Zr Stabilized Ti_5Te_4-Type Hafnium Telluride

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A new Ti_5Te_4-type compound, Zr stabilized hafnium telluride was discovered and characterized with electron crystallography. Microanalyses and preparative work show that Zr stabilizes Ti_5Te_4-type hafnium telluride and destabilizes the competing phase, Hf_3Te_2.

Key words: Hafnium, Zirconium, Ti_5Te_4-Type Structure, Electron Crystallography

Introduction

Hafnium and zirconium are commonly thought to be very similar in chemistry. However, they are surprisingly dissimilar in the chemistry of metal-rich chalcogenides. For instance, Hf_2S [1] and Hf_2Se [2] are comprised of hexagonal close-packed double metal atom layers spaced by sulfur or selenium while both Zr_2S [3] and Zr_2Se [4] crystallize in a Ta_2P-type structure [5]. Zr_2Te [6] and Hf_2Te [7] adopt Sc_2Te- [8] and Nb_2Se-type structures [9], respectively. Hf_3Te_2 [10] has a layered structure consisting of *bcc* metal slabs sandwiched by Te atoms, but no counterpart is reported for zirconium tellurides. Ti_5Te_4-type [11] Zr_5Te_4 was identified a long time ago [12] and recently structurally characterized [13, 14]. Hf_5Te_4 adopting the same structure type was mentioned only [15, 16] by citing unpublished work.

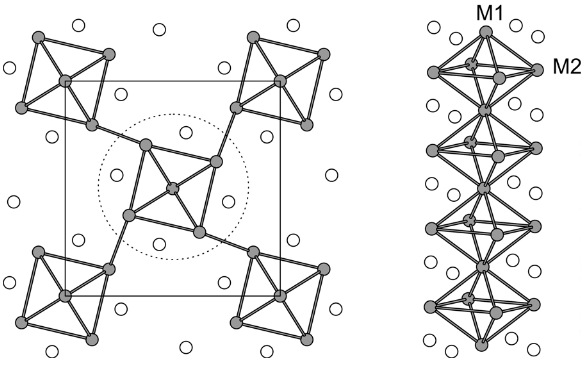

Fig. 1. A projection of the Ti_5Te_4-type structure along the tetragonal *c* axis is shown at the left side. The part marked with a dashed circle in the projection represents a single $^1_\infty[M_5X_4]$ column (M = early transition metal, X = metalloid or post transition metal), which is shown in perspective view at the right. Filled small circles depict early transition metal atoms, open ones metalloid or post transition metal atoms. Two crystallographic sites for early transition metal atoms are denoted as M1 and M2, respectively.

In the Ti_5Te_4-type structure, M_6X_8 clusters (M = early transition metal, X = metalloid or post transition metal) [17] are *trans*-condensed into one-dimensional *bcc* metal columns which are further connected with each other *via* metal-metal bonding (see Fig. 1). More than 10 Ti_5Te_4-type compounds have been reported up to now. It was found that this structure type is adopted only when the valence electron count (VEC) [18] and atomic sizes [19] meet certain criteria. We predicted Ti_5Te_4-type Hf_5Te_4 to exist [19] because the above-mentioned criteria are met in this case. However, it turns out that Ti_5Te_4-type hafnium telluride exists only with the stabilization by zirconium. Here we report the synthesis and characterization of this phase.

Experimental Section

Synthesis: Hf powder (99.6%, including 2 — 3.5% Zr, 325 mesh, Johnson Matthey), Zr rod (99.2+%, including $\leq$ 4.5% Hf, 12.7 mm in diameter, Johnson Matthey) and Te (99.997+%, Preussag) were used as starting materials. Zr was lathed into small pieces before being used. $HfTe_2$ was first prepared in evacuated silica ampoules and then further reduced with Hf and Zr in sealed tantalum tubes which were protected by a silica tube by adding some silica wool. When Zr pieces were used, a short tantalum rod was added and the ampoules were repeatedly shaken during the heat treatment to crush Zr pieces and to homogenize the sample. The ampoules were heated at 1000 °C for about 40 days and then quenched in cool water.

TEM and EDXS: TEM observations and EDXS measurements were performed with a Philips CM30/ST electron microscope which was operated at 300 kV and equipped with an energy dispersive X-ray spectroscopy system (Noran, Silicon detector). High resolution images and selected area electron diffraction (SAED) patterns were recorded with a Slow Scan CCD Camera (Gatan, 1024 × 1024 pixels). The program Crisp [20] was used to process high resolution images.

X-ray powder diffraction: X-ray measurements were made on a Stoe StadiP system equipped with an incident beam curved germanium monochromator. Samples were contained in glass capillaries of 0.2 mm diameter. Data were collected in Debye-Scherrer geometry with a linear position-sensitive detector (2θ range 4°).

Results and Discussion

A sample prepared with stoichiometric quantities of starting materials (Hf:Te = 5:4) shows strong peaks besides reflections of Hf$_3$Te$_2$ on the powder diffraction pattern. According to the equation proposed in our previous publication [19], the unit cell volume of the hypothetical Hf$_5$Te$_4$ phase is predicted to be 428.3 Å^3. Supposing the ratio of a/c is the same as that of Zr$_5$Te$_4$, the lattice constants of the hypothetical Hf$_5$Te$_4$ should be a = 10.63 Å and c = 3.79 Å. Most of the additional peaks observed on the powder pattern can be assigned to this unit cell. The lattice constants refined from powder diffraction data are $a = 10.674(3)$ Å and $c = 3.754(1)$ Å, in good agreement with the predicted values.

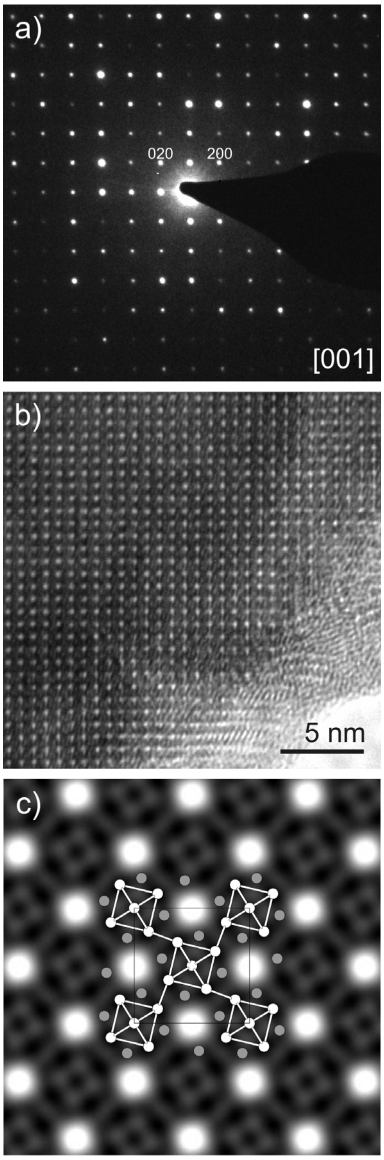

Fig. 2. Selected area electron diffraction pattern (a) and corresponding high resolution image (b) of Ti$_5$Te$_4$-type hafnium telluride with electron beam parallel to [001]. (c) Reconstructed image after lattice averaging, compensating for the contrast transfer function (CTF) and imposing the crystallographic symmetry in projection $P4$. A projection of the structure was superimposed on (c) to highlight the features of the reconstructed image.

The sample has been further examined with TEM and EDXS. Thin Hf$_3$Te$_2$ platelets can be easily identified based on the diffraction patterns. EDXS measurements on 14 Hf$_3$Te$_2$ crystals show an average composition of 58.0% Hf, 1.7% Zr and 40.4% Te, the highest Zr content measured being 2.5%. Ti$_5$Te$_4$-type crystals have also been identified by SAED. These crystals are chunky blocks with irregular shape. In most cases, it is difficult to find a thin enough area for high resolution observations, and even SAED patterns can be of poor quality. A significant enrichment of Zr in these crystals has been observed. Microanalyses made on seven Ti$_5$Te$_4$-type crystals gave an average composition of 48.6% Hf, 7.9% Zr and 43.5% Te, the lowest Zr content being 4.4%. A SAED pattern along the [001] direction and the corresponding high resolution image are shown in Figs 2a and b, respectively. After lattice averaging, compensating for the contrast transfer function (CTF) and imposing the crystallographic symmetry in projection $P4$, the reconstructed image (Fig. 2c) can be interpreted directly as a projection of the Ti$_5$Te$_4$-type structure along [001]. The coordinates of the metal atoms in the ab plane are measured from this image by searching the local maxima of the po-

Table 1. Fractional coordinates of Zr stabilized Ti_5Te_4-type hafnium telluride.

Atoms	Site	*x*	*y*	*z*
Hf1	2*a*	0	0	0
Hf2	8*h*	0.297	0.375	0
Te	8*h*	0.062	0.260	0

Note: The SAED pattern and high resolution image were taken from a crystal of composition 42.0% Hf, 13.7% Zr and 44.3% Te, as determined by EDXS.

Table 2. Interatomic distances (Å) in Zr stabilized Ti_5Te_4-type hafnium telluride.

Hf 1	−2 Hf 1	3.75	Te	−Hf 1	2.85
	−8 Hf 2	3.16		−Hf 2	2.79
	−4 Te	2.85		−2 Hf 2	2.80
				−2 Hf 2	2.81
Hf 2	−2 Hf 1	3.16		−2 Te	3.75
	−2 Hf 2	3.41		−2 Te	4.03
	−2 Hf 2	3.60		−4 Te	4.19
	−2 Hf 2	3.75		−2 Te	4.44
	− Te	2.79			
	−2 Te	2.80			
	−2 Te	2.81			

tential. The potential distribution of Te is smeared out and its coordinates cannot be determined reliably in the same way. Inspection of other structures of the same type reveals that nonmetal atoms are always in contact with five M2 atoms at nearly the same distances and one M1 atom at a slightly longer distance. The coordinates of Te in the *ab* plane have been determined with this geometrical restriction. The shortest distance between Te and Hf2 in the projection is only about 2 Å, approaching the point resolution of the microscope, 1.9 Å. The coordinates along the *c* axis were fixed at 0 or 1/2 from the geometrical considerations. Attempts were not made to refine the structure on basis of the electron diffraction data. A detailed description of processing high resolution images with the program Crisp can be found in a previous publication [21]. The atomic coordinates are listed in Table 1. Supposing the lattice constants of the crystal are the same as those refined from X-ray powder diffraction data, the interatomic distances were calculated (Table 2).

Another phase was identified by TEM. The composition averaged over 8 EDXS measurements is 36.9% Hf, 3.0% Zr and 60.1% Te. The metal to nonmetal ratio in this phase suggests a compound Hf_2Te_3. It is worth noting that the Zr content of this phase is in between that of Hf_3Te_2 and the Ti_5Te_4-type phase. SAED patterns shown in Fig. 3 indicate that this phase is closely related to $HfTe_2$. The strong reflections can be indexed with a unit cell comparable with that of $HfTe_2$. The positions of other reflections show that the structure of this phase is quite different from Hf_2Se_3 [22] and Zr_2Te_3 ($Zr_{1.3}Te_2$) [23]. Besides sharp Bragg reflections diffuse scattering along c^* is observed which, however, is not investigated further.

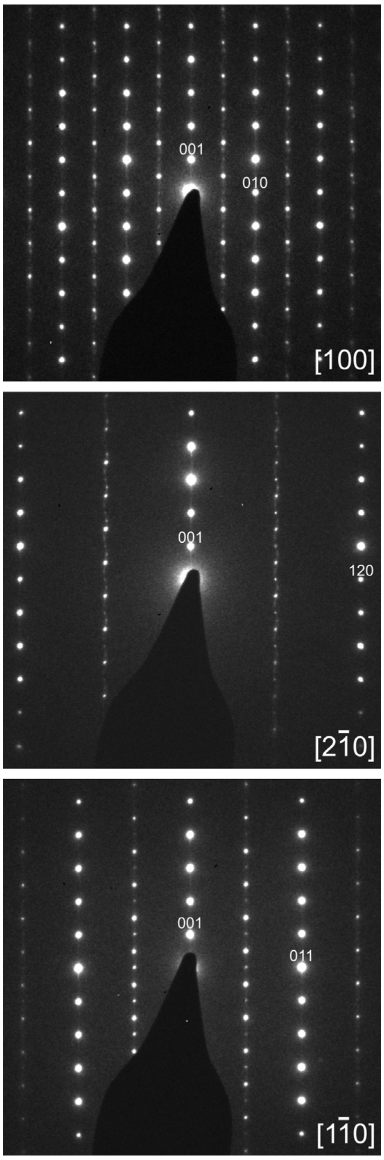

Fig. 3. Selected area electron diffraction patterns of Hf_2Te_3. The indexing is based on a $HfTe_2$-related unit cell.

The significant enrichment of Zr in Ti_5Te_4-type crystals raises the suspicion that it is a Zr stabilized phase, and introducing Zr intentionally into the starting materials may improve the yield of this phase. A sam-

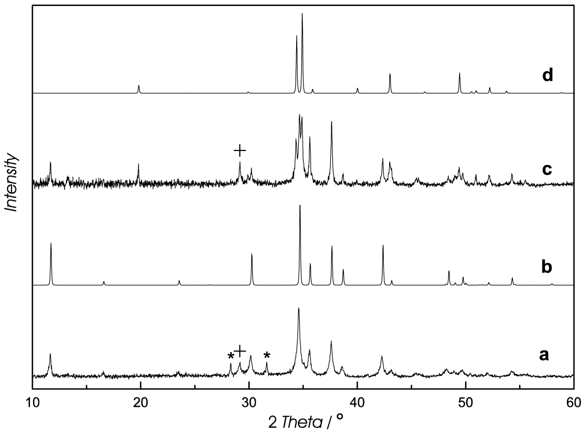

Fig. 4. Experimental powder diffraction patterns of samples with nominal composition $Hf_{4.5}Zr_{0.5}Te_4$ (a) and Hf_5Te_4 (c) (Cu-Kα_1, 1 min/0.1° in 2θ). Simulated patterns of Ti_5Te_4-type hafnium telluride (b) and Hf_3Te_2 (d) are also given for comparison. Peaks marked with "+" and "*" result from impurities of Hf_2Te_3 and monoclinic HfO_2, respectively.

ple with nominal composition Hf: Zr: Te = 4.5: 0.5: 4 was therefore prepared. The X-ray powder diffraction pattern of this sample is shown in Fig. 4 together with that of the stoichiometric one. It can be seen that Zr intentionally added to the starting materials improves the yield of the Ti_5Te_4-type phase greatly. On the other hand, the amount of Hf_3Te_2 in the product is negligible. Clearly, Zr stabilizes the Ti_5Te_4-type structure which consists of one-dimensional *bcc* metal columns, and destabilizes the Hf_3Te_2-type structure built up from two-dimensional *bcc* metal slabs.

It has been found that Hf atoms prefer sites allowing for more metal-metal bonding in the quasi-binary system Hf-Zr-P [24]. Comparing the structures of Hf_2Te and Zr_2Te, Harbrecht and coworkers [6] found that metal atoms in the former have enhanced metal-metal bonding compared to the latter. The preference of Hf to form more metal-metal bonding was explained by the greater expansion of the 5*d* orbitals compared to the 4*d* orbitals of Zr [25]. The Hf_3Te_2-type structure allows for more metal-metal contacts than the Ti_5Te_4-type structure does, so it is preferred by Hf, and the Ti_5Te_4-type structure is adopted only when sufficient Zr is present to stabilize it. Obviously, only a small amount of Zr is enough to stabilize the Ti_5Te_4-type structure or destabilize the Hf_3Te_2-type structure: The highest Zr content in Hf_3Te_2 and the lowest Zr content in the Ti_5Te_4-type structure observed by EDXS are 2.5% and 4.4%, respectively. The finding that the Ti_5Te_4-type structure collects Zr from the starting materials may be exploited to purify Hf metal and, hence, may help to solve a long-standing problem.

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[1] H. F. Franzen, J. Graham, Z. Kristallogr. **123**, 133 (1966).
[2] H. F. Franzen, J. G. Smeggil, B. R. Conard, Mater. Res. Bull. **2**, 1087 (1967).
[3] X. Yao, H. F. Franzen, J. Less-Common Met. **142**, 27 (1988).
[4] H. F. Franzen, L. J. Norrby, Acta Crystallogr. **B24**, 601 (1968).
[5] A. Nylund, Acta Chem. Scand. **20**, 2393 (1966).
[6] G. Örlygsson, B. Harbrecht, Inorg. Chem. **38**, 3377 (1999).
[7] B. Harbrecht, M. Conrad, T. Degen, R. Herbertz, J. Alloys Compds. **255**, 178 (1997).
[8] P. A. Maggard, J. D. Corbett, Angew. Chem. Int. Ed. Engl. **36**, 1974 (1997).
[9] B. R. Conard, L. J. Norrby, H. F. Franzen, Acta Crystallogr. **B25**, 1729 (1969).
[10] R. L. Abdon, T. Hughbanks, Angew. Chem. Int. Ed. Engl. **33**, 2328 (1994).
[11] F. Grønvold, A. Kjekshus, F. Raaum, Acta Crystallogr. **14**, 930 (1961).
[12] L. Brattås, A. Kjekshus, Acta Chem. Scand. **25**, 2350 (1971).
[13] R. de Boer, E. H. P. Cordfunke, P. van Vlaanderen, D. J. W. Ijdo, J. R. Plaisier, J. Solid State Chem. **139**, 213 (1998).
[14] G. Örlygsson, B. Harbrecht, Z. Kristallogr. **214**, 5 (1999).
[15] R. L. Abdon, T. Hughbanks, J. Am. Chem. Soc. **117**, 10035 (1995).
[16] C. C. Wang, R. L. Abdon, T. Hughbanks, J. Reibenspies, J. Alloys Compds. **226**, 10 (1995).
[17] A. Simon, Angew. Chem. Int. Ed. Engl. **20**, 1 (1981).
[18] M. Bouayed, H. Rabaâ, A. Le Beuze, S. Députier, R. Guérin, J. Y. Saillard, J. Solid State Chem. **154**, 384 (2000).
[19] M. He, A. Simon, V. Duppel, Z. Anorg. Allg. Chem. **630**, 535 (2004).
[20] S. Hovmöller, Ultramicroscopy **41**, 121 (1992).
[21] T. E. Weirich, R. Ramlau, A. Simon, S. Hovmöller, X. D. Zou, Nature (London) **382**, 144 (1996).

[22] I. M. Schewe-Miller, V. G. Young Jr., J. Alloys Compds. **216**, 113 (1994).

[23] C. C. Wang, C. Eylem, T. Hughbanks, Inorg. Chem. **37**, 390 (1998).

[24] H. Kleinke, H. F. Franzen, J. Solid State Chem. **136**, 221 (1998).

[25] H. Kleinke, H. F. Franzen, Angew. Chem. Int. Ed. Engl. **35**, 1934 (1996).