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Preparation and Properties of WP_4

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Introduction

Many transition metal polyphosphides MP_4 have recently been prepared. VP_4, CrP_4, and MoP_4 are isomorphous and metallic conductors due to the formation of metal chains in their crystal structure (*1, 2*). Metal pairs are formed in TcP_4 and ReP_4 (*3, 4*). RuP_4 and OsP_4 have α- and β-temperature modifications (*5, 6*). There are no metal–metal bonds in the Ru and Os compounds. The α forms are isostructural with CdP_4. MnP_4 and FeP_4 have also several modifications (*6–10*). The transition metals are divalent in these compounds and metal–metal interactions in their structures were explained by the number of *d* electrons (*5*). In the present investigation, WP_4 was prepared under high pressure.

Sample Preparation

Mixtures of tungsten and red phosphorous having various mixing ratios were reacted at 1000°C for 1 hr under 3 GPa in a cubic type high pressure vessel. Details of the high pressure experiments have already been described (*1, 11*). An unknown phase was observed when the starting composition of P/W was more than 2. It was contaminated with WP_2 when P/W < 4 and with black phosphorous when P/W > 4. X-ray powder diffraction data are summarized in Table I. Black single crystals with metallic luster and with irregular shapes were obtained when the starting mixture of composition P/W = 4 was held at 1000°C for 1 hr and slowly cooled to 600°C over 6 hr and then quenched to room temperature under high pressure of 3 GPa.

Characterization and Discussion

The X-ray powder diffraction data of WP_4 could not be indexed assuming the compound to be isostructural with other MP_4 phases. It was indexed as tetragonal with the aid of Weissenberg photographs. The lattice parameters were refined to be $a = 5.702$ Å, $c = 9.352$ Å by a least-squares procedure. The measured density was 6.2 $g \cdot cm^{-3}$ and the X-ray density was 6.72 $g \cdot cm^{-3}$ assuming four formula units.

Figure 1 shows the density of WP_4 compared with the values for other tungsten phosphides which can be obtained at ambi-

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TABLE I

X-RAY POWDER PATTERN OF WP_4

$H\ K\ L$	I_{obs}	d_{obs}	d_{calc}
0 0 2	vs	4.674	4.674
1 1 0	s	4.030	4.032
1 1 2	vvs	3.057	3.054
2 0 0	m	2.852	2.851
2 1 1	w	2.459	2.460
2 0 2	s	2.433	2.434
1 1 4	s	2.022	2.022
2 2 0	m	2.017	2.016
2 1 3	vw	1.974	1.974
2 2 2	w	1.851	1.851
2 0 4	m	1.808	1.808
3 1 0	s	1.803	1.803
3 1 2	w	1.682	1.682
0 0 6	vw	1.559	1.559

ent pressure in a sealed quartz tube (*12*). The densities of the phosphides can be related to the amounts of phosphorous. WP_4 fits well into the curve in Fig. 1. All compounds in the figure, except black phosphorous and WP_4, can be obtained under an ambient pressure. These results suggest that WP_4 is metastable under normal pressure conditions. Decomposition of WP_4 to WP_2 and to WP was observed for a sample kept at ambient conditions for 3 months.

Electrical resistivity was measured on a pellet of polycrystalline material using the four-probe technique. WP_4 was a metallic conductor; $\rho_{285\ K} = 1.42\ \Omega cm$, $\rho_{89\ K} = 0.99\ \Omega cm$. Magnetic susceptibility was 1.73×10^7 emu $\cdot$ g^{-1} in the range between room temperature and liquid nitrogen. WP_4 does not have exactly the same crystal structure as CrP_4 and MoP_4 although tungsten forms a VIa group with Cr and Mo in the periodic table. CrP_4 and MoP_4 have monoclinic lattices with $a = 5.191$, $b = 10.760$, $c = 5.771$ Å, $\beta = 110.65°$ and $a = 5.313$, $b = 11.139$, $c = 5.820$ Å, $\beta = 110.64°$ respectively. However, WP_4 probably has W chains which are similar to those found in VP_4, CrP_4, and MoP_4.

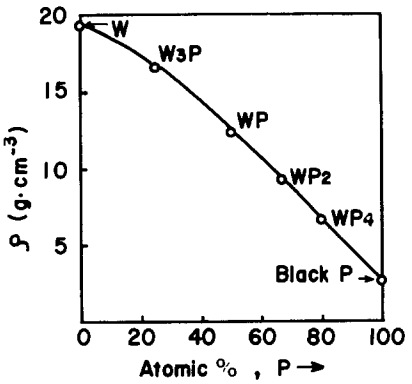

FIG. 1. Densities in the binary system W–P.

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