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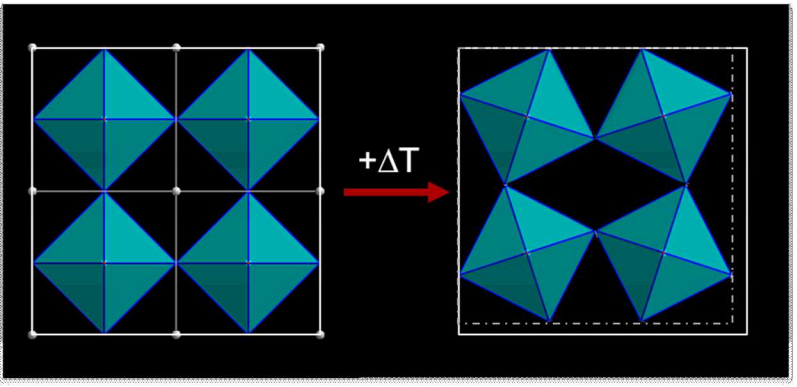

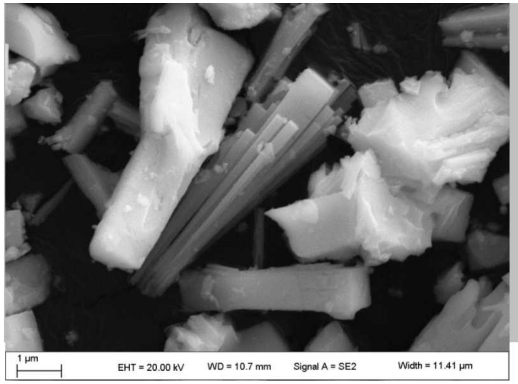

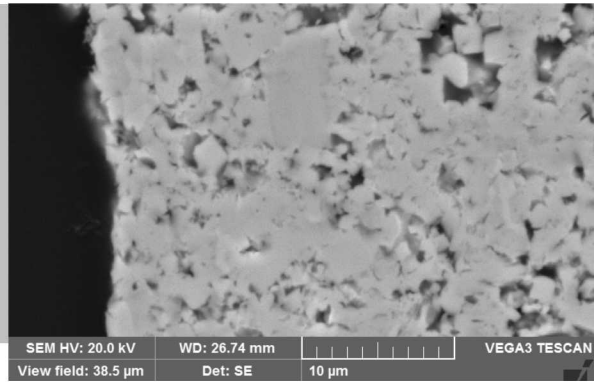

Synthesis and processing of meta-stable negative thermal expansion materials ZrW_2O_8 and $Zr_2WP_2O_{12}$ as a wasteform

Margaret E. Gordon, Charles R. Bryan, Jeffery A. Greathouse, Philippe F. Weck, Eunja Kim, Clay Payne

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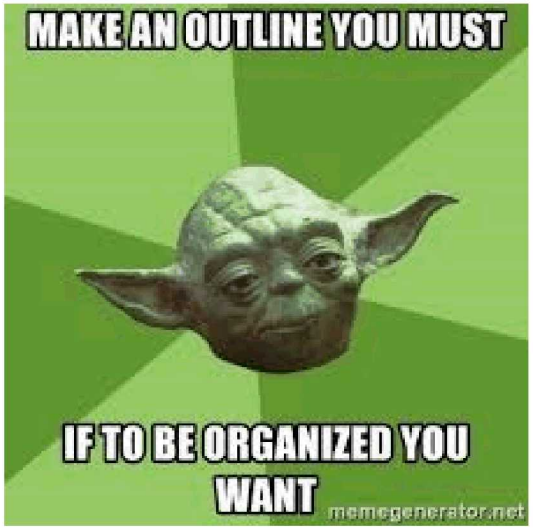
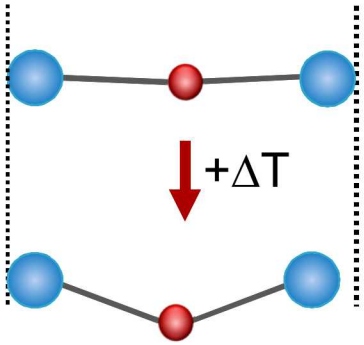
Outline

- Materials with Negative Thermal Expansion – how does that work?
- ZrW_2O_8
- Synthetic approaches, let me count the ways…
- Sintering of ZrW_2O_8 and $Zr_2W_2PO_{12}$



Structural Mechanism of NTE

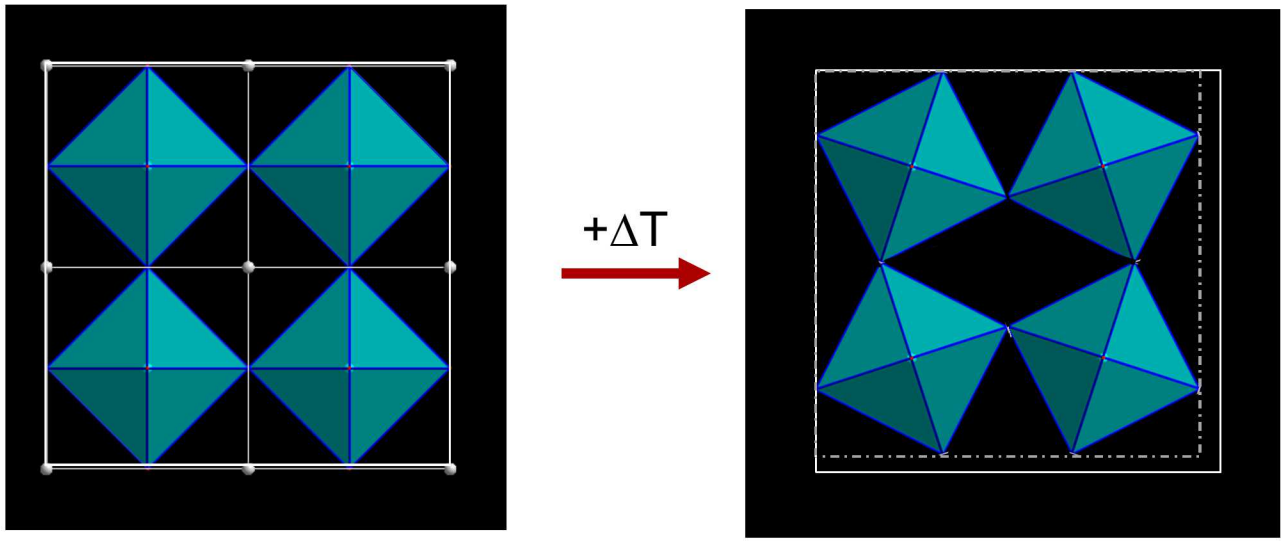


ZrW_2O_8 belongs to a class of materials including ZrV_2O_7, $Sc_2W_3O_{12}$ that display NTE

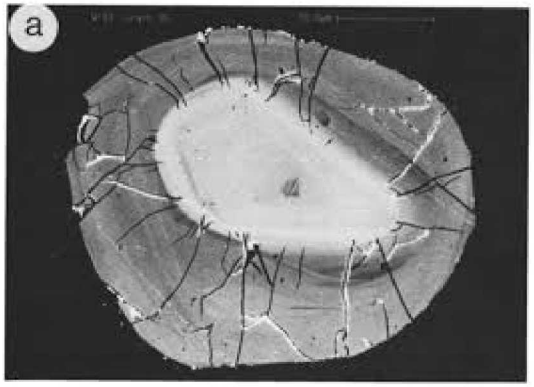
- Nearly linear M – O – M linkages
- Open framework
- Heat causes transverse vibrations in corner sharing polyhedra

Notional Polyhedra
2D area = 4.41 in^2

Tilted 15°
Area = 4.01 in^2, reduced ~9.1%

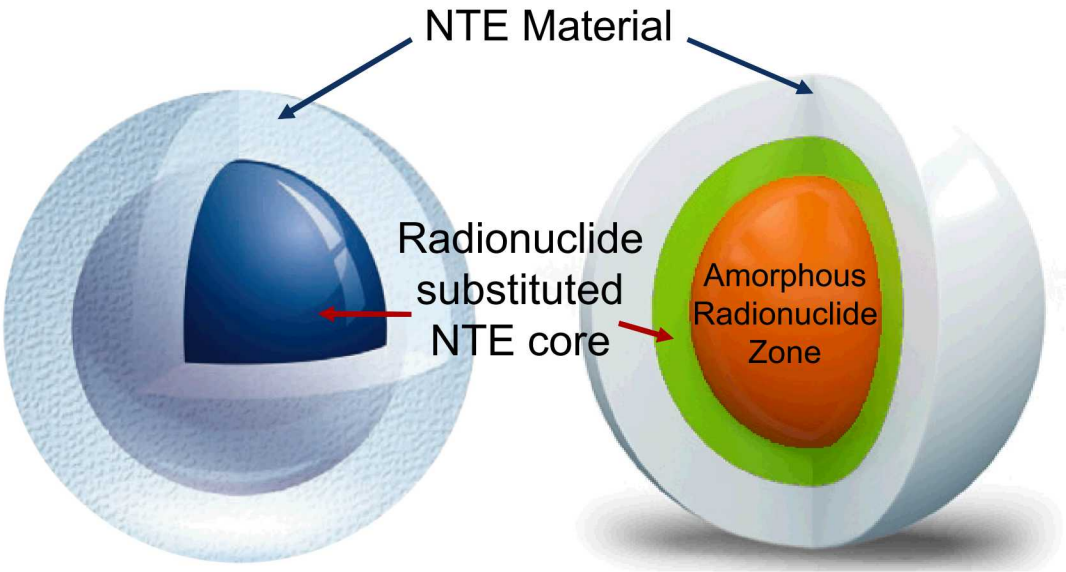


An NTE material as a wasteform?

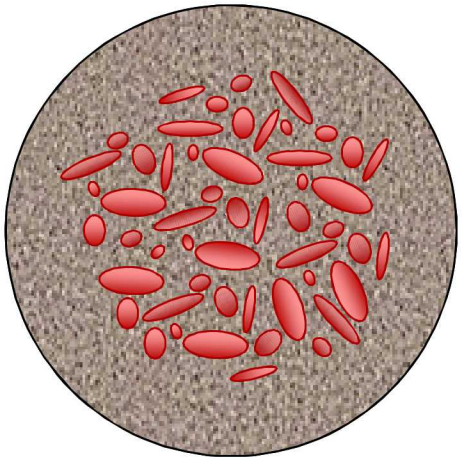


Zircon,
undergoing
metamictization

Lee, J. K. W., and Tromp, J. (1995), Self-induced fracture generation in zircon, *J. Geophys. Res.*, 100(B9), 17753– 17770, doi:10.1029/95JB01682.

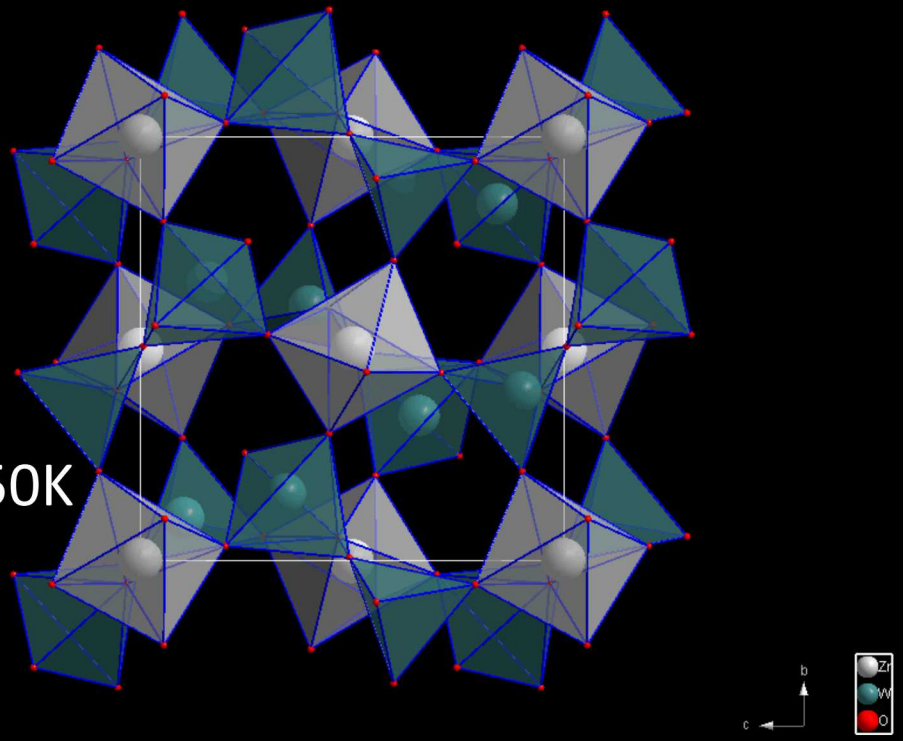


Agglomerate
Matrix = NTE material,
Inclusions = radionuclide substituted NTE material



ZrW_2O_8 Structure & Properties

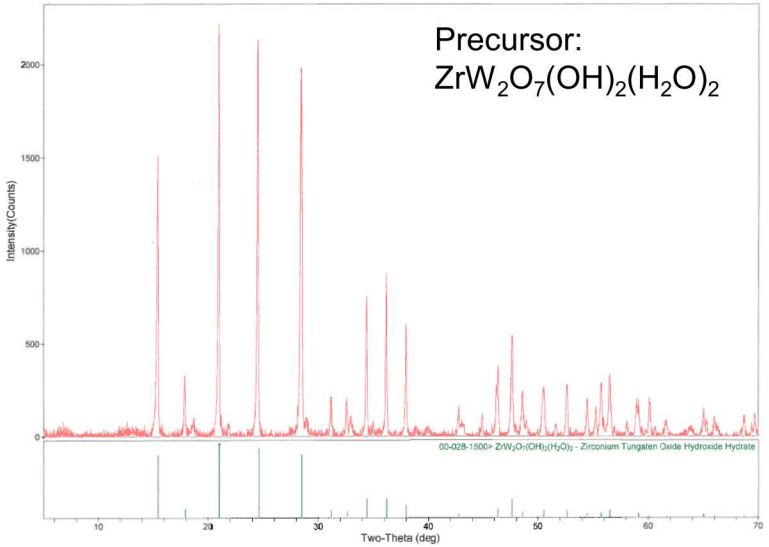
- WO_4 tetrahedra, 3 corner-shared O
- ZrO_6 octahedra, 6 corner-shared O
- Metastable cubic phase (α) displays NTE from 0.3 K to 1050K
- Negative Coefficient of TE (0-430K) = $-8.8 \times 10^{-6}\ K^{-1}$, (430-1050K) = $-4.9 \times 10^{-6}\ K^{-1}$
- B-phase (cubic, NTE), Trigonal phase and high pressure γ–phase display positive thermal expansion



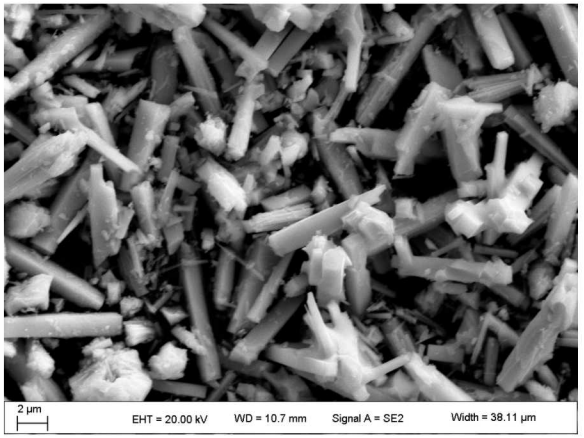
Co-precipitation Synthetic Route

Co-precipitation method of Closmann et al. (J. S. S. Chem. Vol 139, 1998, 424-426):

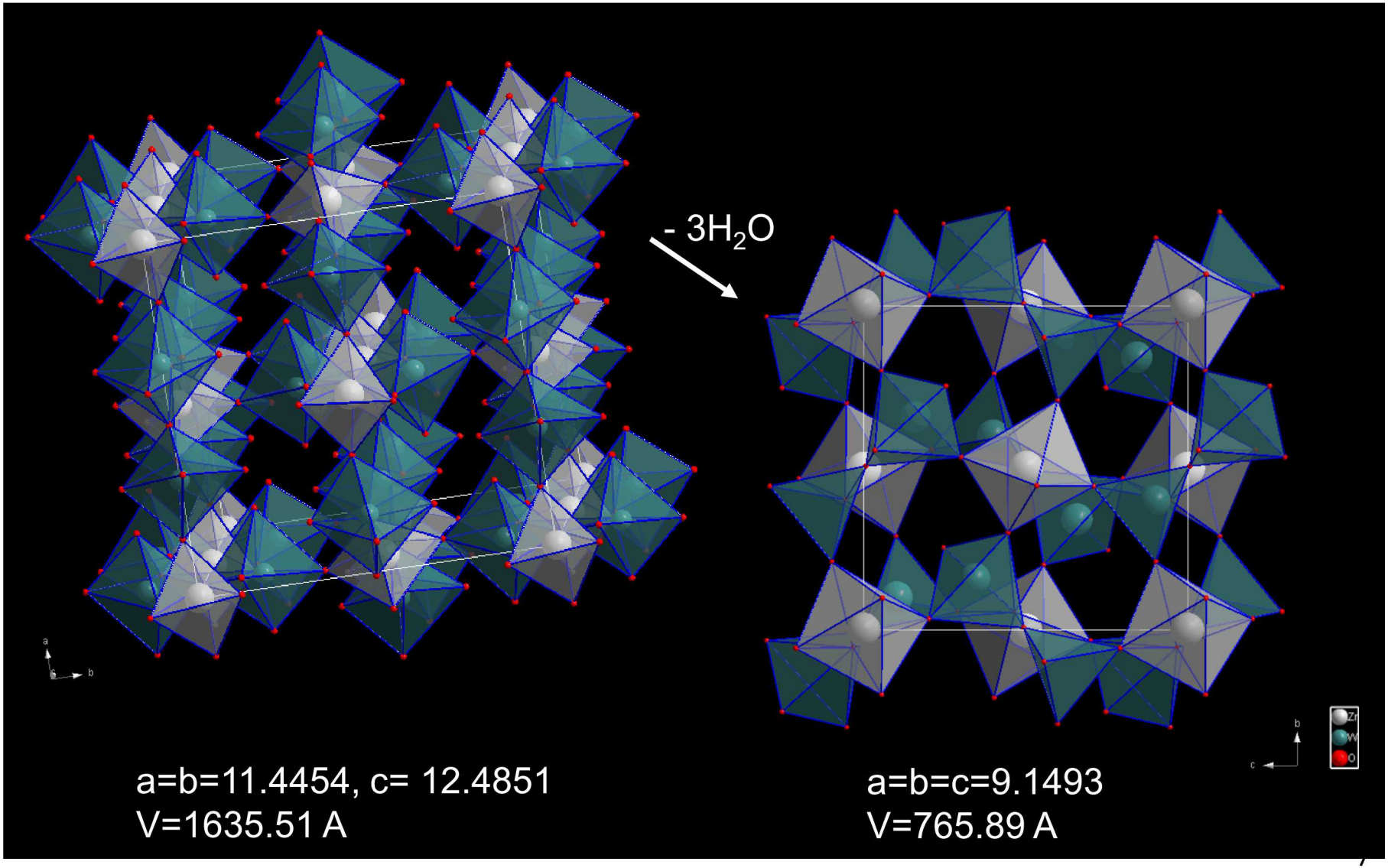
- Simultaneous addition of 50mL 1M ammonium metatungstate and 50 mL 0.5 M zirconium oxychloride to a stirred flask of 25 mL DI H_2O
- Acidify, heat to 130-200 deg C in Parr bomb up to 7 days.
- Resulting precipitate is zirconium tungstate hydroxide hydrate, $ZrW_2O_7(OH)_2(H_2O)_2$



SEM images of precursor $ZrW_2O_7(OH)_2(H_2O)_2$

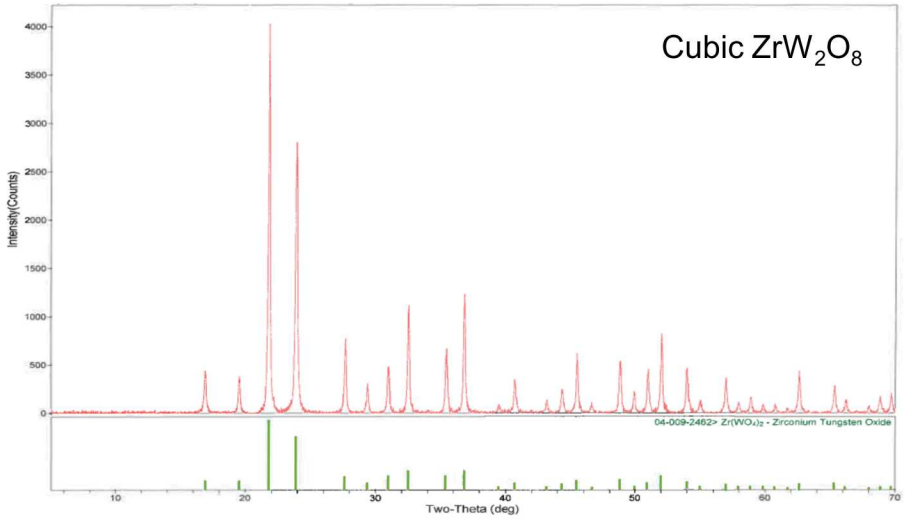


$ZrW_2O_7(OH)_2(H_2O)_2$ to ZrW_2O_8

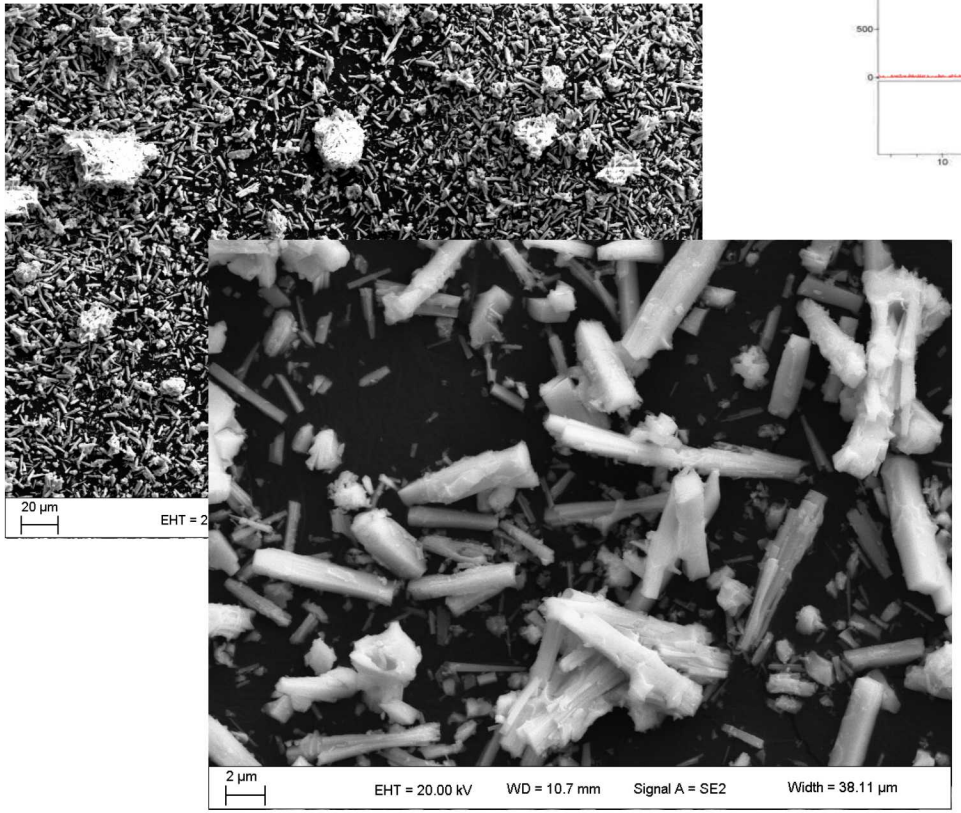


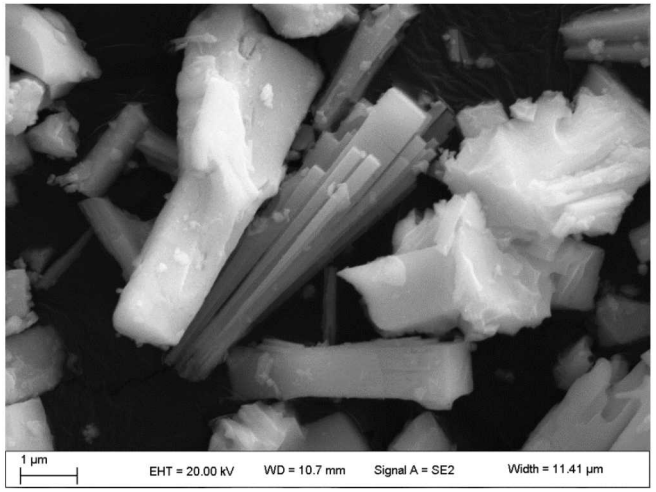
Morphology of resulting ZrW_2O_8

- Heat precursor to 600 deg C for up to 10 hours to convert to cubic ZrW_2O_8.
- ZrW_2O_8 maintains needle morphology of precursor, with defects



SEM images of cubic ZrW_2O_8





Seeded HfW_2O_8/ZrW_2O_8 Syntheses

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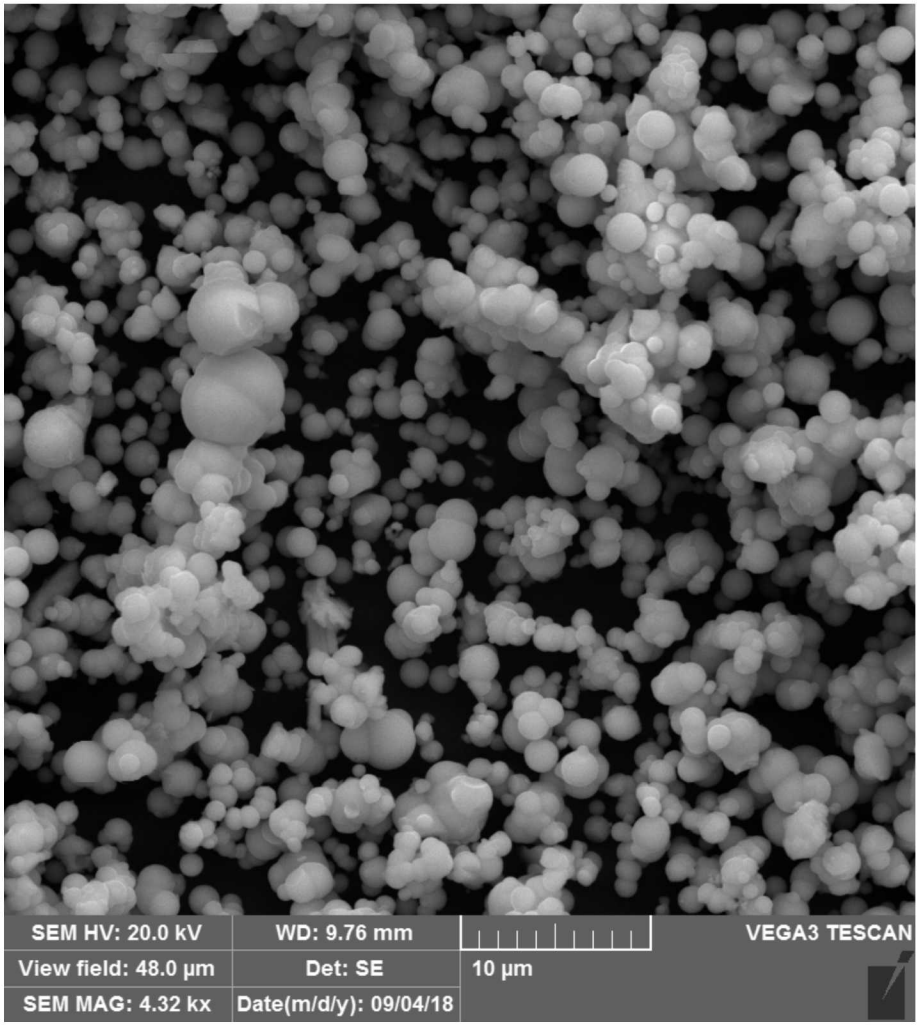
- Seeded growth studied by Lind and Wilkinson, 2002* and others to increase yield and decrease temperature of final heat treatment from >1000 deg C to 500-700 deg C.
- Acidity of co-precipitation method incompatible
  - Dissolution of seeds at low pH
  - Reduced acidity allows impurities to form
- Non-hydrolytic Sol Gel method: modified Teflon pouch approach
  - Add zirconium isopropoxide, WCl_6, $CHCl_3$, and THF to a PTFE pouch and place in a Parr vessel with alcohol or THF backfill. Heat to 100-130 deg C for up to 7 days. Filter to obtain precursor.
  - Heat to 500 deg C for 1 hr, and 740 deg C for 40 min.

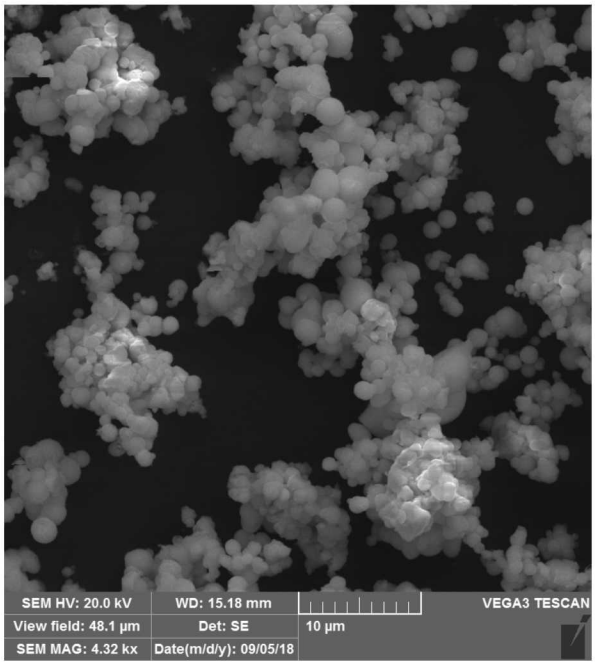
*Lind, C. & Wilkinson, A.P. Journal of Sol-Gel Science and Technology (2002) 25: 51.

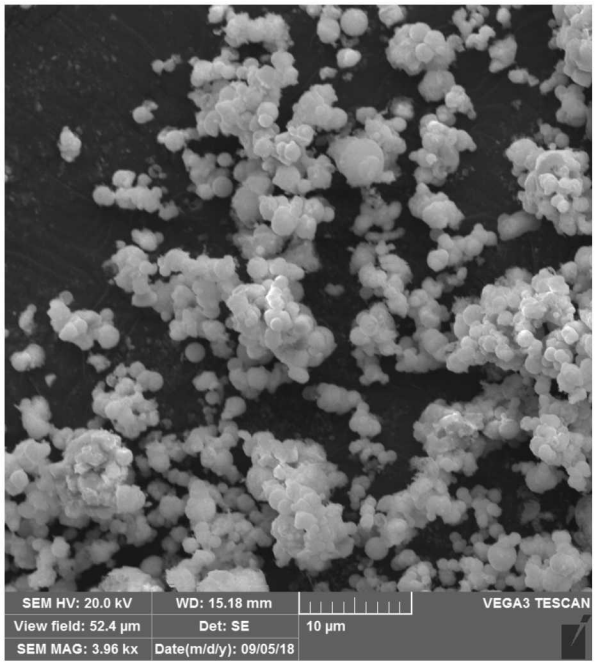
Seeded Precursor

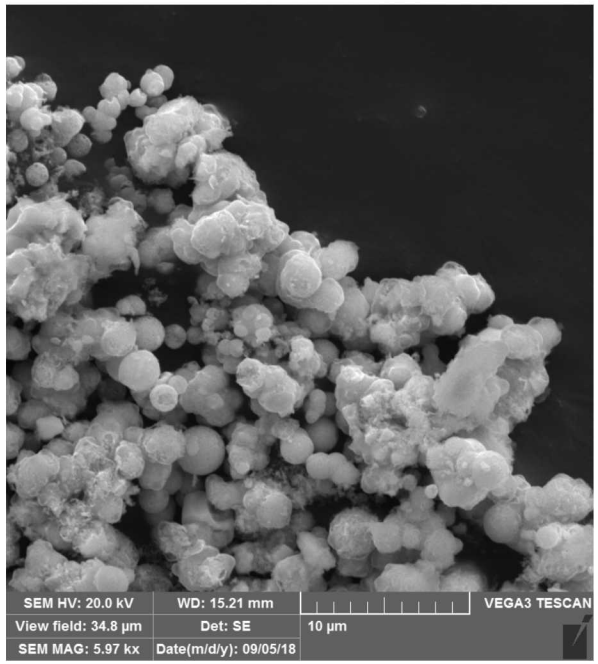


- Precursor was washed with $CHCl_3$ and dried at RT
- XRD confirms presence of crystalline HfW_2O_8 seeds in an amorphous matrix
- Amorphous spheroids range in size from 0.8 to 5 microns

Firing of Seeded Precursor





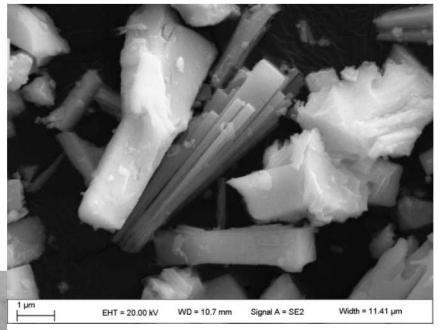


- 30 min 60 min 2 hr
- XRD shows increasing crystalline WO_3 forming after 60 min, and SEM shows coarsening of precursor spheroids

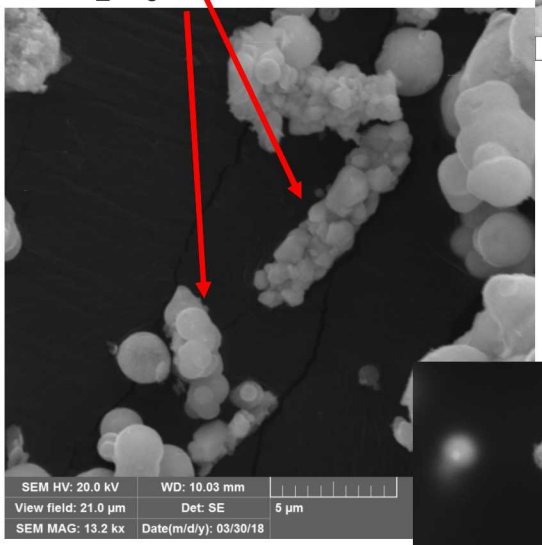
A Look inside…

- Multi-crystalline growth of ZrW_2O_8 on HfW_2O_8 seeds
- All facets of the seeds appear to generate growth
  - Seeds are not fully encased in new crystalline growth
- Decreased size of seeds (increase surface area/gram and surface energy of crystallites) improves yield of ZrW_2O_8,
- Sonication of seeds prior to incorporation improves separation. Likely this prolongs the suspension of seeds in the precursor solution.
- Precursor spheroids not in contact with a seed result in very porous ZrW_2O_8.

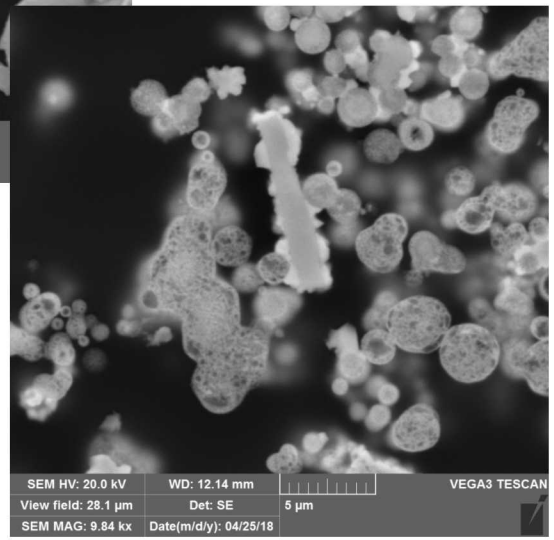
Hf/ZrW_2O_8 Seeds



Growth of ZrW_2O_8 on Seeds



Potted and polished sample showing growth of ZrW_2O_8 on seeds



*Closmann et al. (J. S. S. Chem. Vol 139, 1998, 424-426)

Sintering ZrW_2O_8

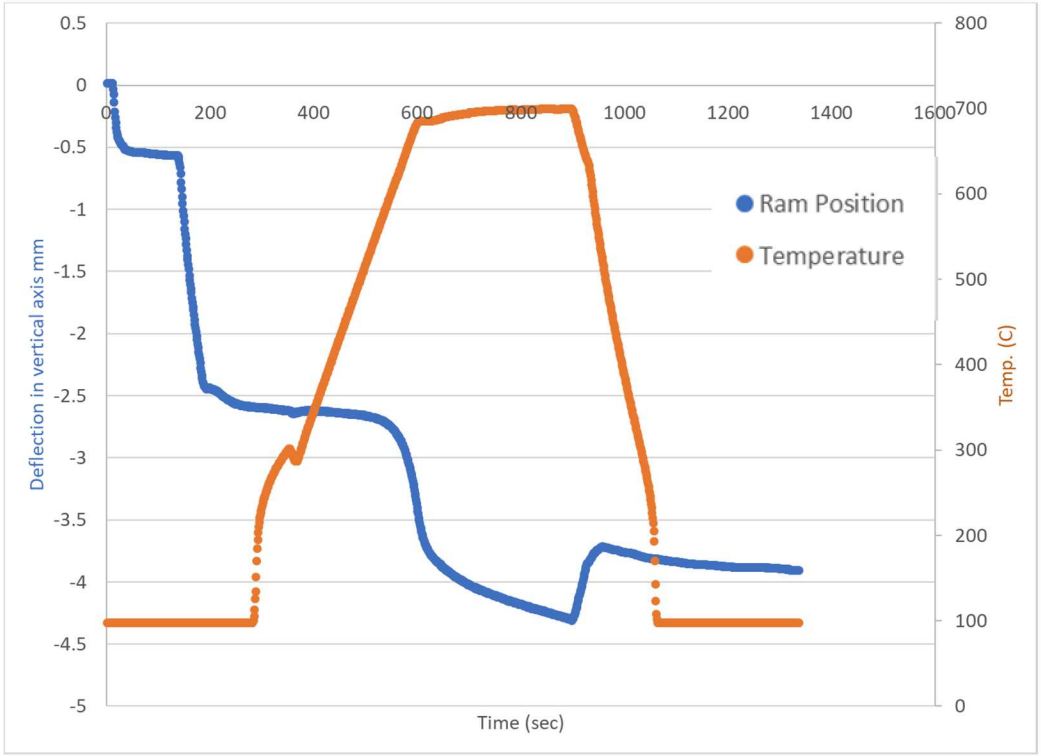
- Metastable nature precludes traditional sintering
- Must apply heat and pressure quickly and precisely to avoid decomposition – Spark Plasma sintering
  - Within a uniaxial press in a vacuum, a current is passed through the sample causing resistive heating
  - Tests carried out at Thermal Technologies, LLC in CA

Sintering of ZrW_2O_8

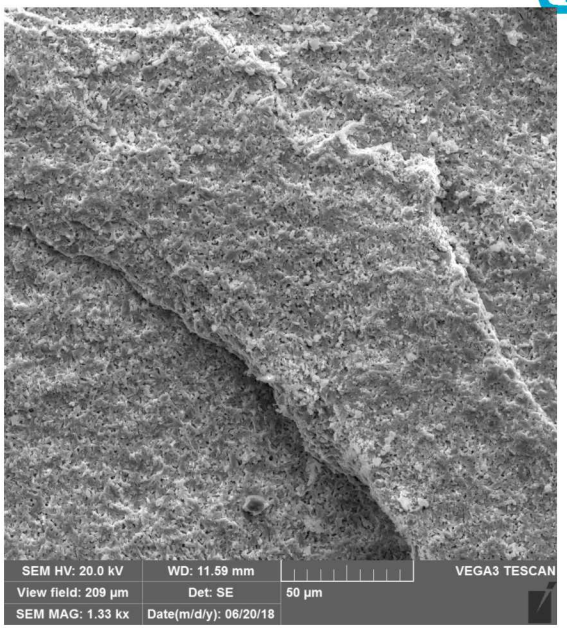
Run	Sample	Temp, C	Pressure	Time	XRD Phase
1	ZrW2O8 (CPI-31A)	1150	30MPa	5 min	WOx, ZrO
2	ZrW2O8 (CPI-31A)	850	30MPa	5	WO3, ZrO
3	ZrW2O8 (CPI-31A)	700	60MPa	5	ZrW2O8
4	Zr2P2WO12 (MG7-61A)	900	30MPa	5	-no xrd
5	Zr2P2WO12 (MG7-61A)	1100	30MPa	5	-no xrd
6	Zr2P2WO12 (MG7-63A)	1200	60MPa	5	Mix of oxides
7	ZrW2O8 (CPI-31A)	600	60MPa	10	orthorhombic
8	Zr2P2WO12 (MG7-63A)	1400	60MPa	10	Zr2P2WO12
9	ZrW2O8 (CPI-31A)	650	60MPa	15	cubic

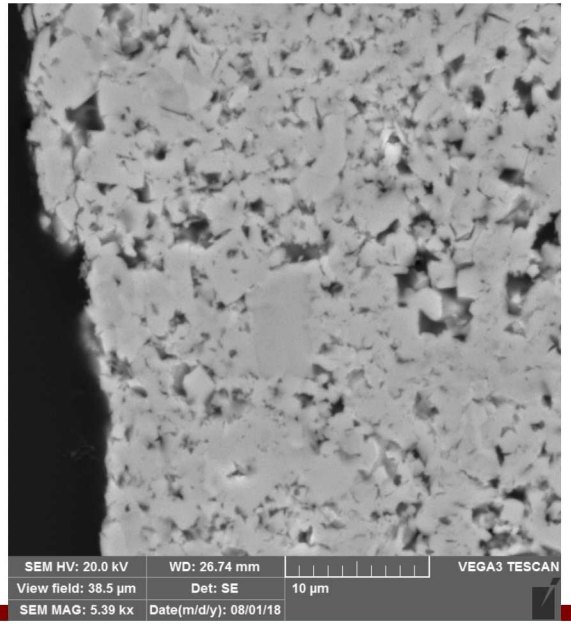
Sintered ZrW_2O_8

Spark Plasma Sintering run

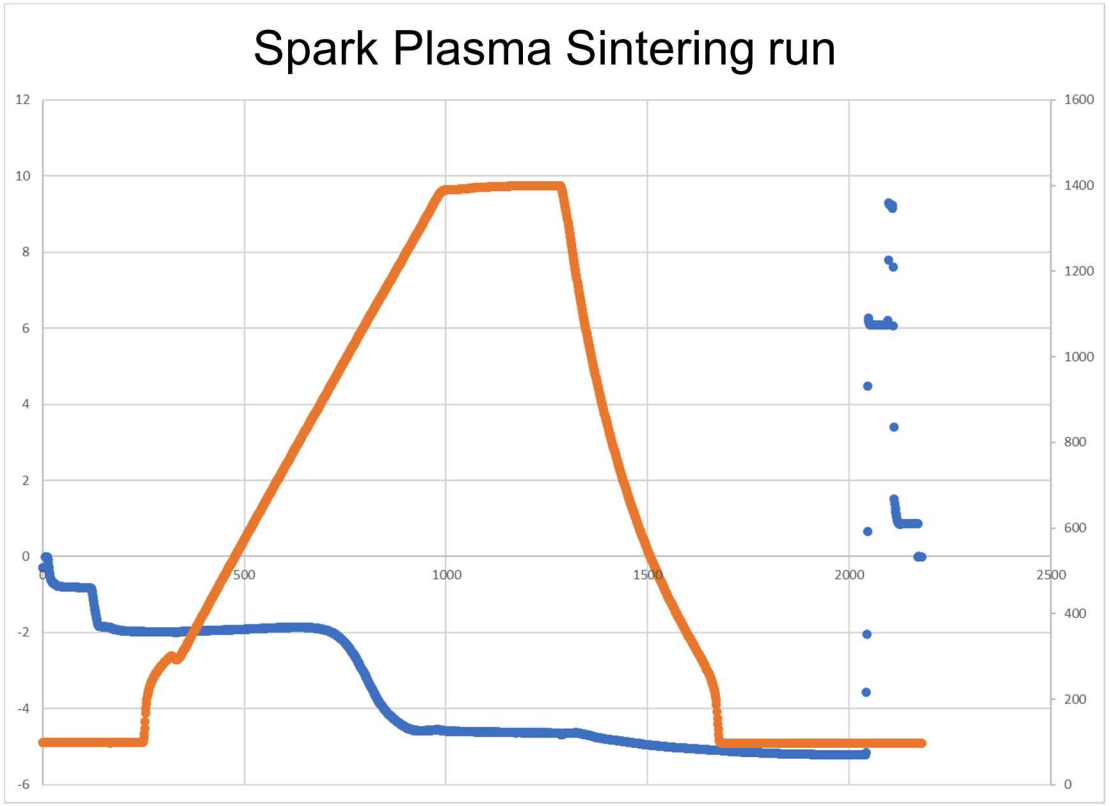


Blue line denotes ram position with time,
Orange line denotes temperature.

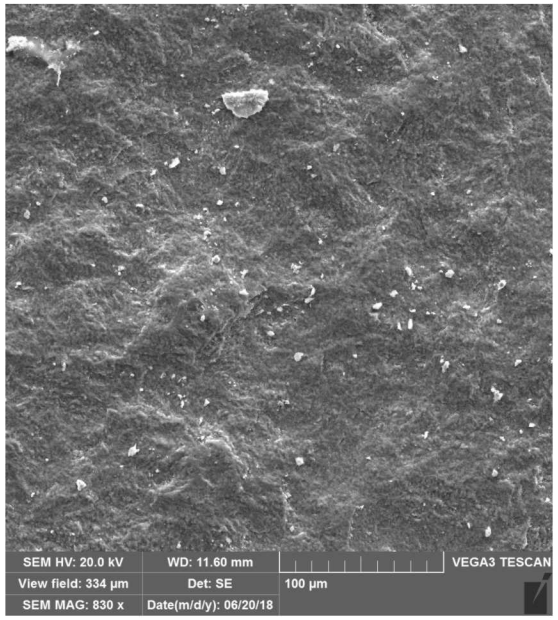


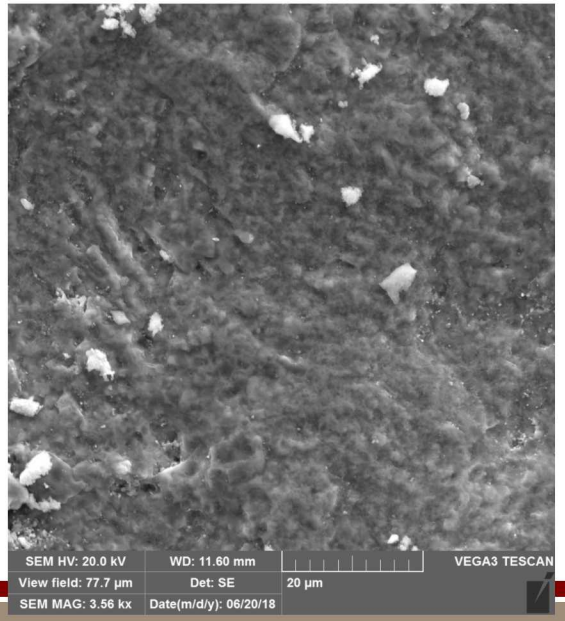


Sintered $Zr_2W_2PO_{12}$



Blue line denotes ram position with time,
Orange line denotes temperature.





Conclusions

- HfW_2O_8 can be used to seed growth of ZrW_2O_8.
  - Seeding the acidic co-precipitation method did not yield phase pure product when the acidity was reduced preserve the seeds.
  - Seeding the non-hydrolytic sol method was successful, but does not yield completely encased seeds. However, crystallite growth on the seeds is dense rather than porous.
  - The final thermal treatment has a narrow window in both time and temperature to avoid impurity formations.
- Sintering of ZrW_2O_8 using the Spark Plasma method can maintain the cubic phase and create a dense piece.
  - Continued work to obtain a more fully densified piece is underway.
  - A related NTE material, $Zr_2W_2PO_{12}$ can also be sintered successfully.
- Thank you!