Experimental report

23/03/2017

Proposal: DIR-142 **Council:** 4/2015

Title: In situ neutron powder diffractioninvestigation on crystal growth Kinetics of black phosphorous

Research area: Chemistry

This proposal is a continuation of 5-25-210

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Samples: black Phosphorous / P

Instrument	Requested days	Allocated days	From	To
D20	4	3	20/11/2015	23/11/2015

Abstract:

In situ neutron powder diffraction investigation on crystal growth kinetics of black phosphorous (DIR-142)

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In a previous experiment (5-25-230) at the diffractometer D20 we followed the formation formation of black phosphorus [1] in situ, an allotrope which serves as precursor material for phosphorene. We were able to substantiate the fast and effective synthesis of black phosphorus upon cooling from elevated temperatures above 500°C down to 200°C within minutes [2]. During this set of experiments the question about the isothermal growth of black phosphorus arose, which were addressed in this experiment (Director Discretionary's Time, DIR-142). All data were recorded temperature dependent using the furnace available at the D20 diffractometer. The wavelength was determined from a $Na_2Ca_3Al_2F_{14}$ standard to be 186.7 pm.
Several ampoules of approx. 4 and 8 cm have been measured during this experiment with various heating and cooling rates and different temperature set points to determine isothermal growth data for the black phosphorus formation. In the first experiment described here (Figure 1) 199,9 mg red phosphorus, 8,0 mg Sn and 3,968 mg SnI_4 were placed in an ampoule of 3.8 cm lengths and 15 mm inner diameter.

Fig.1. 4 cm silica glass ampoule containing red phosphorus, tin and SnI_4 starting materials. The mixture was fully reacted to the final product black phosphorus, measured at various temperatures. Middle: Bulk residue and layered crystals of black phosphorus covered by orange spots of SnI_4. Crystal structure section of black phosphorus with a view parallel the phosphorene sheets. (040) and (132) layers are given.

Due to the silica glass ampoule of 2.5 mm wall thickness a strong background is present (see Figure 2). Nevertheless, several reflections are visible in the neutron diffraction pattern which have been used to follow the formation of black phosphorus and to determine the growth mechanism. Black phosphorus was identified by a Rietveld analysis and lattice parameters are consistent with literature values of a = 332.74(3) pm, b = 1051.24(6) pm, c = 438.81(3) pm, $\alpha = \beta = \gamma = 90°$, space group *Cmce* [2, 3] (not shown).

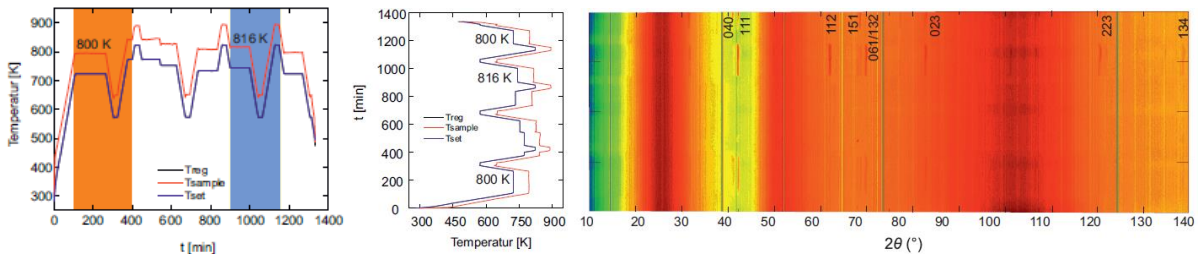

Fig. 2. Full temperature program applied to the ampoule of Figure 1. The blue line is the set temperature of the oven, the red line is the sample temperature, derived by temperature calibration of an ex situ NaCl/KCl measurement. The orange and blue area are taken into account for further discussions. Black phosphorus is formed upon heating to 800 K (orange) and is condensed from the gas phase (blue). Color coding of the intensity: blue (low) to red (high).

The first experiment was performed to prepare black phosphorus, starting from room temperature by heating to 800 K (4 K/min rate) followed by a holding period at this temperature. A detailed overview is given in Figure 3. Black phosphorus is formed at this temperature after an induction period at about 130 min experiment time.

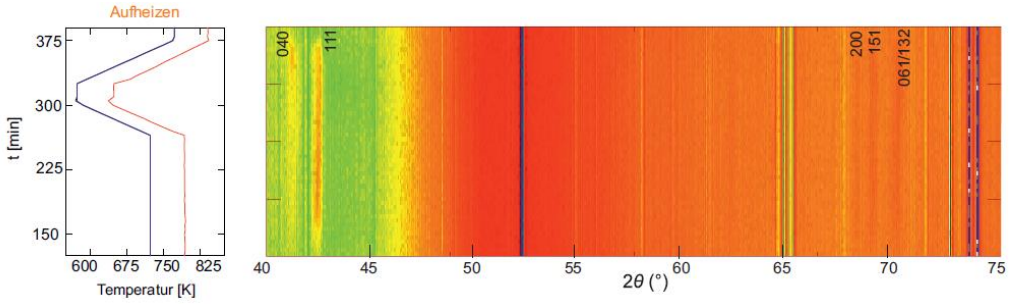

Fig. 3. Section of the temperature program applied to the ampoule of Figure 1 (orange part of Fig. 2) and neutron diffractograms for the isothermal black phosphorus formation at 800 K. Indices of the reflections are given. Non-indexed events and spots are due to detector faults and the silica glass ampoule. Color coding of the intensity: blue (low) to red (high).

The (040) reflection is the first visible one followed by (111). We carefully interpret this as a layer growth in *a*,*c* direction (this is the layer parallel to the phosphorene sheets) followed by a terrace growth to bulk crystals right after. Upon further heating up to 890 K black phosphorus fully disappeared and evaporated into the gas phase (the significant evaporation of solid black phosphorus into the gas phase starts at 830 K).

In a second experiment we investigated the formation/condensation of black phosphorus from the gas phase, cooling down from 890 K to 816 K. A set of diffractograms after cooling is given in Figure 4.

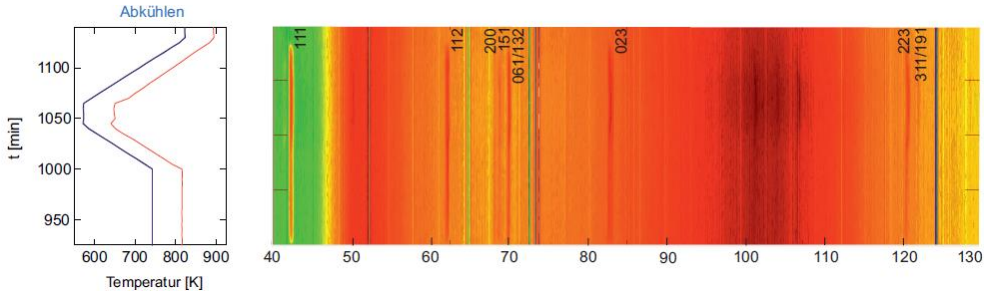

Fig. 4. Section of the temperature program applied to the ampoule of Figure 1 (blue part of Fig. 2) and neutron powder diffractograms for the isothermal black phosphorus formation at 816 K. Formation of black phosphorus by cooling a phosphorus gas phase down to 816 K. Color coding of the intensity: blue (low) to red (high).

In contrast to the previous experiment we did not observe the (040) reflection but a plethora of other ones like (111), (112), (200), (151), (132), (061), (023) and (223) right at the beginning of the crystallization process. A careful interpretation might be that here a direct bulk growth of black phosphorus took place. This is in contrast to the observation of the heating experiment performed before. One has to keep in mind that strong texture effects might occur due to the layered morphology of the crystals which can cause such differences. A fast condensation is obvious by a strong intensity increase of all reflections after cooling down from 816 K at an experiment time of 1000 minutes.

In a third control experiment we repeated experiment 1 and heated a larger amount of starting to 807 K. Literally, we found the same growth behavior than before, the (040) is the first

reflection to be observed, followed by (111) and several others, but now see a much stronger (200) reflection than observed before. This tells us, that strong texture effects are present during the measurements and interpretations towards a specific growth mechanism has to be done with care. In the isotropic growth regime after the observation of all reflections we determined the nucleation rates for the crystallization of black phosphorus in different growing directions.

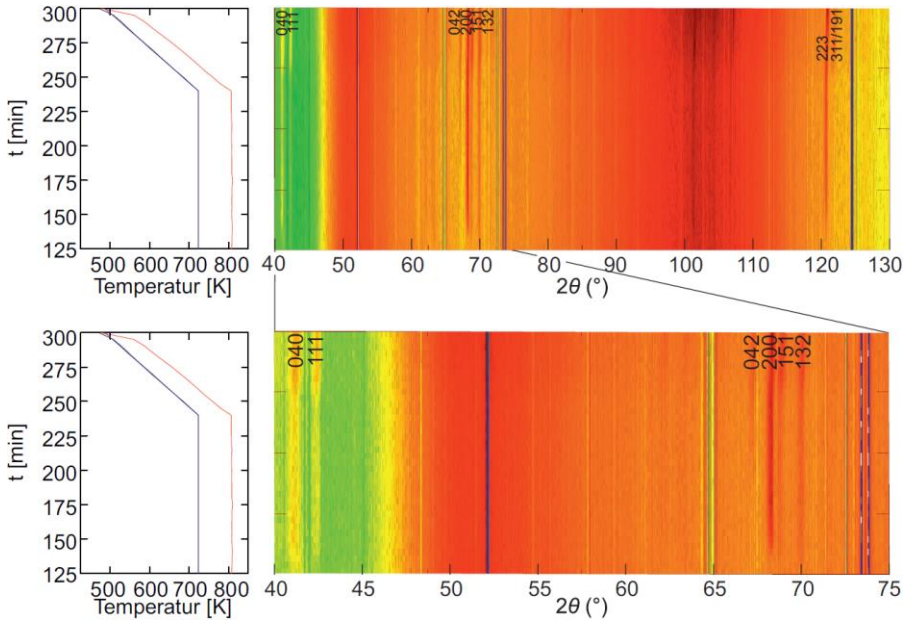

Fig. 5. Section of the temperature program applied to a 7.1 cm ampoule loaded with 400 mg of red phosphorus, 16 mg Sn and 8,032 mg SnI_4. Neutron powder diffractograms for the isothermal black phosphorus formation at 807 K. Formation of black phosphorus by heating the mixture to 807 K. Color coding of the intensity: blue (low) to red (high).

We investigated the growth for different (hkl) layers separately and determined an overall rate for the formation of black phosphorus. For an isothermal nucleation process and the assumption of isotropic particle growth, the Johnson-Mehl-Kolmogorow theory can be used to estimate such rates [4]. Assuming a zero order reaction we found 0.088 s^{-1} for the (132) layer, 0.127 s^{-1} (151), 0.329 s^{-1} (200) and 0.093 s^{-1} (040). We see a three times faster growth in *b* than a phosphorene layer growth in *ac* direction.

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