High Pressure Induced Transformations in NbTe₄ and TaTe₄

E. BJERKELUND and A. KJEKSHUS

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

V. MEISALO *

Division of Pure Physics, National Research Council, Ottawa 2, Canada

Crystallographic phase changes can be induced in many materials by subjecting them to high pressures, but transformations produced at room temperature are generally readily reversible.[1] However, in many cases, especially for substances with a predominant degree of directional (covalent) bonding, the effect of high pressure alone may be insufficient to bring about a phase transition and the additional use of heat treatment has been found necessary in order to facilitate the structural rearrangements. An advantage of this combined high temperature high pressure technique is that it is often possible to retain the high pressure forms in a metastable state at atmospheric pressure by lowering the temperature before releasing the pressure.

Two interesting candidates for a high pressure study are the newly discovered isostructural NbTe₄ and TaTe₄ phases.[3-9] NbTe₄ and TaTe₄ exhibit the stoichiometric compositions implied by the formulae without any appreciable ranges of homogeneity.[5-7] Although some details of their complete structural arrangements still remain unsolved, the essential features appear to be known from structure determinations of the NbTe₄ and TaTe₄ sub-cells.[6,7] (The sub-cells, containing two formula units ($Z_{I,s}=2$), are most conveniently related to the full crystallographic unit cells by $a=\sqrt{2}\,a_s$ and $c=3c_s$, both cells having tetragonal symmetry.) The atomic arrangements deduced for the sub-cells consist of columns of slightly distorted square antiprisms of Te atoms along [001], the antiprisms being coupled along the square

faces. Only half of the antiprismatic holes between the Te atoms is occupied by Nb (Ta) atoms and the ordered distribution of the latter atoms leaves alternate nearest neighbour columns of antiprisms empty. The vacant antiprismatic holes are notably slightly larger than those being occupied. Space-filling considerations together with the fact that the unoccupied portions of the lattices are located mainly in well defined regions of the structures very strongly suggest that NbTe₄ and TaTe₄ should undergo phase transformations (including the possibility of decompositions) when subjected to external pressure.

The initial samples of the NbTe₄ and TaTe₄ phases were prepared as described in the preceding papers [5,6] and the Guinier photographic data (taken with monochromatized $CuK\alpha_1$-radiation and using KCl as internal standard) confirmed the previously deduced [5-7,9] phase relationships in the relevant portions of these systems. The following dimensions of the sub-cells of the normal pressure modifications were obtained after least squares refinements of the diffraction data:

NbTe₄(I): $a_s = 6.499 \pm 0.001$ Å,
$\qquad c_s = 6.836 \pm 0.003$ Å
$\qquad (V_s = 288.7 \pm 0.2$ Å³)
TaTe₄(I): $a_s = 6.514 \pm 0.001$ Å,
$\qquad c_s = 6.810 \pm 0.001$ Å
$\qquad (V_s = 288.9 \pm 0.2$ Å³).

The indicated error limits correspond to twice the standard deviations found in these calculations.

The high pressure cells consisted of ~ 2 mm thick circular disks ($\phi = 6$ mm) of compressed pyrophyllite powder (*i.e.* the pressure transmitting medium) where the samples were situated in throughgoing concentric holes ($\phi = 2$ mm), the top and bottom of the pellets being partly covered with ~ 0.05 mm thick sheets of synthetic mica in order to prevent contact between the samples and the carboloy (grade 999) of the anvils. The samples and the surrounding gaskets were slowly subjected to increasing pressure between a pair of flat-face, Bridgman type anvils, the force being generated with a 500 ton hydraulic press (Manlabs Inc.) which was equipped with an automatic pressure control unit. The maximum loads during the present experiments correspond to average pressures of $20-35$ kb across the 10 or 13 mm diameter working faces of the anvils. However, due to the frictional properties of the sample, pyrophyllite, and carboloy the actual pressure at the position of the sample was con-

* National Research Council Postdoctorate Fellow; on leave from Department of Physics, University of Helsinki, Helsinki 17, Finland.

siderably higher, probably in the range 70—150 kb. The pressings were performed at room temperature and various temperatures up to ~575°C. During the latter experiments the sample and the enclosing pyrophyllite were first compressed to 5—10 kb average pressure and while subjected to these conditions the samples, anvils, and part of the piston system were heated by a surrounding furnace. After reaching the intended temperature, the pressure was increased to the maximum load. The high pressure and temperature conditions were maintained for $\frac{1}{2}$ h, the system was then cooled to room temperature in about $\frac{1}{4}$ h, and finally the pressure was rapidly released. The temperature was measured by a Pt/Pt-Rh thermocouple located as close to the sample as possible. The samples were carefully separated from the embedding pyrophyllite/mica matrix and Guinier type X-ray photographs were taken of the powdered sample materials at room temperature.

The pressings carried out at room temperature gave no evidence of any phase changes in the $NbTe_4$ and $TaTe_4$ samples after the pressure had been released. On the other hand, samples which had been exposed to a combined heating and pressing proved to have undergone marked transitions which were readily reproducible (for ~450 $< t <$ ~550°C). Application of the disappearing phase principle to the Guinier photographs of samples with different initial Nb(Ta)/Te ratios very strongly suggests $NbTe_4$ and $TaTe_4$ as the compositions also of the pressure induced phases. Further support for these formulae is achieved by utilizing the fact that the transformations are reversible, i.e. the original, normal pressure samples (the pure phases or the appropriate mixtures with the neighbouring phases depending on composition) are regenerated by annealing the pressure synthesized samples at ~400—500°C. (The possibility of considerable amounts of additional, pressure produced, amorphous phases being present in the samples is excluded by careful inspection of the X-ray photographs.) The new phases are accordingly considered proper high pressure modifications of $NbTe_4$ and $TaTe_4$ (although this must finally be verified by X-ray studies under pressure) and following Bridgman's scheme of notations the normal and high pressure modifications are denoted phases I and II, respectively. The metastable phase II modifications appear to have an unlimited durability at normal temperature and pressure.

Table 1. Guinier photographic data of $NbTe_4(II)$ and $TaTe_4(II)$ taken with monochromatized $CuK\alpha_1$-radiation.

h k l	$\sin^2\theta \times 10^5$ I_{obs}	
	$NbTe_4(II)$	$TaTe_4(II)$
0 2 0	1352 m	1347 st
0 2 1		2132 w
0 0 2	3148 w	3150 m
0 2 2	4506 vw	4507 vw
1 1 0	4891 w	4874 w
0 4 0	5397 m	5392 w
1 1 1	5680 w	5668 vw
0 4 1	6186 m	6172 w
1 3 0	7589 st	7563 st
1 1 2	8041 st	8014 st
1 3 1	8371 st	8347 st
0 2 3	8433 st	8429 m
0 4 2	8540 w	8536 w
1 3 2	10740 m	10707 w
1 1 3	11989 st	11951 st
0 0 4	12603 m	12584 m
0 6 1	12946 w	12916 w
1 5 1	13768 w	13731 w
0 2 4		13918 vw
1 3 3	14667 m	14632 w
0 6 2	15290 st	15251 m
1 5 2	16119 w	16102 w
1 1 4	17479 w	17455 vw
2 0 0	18205 st	18132 m
2 2 0		19479 w
1 5 3	20060 m	20017 w
1 7 0	21056 m	21054 w
1 7 1		21802 vw
0 8 1	22352 w	22349 w
2 4 0	23607 vw	
1 7 2		24192 vw
2 4 1	24369 vw	24297 vw
1 1 5	24560 vw	
0 8 2⎫ 0 6 4⎭	24736 vw	24702 w
0 4 5	25052 vw	25042 vw
1 5 4	25564 vw	25531 vw
2 2 3	26619 st	26565 st
2 4 2	26745 vw	26646 w
1 3 5	27261 m	27231 m
0 0 6	28343 m	28313 m
0 2 6		29695 vw
2 0 4	30812 vw	30729 w
2 6 1	31121 vw	31084 vw
0 6 5⎫ 1 9 0⎭	31846 vw	31801 vw
1 9 1⎫ 1 5 5⎭	32656 w	32629 w
2 6 2	33495 m	33417 w
1 9 2	34999 vw	34981 vw

Comparison of the Guinier photographs immediately suggested that $NbTe_4(II)$ and $TaTe_4(II)$ are isostructural and the indexing of these data in terms of orthorhombic unit cells (Table 1) indeed confirmed this suggestion:

$NbTe_4(II)$: $\quad a = 3.611 \pm 0.001$ Å,
$\qquad\qquad b = 13.265 \pm 0.002$ Å,
$\qquad\qquad c = 8.681 \pm 0.002$ Å
$\qquad\qquad (V = 415.8 \pm 0.3$ Å$^3)$
$TaTe_4(II)$: $\quad a = 3.618 \pm 0.001$ Å,
$\qquad\qquad b = 13.272 \pm 0.003$ Å,
$\qquad\qquad c = 8.685 \pm 0.002$ Å
$\qquad\qquad (V = 417.0 \pm 0.3$ Å$^3)$.

(The phases have no appreciable ranges of homogeneity.) The diffraction data in Table 1 show definitely systematic extinctions for reflections of the type hkl when $h + k = 2n + 1$ and indicate furthermore very strongly the condition $h0l$ absent when $l = 2n + 1$. The probable space groups are accordingly $C222_1$, $Cmc2_1$, $Ama2$ (a and c interchanged), and $Cmcm$. From the size of the unit cells and the minimum of four equivalent positions in any of the possible space groups, it may safely be concluded that the cell contents are four formula units ($Z_{II} = 4$).

The ratio of the cell volumes per formula unit, $i.e.$ $V_{II}Z_I/V_IZ_{II} = 0.720$ and 0.721 for $NbTe_4$ and $TaTe_4$, respectively, shows that the metastable high pressure modifications are considerably denser than the stable ones. The parameter $V_{II}Z_I/V_IZ_{II}$ has in fact remarkably low values in these cases and this finding must obviously be attributed to the open feature of the $NbTe_4(I)$ and $TaTe_4(I)$ structures.

In view of the previous [5-7] considerations on the chemical bonding scheme in $NbTe_4(I)$ and $TaTe_4(I)$ (concerning mainly the applicability of the generalized $(8 - N)$ rule) it would be of considerable interest to establish the geometries of the coordination polyhedra and, in particular, the numbers of $Nb(Ta) - Nb(Ta)$ and $Te - Te$

bonds in the crystal structures of $NbTe_4(II)$ and $TaTe_4(II)$. All efforts devoted to the exploration of the structural arrangements in the latter modifications have hitherto been unsuccessful, but the work is continuing in connection with a programme for determination of their relevant physical properties.

Finally it is worth reporting that several other niobium and tantalum chalcogenides have been subjected to a similar high temperature high pressure treatment, but phase transformations have hitherto only been detected for $NbTe_4$ and $TaTe_4$.

1. Bridgman, P. W. *The Physics of High Pressure*, G. Bell & Sons, Ltd., London 1952.
2. Ukrainskii, Yu. M., Novoselova, A. V. and Simanov, Yu. P. *Russ. J. Inorg. Chem. (English Transl.)* **4** (1959) 60.
3. Novoselova, A. V., Grigorjan, L. A. and Simanov, Yu. P. *Dokl. Akad. Nauk SSSR* **135** (1960) 864.
4. Grigorjan, L. A., Simanov, Yu. P. and Novoselova, A. V. *Dokl. Akad. Nauk SSSR* **135** (1960) 1133.
5. Bjerkelund, E. and Kjekshus, A. *Z. anorg. allgem. Chem.* **328** (1964) 235.
6. Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **18** (1964) 690.
7. Bjerkelund, E. and Kjekshus, A. *J. Less-Common Metals* **7** (1964) 231.
8. Revolinsky, E., Brown, B. E., Beerntsen, D. J. and Armitage, C. H. *J. Less-Common Metals* **8** (1965) 63.
9. Selte, K., Bjerkelund, E. and Kjekshus, A. *J. Less-Common Metals* **11** (1966) 14.