The Preparation and X ray Characterization of HfTe$_{2-x}$, $x = 0.061$

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The phase HfTe$_{2-x}$, $x = 0.061$, characterized by the space group $P\bar{3}m1$, was prepared by a vapor transport technique. The unit cell parameters are: $a = 3.9492 \pm 4$ Å and $c = 6.6514 \pm 7$ Å. A description of the structure is presented based on nonstoichiometry in the tellurium sublattice and random but unequal distribution of hafnium atoms on two possible sites.

Introduction

A review by Haraldsen (*1*) in 1966 summarizes the structural chemistry of the Group IVB, VB and VIB transition metal tellurides in addition to various other transition metal chalcogen and pnicogen systems. This article points out the lack of information concerning the Hf–Te system over the entire composition range. McTaggert and Wadsley (*2*) in 1958 reported preparing both the sesquitelluride and monotelluride of Hf. Neither chemical composition nor density data were listed for the monotelluride phase. For the sesquitelluride only a unit cell formula, Hf$_{1.333}$Te$_2$, was presented while an experimental density value was not reported. The lattice parameters and symmetry of this phase were deduced from X ray powder diffraction patterns, but the interplanar spacings, Miller indices and relative intensities of the various diffraction lines were not listed. McTaggert and Wadsley prepared their samples by the direct reaction of the elements or by the thermal degradation of more chalcogen-rich phases at or below 900°C. Recent work (*3–5*) has shown that these experimental techniques are unsuitable for preparing many transition metal chalconide phases. The problems most likely encountered with these two techniques are, in the former, the incomplete reaction of the metal and, in the latter, the relatively low vapor pressure of the chalcogen at 900°C or lower reduces the reaction rate to the extent that a more metal-rich phase does not form in a reasonable length of time. High temperature annealing above 1300°C has been successfully used to prepare transition metal chalconides at or below the 1:1 stoichiometry while vapor transport techniques have been fruitfully employed to yield crystals of chalcogen-rich phases (*6*). The experimental work reported here resulted from an initial examination of the Hf–Te system by vapor transport techniques.

Experimental Methods

The hafnium telluride discussed in this paper was produced from filings of 96.5% Hf containing 3.5% Zr metal from Amax Specialty Metals, Inc. and 99.999% Te from United Minerals and Chemical Corporation. The elements were weighed out to give the 1:1 stoichiometry, sealed in 8 mm quartz tubes evacuated to 10^{-2} Torr and heated at 500°C for 5 days. Approximately 0.2 g of this material was then placed into a 2.5 cm diameter quartz tube about 20 cm long. About 10 mg NH$_4$I (J. T. Baker Chemical Co., Reagent Grade) which had been dried at 120°C was added to the ampoule. The ampoule was then evacuated to 10^{-2} Torr, sealed off and placed into a horizontal furnace. The temperature at the end containing the HfTe charge was maintained at 900°C ($\pm$10°C) and the other end at 680°C ($\pm$10°C). After several days, plate-like golden crystals several millimeters in diameter were produced at the cooler end. The crystals were quite stable in dry air. On the other hand, they degraded rather rapidly in humid air. Consequently the crystals were kept either in their unopened transport tubes or

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in a desiccator under a vacuum of 10^{-2} Torr until they were used.

X ray examination of this phase was accomplished by Debye-Scherrer powder and Weissenberg single crystal techniques using Ni-filtered $CuK\alpha$ radiation. Samples for the Debye-Scherrer method were prepared by grinding the crystals under toluene in an agate mortar and then rapidly sealing up the resultant powder in a glass capillary. Zr could conceivably have transported from the Hf (3.5% Zr)–Te starting material first to form zirconium telluride nuclei around which the hafnium telluride grew epitaxially. A scanning electron microscope with a solid state detector attached was used to examine freshly cleaved cross-sectional areas of a number of transported crystals to look for regions rich in Zr. In comparing the middle and outer regions of these crystals, no variation in concentration of Zr was observed. The electron microprobe was then used to determine Zr quantitatively. The amount of Zr detected after examining numerous large rectangular growth faces and cleaved narrow cross-sectional areas was 0.06 ($\pm$5) wt %. This amount of Zr can be expressed by the formula $Hf_{0.997}Zr_{0.003(\pm 2)}Te_{1.939}$, assuming that the Zr present substitutes for an equal number of Hf atoms, but would have no significant effect upon the results presented here. Samples were analyzed for Hf by ignition in air and weighing as HfO_2. X ray phase identification of the ignited residue was by the Debye-Scherrer method.

The density of this phase is 7.873 ± 3 g/ml as determined with pycnometer at 26°C using toluene as the displaced liquid.

Results

The combination of density measurements and ignition results unambiguously defines the composition of this phase to be $HfTe_{1.939(\pm 3)}$ or $HfTe_{2-x}$, $x = 0.061$.

Although the X ray powder pattern could be interpreted as having trigonal or hexagonal symmetry, the single crystal data clearly shows that $HfTe_{2-x}$ exhibits trigonal symmetry and belongs to the centric space group $P\bar{3}m1$. The lattice parameters, $a = 3.9492 \pm 4$ Å and $c = 6.6514 \pm 7$ Å, were obtained by a least squares treatment of the back reflection lines of a Debye-Scherrer powder pattern using Ni-filtered $CuK\alpha$ radiation ($\lambda_{\alpha_1} = 1.54051$ Å and $\lambda_{\alpha_2} = 1.54433$ Å). Table I lists the powder data. The calculated d values were obtained from the lattice constants

TABLE I

POWDER DATA FOR $HfTe_{2-x}$, $x = 0.061$ [a]

h k l	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}
0 0 1	6.492	6.651	m	2
1 0 0	3.295	3.420	w	4
0 0 2		3.326		1
1 0 1	3.011	3.042	s—	100
1 0 2	2.372	2.384	s	93
0 0 3	2.207	2.217	m	3
1 1 0	1.968	1.975	w	5
1 1 1	1.889	1.893	w=	1
1 0 3	1.855	1.860	m	19
0 0 4	1.659	1.663	s—	9
2 0 1		1.656		16
2 0 2	1.518	1.521	m	23
1 0 4	1.492	1.495	w=	4
1 1 3	1.478	1.476	w—	5
2 0 3	1.354	1.354	w	7
1 1 4	1.269	1.272	m+	23
2 1 1		1.270		13
1 0 5	1.238	1.240	w	6
2 1 2	1.202	1.205	m	22
3 0 0	1.139	1.140	w—	8
2 1 3	1.115	1.117	w	7
1 0 6	1.053	1.055	w	8
2 0 5	1.049	1.049	w—	4
2 1 4	1.021	1.021	w—	2
3 0 3	1.014	1.014	w=	2
2 2 0	0.9870	0.9873	w—	7
2 2 1	0.9769	0.9766	w=	~0
0 0 7	0.9503	0.9502	w—	1
3 0 4	0.9390	0.9403	w+	11
3 1 1		0.9391		7
2 0 6	0.9305	0.9302	w	7
1 2 5	0.9269	0.9271	w	7
1 0 7	0.9153	0.9155	w—	1
3 1 2	0.9120	0.9122	w+	10
2 2 3	0.9020	0.9019	w=	2
3 1 3	0.8720	0.8721	w—	4
1 1 7	0.8562	0.8562	w+	6
2 2 4	0.8490	0.8490	m—	15
4 0 1	0.8480	0.8480	w	4
2 1 6	0.8416	0.8415	m—	19
0 0 8	0.8314	0.8314	w	2
2 0 7	0.8303	0.8306	w	2
4 0 2	0.8280	0.8281	w	9
1 3 4	0.8235	0.8239	w=	3
1 0 8	0.8079	0.8079	w=	6
4 0 3	0.7975	0.7978	w=	7
3 2 1	0.7790	0.7792	m—	25

[a] Calculated using a value for the thermal parameter of both Hf and Te equal to zero.

previously given. Even though care was taken to prepare a random powder sample, the hexagonal platelets of $HfTe_{2-x}$ produced orientation effects

in the powder pattern by intensifying the 00l reflections. The values of I_{calc} were calculated using Yvon, Jeitschko and Parthé's program (7) for a structure suggested later in the discussion.

To verify that the structure of $HfTe_{2-x}$ was most probably the CdI_2 structure, i.e., Hf at 0, 0, 0 and Te at $\pm(1/3, 2/3, 1/4)$, Yvon, Jeitschko and Parthé's program (7) was used to calculate the intensities of the 00l reflections. The intensity values for the assumed structure are listed in the third column of Table II. Also listed in this table are the visually estimated intensities of the 00l reflections obtained from the Weissenberg single crystal photographs. Obviously the agreement between the two sets of intensity values is far from satisfactory.

Attempts were then made to determine a structure which yielded better agreement between the observed and calculated 00l intensity values. Intensity data were calculated for several trial structures which were subject to the following constraints:

1. The stoichiometry $HfTe_{1.939}$;
2. Random occupancy of two different sites, 0, 0, 0 and 0, 0, 1/2, by Hf such that the sum of the occupation factors for the two sites was 1.00;
3. The Te atom at $\pm(1/3, 2/3, 1/4)$ in the CdI_2 structure could exhibit a slight displacement of the z parameter from 0.25.

Only 00l intensities were used in this determination because it was assumed that $HfTe_{2-x}$ basically exhibits a layered structure very similar to that for CdI_2 with only Hf atoms or Te atoms in a given layer. The thermal parameters for both Hf and Te were set equal to 0.0 in these calculations. No attempt was made to correct the observed intensities for absorption effects. To a first order approximation, absorption and thermal effects will tend to cancel each other. Some of the possible structures and their associated 00l intensities are listed in Table II. The structure giving the best intensity agreement has Hf atoms randomly distributed over the two sites, 0, 0, 0 and 0, 0, 1/2, with the majority of the Hf atoms (~2/3) occupying the site 0, 0, 0 and Te atoms slightly displaced from z equals 0.25 to 0.27.

Discussion

The structure of $HfTe_{2-x}$, although inherently quite simple, nevertheless manifests a number of interesting aspects.

The form of nonstoichiometry exhibited by $HfTe_{2-x}$ is quite unusual in that the deviation from the normal 1:2 stoichiometry arises from random vacancies on the Te sublattice rather than from metal vacancies. A common form of structural variation on the CdI_2 structure and other related layered structures is the random insertion of metal atoms above the 1:2 stoichiometry into empty octahedral or trigonal prismatic interstices formed by a complete nonmetal sublattice, e.g., $V_{1+x}S_2$ (8), $2S-Nb_{1+x}S_2$ (8, 9), $2S-Ta_{1+x}S_2$ (10).

TABLE II

OBSERVED AND CALCULATED 00l INTENSITIES FOR TRIAL STRUCTURES OF $HfTe_{2-x}$, $x - 0.061$

			Calculated intensities					
		1[a]	1.00	0.50	0.67	1.00	0.33	0.67
	Observed	2	0.00	0.50	0.33	0.00	0.67	0.33
h k l	intensity	3	0.25	0.25	0.25	0.27	0.27	0.27
0 0 1	2.0		44.3	0.0	10.5	28.1	27.3	2.3
0 0 2	1.0		1.2	3.7	2.6	0.9	2.3	1.8
0 0 3	4.0		2.9	0.0	0.7	6.1	0.2	3.8
0 0 4	10.0		6.6	19.3	13.5	5.3	13.2	10.6
0 0 5	0.3		0.6	0.0	0.1	0.0	1.7	0.2
0 0 6	0.3		0.0	0.1	0.1	0.0	0.0	0.0
0 0 7	1.0		0.3	0.0	0.1	1.1	0.3	1.0
0 0 8	2.5		2.1	6.2	4.3	1.1	2.7	2.1

[a] (1) Occupation factor for Hf at 0, 0, 0; (2) occupation factor for Hf at 0, 0, 1/2; (3) z parameter for Te.

At first glance, the Te atom in this structure appears to be shifted in a direction away from the majority of metal atoms and so away from maximum metal–nonmetal bonding. A useful tool, however, by which the extent of the bonding between the Hf and Te atoms in $HfTe_{2-x}$ can be quantitatively evaluated is the empirical bond order relationship derived by Pauling (11):

$$D(n) = D(1) - 0.600 \log n,$$

where $D(n)$ represents a bond distance of order n. The value of $D(1)$ is obtained as the sum of the single bond metallic radius for Hf, 1.442 Å, and the tetrahedral covalent radius for Te, 1.32 Å (11). The two different Hf–Te distances in this structure calculated from the lattice parameters and assuming the z parameter for Te is 0.27 are 2.90 Å for the Te to the Hf at the origin and 2.75 Å for the Te to the Hf at 0, 0, 1/2. The corresponding Pauling bond orders associated with these distances are 0.59 and 1.06, respectively. Accordingly, the total number of two electron bonds formed by the Hf at the origin with occupation factor 2/3 to the six Te atoms octahedrally surrounding it is equal to $6 \times 2/3 \times 0.59$ or 2.36. Similarly the total number of two electron bonds formed by the Hf at 0, 0, 1/2 to the six Te atoms octahedrally surrounding it is $6 \times 1/3 \times 1.06$ or 2.12. This calculation ignores the slight deficit in Te from stoichiometric $HfTe_2$, the effect of which would be to multiply each of the above bond orders by 0.97, yielding total two electron bonds of 2.29 and 2.06, respectively. Accordingly by an uneven distribution of metal atoms on the two different sites and by a slight displacement of the Te atom, the extent of bonding of the Te to the two different Hf atoms is very nearly equal.

The result of this simple calculation forms the basis for a plausible suggestion for the bonding in $HfTe_{2-x}$ to account for both the unequal distribution of metal atoms on the two sites and the slight displacement of the Te atoms from the ideal z value of 0.25.

Structures for $HfTe_{2-x}$ are not formed in which the metal atoms are located either totally at the origin or else half at the origin and half at 0, 0, 1/2 (a NiAs type structure). The latter structure might be unstable due to the large number of vacancies (50%) occurring in the metal layers. On the other hand, the observed structure involves an increase in entropy over the ideal CdI_2 structure by locating the metal atoms at two positions rather than just one position. The slight displacement of the Te atom will also tend to increase the entropy of the observed structure above that expected for the CdI_2 structure.

In view of the fact that the $HfTe_{2-x}$ phase reported here exhibits a defect structure, it is very interesting to speculate that under different growth conditions variations could be observed in the overall stoichiometry of the phase, the form of vacancies present, the distribution of metal atoms among the various lattice sites and even changes in the z parameter of the Te atom.

Conclusion

The phase $HfTe_{2-x}$, $x = 0.061$, has been prepared by high temperature vapor transport techniques. The symmetry, lattice parameters, composition and density of this phase have been reported, and a possible structure has been suggested and discussed.

Acknowledgment

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