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X-ray Investigations in the System U—N—Te

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The crystal structures of the ternary compounds in the system U—N—Te were investigated. The compounds were prepared in a powder form by reacting $UN + X\,Te$ ($0.4 \leqslant X \leqslant 2.0$). Powdered uranium mononitride, UN, and elementary tellurium were mixed in the desired proportions and subsequently heated at 900—1000 °C in evacuated and sealed quartz tubes. The powder diagrams were taken with a Philips diffractometer (CuK_α radiation). The compounds having the following crystal structures and lattice parameters were found:

Compound	Lattice parameters/Å	Structure type
U_2N_2Te	$a = 3.963$ $c = 12.561$	La_2O_2Te
UNTe	$a = 3.929 \pm 002$ $c = 7.617 \pm 0.003$	PbFCl

The structure of UNTe is discussed in more detail; the unit-cell dimensions, atomic parameters, and interatomic distances have been determined. Comparison between the calculated and observed intensity values shows the best agreement for the variable atomic parameters $u = 0.165$ and $v = 0.624$.

INTRODUCTION

The crystal structures of U_2N_2Te, U_2O_2Te and UOTe were described by Benz and Zachariasen[1], Breeze and Brett[2,3] Klein, Haneveld and Jellinek[4] and Marsaik and coworkers[5,6]. Compound U_2N_2Te was prepared in two different ways. In the first procedure, the cold-pressed powder mixtures of the binary compounds were placed in a tungsten crucible covered with a lid, and reacted in a nitrogen atmosphere for 2 hours at 1200 °C ($UTe + UN + 1/2\ N_2 = U_2N_2Te$). In the second procedure the stoichiometric mixtures of uranium mononitride and tellurium were heated in a silica tube for one month at 1000 °C ($UN + 1/2\ Te = U_2N_2Te$). By both methods, pure compound U_2N_2Te was obtained. U_2N_2Te has a body-centered tetragonal structure (structure type La_2O_2Te, space group I4/mmm) with the following unit-cell parameters: $a = (3.9631 \pm 0.0002)$ Å, $c = (12.561 \pm 0.002)$ Å.

In the investigation of the U—O—Te—C, system by electron microprobe analysis, Breeze and Brett[2,3] found a new oxy-uranium telluride, approximately of the composition U_2O_2Te. The X-ray patterns of this compound was indexed on a tetragonal unit-cell with the parameters $a = (3.9460 \pm$

$\pm$ 0.0002) Å, $c = (12.564 \pm 0.004)$ Å. U_2O_2Te is of the La_2O_2Te structure type (space group I4/mmm.) Consequently, both compounds U_2N_2Te and U_2O_2Te are isostructural with La_2O_2Te.

The tetragonal crystal structure of the compound UOTe (structure type PbFCl, space group P4/nmm) was previously reported by Klein, Hanneveld and Jellinek[4]. They found the following parameters: $a = 4.004$ Å, $c = 7.491$ Å, and the atomic positions: $z_U = 0.173 \pm 0.001$, $z_{Te} = 0.629 \pm 0.002$. Breeze and Brett[2] gave the following values of the parameters for the same compound: $a = (4.0141 \pm 0.0003)$ Å, $c = (7.4940 \pm 0.0008)$ Å. Mursaik and coworkers[5,6] investigated the magnetic structure of UOTe by neutron diffraction at 4.2 K and 78 K. The best agreement between the calculated and the observed intensities was obtained for the atomic positions $z_U = 0.174 \pm 0.001$ and $z_{Te} = 0.630 \pm 0.001$. In these papers the symmetry of the magnetic unit-cell and the space group of UOTe were reported in detail.

EXPERIMENTAL

Binary compound UN was prepared by reaction of the metal with the gaseous non-metal. In the massive state uranium reacts very slowly with the nitrogen gas. Uranium reacts with nitrogen more rapidly when the metal is in the form of a fine powder. Therefore, the uranium powder was prepared by repeated hydriding and de-hydriding of carefully cleaned uranium filings. The surface oxide film of the uranium filings to be hydrided was first removed by washing with nitric acid and ethanol. The preparation of uranium mononitride involved the following stages: first, hydrogen was passed over the uranium filings for 2—3 hours at 250—270 °C; the temperature was then gradually raised to 900 °C and hydrogen replaced by nitrogen; the completion of this reaction gave a higher nitride, UN_x. Finally, the temperature was raised to 1400 °C in vacuum to degrade UN_x to uranium mononitride[7,8]. Uranium mononitride was obtained as a dark gray powder. The X-ray powder diffraction patterns were sharp and indicated a lattice constant of 4.88 Å.

The compounds of the ternary system U-N-Te were prepared in powder form by reacting UN + X Te ($0.4 \leqslant X \leqslant 2.0$). Binary compound UN and elementary Te were mixed in the proportion desired, cold-pressed and then reacted in a sealed evacuated quartz tube at 900—1000 °C for *cca* 10 days. The samples for X-ray diffraction studies were easily crushed in an agate mortar under benzene or acetone. All X-ray diffraction patterns were obtained by means of a recording Philips PW 1010 diffractometer. The patterns were taken by using nickel-filtered CuK_α radiation. The density was determined only for compound UNTe (1 : 1 : 1), by the pycnometer method with the use of decalin. This sample was also chemically analyzed for nitrogen by the Dumas method.

RESULTS AND DISCUSSION

The results of the X-ray analysis of the U—N—Te system are given in Table I.

As seen from Table I, the only product formed is UNTe in the reaction UN + Te, and in the reaction UN + (0.4 to 0.6) Te the compound U_2N_2Te is formed. In the reaction of UN + (0.7 to 0.9) Te it is probable that the $UNTe_{0.7}$intermediate phase is formed. The X-ray diagrams of the products of the reactions UN + Te, UN + 0.7 Te, UN + 0.8 Te and UN + 0.5 Te are shown in Figure 1. These diagrams present the migration of the diffraction peaks from larger angles for UNTe over the intermediate phase for $UNTe_{0.7}$ + + UNTe to smaller angles for U_2N_2Te.

The X-ray patterns of UNTe were indexed on the basis of a tetragonal unit cell with $a = 3.958$ Å and $c = 7.630$ Å. In analogy to U_2N_2Te and U_2O_2Te, UNTe was assumed to be isostructural with UOTe, with two formula units per unit-cell and the atoms at the following sites:

2 U	in	2(c) : 1/2, 0, u	0, 1/2, $\bar{u}$
2 Te	in	2(c) : 1/2, 0, v	0, 1/2, $\bar{v}$
2 N	in	2(a) : 0, 0, 0	1/2, 1/2, 0

TABLE I

X-ray results of the U-N-Te samples heated at 900—1000 °C

Reaction	Heating conditions	Results of X-ray analysis
UN + 0.4 Te	900 °C, 215 h, slowly cooled	$U_2N_2Te + UO_2 + UN$
UN + 0.5 Te	900 °C, 215 h, slowly cooled	$U_2N_2Te + UO_2$
UN + 0.6 Te	900 °C, 215 h, slowly cooled	$U_2N_2Te + UO_2$
UN + 0.7 Te	900 °C, 318 h, slowly cooled	$UNTe_{0.7}$
UN + 0.8 Te	900 °C, 280 h, 1 K/min	$UNTe_{0.7}$
UN + 0.9 Te	900 °C, 280 h, 1 K/min	$UNTe_{0.7}$
UN + Te	900 °C, 280 h, 1 K/min	UNTe
UN + Te	900 °C, 240 h, tempered	UNTe
UN + Te	1000 °C, 259 h, tempered	UNTe
UN + 2 Te	900 °C, 280 h, tempered	UNTe + Te + UO_2
UN + 2 Te	1000 °C, 259 h, 1 K/min	UNTe + Te + UO_2

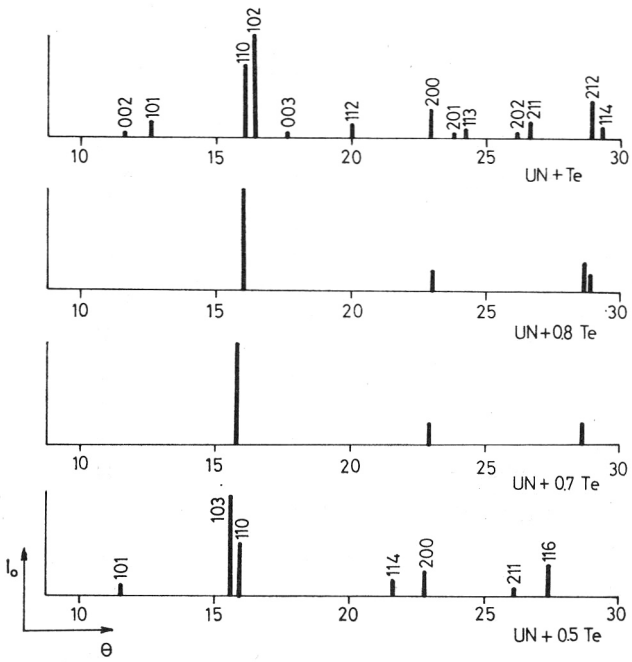

Fig. 1. X-Ray diagrams for the samples UN + x Te

TABLE II

X-ray diffraction data for UNTe

$h\ k\ l$	d_o	d_c	I_o	I_c
0 0 1	7.69	7.62	4	4
0 0 2	3.818	3.815	3	4
1 0 1	3.509	3.510	15	22
1 1 0	2.797	2.798	68	59
1 0 2	2.745	2.745	100	103
0 0 3	2.541	2.544	2	3
1 1 2	2.254	2.256	8	8
2 0 0	1.976	1.977	27	25
0 0 4 2 0 1	1.909	1.914	4	5
1 1 3	1.881	1.893	5	8
2 0 2	1.751	1.756	2	2
1 0 4 2 1 1	1.719	1.723	15	7
2 1 2	1.600	1.605	44	41
1 1 4	1.571	1.575	11	12
2 2 0	1.394	1.398	6	8
2 0 4 2 2 1	1.368	1.374	7	7

TABLE III

Interatomic distances (δ) for UNTe and the other uranium tellurides, nitrides and oxytellurides

Compound	Structure	Atoms	δ/Å	Ref.
UNTe	tetragonal	U-4 Te U-1 Te U-4 N N-4 N Te-4 N Te- Te	3.21 3.49 2.33 2.78 3.47 3.36	
UTe	cubic	U-6 Te	3.08	9
UTe_2	orthorhombic	U-2 Te_I U-4 Te_{II} U-2 Te_I	3.08 3.19 3.205	10
UN	cubic	U-6 N	2.44	9
UOTe	tetragonal	U-4 Te U-1 Te U-4 O O-4 O	3.20 3.42 2.39 2.83	4, 11
U_2O_2Te	tetragonal	Te-8 U	3.35	3
U_2N_2Te	tetragonal	U-4 Te U-4 N	3.42 2.31	1

Table II presents the diffractometer data for UNTe, containing the comparison of the observed and calculated relative intensities for the variable atomic parameters $u = 0.165$ and $v = 0.624$, together with the observed and the calculated d values.

It is seen that the observed and the calculated intensities are in good agreement (R factor is 0.125). The calculated intensities were obtained from the expression:

$$I \propto (1 + \cos^2 2\Theta) \cdot (\sin^2 \Theta \cos \Theta)^{-1} \cdot m \cdot F^2$$

where Θ is the Bragg angle, m the multiplicity factor and F the structure factor.

The measured density of 10.24 g/cm³ is in good agreement with the theoretical density 10.35 g/cm³ calculated from the UNTe unit-cell dimensions. The results of the chemical analysis show 3.16% N; the theoretical content is 3.64% N.

REFERENCES

1. R. Benz and W. H. Zachariasen, *Acta Crystallogr.* **B26** (1970) 823.
2. E. W. Breeze, N. H. Brett and J. White, *J. Nucl. Mater.* **39** (1971) 157.
3. E. W. Breeze and N. H. Brett, *J. Nucl. Mater.* **40** (1971) 113.
4. A. J. Klein Haneveld and F. Jellinek, *J. Inorg. Nucl. Chem.* **26** (1964) 1127.
5. A. Mursaik and J. Niemec, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **13** (1965) 291.
6. A. Mursaik, W. Suski and J. Leciejewicz, *Phys. Status Solidi* **34** (1969) 157.
7. M. Allbutt and R. M. Dell, *J. Nucl. Mater.* **24** (1967) 1.
8. M. Allbut, A. R. Junkinson and R. F. Carney, *Proc. Brit. Ceram. Soc.* No. **7** (1967) 111.
9. M. Allbutt and R. M. Dell, *J. Inorg. Nucl. Chem.* **30** (1968) 705.
10. A. J. Klein Haneveld and F. Jellinek, *J. Less-Common Metals* **21** (1970) 45.
11. F. Hulliger, *J. Less-Common Metals* **16** (1968) 113.

SAŽETAK

Rendgenografska istraživanja u sistemu U—N—Te

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Istraživane su kristalne strukture ternarnih spojeva u sistemu U—N—Te. Spojevi su priređeni reakcijom UN + X Te ($0{,}4 \leqslant X \leqslant 2{,}0$). Praškasti uran-mononitrid, UN, i elementarni telur pomiješani su u odgovarajućim količinama i grijani na 900—1000 °C u evakuiranima kvarcnim ampulama. Rendgenogrami praha snimani su Philipsovim difraktometrom upotrebom filtriranog CuK_α-zračenja.

Osim već od prije poznatog spoja U_2N_2Te nađen je i novi spoj UNTe, koji pripada tetragonskom sustavu i prostornoj grupi P4/nmm. Nađeno je da spoj UNTe ima slijedeće parametre jedinične ćelije: $a = 3.929$ Å i $c = 7.617$ Å. Usporedba opaženih i izračunanih vrijednosti intenziteta za UNTe pokazuje najbolje slaganje ako se za varijabilne atomske koordinate uzmu vrijednosti $u = 0.165$ (za uran) i $v = 0.624$ (za telur).

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