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Synthesis of Nanocrystalline BP via Benzene-Thermal Co-reduction of PCl_3 and BBr_3

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Nanocrystalline boron phosphide (BP) powders 10 to 40 nm in size have been synthesized via a sodium co-reduction of PCl_3 and BBr_3 in benzene at 300 °C. X-ray diffraction data show a cubic pattern with lattice constant $a = 4.539$ Å.

Boron phosphides, used as refractory and wide-gap semiconductors, have attracted considerable interest for their superior physical properties, such as outstanding high-temperature stability[1] and high thermoelectric powers for direct energy conversion.[2,3] These properties suggest many uses in modern technology. For example, they would be promising materials for large-surface-area liquid junction solar cells.[4,5]

Boron phosphides were traditionally synthesized via various high-temperature reactions (up to 1000 °C).[6] They were also prepared by pyrolysis of phosphinoborane compound precursors.[7,8] However, it is difficult to obtain boron phosphide nanomaterials by these methods. On the other hand, various deposition methods have been used to prepare films of boron-phosphorus compounds.[9–12] Recently, we synthesized ultrafine cubic BP by reacting amorphous boron powders with PCl_3 and alkali metals through a solvothermal method.[13] As the boron source is chemically inert, we propose a new route to nanocrystalline BP by benzene-thermal co-reduction of PCl_3 and BBr_3 using metallic sodium as a reductant. The reaction can be described as follows:

$$\mathrm{PCl_3 + BBr_3 + 6Na \xrightarrow[300^{\circ}C]{Benzene} Cubic\text{-}\ BP + 3NaCl + 3NaBr} \tag{1}$$

In this reaction, nascent phosphorus and boron are generated in the reduction of PCl_3 and BBr_3 by metallic sodium, and they combine to form nanocrystalline BP. Benzene serves as the solvent and reaction medium to control the reaction velocity and product morphology.

In the benzene-thermal synthesis of cubic BP, PCl_3 and BBr_3 were co-reduced by metallic sodium. PCl_3 (analytical pure grade) and BBr_3 (99.99%, Shanghai Pharmaceutical Corporation) were used without further purification. 15 mL of analytical pure grade benzene, 3 grams of sodium (13.0×10^{-2} moles), 2 mL of PCl_3 (2.30×10^{-2} moles) and 2 mL of BBr_3 (2.08×10^{-2} moles) were put into a glass tube and placed in a stainless steel autoclave. The autoclave has a capacity of some 55 mL. Before sealing the autoclave, approximately 5 mL of benzene was put into the autoclave (outside the glass tube) to balance heat and pressure. The autoclave was sealed and heated at 300 °C for 12 h, followed by cooling to room temperature outside the furnace. The obtained sample from the glass tube was washed several times with absolute ethanol, distilled water, and acetone to remove sodium chloride, bromide, and other impurities. The final product was vacuum-dried at 60 °C for 12 h. 0.645 grams of dark brown powder was obtained.

The product was analyzed by powder X-ray diffraction (XRD) on a Japan X-ray Rigaku D/max rA X-ray diffractometer with Cu Kα radiation (wavelength $\lambda = 1.54178$ Å). A scan rate of 0.06°/s was applied to record the pattern. Figure 1 shows the XRD pattern of the as-prepared BP sample. The four peaks at d-spacings of 2.6200, 2.2690, 1.6044 and 1.3686 Å were indexed as cubic BP ((111), (002), (022) and (113)). The rms error of fit was 4.384×10^{-5}, with the lattice constant $a = 4.539$ Å, in good agreement with $a = 4.538$ Å (JCPDS card# 76-2485). As the reaction is strongly exothermic, the local temperature may temporarily go higher than 300 °C. As a result, small amounts of amorphous carbon were produced by pyrolysis of benzene. In Fig. 1, a very broad, weak bulge centered at 2θ about 26 degrees indicated the co-existence of amorphous carbon. NaCl and NaBr were removed in purification. Therefore, diffraction lines of these substances did not appear.

Morphology was examined on a Japan Hitachi 800 transmission electron microscope using an accelerating voltage of 200 kV. The TEM image and TED pattern are shown in Fig. 2. As nanoparticles have extremely small dimensions and a high surface energy, it is easy for them to aggregate into secondary particles. In Fig. 2 (left), the product exhibits agglomerated particle morphology. Some amorphous carbon may cling to and disperse between the BP primary particles. The agglomerated particle size was estimated to be in the range of 10 to 40 nm. The TED pattern in Fig. 2 (right) confirms the nanocrystallinity of BP, in which the diffraction ring diameters and intensities correspond well to the cubic phase of BP.

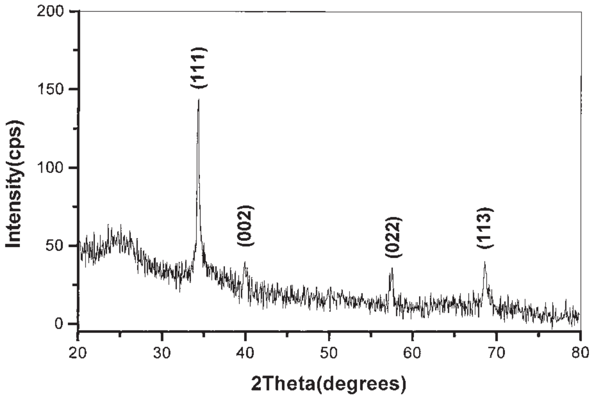

Fig. 1. XRD pattern of the as-prepared nanocrystalline BP.

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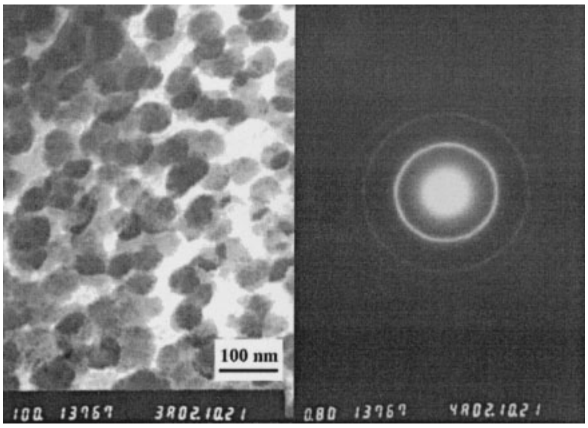

Fig. 2. Transmission electron microscope (TEM) image (left) and transmission electron diffraction (TED) pattern (right) of the as-prepared nanocrystalline BP. The three diffraction rings from inner to outer can be indexed to (111), (022) and (113) planes of the cubic BP phase, respectively.

In summary, nanocrystalline cubic BP powders of about 10 to 40 nm in diameter have been successfully prepared via a benzene-thermal synthesis by metallic sodium co-reduction of PCl_3 and BBr_3 at 300 °C for 12 h. Although the reaction is much more exothermic than the previous work, the reaction was tempered and particle size was controlled by benzene.[13] This study shows that solvothermal synthesis can be an efficient technique for preparing BP nanomaterials.

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