



Two convenient low-temperature routes to single crystals of plutonium dioxide



Nathan A. Meredith^b, Shuao Wang^c, Juan Diwu^c, Thomas E. Albrecht-Schmitt^{a,*}

^a Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, United States

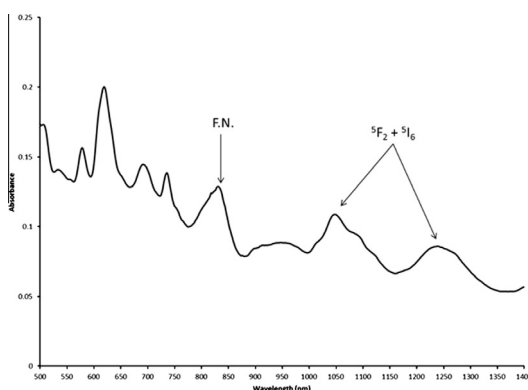
^b Departments of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, United States

^c School of Radiation Medicine and Protection and School of Radiological and Interdisciplinary Sciences, Soochow University, Suzhou, Jiangsu 215123, China

HIGHLIGHTS

- Two low-temperature routes to the growth single crystals of plutonium dioxide.
- Safer methods of preparing PuO₂ single crystals that do not involve solid-state synthetic techniques.
- Solvothermal crystal growth of plutonium dioxide.

GRAPHICAL ABSTRACT



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ABSTRACT

During the solvothermal synthesis of a low-dimensional borate, $\text{KB}_5\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, in the presence of Pu(III), single crystals of plutonium dioxide unexpectedly formed. Single crystals of PuO₂ also formed during the hydrothermal synthesis of another borate, $\text{Na}_2\text{B}_5\text{O}_8(\text{OH}) \cdot 2\text{H}_2\text{O}$, in the presence of Pu(III). The reactions were conducted at 170 °C and 150 °C, respectively, which are much lower temperature than previously reported preparations of crystalline PuO₂. Yellow–green crystals with a tablet habit were characterized by single crystal X-ray diffraction and solid-state UV–vis–NIR absorption spectroscopy. The crystal structure was solved by direct methods with $R_1 = 1.26\%$ for 19 unique observed reflections. PuO₂ is cubic, space group $Fm\bar{3}m$, and adopts the fluorite structure type. The lattice parameter was determined to be $a = 5.421(5) \text{ \AA}$ giving a volume of $159.3(2) \text{ \AA}^3$. The absorption spectrum is consistent with Pu(IV).

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1. Introduction

With the end of the Cold War and the dismantling of nuclear weapons in the U.S. and Russia, there have been developing

* Corresponding author. Present address: Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way, 310 DLC, Tallahassee, FL 32306–4390, United States. Tel.: +1 850 645 0477.

E-mail address: talbrechtschmitt@gmail.com (T.E. Albrecht-Schmitt).

concerns about the diversion of ²³⁹Pu during interim storage or disposal. One proposed solution to alleviate such concerns is to incorporate plutonium into the nuclear fuel cycle. This process would involve recovering Pu metal from weapons, oxidizing it to plutonium dioxide, and blending the oxide with depleted UO₂ to create mixed-oxide (MOX) reactor fuels [1].

The most commonly applied method for the preparation of PuO₂ in the nuclear industry is the calcination of Pu(III) or Pu(IV) oxalate – Pu₂(C₂O₄)₃ or Pu(C₂O₄)₂. In this process, Pu(NO₃)₄

solutions are reacted with oxalic acid to precipitate the oxalate species, which is subsequently calcined in air at temperatures from 450 to 1050 °C with the most typical being approximately 700 °C [2–4]. The resulting powdered phase is then mixed with UO₂ and pressed into fuel pellets [5]. Other procedures, including direct thermal denitration at 550 °C [6] and oxidation of plutonium hydride via the nitride between 850 and 950 °C (the HYDOX process) [7], have also been developed for the preparation of plutonium dioxide powders.

Despite the emphasis on powdered and ceramic samples for use in MOX fuel, the growth of bulk single crystals of plutonium dioxide is still desirable for such purposes as studies of electrical and magnetic properties in both the pure oxide and mixed phases [8,9]. Phipps and Sullenger reported the preparation of single crystalline plutonium dioxide by dissolving a powdered sample in a 70% SiO₂/30% Na₂O sodium silicate glass followed by heating at 1300 °C [10]. Benedict and co-workers were able to synthesize single crystals of plutonium dioxide in a high temperature CsCl melt (550 °C) that was sparged with an oxygen–chlorine gas mixture [11]. Schlecter was able to prepare single crystals of plutonium dioxide by the thermal decomposition of Pu(SO₄)₂ in either a KCl–PbCl₂ or LiCl–KCl eutectic at a temperature of 800 °C [12]. Finch and Clark reported a high-temperature flux growth of plutonium dioxide single crystals using a Li₃O–MoO₃ solvent at 1300 °C [13]. More recently, Modin and coworkers reported on the growth of PuO₂ single crystals via a 5% PuO₂–95% MoO₂ flux at 1100 °C [14].

We have recently become interested in investigating the interstitial incorporation of Pu(III) and Pu(IV) in low-dimensional borate phases to determine the potential of these phases to reduce the mobility of actinides during long-term geologic disposal [15]. In an attempt to prepare KB₅O₇(OH)₂·2H₂O in the presence of Pu(III) via the synthesis of Zhang and coworkers [16], single crystals of PuO₂ unexpectedly formed in the reaction product. Similarly, PuO₂ single crystals formed during the preparation of Na₂B₅O₈(OH)·2H₂O in the presence of Pu(III) by the procedure of Li and Liu [17]. We herein report the synthetic conditions and characterization of these crystals.

2. Experimental

2.1. Synthesis

All studies with plutonium were conducted in a nuclear science facility that is equipped with HEPA filtered hoods and negative pressure gloveboxes that are ported directly into the hoods. All free-flowing solids are worked with in gloveboxes, and products are only examined when coated with either water or Krytox oil and water. There are significant limitations in accurately determining yield with plutonium because this requires drying, isolating, and weighing a solid, which poses certain risks, as well as manipulation difficulties given the small quantities employed in the reactions.

PuO₂ was firstly prepared by the solvothermal reaction under autogeneous pressure of weapons-grade plutonium(III) trichloride (²³⁹PuCl₃, 94% ²³⁹Pu with 6% ²⁴⁰Pu and trace amounts of other Pu isotopes and ²⁴¹Am), boric acid (H₃BO₃, 99.99%, Acros Organics), and potassium hydroxide (KOH) in a deionized water–pyridine (≥99%, Sigma–Aldrich) mixture. All materials were used as received. A typical reaction involved combining 4 mg of PuCl₃, 18 mg of H₃BO₃, and 4 mg of KOH in a 10 mL PTFE autoclave liner containing 335 μL of pyridine and 88 μL of deionized water. The mixture was sealed in an autoclave and heated at 170 °C for 7 days and cooled to room temperature. The solid product was isolated by rinsing the solid with room temperature deionized water followed by ethanol. The solid was left to stand for several hours while the ethanol and any remaining pyridine evaporated.

In the second method, PuO₂ was prepared under hydrothermal conditions by reacting plutonium trichloride, boric acid (H₃BO₃, 99.99%, Acros Organics), and sodium carbonate (Na₂CO₃, ACS reagent grade, Matheson Coleman Bell) in water. All materials were used as received. A typical reaction involved combining 3 mg of PuCl₃, 618 mg of H₃BO₃, and 218 mg Na₂CO₃ in a 10 mL PTFE autoclave liner containing 500 μL of deionized water. The mixture was sealed in an autoclave and heated at 150 °C for 3 days and cooled to room temperature over 2 days. The solid product was isolated by rinsing the solid with room temperature deionized water and was left to stand for several hours.

2.2. Crystallographic studies

A crystal of PuO₂ from the solvothermal reaction was mounted on a CryoLoop with Krytox oil and optically aligned on a Bruker APEXII Quazar X-ray diffractometer using a digital camera. Initial intensity measurements were performed using an IμS X-ray source, a 30 W microfocussed sealed tube (Mo Kα, λ = 0.71073 Å) with high-brilliance and high-performance focusing Quazar multi-layer optics. Standard APEX II software was used for determination of the unit cell and data collection control. The intensities of the reflections of a sphere were collected by a combination of four sets of exposures. Each set had a different φ angle for the crystal, and each exposure covered a range of 0.5° in ω. A total of 1464 frames were collected with an exposure time per frame of 30 s. SAINT software was used for data integration, including Lorentz and polarization corrections. Semiempirical absorption corrections were applied using the program SCALE (SADABS) [18]. The crystal structure of PuO₂ was solved by direct methods and all atoms were refined anisotropically using the SHELXTL software.

2.3. UV–Vis–NIR absorption spectroscopy

UV–Vis–NIR data were acquired from freshly harvested crystals of PuO₂ that formed in both reactions using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slides under Krytox oil, and the spectra were collected from 500 to 1400 nm. The exposure time was optimized automatically by the Craic software.

3. Results and discussion

3.1. Synthesis and isolation

During the solvothermal preparation, the reagents used were added in the sequence PuCl₃, water, H₃BO₃, KOH, and pyridine. The initial plutonium(III) solution in water was dark blue–purple. Immediately following the addition of KOH, the solution became yellow–green which is characteristic of plutonium(IV) and most likely suggests the formation of a tetravalent hydroxide species. In the hydrothermal reaction, the Na₂CO₃ and H₃BO₃ were added followed by water and then PuCl₃. In this case, the solution remained dark blue–purple. When the reaction vessels were reopened after the reaction, the solution color was yellow–green again indicating the presence of plutonium(IV). This was further confirmed by absorption spectroscopy. The oxidation of Pu(III) to Pu(IV) in air is expected at these temperatures. The PTFE liners used to contain these reactions do not exclude oxygen from the atmosphere, and this oxidizes Pu(III) to Pu(IV). The oxidation of Pu(III) to Pu(IV) is also spontaneous at high pH owing to the remarkable insolubility of Pu(OH)₄.

Following the reaction and isolation of the solid product, several distinct phases were identified in the solvothermal reaction. Yellow–green crystals with a tablet habit were isolated. Also present

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