



A fast low-pressure transport route to large black phosphorus single crystals

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ABSTRACT

Black phosphorus, a promising candidate for lithium battery electrodes, can be prepared by a low-pressure transport reaction route representing the first effective and scalable access to this element modification. Crystal sizes larger than 1 cm were obtained at low-pressure conditions in silica ampoules. X-ray phase analyses, EDX, ICP-MS and optical microscopy were applied to characterize the resulting black phosphorus. The present method drastically improves the traditional preparation ways like mercury catalysis, bismuth-flux or high-pressure techniques and represents an easy, non-toxic, fast and highly efficient method to achieve black phosphorus. In contrast to a previously reported low-pressure route the present transport reaction allows an up-scaling to higher masses of starting materials, a larger black phosphorus yield and faster reaction time under retention of the high product crystallinity.

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1. Introduction

Phosphorus is an exciting element with an extraordinary variety of structural and physical properties [1] featuring four crystalline allotropes and a barely characterized amorphous red form at standard conditions. From red, white, violet, fibrous and black phosphorus the latter is the one with the highest density and the lowest reactivity [2–9].

Black phosphorus can be prepared traditionally by high-pressure routes from white or red phosphorus [10–12], mercury catalysis [13] or by recrystallization from a Bi-flux [14–16]. According to a potential use in industrial applications none of the mentioned methods are practicable due to low throughput, high toxicity or non-economic workup procedures. Large crystals of black phosphorus, suitable for the determination of physical properties, were successfully prepared by the high-pressure routes [17]. The availability of such large crystals improved the knowledge of the physical properties drastically but prevented the preparation of large sample amounts for industrial applications. A growing interest in black phosphorus is connected to the anisotropic structural features, which makes black phosphorus interesting as an electrode material for rechargeable lithium-ion batteries [18]. Due to the good electrochemical performance the black phosphorus has a reasonable potential to be used in form of a carbon–black phosphorus composite. Recently, a surprisingly low-pressure route was reported, using a mineralizer as reaction promoter, which allows the production of high-quality phos-

phorus at non-toxic conditions [19]. Thermodynamic calculations, extensive preparative work and phase analyses showed that the transformation of red into black phosphorus can be realized via a SnI_4 mineralization, an excess of red phosphorus and Au_3SnP_7 [20] as an important side-product. The transformation took place without the presence of a temperature gradient. Crystals of 1–2 mm in diameter were grown within 10 days. The applied mineralization principle itself is part of a developed synthesis principle based on the concepts introduced by Schäfer in the last century [21] which has also successfully been transferred to binary (Cu_2P_{20}) and ternary polyphosphides ($\text{M}_3\text{SnCuP}_{10}$ and M_3SnP_7 with $M = \text{Ag, Au}$ [22–24]).

2. Experimental section

2.1. Synthesis

The mineralizer SnI_4 was prepared from tin powder (1.2 g, 99.995%, Chempur) and iodine (4.0 g, resublimed, 99.999%, Chempur) in 25 ml toluene. The starting materials were refluxed for approximately 30 m until the violet color of the dissolved iodine disappeared. After decanting the hot solution from the remaining tin the orange crude product was crystallized at room temperature. The crude product was finally recrystallized from toluene and dried over molecular sieve.

AuSn was prepared in a sealed evacuated silica ampoule using an equimolar mixture of gold (Heraeus, >99.9%) and tin (Heraeus, 99.999%). A H_2/O_2 burner was used to melt the starting materials.

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After homogenization of the product the purity of AuSn was checked by X-ray powder diffraction and the phase-pure starting material was used without further purification. AuSn acts as a binary precursor to accelerate the reaction to the polyphosphide Au_3SnP_7 at elevated temperatures prior to the transport reaction.

Red phosphorus (500 mg, electronic grade, 99.999+%, Chempur) and AuSn (364 mg) were transferred to a silica ampoule of 10 cm length and an inner diameter of 10 mm. Ten milligram of SnI_4 was added and the ampoule was evacuated to pressures lower than 10^{-3} mbar. The sealed ampoule was transferred to a muffle furnace and was placed horizontally in the middle of the furnace chamber. After heating to 673 K within 1 h the temperature was held at that temperature for 2 h. In the following the temperature was raised to 873 K (1 h) and kept constant at this temperature for 23 h. In a next step the temperature was reduced to 773 K applying a cooling rate of 40 K/h and kept at that temperature before the oven was switched off. The ampoule was cooled down to room temperature within 4 h. This procedure results in the formation of black phosphorus with crystal sizes larger than 1 cm. The efficiency of the preparation process can be substantiated by a reduction of the total reaction time and the amount of AuSn to 10 h (holding time at 923 K) and 200 mg, which results in a comparable conversion ratio with slightly smaller (approx. 0.5 cm) black phosphorus crystals. A total conversion of the red to black phosphorus can be achieved by a prolongation of the reaction time to 70 h at 923 K (see below).

2.2. X-ray powder diffraction

Phase-analytical XRD experiments were performed for all starting materials and products using Guinier-cameras, operated with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Image plate technology was used as detection unit. Data were collected in the 2θ range of $15\text{--}60^\circ$ with α -quartz (Guinier) as an internal standard. Data read-out of the image plates was done using a BAS 1800 reader (Fuji), and the WinXpov program package was used for indexing and refinement purposes.

2.3. EDX analysis

Semi-quantitative analyses of our black phosphorus product were performed using a Leica 420i scanning electron microscope equipped with an energy dispersive detector (EDX, Oxford). GaP, Au and Sn were used as standards for calibration. A voltage of 20 kV was applied to the samples.

2.4. ICP-MS measurements

Quantitative analyses of our black phosphorus product were done by inductive coupled plasma (ICP)-mass spectrometry (MS) measurements using an ICP-MS 7500ce (Agilent Technologies, USA) fitted with an ApexQ (Elemental Scientific Inc., USA) unit. Target elements were tin, iodine and gold. An external calibration was performed with an internal standard solution of ^{103}Rh ($c = 1 \mu\text{g L}^{-1}$) prior to the experiments. Calibration solutions (deionized water and 5 mL HNO_3 (suprapure, Merck)) with tin, iodide and gold concentrations of $0\text{--}5 \mu\text{g L}^{-1}$ were used.

Up to 2.8 mg of sample was dissolved in 5 ml HNO_3 (suprapure, 65%, Merck) and was diluted to a total volume of 50 mL afterwards. A rhodium standard solution (^{103}Rh solution, $c = 1 \mu\text{g L}^{-1}$) was added as internal standard prior to the ICP measurements.

3. Results and discussion

After a reaction time of 32.5 h black phosphorus was achieved via a transport reaction featuring crystal sizes up to 1.5 cm in diameter. At a corner of the ampoule, the formation of the bulk residue represented by Au_3SnP_7 [20], AuSn [25], Sn_4P_3 [26,27] and AuSn_2 [28,29] could be detected (Fig. 1).

X-ray powder diffractograms were measured for all reaction products and all crystalline products were identified (see Fig. 2 and 3).

The Guinier-powder pattern of black phosphorus shows a texture effect in good accordance with the flat-bed preparation of the sample (see Fig. 4).

This texture effect was reduced prior to the measurements by a careful preparation of the flat-bed sample. The finely ground powder was transferred to the sample holder (X-ray transparent foil) without pressing the powder onto the foil in order to achieve an almost random orientation of the anisotropic crystals relative to the beam. Nevertheless, a remarkable good crystallinity can be estimated from the overall intensity and the reflection half width of the black phosphorus data.

The total amount of starting materials like Au, Sn and I in the reaction product was verified by ICP-MS measurements. Three different single crystals were selected from an 873 K preparation in order to verify the purity of black phosphorus. The crystals were separated from the bulk material without any further workup or purification steps. Au, Sn and I_2 were selected as target elements for quantitative analyses. A summary of the ICP-MS experiments is given in Table 1.

The first two measurements prove the purity of black phosphorus in good accordance with the starting purity of red phosphorus of 99.999+at%. The third sample was chosen to point

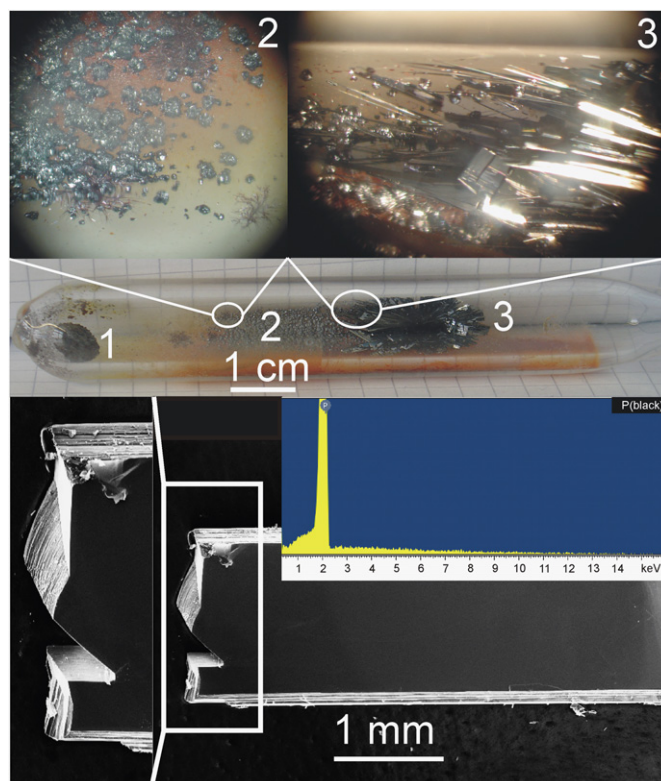


Fig. 1. Silica ampoule after the reaction procedure. 1, 2 and 3 represent the bulk residue, violet phosphorus and the main product black phosphorus. No impurity was found after EDX and ICP-MS analyses for the black phosphorus crystals. A typical EDX spectrum is given.

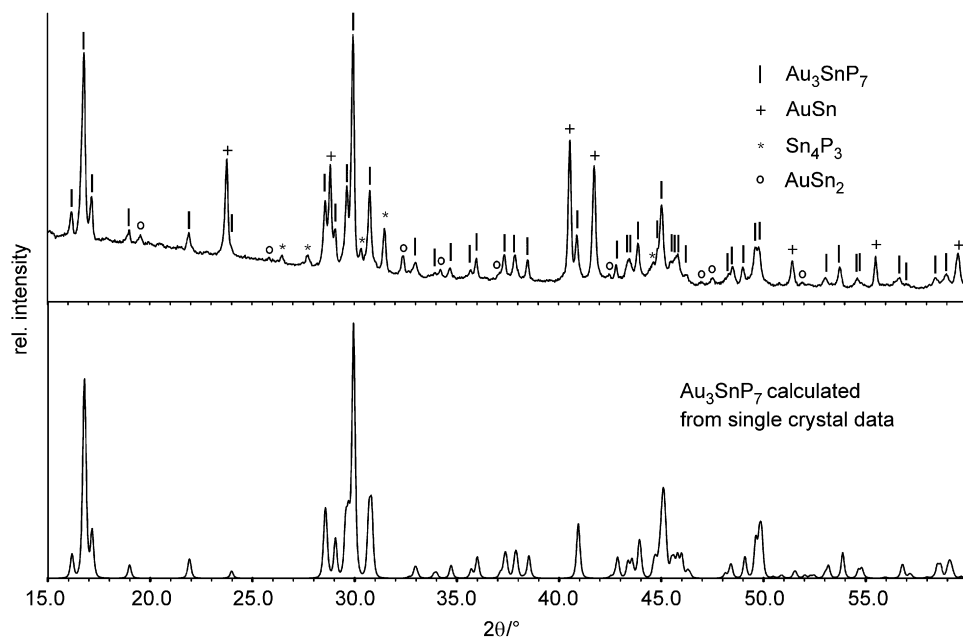


Fig. 2. Top section: X-ray powder pattern ($\text{CuK}\alpha_1$ radiation, 293 K) of the bulk residue (1 in Fig. 1). Au_3SnP_7 , AuSn , Sn_4P_3 and AuSn_2 were identified as reaction products. Bottom section: Calculated X-ray powder pattern ($a = 6.343(3)$, $b = 10.955(3)$, $c = 6.372(3)$ Å, $\beta = 108.63(2)^\circ$, $P2_1/m$ [21]) of Au_3SnP_7 . It represents the main phase beside AuSn , Sn_4P_3 and AuSn_2 (in decreasing order of appearance, citations see main text).

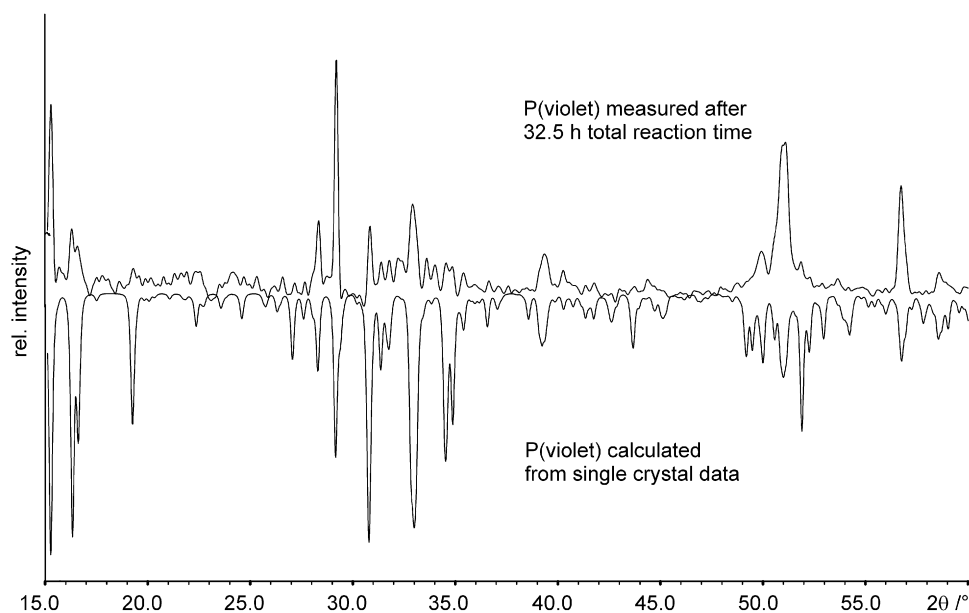


Fig. 3. X-ray powder pattern ($\text{CuK}\alpha_1$ radiation, 293 K) of violet phosphorus (2 in Fig. 1). The good crystal quality of violet phosphorus is remarkable after the short reaction time of 32.5 h. Structure data for violet phosphorus are taken from the literature [7].

out the fact that the mineralizer SnI_4 can be condensed via the gas phase on top of the crystals. Nevertheless, a simple purification step like refluxing in hot toluene can reduce the amount of impurities, if necessary. It has to be stated at this point that the total amount of impurities are smaller than 0.002(1)at% in average.

Violet phosphorus is expected to be the stable phase at the applied temperature without the use of a mineralizer [30]. It seems to be an intermediate step in the transformation from red to black phosphorus under the applied conditions. Prolonging the reaction time longer than 32.5 h or increasing the reaction temperature to 923 K led to a further transformation of the violet to black phosphorus, eventually up to a full conversion (Fig. 5).

With the increase of temperature a reduction of the crystal sizes was observed compared with the reaction at 873 K. It was shown that phosphorus in form of P_4 and P_2 fragments is the only transport relevant species out of all starting materials and possible gas-phase molecule in the present case [19]. The very fast growth of black phosphorus within 32.5 h and a small temperature gradient to crystals larger than 1 cm can only be explained by a rapid gas-phase reaction from these phosphorus fragments (mainly P_4 and P_2) at the reaction temperature. No other possible transport species like tin iodides, gold iodides, iodine itself, phosphorus iodides or tin phosphides show reasonable transport efficiencies at the applied temperature [19]. We have determined the temperature gradient within the ampoule

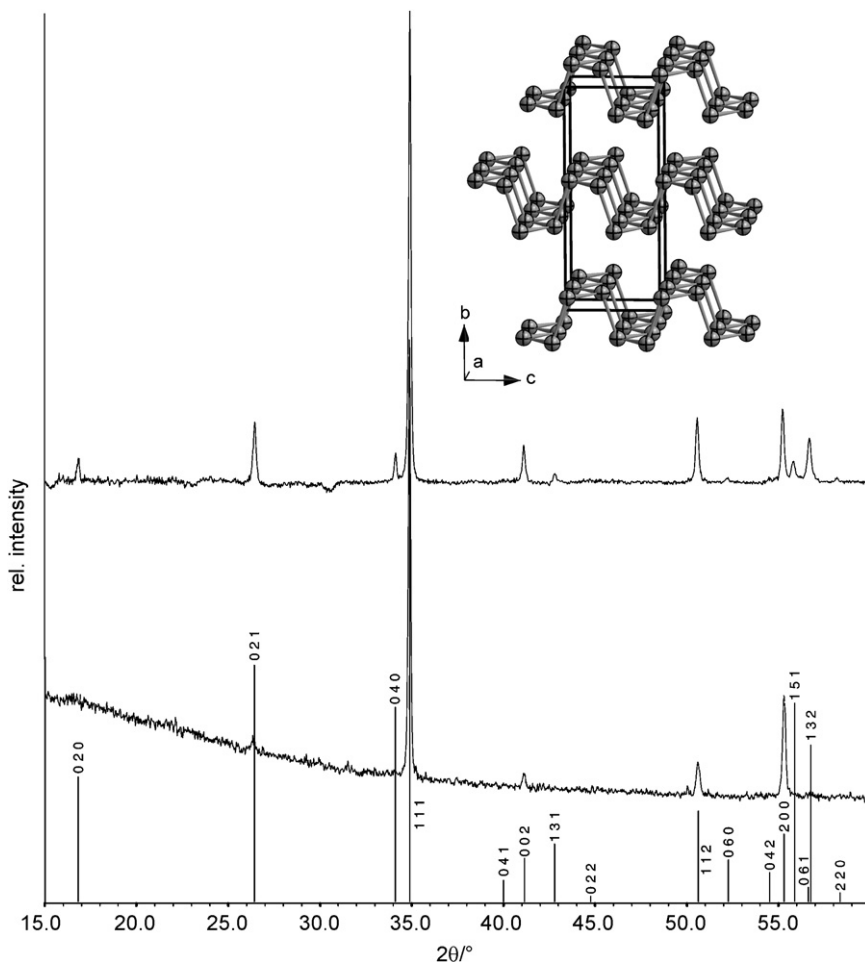


Fig. 4. X-ray powder pattern ($\text{CuK}\alpha_1$ radiation) and calculated pattern of black phosphorus (3 in Fig. 1, structure data from [19]). A texture effect due to the pronounced contribution of the ac -plane parallel to the X-ray beam (plate-like crystals, for structure details see inset) led to the complete loss of intensity for all $0k0$ reflections and significantly wrong intensities for all reflections with a k contribution. After a careful preparation of the flat-bed sample the texture problem was significantly reduced (top diffractogram). Hkl indices are given for all reflections.

Table 1
Results from ICP-MS measurements of three different samples

Sample no.	1	2	3
Au	5.3×10^{-7}	3.2×10^{-6}	1.2×10^{-6}
Sn	1.9×10^{-4}	1.3×10^{-4}	4.5×10^{-4}
<i>I</i>	5.5×10^{-4}	1.8×10^{-4}	2.2×10^{-3}
Total	7.4×10^{-4}	3.1×10^{-4}	2.6×10^{-3}

Values in at%.

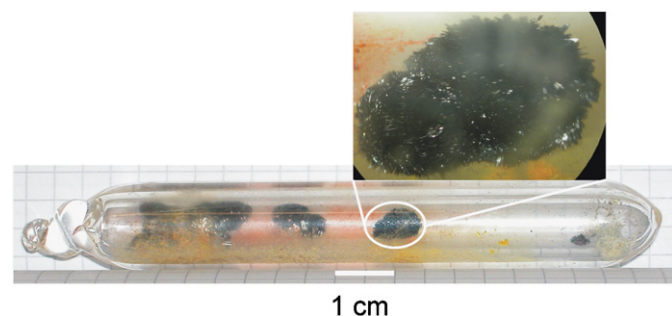


Fig. 5. Silica ampoule after a reaction time of 75 h and a maximum reaction temperature of 923 instead of 873 K.

from measurements with an external thermocouple close to the top and the middle of the ampoules and found a gradient of about 45 K at 873 and at 773 K. The exact application of the reported temperature program is important to grow black phosphorus in the presented way. A deviation from the program led to the formation of white or violet phosphorus as the main phase beside only small or no amounts of black phosphorus. Obviously the combination of different minority gas-phase species, the majority phosphorus components and some very complex and temperature dependent gas-phase equilibria are responsible for the fast formation of black phosphorus. More detailed studies of these phenomena are currently underway to achieve a full understanding of the growing mechanism of black phosphorus.

4. Conclusion

The reported transport reaction led to the formation of large black phosphorus crystals within reasonable short reaction times. It represents a significant improvement in preparation time and achievable crystal size compared with traditional methods like mercury catalysis, high-pressure synthesis and bismuth-flux methods. The present method also drastically improves the previously reported low-pressure route to black phosphorus in the overall product amount per reaction and maybe is suitable to

bring the compound a little bit more into the focus of materials scientists for electrochemical applications. Now a defined crystalline product is available at very high purity with no additional workup steps necessary, prior to use. Up-scaling to higher product amount is only dependent on the size of the ampoule and furnace. A reduction of the amount of the starting material AuSn and the mineralizer SnI₄ is also possible in order to minimize the production costs and to optimize the conversion rate.

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