New Hafnium Phosphides

TORSTEN LUNDSTRÖM and
PILAI TANSURIWONGS

*Institute of Chemistry, University of Uppsala,
Uppsala, Sweden*

In earlier investigations of the hafnium phosphorus system, three hafnium phosphides have been reported. The existence and structure of HfP was reported by Jeitschko and Nowotny in 1962.[1] The preparation and characterization of HfP_2 was made by Hulliger[2] somewhat later. Hf_3P was prepared recently.[3]

As a part of crystal-chemical investigations on the phosphides of group IV and V metals it was decided to reinvestigate the Hf—P system. The aim of this investigation was to establish the two-phase equilibria of the system at one temperature.

The compounds were prepared by reacting turnings from zone-refined polycrystalline bars of hafnium, containing 3 % zirconium (from Koch-Light, claimed non-metallic impurities less than 10 ppm C, 10 ppm H_2, 10 ppm N_2 and 50 ppm O_2) and red phosphorus of better than 99 % purity. Optimum conditions for the reaction in evacuated silica capsules were 3 days at 850°C. The reaction products, invariably consisting of HfP and Hf in the region Hf—HfP, were then arc-melted under purified argon and heat-treated at 1000°C for 5—10 days. In some cases a further heat-treatment was carried out, but no significant differences were observed on the powder patterns.

The X-ray analysis of the specimens was performed with Guinier-Hägg type focussing cameras using Cu$K\alpha_1$ or Cr$K\alpha_1$ radiation. The cell dimensions given in Table 1 are based on silicon as internal calibration standard with $a = 5.43054$ Å. The observed and calculated θ-values were matched using the least-squares program CELSIUS, written by J. Tegenfeldt, Institute of Chemistry, Uppsala.[4] It should be

Table 1. Cell dimensions for hafnium phosphides in two-phase regions.

Nominal comp.	Heat treatment	Observed phases	Cell dimensions(Å)		Standard dev.(Å)	Cell volume(Å^3)
$HfP_{0.25}$	1000°C, 6 d.	Hf + Hf_3P	Hf	$a =$ 3.211		45.6
				$c =$ 5.106		
			Hf_3P	$a =$ 10.6683	0.0005	602.6
				$c =$ 5.2948	0.0005	
$HfP_{0.44}$	1000°C, 5 d.	Hf_3P + Hf_2P	Hf_3P	$a =$ 10.6696	0.0003	602.8
				$c =$ 5.2954	0.0002	
			Hf_2P	$a =$ 15.0398	0.0016	659.2
				$b =$ 12.2770	0.0014	
				$c =$ 3.5701	0.0001	
$HfP_{0.57}$	1000°C, 7 d.	Hf_2P + Hf_3P_2	Hf_2P	$a =$ 15.0577	0.0012	661.5
				$b =$ 12.2954	0.0013	
				$c =$ 3.5728	0.0004	
			Hf_3P_2	$a =$ 10.1359	0.0014	357.5
				$b =$ 3.5770	0.0005	
				$c =$ 9.8603	0.0012	
$HfP_{0.80}$	1000°C, 6 d.	Hf_3P_2 + HfP	Hf_3P_2	$a =$ 10.1401	0.0008	358.5
				$b =$ 3.5774	0.0003	
				$c =$ 9.8829	0.0012	
			HfP	$a =$ 3.6461	0.0003	142.3
				$c =$ 12.3614	0.0011	
$HfP_{1.30}$	1000°C, 5 d.	HfP + HfP_2	HfP	$a =$ 3.6501	0.0001	142.8
				$c =$ 12.3796	0.0003	
			HfP_2	$a =$ 6.4676	0.0003	195.7
				$b =$ 3.4986	0.0003	
				$c =$ 8.6476	0.0004	

noted, that the systematic errors in some cases may be greater than the errors indicated by the standard deviations of Table 1. The estimated accuracy is ± 0.04 %.

The results of this investigation are collected in Table 1, which shows the cell dimensions of two previously unknown phases as well as those of the phases reported earlier. The lattice parameters of HfP_2 agree well with those reported by Hulliger,[2] while the small variation in the cell dimensions of HfP indicates a homogeneity range for this phase at 1000°C. No HfP of NaCl type structure was found in arc-melted alloys, although this structure has been reported to exist above 1600°C.[5] Furthermore, HfP was heat-treated at 1300°C for 40 h and at 1600°C for 10 h in a high-frequency furnace under a purified argon atmosphere and then quenched in water-cooled vacuum-oil. No NaCl type structure could be detected in the samples after this treatment. The thermal stability of HfP_2 is the highest among the diphosphides of group IV metals, HfP_2 being only slightly decomposed at 1000°C. In contrast, the decomposition of TiP_2 is significant at 600°C and according to Irani and Gingerich[5] appreciable amounts of phosphorus are evolved by ZrP_2 at 850°C. Thus the thermal stability of the group IV diphosphides increases in order $TiP_2 < ZrP_2 < HfP_2$.

Hf_3P was reported by Ganglberger *et al.*[3] to belong to the Ti_3P type structure. This result was corroborated through the observation of reflections for which $h + k + l = 2n + 1$. However, the cell dimensions of this phase (see Table 1) are in less good agreement with those reported, $a = 10.98$ Å and $c = 5.35$ Å. The cause of such a large discrepancy can certainly not be inaccurate measurement of the cell dimensions. The samples of Ganglberger *et al.* were, however, prepared through sintering of hafnium-phosphide powder at 2300°C in a hydrogen atmosphere.[6] Furthermore, the cell volume obtained by us, 602.6 Å^3, is smaller than that[7] of Zr_3P, 624.5 Å^3, as expected from the metal radii, while the cell volume of Ganglberger *et al.* is larger than that of Zr_3P. Thus it seems reasonable to assume that hydrogen is soluble to some extent in Hf_3P.

The cell dimensions of Hf_2P indicated that the structure might be isotypic with that of Ta_2P, recently determined by Nylund.[8] A Weissenberg film from a single-crystal of Hf_2P was then compared with that from Ta_2P, and the isotypism was confirmed. The cell dimensions given in Table 1 show small variations, which indicates a limited range of homogeneity.

Single-crystals of the phase designated Hf_3P_2 in Table 1 were selected from an arc-melted sample with the nominal composition $HfP_{0.75}$. The composition Hf_3P_2 deduced from density considerations is somewhat uncertain, but will be definitely settled through a structure determination. The symmetry is orthorhombic, and the cell dimensions, given in Table 1, indicate a certain range of homogeneity.

Acknowledgements. The authors wish to thank Prof. Gunnar Hägg for his kind interest and for all facilities put to our disposal. This investigation was supported by grants from the *Swedish Natural Science Research Council.*

1. Jeitschko, W. and Nowotny, H. *Monatsh.* **93** (1962) 1107.
2. Hulliger, F. *Nature* **204** (1964) 775.
3. Ganglberger, E., Nowotny, H. and Benesovsky, F. *Monatsh.* **97** (1966) 1696.
4. Tegenfeldt, J. *Institute of Chemistry, Uppsala. Unpublished.*
5. Irani, K. S. and Gingerich, K. A. *J. Phys. Chem. Solids* **24** (1963) 1153.
6. Ganglberger, E. *Private communication.*
7. Lundström, T. *Acta Chem. Scand.* **20** (1966) 1712.
8. Nylund, A. *Acta Chem. Scand.* **20** (1966) 2393.

Received January 20, 1968.