Papers

D5

Crystal Structures of Some Complex Chlorides of Trivalent and Tetravalent Plutonium[+]

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The compounds K_2PuCl_5, Rb_2PuCl_5, K_2PuCl_6, and Rb_2PuCl_6 have been prepared. The latter two compounds were verified to contain only Pu(IV) by chemical analysis and spectrophotometry in solid and solution. The crystal structures of these compounds were determined by x-ray powder (Debye–Scherrer and Guinier) diffraction. The results are as follows:

K_2PuCl_5: Orthorhombic, Pnma, K_2PrCl_5 type [1]. $a = 12.675 \pm 0.003$, $b = 8.728 \pm 0.002$, $c = 7.970 \pm 0.002$ Å.

Rb_2PuCl_5: Orthrohombic, Pnma, K_2PrCl_5 type [1]. $a = 13.078 \pm 0.005$, $b = 8.908 \pm 0.003$, $c = 8.177 \pm 0.004$ Å.

K_2PuCl_6: Monoclinic, C2/m, distorted K_2PtCl_6 type. $a = 10.45 \pm 0.03$, $b = 10.12 \pm 0.03$, $c = 10.47 \pm 0.05$ Å; $\beta = 92.7 \pm 0.2°$ (tentative assignment).

Rb_2PuCl_6: Hexagonal, $P6_3mc$, Rb_2GeF_6 type [2]. $a = 7.374 \pm 0.005$, $c = 11.91 \pm 0.001$ Å.

1 G. Meyer and E. Hüttl, *Z. Anorg. Allg. Chem., 497,* 191 (1983).
2 L.R. Morss and J. Fuger, *Inorg. Chem., 8,* 1433 (1969).

[+] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under contract number W-31-109-ENG-38.

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D6

The Vapor Pressure of Americium Trichloride

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The saturation vapor pressure of americium trichloride has been measured by means of a new technique using 100 to 200 micrograms of $AmCl_3$. The trichloride is prepared in an x-ray capillary using the classical Fried-Davidson method, and is identified by means of its x-ray pattern. The capillary is transferred to the vapor pressure apparatus, its tip is broken, and the contents are sublimed into the vapor pressure cup. The cup is next suspended in a bath of molten tin, and the buoyancy is measured by the deflection of a quartz fiber torsion balance, from which the cup is suspended. A detailed description of the measurement will be given. The vapor pressure of $AmCl_3$ may be described by the equation:

$$\log p\ (\text{mm Hg}) = -\frac{(13157 \pm 515)}{T} + (11.94 \pm 0.67)$$

The thermodynamic parameters derived from the vapor pressure measurement will be reported.

D7

Recent Achievements in Single Crystal Growth of Actinide Compounds

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Important progress has been achieved in solid state physics of the element uranium since large and perfect single crystals of uranium metal and compounds are available. To allow similar progress in the solid state physics of the other actinide elements, a large effort has been undertaken at the European Institute for Transuranium Elements to grow single crystals of actinide compounds with cubic crystal structure like the dioxides, the monopnictides, the monochalcogenides, and some intermetallic compounds.

The single crystals enable the measurement of physical properties related to the electronic structure in order to extend the knowledge of chemical bonding in the 5 f transition elements.

The different steps allowing the preparation of actinide samples for solid state physics investigations are:

- preparation of actinide metals
- refining of actinide metals
- preparation of compounds by direct synthesis

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 monopnictides. Actinide monopnictide single crystals are grown by the mineralisation technique. Large single crystals (up to 1/2 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, 1 = 5 cm) was prepared.

D8

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 (1–100 mm^3) with well formed natural faces and a high degree of perfection.

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 $2PbO\text{-}V_2O_5$ flux has been chosen because of its [1, 2].

i) low vapour pressure even at high temperature (1300 °C)

ii) compatibility with platinum

iii) viscosity.

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

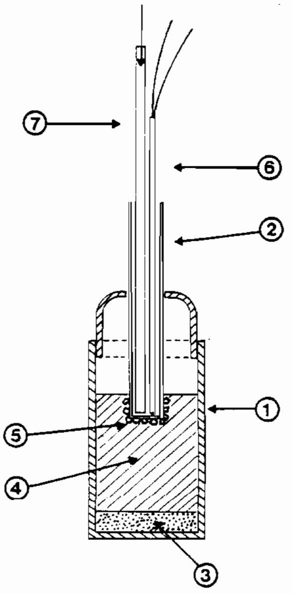

Fig. 1. Apparatus for high temperature solution growth of actinide dioxide single crystals (temperature gradient method). 1. platinum crucible. 2. platinum tube. 3. nutrient. 4. solvent. 5. single crystals. 6. thermocouple. 7. alumina tube for gas cooling.

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

TABLE I. Experimental Conditions and Results.

Compound	$Pb_2V_2O_7$ (g)	AnO_2 powder (g)	Crucible temp. (°C)	Temp. gradient $\Delta T/1$ (°C/cm)	Reaction time (days)	Single crystals (mm^3)
ThO_2	36	1.8	1250	50	7	pale-yellow octahedrals 2 × 2 × 2
NpO_2-doped ThO_2						pink octahedrals
a) 0.1%	20	5.0	1200	50	7	1.5 × 1 × 1
b) 1.0%	20	5.0	1200	50	15	2 × 1 × 1
NpO_2	20	11.0	1100	25	10	black cubes 2.5 × 2 × 1.5
PuO_2	20	6.4	1100	25	15	black cubes 0.8 × 1 × 0.5