Synthesis and Characterization of Doped CeO_2 as a Surrogate Nuclear Fuel

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I. Background

Motivation for Research

- Nuclear energy continues to provide safe, productive energy, but can be improved.
- During the fission process, gasses are released into the fuel-cladding gap, lowering the thermal conductivity of the gap which leads to the reduction in efficiency and reliability of the fuel. [1]
- Increase in fuel grain size leads to an increase in the retention of fission gases.
- This study analyzes the impact of MnO_2 and TiO_2 additives on the grain size and microstructure of CeO_2 as a surrogate nuclear fuel for UO_2.

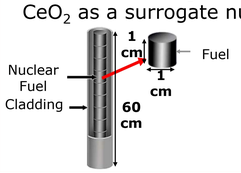

Figure 1. *Schematic representation of a nuclear fuel and cladding of typical dimensions. [2]*

Surrogate Nuclear Fuels

- CeO_2 can be used as a surrogate fuel for UO_2 due to similar thermodynamic properties and crystal structure (Figure 2). [3]
- Handling and processing highly radioactive materials produce many challenges.
- Surrogate fuels can resolve some of these challenges by:
  - Increasing experimental timeliness
  - Reducing cost
  - Reducing radioactive exposure

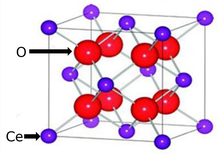

Figure 2. *CeO_2 and UO_2 have the same fluorite crystal structure. [4]*

II. Experimental

Materials Synthesis

- As-received CeO_2 was doped with MnO_2, and TiO_2 powders to obtain desired dopant concentrations.
- Each powder mixture was planetary ball milled at 250 rpm for 6 hours and high energy planetary ball milled (HEPBM) at 500 rpm for 1 hour to reduce the particle size and incorporate the dopants into the CeO_2 lattice.
- HEPBM powders were mixed with 0.45 wt% ethylene bis-stearamide (EBS) binder to improve pellet integrity prior to powders being pressed into pellets.
- Green pellets were pressed using a dual action die set at 150 MPa to obtain maximum theoretical density (TD).
- TiO_2-doped CeO_2 samples were sintered at 1600°C, while sintering temperatures ranged from 1200°C to 1550°C for MnO_2-doped CeO_2 samples.
- Samples were polished to 0.5 µm and thermally etched approximately 150°C below sintering temperature for characterization techniques.

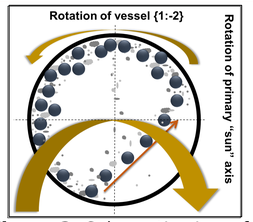

Figure 3. *Schematic view of planetary ball mill motion.*

Characterization Techniques

- X-Ray diffraction (XRD), with a lanthanum hexaboride (LaB_6) standard, was used for phase purity and dopant incorporation analysis.
- Optical microscopy and scanning electron microscopy (SEM) was used for pellet grain size and microstructure analysis.
- Energy dispersive spectroscopy (EDS) was used for a qualitative chemical analysis.
- Inductively coupled plasma mass spectroscopy (ICP-MS) was used for a quantitative chemical analysis.

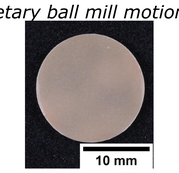

Figure 4. *Sintered TiO_2-doped CeO_2 pellet.*

III. Results

XRD Analysis of Doped Cerium Dioxide

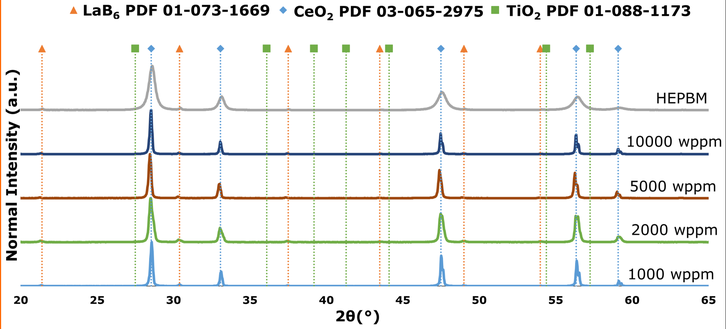

Figure 5. *XRD of HEPBM and sintered TiO_2-doped CeO_2 indicates CeO_2 phase is maintained with no secondary TiO_2 peaks present. All HEPBM TiO_2-doped CeO_2 powders produced equivalent patterns and are combined on this plot.*

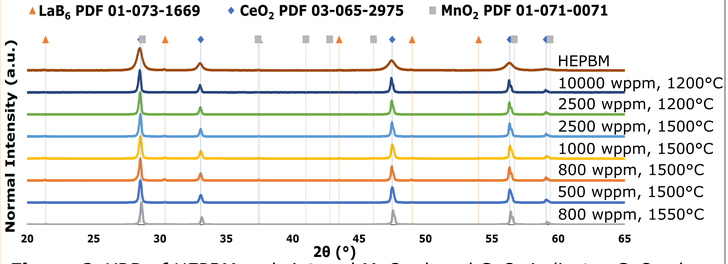

Figure 6. *XRD of HEPBM and sintered MnO_2-doped CeO_2 indicates CeO_2 phase is maintained with no secondary MnO_2 peaks present. All HEPBM MnO_2-doped CeO_2 powders produced equivalent patterns and are combined on this plot. MnO_2 dopant concentrations and sintering temperatures are labeled accordingly.*

Grain Size Analysis of Sintered Pellets

- Top surface and cross sections for each sample variant were imaged using an optical microscope and SEM, and the images were used to perform grain size analysis using ASTM E112-12. [5]
- Combining the top surface and cross section data results in a range of the average grain size for TiO_2-doped and MnO_2-doped CeO_2 (Figure 7).

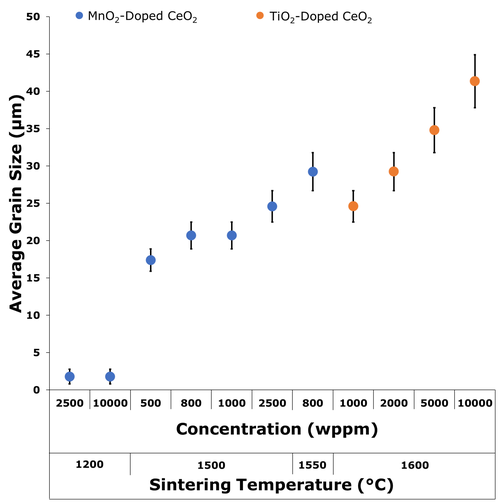

Figure 7. *Average grain size range of MnO_2-doped and TiO_2-doped CeO_2.*

Microstructural Analysis

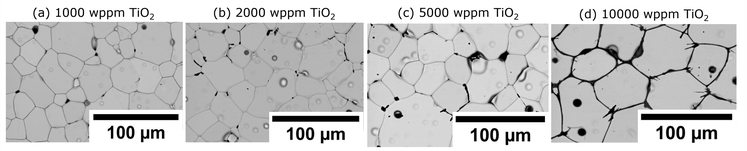

Figure 8. *SEM images of TiO_2-doped CeO_2 samples show grain size, porosity and uniformity of samples. As dopant concentration is increased, sample grain size and porosity increase, reducing the density.*

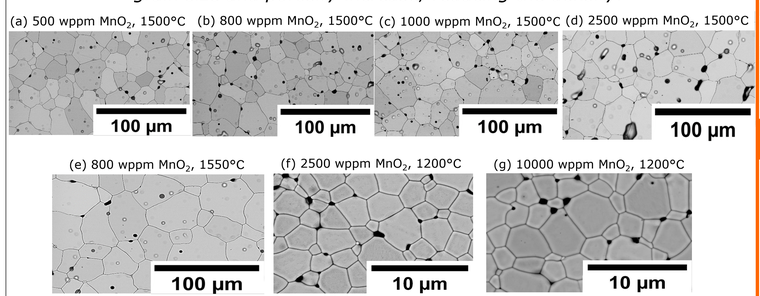

Figure 9. *SEM images of MnO_2-doped CeO_2 samples show grain size, porosity and uniformity of samples. Sintering temperature is labeled for each sample. Samples sintered at 1500°C increased in porosity with dopant concentration (a-d).*

Qualitative Chemical Analysis

- EDS performed on each sample variant is qualitative due to instrument detection limits (approximately 1 wt%).
- Trace amounts of Si were detected on samples and is likely due to the crucible used during sintering and thermal etching processes.
- EDS identified Ti^+ in TiO_2-doped samples of concentrations ≥ 2000 wppm, while no Mn^+ was detected in MnO_2-doped samples.

Quantitative Chemical Analysis

Table 1. *Using Archimedes density for calculations, density values assume a single phase and stoichiometric CeO_2 with a reference density of 7.128 g/cm³. ICP-MS provides concentrations of HEPBM and sintered powders. [6]*

Sample Identification	Sintering Temperature (°C)	Percent of Theoretical Density (%)	Target Cation Concentration (wppm)	Actual HEPBM Cation Concentration (wppm)	Actual Sintered Cation Concentration (wppm)
		TiO_2			
1000 wppm	1600	93 ± 0.5	600	364 ± 13%	334 ± 13%
2000 wppm		95 ± 0.5	1199	711 ± 13%	729 ± 13%
5000 wppm		93 ± 0.5	2998	1835 ± 13%	640 ± 13%
10000 wppm		90 ± 0.5	5995	3537 ± 13%	1043 ± 13%
		MnO_2			
2500 wppm	1200	96 ± 0.5	1580	1516 ± 14%	1355 ± 14%
10000 wppm		96 ± 0.5	6319	5441 ± 14%	5038 ± 14%
500 wppm	1500	97 ± 0.5	316	295 ± 14%	124 ± 14%
800 wppm		96 ± 0.5	506	447 ± 14%	179 ± 14%
1000 wppm		95 ± 0.5	632	241 ± 14%	203 ± 14%
2500 wppm		90 ± 0.5	1580	1516 ± 14%	311 ± 14%
800 wppm	1550	94 ± 0.5	506	447 ± 14%	171 ± 14%

IV. Discussion

- MnO_2-doped samples: 800 wppm MnO_2 samples sintered at 1550°C resulted in the largest grain size with a uniform microstructure and a %TD ≥ 94 ± 0.5 (Figure 9.e).
- TiO_2-doped samples: Increasing TiO_2 dopant concentration resulted in an increased grain size with decreasing %TD (Table 1), likely due to exceeding the solubility limit of TiO_2 in CeO_2 (Figure 8.d).
- For HEPBM powders, ICP-MS data indicates an average 40% and ≤ 15% error in target doping concentrations for TiO_2 and MnO_2 dopant concentrations, respectively.
- The doping process will be further refined.
- Further analysis will be performed on the samples to confirm the Si contaminant source and its impact.

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References

[1] J. Rest, et al., Fission gas release from UO_2 nuclear fuel: A review, *J. Nucl. Mater.* 513 (2019) 310–345.
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[5] ASTM Standard, E112-12: Standard Test Methods for Determining Average Grain Size, ASTM Int. E112-12 (2013) 1–27. https://doi.org/10.1520/E0112-12.1.4
[6] J.T. Dunwoody, and A.T. Nelson, "Cerium Dioxide Pellet Fabrication and Characterization," Los Alamos National Laboratory, (2017).

Acknowledgements

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