EUROPEAN SYNCHROTRON RADIATION FACILITY
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Experiment Report Form

	Experiment title: Nanoparticles of metal-metalloid compounds: studying their reactivity in molten salts to discover functional solids	**Experiment number**:
Beamline: ID11	**Date of experiment**: from: 08 september 2021 to: 14 september 2021	**Date of report**: 13/09/2021
Shifts: 18	**Local contact(s)**: Jonathan WRIGHT	*Received at ESRF:*

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Report:

1. Objectives

In this experiment, we have scrutinized by *in situ* X-ray diffraction chemical reactions into inorganic molten salts. The aim was two-fold:

(1) Understand phase transformations during the reaction of metal nanoparticles with metalloid sources, which yield *ex situ* nanoparticles of compounds highly relevant for electrocatalysis of water splitting;

(2) Screen reaction conditions in the search for new phases occuring as intermediate during reactions, in order to identify the conditions of their synthesis *ex situ* in the lab.

The high flux and high energy 90 keV incident beam accessible at ID11 was necessary to assess the systems of interest mainly for two reasons: (i) the chemical species of interest were diluted; (2) the molten salt media were alkali and alkaline earth halides, highly X-ray absorbing.

2. Set-up of the experimental station

The experiment was the first opportunity to test on site a new capillary oven we have designed for performing reactions into molten salts while enabling *in situ* analysis. The first shift of the experiment was dedicated to setting up the oven on the beamline (**Figure 1**) and adjusting the geometry of the hutch to the reach the q range required for the experiment. The open design enables probing the medium in the capillary by X-ray diffraction at ID11 but also by X-ray absorption on other beamlines. The capillary holder is specifically designed to enable liquid phase reactions in the capillary while flowing gas (here inert argon gas) for air sensitive reactions. Overall, this installation was a success, the capillary position was highly reliable, as well as gas flow and the air tight capillary holder. These features allowed very fast exchange of samples, even if all of them where stored in an argon filled glovebox of the central chemistry lab. Compared to a previous installation we had tested at

DIFFABS beamline on SOLEIL, this set-up is an important progress for reliably acquiring data in a portable way on different beamlines for different techniques. Nonetheless, further improvements are required, especially enhancement of the thermal regulation through better insulation in order to ensure smoother temperature profiles.

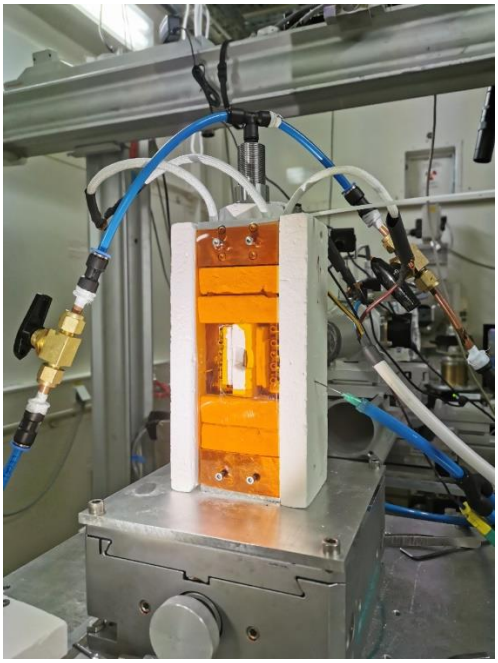

Figure 1. Picture of the molten salt capillary oven set up on ID11.

After adjusting analysis and detection conditions, the remaining shifts were dedicated to the analysis of reactions in molten salts. Most experiments were performed at 10 °C min^{-1} heating rate, which was identified as suitable to ensure crystallization to take place in the systems of interest in the lab. The capillaries were scanned continuously and diffractograms were acquired for 1.5 s at 10 positions of the capillaries. Hence, for each position, a diffractometer was assessed every ca. 30 s. The experiments dedicated to the understanding of reactions performed in the lab were performed with a dwell time of 10 to 30 min at the target temperature, according to the lab procedure. The other set of experiments dedicated to screening of reaction conditions were performed with only a ramp at 10 °C min^{-1} up to 750 or 1000 °C in some specific cases.

3. Monitoring of reactions within the nickel-boron-silicon and nickel-boron-phosphorus composition spaces

We have studied 40 reactions to explore the reaction between nickel precursors (metal nanoparticles or salts) with a boron source ($NaBH_4$) and a silicon source (Na_4Si_4) or a phosphorus source (phosphines or red phosphorus). These experiments provided very beneficial results to (1) identify the crystallization sequences during reactions and then the conditions required for *ex situ* selective synthesis of a given phase; (2) explore in only one synthesis the whole temperature range at given positions in the composition spaces, in order to identify possible new metastable compounds.

A typical set of data acquired during heating is displayed **Figure 2**, for the example of the reaction between $NiCl_2$, Na_4Si_4 and $NaBH_4$ in the molten eutectic mixture LiCl:KCl. The low temperature diffractograms exhibit high intensity diffraction peaks that correspond to the initial salts LiCl and KCl, which provide the molten salt medium upon melting (~360 °C), as observed by the disappearance of these peaks. Melting of the reaction medium is accompanied by the appearance of a strong scattering signal, which will be further analyzed in the near future by PDF. Further heating of the molten medium is accompanied by the growth of a new set of peaks, which are ascribed to the crystallization of one or several phases. Among those, one can identify $Ni_{21}Si_{12}$, although some more diffraction peaks may hint at additional phases. Further heating at 750 °C triggers the crystallization of the ternary compound Ni_6Si_2B at the expanse of the intermediate phases. Ni_6Si_2B crystallization starts at about 500 °C. This phase has been only sparsely described and only from bulk solid-state

synthesis or from the elemental melt at 950 °C.[1,2] We succeed to obtain it as a pure phase *in situ* at 750 °C, which is consistent with our *ex situ* lab experiments. Moreover, these *in situ* experiments show that this phase starts to crystallize at surprisingly low temperatures compared to the reported phase diagram. *Ex situ* lab scale experiments also demonstrate that the material is obtained as nanoparticles, thus providing the first occurrence of a ternary Ni_6Si_2B phase at the nanoscale. The intermediate formation of $Ni_{31}Si_{12}$ indicates that the ternary phase occurs through a series of crystallization events, where Si is first combined with Ni, followed by boron.

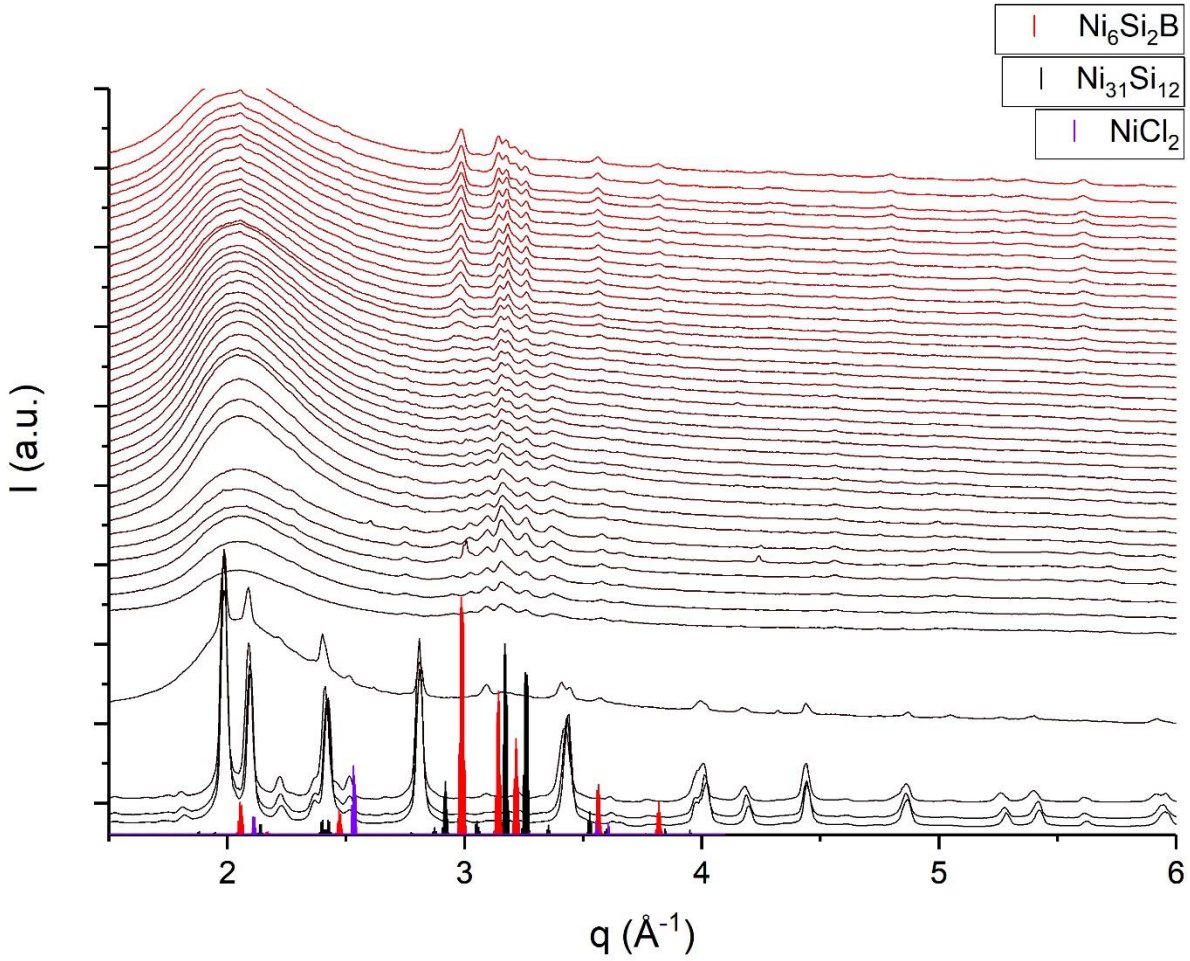

Figure 2. Series of XRD patterns recorded *in situ* during heating of a mixture of Na_4Si_4, $NaBH_4$ and $NiCl_2$ in a eutectic mixture of LiCl and KCl.

PDF analysis will be performed in the near future to analyze the structure of the ionic melt and of the identified crystalline phases appearing. We also observe in some cases the absence of XRD peaks in the first 50 °C after melting .

4. Monitoring reactions within the iron-boron composition space: feasability study

In another series of experiments, we have assessed the possibility to monitor the synthesis of iron boride FeB nanoparticles in a molten LiCl-KCl mixtures. **Figure 3** shows an experiment simulating the *ex situ* synthesis in the lab. The diffraction peaks of the targeted phase clearly appear after the salt melted, which confirms that the reaction takes in the molten medium. Before melting, a series of diffraction peaks appera in addition to those of the salts. Further examination is required to identify this component.

These results also show that we can study the crystallization of Fe- and B-based nanomaterials. This is particularly interesting in the perspective of further experiments in the future, for assessing the synthesis conditions for Fe-based 2D materials.

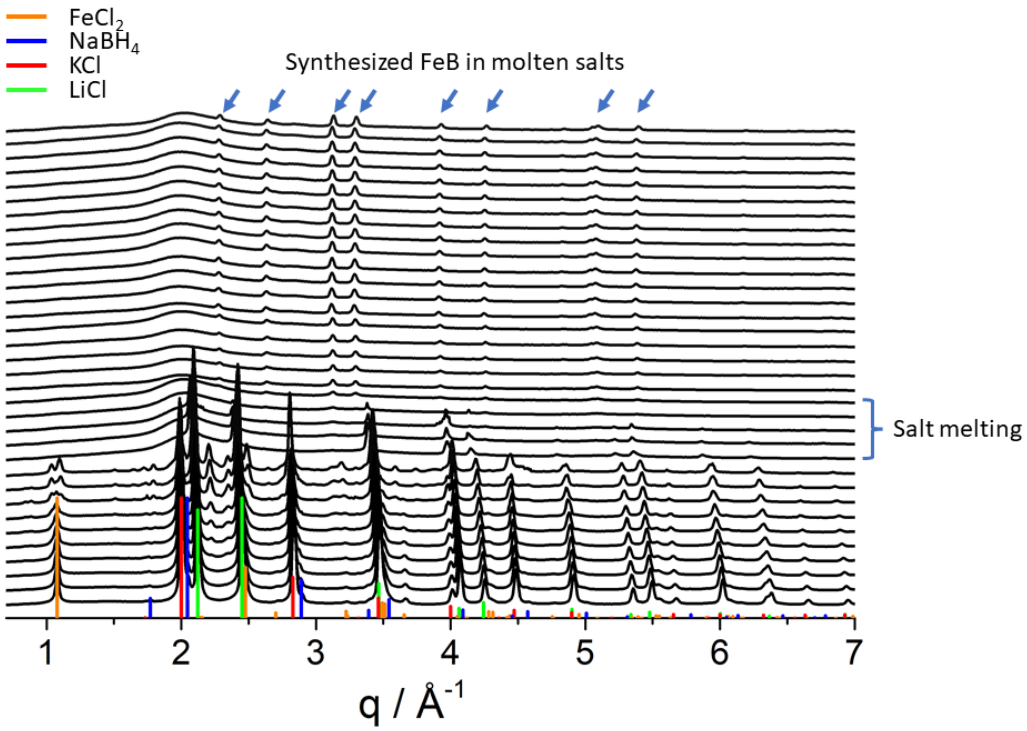

Figure 3. Series of XRD patterns recorded *in situ* during heating up to 600 °C of a mixture $FeCl_2$, $NaBH_4$ in a LiCl:KCl eutectic molten salts. The intense diffraction peaks observed at low temperature correspond to the solid LiCl and KCl salts. They disappear upon melting at 360 °C.

5. Conclusions

Overall, the experiment was fruitful in the following sense:

- It validated the design of our multipurpose oven for high temperature liquid-phase reactions. It also enabled identifying the future tracks for optimization.
- It allowed identifying the crystallization sequence, then the formation mechanisms of several binary and ternary metal-p block elements. This knowledge sheds a new light on reaction mechanisms in molten salts. It will also enable selecting the conditions for *ex situ* synthesis of nanomaterials that could not be reached before, thus hindering the study of their properties.
- Further analysis is now required to track the appearance of unidentified XRD peaks, which might indicate the occurrence of new compounds, which will then require further work for identification.

Conditions of the experiment:

This was the first experiment of the group on ID11. The local team provided excellent conditions for the experiment, and was very helpful for data retrieval and analysis. There were a series of loss of computer connection with the hutch, which resulted overall in the loss of 1 shift. Except this problem, the outcome of the experiment is very positive. Further data analysis is on the way to initiate rapidly the writing of a scientific paper on these first findings.

6. References

(1) Rundqvist, S.; Jellinek, F. The Structures of Ni_6Si_2B, Fe_2P and Some Related Phases. *Acta Chemica Scandinavica* **1959**, *13*, 425–432.

(2) Lugscheider, V. E.; Reimann, H.; Knotek, O. Das Dreistoffsystem Nickel-Bor-Silicium*. *Montscheft für Chemie* **1975**, *106*, 1155–1165.