The Non-metal Rich Region of the Hf–Te System

LEIF BRATTÅS and ARNE KJEKSHUS

Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

Only one previous investigation of the hafnium tellurides appears to have been carried out.[1] This led to the identification of only a single phase (*viz.* Hf_2Te_3), a finding which is surprising in view of what has been found for closely related systems (*cf.*, *e.g.*, Pearson[2]). For this reason we decided to undertake a systematic phase analysis of the Hf-Te system. However, it proved impossible to make use of a single technique for synthesis throughout the whole system. The methods described here are accordingly suitable only for examination of non-metal rich hafnium tellurides. Hence, somewhat unintentionally, this study also forms a direct continuation of the research programme on transition metal polychalcogenides performed at this Institute.

Experimental. Samples were prepared from 99.9 % Hf (this figure excludes a content of ∼ 3 % Zr; turnings from crystal bars) and 99.999 % Te from Koch-Light Laboratories, Ltd. in two ways. Firstly, by direct reaction between the elements, the conditions being 500 − 800°C for temperature, 5 − 14 days for period of heat treatment, and slow cooling or quenching depending on composition. Secondly, by chemical transport reactions, using iodine as the transport agent. Further description of the experimental conditions is presented below.

X-Ray powder photographs were taken in a Guinier type camera of 80 mm diameter with monochromatized $CuK\alpha_1$-radiation ($\lambda = 1.54050$ Å) using KCl as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data and the indicated error limits correspond to twice the standard deviations obtained in these calculations.

Single crystal X-ray (oscillation, Weissenberg, and precession) photographs were taken with Zr-filtered $MoK\alpha$-radiation.

Neutron activation analyses were employed in the determination of composition. The samples were weighed and then activated for 2 h in a neutron flux of 4×10^{12} n/cm²sec. After storing for 3 days the induced activities of

[181]Hf and [131]Te were measured on a 400 channel γ-spectrometer. Samples of the pure elements were treated in a similar way and utilized as standards. Chemical analyses were also obtained using electron microprobe equipment; the elements being used as standards.

Results. It proved to be rather difficult to obtain consistent, reproducible results for samples containing less than ∼ 60 atomic % Te. A part of this difficulty arises from the presence of an apparently unavoidable interfering reaction between the sample and the quartz container (easily observable < ∼ 58 atomic % Te, at 800°C), which *inter alia* leads to HfSiTe (*cf.* Ref. 3). The effects of this reaction can be reduced (but not eliminated) by placing the samples in alumina crucibles inside the silica tubes. The contamination is quite variable, even for samples with the same initial composition. The results obtained on contaminated samples are not included in this paper, however.

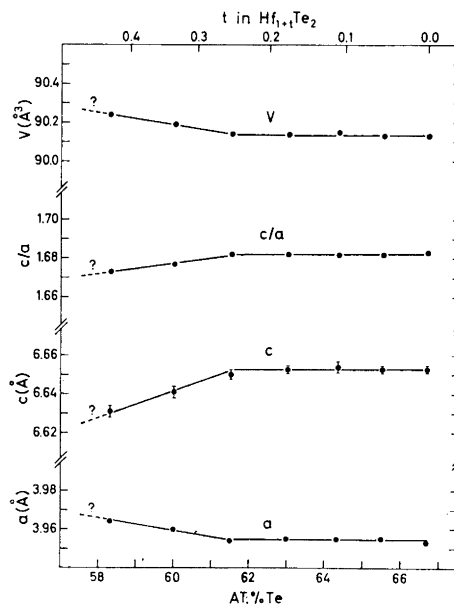In order of increasing non-metal content, the following phases were obtained:

Fig. 1. Unit cell dimensions *versus* composition for the $Hf_{1+t}Te_2$ phase. The vertical bars represent uncertainties when the calculated error limit (twice the standard deviation) exceeds the size of the symbol.

(i) *The $Hf_{1+t}Te_2$ phase.* A hexagonal phase was observed in samples containing $\sim 58 - \sim 75$ atomic % Te. The variation of the unit cell dimensions with composition is shown in Fig. 1. There is an appreciable region of homogeneity, the composition range extending from $< \sim 58$ to 61.5 ± 0.3 atomic % Te at 800°C. A more accurate estimation of the Te-poor phase limit is impossible due to the reaction between Hf, Te, and SiO_2 (*vide supra*). This phase, which is designated $Hf_{1+t}Te_2$ ($0.25 \pm 0.02 \leqq t < \sim 0.43$), has a structure of the intermediate $Cd(OH)_2/NiAs$ type (*cf.*, *e.g.*, Ref. 4) and is accordingly identical with that reported at a composition of Hf_2Te_3 by McTaggart and Wadsley.[1]

A convenient procedure for preparation of pure $Hf_{1+t}Te_2$ is as follows: Firstly, the components are heated at 600°C for 5 days, and then cooled slowly to room temperature. The sample is afterwards subjected to crushing and reannealed at 600°C for another period of 5 days. After intermediate crushing, the concluding heat treatment is performed at 800°C for 7 days.

A considerable number of single crystals of the $Hf_{1+t}Te_2$ phase were found in the capsules after the heat treatments. Freshly prepared samples have a brass-like colour, but surface oxidation rapidly forms a black coating.

The $HfTe_3$ phase. A new phase was observed in samples with $\geqq 70$ atomic % Te, when these were made by direct reactions between the elements at ~ 500°C. No extended range of homogeneity of this phase exists and the composition is unequivocally determined to be $HfTe_3$. $HfTe_3$ undergoes thermal decomposition to the $Hf_{1+t}Te_2$ phase at ~ 600°C.

Attempts have been made to synthesize single crystals of $HfTe_3$ by chemical transport reactions. A variety of different thermal conditions and concentrations of the transport agent were tried during these syntheses, but this endeavour failed, the crystals obtained invariably being of the $HfTe_5$ phase (*vide infra*).

$HfTe_3$ crystallizes monoclinically with unit cell dimensions: $a = 5.879(2)$ Å, $b = 3.902(1)$ Å, $c = 10.056(3)$ Å, $\beta = 97.98(3)$°. Comparison of observed and calculated X-ray intensities confirms that the structure is of the $ZrSe_3$ type.[5] Hence, $HfTe_3$ is isostructural with the previously known trichalcogenides of the Group IVA elements (*cf.*, *e.g.*, Ref. 6), and its existence is thus in accordance with all expectations.

The $HfTe_5$ phase. Rather surprisingly, there is an even more non-metal rich hafnium telluride than $HfTe_3$. This compound has been obtained exclusively by the chemical transport technique, which very strongly suggests that its preparation involves irreversible paths. The most suitable transport conditions were obtained by applying a temperature gradient of $\sim \frac{1}{3}$°C/mm along a ~ 150 mm long (evacuated and sealed) silica capsule, with the hot end containing a mixture of Hf and Te at ~ 500°C. An iodine concentration of ~ 5 mg/ml capsule volume yielded a considerable number of needle shaped crystals at the cold end of the capsule after 7 days.

Chemical analyses of the crystals by the neutron activation technique gave 21.2 weight % Hf and 74.2 weight % Te. (The maximum relative uncertainties are estimated to be about 10 and 20 % for Hf and Te, respectively). Examination of transverse sections of the crystals by electron microprobe analysis showed these to be homogeneous. The quantitative analyses according to the latter technique gave 19.8 weight % Hf, 1.8 weight % Zr, and 77.8 weight % Te, with estimated relative error limits of < 5 % for each component. These results together with the crystallographic data (*vide infra*) provide support for the formula $HfTe_5$. The compound has almost certainly no appreciable range of homogeneity.

Oscillation, Weissenberg, precession, and Guinier photographs show that $HfTe_5$ belongs to the orthorhombic system with the following unit cell dimensions: $a = 13.730(2)$ Å, $b = 3.9743(5)$ Å, $c = 14.492(2)$ Å. The cell content appears to be four formula units. The systematic extinctions in the diffraction data are of the type $hk0$ absent when $h + k = 2n + 1$. The possible space groups are accordingly limited to $Pmmn$ and $Pmn2_1$ (b and c interchanged). Determination of the crystal structure of $HfTe_5$ is in progress.

1. McTaggart, F. K. and Wadsley, A. D. *Australian J. Chem.* **11** (1958) 445.
2. Pearson, W. B. *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon, Oxford-London-Edinburgh-New York-Toronto-Paris-Braunschweig 1967, Vol. II.
3. Onken, H., Vierheilig, K. and Hahn, H. *Z. anorg. allgem. Chem.* **333** (1964) 267.