figure 2** shows the XRD patterns record during the the crystallization of Cu_7PS_6 in 2.5 mm capillaries filled with a wool glass on top of the molten medium to avoid sulfur evaporation. Room temperature reference patterns on top were extracted from the PDF4+ database. We have monitored the reaction in LiCl/KCl of lab-made copper sulfide $Cu_{1.8}S$ nanoparticles as metallic precursor and sulfur source, red phosphorus as phosphorus source and additional commercial sulfur S_8. We identify only two main stages on the heatmap during the heating up. First, the

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initial powdered mixture is solid, made mainly of KCl and LiCl, where $Cu_{1.8}S$ nanoparticles are detected by the main peak at 3.2 A^{-1}. Immediately after the salt melts, around 300 °C, the Cu_7PS_6 ternary phase transforms instantaneously without any intermediate phase.
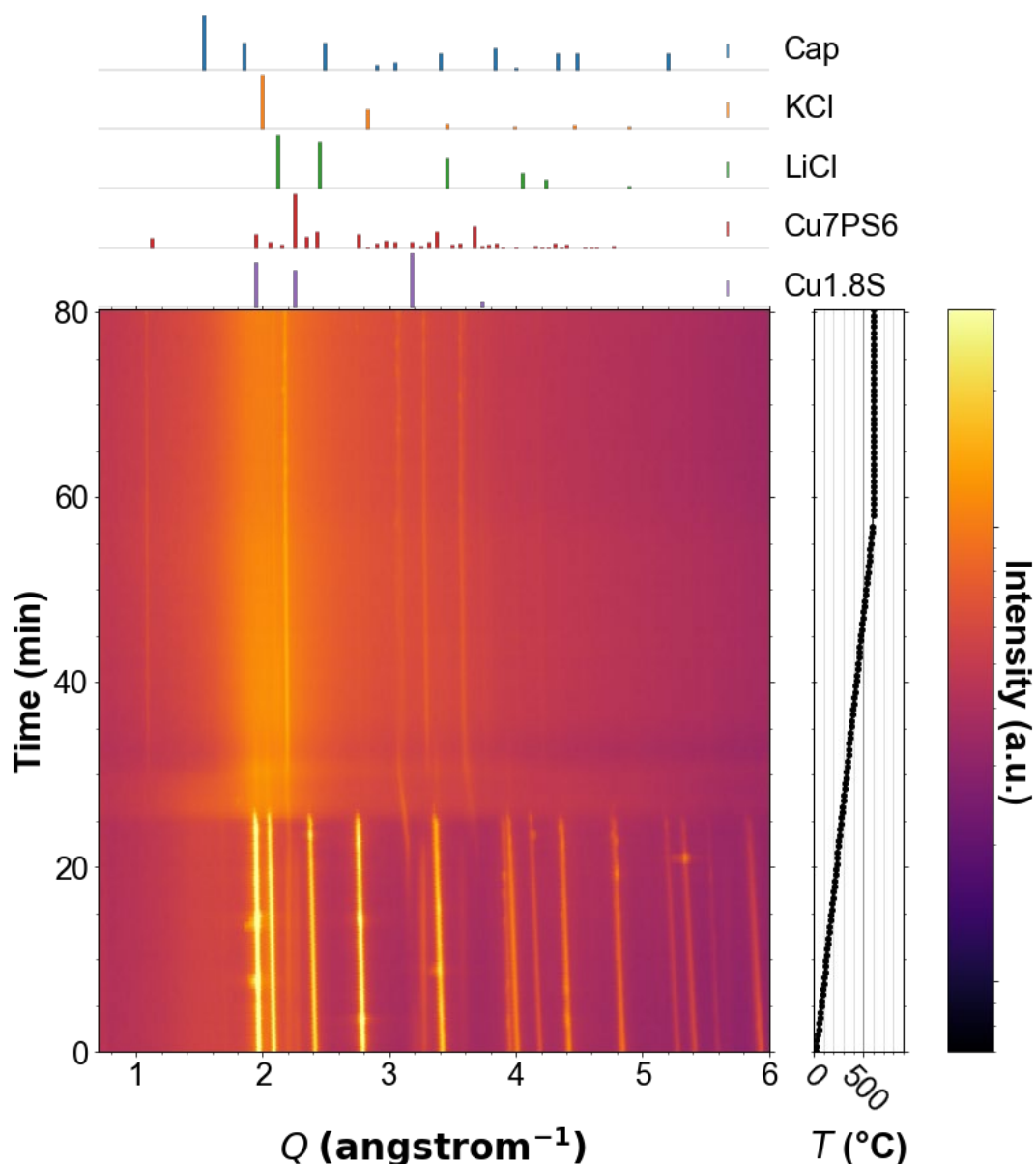

Figure 3. *In situ XRD patterns recorded during the synthesis of Cu₇PS₆, with corresponding room temperature reference patterns from the PDF4+ database on the top.*

4. *In situ* PDF experiments

We have monitored some of the aforementioned experiments a second time in total X-ray scattering mode, but bringing the detector closer to the same to get access to a Q range up to 25 Å⁻¹. These experiments require further data processing to be discussed in depth.

5. Conclusion and use of the beamtime

Overall, we have assessed about 15 reaction mixtures in alkal chloride salts with various p-block element sources (Na_4Si_4, Si nanoparticles, red phosphorus, Li_3P and sulfur) and metallic precursors ($CuCl_2$, Cu_2S bulk and $Cu_{1.8}S$ nanoparticles). This range of reactions enables identifying key parameters that can drive the formation of intermediates and then modify reaction pathways. Especially, we have highlighted the unexpected role of redox reactions and of the initial phosphorus oxidation state. Although further analysis is required to fully assign all XRD patterns, we anticipate that this new understanding will be of prime importance to design further experiments (in our lab but also on *in situ* XRD beamlines) targeting specific compounds.

The beamtime was operated very smoothly thanks to the dedication of the local manager. We have however experienced damages on our *in situ* oven, which forced regular interruptions to replace particular pieces. We will address these difficulties by changing the design for the future experiments.