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Crystal growth of actinide dioxides by chemical transport

J. C. Spirlet, E. Bednarczyk, I. Ray and W. Müller

Commission of the European Communities, Joint Research Centre, European Institute for Transuranium Elements, Postfach 22 66, D-7500 Karlsruhe 1, F.R.G.

Résumé. — Des monocristaux de dioxydes d’actinides (U, Np) ont été préparés par la méthode de transport chimique en phase gazeuse, utilisant le tétrachlorure de tellure comme agent de transport. La réaction de transport est réalisée dans des cellules de quartz scellées sous vide et placées dans un four à gradient de température entre 1 075 °C et 975 °C. Les monocristaux obtenus ont des dimensions comprises entre le mm et le cm. Les oxydes ont été identifiés et caractérisés par les méthodes de Debye-Scherrer et de Weissenberg.

Abstract. — Actinide (U, Np) dioxide single crystals were grown by a chemical transport reaction using tellurium tetrachloride as transporting agent. The oxides were transported from 1 075 to 975 °C in vacuum sealed quartz bulbs. Single crystal sizes were in the mm to cm range. The oxides were identified and characterized by the Debye-Scherrer and Weissenberg methods.

I. Introduction. — The chemical transport reaction method with \( \text{TeCl}_4 \) as transporting agent is widely used to grow crystals of a large number of refractory oxides (Table I). This method allows the preparation of crystals up to some cm in size with well formed natural faces and with low defect density.

Actinide dioxide single crystals are required for solid state investigations such as neutron diffraction and optical reflectivity. Large single crystal faces are also suitable for the electronic properties study by photoelectron spectroscopy.

The successful preparation of large and good quality crystals of uranium dioxide [1, 2] encouraged us to extend this method to other actinide dioxides.

The mechanism of the chemical transport with \( \text{TeCl}_4 \) as described in equation (1) is generally accepted for the transport of \( \text{TiO}_2, \text{ZrO}_2, \text{HfO}_2 \) [1].

\[
\text{MeO}_2 + \text{TeCl}_4 + \text{Cl}_2 \xrightarrow{1 075 - 975 \, \degree \text{C}} \text{MeCl}_4 + \text{TeO}_2 .
\] (1)

For other oxides, including those of the actinides, the transport mechanism is complicated by the presence of stable oxichlorides \( \text{MeO}_2\text{Cl}_2 \).

2. Experimental. — The transport reaction is carried out in a quartz bulb (25 mm in diameter,
CRYSTAL GROWTH OF ACTINIDE DIOXIDES BY CHEMICAL TRANSPORT

150 mm long) in a temperature gradient furnace mounted in a glove box.

Sintered pellets of the starting oxide (10-20 g) are introduced into the carefully cleaned bulb (HNO₃, detergent, distilled water). The bulb is evacuated and sealed under a vacuum of 10⁻⁶ torr with a plasma torch.

The number of nucleation centres in the crystallization zone due to the possible presence of oxide traces on the walls is reduced by heating this zone to 1050 °C for 12 hours. The crystals are grown at 975 °C maintaining the oxide feed at 1 075 °C for 2 weeks (Fig. 1).

3. Results. — The results of the growth experiments of UO₂, NpO₂ single crystals are summarized in table II. The transporting rate of the oxides is about 20 mg/h. By careful nucleation control, large single crystals (up to 1 × 0.5 × 0.5 cm) are obtained (UO₂, Fig. 2). Poor nucleation control results in a large number of small crystals (1-3 mm³, NpO₂, Fig. 3). The most commonly found crystal habits for UO₂ are large prisms, platelets and octahedra. For NpO₂, small cubes were obtained (Fig. 4).

The lattice parameters measured by the Debye-Scherrer and the Weissenberg methods are in good agreement with the literature values.

Table II. — Results of the growth experiments.

<table>
<thead>
<tr>
<th>Feed quantity (g)</th>
<th>UO₂</th>
<th>NpO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transported quantity (g)</td>
<td>8</td>
<td>4.8</td>
</tr>
<tr>
<td>Time (d)</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Transporting speed (mg/h)</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>Lattice parameter measured</td>
<td>5.470</td>
<td>5.434</td>
</tr>
<tr>
<td>Literature</td>
<td>5.468</td>
<td>5.434</td>
</tr>
<tr>
<td>Dimensions (cm)</td>
<td>1 × 0.5 × 0.5</td>
<td>0.1 × 0.1 × 0.1</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>prisms</td>
<td>cubes</td>
</tr>
<tr>
<td></td>
<td>octahedra</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. — Temperature profile in the furnace during the growth of UO₂ single crystals.

Fig. 2. — UO₂ single crystals in the quartz bulb.

Fig. 3. — NpO₂ single crystals.

Fig. 4. — Scanning electron micrograph of NpO₂ single crystals.
References