

Low-Temperature Synthesis of Uranium Tetraboride by Solid-State Metathesis Reactions

Anthony J. Lupinetti,^{*,†} Julie L. Fife,[‡] Eduardo Garcia,[†] Peter K. Dorhout,[§] and Kent D. Abney[†]

Nuclear Materials Technology Division (NMT-2), Mail Stop E511, and Chemistry Division, Isotope and Nuclear Chemistry Group (C-INC), Mail Stop J514, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, and Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received October 25, 2001

A novel synthesis of uranium tetraboride (UB₄) by solid-state metathesis reaction is demonstrated. This approach significantly lowers the temperature required to synthesize this material to ≤ 850 °C. When UCl₄ is reacted with 2 equiv of MgB₂ at 850 °C, crystalline UB₄ is formed. Powder X-ray diffraction and ICP-AES data support the reduction of UCl₄ to UCl₃ as the initial step in the reaction. The UB₄ product is purified by washing with water.

The Department of Energy strategy for plutonium has shifted focus within the past decade from production and recycling to stabilization and disposal. This change results from the reduction in the nuclear stockpile and the accompanying need for plutonium disposition. Today's strategy uses plutonium oxide as the optimum intermediate (i.e., <50-year) storage form, even though Haschke reported that PuO₂ slowly reacts with moisture to form hydrogen, causing numerous safety and storage concerns.¹ Our work focuses on the preparation of actinide borides as an alternative intermediate storage form for actinide elements. These materials would offer the prospect of highly refractory boride phases of plutonium and other actinides that are stable to moisture, are highly compact, and will have many of the desired nonproliferation physical characteristics (e.g., chemical inertness and stability to radiolytic decay).

The area of actinide borides is underdeveloped, in part due to the high temperatures required to produce these materials.² The total list of known binary thorium- and uranium-boride phases includes only ThB₄, ThB₆, ThB₆₆, UB₂, UB₄, and UB₁₂, with little information reported on their chemical properties.³ In contrast, plutonium borides have

been synthesized at lower temperatures but require the use of molten plutonium (800 °C), which is extremely corrosive,⁴ or the use of PuH₃ (900 °C).⁵ Plutonium borides are known to be refractory, but other properties such as chemical behavior and stability have not been evaluated. In contrast, many transition metal and lanthanide borides, such as ZrB₂,^{6,7} and LaB₆,⁸ have been extensively studied and have been used as refractory materials and corrosion-resistant coatings. It is therefore expected that some actinide-boride phases will also be corrosion resistant.

During the past two decades significant advances have been made in the low-temperature synthesis of highly refractory materials.^{9,10} New methods, such as molecular precursors, preceramic polymers, chemical vapor deposition, sol-gel and hydrothermal syntheses, low-temperature molten salts, self-propagating high-temperature synthesis (SHS), and solid-state metathesis reactions (SSM), virtually eliminate the problems associated with slow solid-state diffusion by mixing the constituents of the ceramic at a molecular level. SHS and SSM methods have been used successfully to synthesize transition metal borides, nitrides, and oxides and actinide oxides and nitrides at low to moderate temperatures.^{11,12,13} The key to low-temperature synthesis is identification of suitable precursors that lead to ceramic materials having the desired physical characteristics described above.

Our approach focuses on the use of solid-state metathesis reactions for the production of new actinide boride materials, specifically uranium borides as proof of concept for pluto-

* Author to whom correspondence should be addressed. E-mail: lupi@lanl.gov.

[†] Nuclear Materials Technology Division (NMT-2), Mail Stop E511, Los Alamos National Laboratory.

[‡] Chemistry Division, Isotope and Nuclear Chemistry Group (C-INC), Mail Stop J514, Los Alamos National Laboratory.

[§] Colorado State University.

(1) Haschke, J. M.; Allen, T. H.; Morales, L. A. *Science* **2000**, 287, 285.

(2) Eick, H. A.; Mulford, R. N. R. *J. Inorg. Nucl. Chem.* **1969**, 31, 371.

(3) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*; Chapman and Hall: New York, 1986; pp 56, 280, 317 for Th, U, and Pu, respectively.

(4) Eick, H. A. *Inorg. Chem.* **1965**, 4, 1237.

(5) Skavdahl, R. E.; Chikilla, T. D.; McNeilly, C. E. *Trans. Am. Nucl. Soc.* **1964**, 7, 403.

(6) Su, K.; Sneddon, L. G. *Chem. Mater.* **1993**, 5, 1659.

(7) Rao, L.; Gillan, G.; Kaner, R. B. *J. Mater. Res.* **1995**, 10, 353.

(8) Kher, S. S.; Spencer, J. T. *J. Phys. Chem. Solids* **1998**, 59, 1343.

(9) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, 14, 297.

(10) Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, 62, 889.

(11) Gillan, E. G.; Kaner, R. B. *Chem. Mater.* **1996**, 8, 333.

(12) Parkin, I. P.; Fitzmaurice, J. C. *J. Mater. Sci. Lett.* **1994**, 13, 1185.

(13) Parkin, I. P.; Fitzmaurice, J. C. *New J. Chem.* **1994**, 18, 825.

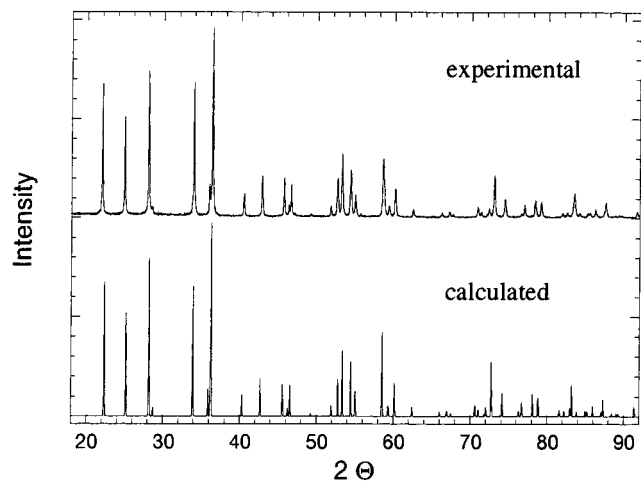
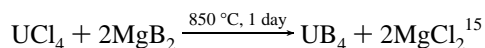


Figure 1. Powder X-ray diffraction pattern for the water-washed solid product from the reaction of $\text{UCl}_4 + 2\text{MgB}_2$ for 1 day at $850\text{ }^\circ\text{C}$ (top) and a powder X-ray diffraction pattern of UB_4 calculated from single-crystal data (bottom).

nium boride materials. Typically, 50–250 mg of UCl_4 and 2 equiv of MgB_2 were reacted in a vacuum-sealed 1.5 mL quartz tube and heated to $850\text{ }^\circ\text{C}$ for 1 day:¹⁴



After reaction, the tubes were opened and the contents washed in water to remove soluble salts. The sample was then rinsed with ethanol and dried. In Figure 1, a powder X-ray diffraction (pXRD) pattern of the washed product is compared with a UB_4 pattern calculated from single-crystal data. From the similarity of the experimental pattern and the calculated pattern, it is clear that UB_4 is the only crystalline phase readily identified in the remaining solid.

The reaction of UCl_4 with substoichiometric amounts of MgB_2 produces a mixture of crystalline phases composed of UB_4 , UCl_3 , and MgCl_2 . X-ray powder diffraction patterns of the reactions of $\text{UCl}_4 + x\text{MgB}_2$ ($x = 0.5, 1, 2, 2.5$) for reactions conducted at $850\text{ }^\circ\text{C}$ for 1 day are shown in Figure 2. As the amount of MgB_2 in the reaction increases, the amount of UCl_3 remaining in the reaction decreases while the amount of UB_4 produced increases. The presence of UCl_3 in the reaction mixture was also confirmed by single-crystal X-ray diffraction. This evidence suggests that MgB_2 acts as a reducing agent as well as a boron source:



To support this hypothesized reduction of UCl_4 to UCl_3 and in order to better understand the nature of the reaction products, two sets of samples were taken for ICP-AES analysis. First, the reaction products were washed with 40 mL of distilled water and the filtrate was collected. Separately, the water-insoluble, solid products were dissolved in

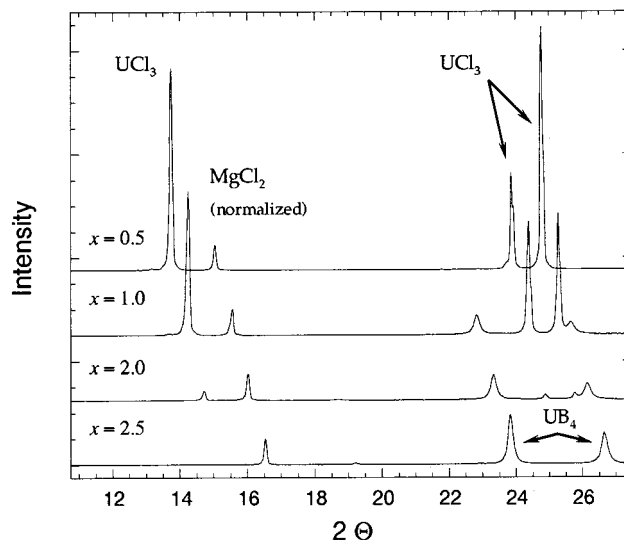


Figure 2. Powder X-ray diffraction patterns of the crude products of the reaction of UCl_4 with (a) 0.5 MgB_2 , (b) 1 MgB_2 , (c) 2 MgB_2 , and (d) 2.5 MgB_2 at $850\text{ }^\circ\text{C}$ for 1 day. The powder patterns are normalized to a constant MgCl_2 peak height. The x -axis corresponds to pattern a; patterns b–d are offset by $+0.5^\circ$ in 2θ from the pattern above for clarity. All powder patterns were taken with the sample under a dry, inert atmosphere.

20 mL of 3.2 M HNO_3 . Any unreacted UCl_4 , as well as UCl_3 and MgCl_2 produced, will dissolve in the water; unreacted MgB_2 and UB_4 produced are insoluble in water and will remain in the solid. The resulting samples were analyzed for uranium, magnesium, and boron content and compared with the initial amounts present in the reaction. At 0.5 equiv of MgB_2 , almost all of the uranium (96%) and magnesium (83%) is present in the filtrate, which is consistent with the production of soluble UCl_3 and MgCl_2 as proposed above. This is also consistent with the lack of UB_4 and MgB_2 in the pXRD pattern of this sample (Figure 2a). The lack of significant quantities of uranium (3%) and magnesium (1%) in the $x = 0.5$ solid is consistent with the formation of elemental boron as the only boron-containing product in the reduction reaction proposed above (i.e., no MgB_2 remains and no UB_4 has yet been formed).

With increasing amounts of MgB_2 (i.e., $x = 0.5$), the amount of uranium in the filtrate is expected to decrease and the amount in the solid increase due to the conversion of soluble UCl_3 into insoluble UB_4 . Indeed, at $x = 2.5$, 90% of the uranium is in the solid product. If all of the uranium in the solid samples is in the form of UB_4 , the elemental boron in $x = 0.5$ must be converted to UB_4 as x approaches 2.5 (Figure 2d). For all values of x , less than 4% of the magnesium is in the solid product; thus, all of the magnesium is dissolved in the filtrate (presumably as MgCl_2). This is consistent with the observation that no magnesium uranium boride ternary phases are present in the pXRD patterns.

Experiments were also conducted to determine the effect of time (1–5 days) and temperature ($600\text{--}850\text{ }^\circ\text{C}$) on the reaction of UCl_4 with 2 equiv of MgB_2 . In all cases, the products were the same: UB_4 , UCl_3 , and MgCl_2 . The major difference in these reactions is the crystallinity of UB_4 ; as might be expected, longer reaction times and higher temperatures yield a more crystalline product.

(14) Note: Although depleted uranium (^{238}U) was used in these studies, care must still be taken in the handling and disposal of starting materials and products as they are still α particle emitters. Sealed ampules were run in furnaces in a fume hood to prevent contamination issues in the case of a tube rupture.

(15) $\Delta H_{\text{rxn}} = -58\text{ kcal/mol}$.

COMMUNICATION

In this paper, we have shown that UCl_4 can be converted in high yield (90+% by ICP-AES based on total uranium) to the refractory boride UB_4 by solid-state metathesis methods. No other uranium boride compounds were observed in these studies. These methods allow for the formation of crystalline boride materials at low temperatures (i.e., 600–850 °C) using quartz reaction vessels. We plan to combine metathesis reactions and low-temperature molten salt fluxes in future studies to probe the reaction chemistry of other actinide halides and boron-containing materials.

Acknowledgment. The authors thank Mr. Ryan Hess, Mr. Antonio Maestas, Dr. Warren Oldham, and Dr. Susan

Oldham for useful discussions and assistance during the course of these experiments and Dr. Brian Scott for the use of his powder X-ray diffractometer. The authors would also like to thank Ms. Brandy Duran for running the ICP-AES samples. This work was performed under the auspices of the Department of Energy, Los Alamos National Laboratory Nuclear Weapons Program Office. Los Alamos National Laboratory is operated by the University of California for the U.S. Department of Energy under Contract W-7405-ENG-36.

IC015607A