CHEMISTRY

Ya. Kh. Grinberg, Z. S. Medvedeva, A. A. Eliseev, É. G. Zhukov

1965

SovietRxiv

Fig. 1. Plate-like and dendritic BP crystals (18×)

Figure 1: Fig. 1. Plate-like and dendritic BP crystals (18×)

Fig. 2. Three-dimensional BP crystals (36×)

Figure 2: Fig. 2. Three-dimensional BP crystals (36×)

Abstract

Full Text

CHEMISTRY

Ya. Kh. Grinberg, Z. S. Medvedeva, A. A. Eliseev, É. G. Zhukov

PREPARATION OF SINGLE CRYSTALS OF BORON PHOSPHIDE BP FROM THE GAS PHASE

(Presented by Academician I. V. Tananaev, 7 VII 1964)

Until recently, the preparation of single crystals of various substances from the gas phase was limited to sublimation processes—sublimation in the presence of a temperature gradient. This requires a sufficiently high vapor pressure of the compound and comparable volatility of its constituent components. These difficulties can be overcome if a carrier component is introduced into the reaction space, one which interacts with the starting substance by a reversible reaction and forms gaseous compounds with it. Their transfer in a temperature gradient into a region with a smaller equilibrium constant ensures separation of the primary solid phase in the form of single crystals (1). For many refractory compounds this is the simplest method for obtaining the most perfect single crystals. The choice of the temperature gradient in the reaction space and of the temperature in the crystallization zone has a decisive influence on such a process. The present work is devoted to determining the influence of these factors on the crystallization of boron phosphide BP.

Fig. 1. Plate-like and dendritic BP crystals (18×)

Fig. 2. Three-dimensional BP crystals (36×)

The starting substance was BP powder (purity 99.998%), previously synthesized from the elements at a temperature of 1100–1150° under a phosphorus vapor pressure of 4–5 atm (2). Excess boron was removed by prolonged boiling in aqua regia. Elements of group VI of the periodic system, forming volatile compounds with boron, were used as carriers. Before the experiment, the reaction space was evacuated to 10^{-5} mm Hg. The process was carried out at 900–1200° with

Fig. 3. View of a BP single crystal. The arrow is labeled "X-ray beam" ; the face is labeled {110}.

Figure 3: Fig. 3. View of a BP single crystal. The arrow is labeled "X-ray beam" ; the face is labeled {110}.

different temperature gradients ΔT between the crystallization and "source" zones. The temperature was maintained with an accuracy of ±5°.

Experiments carried out with different temperature gradients at a constant crystallization temperature showed that ΔT mainly deter–

increases the number of nuclei. Since transport limited by the diffusion process is directly proportional to the temperature gradient (^{1}), at large ΔT a strong supersaturation is created in the crystallization zone, owing to which the number of nuclei increases sharply. Reducing ΔT to 20–40° makes it possible to sharply decrease the number of crystallization centers, and each of them under these conditions forms a more perfect single crystal.

A change in the crystallization temperature at constant ΔT showed that this factor mainly affects the shape of the crystals.

Fig. 3. View of a BP single crystal

At high temperatures, predominantly plate-like and dendritic growth is observed (Fig. 1), with the dendrites often elongated along one axis and growing from a common center. Lowering the temperature promotes the formation of bulk single crystals with well-developed faces having a mirror-like surface. The crystals obtained were transparent and pink in color. Their dimensions did not exceed 2 × 2 × 1 mm.

Calculation of powder patterns of the crystals confirmed that BP crystallizes in a cubic lattice of the ZnS type with an identity period a = 4.538 Å. This exactly corresponds to the parameter calculated from the X-ray pattern of the starting powder and to the literature data (^{3}), which indicates the absence of appreciable solubility of the carriers used in boron phosphide. Spectral analysis showed that the amount of carrier in BP did not exceed 10^{-3}%.

Bulk single crystals had a complex faceting characteristic of compounds with a cubic structure (^{4}), and a varied habit (Fig. 2): an octahedron, a tetragonal pyramid, and also combinations of multifaceted prisms and pyramids with triangular and square faces.

The crystals were studied by the Laue method (with CuK_α radiation) and by rocking (in an RKOP-type camera). On the rocking X-ray pattern of one of the crystals, a horizontal symmetry line is clearly revealed, which corresponds to the plane m, perpendicular to the direction around which the rocking was performed. The same symmetry line is also observed on three Lauegrams taken at intervals of 60°. The identity period of the single crystal along the rocking axis proved to be 6.36 Å, which corresponds to the face diagonal of the cube. Consequently, the single crystal studied (Fig. 3) was photographed in the direction [110].

All crystals had n-type conductivity and showed rectification at a point contact.

The thermo-e.m.f., measured by the compensation method in the temperature interval 20–150°, proved to be ~ 260 μV/deg, and the microhardness of differently oriented faces was $H = 4000$ kg/mm^2.

The authors express their sincere gratitude to Professor N. P. Luzhnaya for her constant interest in the work.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

Received
23.VI.1964

REFERENCES

1. H. Schäfer, *Chemische Transportreaktionen*, Verlag Chemie, GmGH, Veskheim, 1961.
2. P. Popper, T. Ingles, *Nature*, **179**, 1075 (1957).
3. S. Rundquist, XVI Congr. Intern. de Chimie pure et appliquee, Paris, 1957, p. 539.
4. A. E. Fersman, *Crystallography of Diamond*, Publishing House of the Academy of Sciences of the USSR, 1955.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.