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 + XTe (0.4 ≤ X ≤ 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 (CuKα radiation). The compounds having the following crystal structures and lattice parameters were found:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameters/Å</th>
<th>Structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₂N₂Te</td>
<td>a = 3.963</td>
<td>La₂O₂Te</td>
</tr>
<tr>
<td></td>
<td>c = 12.561</td>
<td></td>
</tr>
<tr>
<td>UNTe</td>
<td>a = 3.929 ± 002</td>
<td>PbFCl</td>
</tr>
<tr>
<td></td>
<td>c = 7.617 ± 0.003</td>
<td></td>
</tr>
</tbody>
</table>

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 U₃N₂Te, U₂O₂Te and UOTe were described by Benz and Zachariasen¹, Breeze and Brett²,³ Klein, Haneveld and Jellinek⁴ and Marsaik and coworkers⁵,⁶. Compound U₂N₂Te 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 N₂ = U₂N₂Te). 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 = U₂N₂Te). By both methods, pure compound U₂N₂Te was obtained. U₂N₂Te has a body-centered tetragonal structure (structure type La₂O₂Te, space group I₄/mmm) with the following unit-cell parameters: $a = (3.9631 ± 0.0002)$ Å, $c = (12.561 ± 0.002)$ Å.

In the investigation of the U—O—Te—C, system by electron microprobe analysis, Breeze and Brett²,³ found a new oxy-uranium telluride, approximately of the composition U₂O₂Te. The X-ray patterns of this compound was indexed on a tetragonal unit-cell with the parameters $a = (3.9460 ±$
The tetragonal crystal structure of the compound UOTe (structure type PbFCl, space group P4/nmm) was previously reported by Klein, Hanneveld and Jellinek. They found the following parameters: \( a = 4.004 \pm 0.001 \text{ Å}, \ c = 7.491 \pm 0.004 \text{ Å} \). Breeze and Brett gave the following values of the parameters for the same compound:

\[
a = (4.0141 \pm 0.0003) \text{ Å}, \ c = (7.4940 \pm 0.0008) \text{ Å}
\]

Mursaik and coworkers 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, UNx. Finally, the temperature was raised to 1400 °C in vacuum to degrade UNx to uranium mononitride. 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 \( \leq X \leq 2.0 \)). 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\(_\alpha\) 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\(_2\)N\(_2\)Te 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\(_2\)N\(_2\)Te.
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 \( \text{U}_2\text{N}_2\text{Te} \) and \( \text{U}_2\text{O}_2\text{Te} \), UNTe was assumed to be isostructural with UOTe, with two formula units per unit-cell and the atoms at the following sites:

\[
\begin{align*}
2\text{U} & \text{in } 2(c) : 1/2, 0, u & 0, 1/2, \bar{u} \\
2\text{Te} & \text{in } 2(c) : 1/2, 0, v & 0, 1/2, v \\
2\text{N} & \text{in } 2(a) : 0, 0, 0 & 1/2, 1/2, 0
\end{align*}
\]

**TABLE I**

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heating conditions</th>
<th>Results of X-ray analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN + 0.4 Te</td>
<td>900 °C, 215 h, slowly cooled</td>
<td>( \text{U}_2\text{N}_2\text{Te} + \text{UO}_2 + \text{UN} )</td>
</tr>
<tr>
<td>UN + 0.5 Te</td>
<td>900 °C, 215 h, slowly cooled</td>
<td>( \text{U}_2\text{N}_2\text{Te} + \text{UO}_2 )</td>
</tr>
<tr>
<td>UN + 0.6 Te</td>
<td>900 °C, 215 h, slowly cooled</td>
<td>( \text{U}_2\text{N}_2\text{Te} + \text{UO}_2 )</td>
</tr>
<tr>
<td>UN + 0.7 Te</td>
<td>900 °C, 318 h, slowly cooled</td>
<td>UNTe ( 0.7 )</td>
</tr>
<tr>
<td>UN + 0.8 Te</td>
<td>900 °C, 280 h, 1 K/min</td>
<td>UNTe ( 0.7 )</td>
</tr>
<tr>
<td>UN + 0.9 Te</td>
<td>900 °C, 280 h, 1 K/min</td>
<td>UNTe ( 0.7 )</td>
</tr>
<tr>
<td>UN + Te</td>
<td>900 °C, 240 h, 1 K/min</td>
<td>UNTe</td>
</tr>
<tr>
<td>UN + Te</td>
<td>900 °C, 259 h, tempered</td>
<td>UNTe</td>
</tr>
<tr>
<td>UN + 2 Te</td>
<td>1000 °C, 259 h, tempered</td>
<td>UNTe + Te + \text{UO}_2</td>
</tr>
<tr>
<td>UN + 2 Te</td>
<td>1000 °C, 259 h, 1 K/min</td>
<td>UNTe + Te + \text{UO}_2</td>
</tr>
</tbody>
</table>

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

**X-ray diffraction data for UNTe**

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

### TABLE III

**Interatomic distances ($\delta$) for UNTe and the other uranium tellurides, nitrides and oxytellurides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Atoms</th>
<th>$\delta$/Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNTe</td>
<td>tetragonal</td>
<td>U-4 Te</td>
<td>3.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-1 Te</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-4 N</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N-4 N</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Te-4 N</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Te- Te</td>
<td>3.36</td>
<td></td>
</tr>
<tr>
<td>UTe</td>
<td>cubic</td>
<td>U-6 Te</td>
<td>3.08</td>
<td>9</td>
</tr>
<tr>
<td>UTe$_2$</td>
<td>orthorhombic</td>
<td>U-2 Te$_I$</td>
<td>3.08</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-4 Te$_{II}$</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-2 Te$_I$</td>
<td>3.205</td>
<td></td>
</tr>
<tr>
<td>UN</td>
<td>cubic</td>
<td>U-6 N</td>
<td>2.44</td>
<td>9</td>
</tr>
<tr>
<td>UOTe</td>
<td>tetragonal</td>
<td>U-4 Te</td>
<td>3.20</td>
<td>4, 11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-1 Te</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-4 O</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-4 O</td>
<td>2.83</td>
<td></td>
</tr>
<tr>
<td>U$_2$O$_2$Te</td>
<td>tetragonal</td>
<td>Te-8 U</td>
<td>3.35</td>
<td>3</td>
</tr>
<tr>
<td>U$_2$N$_2$Te</td>
<td>tetragonal</td>
<td>U-4 Te</td>
<td>3.42</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-4 N</td>
<td>2.31</td>
<td></td>
</tr>
</tbody>
</table>
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:

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

where $\Theta$ is the Bragg angle, $m$ the multiplicity factor and $F$ the structure factor.

The measured density of 10.24 g/cm$^3$ is in good agreement with the theoretical density 10.35 g/cm$^3$ 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


SAZETAK

Rendgenografska istraživanja u sistemu U—N—Te

R. Trojko i Z. Despotović

Istraživane su kristalne strukture ternarnih spojeva u sistemu U—N—Te. Spojevi su priređeni reakcijom UN + XTe (0,4 ≤ X ≤ 2,0). Praškasti uran-mononitrild, UN, i elementarni telur pomiješani su u odgovarajućim količinama i grijani na 900—1000 °C u evakuiranim kvarcnim ampulama. Rendgenogrami praha snimljeni su Philipsovim difraktometrom upotrebom filtriranog CuK$_\alpha$-zračenja.

Osim već od prije poznatog spoja $\text{U}_2\text{N}_2\text{Te}$ nađen je i novi spoj UNTe, koji pripada tetragonskom sustavu i prostornoj grupi P4/nmm. Nađeno je da spoj UNTe ima slijedeće parametre jedinične celije: $a = 3.929$ 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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