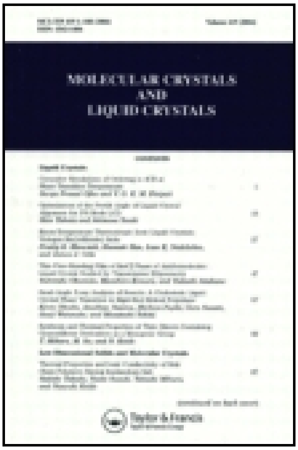

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Growth of Large Single Crystals of Black Phosphorus at High Pressures and Temperatures, and its Electrical Properties

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GROWTH OF LARGE SINGLE CRYSTALS OF BLACK PHOSPHORUS AT HIGH PRESSURES AND TEMPERATURES, AND ITS ELECTRICAL PROPERTIES

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The crystal growth of black phosphorus(B.P.) and its electrical properties have been studied at high pressures and high temperatures. A wedge type cubic anvil high pressure apparatus was used in the present experiments. From the measurement of the electrical resistance the melting points of B.P. have determined at high pressures. When B.P. is melted in the carbon furnace and slowly cools at 2.3 GPa, the large single crystals have often been grown. The size of the largest one is 4 mm in diameter and 5 mm in length. The anisotropic resistivity within the layers(ac-plane) has been observed. The resistivities along the a-, c- and b(perpendicular to the layer)-axes were about 0.1, ~ 1 and $10^2 \sim 10^3$ Ωcm, respectively at atmospheric pressure. The resistivity along the a-axis was insensitive to pressure; on the other hand, the resistivities along the c- and b- axes decreased rapidly with increasing pressure at room temperature. The resistivity along the b-axis was about two orders of magnitudes larger than that of the a- and c- axes at 3.0 GPa. The intrinsic energy gaps observed in the single crystals were isotropic within the experimental error at atmospheric and high pressure. The electrical properties of B.P. are compared with the result of the band structure calculated by Asahina et al.

INTRODUCTION

The physical properties of layered materials have been a subject of considerable interest in recent years. Black phosphorus(B.P. , hereafter) is a narrow gap semiconductor with an infinite puckered layer structure. Bridgman reported in 1914 that B.P. can be prepared from white phosphorus at 1.2 GPa(12 kbar) and at 200°C[1]. Some electrical and optical properties of polycrystalline B.P. produced at high pressures and at high temperatures were studied by Keyes[2] and Warschauer[3]. The B.P. is a p-type semiconductor with room temperature resistivity about 1 Ωcm and has an intrinsic energy gap of about 0.35 eV. An optical absorption edge is found in the 2 to 6 μ region.

The crystal structure of B.P. has been determined, the lattice is orthorhombic with eight atoms per unit cell and lattice parameters a = 3.31 A, b = 10.48 A, c = 4.38 A[4,5]. The atoms are arranged in puckered layers; in a layer each atom is joined by covalent bonds to three neighbors, while the layers are held together by van der Waals forces. The crystal structure is shown in Fig. 1.

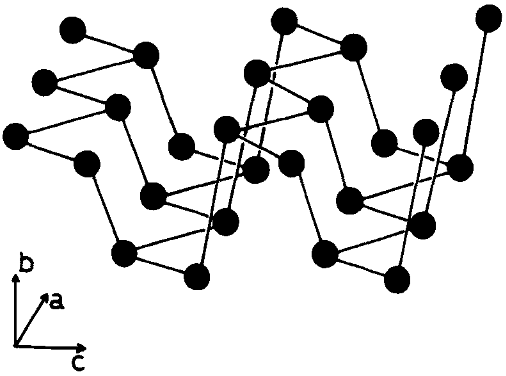

FIGURE 1 A part of an infinite puckered layer of phosphorus atoms parallel with the (010) plane in the structure of black phosphorus.

The linear compressibilities of polycrystalline B.P. have been determined using newtron powder diffraction by Cartz et al.[6]. The markedly anisotropic compression has been observed. The interesting part of their results is that a very large anisotrophy exists for compression within the layers.

Maruyama et al. have reported the electrical properties of B.P. single crystals prepared from a solution of white phosphorus in liquid bismuth[7]. The electrical resistivity along the a-axis(needle axis direction) is 0.3∿5 Ωcm at room temperature. The intrinsic band gap energy is 0.31 eV.

Asahina et al. have calculated the band structure of B.P. using the self-consistent pseudopotential method, and have found that in spite of the layered structure the effective masses in the b-axis are even smaller than those in the inplane c-direction[8]. The single crystals of B.P. prepared from bismuth solution are obtained as needle and thin rod form. Thus, the single crystals are still too small to measure the anisotropy in the resistivity.

We have been grown large single crystals of B.P. at high pressures and high temperatures using a wedge type cubic anvil high pressure apparatus[9], and have measured the electrical resistivity of the large single crystals as a function of temperature and pressure from 25 to 1200°C and from atmospheric pressure to 4.0 GPa.

In this paper the electrical anisotropy and the energy gap of the large single crystals of B.P. will be discussed.

EXPERIMENTAL

A wedge type cubic anvil high pressure apparatus developed by Wakatuki et al. was used in the present experiments[10]. The apparatus actuated with a 600 ton oil press has six anvils of 16 mm on an edge of top square. The pyrophyllite sample holder is formed into a cube of 21 mm on an edge.

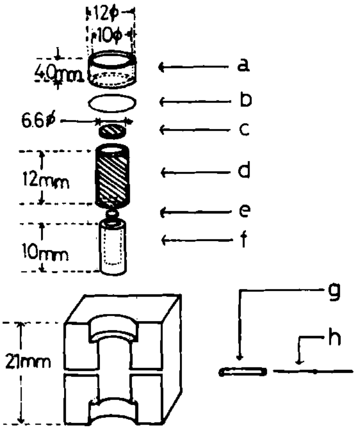

FIGURE 2 The sample assymbly for the preparation and crystal growth of B.P. in the pyrophyllite sample holder,

a) current ring, b) metal plate, c) carbon disk, d) carbon furnace, e) disk, f) cylinder, g) ceramic tube, h) thermocouple.

Figure 2 illustrates the sample assymbly for the preparation and the crystal growth of B.P. at 2 to 4 GPa and 500 to 1200°C. The electrical resistivity along each crystallographic direction of single crystals were measured with an ordinary four or two point method with platinum wire and silver paste. The sample assymbly for the measurement a resistivity at high pressures and high temperatures is shown in Fig. 3.

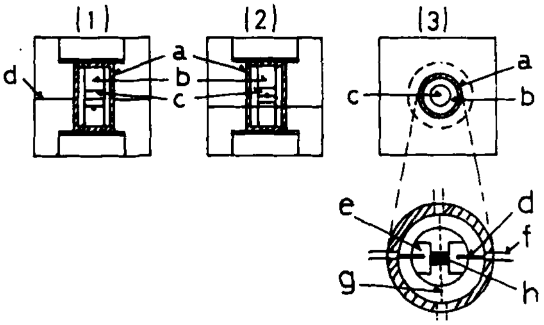

FIGURE 3 The sample assymbly for the measurement of electrical resistance, a) carbon furnace, b) pyrophyllite, c) disk, d) current lead, e) metal, f) ceramic tube, g) thermocouple, h) specimen.

RESULTS AND DISCUSSION

The crystalline B.P. was originally prepared by Bridgman by heating white phosphorus to 200°C at 1.2 GPa1). Jacobs found an amorphous form of B.P.11). Pätz made a study of the temperatures and pressures at which white phosphorus transforms to B.P.12). We have produced B.P. by heating white or red phosphorus at high pressures. Figure 4 shows powder X-ray patterns of B.P. prepared in the temperature range 200 - 500°C at 3.8 GPa. Solid structure of B.P. changes from amorphous to polycrystalline form depending on the applied pressure and temperature. Butuzov reported that a melting point of B.P. is about 1000°C at 1.8 GPa13). From the measurement of the electrical resistance of B.P. at high pressures and high temperatures, the effect of pressure on the melting point has been studied.

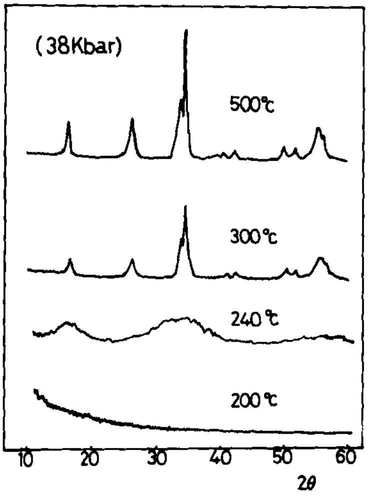

FIGURE 4 Powder X-ray patterns of B.P. prepared from white phosphorus at 3.8 GPa

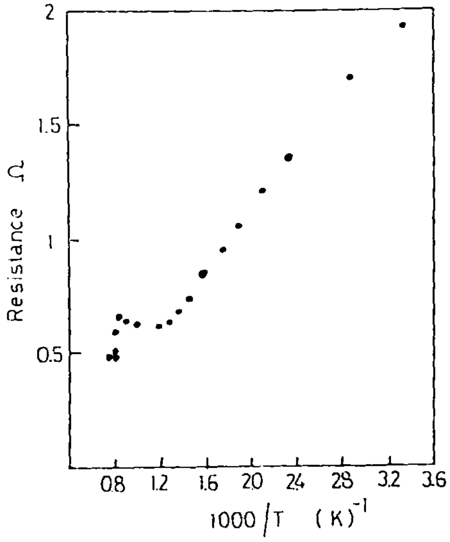

FIGURE 5 The electrical resistivity of polycrystalline B.P. plotted as a function of reciprocal temperature at 2.6 GPa

Figure 5 exhibits the electrical resistivity of polycrystalline B.P. plotted as a function of reciprocal temperature at 2.6 GPa. The resistivity decreased with increasing temperature up to about 820°C. Above this temperature the resistivity slightly increased with increasing temperature, reached a maximum at about 980°C, dropped abruptly with temperature. This is due to a phase transition from solid to liquid. We suggest that the temperature of the resistivity maximum is the melting point. Liquid B.P. behaved as a liquid metal at high pressures. The melting temperature increased with increasing pressure at the rate of 120°C/GPa. B.P. does not melt at atmospheric pressure but it decomposed to P_4 molecules in inert gases or in vacua around 490°C[9,14].

When B.P. is melted in a carbon furnace and slowly cools at about 2.3 GPa, large single crystals have often been grown. The size of the largest one was 4 mm in diameter and 5 mm in length. This is easily cleaved and exhibits a flakiniss similar to mica. Figure 6 indicates a cleavage plane(ac-plane) of B.P. single crystal. The flake shows metallic luster like silver and have a flexible. A long axis within the plane is parallel to the crystallographic a-axis, a short one is parallel to the c-axis. The b-axis which consists of layers separated by van der Waals forces is perpendicular to the cleavage plane.

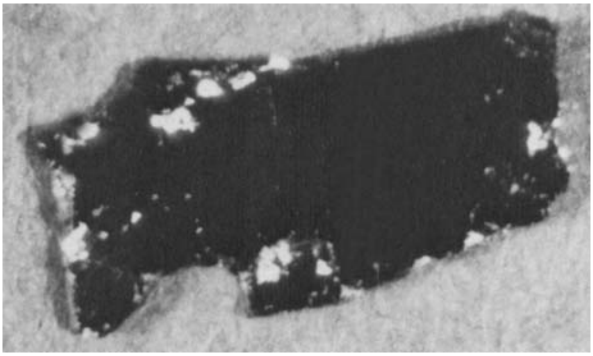

FIGURE 6 The cleavage plane of B.P. single crystal, size: 4 x 2 x 0.2 mm^3

The structure of B.P. is composed of corrugated double layers; each atoms is jointed by covalent bonds to three neighbors within the layers, each layer consists of two sets of zig-zag chains along the a-axis, the bond length along the chain is 2.221 A, bond angle is 96.5°. These are insensitive to pressure. This means a near zero compressibility in the a-direction. On the other hand, the linear compressibility in the c-didection within the layers is several orders of magnitudes larger than that in the a-direction. The compression is so anisotropic within the layers. For shortening a weak van der waals bonds with pressure the large compressibility has been observed along the b- axis. The data on the average linear compressibility6) are summarized in Table 1.

Table 1 Physical Properties Of Black Phosphorus

	Single Crystal			Poly-crystal
	a-axis	c-axis	b-axis	
Resistivity Ω·cm, at Atmospheric pressure	0.1	~1	10^2~10^3	1
Intrinsic Energy Gap, eV at atmospheric pressure	0.3 ~ 0.4			0.3 ~ 0.4
Resistivity Ω·cm 2.6 GPa	0.01	0.01	0.2	0.15
Intrinsic Energy Gap, eV 2.6 GPa	0.004 ~ 0.009			0.04
Effective Mass Hole a)	0.17	0.71	0.59	average 0.34
m^*/m_0 Electron	0.16	0.81	0.24	0.26
Linear Compressibility b) $\times 10^{-4}$ GPa^{-1}	0.7	124	119	

a) Asahina et al., Ref. 8, b) cartz et al., Ref. 6

Since the crystal structure is highly anisotropic, it expected that the electrical resistivity in the single crystals is very anisotropic. The resistivities along the a- and c-axis were about 0.1 Ω·cm and ~1 Ω cm, respectively at room temperature. The anisotropic resistivity within the layers has been observed. The resistivity along the b-axis (perpendicular to the layer) was 10^2~ 10^3 Ω·cm. Asahina et al. have found that as is given in Table 1, the effective masses in the b-direction are even smaller than those in the in-plane the c-direction, and have suggested that the electrical properties of B.P. may not be two dimensional8). However, as mentioned above, the resistivities in large single crystals show the character as a layered material at atmospheric pressure.

Figure 7 depicts the electrical resistivity in single

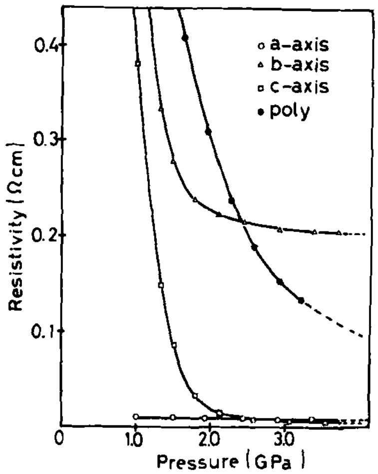

FIGURE 7 The effect of pressure on the electrical resistivity of B.P. single crystals at room temperature

crystals and polycrystals of BP as a function of pressure at room temperature. The resistivity along the a-axis was insensitive to pressure. Since the covalently bonded chains of atoms along the a-direction is very rigid, the overlap of electron cloud on P atoms does not almost increase at high pressures. On the other hand, the resistivity along the c-axis decreased rapidly with increasing pressure up to near 2.5 GPa and levelled off at higher pressures. The lowest P - P distance between adjacent chains within the layers reduces from 3.33 A at atmospheric pressure to 3.21 A at 2.66 GPa6). A marked reduction of the resistivity along the c-axis arises from an increase of interchain interaction with pressure. The values of the resistivities along the a- and c-axes became to be nearly equal at around 2.5 GPa. The electrical anisotropy in the layers almost disappered above this pressure. The resistivity along the b-axis sharply decreased with pressure in the low pressure region because of a marked shortening of the van der Waals bond between the layers. However, the resistivity at 3.0 GPa was about two orders of magnitudes larger than that of the a- and c-axes. These results suggest that orthorhombic B.P. may be transformed to the ordinary layered structure which is electrically isotropic within the layers at higher pressures. Jamieson has reported15) that the orthorhombic B.P. is transformed to a structure of the type arsenic A7 at around 6.0 GPa. In this structure a phosphorus atom has three neighbors at 2.13 A and the interlayer van der Waals distance is 3.27 A. Two dimensional character in B.P. has remained in the denser arsenic structure.

The intrinsic energy gaps were from 0.004 to 0.009 eV at 2.6 GPa. The anisotropic energy gap has not observed within the experimental error at atmospheric and high pressure. Asahina et al have calculated that the energy gap decreases at the rate of 0.23 eV/GPa. The experimental values were 0.11 - 0.15 eV/GPa. These are significantly smaller than the calculated value.

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