

## A Benzene-Thermal Synthesis of Cubic Boron Phosphide (BP) Ultrafine Powders

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Ultrafine boron phosphide (BP) with cubic cell was synthesized via a benzene-thermal reaction of boron powder and phosphorus trichloride ( $\text{PCl}_3$ ) with metallic lithium or sodium at  $350^\circ\text{C}$  in an autoclave; initiating a new route and developing a facile technique for preparing BP.

Cubic boron phosphide BP is a semiconductor with an indirect band gap of  $2\text{ eV}$ .<sup>1,2</sup> Due to its outstanding chemical, mechanical, optical, and thermal properties, it is one of the most promising high-temperature thermoelectric materials.<sup>3-6</sup> In preparation of boron-phosphorus compounds, cubic boron phosphide with zinc blende structure was traditionally prepared by various high-temperature reactions (up to  $1000^\circ\text{C}$ ), such as boron reacting with phosphorus,  $\text{Zn}_3\text{P}$  or  $\text{PH}_3$ , hydrogen reduction of  $\text{BCl}_3$  in the presence of phosphorus, metathesis reactions of  $\text{BCl}_3$  with  $\text{PH}_3$ ,  $\text{Zn}_3\text{P}$  or  $\text{AlP}$ , and pyrolysis of  $\text{BCl}_3$  and  $\text{PCl}_3$  mixtures.<sup>3-5</sup> Rhombohedral boron phosphide ( $\text{B}_{12}\text{P}_2$ ) films have been synthesized at  $1100^\circ\text{C}$  by chemical vapor deposition.<sup>7,8</sup> However, synthesis of cubic BP was rarely investigated because of the difficulty of preparing this low-compressibility material. As solvothermal synthetic method has been successfully used in preparing various nanocrystallites, such as diamond,<sup>9</sup> cubic boron nitride,<sup>10,11</sup> silicon carbide,<sup>12</sup> and chalcogenides,<sup>13</sup> in this letter, we develop a benzene-thermal route to ultrafine cubic BP.

In benzene-thermal route to cubic BP, a typical reaction was that 0.973 grams of powdered boron (300 mesh), appropriate amount of  $\text{PCl}_3$ , benzene and excessive metallic lithium or sodium were added in a quartz tube and sealed in a stainless steel autoclave. The autoclave was heated at  $350^\circ\text{C}$  for 10 h followed by naturally cooling to room temperature out of the furnace. The obtained sample was washed with 36 wt% hydrochloric acid, 45 wt% nitric acid, distilled water, absolute alcohol and acetone to remove impurities. The final product was vacuum-dried at  $60^\circ\text{C}$  for 8 h. Brownish-gray powder sample was obtained.

The X-ray powder diffraction (XRD) pattern was recorded on a Rigaku Dmax rA X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (wavelength  $\lambda = 1.54178\text{ \AA}$ ). The XRD pattern (Figure 1) shows strong peaks of the crystalline BP. All the peaks were indexed to the face centered cubic cell of BP phase (S.G. F-43m), with lattice constant  $a = 4.536\text{ \AA}$ , in good agreement with  $a = 4.538\text{ \AA}$  (JCPDS card# 11-119).

X-ray photoelectron spectroscopy (XPS) spectra of the sample were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized  $\text{Mg K}\alpha$  X-rays as the excitation source. The wide-scan XPS spectrum indicated presence of B and P. Small amounts of carbon and oxygen were also detected. They may come from adsorption, impurities or contamination. The  $\text{P } 2\text{p}_{3/2}$  spectrum (Figure 2a) shows a peak at  $130.32\text{ eV}$ . It corresponds to the phosphorus

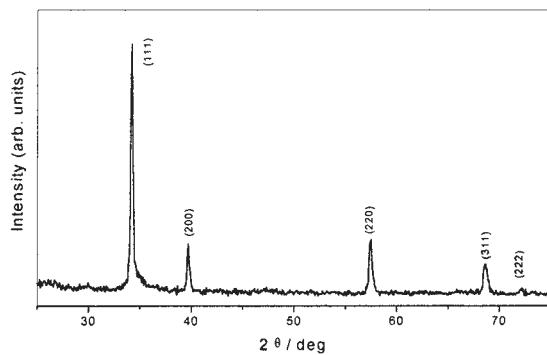


Figure 1. XRD pattern of as-prepared cubic BP sample.

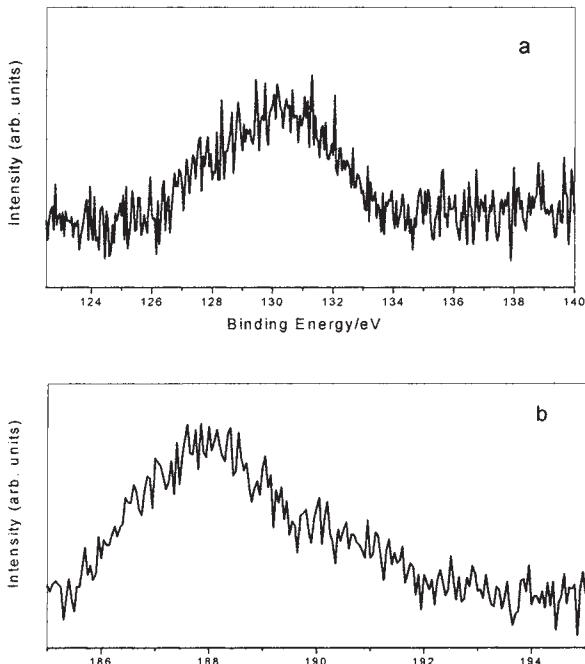
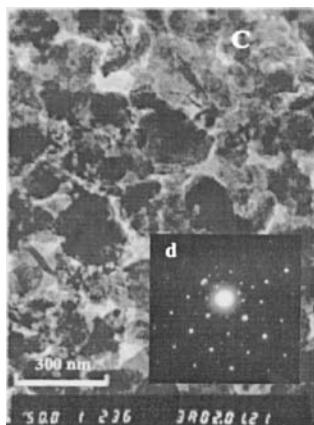


Figure 2. XPS spectra of the cubic BP sample (a,  $\text{P } 2\text{p}_{3/2}$  region; b,  $\text{B } 1\text{s}$  region).

bonded with boron, which has a binding energy of  $\text{B } 1\text{s}$  centered approximately at  $188.12\text{ eV}$ , as shown in Figure 2b, indicating phosphorus combined with boron forming boron phosphide.<sup>14</sup> The mole ratio of B : P is  $1 : 0.942$ , which is very close to that of BP.

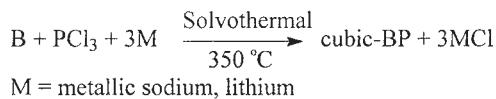
Transmission electron microscopy (TEM) image (Figure 3c) was recorded on a Hitachi 800 transmission electron microscope. It shows particle morphology with granular size of 50 to 210 nm in diameter. Selected area transmission electron diffraction (TED)



**Figure 3.** TEM (c) and TED (insert d) of as-prepared cubic BP sample (scale bar, 300 nm).

pattern (insert Figure 3d) is consistent with high crystallinity of cubic BP.

In the solvothermal reaction to BP, active nascent phosphorus was produced from reducing  $\text{PCl}_3$  by alkali metal. The phosphorus reacted with boron forming boron phosphide at  $350^\circ\text{C}$ . The reaction can be described as follow:



The yield relative to stock boron was calculated as about 78%. The actual yield may be larger due to the BP loss in purification. This work initiates a new route and develops a facile technique for preparing ultrafine cubic BP.

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