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SYNTHESIS AND PROCESSING OF META-STABLE NEGATIVE THERMAL EXPANSION MATERIALS, ZIRCONIUM TUNGSTATE AND ZIRCONIUM PHOSPHOTUNGSTATE (ZRW_2O_8 AND $ZRWP_2O_{12}$)

Margaret E. Gordon[1], Jeffery A. Greathouse[1], Philippe F. Weck[1], Eunja Kim[2], and Charles R. Bryan[1]

[1]Sandia National Laboratories, Albuquerque, New Mexico 87185, USA, megord@sandia.gov
[2]Department of Physics and Astronomy, University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas, Nevada 89124, USA

Synthetic routes and Direct Current Sintering were investigated to form core-shell structured materials or pellets of negative thermal expansion materials, ZrW_2O_8 and $Zr_2WP_2O_{12}$ to be used as a radionuclide wasteform. The solution synthetic routes, while successful in the growth of additional phase pure ZrW_2O_8 on the surface of the ZrW_2O_8 seeds, did not completely encapsulate them. Via Direct Current Sintering, a narrow temperature band of phase stability for ZrW_2O_8 was identified from 650-700 ºC at a pressure of 60 MPa. The pellet was partially sintered, showing some void spaces by SEM. $Zr_2WP_2O_{12}$ necessitated much higher temperatures to maintain phase purity, at 1400 ºC and produced a dense pellet.

I. INTRODUCTION

Although thermal expansion is the rule, a select subclass of materials exists that contracts under thermal stress – so called negative thermal expansion (NTE) materials. Many of these materials exhibit anisotropic negative thermal expansion – contraction in one or two dimensions with expansion in the third. This characteristic typically is limited to a narrow temperature range. Zirconium tungstate (ZrW_2O_8) is among the few known materials exhibiting isotropic negative thermal expansion over a broad temperature range, including room temperature where it crystallizes in the acentric cubic α-ZrW_2O_8 phase. (1) Isotropic NTE materials are important for technological applications requiring thermal-expansion compensators in composites designed to have overall zero or adjustable thermal expansion. Two characteristics of ZrW_2O_8 and $Zr_2WP_2O_{12}$ are important for this work – both can accommodate substitution, and secondly these materials contract upon amorphization. Metamictization of a radionuclide substituted ZrW_2O_8 or $Zr_2WP_2O_{12}$, therefore, would not cause damaging expansion and cracking. Fabrication of a wasteform with a shell of an NTE material such as ZrW_2O_8 or $Zr_2WP_2O_{12}$ and a core of radionuclide substituted material would potentially limit the radiation damage due to radionuclide release.

The phases of ZrW_2O_8 and $Zr_2WP_2O_{12}$ that display negative thermal expansion are stable to >950 K and to >1600 K respectively, with coefficients of thermal expansion of -8.8×10^{-6} K^{-1} and -6×10^{-6} K^{-1}.1, 2 In this work, we have adapted solution routes in a new fashion using a PTFE Teflon™ pouch to synthesize ZrW_2O_8 and its phosphorous analog $Zr_2WP_2O_{12}$. The characterized phase pure products were then sintered into pellets. A sintering protocol to maintain phase purity while achieving high densification was identified for both materials, with that for $Zr_2WP_2O_{12}$ employing 60MPa of pressure at 1400 ºC. Scanning Electron Microscopy, Powder X-ray diffraction, pycnometry, Raman spectroscopy and Fourier transform Infrared Spectroscopy were used to corroborate density, morphology and phase results.

II. EXPERIMENTAL

IIa. Synthesis of ZrW_2O_8

All reagents were used as received. The following synthesis was modified from that of Lind et al.(2) To avoid the use of a glove box, a PTFE Teflon ® pouch synthetic technique was used. Virgin Teflon sheeting, in a thickness of 0.5 mm, was cut in a rectangle (sized to fit in a parr vessel), folded and then heat sealed using a thermal impulse heat sealer to make a rectangular reaction pouch. Then, 1.35 g WCl_6 (Aldrich) and 5mL $CHCl_3$ (Aldrich) was added to the pouch before sealing the top while expelling as much air as possible. The closed pouch was placed in an ice bath. A second solution of 0.66 g Zirconium (IV) propoxide 70% in 1-propanol dissolved in 8 mL THF and 2 mL of diisopropyl ether was mixed separately. The zirconium solution then was loaded into a syringe and added slowly while stirring by inserting the needle through the top of the pouch. After the addition, the pouch is resealed. The whole solution was stirred at room temperature for 60 minutes during which the solution turned midnight blue. The pouch was then loaded into a Parr vessel and backfilled to 30% full with 1-propanol and heated to 110 ºC or 7 days.

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The dark blue powder intermediate was removed from the Parr vessel and Teflon pouch, washed with $CHCl_3$ and then centrifuged and decanted to recover the solids. The solids were then vacuum dried.

The final product of ZrW_2O_8 was obtained by firing at 500 ºC for 1 hour, then heating to 740 ºC for 40 minutes before quenching to room temperature. A Hafnium substituted analog was synthesized by replacing 50% of the zirconium (molar amount) with hafnium isopropoxide (Aldrich).

IIb. Synthesis of $Zr_2WP_2O_{12}$

All reagents were used as received. All reagents were tested via thermogravimetric analysis to determine actual molar amounts of Zr, P, and W respectively. The molar ratio Zr/P/W was held to 2/1/2 throughout the synthesis. (3)

0.9021 g Ammonium paratungstate $(NH_4)_{10}(H_2W_{12}O_{42})$*x$H_2O$ (Aldrich) was mixed with 30 mL DI H_2O. 1 g of Ammonium Phosphate monobasic (Aldrich), $NH_4H_2PO_4$, was mixed with 20 mL H_2O. These solutions were combined, covered, and stirred for a minimum of 60 min and up to 24 hours.

2.5271 g zirconyl oxychloride octahydrate (Aldrich) was mixed with 5mL DI H_2O and stirred until dissolved. This Zr solution was then slowly added dropwise to the phospho-tungsten solution while stirring. After an additional 90 minutes of stirring, the pH was measured using pH paper to be highly acidic, <1.

The solution was placed in a Teflon lined Parr vessel and placed in an oven at 130º C for 48 hours.

Upon removal from the Parr vessel, the fine white precipitate was filtered and washed with DI water. After drying in an oven at 80 ºC overnight, the precipitate was fired in a 900ºC furnace for 4 hours, removed, and allowed to cool to room temperature. The $Zr_2WP_2O_{12}$ phase was confirmed by XRD.

IIc. Sintering Experiments

Spark plasma sintering was performed at Thermal Technologies LLC in Santa Rosa, CA. Approximately 3 grams of either ZrW_2O_8 or $Zr_2WP_2O_{12}$ was loaded into a 1 cm diameter press lined with a graphite sheet. The press was placed in Thermal Technologies Direct Current Sintering furnace (DCS-25). The sample is resistively heated while pressure is applied. See Figures 1 and 2.

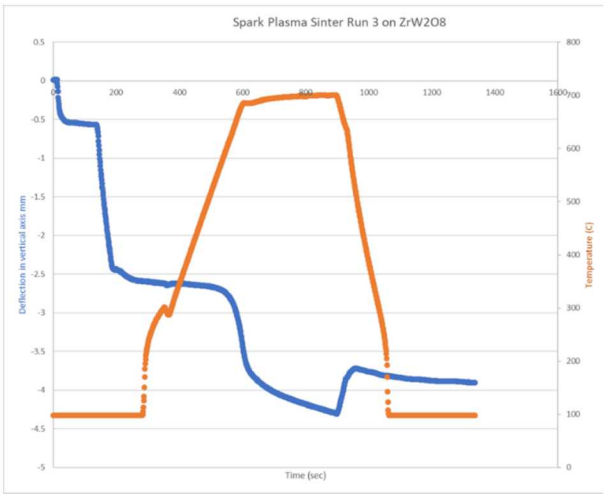

Fig. 1. Sintering procedure for ZrW_2O_8. Maximum applied temperature was 700 ºC (orange line), maximum pressure was 60 MPa, both held for 5 minutes. The blue line denotes the ram position.

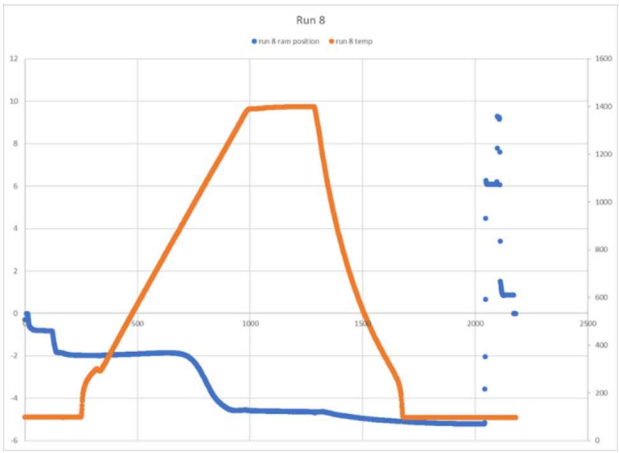

Fig. 2. Sintering procedure for $Zr_2WP_2O_{12}$. Maximum applied temperature was 1400 ºC (orange line), maximum pressure was 60 MPa, both held for 5 minutes. The blue line denotes the ram position.

III. RESULTS AND DISCUSSION

The use of a core-shell material as a wasteform requires complete encapsulation of the radionuclide rich core phase by a shell material that contains no radionuclide. To achieve this synthetically, we pursued the growth of crystalline ZrW_2O_8 on Hf-substituted ZrW_2O_8 seeds simply by adding 20 wt% or less of the seeds to the synthesis in the Teflon pouch. XRD confirmed the desired phase remained ZrW_2O_8 (the Hf analog is iso-structural). The sample was then potted with epoxy and polished to reveal a cross-section of the synthesized material. See Figures 3 and 4. While some growth was visible on the seeds, complete encapsulation was not achieved. Further,

the ZrW_2O_8 formed apart from the seeds was highly porous.

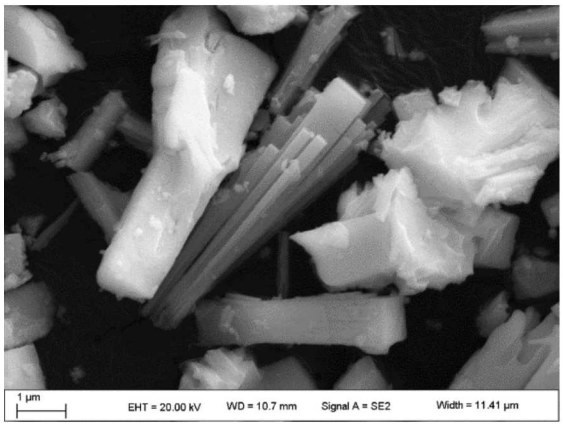

Figure 3. SEM of HF/ZrW_2O_8 seeds, approximately 1x1x5 µm in dimension.

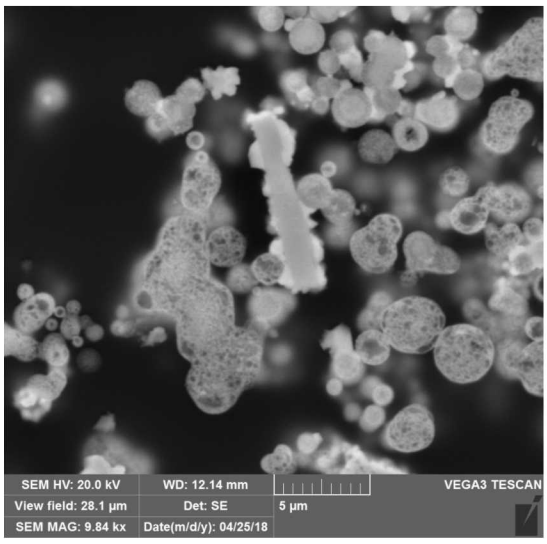

Figure 4. SEM of a potted and polished sample of ZrW_2O_8 growth on Hf/ZrW_2O_8 seeds. Note at the center of the image, a seed with some crystalline overgrowth.

While the metastable nature of ZrW_2O_8 precludes traditional sintering that requires long periods of high heat and pressure, spark plasma sintering or direct current sintering was attractive. In direct current sintering, a current is directed through the sample to provide resistive heating. The sample heats rapidly, reaching 1000 ºC in about 10 minutes, and cooling equally quickly. A ram applies a programmed force to the sample over the course of the experiment.

Using this scheme, several pellets were pressed over a range of temperatures, pressures, and time. See Table 1.

Sample	Temp. ºC	Pressure, MPa	Time, min	Maintained phase?
ZrW_2O_8	1150	30	5	No
ZrW_2O_8	850	30	5	No
ZrW_2O_8	700	60	5	Yes
ZrW_2O_8	600	60	10	No
ZrW_2O_8	650	60	15	Yes
$Zr_2WP_2O_{12}$	900	30	5	No
$Zr_2WP_2O_{12}$	1100	30	5	No
$Zr_2WP_2O_{12}$	1200	60	5	No
$Zr_2WP_2O_{12}$	1400	60	10	Yes

For ZrW_2O_8 to maintain its phase, a narrow temperature band between 650 ºC and 700 ºC is required, otherwise WO_3 and ZrO_2 begins to form. In figure 1, which depicts the ZrW_2O_8 run at 700 ºC, it is clear that the ram position (blue line) had not reached a steady state after 5 minutes at 700 ºC indicating that the sample was not completely dense. The SEM (Figure 5) confirms that the pellet contained numerous small void pockets. The lower temperature ZrW_2O_8 samples (600 ºC and 650 ºC) that were held for longer periods of time also did not achieve a stable ram position and were not completely dense. Of note in the SEM, however, the particles have sintered together indicating that with additional trials, a dense pellet with good integrity could be achieved.

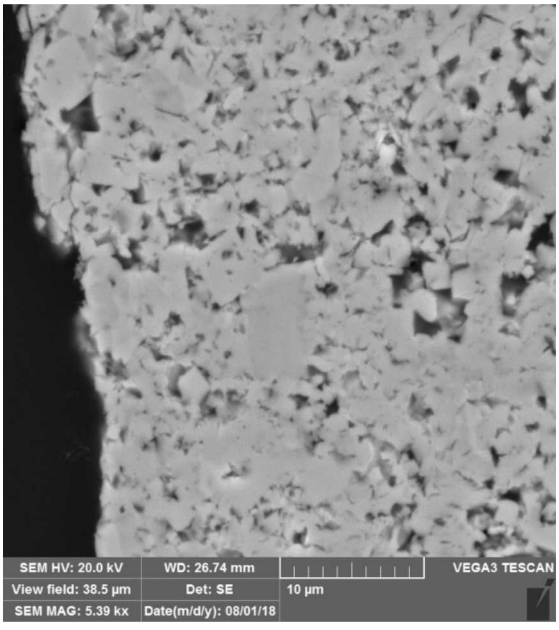

Figure 5. A potted and polished sintered sample of ZrW_2O_8 showing incomplete densification.

For $Zr_2WP_2O_{12}$, the highest temperature run pellet, 1400 ºC, showed a stable ram position at the end of 10 minutes. See Figure 2, blue line. The small decline in the ram position during the cooling phase is a result of the die contraction, and not further sample compression, as in this experiment, the die was not released until after cooling was complete. Excursions in the ram positions near the end of the experiment are a result of the die release.
The SEM of this pellet does not show visible void pockets, rather showing a uniform surface. See Figure 6.

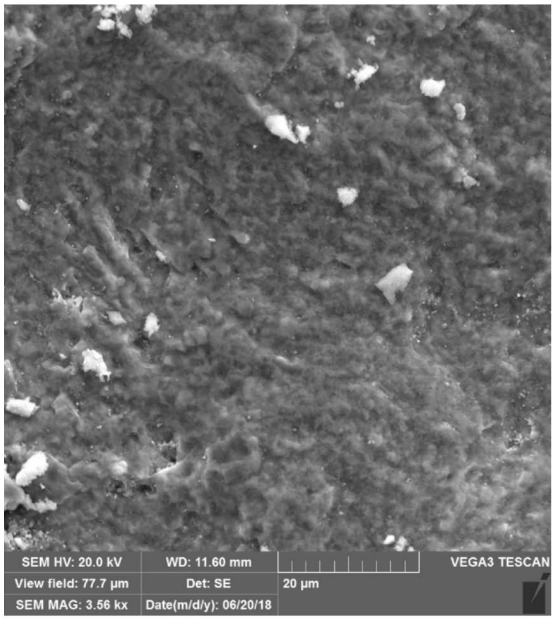

Figure 6. An SEM of a $Zr_2WP_2O_{12}$ sample sintered at 1400 ºC.

IV. CONCLUSIONS

The ability to form a core-shell material from a negative thermal expansion material was investigated through solution synthesis and direct current sintering. In order for this strategy to produce a viable wasteform, it must create a completely encapsulated core.

In the solution synthesis routes of ZrW_2O_8, incomplete coverage of the core "seeds" was observed. The presence of highly porous secondary formations occurring alongside the partially covered seeds prevented performing sequential syntheses to encase the seeds. Further avenues to eliminate the secondary porous formations and increase core encapsulation are being explored.

The creation of larger core-shell pellets was also investigated. Controlling the temperature during direct current sintering of both ZrW_2O_8 and $Zr_2WP_2O_{12}$ samples successfully created pieces that maintained their original phases. The $Zr_2WP_2O_{12}$ pellet appeared dense, while the ZrW_2O_8 pellet shows significant void spaces. From these results, we plan to create a sintered core-shell pellet of these NTE materials through strategic sample loading into the direct current sintering pellet press. Parallel efforts in modeling and leaching experiments will assist in validating this strategy in a wasteform.

ACKNOWLEDGMENTS

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REFERENCES

1. T. A. Mary, J. SO. Evans, T. Vogt, A.W. Sleight, "Negative Thermal Expansion from 0.3 to 1050 Kelvin in ZrW2O8." *Science,* **272**, *5258*, 90 (1996).
2. C. Lind, A. Wilknison, P. Pattanaik, "A new Polymorph of ZrW2O8 prepared using Nonhydrolyitc sol gel chemistry" Journal of Sol-Gel Science and Technology, **55**, *1*, 111 (2010)
3. Isobe, T, Umezome, T, Kameshima, Y, Nakajima, A & Okada, K, "Preparation and properties of negative thermal expansion Zr2WP2O12 ceramics" *Materials Research Bulletin*, **44**, *11*, 2045-2049 (2009)