

between the elements of the highest available purity

- crystal growth
- characterization, orientation and encapsulation of the the single crystals.

Actinide dioxides. Actinide dioxide single crystals are obtained by chemical vapour transport (UO_2 , NpO_2) using TeCl_4 as transporting agent or by high temperature solution growth with lead vanadate as solvent (ThO_2 , NpO_2 , PuO_2).

Actinide mononictides. Actinide mononictide single crystals are grown by the mineralisation technique. Large single crystals (up to $1/2 \text{ cm}^3$) of PuAs, PuSb, PuBi were prepared.

Actinide intermetallic compounds. Pulling from the levitated melt in a Hukin crucible by the Czochralski technique allows the preparation of intermetallic compound single crystals (AnX_3 or Laves phases). A single crystal of PuFe_2 (θ 4 mm, l = 5 cm) was prepared.

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Single Crystal Growth of Actinide Dioxides

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High temperature solution growth (HTSG) is a very successful method to grow single crystals of refractory oxides. Crystallisation is obtained from solutions of oxides in molten salts by slow cooling, solvent evaporation or by transport in a temperature gradient. High temperature solution growth produces small single crystals ($1\text{--}100 \text{ mm}^3$) with well formed natural faces and a high degree of perfection.

TABLE I. Experimental Conditions and Results.

Compound	$\text{Pb}_2\text{V}_2\text{O}_7$ (g)	AnO_2 powder (g)	Crucible temp. ($^\circ\text{C}$)	Temp. gradient $\Delta T/l$ ($^\circ\text{C}/\text{cm}$)	Reaction time (days)	Single crystals (mm^3)
ThO_2	36	1.8	1250	50	7	pale-yellow octahedrals $2 \times 2 \times 2$
NpO_2 -doped ThO_2						pink octahedrals
a) 0.1%	20	5.0	1200	50	7	$1.5 \times 1 \times 1$
b) 1.0%	20	5.0	1200	50	15	$2 \times 1 \times 1$
NpO_2	20	11.0	1100	25	10	black cubes $2.5 \times 2 \times 1.5$
PuO_2	20	6.4	1100	25	15	black cubes $0.8 \times 1 \times 0.5$

In order to prepare actinide dioxide single crystals the thermal gradient method was adopted. In this process, relatively small solvent quantities are necessary. The yield is high (up to 80%) and a detailed knowledge of the solvent-actinide oxide system is not necessary, the temperature remaining constant during the process. The $2\text{PbO}\cdot\text{V}_2\text{O}_5$ flux has been chosen because of its [1, 2].

i) low vapour pressure even at high temperature ($1300 \text{ }^\circ\text{C}$)

ii) compatibility with platinum

iii) viscosity.

The apparatus used to grow actinide dioxide single crystals is shown in Fig. 1.

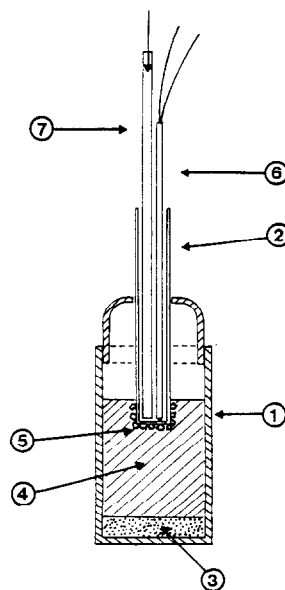


Fig. 1. Apparatus for high temperature solution growth of actinide dioxide single crystals (temperature gradient method). 1. platinum crucible. 2. platinum tube. 3. nutrient. 4. solvent. 5. single crystals. 6. thermocouple. 7. alumina tube for gas cooling.

The platinum crucible containing the flux and the nutrient (oxide powder or pressed pellets) is heated in

a resistance furnace. Cold gas (nitrogen) is injected into a platinum tube to obtain a suitable temperature gradient. The single crystals are growing on the platinum tube.

Single crystals of thorium, neptunium, and plutonium dioxide have been grown as well as Np doped thorium dioxide.

The experimental conditions and results are summarized in Table I.

The average growth rate for all the actinide dioxides is about 1 mm/week. The single crystals have been characterized by X-ray diffraction (Debye-Scherrer, Gandolfi, Laue). A more complete characterization including the determination of the oxygen/metal ratio and a panoramic analysis of the impurities and the detection of inclusions is in progress.

1 B. M. Wanklyn, *J. Cryst. Growth*, 7, 368–370, (1970).

2 G. Garton, S. H. Smith and B. M. Wanklyn, *J. Cryst. Growth*, 13/14, 588–592 (1972).

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Phase Relations and Structures of Protactinium Hydrides

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The metal–hydrogen systems of the lighter actinides (Th–Am) have in general been well characterized, but a conspicuous gap occurs at Pa + H. Only the results of two X-ray diffraction studies have been described [1, 2]; Sellers *et al.* [1] reported that the elements reacted at 523 K to form a cubic β -UH₃-type hydride with $a = 664.8$ pm. Later work by Dod showed that the products formed between 373 and 573 K had the cubic α -UH₂-type structure with $a = 415.4$ pm, while that formed at 473 K gave a new diffraction pattern which was not indexed or correlated with a known structure. The present study was initiated after suitable quantities of ²³¹Pa (0.052 mass% impurity) were prepared in our institute.

Temperature–pressure–composition data were measured with a gold-lined Seivert's apparatus in the experimental range $373 < T < 795$ K and $10 \mu\text{bar} < P < 45$ bar. Metal samples (0.15–0.21 g) were contained in a W cell. Samples for X-ray studies were prepared along hydriding and dehydriding isotherms and were cooled at constant composition. Diffraction data were obtained by the Debye–Scherrer method.

The pressure–composition isotherms measured during hydriding and dehydriding are similar, but

large hysteresis effects are encountered. Results of extensive studies indicate that equilibrium is defined by the dehydriding pressures. At low H/Pa, hydrogen dissolves in the bct metal to form phase I. The hydrogen-saturated metal coexists with hydride for $H/Pa < 1.3$. Isotherms for $T > 500$ K show that the phase II hydride exists across the range $1.3 \leq H/Pa \leq 1.7$, and that a second diphasic region occurs for $1.7 < H/Pa < 2.0$. Phase III forms in the range $2.0 \leq H/Pa \leq 3.0$. At $T < 500$ K, a continuous solid solution designated phase IV exists across the entire range $1.3 \leq H/Pa \leq 3.0$.

Diffraction data for phase II show that it is identical to the new hydride observed by Dod [2]. The reflections are indexable on fcc with parameters which vary from 914.4(6) pm at $H/Pa = 1.3$ to 919.8(2) pm at $H/Pa = 1.7$. Phases III and IV have β -UH₃-related and α -UH₃-related structures, respectively. The cubic parameter of phase III is 656.7(5) pm at $H/Pa = 2.0$ and 664.2(6) pm at $H/Pa = 2.9$. The parameters of phase II and III hydrides obtained along hydriding isotherms are consistently larger than those reported here for dehydriding samples. The phase IV parameter, 415.7(7) pm, is constant.

Metal atom coordinates for the phase II structure have been determined using powder intensities. The measured hydride density of $11.2 \pm 1.2 \text{ g cm}^{-3}$ is in good agreement with the 11.79 g cm^{-3} value calculated for $Z = 24$ formula units of PaH_{1.67} per unit cell. The lattice parameters and intensities are similar to those of compounds with metal atoms in the MgCu₂(C15) arrangement, which served as a model. The d-values and calculated intensities for space group Fd3m with Pa on fixed positions 8 (a) and 16 (d) are presented with observed data in Table I.

Identification of this unique actinide hydride structure is particularly significant. The upper and lower boundaries of phase II correspond to the ideal stoichiometries Pa₃H₄ and Pa₃H₅, respectively, but it is not obvious why this complicated arrangement is stable in Pa + H at high temperatures. Protactinium occupies both Mg and Cu sites in the MgCu₂ arrangement, which is found for spinel, cubic AB₂ Laves hydrides and ThZr₂H₇. The behavior of Pa is most similar to that of the Th–Zr alloy in that neither metal exists in the MgCu₂ arrangement prior to reaction with hydrogen [3].

The two types of metal positions in Pa₃H_x are non-equivalent, and the phase must be looked upon as a 'pseudo-ternary' hydride. Each Pa on a Mg site is surrounded by 12 Pa on Cu sites at distances of 382.7 pm and by 4 Pa on Mg sites at 399.7 pm. Each metal on a Cu site is surrounded by 6 Pa on Cu sites at distances of 326.4 pm, which is similar to the inter-atomic distance in Pa metal (321.5 pm). The metals on Cu sites form an infinite three dimensional network composed of two-dimensional sheets having metal positions like those of the (110) planes of bct