Crystal Structure Refinement of the κ-phase in the Hf−Mo−P System

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The crystal structure of κ-(Hf−Mo−P) has been determined using X-ray single-crystal diffractometry. κ-(Hf−Mo−P) crystallizes in the space group $P6_3/mmc$ (No. 194) with the cell dimensions: $a = 8.6236(4)$ Å, $c = 8.6101(6)$ Å. The structure has been refined on F^2 to an $R(F^2)$-value of 0.1286 without excluding any reflexions. κ-(Hf−Mo−P) is isostructural with κ-Hf_9Mo_4Ni but some hafnium substitution occurs on the molybdenum sites. According to the final refinement the composition is $Hf_{9+x}Mo_{4-x}P$ with $x = 0.29(4)$.

In a recent communication[1] κ-type phases were reported to occur in the ternary systems Hf−Mo−{Si, P, S} and Hf−Mo−{Ge, As, Se}. It was observed that the unit cell volumes increased in the order κ-(Hf−Mo−Si)→κ-(Hf−Mo−P)→κ-(Hf−Mo−S), and an analogous observation was also made for the Ge, As, Se series. This feature cannot be explained in terms of nonmetal atom size effects, since the normal sizes of the nonmentals concerned decrease for both series of compounds. Vacancies or atomic substitutions in the structure might presumably be responsible for the anomalous cell volume trend, and it was therefore decided to examine some of the κ-phase structures in greater detail by accurate X-ray diffraction methods. In the present paper the results from an X-ray single-crystal refinement of κ-(Hf−Mo−P) are reported.

EXPERIMENTAL

Preparation and phase analysis. The starting materials and the method of synthesis have been described in an earlier paper.[1] Powder photographs showed diffraction lines solely from κ-(Hf−Mo−P), indicating that the sample was a single phase.

Chemical analysis. Phosphorus. The sample was dissolved in a mixture of fuming nitric acid, hydrofluoric acid and sulfuric acid with addition of perchloric acid to complete the oxidation of phosphorus. After evaporation and heating to fumes of sulfuric acid the residue was taken up in water and hydrofluoric acid. In an aliquot of this solution the phosphorus was determined spectrophotometrically according to Murphy and Riley[2] after addition of boric acid.

Molybdenum. The sample was dissolved in a mixture of sulfuric, hydrofluoric, nitric and perchloric acids, the solution evaporated and heated to fumes of sulfuric acid and the residue taken up in water. The precipitate of hafnium phosphate was removed by filtration and molybdenum determined in the filtrate by reduction in a cadmium reductor and titration with permanganate.

Hafnium. The sample was dissolved and treated as for molybdenum, and hafnium was determined separately in precipitate and solution. Hafnium remaining in the solution was precipitated with mandelic acid and the precipitate ignited to and weighed as HfO_2. The hafnium phosphate precipitate was fused with sodium carbonate and the melt extracted with water to remove phosphate. The residue was fused with potassium pyrosulfate, the melt brought into solution and hafnium precipitated with ammonia and ignited to HfO_2. The result for Hf includes Zr and the calculation was based on the assumption of 3 weight percent of Zr in the hafnium as analyzed in the hafnium used for the synthesis. The result of the analysis was: 80.5(2) % Hf+Zr, 18.14(2) % Mo and 1.48(2) % P.

X-Ray diffraction measurements and data reduction. X-Ray powder photographs were taken using a Guinier-Hägg-type focusing camera with $CrK\alpha_1$ radiation ($\lambda = 2.289753$ Å) and Si ($a = 5.431065$ Å)[3] as internal standard. The unit cell dimensions were refined using the local program CELNE.[4] After

several attempts a small fragment was found which proved to be a single crystal when examined in a Weissenberg camera. A Nonius CAD 4-F diffractometer controlled by a PDP 8/A computer was used to record the intensity data. Graphite-monochromatized MoKα radiation ($\lambda = 0.71069$ Å) and the $\omega/2\theta$-scan technique were employed. During the data collection four reflexions were used as monitors and checked after every 20th reflexion scanned. The intensity of these monitors had been reduced by about 2.5 % at the end of the data collection and a linear correction was applied. F_o^2 and $\sigma_c(F_o^2)$ values were obtained from the integrated peak intensities by applying corrections for background, Lorentz and polarization effects (assuming the monochromator to be ideally imperfect), and for absorption. The crystal was of irregular shape and was approximated with five boundary planes to a polyhedron with dimensions of the order of $0.04 \times 0.03 \times 0.02$ mm. Corrections for absorption were applied using the Gaussian grid method and a calculated linear absorption factor of 874 cm^{-1}. The transmission factors were found to vary from 0.19 to 0.41. In total 2736 reflexions up to $100.0°$ in 2θ were recorded which included the 24 symmetry related reflexions of the form $\{21\bar{3}2\}$ which were used to check the absorption correction. After averaging equivalent reflexions 1130 remained.

Calculations. All calculations were performed with a NORD 100 computer using a system of programs described by Lundgren.[5]

STRUCTURE ANALYSIS AND RESULTS

The diffraction symmetry and the systematic absences of reflexions confirmed the space group to be $P6_3/mmc$ (No. 194) as in the case of κ-(Hf−Mo−B)[6] and κ-(Hf−Mo−Ni).[7] The structure was refined using a full-matrix least-squares program using the atomic coordinates of κ-(Hf−Mo−Ni)[7] as initial values for the positional parameters, with phosphorus replacing nickel. The atomic scattering factors for neutral atoms were used and corrected for anomalous dispersion[8] (real as well as imaginary parts). The quantity minimized was $\Sigma w(|F_o^n| - k^n \cdot |F_o^n|)^2$ with $n = 1$ or 2 and the weight w was given by

$$w^{-1} = \sigma_c^2(F_o^n) + (p \cdot |F_o^n|)^2$$

where σ_c is the standard deviation of F_o^n based on counting statistics and p an empirical parameter chosen to obtain a satisfactory weight analysis (p was 0.04 in the final refinement). The agreement indices are defined as

$$R(F^n) = \Sigma(|F_o^n| - |F_c^n|)/\Sigma|F_o^n|$$

$$R_w(F^n) = [\Sigma w(|F_o^n| - |F_c^n|)^2/\Sigma|F_o^n|^2]^{1/2}$$

with $n = 1$ or 2, and where F_o has been multiplied by $1/k^n$.

During a preliminary refinement based on F it was obvious that the strongest observed values F_o were consistently lower than the calculated values F_c. An isotropic extinction correction was therefore applied including the whole material (2736 reflexions). The largest extinction correction was 37 %. The internal consistency factor for symmetry related reflexions (defined analogously to the conventional agreement factor) decreased from 4.71 % to 3.80 %. All subsequent refinements were based on the averaged extinction-corrected F^2 data.

The following refinement was based on the 650 strongest reflexions $[> 3\sigma_c(F_o^2)]$ and an $R(F)$-value of 0.1084 was obtained. In order to avoid bias of the input data by the exclusion of "unobserved" reflexions[9,10] all reflexions were included yielding an $R(F)$-value of 0.1330. Since the crystal was rather small, the measured intensities were weak and more than 40 % of the reflexions had an intensity less than $3\sigma_c(F_o^2)$. The agreement factors for a refinement omitting observations with $F_o^2 < 3\sigma_c(F_o^2)$ were hence much lower than those for a refinement using the complete material (Table 1). The standard deviations obtained using all reflexions were however about 20 % smaller than those based on the restricted material. Introduction of anisotropic temperature factors improved the agreement

Table 1. R-Factors from isotropic and anisotropic refinements on F^2 of κ-(Hf−Mo−P).

No. of refl.	No. of param.	$R(F^2)$	$R_w(F^2)$	$R(F)$
Isotropic refinement				
650($>3\sigma$)	10	0.1084	0.1458	0.0690
1130	10	0.1330	0.1636	0.1234
Anisotropic refinement				
1130	19	0.1303	0.1571	0.1227
1130[a]	21	0.1286	0.1537	0.1216
1130[b]	22	0.1284	0.1537	0.1216
1130[c]	23	0.1284	0.1537	0.1216

[a] Substitution of Hf on the positions 6h and 2a. [b] P vacancies on the position 2c. [c] Oxygen present on the position 6g.

Table 2. Structure data for κ-$Hf_{9.29}Mo_{3.71}P$. Standard deviations are given in parentheses. Space group $P6_3/mmc$ (No. 194), $Z = 2$. Cell dimensions: $a = 8.6236(4)$ Å, $c = 8.6101(6)$ Å. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)]$.

Atom	Position	Positional parameters $x(y=2x)$	z	$U_{ij} \times 10^4$ (Å²) U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy (%)
Hf(1)	12k	0.19879(5)	0.04836(8)	48(2)	56(2)	49(2)	$U_{22}/2$	$U_{23}/2$	−9(2)	100
Hf(2)	6h	0.53992(7)	1/4	47(2)	82(4)	54(3)	$U_{22}/2$	0	0	100
Mo(1) Hf(3)	6h	0.88991(12)	1/4	31(5)	26(6)	29(5)	$U_{22}/2$	0	0	93.3(1.1) 6.7(1.1)
Mo(2) Hf(4)	2a	0	0	39(8)	U_{11}	43(11)	$U_{11}/2$	0	0	91.6(2.2) 8.4(2.2)
P	2c	1/3	1/4	29(23)	U_{11}	24(35)	$U_{11}/2$	0	0	100

factors somewhat (see Table 1) and a Hamilton *R*-factor significance test[11] favoured the anisotropic model at the 99.5% confidence level. Due to the experimental difficulties in making a proper geometrical description of the crystal and the very strong absorption, the intensity data could, however, suffer from systematic errors. A ΔR normal probability plot[12] after the refinement, including all 1130 reflexions gave a least-squares line with a slope of 1.33 and an intercept of 0.14 in the interval $|\Delta R| < 4.0$ (11 reflexions outside). All points were very close to a straight line. This indicates that the Hamilton test may not be invalidated by the influence of systematic errors.

At this stage of refinement a Fourier difference synthesis was calculated. It indicated excess

Table 3. Interatomic distances (Å) for κ-$Hf_{9.29}Mo_{3.71}P$. Distances shorter than 4.00 Å are listed. The estimated standard deviations are less than 0.001 Å for all distances.[a]

Hf(1)−P	2.656	Mo(1)−2Mo(2)	2.709
Mo(1)	2.890	2Mo(1)	2.848
Mo(2)	2.998	2Hf(1)	2.890
2Hf(1)	3.084	2Hf(2)	2.897
2Mo(1)	3.107	4Hf(1)	3.107
2Hf(2)	3.221		
2Hf(2)	3.228	Mo(2)−6Mo(1)	2.709
Hf(1)	3.472	6Hf(1)	2.998
2Hf(1)	3.481		
		P−6Hf(1)	2.656
Hf(2)−2Mo(1)	2.897	3Hf(2)	3.086
P	3.086		
4Hf(1)	3.221		
4Hf(1)	3.228		
2Hf(2)	3.279		

[a] The sites Mo(1) and Mo(2) are partly occupied by hafnium.

scattering power associated with both the molybdenum sites. The possibility of hafnium substitution on these sites was therefore tested. Refinement gave the value of 6.7(1.1) % for the occupancy parameter of hafnium on the position 6h and the value of 8.4(2.2)% on the position 2a. Although no other deviations were detected in the difference synthesis two other modifications of the structure model were tried. First, the possibility of phosphorous vacancies on the site 2c was tested and secondly, the site 6g was assumed to be partly occupied by oxygen as in κ-(Hf−Mo−Ni).[7] None of these two refinements indicated any deviation from the initial model. *R*-Values for the different refinements are listed in Table 1.

No further improvements were attempted and the results from the final refinement, including Hf/Mo substitution on the sites 6h and 2a are presented in Table 2. Corresponding interatomic distances are given in Table 3. The total number of parameters varied was 21 (one scale factor, 4 positional parameters, 2 occupancy parameters and 14 anisotropic thermal vibration parameters).

A list of observed and calculated structure factors has been deposited at the Institute of Chemistry, Uppsala, and can be obtained on request.

DISCUSSION

As mentioned in the introduction, the purpose of the present investigation was to determine whether crystal defects, such as atomic substitutions or vacancies, might be responsible for the observed cell volume anomaly in the two series of κ-phases: κ-(Hf −Mo−{Si, P, S}) and κ-(Hf−Mo−{Ge, As, Se}). For the only κ-phase structures examined earlier by high-precision diffraction techniques,[7,13] the defects

observed were associated with the nonmetal sublattice. In κ-(W $-$Co$-$C) there were vacancies on the $2c$ carbon positions, and in κ-(Hf $-$Mo$-$Ni) the $6g$ position was partially occupied by oxygen. In an earlier report [1] it was therefore suggested that the observed cell volume anomaly might be connected with the distribution of the nonmetal atoms in the structure. The present results of the structure refinement indicate, however, that atomic substitutions in the metal sublattice may be the cause of the cell volume anomalies. The $2c$ position is completely occupied by phosphorus (and the $6g$ position is empty), while Hf/Mo substitution occurs on both the $2a$ and the $6h$ molybdenum sites (see Fig. 1). The composition corresponds to the formula $Hf_{9.29(4)}Mo_{3.71(4)}P$. The results of the chemical analysis give the formula $Hf_{9.20(2)}Mo_{3.80(2)}P_{0.96(1)}$, calculated on the basis of thirteen metal atoms per formula unit. Although the powder photographs showed diffraction lines from the κ-phase only, the presence of minor amounts of impurity phases in the sample cannot be excluded. Assuming for instance the presence of 1% by weight for each of Hf and $HfMo_2$ (which would probably be below the limits of detection), the composition of the κ-phase would be $Hf_{9.27(2)}Mo_{3.73(2)}P_{0.98(1)}$. Accordingly, the results of the structure refinement and the chemical analysis agree to within experimental errors.

It seems very likely that an increasing degree of Hf/Mo substitution in the series κ-(Hf $-$Mo$-$Si), κ-
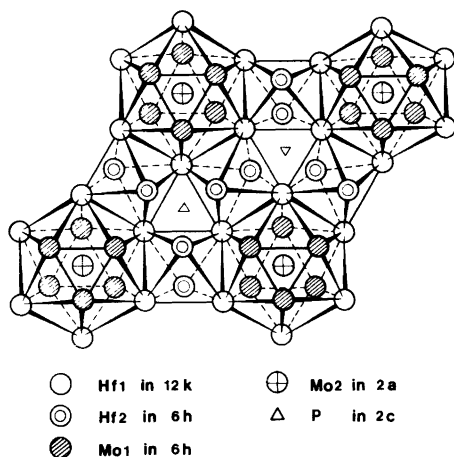

○   Hf1 in 12k   ⊕   Mo2 in 2a
◎   Hf2 in 6h   △   P   in 2c
◍   Mo1 in 6h

Fig. 1. The structure of κ-(Hf$-$Mo$-$P) projected along the hexagonal axis. The sites Mo1 and Mo2 are partly occupied by hafnium.

(Hf$-$Mo$-$P), κ-(Hf$-$Mo$-$S) (and analogously in the series containing Ge, As and Se) is entirely responsible for the cell volume anomaly. This hypothesis is supported by a simple estimation of the cell volume effects produced by Hf/Mo substitution. Assuming that the unit cell volumes are proportional to the sums of the atomic volumes of the constituent elements, the calculated unit cell volume for κ-(Hf$-$Mo$-$P) (using the occupancy parameters obtained from the present structure refinement) is:

$$(18.57r_{Hf}^3 + 7.43r_{Mo}^3 + 2r_P^3)s = 96.290s,$$

where s is a proportionality constant, $r_{Hf} = 1.58$ Å, $r_{Mo} = 1.40$ Å (Goldschmidt radii for 12-coordination) and $r_P = 1.10$ Å (Pauling covalent radius). For κ-(Hf$-$Mo$-$Si) a similar calculation, assuming a completely ordered distribution of all atoms, yields the value

$$(18r_{Hf}^3 + 8r_{Mo}^3 + 2r_{Si}^3)s = 96.148s.$$

This indicates that a greater degree of Hf/Mo substitution in κ-(Hf$-$Mo$-$P) may well outweigh the influence of the larger Si atom ($r_{Si} = 1.17$ Å) as compared with P.

In order to substantiate the present hypothesis, a single crystal refinement of the κ-(Hf$-$Mo$-$Ge) structure has been started. κ-(Hf$-$Mo$-$Si) would be preferable for a study, but unfortunately all attempts to grow single-crystals of this material have been unsuccessful.

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