J. Am. Chem. Soc. 1993, 115, 6126–6130

$Hf_{10}Ta_3S_3$, a New Structure Type Related to γ-Brass: Confirmation of Hume–Rothery and Brewer–Engel Electron Concentration Rules

Gregory A. Marking and Hugo F. Franzen*

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received December 14, 1992

Abstract: A new structure which can be described as a "stuffed" γ-brass has been found in the Hf/Ta/S system. It is unusual in that the γ-brass structure is unknown for early transition metals and it is the first reported example of a "stuffed" γ-brass. In this compound the metal clusters and their relative positions are those characteristic of the *bcc* γ-brass. The sulfur may contribute to the conduction band increasing the metal s–p electron to atom ratio to around 21/13 as is found for γ-brasses. Single-crystal and Rietveld powder refinements have been performed, and the resulting interatomic distances along with the stoichiometry can be used to infer the metal site occupancies.

Introduction

A number of complex, novel structures have been found in metal-rich systems. Among the most interesting are Hf_2S,[1] Ta_6S,[2] $Nb_{21}S_8$,[3] $Nb_{1.72}Ta_{3.28}S_2$,[4] and $Nb_{0.95}Ta_{1.05}S$[5] (Ta_2Se type[6]), compounds that have led to a deeper understanding of chemical bonding in metal-rich systems. Continued high-temperature investigations into ternary metal-rich sulfide systems have recently led to the novel "stuffed" γ-brass structure ($Hf_{10}Ta_3S_3$) reported here.

The structure of this new compound agrees with ideas about M–M and M–S bonding which grew out of previous metal-rich sulfide research, and other ideas pertaining to binary alloy γ-brasses[7,8] (e.g. Cu_5Zn_8) are applicable as well. This new early transition metal sulfide forms in a modification of one of the structures for which the Hume–Rothery electron concentration rules[9] were developed in late transition and main group metal alloys and therefore has interesting theoretical implications.

Experimental Section

Synthesis. The new compound $Hf_{10}Ta_3S_3$ is easily prepared with approximately 90% wt fraction by arc-melting (10 V, 75 A) pellets of the appropriate quantities of the metals and metal sulfides in an Argon atmosphere for 1 min. These pellets cannot be inverted and remelted to prepare homogeneous samples since they tend to violently shatter due to extreme brittleness. A typical reaction mixture is as follows:

$$7Hf + {}^{3}/{}_{2}Hf_2S + {}^{3}/{}_{2}Ta_2S = Hf_{10}Ta_3S_3$$

The binary metal sulfides were prepared by direct combination of the elements in sealed evacuated quartz tubes which were heated at 400 °C until sulfur vapor could not be visually detected and then annealed at 800 °C for up to 1 week. Hf_2S was then pelletized and arc-melted to promote homogenization. The Nb and Zr substituted compounds can also easily be prepared in the same fashion with starting stoichiometries of $Hf_{10}TaNb_2S_3$ and $Hf_{8.25}Zr_{1.75}Ta_3S_3$ although the resulting phase fractions are not as high. Subsequent high-temperature annealing (>1400 °C) has little effect on the parent compound but leads to phase separation and/or disproportionation of the substituted compounds.

The sample which yielded the single crystal used in this study had a starting composition of $Hf_{10}Ta_3S_3$ with a weight loss <1% observed upon arc-melting. SEM–EDS analysis of this arc-melted samples gave a stoichiometry of $Hf_{10.1}Ta_{2.9}S_{2.9}O_{0.1}$ for the major phase with an estimated error of <0.5 wt %. The presence of oxygen was minimal and therefore neglected.

Phase analyses performed on a variety of samples through Guinier powder film techniques suggest that there is a small Ta, Hf substitutional phase width which is centered around $Hf_{10}Ta_3S_3$. The authors have chosen to use this stoichiometry as representative of the structure throughout the manuscript. However, all discussion of the X-ray single-crystal results refer to a sample of composition $Hf_{10.1}Ta_{2.9}S_3$ as obtained from SEM–EDS results.

Single-Crystal Refinement. Suitable single crystals are difficult to find because the arc-melting technique of synthesis leads to twinning (common for the γ-brasses) and microcrystalline samples. A small irregularly shaped crystal was selected from the crushed sample of $Hf_{10}Ta_3S_3$ mentioned above and mounted on a glass fiber. An intensity data set for this crystal was collected (then recollected at a slower speed in an attempt to lower the thermal parameter esd's) on a Rigaku AFC6R diffractometer using monochromated Mo Kα radiation and the ω–2θ scan technique out to 60° to 2θ. The observed intensities were corrected for Lorentz polarization and absorption effects. Refinement of the recollected data resulted in significant improvement of the *R* factors but not of the thermal parameter esd's. The crystal data for refinement of the second data set are reported in Table I. Inclusion of unobserved reflections into the full-matrix least-squares refinement did not affect the results.

The structure was initially refined using TEXSAN[10] software in the space group $I\bar{4}3m$, which is the space group of many γ-brasses, until it became evident that sulfur and M4 had exceedingly large thermal parameters. Upon lowering the symmetry to a subgroup, $I23$, the S and M4 sites are changed significantly (as discussed later) and the refinement proceeded smoothly to completion. Anomalous dispersion effects allowed the selection of the proper enantiomer. The sulfur position cannot be refined anisotropically, which may be due to movement along the free parameter as evidenced by elongated thermal ellipsoids obtained for sulfur from DIFABS[11] absorption corrected refinements. The esd's for the thermal parameters of the S and the two metal positions within bonding distance of the S (M3 and M4) are large, which also suggests thermal motion for the sulfur. Positional and anisotropic thermal parameters for this crystal are reported in Tables II and III.

The Laue class of space group $I23$ is $m\bar{3}$, which is a proper subgroup of the symmetry group of the lattice, $m\bar{3}m$, and therefore merohedral twinning is a possibility. The large thermal parameter esd's for M3, M4, and S are also indications that twinning may have occurred although

---

(1) Franzen, H. F.; Graham, J. *Z. Kristallogr.* **1966**, *123*, 133.

(2) (a) α-Ta_6S: Franzen, H. F.; Smeggil, J. G. *Acta Crystallogr.* **1970**, *B26*, 125. (b) β-Ta_6S: Harbrecht, B. *J. Less-Common Met.* **1988**, *138*, 225.

(3) Franzen, H. F.; Beineke, T. A.; Conard, B. R. *Acta Crystallogr.* **1968**, *B24*, 412.

(4) Yao, X.; Franzen, H. F. *J. Am. Chem. Soc.* **1991**, *113*, 1426.

(5) Yao, X.; Miller, G. J.; Franzen, H. F. *J. Alloys Comp.* **1992**, *183*, 7.

(6) Harbrecht, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1660.

(7) (a) Westgren, A.; Phragmén, G. *Phil. Mag.* **1925**, *50*, 311. (b) Heidenstam, O. V.; Johansson, A.; Westman, S. *Acta Chem. Scand.* **1968**, *22*, 653.

(8) Edström, V.-A.; Westman, S. *Acta Chem. Scand.* **1969**, *23*, 279.

(9) Hume-Rothery, W.; Raynor, G. V. *The Structure of Metals and Alloys*; Institute of Metals: London, 1962.

(10) *TEXSAN: Single Crystal Structure Analysis Software, Version 5.0*; Molecular Structure Corp.: The Woodlands, TX, 1989.

(11) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

0002-7863/93/1515-6126\$04.00/0

Table I. Crystal Data for "Stuffed" γ-Brass $Hf_{10}Ta_3S_3$

formula	$Hf_{10.1}Ta_{2.9}S_3$
space group	$I23$ (No. 197)
a, Å	10.832(1)
V, Å^3	1270.9(1)
Z	4
d_{calc}, g/cm^3	12.667
cryst size, mm^3	0.13 × 0.06 × 0.04
μ(Mo Kα), cm^{-1}	1063.5
data collcn instrument	Rigaku AFC6R
radiation (monochromated in incident beam) (λ, Å)	Mo Kα (0.710 69 Å)
orientation reflcns: no; range (2θ), deg	13; 16.0–17.7
temp, °C	23
scan method	2θ–ω
octants measd	hkl
data collcn range, 2θ, deg	0–60
no. of reflcns measd	1063
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	357, 195
no. of params refined	23
transm factors: max, min	1.000, 0.2669
abs corr	ψ scans
R,[a] R_w,[b] GOF[c]	0.034, 0.035, 0.84
largest shift/esd, final	0.011
largest peak, e/Å^3	3.237
largest negative peak, e/Å^3	−3.648

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] GOF $= \sum((|F_o| - |F_c|)/\sigma_i)/(N_{obs} - N_{params})$.

Table II. Positional Parameters for $Hf_{10}Ta_3S_3$

atom	site	x	y	z	B_{eq}, Å^2
IT = M1	x, x, x	0.0971(2)			0.2051(7)
OT = M2	x, x, x	0.8399(3)			0.180(1)
OH = M3	$x, 0, 0$	0.3368(3)			0.4(1)
CO = M4	x, y, z	0.2964(2)	0.2816(2)	0.0671(2)	0.5(1)
S	$x, {}^1/_2, 0$	0.673(2)			0.7(2)

Table III. Anisotropic Thermal Parameters (Å^2 × 10^3) for $Hf_{10}Ta_3S_3$

site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M1	2.597(9)	U_{11}	U_{11}	1.3(7)	U_{12}	U_{12}
M2	2.28(1)	U_{11}	U_{11}	0(1)	U_{12}	U_{12}
M3	3(2)	2(1)	9(2)			2(1)
M4	6(1)	5(1)	10(1)	0.2(8)	−0.1(9)	−0.6(8)

movement of the sulfur along its free positional parameter satisfactorily explains these esd's. For these reasons, the structure of $Hf_{10}Ta_3S_3$ was refined as a merohedral twin (and trill) using all possible unique twinning laws. A modification (SFLS, M. Eitel (1985) and H. Bärnighausen (1986), Universität Karlsruhe) of the program ORFLS[12] was used for refinement of an isotropic model which converged with a twin fraction of 2.47% for twinning across a diagonal mirror, e.g. σ_{x-y}, and the Hamilton R factor test shows that this result is significant to slightly greater than 95% probability. This small amount of possible merohedral twinning does not significantly alter the results reported in this paper for $Hf_{10}Ta_3S_3$ as a single crystal.

A check for disordered twinning (small domain size) was also performed by splitting all atomic positions between possible sites and refining positions and occupancies. All twin occupancies either went to zero or else their positions refined to the same values as found for the single crystal within esd's, and it is concluded that disordered twinning is not observed.

Powder Refinements. X-ray powder data for the bulk samples, $Hf_{8.25}Zr_{1.75}Ta_3S_3$ and $Hf_{10}TaNb_2S_3$, were collected on a Scintag XDS 2000 (45 kV, 30 mA) diffractometer using Cu Kα radiation with a Kevex Peltier detector (8.04 keV, 300 eV window) over a range 10–160° in 2θ at a scan rate of 6 s/step with a 0.02° step size. Full profile Rietveld refinements were performed using GSAS software[13] and a starting model based on the single-crystal results. The residuals, metal occupancies, and phase fractions are reported in Table IV.

Table IV. Rietveld Refinement Results for $Hf_9ZrTa_3S_3$ and $Hf_{10}TaNb_2S_3$

	$Hf_9ZrTa_3S_3$	$Hf_{10}TaNb_2S_3$
R_{wp}	9.16	7.74
R_p	7.02	5.99
phase fraction (wt % of bulk)	88	59

	site occ	
	% Zr	% Nb
M1	5.3	56.1
M2	6.3	40.2
M3	7.5	2.0
M4	6.8	0

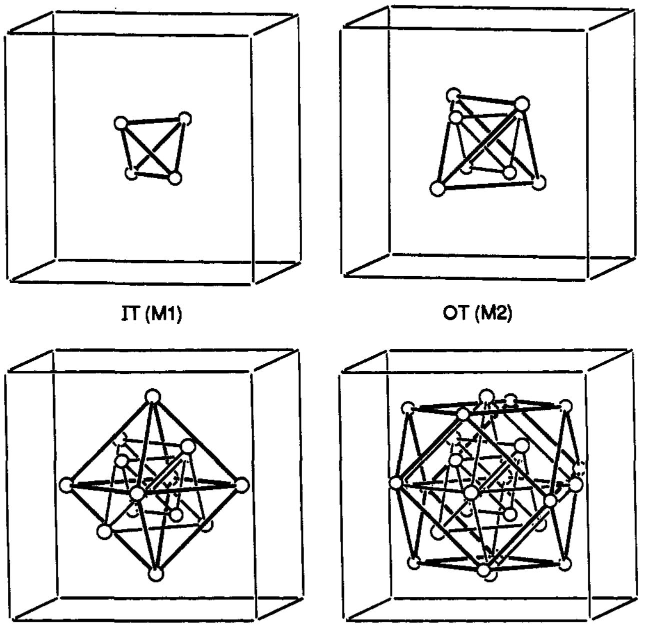

Figure 1. Polyhedra composing the 26 atom units found in γ-brasses.

Discussion

Atomic Positions. The metal atoms in $Hf_{10}Ta_3S_3$ occupy the same positions as those in Cu_5Zn_8 with one small difference for the M4 site. The metal sites can be described as *bcc* packing of 26 atom units which are composed of the following polyhedra[14] (Figure 1): M1 forms a tetrahedron centered at the origin and denoted as the inner tetrahedron (IT), M2 caps the faces of the IT forming a larger tetrahedron denoted as the outer tetrahedron (OT), M3 caps the edges of the OT forming a large octahedron (OH), and M4 approximately caps the edges of the OH forming an enveloping cuboctahedron (CO) with the M3 atoms slightly protruding out of the centers of the rectangular faces.

Examination of Cu_5Zn_8 (Figure 2) reveals channel-like areas along the face bisectors at positions $x, {}^1/_2, 0$. These channels are too constricted to contain any elements except possibly hydrogen in Cu_5Zn_8, but in $Hf_{10}Ta_3S_3$ the unit cell is expanded (due mainly to the larger metal atoms Hf and Ta) so that sulfur can fit beautifully into the channels (Figure 3).

In the space group $I\bar{4}3m$ of the γ-brasses, any atom at $x, {}^1/_2, 0$ also has symmetry-equivalent positions at $\bar{x}, {}^1/_2, 0$ and $x + {}^1/_2, {}^1/_2, 0$ and $\bar{x} + {}^1/_2, {}^1/_2, 0$. Due to sulfur–sulfur repulsion, the 24-fold site $x, {}^1/_2, 0$ can only be 50% occupied by sulfur in this space group.

Upon lowering of the symmetry to $I23$, the $x, {}^1/_2, 0$ site is split into two 12-fold sites $x, {}^1/_2, 0$ and $x + {}^1/_2, {}^1/_2, 0$ and the M4 site, x, x, z, loses symmetry to become an x, y, z site. The sulfur is found to order into one of the split $x, {}^1/_2, 0$ sites, and the M4

---

[12] *ORFLS: A Fortran Crystallographic Least Squares Program*; U.S. Atomic Energy Commission Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

[13] Larson, A. C.; Von Dreele, R. B. *Generalized Crystal Structure Analysis System*; LANSCE, MS-H805; Los Alamos National Laboratory: Los Alamos, NM 87545.

[14] Bradley, A. J.; Jones, P. *J. Inst. Met.* **1933**, *51*, 131.

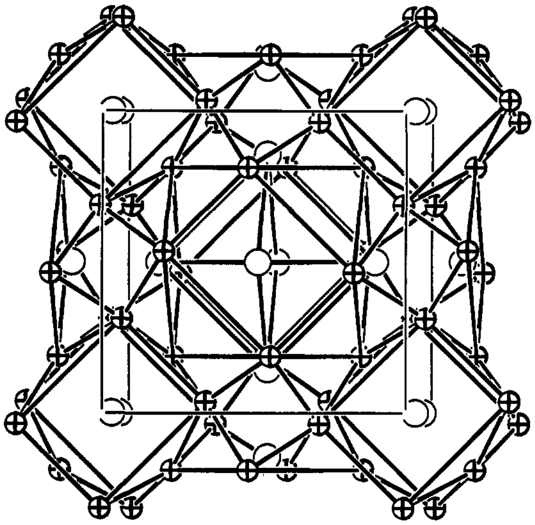

Figure 2. OH and CO metal framework showing channel-like voids of Cu_5Zn_8.

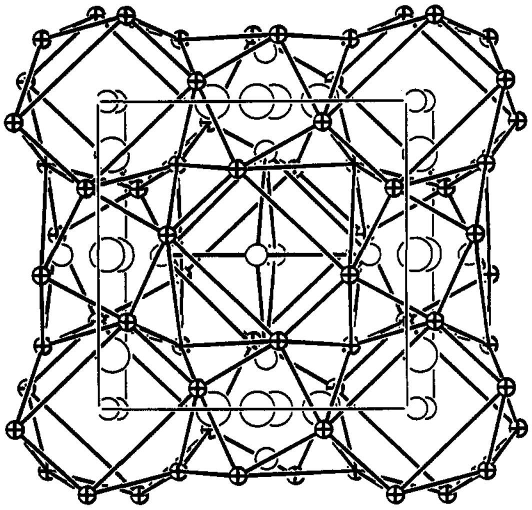

Figure 3. OH and CO framework showing sulfur positions in channels of $Hf_{10}Ta_3S_3$. Sulfur on front and back faces is not shown.

atoms rearrange slightly to accommodate the sulfur maximizing M–S bonding without the significant loss of M–M bonding.

Metal Site Occupancies. Since Hf and Ta are nearly identical scatterers of Mo Kα X-radiation, the metal site occupancies cannot be directly refined in $Hf_{10}Ta_3S_3$. However, bonding ideas, interatomic distances, Rietveld refinements of the Zr- and Nb-substituted phases, bond-order calculations, and the stoichiometry provide insights into the probable site occupancies. The interatomic distances for $Hf_{10}Ta_3S_3$ are given in Table V, and the refined metal occupancies for the two phases $Hf_{10}TaNb_2S_3$ and $Hf_9ZrTa_3S_3$ are given in Table IV.

Hafnium is more electropositive than tantalum forming stronger M–S bonds, and Ta has an additional bonding electron relative to Hf and thus is favored in sites with only M–M bonds. Therefore, one expects Hf to be found in the M–S bonding sites (M3 and M4) and Ta to be found in M–M bonding sites (M1 and M2). Assuming that Zr substitutes for Hf and that Nb substitutes for Ta, the refined occupancies for the substituted Zr and Nb compounds agree with the expected site occupancies above. Nb shows a dramatic preference for the M1 and M2 (Ta) sites with Zr showing a much lesser preference for the M3 and M4 (Hf) sites.

Accordingly, one makes the following assignments: M1 = Ta, M2 = Ta, M3 = Hf, and M4 = Hf. This leads to an idealized site assignment and stoichiometry of $Hf_9Ta_4S_3$ which is close to, but not the same as, the experimentally known stoichiometry. This suggests that at least one of the four metal sites has mixed occupancy, a phenomenon that is common to ternary metal-rich sulfides.[4,5,15] Since Ta has a smaller radius than Hf ($r_{Ta} = 1.343$ Å; $r_{Hf} = 1.442$ Å),[16] it is expected that $d_{Ta\text{-}Ta} < d_{Ta\text{-}Hf} < d_{Hf\text{-}Hf}$, and comparison of the distances from M1 and M2 to M3 and M4 indicates that M2 has mixed Ta/Hf occupancy.

Table V. Interatomic Distances <3.8 Å for $Hf_{10}Ta_3S_3$

M1-3M2	2.948(5)	M4–S	2.497(3)
M1-3M4	2.960(4)	M4–S	2.604(8)
M1-3M1	2.974(6)	M4–M1	2.9604(8)
M1-3M3	2.993(3)	M4–M2	3.058(6)
		M4–M2	3.157(2)
M2-3M1	2.948(5)	M4–M3	3.166(2)
M2-3M4	3.058(6)	M4–M3	3.346(2)
M2-3M3	3.111(3)	M4–M3	3.398(3)
M2-3M4	3.157(2)	M4–2M4	3.405(4)
		M4–2M4	3.464(2)
M3-2S	2.58(1)	M4–2M1	3.530(2)
M3-2M1	2.993(3)		
M3-2M2	3.111(3)	S–2M4	2.497(3)
M3-2M4	3.166(2)	S–2M3	2.58(1)
M3-2M4	3.346(2)	S–2M4	2.604(8)
M3-2M4	3.398(3)	S–S	3.75(2)
M3-M3	3.535(6)		

Table VI. Calculated Bond Orders in Different Occupancy Models for $Hf_{10}Ta_3S_3$

metal site	occ % Ta	expected valence	calcd bond order
		Stoichiometric Model	
IT	100	5.00	4.98
OT	100	5.00	3.73
OH		4.00	4.28
CO		4.00	3.99
		Statistical Model	
IT	22.3	4.22	7.34
OT	22.3	4.22	5.24
OH	22.3	4.22	4.29
CO	22.3	4.22	3.92
		Proposed Model	
IT	100	5.00	5.23
OT	45	4.45	4.59
OH		4.00	4.41
CO		4.00	4.13

Bond-order calculations on the refined structure of $Hf_{10}Ta_3S_3$ using the Pauling bond-order equation,[16] $D(1) = D(n) - 0.6 \log n$, also suggest mixed-metal occupancy primarily on the M2 site. Assuming that the total bond orders for particular metal sites will scale like the expected valences of those sites, that pure Hf and pure Ta will exhibit valences of 4 and 5 respectively, and that the radius for a particular site will be directly proportional to its composition, one can calculate the bond orders of the metal sites for differing models of occupancy (Table VI). The stoichiometric model results in a large discrepancy between the expected valence and the calculated bond order only for the M2 (OT) site. The total metal occupancies were then constrained to the experimental stoichiometry, and other models of occupancy were investigated. The model of statistical occupancy on all metal sites give poor agreement, and the proposed occupancy model gives the best agreement between the expected and calculated values. In a recently completed investigation of $Zr_{6.45}Nb_{4.55}P_{4.0}$[17] it was possible to refine the occupancies because of anomalous dispersion, and excellent agreement with occupancies based on bond-orders was obtained.

---

(15) Yao, X.; Marking, G.; Franzen, H. F. *Ber Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1552.

(16) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithica, NY, 1948.

(17) Marking, G. A.; Franzen, H. F. *Mater. Chem.* **1993**, *5*, 678.

Table VII. Reported Site Occupancies for $Hf_{10}Ta_3S_3$ and Pd_3Zn_{10}

site	$Hf_{10}Ta_3S_3$	Pd_3Zn_{10}
IT (M1)	Ta	Zn
OT (M2)	45% Ta, 55% Hf	Pd
OH (M3)	Hf	33% Pd, 67% Zn
CO (M4)	Hf	Zn
S	S	

These metal site occupancies for $Hf_{10}Ta_3S_3$ cannot be inferred using longstanding arguments that would apply if this compound were strictly a binary allow type of γ-brass. For γ-brasses, M_xN_y, the structure (I, F, P) and the site occupancies have been shown to be determined by the following factors:[18] (1) Avoiding contacts between the larger atoms when $R_M/R_N > 1.10$ and $x/y < 0.3$, (2) obtaining a relatively high packing fraction, and (3) maximizing the number of contacts between unlike atoms, M–N. The first factor, which dominates the choice of structure, has no relevance since R_{Hf} and R_{Ta} are <10% different. With no size-imposed restrictions the choice of structure is of the highest symmetry, *I*-centered cubic.

The second factor appears to be relevant to the packing within the Hf–Ta clusters although the atoms isolate the 26-atom metal units so that the *bcc* packing is not condensed to the degree found in binary alloy γ-brasses. If one compares the normalized Hf and Ta radii ($R_{Hf} = 1.02$, $R_{Ta} = 0.94$) to the ideal calculated radii giving the highest packing fraction[18] ($R_{IT} = 0.888(2)$, $R_{OT} = 0.906(4)$, $R_{OH} = 1.000(2)$, $R_{CO} = 1.058(2)$), one obtains the same idealized $Hf_9Ta_4S_3$ site assignments as discussed above: IT = Ta, OT = Ta, OH = Hf, and CO = Hf. The relative radii of Hf and Ta are thus nearly ideal for packing into 26-atom clusters which stabilize $Hf_{10}Ta_3S_3$ in a γ-brass type structure.

The third determining factor is not directly applicable to the "stuffed" γ-brass structure because the presence of 5d orbitals on the metals dramatically increases the metal–metal bonding capacity between metal atoms, and also the presence of the sulfur atoms makes metal–sulfur bonding an important factor. In γ-brasses such as Cu_5Zn_8, the unlike metal–metal interactions may be viewed as the most bonding, but in the "stuffed" γ-brass this is no longer true. Ta–Ta and Hf–S bonding are as important as Hf–Ta bonding in this structure.

In the reported M_3N_{10} γ-brass, Pd_3Zn_{10},[8,18] there are 8 M atoms on the OT sites and 4 M atoms on the OH sites with 40 N atoms occupying all remaining sites, maximizing the number of M–N contacts. In $Hf_{10}Ta_3S_3$, a $N_{10}M_3S_3$ "stuffed" γ-brass, they are 8 M atoms on the IT sites and 4 M atoms on the OT sites with the 40 N atoms occupying all remaining sites, which effectively minimizes the number of unlike M–N contacts but maximizes d electron bonding as well as the packing fraction. Table VII shows the reported site occupancies of $Hf_{10}Ta_3S_3$ and Pd_3Zn_{10} for comparative purposes.

Electron Compounds.[9] Electron counting rules, in particular the Hume–Rothery rules,[9] have played an important role in solid-state chemistry and materials science although they have not been well understood theoretically. Recently, the concept of second moment scaling has been shown to lead to the Hume–Rothery electron concentration rules for alloys,[19] and the existence of the new γ-brass-like compound reported here presents a significant test for this approach. The unavailability of reliable Hückel parameters for Hf and Ta precluded a meaningful application of the theory at this time, however.

The γ-brasses were observed to form alloys with a ca. 20/13 to 22/13 ratio of s and p electrons to metal atoms, and it is of interest to examine whether $Hf_{10}Ta_3S_3$, being a "stuffed" γ-brass, follows this rule as well. According to the ideas of Engel as modified by Brewer,[20] the s and p electrons determine structure, and Ta tends to have the configuration $d^{3.5}sp^{0.5}$ in alloys, while Hf tends to have two possible configurations, $d^{2.5}sp^{0.5}$ for bcc structures and $d^{2.3}sp^{0.7}$ for hcp structures. The promotional energies required for the excited-state configurations are compensated by bonding interactions. Zr also tends to have two possible configurations in alloys, bcc $d^{2.7}sp^{0.3}$ and hcp $d^{2.3}sp^{0.7}$. If the hcp configuration for Hf contributed substantially to the electronic structure of the "stuffed" γ-brass, Zr would readily substitute for Hf because their hcp configurations are identical. That this is not observed suggests that the correct configuration for Hf is that corresponding to bcc. The configurations corresponding to bcc for Hf and Zr are different, and thus the small amount of substitution of Zr for Hf observed in this structure can be understood in terms of the $d^{2.3}sp^{0.7}$ configuration of Hf. Futhermore, the bcc modification of Hf is found at high temperatures ($T \geq 1743$ °C) and the "stuffed" γ-brass is synthesized at high temperatures by arc-melting. For these reasons we have chosen to use the bcc electron configurations to count s and p electrons as 3 × 1.5 for Ta plus 10 × 1.5 for Hf for a total of 19.5 metal s–p electrons. An idea common to both the Hume–Rothery rules and the Brewer-Engel correlation is that the s and p conduction electrons determine the long-range order of the crystal structure, and according to the Brewer–Engel ideas, the d-electron interactions are primarily short range, i.e. to nearest neighbors. If these ideas are appropriate to the stuffed γ-brass, a proposal that suggests theoretical investigation, it is necessary that the $Hf_{10}Ta_3S_3$ formula unit provides approximately 20–22 electrons for the s–p conduction band and thus that approximately 0.5–2.5 s–p electrons are donated by the three sulfur atoms.

Table VIII. Electrons/Metal Atom for Six Different Compounds Using Brewer's High-Temperature *bcc* Configurations

composn	e/a[a]	composn	e/a[a]
Form as γ-Brass Structures			
$Hf_{10}Ta_3S_3$	19.5	$Hf_{10}TaNb_2S_3$	18.5
$Hf_9ZrTa_3S_3$	19.3		
Form as κ-Phase Structures			
$Hf_{10}Nb_3S_3$	18.0	$Zr_{10}Nb_3S_3$	16.0
$Zr_{10}Ta_3S_3$	17.5		

[a] e/13 metal atoms. Sulfur electrons are not included.

The fact that compounds with this structure did not form for $Hf_{10}Nb_3S_3$, $Zr_{10}Ta_3S_3$ or $Zr_{10}Nb_3S_3$ (which form in a κ-phase structure instead[21]) is not surprising because the structures of the metal-rich binary sulfides[22] of the 5d transition metals (Ta_6S,[2] Ta_2S,[23] Ta_3S_2,[24] and Hf_2S[1]) differ substantially from those of the 4d transition metals ($Nb_{21}S_8$,[3] $Nb_{14}S_5$,[25] Zr_9S_2,[26] Zr_2S[27]). This difference in the Hf–Zr case has been rationalized through the Brewer–Engel correlation,[28] and it appears likely that interactions of the f shell with the outer electrons yielding significant differences in the excited-state energies are of importance in the formation of metal-rich structure by 5d metals.

Continuing with the Brewer–Engel analysis, and counting 1.3 s and p electrons for Zr and 1.0 for Nb, as suggested by Brewer (in the high-temperature *bcc* structure in the case of Zr), yields the electron counts given in Table VIII. It therefore appears

---

(18) Pearson, W. B.; Brandon, J. K.; Brizard, R. Y. *Z. Kristallogr.* **1976**, *143*, 417.

(19) Hoistad, L. M.; Lee, S. *J. Am. Chem. Soc.* **1991**, *113*, 8216.

(20) Brewer, L. In *Alloying*; Walter, J. L., Jackson, M. R., Sims, C. T., Eds.; ASM International: Metals Park, OH, 1988; Chapter 1.

(21) Marking, G. A.; Franzen, H. F. Unpublished research.

(22) Franzen, H. F. *Prog. Solid State Chem.* **1978**, *12*, 1.

(23) Franzen, H. F.; Smeggil, J. G. *Acta Crystallogr.* **1969**, *B25*, 1736.

(24) (a) Hughbanks, T. *Prog. Solid State Chem.* **1989**, *19*, 329; (b) Wada, H.; Onada, M. *Mater. Res. Bull.* **1989**, *24*, 191. (c) Kim, S.-J.; Nanjundaswamy, K. S.; Hughbanks, T. *Inorg. Chem.* **1991**, *30*, 159.

(25) Chen, H.-Y.; Tuenge, R. T.; Franzen, H. F. *Inorg. Chem.* **1973**, *12*, 552.

(26) Chen, H.-Y.; Franzen, H. F. *Acta Crystallogr.* **1972**, *B28*, 1399.

(27) Conard, B. R.; Franzen, H. F. *High Temp. Sci.* **1971**, *3*, 49.

(28) Franzen, H. F.; Smeggil, J. G.; Conard, B. R. *Mater. Res. Bull.* **1967**, *2*, 1087.

significant, within the context of the Hume–Rothery rules and the Brewer–Engel correlation, that $Hf_{10}Nb_3S_3$, $Zr_{10}Ta_3S_3$ and $Zr_{10}Nb_3S_3$ all crystallize in the κ-phase structure, i.e., sufficient substitution to decrease the s–p electron count below a critical count destabilizes the γ-brass structure.

Conclusions

A new compound $Hf_{10}Ta_3S_3$ has been found to crystallize in a new structure type which is similar to the known γ-brasses. This structure type is unique in that it is the only reported "stuffed" γ-brass type structure. The metal components, Hf and Ta, are larger in size and more electropositive than the metals found in "normal" γ-brasses (e.g. Cu and Zn), and because of the larger metallic radii, sulfur can be incorporated into the structure where it plays an integral role in stabilizing this phase relative to others.

A suggestion was made which preserves the Hume–Rothery and Brewer–Engle electron concentration rules, two of the major pillars supporting the idea of correlation of structure and electron concentration. According to this suggestion the metal atoms provide approximately 19.5 s and p electrons per formula unit and the sulfur atoms donate approximately an additional 0.5–2.5 electrons to the s–p bands with the result that $Hf_{10}Ta_3S_3$ can be considered a 20/13 to 22/13 electron compound just as a normal γ-brass. Further experimental and theoretical work is strongly suggested by this novel structure in order to determine if and to what extent the Hume–Rothery electron concentration rules and the Brewer–Engel correlation apply.

Acknowledgment. The Ames Laboratory is operated for DOE by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of the Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy.

Supplementary Material Available: A listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.