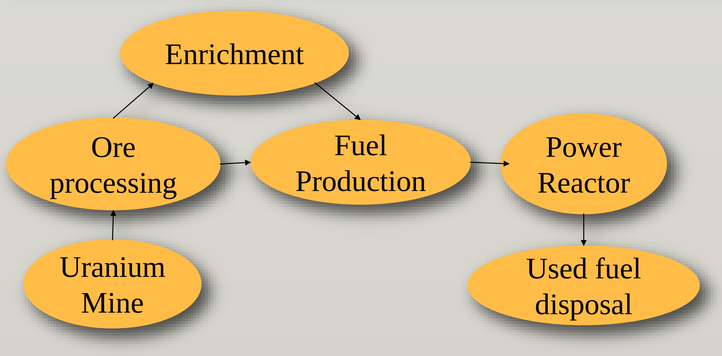
Solid state synthesis of $Nd_2Zr_2O_7$ and study of its thermal properties using in-situ X-ray diffraction

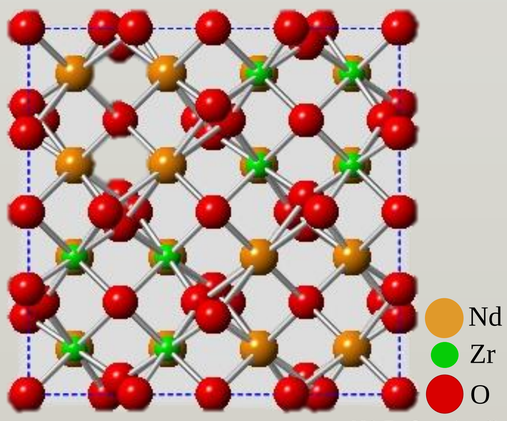
Kalie Knecht[1], Caitlin Taylor[2], William Weber[2,3], and Maulik Patel[2]

1. Nuclear Engineering, University of Tennessee, Knoxville, TN 37996, USA.
2. Materials Science & Engineering, University of Tennessee, Knoxville, TN 37996, USA.
3. Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

Pyrochlores ($A_2B_2O_7$) have been researched extensively for their potential as candidate materials for the immobilization of actinides. Zirconate pyrochlores such as $Nd_2Zr_2O_7$, where Nd acts as a surrogate for actinides like Am, are promising because they remain crystalline, even at very high doses of damage accumulation, while undergoing an order-disorder transformation. During the first several hundred years a waste form will primarily experience an elevated temperature state due to β-decay processes. Understanding dynamical thermal effects on structural modifications is therefore of fundamental importance. The present work details the synthesis of $Nd_2Zr_2O_7$ pyrochlore, results of X-ray diffraction (XRD) under ambient conditions, and an in-situ *high temperature x-ray diffraction (HTXRD) experiment to study thermal expansion coefficient in $Nd_2Zr_2O_7$.*



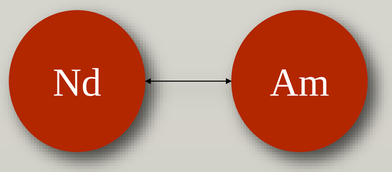
In the United States, the nuclear fuel cycle is open ended. This means that at the end of the fuel cycle, there is waste to be disposed of (1).

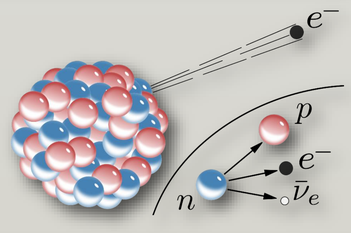


$Nd_2Zr_2O_7$ unit cell

Zirconate pyrochlores ($A_2Zr_2O_7$) make a good waste form because they remain crystalline even at very high doses of damage accumulation (2).

Actinides of a similar size as the A-site cation in zirconate pyrochlores will take their place in the crystalline lattice. Actinides such as Am will take the place of Nd in $Nd_2Zr_2O_7$ due to similarities in radii.

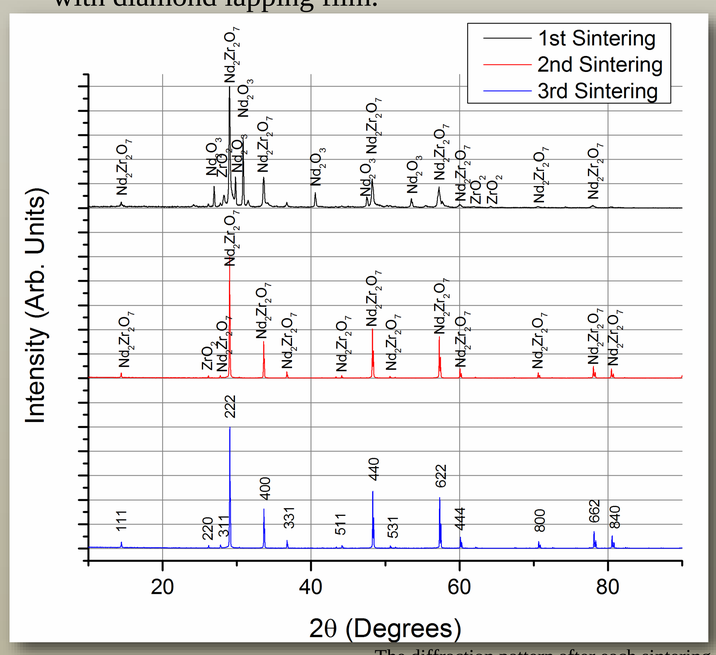




In the first several hundred years, the nuclear waste form will experience an elevation in temperature due to β-decay processes. Because of this, it is important to understand the thermal properties of nuclear waste form candidates.

Synthesis of $Nd_2Zr_2O_7$

1. Nd_2O_3 and ZrO_2 powders were calcined at 800°C to ensure proper stoichiometry due to the hygroscopic nature of Nd_2O_3.
2. Stoichiometric amounts of Nd_2O_3 and ZrO_2 were wet mixed for 8 hours.
3. The mixed powder was pressed into 13 mm diameter pellets.
4. The pellets were sintered for 48 hours at 1200 °C
5. The pellets were wet mixed for 18 hours. The mixed powder was pressed into 13 mm diameter pellets. The pellets were sintered for 72 hours at 1400 °C.
6. The pellets were wet mixed a final time for 18 hours. The mixed powder was pressed into 13 mm diameter pellets. The pellets were sintered for 196 hours at 1500°C.
7. The pellets were cut into 1.5 mm thick pellets with a diamond saw and polished with diamond lapping film.

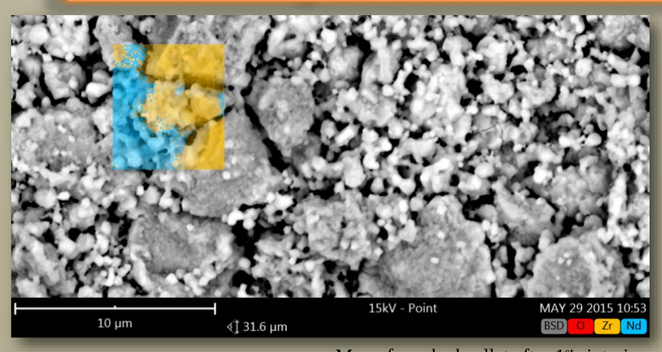


The diffraction pattern after each sintering

The diffraction pattern of the sample was recorded after each sintering to monitor the formation of $Nd_2Zr_2O_7$.

A polished final sample

Scanning Electron Microscopy (SEM)



Map of cracked pellet after 1st sintering

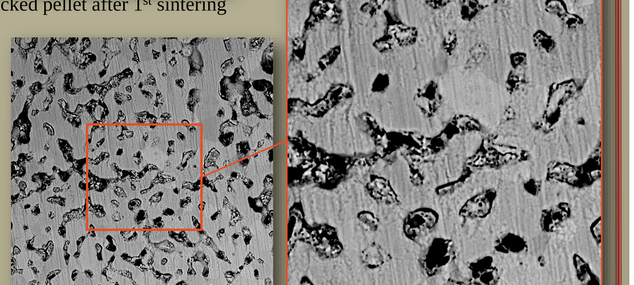
Scanning electron microscopy (SEM) was used to observe a cracked pellet after first the first sintering. The Phenom Pro-suite Element Identification program was used to map the sample.

The density of the final sample was measured using Archimedes method.

Measured density = **5.01(6) g/cm³**

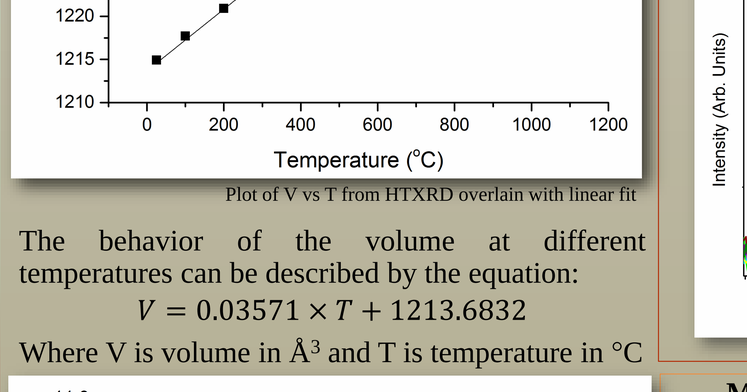
Theoretical density = **6.45 g/cm³**

77.8% theoretical density was achieved in synthesis.



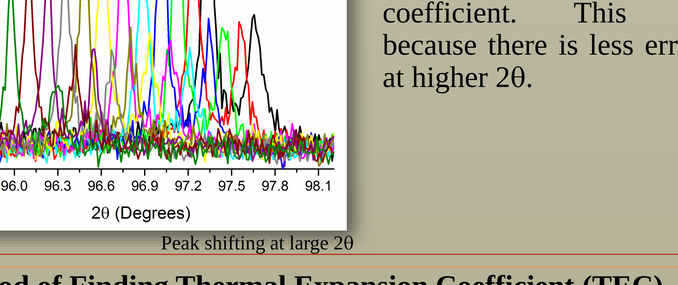
SEM image of pellet after high temperature experiment

HTXRD of Nd_2Zr_2O7 to find its thermal expansion coefficient



Panalytical Empyeran XRD machine with Anton Paar high temperature stage

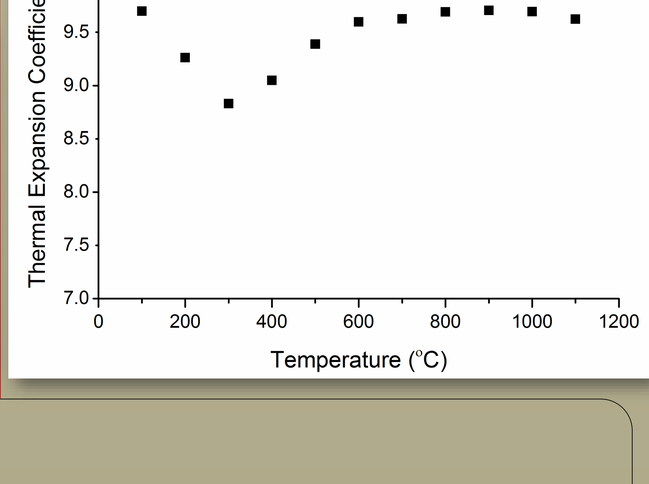
Between each scan, the temperature was raised 100°C and given 10 minutes to equilibrate. There was a short scan at lower 2θ and a long scan at higher 2θ.



Temperature Profile of HTXRD Experiment

HTXRD was conducted using an Panalytical Empyrean with an Anton Paar High Temperature stage that can reach temperatures of up to 1200 °C.

All of the diffraction data was fit using cmpr (3).

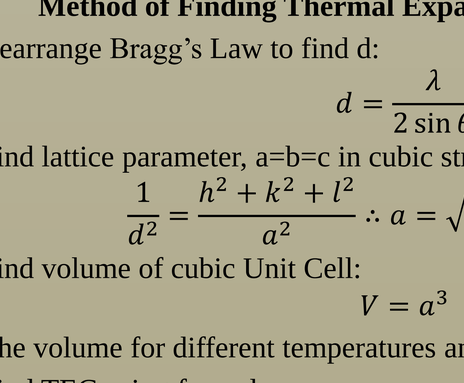


Plot of V vs T from HTXRD overlain with linear fit

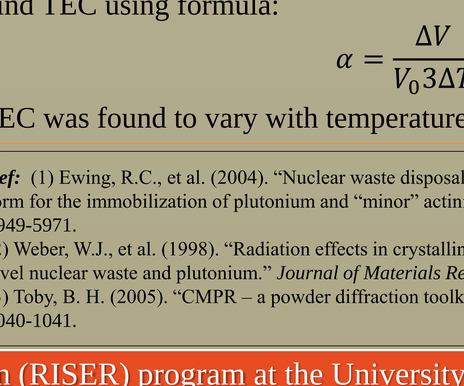
The behavior of the volume at different temperatures can be described by the equation:

$$V = 0.03571 \times T + 1213.6832$$

Where V is volume in Å³ and T is temperature in °C



Peak shifting at small 2θ



Peak shifting at large 2θ

If the diffraction patterns for different temperatures were plotted together, the peaks shift left at higher temperatures. This is a qualitative indicator of expansion. The shifting of the peaks is more evident at higher 2θ.

The higher 2θ peaks were used for finding volume and thermal expansion coefficient. This is because there is less error at higher 2θ.

Method of Finding Thermal Expansion Coefficient (TEC)

Rearrange Bragg's Law to find d:

$$d = \frac{\lambda}{2\sin\theta}$$

Find lattice parameter, a=b=c in cubic structure:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \therefore a = \sqrt{d^2(h^2+k^2+l^2)}$$

Find volume of cubic Unit Cell:

$$V = a^3$$

The volume for different temperatures an be found above.

Find TEC using formula:

$$\alpha = \frac{\Delta V}{V_0 3\Delta T}$$

TEC was found to vary with temperature (see figure to the left).

Conclusions:

- The thermal expansion coefficient of $Nd_2Zr_2O_7$ varies with temperature
- Since actinides undergo α-decay in waste forms, the samples will be implanted with He, an α-decay product, and the lattice expansion due to He as a function of temperature will be studied.

Ref: (1) Ewing, R.C., et al. (2004). "Nuclear waste disposal – pyrochlore, A2B2O7…: Nuclear waste form for the immobilization of plutonium and "minor" actinides." *Journal of Applied Physics*. **95**(1): 5949-5971.
(2) Weber, W.J., et al. (1998). "Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium." *Journal of Materials Research*. **13**(6): 1434-1484.
(3) Toby, B. H. (2005). "CMPR – a powder diffraction toolkit," *Journal of Applied Crystallography* **38**. 1040-1041.

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