Self-Propagating High-Temperature Synthesis of Boron Subphosphide $B_{12}P_2$

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Abstract—Two new methods to produce nanopowders of $B_{12}P_2$ boron subphosphide by self-propagating high-temperature synthesis have been proposed. Bulk polycrystalline $B_{12}P_2$ with microhardness of $H_V = 35(3)$ GPa and stability in air up to 1300 K has been prepared by sintering these powders at 5.2 GPa and 2500 K.

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Icosahedral boron subphosphide $B_{12}P_2$ is a promising superhard material with theoretical hardness of $H_V = 37$ GPa [1] and high thermal and chemical stability [2]. It may be produced by three methods: (i) thermal decomposition of BP boron phosphide at temperatures above 1500 K in a reducing atmosphere [3], (ii) direct interaction between the elements at $T > 1600$ K under argon pressure of 50 bar [4], and (iii) reaction between boron and phosphorus halogenides [5]. $B_{12}P_2$ single crystals can be grown both by crystallization from flux solutions [5] and gas–transport reactions [3, 5]. However, technologies based on the above methods are complex and labor intensive, which prevents practical applications of boron subphosphide.

Earlier we have developed a method to produce BP boron phosphide free of $B_{12}P_2$ impurity by interaction of boron phosphate and magnesium according to the

$$BPO_4 + 4Mg = BP + 4MgO.$$  (1)

reaction in the mode of self-propagating high-temperature synthesis (SHS) [6]. As a result of side reactions and partial oxidation by air oxygen, the yield of the desired product (BP) is relatively low (~35% of the theoretical one), which, however, is compensated by the method simplicity and availability of the reagents used.

The aim of the present work was to develop efficient SHS methods of producing single-phase boron subphosphide by elaborating experimental approaches proposed in [6]. As a result of our studies two schemes of $B_{12}P_2$ synthesis were suggested.

Scheme 1. The synthesis was performed by changing the precursor stoichiometry, i.e. instead of BPO$_4$ we used a boron phosphate glass of $B_{12}P_2O_{23}$ composition produced by evaporation of a mixture of boric (Alfa Aesar, 99.8 %) and orthophosphoric (Alfa Aesar, 85% aq. sol.) acids in distilled water (3.2 : 1 : 2.1 weight ratio) at 520 K with subsequent annealing of the product in a muffle furnace at 770 K. The mixture of as-prepared $B_{12}P_2O_{23}$ glass (~200 μm) and metallic magnesium (Alfa Aesar, 99.8 %, 325 mesh) in the 1 : 1 weight ratio was pressed in a steel die at 10 t load into 2.2-g pellets 20 mm in diameter and 4 mm in height. The reaction was performed in a dynamic argon atmosphere (pressure of 1 bar, consumption of 50 cm$^3$/s) in the originally designed SHS apparatus described elsewhere [7]. The pellets placed on a substrate of pressed MgO were fired with an AC-heated graphite foil ribbon; the quantity of heat released on the ribbon was comparable with the thermal effect of the reaction (2). According to our estimations, the temperature in the course of the reaction was no less than 1300 K. After burning the weight of pellets decreased by ~6% (a part of the substance was taken away with the argon flow). The equation of the reaction may be written as

$$B_{12}P_2O_{23} + 23Mg = B_{12}P_2 + 23MgO.$$  (2)

After boiling the resulting products in 20% hydrochloric acid for 30 min, there forms a brown residue, which is $B_{12}P_2$ containing no more than 3 vol % BP (Fig. 1a). The presence of a small BP impurity may be
explained by the fact that the initial boron phosphate glass contained some amount of crystalline BPO₄. The yield of B₁₂P₂ made about 51% of the theoretical one according to reaction (2).

In the comparison experiments similar pellets were annealed at 870 K in a closed crucible in a muffle furnace for 20 min. After treating the reaction products with hydrochloric acid, the yield of B₁₂P₂ was 65% of theoretical by reaction (2). In this case, however, the BP impurity content increased up to ~10 vol %.

Scheme 2. The aim was achieved by the variation of the reducing agent stoichiometry during the reduction of boron phosphate by the reaction

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2\text{BPO}_4 + 5\text{MgB}_2 + 3\text{Mg} = \text{B}_{12}\text{P}_2 + 8\text{MgO}. \tag{3}
\]

As a reducing agent the mixture of magnesium diboride (Alfa Aesar, 99%, 100 mesh) and metallic magnesium (Alfa Aesar, 99.8%; 325 mesh) in the weight ratio 3 : 1 was used. The SHS reaction was carried out according to the procedure similar to that used in scheme 1. A decrease in the pellets weights was ~3%. After boiling the products in 20% hydrochloric acid for 30 min, the light-grey residue was single-phase B₁₂P₂ (see Fig. 1b). The yield of boron subphosphide was 76% of theoretical by reaction (3). Similar pellets annealed in a muffle furnace in a closed crucible at 870 K for 20 min after washing in 20% hydrochloride acid allow us to produce B₁₂P₂ with a 71% yield, and in this case the BP content increases up to 16 vol %.

Relatively low (50–75%) yields of the desired product by reactions (2) and (3) are due to a number of side reactions (the formations of magnesium phosphide, diboride and borate; boron and phosphorus oxides, etc.), which, however, as in the case of BP [6], is compensated by the simplicity of the method and availability of the reagents used.

The X-ray diffraction analysis of the products was performed on an Equinox 1000 Inel diffractometer (CuKα₁ radiation, \(\lambda = 1.540598 \text{ Å}\)). The lattice parameters of boron subphosphide samples prepared according to schemes 1 and 2 are \(a = 5.985(3) \text{ Å}, c = 11.842(9) \text{ Å}\) and \(a = 5.988(3) \text{ Å}, c = 11.836(7) \text{ Å}\), respectively, which agrees well with the values reported for B₁₂P₂ with stoichiometry close to the ideal [4]. The sizes of coherent scattering areas (CSA) estimated from the diffraction lines broadening using Williamson–Hall method [8] were 20–30 nm regardless of the production scheme.

The morphology of B₁₂P₂ powders was studied on a Supra 40VP Carl Zeiss high-resolution scanning electron microscope. According to the data obtained, the B₁₂P₂ powders consist of isotropic grains with sizes of 50–90 nm irrespective of the production scheme (Fig. 2). A comparison of these values with the CSA sizes allows a conclusion that B₁₂P₂ grains observed in the electron microscope (see Fig. 2) are aggregates of several crystallites. The local element analysis of washed boron subphosphide powders was made on a Leica S440 electron microscope with an EDS Princeton Gamma-Tech energy-dispersive spectrometer. According to the data obtained, for all samples the B : P ratio is 6 : 1, and total impurities concentration (Mg, O, Cl, Al, and Si) does not exceed 0.7 at %.

The phase purity of the boron subphosphide samples was also verified by Raman scattering. Raman spectra were excited by a He-Ne laser (\(\lambda = 632.8 \text{ nm}\), beam size = 10 μm) and recorded on a Horiba Jobin Yvon HR800 micro-Raman spectrometer. The Raman spectra of washed reaction products are shown in Fig. 3. All