Experimental Report

11/08/2015

Proposal:	**5-25-230**	**Council:**	4/2014
Title:	In situ neutron powder diffractioninvestigation on synthesis of black Phosphorus via mineralisation route		

This proposal is continuation of: 5-25-210

Researh Area: Chemistry

Main proposer: **KOEPF Marianne**

Experimental Team: AUER Henry
GOETZE André
KOHLMANN Holger
KOEPF Marianne

Local Contact: HANSEN Thomas

Samples: black Phosphorus

Instrument	Req. Days	All. Days	From	To
D20	1	1	06/10/2014	07/10/2014

Abstract:

The formation and crystal growth of black Phosphorus by a transport reaction has not been clarified to date. We propose to investigate both at D20 with an in situ experiment. Black Phosphorus is an interesting candidate as anode material for Lithium- and Sodium-ion batteries. Therefore, the exploration of the formation and growth is essential to understand its reactivity and electrochemical behaviour, as well as the stability in relation to its other allotropes.

A mixture of red Phosphorus will be reacted with tin and tin iodide enclosed in a silica glass ampoule. By heating it up to 923 K and holding it at lower temperatures the formation of black Phosphorus will be initiated. The growth will be investigated under isothermally conditions in two consecutive experiments at 773 K and 723 K afterwards. A furnace with a Vanadium heating element, belonging to D20 will be used. The reaction rate as well as the growth kinetics will be analysed to achieve a crystal growth model of the formation of black Phosphorus.

In situ neutron powder diffraction investigation on the synthesis of black phosphorus via mineralisation route (5-25-230)

Marianne Köpf, Tom Nilges, Technical University Munich, Munich, Germany;

Holger Kohlmann, Leipzig University, Leipzig, Germany

Within this experiment the synthesis of black phosphorus (b-P) [1] via the mineralisation route [2, 3] was investigated *in situ* using neutron powder diffraction at D20. The reactants (red P, Sn and SnI_4) were enclosed within evacuated silica glass ampoules and the reaction was performed in a furnace with vanadium heating element. This furnace is belonging to D20. Data were collected every 5 min at a wavelength of λ = 186.71(2) pm.

The conditions of reaction account for a non-standard procedure and so adjustments of the equipment had to take place. Challenges in preparing the furnace setup and changing equipment reduced the allocated measurement time to approximately 16 h. Another task consisted of the calibration of the provided V-furnace. So an *in situ* calibration was performed within the second run. By adding some NaCl to the V-hull the temperature of the system was calculated via the indexed lattice parameters and the coefficient of expansion for NaCl [4]. The indexing was started with data of Barrett and Wallace [5].

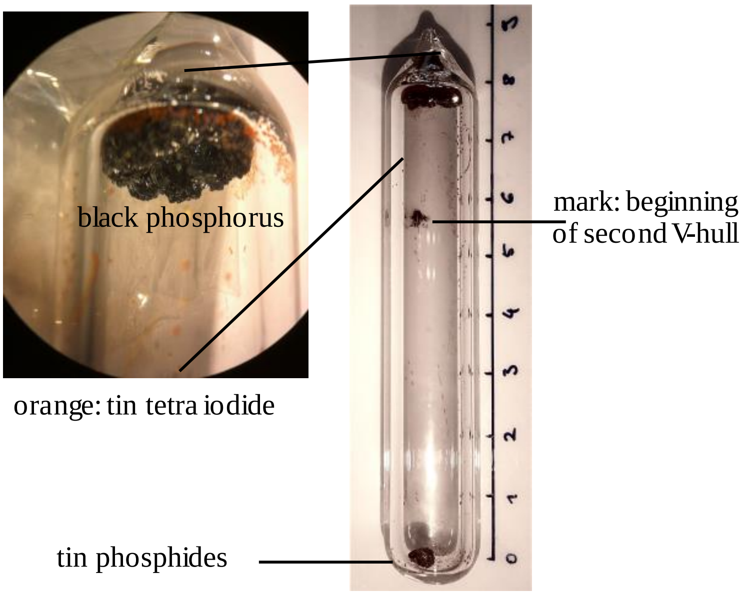

Figure 1. Ampoule of second run on synthesis of b-P.

Therefore, two shortened synthesis runs were performed. In the setup the thermocouple was placed close to the sample. During the first run, synthesis was carried out expecting the displayed temperature of the thermocouple, being similar to the sample temperature. While the first heating ramp few reflections of b-P were detected over 50 min, then they vanished and synthesis failed. A temperature window in which b-P crystallises without decomposing again is derived from this data to about 25 K.

In the second run heating was adjusted whilst performing the experiment, using the known coefficient of expansion of NaCl, as described above. An unexpected high temperature dependent discrepancy up to 108 K was observed between calculated and displayed temperature. This might be the reason of synthesis failure in the first run. During the second approach, synthesis of b-P was performed perfectly, see figure 1. However, the sink of the transport reaction was above the boundaries of the neutron beam. After finishing the *in situ* experiment, the ampoule was placed upside-down within the setup and a final measurement of about 5 min was performed, in order to verify the formation of b-P. Analysing this data the cell parameters for b-P were indexed and refined to a = 332.74(3) pm, b = 1051.24(6) pm, c = 438.81(3) pm, $\alpha = \beta = \gamma = 90°$ and GOF = 1.20, $R_P = 1.83$ and $wR_P = 2.39$ starting with data from Brown and

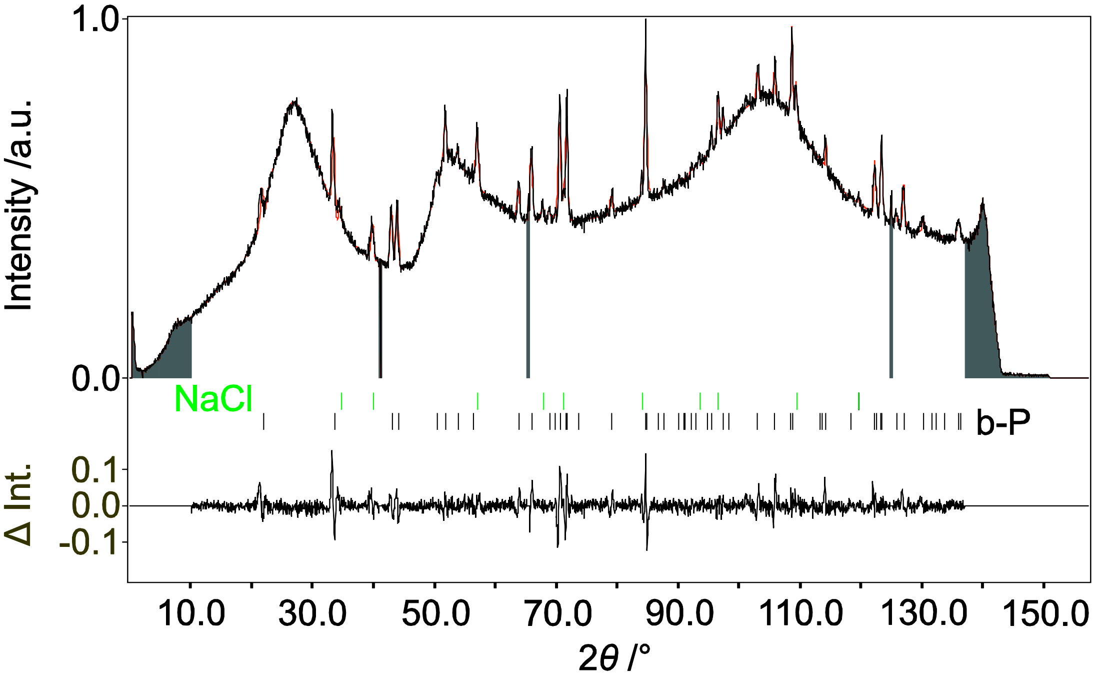

Figure 2. Neutron powder diffractogram of b-P and NaCl collected within 5 min at 390 K. Measurement is pictured in black, refinement diffractogram in red, parts which were omitted due to detector defect, are highlighted in grey. The (hkl) positions of b-P (black) and NaCl (green) are also shown. Indexing and refining of b-P resulted in a = 332.74(3) pm, b = 1051.24(6) pm, c = 438.81(3) pm, $\alpha = \beta = \gamma = 90°$. GOF = 1.20, $R_P = 1.83$ and $wR_P = 2.39$.

Rundqvist (a = 331.36(5) pm, b = 1047.8(1) pm, c = 437.63(5) pm, $\alpha = \beta = \gamma = 90°$)[1], using Jana2006 [6]. The indexed values of NaCl resulted in a temperature of 390 K for this measurement. The neutron powder data diffractogram is shown in Figure 2. Both, the collected data as well as the optical impression show perfect growing conditions for crystals of b-P.

In summary in the first experiment it was possible to find the temperature window in which b-P is crystallising without decomposing. With 25 K this window is very small. In the second run it was possible to adjust conditions for perfect crystal growth of b-P and an unexpected high temperature depended discrepancy of displayed and calculated temperature of the sample was obtained. The experiments show, in further investigations a geometrical limit for the gaseous phase transport has to be installed to keep the sink of reaction within the boundaries of the neutron beam. The evaluation of the growing mechanism, detection of possible intermediates and determination of its crystal growing kinetics are still open to perform. So, some further experiments with other ampoule geometries, e.g. shorter ampoules, will result in the needed data to gain the crystal growth kinetics of b-P.

---

[1] A. Brown, S. Rundqvist, *Acta Crystallogr.* **1965**, *19*, 684-685.

[2] S. Lange, P. Schmidt, T. Nilges, *Inorg. Chem.* **2007**, *46*, 4028-4035.

[3] M. Köpf, N. Eckstein, D. Pfister, C. Grotz, I. Krüger, M. Greiwe, T. Hansen, H. Kohlmann and T. Nilges, *Journal of Crystal Growth* **2014**, *405*, 6-10.

[4] F. D. Enck, J. G. Dommel, *J. Appl. Phys*. **1965**, *36*, 839-844.

[5] W. T. Barrett, W. E. Wallace, *J. Am. Chem. Soc.* **1954**, *76*, 366-369.

[6] V. Petricek, M. Dusek, L. Palatinus, *Z. Kristallogr.* **2014**, *229*, 345-352.