Electronic Supplementary Information (ESI) for

Ultra-Fast Mechanochemical Synthesis of Boron Phosphides, BP and $B_{12}P_2$

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Experimental details and comments

Boron phosphate BPO_4 is the third boron containing substance (after sodium borate $Na_2B_4O_7$ and boric acid H_3BO_3) easily commercially available. CAS Number: 13308-51-5.

In our work BPO_4 has been synthesized by a simple reaction of boric acid (Alfa Aesar, 99.8 %) with orthophosphoric acid (Alfa Aesar, 85% aq. sol.) according to the method described in Ref. 18 (see references list in the main text) in an alumina crucible at 520 K with subsequent annealing of the obtained product in a muffle furnace at 770 K in 90-95% yield. The dried BPO_4 powder was sieved to obtained particles sizes below 200 μm.

There are several advantages for the use of BPO_4 as a precursor for the synthesis of boron phosphides. This precursor achieves excellent stoichiometry, low trace impurity content, and homogeneity approaching the maximum theoretically possible. Boron and phosphorus atoms are already mixed on an atomic scale thus providing higher reactivity and more homogeneous products.

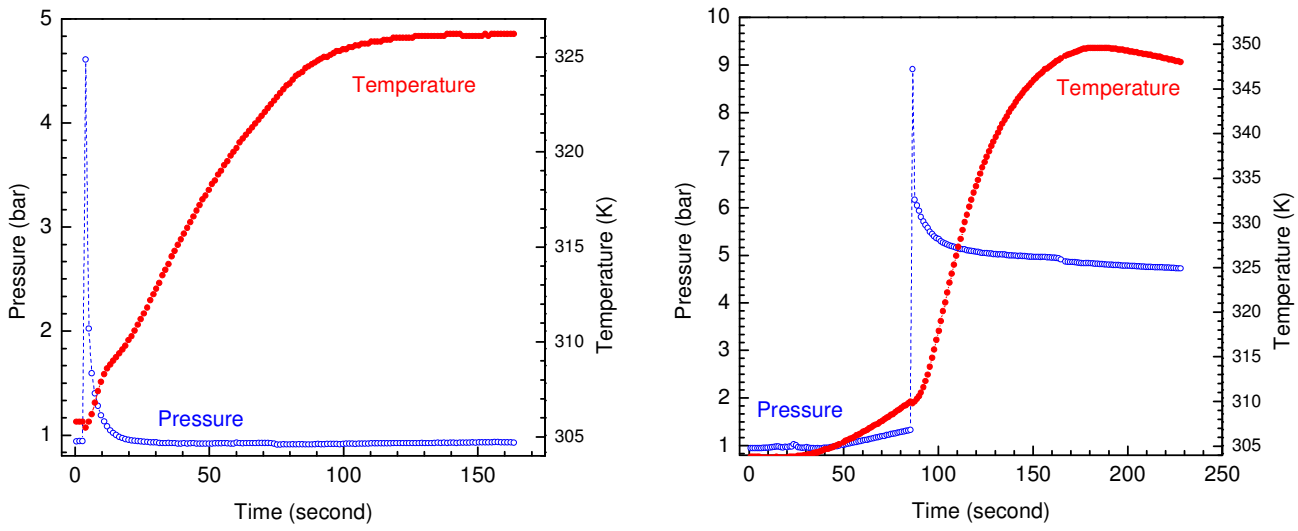


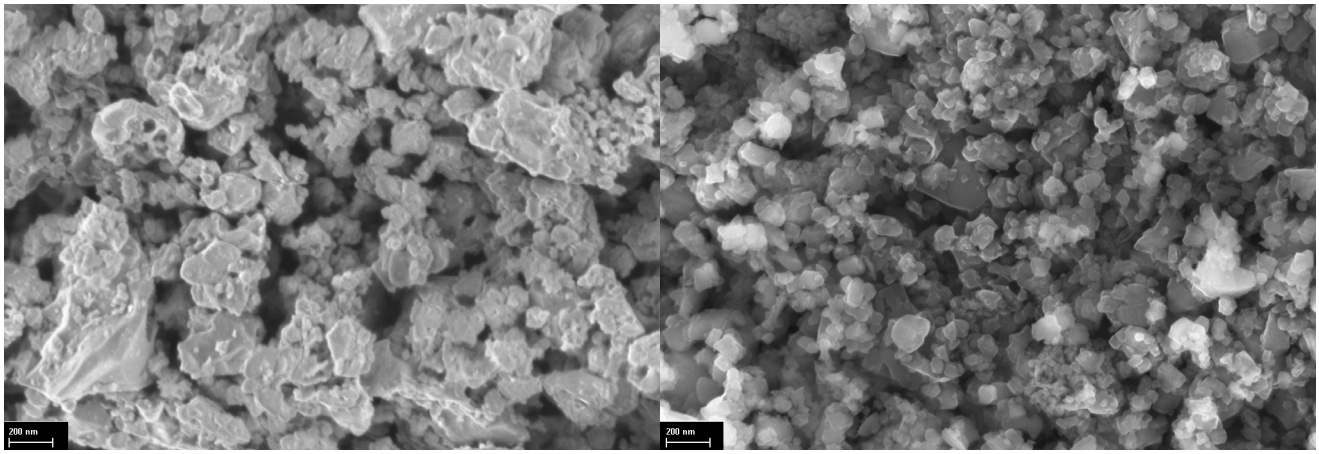
Fig. S1. Pressure and temperature variations in the vial during reactive milling of (*a*) BPO_4 and 4Mg mixture (60 sec real time milling), and (*b*) BPO_4, Mg and MgB_2 (120 sec real time milling). The temperature reading stands only for the overall temperature of the vial.

Fig. S1 shows a typical variation of the gas pressure and the integrated temperature in the vial during the milling-induced reaction at 700 RPM and after switching off the mill's rotation. The increase of the temperature in the container gave a signal corresponding to the sensitive gas pressure sensor. At first, during a few seconds, temperature and pressure are stable. A sharp pressure peak of about 4–12 bars was then monitored reflecting the start of a strong exothermal reaction in the powder mixture. As was shown in additional experiments, the incubation period, i.e. the milling time under high speed up to this peak, was 6–20 seconds for the reaction of pure BPO_4 and Mg. This incubation time is increased up to 160–220 seconds by addition of inert diluent (sodium chloride). The sharp pressure peak could be attributed to the

presence of water (not more then 0.4 wt %) in initial BPO_4 and to the brutal dilatation of the gases present in the milling jar. This pressure peak can also correspond to the formation of small amounts of gaseous products as a result of side reactions in experimental mixture (perhaps elemental phosphorus). This last point is confirmed by the presence of a small phosphorus smell after unloading.

As can be seen in Fig. S1a, the integrated temperature during milling increased from 306 to 326 K. Two sections on the temperature curve are clearly visible. The first slope is 0.50 K/sec and the second one is 0.27 K/sec. In the case of $B_{12}P_2$ synthesis the temperature curve has different shape (Fig. S1b): the first slope is 0.10 K/sec and the second one is 0.80 K/sec. Note that in the free-running experiment (BPO_4 loading without Mg) temperature slowly increases with a rate of about 0.02 K/sec caused mainly by internal friction and impact processes.

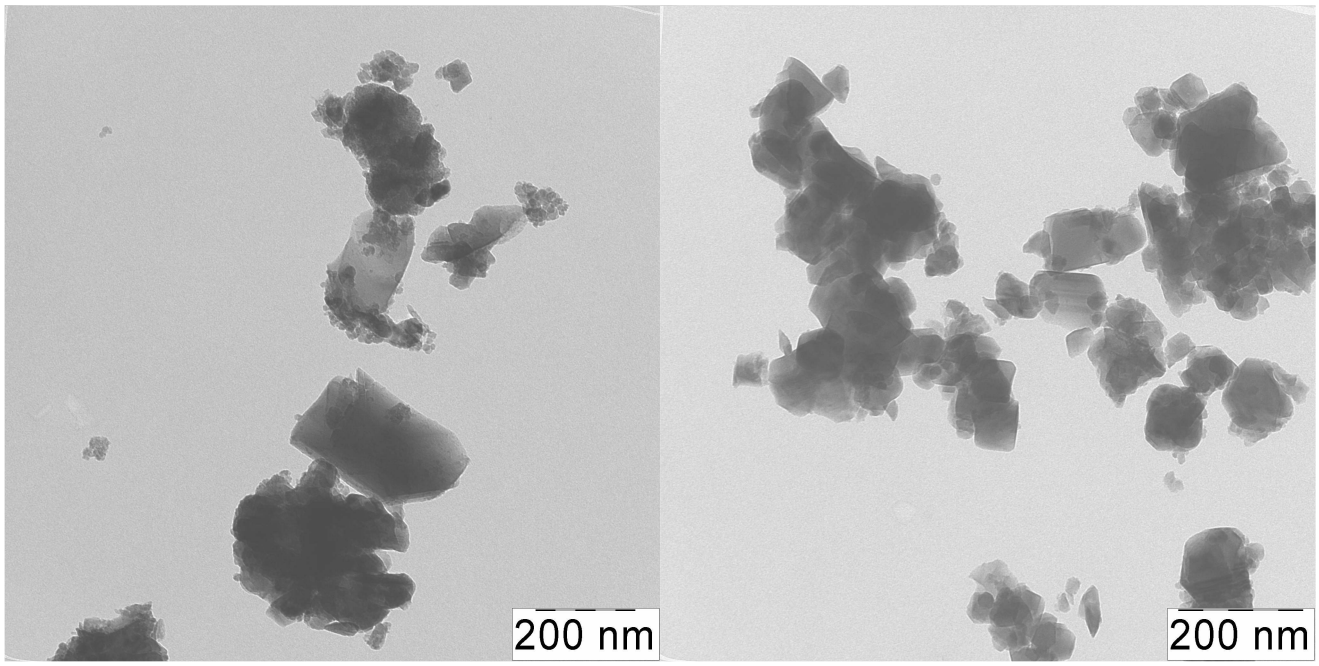
Characterization of BP and $B_{12}P_2$ powders



(*a*) (*b*)

Fig. S2. Representative SEM micrographs (100 000×) of the washed samples of (*a*) cubic BP and (*b*) icosahedral $B_{12}P_2$ produced by the mechanochemical synthesis.

High resolution SEM images show the rough and irregular characteristics of the surface of the BP particles (left image) and roughly spherical $B_{12}P_2$ particles (right image).

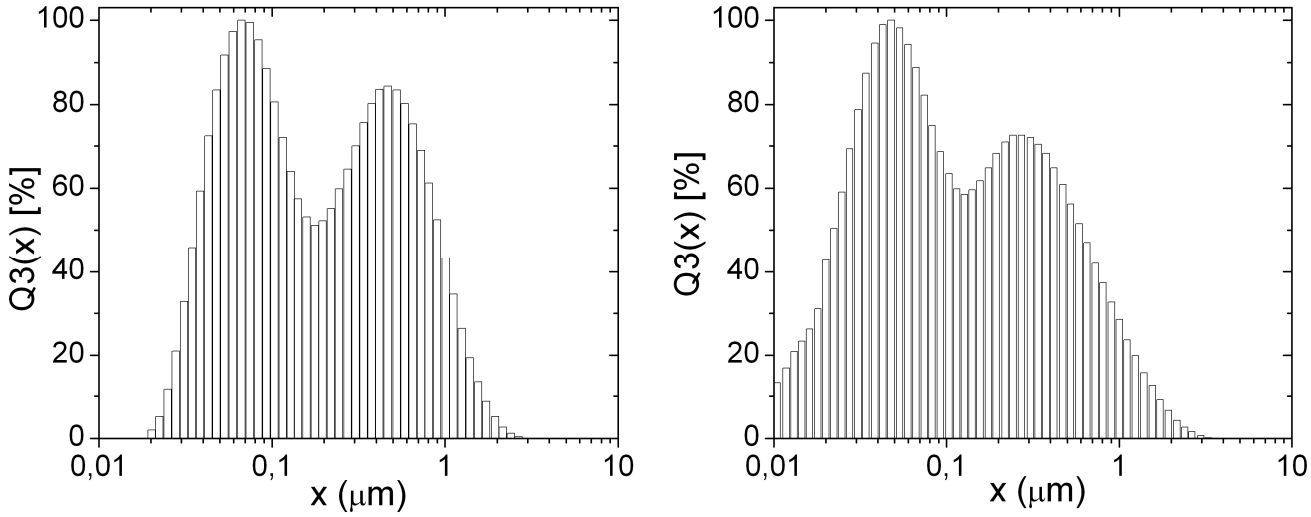


(*a*) (*b*)

Fig. S3. Representative bright-field TEM micrographs of the washed samples of (*a*) cubic BP and (*b*) icosahedral $B_{12}P_2$ produced by the mechanochemical synthesis.

It is revealed that BP powder (left figure) consists of nanoparticles with size distribution ranging from 25 to 80 nm, with a few large grains with sizes of about 100-200 nm, which is in agreement with SEM studies and the crystalline size calculated from XRD data. The $B_{12}P_2$ powder (right figure) consists of

smaller (compared to BP) particles having equiaxed morphology with size distribution ranging from 13 to 60 nm, and the part of large grains is quite modest.



(*a*) (*b*)

Fig. S4. The particle size distribution (laser diffraction) for the washed samples of (*a*) cubic BP and (*b*) icosahedral $B_{12}P_2$ produced by the mechanochemical synthesis.