	Experiment title: **Merging molten salt experiments with high pressure methods for synthesis of novel nanomaterials**	**Experiment number**: **MB5694**
Beamline:	**Date of experiment**: from: 18.07.2023 to: 22.07.2023	**Date of report**: 09/09/2023
Shifts:	**Local contact(s)**: Gaston Garbarino (email: gaston.garbarino@esrf.fr) Angelika Rosa (email: arosa@esrf.fr)	*Received at ESRF:*

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Report:

Aim of the proposal:

This proposal aimed at initiating a **new synthesis method** to deliver novel nanomaterials, by performing **chemical reactions in molten salts as liquid reaction media at elevated pressures** (2-15 GPa) **and high temperatures** (600-1100 °C). This approach takes inspiration from Nature, where some minerals with prominent physico-chemical properties like rubies form in evaporates in such PT conditions in the Earth's crust (Portehault et al 2022). We aimed to monitor reaction pathways as a function of pressure and temperature, by performing in situ X-Ray Diffraction (XRD) coupled with ESRF- developped resistive heating diamond anvil cell setups (Rosa et al. 2016), to identify reaction intermediates and products of synthesis at elevated PT conditions. This approach has never been done before. Our first attempt was to understand how structural transformations during liquid-phase syntheses are impacted by the nanoscale and by high pressures; and subsequently (2) identify promising compounds that could be isolated in the lab with large volume high pressure devices in order to design new electrocatalysts for H_2 production from water.

As a general strategy, we followed the room pressure protocols for the nanoparticle syntheses in molten salts [e.g. Portehault, et al. 2022 et Song et al. 2022], and we applied it to high pressure devices.

For a first study, from the planned Fe/Ni-Si system, we focused on the Ni-Si sub-system for which we have previously succeeded to reach diverse nanomaterials in molten salts at room pressure (Kumar et al. 2020 and Fig. 1A) and for which literature reports a rich high-pressure structural diversity (Dobson et al. 2016 and Fig. 1B). By capitalizing on the recent development of the resistive heated diamond anvil cells (RH-DACs) at ESRF, we applied two types of RH-DACs: external and internal. In collaboration with our beamline scientist we aimed to expand the use of this device to synthesis using molten salts and reach the mentioned PT conditions to obtain high quality diffraction patterns during heating of the reaction media.

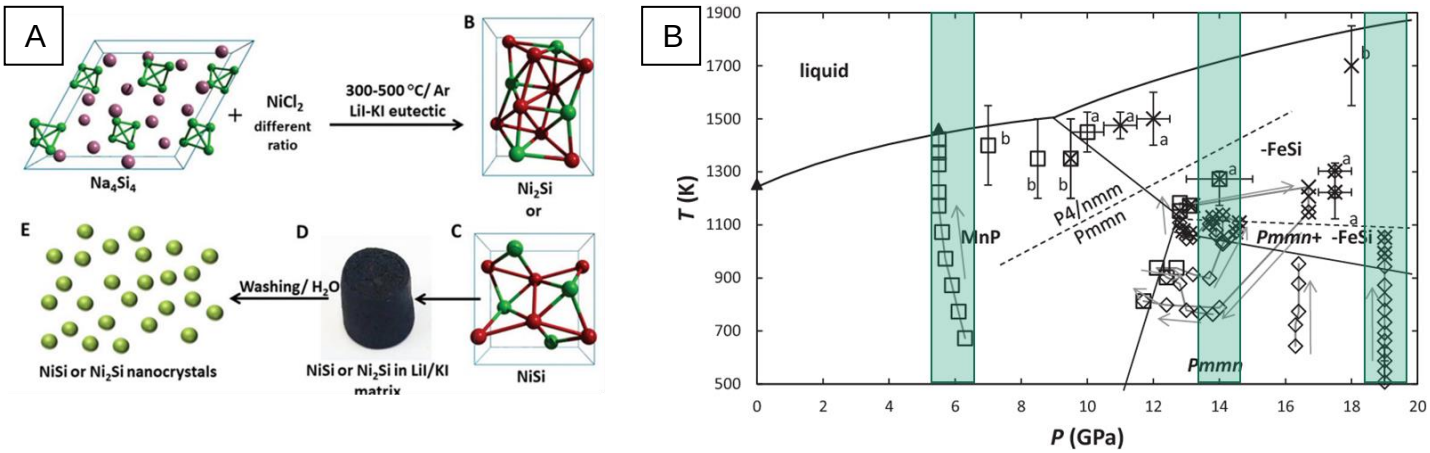

Fig. 1: A) Room pressure synthesis ptotocols for Ni_2Si and NiSi nanoparticules from Kumar et al. 2020; B) Phase diagram of the Ni-Si system at elevated PT conditions (Dobson et al., 2016)

Setup and Results:

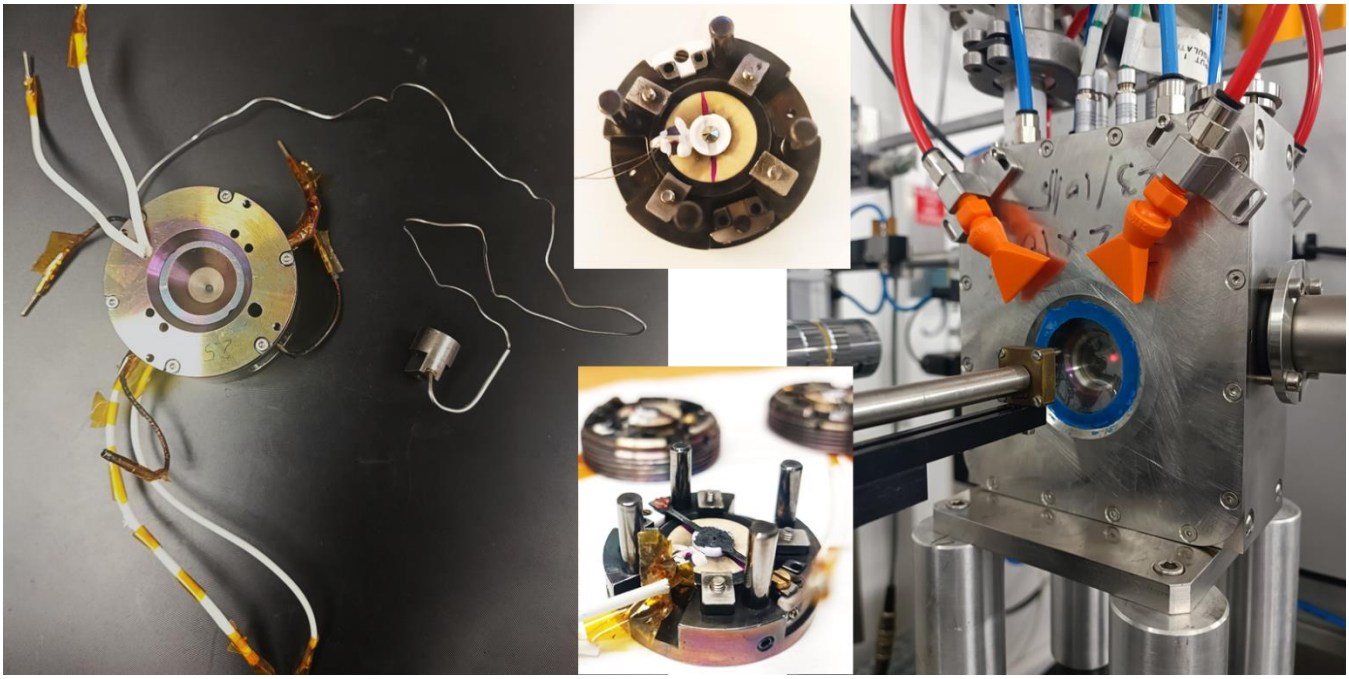

Fig. 2: Illustrations of the RH-DACs, particularly the internal heating cell which has been assembled and loaded in the glowebox prior to the beamtime in collaboration with the beamline scientists. On the right photo we see the glow coming from the cental part of the DAC, where se sample is placed. The cells are installed in the vacuum chamber to avoid oxidation of all the heating parts.

We have requested 4 cells for this experiment. Two cells for external resistive heating, which can reach max 600 °C eqipped with diamonds of 600 microns (for the lower pressures 2-5 GPa) and two cells with the internal heating system, possible to reach 900 °C, equipped with 500 and 350 micron culet diamonds (to reach 5-15 GPa). The cells were prepared during one week preparation session prior the beamtime. The external resistive heating cells required only gasket indentation, sample chamber drilling. The internal resistive heating cells requred special preparation lead by the beamline scientist A. Rosa with the help of the PI of this proposal. Firstly the gaskets were indented and drilled, subsequently the glue holding the diamonds was partly detached in order to let thermocouples to touch the diamonds for temperature measurements. The thermocouples were fixed to the cell seats using two types of glue (ceramic and condictive) in order to well isolate them from the oven part of the cell. Lastly the ceramic heater holders were put on top of the diamonds (small picture on the top of **Fig. 2**) and fixed with metallic contact arms and filled with the conductive graphite glue (small picture in the bottom of **Fig. 2**). The cells were left in a vacuum oven for 24 h, in order to improve the performance of the graphite ovens, reduce the porosity and set all parts in place. All the loadings were performed in the glove-box, as the reaction mixtures were sensitive to air.

In case of reaction with the diamonds, we have prepared several mixes, including the planned Ni-Si synthesis mix but also other chemical systems towards the synthesis of $CuBS_2$ and BP in molten salts. Due to the steep melting curve of all salts, we decided to use the eutectic LiI+KI eutectic mixture, which melts at room pressure at 350°C.

We performed 4 experiments:

- **External-RH-DAC:**
  - **NiSi_01_HT**:
    Salt: eutectic LiI :KI + precursors: Na_4Si_4 + $NiCl_2$
    first increasing P to 6 GPa (56 bars), then up to **600° C,** decreasing the pressure towards melting of the salt, when back to 0 bar – melting and then increasing pressure on the membrane until 56 bars. It appeared difficult to estimate precisely the pressure after melting of KI, but the pressure was probably in the range 1-2 GPa.
  - **BP_01_HT**:
    Salt: eutectic LiI:KI + precursors: $NaBH_4$ + red phosphorus
    first increasing P to 2 GPa (44 bars), then up to **600 °C**, decreasing the pressure towards melting of the salt, when back to 0 bar – melting and then increasing pressure on the membrane until 58 bars. It appeared difficult to estimate precisely the pressure after melting of KI, but the pressure was probably in the range 1-2 GPa, but according to the cell parameters of the Re gasket: 3 GPa

- **Internal-RH-DAC:**
  - **NiSi_02_HT**:
    Salt: eutectic LiI+KI + precursors: Na_4Si_4 + $NiCl_2$
    first increasing P to 2 GPa (25 bars), then up to **900 °C**, at which melting happened and then increasing P on the membrane until 58 bars. According to Re, P = 4 GPa
  - **CuBS2_01_HT**:
    Salt: eutectic LiI+KI + precursors: Cu_2S + S + B
    first increasing P to 4 GPa (46 bars), then up to **800 °C**, at 720° C melting and then increasing shrinking of the sample chamber, decrease of the sample signal, up to 800°C and 60 bars of membrane pressure (P ~4GPa)

To sum up this first attempt of synthesis using molten salts and DAC resistive heating systems, the main challenge was to melt the salt eutectic mixes at the target PT conditions. Each time we had to decrease the pressure in order to obtain the molten reaction medium. This has caused difficulties in estimating the pressure of the synthesis reaction. Besides, the molten salts appeared as very corrosive towards diamonds. However a strong diffuse scattering signal from the eutectic molten salt has been recorded in all 4 performed synthesis with success (e.g. **Fig. 3**). The data analysis is in

progress, together with Paris Edinbourg experiments in parallel, in order to capture the melt at elevated PT conditions and perform the synthesis.

The results of this beamtime are essential for continuation of the PhD thesis of A. Séné and will be continued further by a new PhD candidate in our team, hired both in the LCMCP and IMPMC.

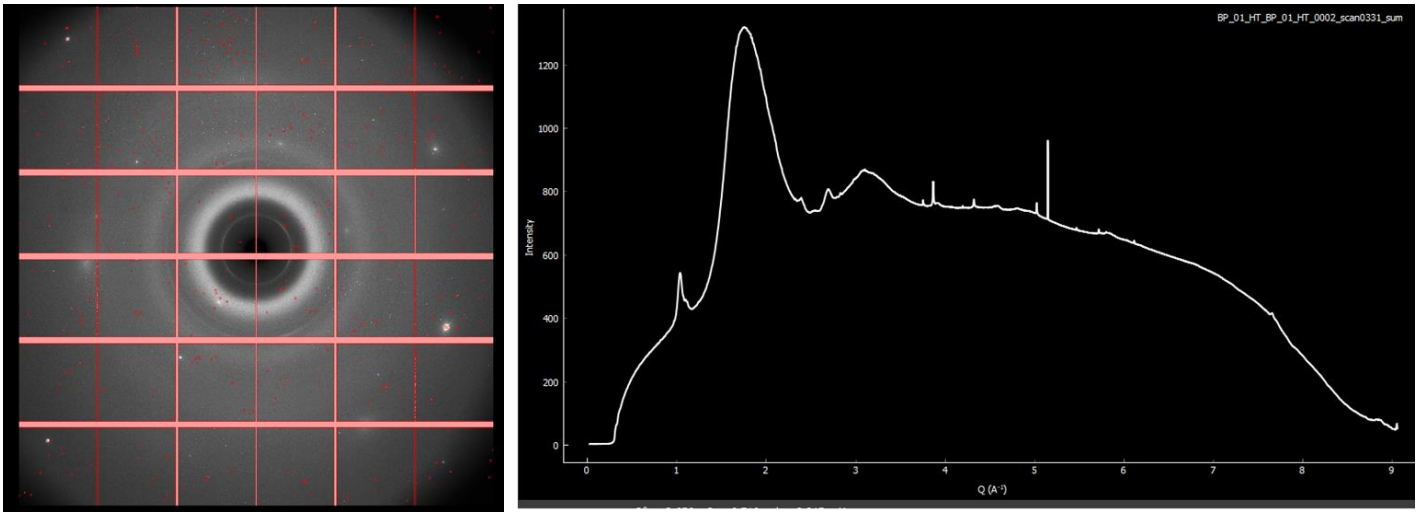

Fig. 3: Diffuse scattering signal from the molten salt eutectic mixture of LiI+KI together with some grains of the synthetised new phase at 600°C and 3 GPa (BP_01_HT experiment).

Conclusion and use of the beamtime:

As a first outcome of the beamtime, we achieved the planned PT conditions using the novel stups for external and internal RH-DACs. We succeeded to melt the salt and conduct the synthesis in the molten state, but we also detected an unexpected reactivity of the molten salt with diamonds.
Another difficulty was the evaluation of pressure. Inded, the estimatation of pressure using the Re equation of state was not reliable at the low P that was required to kep the salt melted.Thanks to the newly published equation of state of KI (Fréville et al 2023), we could however evaluat it roughly.

Unfortunetely we broke most of the diamonds. Most likely due to reaction between the molten salts and diamonds. The large change in volume upon melting could also play a role in these events.

References:

Dobson D.P., Hunt S.A., Ahmed J., Lord O.T., Wann E.T.H., Santangeli J., Wood I.G., Vočadlo L., Walker A.M., Thomson A.R., Baron M.A., Mueller H.J., Lathe C., Whitaker M., Morard G., Mezouar M. (2016) The phase diagram of NiSi under the conditions of small planetary interiors. Phys. Earth Planet. Inter. 261(B), 196–206.

Fréville R., Agnès Dewaele, Nicolas Guignot, Gaston Garbarino & Mohamed Mezouar (2023) Equation of state of KI up to 150 GPa, High Pressure Research, 43:3, 251-261,

Kumar R., Mounib Bahri, Yang Song, Francisco Gonell, Cyril Thomas, et al.. Phase selective synthesis of nickel silicide nanocrystals in molten salts for electrocatalysis of the oxygen evolution reaction. Nanoscale, 2020, 12 (28), pp.15209-15213.

Portehault , D., Gómez-Recio, I., Baron, M.A., Musumeci, V., Aymonier, C., Rouchon, V., and Le Godec, Y. (2022) Geoinspired syntheses of materials and nanomaterials. Chemical Society Reviews 51(2149)

Rosa, A. D., N. Hilairet, S. Ghosh, J.-P. Perrillat, G. Garbarino, and S. Merkel (2016), Evolution of grain sizes and orientations during phase transitions in hydrous Mg2SiO4, J. Geophys. Res. Solid Earth, 121, 7161–7176.

Song, Y., Casale, S., Miche, A., Montero, D., Laberty-Robert, C., Portehault, D. (2022) Converting silicon nanoparticles into nickel iron silicide nanocrystals within molten salts for water oxidation electrocatalysis, Journal of Materials Chemistry A, 10, 1350.