JOURNAL OF SOLID STATE CHEMISTRY **57**, 373–378 (1985)

Crystal Structure Refinements of the κ Phases in the Hf–Mo–Se and Hf–Mo–Ge Systems

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Received June 27, 1984; in revised form October 31, 1984

The crystal structures of κ-(Hf–Mo–Se) and κ-(Hf–Mo–Ge) were determined using X-ray single-crystal diffractometry. Both structures crystallize in the space group $P6_3/mmc$ (No. 194) with the unit-cell dimensions $a = 8.6995(4)$ Å, $c = 8.6234(7)$ Å for κ-(Hf–Mo–Se) and $a = 8.6394(4)$ Å, $c = 8.6827(5)$ Å for κ-(Hf–Mo–Ge). The structures have been refined on F^2 to $R(F^2)$ values of 0.0784 and 0.0661, respectively. κ-(Hf–Mo–Se) and κ-(Hf–Mo–Ge) are isostructural with κ-(Hf–Mo–P) with a variable degree of hafnium substitution on the molybdenum sites of the structure. In κ-(Hf–Mo–Ge) germanium vacancies were found to occur on the trigonal prismatic 2*c* site and the phase was also found to contain oxygen on the octahedral 6*g* site. According to the final refinements the compositions are $Hf_{9+x}Mo_{4-x}Se$ with $x = 0.40(2)$ and $Hf_{9+x}Mo_{4-x}Ge_yO_z$ with $x = 0.25(2)$, $y = 0.88(1)$, and $z = 1.47(12)$.

Introduction

The κ phases in the ternary systems Hf–Mo–{Si, P, S, Ge, As, Se} have been reported to possess ranges of homogeneity (*1*). The structural mechanism mainly responsible for the extension of the homogeneity ranges was proposed to be a variable degree of hafnium substitution on the molybdenum sites in the κ phase. This type of substitution had earlier been found to occur in the κ-(Hf–Mo–P) phase (*2*). The present investigation provides results from X-ray single-crystal structure refinements for a κ phase in the Hf–Mo–Se system and an oxygen-containing κ phase in the Hf–Mo–Ge system.

Experimental

Preparation and Phase Analysis

The starting materials and the method of synthesis have been described earlier (*3*). The alloy in the Hf–Mo–Se system showed diffraction lines exclusively from the κ-(Hf–Mo–Se) phase as revealed by powder photographs. In the course of the synthetic work on Hf–Mo–Ge alloys it was observed that very long annealing times were required for κ-phase formation. However, in one experiment where accidental contamination by oxygen had occurred, the κ phase formed very rapidly. It was suspected that this behavior might be connected with the

0022-4596/85 $3.00

occurrence of a quaternary κ-(Hf–Mo–Ge–O) phase, and in order to substantiate this hypothesis a single crystal from the oxygen-containing alloy was selected for structure analysis. Powder diffraction examination of the alloy indicated the presence of trace amounts of Hf_3Ge and $HfMo_2$.

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 (λ = 2.89753 Å) and Si (a = 5.431065 Å) (*4*) as internal standard. The unit-cell dimensions were refined using the local program CELNE (*5*). The intensity data for both crystals were recorded using the same equipment and experimental conditions as for κ-(Hf–Mo–P) (*2*), and information on the data collection and the processing parameters is given in Table I. 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). Corrections for absorption were also applied using the Gaussian grid method. The rather irregular shapes of the crystals were approximated to polyhedra by a suitable number of boundary planes.

TABLE I

DATA COLLECTION AND PROCESSING PARAMETERS[a]

Parameter	κ-(Hf–Mo–Se)	κ-(Hf–Mo–Ge)
2θ limit (°)	100.0	100.0
No. reflections collected	2798	2773
No nonequivalent	1160	1150
R_{equiv}[b]	0.0817	0.0735
Test reflections		
Number	4	4
Interval	20	20
Intensity decrease (%)	10.7	11.0
Correction	Linear	Linear
$\mu(MoK\alpha)$ (cm^{-1})	888	888
Crystal dimensions (μm)	25 × 40 × 40	30 × 40 × 40
No. of boundary planes (abs. corr.)	5	6
Transmission values	0.10–0.31	0.11–0.27
R_{equiv} (abs. corr. applied)[b]	0.0468	0.0565

[a] Graphite-monochromatized $MoK\alpha$ radiation (λ = 0.71069 Å) was used for the collection of the intensity data.

[b] $R_{equiv} = \sum_{i,n} |I_{i,n} - \langle I_n\rangle| / \sum_{i,n} I_{i,n}$, where $\langle I_n\rangle$ is the average intensity of a group of equivalent reflections.

Calculations

All calculations were performed with a NORD100 computer using a system of programs described by Lundgren (*6*).

Structure Analysis and Results

The diffraction symmetry and the systematic absences of reflections confirmed the space group of the compounds to be $P6_3/mmc$ (No. 194) as in the case of the earlier single-crystal structure refinements of κ phases (*2, 7, 8*). The structures were refined using a full-matrix least-squares program, with the atomic coordinates of κ-(Hf–Mo–P) (*2*) as initial values for the positional parameters, and with selenium and germanium, respectively, replacing phosphorus. The atomic scattering factors for neutral atoms were used, corrected for anomalous dispersion (*9*) (real as well as imaginary parts). The quantity minimized was $\Sigma w(|F_o^n| - k^n \cdot |F_c^n|)^2$ 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 is an empirical parameter chosen to obtain a satisfactory weight analysis (p was 0.042 for κ-(Hf–Mo–Se) and 0.050 for κ-(Hf–Mo–Ge) in the final refinement). The residual values $R(F^n)$ and $R_w(F^n)$ have been defined elsewhere (*2*).

During the preliminary refinements based on F it was obvious that the strongest observed F_o values were consistently lower than the calculated F_c values. The strongest reflection for both crystals, 004, was omitted and isotropic extinction corrections were applied on the remaining reflections (2797 and 2772 reflections for κ-(Hf–Mo–Se) and κ-(Hf–Mo–Ge), respectively). The largest extinction corrections were 13% for

TABLE II

STRUCTURE DATA FOR κ-(Hf–Mo–Se)

Atom	Position	Positional parameter x ($y = 2x$)	z	$U_{ij} \times 10^4$ (Å^2) U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy (%)
Hf(1)	12k	0.19608(3)	0.04704(5)	75(1)	78(1)	39(1)	$U_{22}/2$	$U_{23}/2$	−10(1)	100
Hf(2)	6h	0.54318(4)	$\frac{1}{4}$	68(1)	97(2)	46(2)	$U_{22}/2$	0	0	100
Mo(1)	6h	0.89013(6)	$\frac{1}{4}$	66(3)	55(3)	13(3)	$U_{22}/2$	0	0	88.2(7)
Hf(3)										11.8(7)
Mo(2)	2a	0	0	55(4)	U_{11}	10(6)	$U_{11}/2$	0	0	95.7(1.1)
Hf(4)										4.3(1.1)
Se	2c	$\frac{1}{3}$	$\frac{1}{4}$	129(6)	U_{11}	9(9)	$U_{11}/2$	0	0	100

Note. Standard deviations are given in parentheses. Space group $P6_3/mmc$ (No. 194), $Z = 2$. Cell dimensions: $a = 8.6995(4)$ Å, $c = 8.6234(7)$ Å. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$.

κ-(Hf–Mo–Se) and 42% for κ-(Hf–Mo–Ge). All subsequent refinements were based on the two averaged extinction-corrected F^2 data sets.

The refinements of the two structures were carried out analogously with the refinements of the κ-(Hf–Mo–P) phase (*2*). All reflections except 004 were included, and anisotropic temperature factors were used.

κ-(*Hf–Mo–Se*)

A ΔR normal probability plot (*9*) after the final refinement including all reflections gave a least-squares line with a slope of 1.15 and an intercept of 0.17 in the interval $|\Delta R| < 4.0$ (11 reflections outside). All points were close to a straight line. No deviations from the initial model were indicated by a Fourier difference synthesis. Final structural parameters are presented in Table II and interatomic distances in Table III. The small values of the U_{33} parameters as compared to those of U_{11} and U_{22} could possibly be an artifact due to the approximate character of the absorption correction. The total number of parameters varied was 21 (1 scale factor, 4 positional parameters, 2 occupancy parameters, and 14 anisotropic thermal vibration parameters). The largest correlation coefficients between occupancy and thermal parameters were less than 0.60. Final R values were $R(F^2) = 0.0784$ and $R_w(F^2) = 0.0967$.

κ-(*Hf–Mo–Ge*)

Two deviations from the initial model were indicated by a Fourier difference synthesis. First, there was a negative region at the 2c germanium position, and second

TABLE III

INTERATOMIC DISTANCES (Å) FOR κ-(Hf–Mo–Se)

Hf(1)– Se	2.709	Mo(1)–2Mo(2)	2.718
Mo(1)	2.872	2Mo(1)	2.867
Mo(2)	2.982	2Hf(1)	2.872
2Hf(1)	3.064	2Hf(2)	2.921
2Mo(1)	3.105	4Hf(1)	3.105
2Hf(2)	3.233		
2Hf(2)	3.286	Mo(2) –6Mo(1)	2.718
Hf(1)	3.500	6Hf(1)	2.982
2Hf(1)	3.582		
Hf(2)–2Mo(1)	2.921	Se–6Hf(1)	2.709
Se	3.162	3Hf(2)	3.162
2Hf(2)	3.223		
4Hf(1)	3.233		
4Hf(1)	3.286		

Note. Distances shorter than 4.00 Å are listed. The estimated standard deviations are less than 0.001 Å for all distances. The sites Mo(1) and Mo(2) are partly occupied by hafnium.

TABLE IV

STRUCTURE DATA FOR κ-(Hf–Mo–Ge–O)

Atom	Position	Positional parameters		$U_{ij} \times 10^4$ (Å²)						Occupancy (%)
		x ($y = 2x$)	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
Hf(1)	12k	0.19912(2)	0.04652(4)	57(1)	72(1)	87(1)	$U_{22}/2$	$U_{23}/2$	0(1)	100
Hf(2)	6h	0.54074(3)	$\frac{1}{4}$	52(1)	68(2)	70(2)	$U_{22}/2$	0	0	100
Mo(1)	6h	0.89093(5)	$\frac{1}{4}$	48(2)	40(2)	45(3)	$U_{22}/2$	0	0	93.9(6)
Hf(3)										6.1(6)
Mo(2)	2a	0	0	49(3)	U_{11}	51(6)	$U_{11}/2$	0	0	93.4(1.0)
Hf(4)										6.6(1.0)
Ge	2c	$\frac{1}{3}$	$\frac{1}{4}$	63(6)	U_{11}	39(10)	$U_{11}/2$	0	0	88(1)
O	6g	$\frac{1}{2}$	0	—[a]	—	—	—	—	—	49(4)

Note. Standard deviations are given in parentheses. Space group $P6_3/mmc$ (No. 194), $Z = 2$. Cell dimensions: $a = 8.6396(4)$ Å, $c = 8.6827(5)$ Å. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$.

[a] $B_{iso} = 1.6(4)$ Å².

there was some scattering power associated with the 6g position. These features were incorporated into the final refinement, assuming germanium vacancies on 2c and oxygen occupation of 6g. A ΔR normal probability plot (*9*) including all reflections gave a least-squares line with a slope of 1.08 and an intercept of 0.18 in the interval $|\Delta R| < 4.0$ (4 reflections outside). Final structural parameters are presented in Table IV, interatomic distances in Table V, and the structure in Fig. 1. The total number of parameters varied was 24 (as for κ-(Hf–Mo–Se) with the addition of one occupancy factor for Ge, and one occupancy parameter and one isotropic thermal vibration parameter for oxygen). The largest correlation coefficients between occupancy and thermal parameters were less than 0.66. Final R values were $R(F^2) = 0.0661$ and $R_w(F^2) = 0.0816$.

Lists of observed and calculated structure factors for both structures have been deposited at the Institute of Chemistry, Uppsala, and can be obtained on request.

Discussion

As discussed in Ref. (*1*) the crystallographic formula of ternary κ phases can be expressed as $Hf_{9+x}Mo_{4-x}X_y$, where x denotes the degree of hafnium substitution on the molybdenum sites, X is the nonmetal, and y denotes the nonmetal content. The primary aim of the present study was to

TABLE V

INTERATOMIC DISTANCES (Å) FOR κ-(Hf–Mo–Ge–O)

Hf(1) –2 O	2.326	Mo(1)–2Mo(2)	2.716
Ge	2.675	2Mo(1)	2.827
Mo(1)	2.906	2Hf(1)	2.906
Mo(2)	3.007	2Hf(2)	2.914
2Hf(1)	3.087	4Hf(1)	3.131
2Mo(1)	3.131	4O	3.718
2Hf(2)	3.229		
2Hf(2)	3.249	Mo(2)–6Mo(1)	2.716
2Hf(1)	3.479	6Hf(1)	3.007
Hf(1)	3.533		
		Ge–6Hf(1)	2.675
Hf(2)–2 O	2.255	3Hf(2)	3.104
2Mo(1)	2.914	6 O	3.306
Ge	3.104		
4Hf(1)	3.229	O–2Hf(2)	2.255
4Hf(1)	3.249	4Hf(1)	2.326
2Hf(2)	3.264	2Ge	3.306
		4Mo(1)	3.718

Note. Distances shorter than 4.00 Å are listed. The estimated standard deviations are less than 0.001 Å for all distances. The sites Mo(1) and Mo(2) are partly occupied by hafnium.

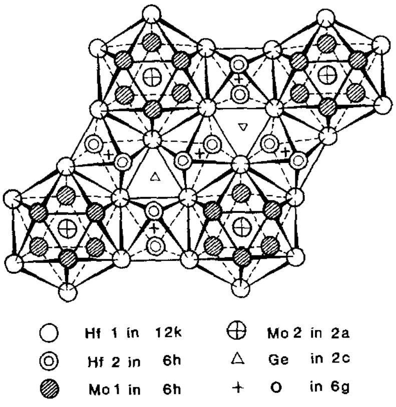

FIG. 1. The structure of κ-(Hf–Mo–Ge–O) projected along the hexagonal axis. The sites Mo(1) and Mo(2) are partly occupied by hafnium.

determine the degree of Hf/Mo substitution and to examine the filling of the nonmetal sites in the two κ phases.

The occurrence of hafnium substitution on the molybdenum sites was confirmed for both compounds. According to the refinements the degree of Hf/Mo substitution was $x = 0.40(2)$ for κ-(Hf–Mo–Se) and $x = 0.25(2)$ for κ-(Hf–Mo–Ge–O) (see Tables II and IV). It should be noted that the κ phases have extended ranges of homogeneity, which have been proposed to be due mainly to a variable degree of Hf/Mo substitution (*1*), and Hf/Mo atomic ratios differing from those obtained for the present crystals might accordingly occur in other preparations. The width of the homogeneity range of the κ-(Hf–Mo–Ge) phase is quite limited, the unit-cell volume varying only between 561.28 and 561.44 Å^3 (*1*). Also the unit-cell volume of the oxygen-containing κ-(Hf–Mo–Ge–O) phase of the present study falls within this interval. The homogeneity range of the κ-(Hf–Mo–Se) phase, however, has a considerably larger extension (*1*). Assuming the unit-cell volume of κ-(Hf–Mo–Se) to be proportional to the sums of the atomic volumes of the constituent elements, the calculated unit-cell volume V is

$$V = 2[(9 + x) \cdot r_{\mathrm{Hf}}^3 + (4 - x) \cdot r_{\mathrm{Mo}}^3 + r_{\mathrm{Se}}^3] \cdot s$$

where s is a proportionality constant, $r_{\mathrm{Hf}} = 1.58$ Å, $r_{\mathrm{Mo}} = 1.40$ Å, (Goldschmidt radii for 12-coordination) and $r_{\mathrm{Se}} = 1.14$ Å (Pauling covalent radius). Inserting the values $x = 0.40$ and $V = 565.19$ Å^3 as determined for the κ phase presently investigated by single-crystal X-ray diffractometry, the value of s obtained is 5.83. Using this value, the degree of hafnium substitution in the κ phase can be estimated from the maximum and minimum unit-cell volumes observed for κ-(Hf–Mo–Se) (566.40 and 564.03 Å^3 according to Ref. (*1*)). As a result, the composition of the κ phase, expressed in terms of the formula $\mathrm{Hf}_{9+x}\mathrm{Mo}_{4-x}\mathrm{Se}$, is estimated to vary between $x = 0.49$ (three-phase equilibrium $\kappa + \alpha - \mathrm{Hf} + \beta$-Hf(Mo)) and $x = 0.32$ (three-phase equilibrium $\kappa + \mathrm{HfMo}_2 + \mathrm{Hf}_2\mathrm{Se}$) at 1850 K.

The position 2*c* is fully occupied by nonmetal atoms in both κ-(Hf–Mo–Se) and κ-(Hf–Mo–P) (*2*). However, nonmetal vacancies are found to occur in the κ-(Hf–Mo–Ge–O) phase, where the site 2*c* is occupied only to 88% (Table IV). This feature might be associated with the rather small size of this site compared to the radius sum of hafnium and germanium. As seen from Table V the Hf–Ge distance is only 2.675 Å, while the radius sum is 2.80 Å, using the Goldschmidt radius of hafnium (1.58 Å) and the Pauling covalent radius of germanium (1.22 Å). In contrast, the Hf–{Se,P} distances in κ-(Hf–Mo–Se) and κ-(Hf–Mo–P) (2.709 Å (Table III) and 2.656 Å (*2*)) are close to the radius sums for hafnium and nonmetal, 2.72 and 2.68 Å, respectively, using the Pauling covalent radii of selenium (1.14 Å) and phosphorus (1.10 Å).

A second noteworthy feature of the germanium-containing κ phase crystal is the scattering power associated with the 6*g* position. Considering the oxygen contamination of the alloy, and the fact that oxygen occupies the 6*g* position in ternary κ-oxides (*10*), the most reasonable interpretation seems to be an occupation of 6*g* by oxygen to the extent of about 49% (Table IV). As mentioned before, the presence of minor amounts of oxygen greatly promotes the κ-phase formation on annealing, indicating that the kinetic factors are much more favorable for quaternary κ-(Hf–Mo–Ge–O) than for ternary κ-(Hf–Mo–Ge).

Acknowledgments

The author is deeply indebted to Professor S. Rundqvist for valuable discussions and criticism of the manuscript. Thanks are also due to Mr. H. Karlsson for assistance with the diffractometer recordings. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

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