SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Konstantin Bauer
FACULTY ADVISOR:	Professor Khachatur Manukyan
PROJECT PERIOD:	Spring 2023
PROJECT TITLE:	Combustion synthesis and characterization of thorium oxide
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**( ) Energy Conversion and Efficiency** **(☒) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Produce thorium solutions with varying fuel-to-oxidizer ratios	We were able to produce thorium solutions of fuel-to-oxidizer ratios from 0 to 1.5.	100
Produce thorium-uranium solutions	We were able to produce thorium-uranium solutions with fuel-to-oxidizer ratios of 0 and 1.5 and of varying percentages of uranium.	100
Perform combustion synthesis on solutions	We performed combustion synthesis on all the pure thorium solutions and on all of the 1.5 fuel-to-oxidizer ratio thorium-uranium solutions. This process remains to be completed for some of the 0 fuel-to-oxidizer ratio solutions thorium-uranium solutions.	80
Analyze the powders resulting from combustion synthesis	We were able to analyze all of the powders we produced with powder X-ray diffraction or with transmission electron microscopy.	100

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	N/A
EXTERNAL AWARDS RECEIVED	N/A
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	N/A
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	N/A
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	N/A
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	N/A
INTERNAL COLLABORATIONS FOSTERED	N/A
EXTERNAL COLLABORATIONS FOSTERED	N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	N/A
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	N/A

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

Yes, I very much enjoyed my research experience this semester. My expectations were fully met, and I gained lots of experience and skills through my research. I thoroughly enjoyed working with Professor Manukyan and his graduate student Noah Cabanas and appreciated the opportunity to be able to work side-by-side with Noah. All other lab personnel were extremely friendly and helpful. I can't think of anything that could have been done to improve my experience, but we do plan to continue work on this research project in the beginning of next semester.

Combustion synthesis and characterization of thorium oxide

Konstantin Bauer

May 12, 2023

1 Introduction

Nuclear reactors have long provided a sustainable and efficient way to generate energy. Typically, uranium dioxide (UO_2) has been used as a fuel for these reactors as it has been well-studied and is cost-effective. However, uranium-based fuels have concerns in nonproliferation, abundance, and waste.

Thorium dioxide (ThO_2) is a nuclear fuel material that addresses many of the drawbacks of uranium dioxide fuel. It is about three times more abundant in the Earth's crust and produces less radioactive waste [1]. However, it too has drawbacks – the main one being that it is rather difficult to sinter thorium into a fuel pellet, limiting its economic viability. The difficulty with producing the pellets has to do with the crystalline structure of thorium. The large (1 μm) grain size of thorium makes it hard to achieve the high-density pellets required [1], and as such, higher temperatures and pressures are needed (when compared to uranium) to synthesize the pellets. This makes for a more costly process.

This research project aimed to address this drawback of thorium dioxide by producing amorphous (or nanocrystalline) thorium dioxide. Since amorphous/nanocrystalline ThO_2 will not have the large grain structures that crystalline thorium has, we want to see if amorphous ThO_2 can reduce the temperatures needed for sintering and lead to an easier process of producing fuel pellets. Further, since actual thorium fuel requires some uranium oxide incorporated into it, we will aim to produce thorium-uranium powders and analyze them to see how uranium incorporates into amorphous thorium.

To produce the ThO_2 powders, the combustion synthesis technique was used. Combustion synthesis is a technique in which some solution is heated, and after some time, a self-propagating exothermic reaction occurs which produces a powder from the solution [2].

2 Methods

Our first task was to create thorium (Th)-acetylacetone (AcAc) solutions of various fuel-to-oxidizer ratios (φ) and thorium concentrations. The fuel-to-oxidizer ratios ranged from 0 to 1.5, and 0.25M was the thorium concentration. To do this, we measured the appropriate masses of thorium nitrate hexahydrate and dissolved the different masses in solutions of 2-methoxy using sonication to ensure full dissolution. The appropriate volume of AcAc was then added to the solution to make the desired fuel-to-oxidizer ratio.

Combustion synthesis was then performed on the solutions. 2mL of the solutions was placed in a reaction vessel on a hot plate, and the hot plate was set to 300C. This process was conducted in a fume hood at a controlled pressure and airflow. The solution boiled off and decreased in volume until it reached a critical point and combusted, resulting in a ThO_2 powder. A thermocouple was used to measure the temperature of this whole process, and videos were taken of the combustion synthesis.

The crystallinity of the various powders was then analyzed using powder X-ray diffraction (PXRD) and are shown in Figures 1 and 3.

A similar process was conducted for thorium-uranium solutions. A stock uranium solution was created by dissolving uranyl nitrate in 2-methoxy, and the appropriate amount of AcAc was added to ensure that the final solutions all had a 1.5 fuel-to-oxidizer ratio. Thorium solutions of different concentrations were then mixed with the appropriate amount of the stock solution to produce a thorium-uranium solution of the desired ratio of thorium to uranium. Th:U ratios ranged from 0:100 to 100:0.

The same combustion synthesis and PXRD process were performed on the thorium-uranium solutions. In addition, the 5% and the 25% uranium solutions were analyzed under a transmission electron microscope (TEM). High-quality images showing the grain structures of the powders were obtained with this.

3 Discussion

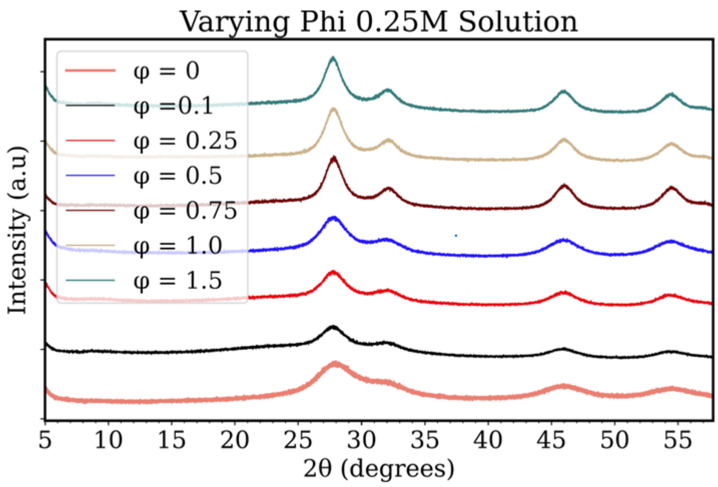

Figure 1: PXRD data from the thorium powders of varying fuel-to-oxidizer ratios.

Through the PXRD analysis of the varying φ thorium solutions, Figure 1 was obtained. A sharper peak corresponds to a more crystalline structure, so we see that as the fuel-to-oxidizer ratio increased, so did the crystallinity.

Figure 2a shows an example of the data obtained from the thermocouple. For all samples, there is a sharp increase at the ignition point (Tg) followed by rapid cooling after reaching the maximum temperature. Qualitative data about the reaction was also obtained. We observed that the higher φ solutions combusted more rapidly, were a darker color, and were often without a flame. The lower φ solutions took longer to combust, achieved a light color before combusting, and often produced a flame. Figure 2b shows this visible flame and a large release of gas for $\varphi = 0.75$.

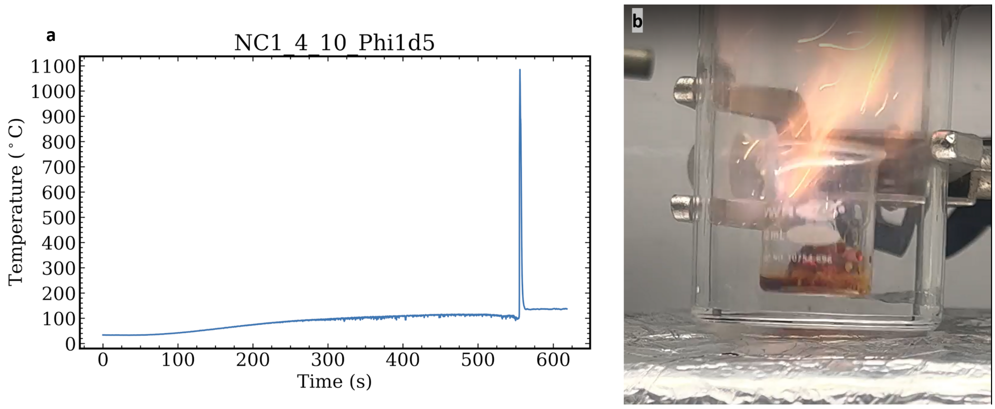

Figure 2: 2a. A temperature vs. time graph obtained with the thermocouple for a combustion synthesis reaction. 2b. A photo in the middle of the combustion reaction for a φ of 0.75.

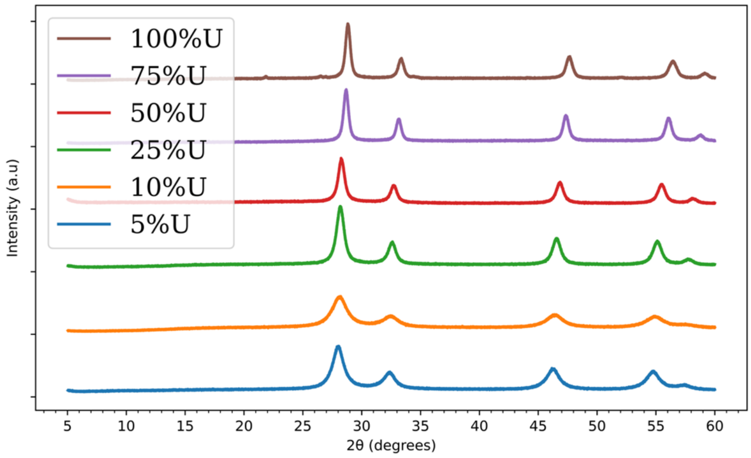

Figure 3: PXRD data for the thorium-uranium powders. The amount of uranium is indicated in the legend. φ was held constant at 1.5.

Figure 3 shows the PXRD data for the thorium-uranium solutions. We see that the bottom 3 peaks (5%, 10%, 25%) all line up well. However, there is a noticeable shift to the right in the red peak (50% Th, 50% U) and again for the peaks above it. The peaks are shifting over to the location of the peak in the pure UO2 sample (the top peak).

From Figure 4a, we can see that there are many small crystalline grains, but there is no larger, uniform atomic structure. This agrees well with what we see in Figure 3 (the orange line corresponds the 5% U powder). From Figures 4b and 4c, we can see that thorium and uranium have incorporated uniformly into one another.

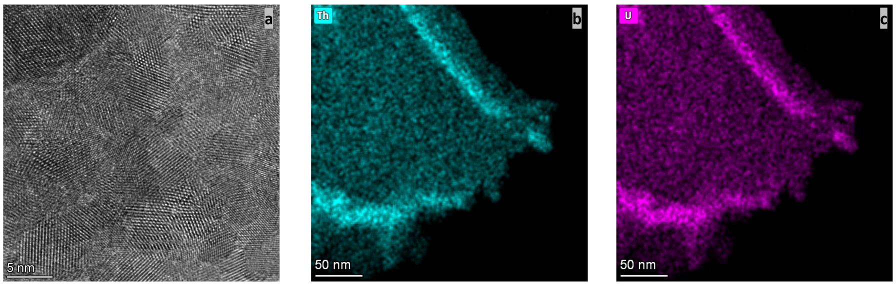

Figure 4: Figures corresponding to the 5% uranium Th-U powder: 2a. TEM image of a grain of the powder. 2b. Thorium elemental analysis of a grain. 2c. Uranium elemental analysis of the same grain.

4 Conclusions

We have shown that amorphous/nanocrystalline ThO_2 can be produced through the combustion synthesis method. By varying the fuel-to-oxidizer ratio of the thorium solutions, we were able to produce thorium oxide powders of varying crystallinity, and we further showed that it is possible to incorporate uranium into the thorium dioxide and still produce amorphous and low crystalline powders through combustion synthesis. Through TEM analysis, we see that the thorium and uranium were incorporated uniformly into one another.

In the future, now that we have shown we can produce thorium oxide, we can investigate the sintering capability of materials, as well as investigate how the materials behave after irradiation to better understand potential morphology changes that may impact it as fuel. This work would occur at the beginning of the next semester.

5 References

1. Humphrey, U. E., & Khandaker, M. U. (2018). Viability of thorium-based nuclear fuel cycle for the Next Generation Nuclear Reactor: Issues and Prospects. Renewable and Sustainable Energy Reviews, 97, 259–275. https://doi.org/10.1016/j.rser.2018.08.019

2. Varma, A., Mukasyan, A. S., Rogachev, A. S., & Manukyan, K. V. (2016). Solution combustion synthesis of nanoscale materials. Chemical Reviews, 116(23), 14493–14586. https://doi.org/10.1021/acs.chemrev.6b00279