Understanding thermal stability in doped zirconia aerogels for high temperature applications

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Structure and Properties of Porous Ceramics
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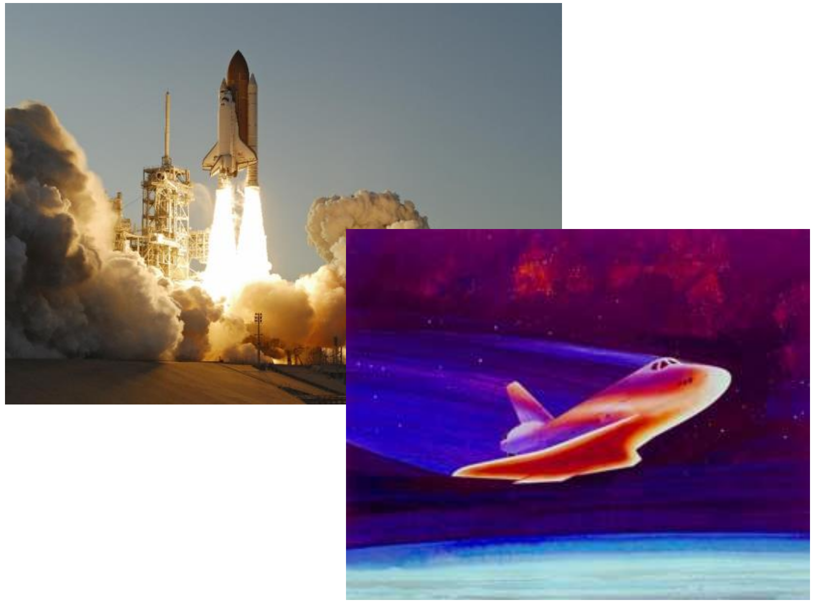
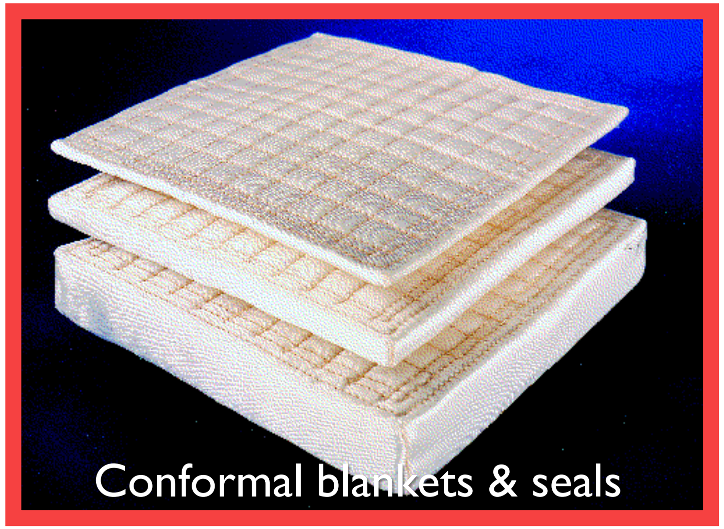
Developing lightweight, high-performance aerospace thermal protection systems (TPS)



TPS Needs:
Manage heat loads
Withstand mechanical loads
Lightweight
Reusable when possible


Advanced composites


Reusable ceramic tiles & coatings

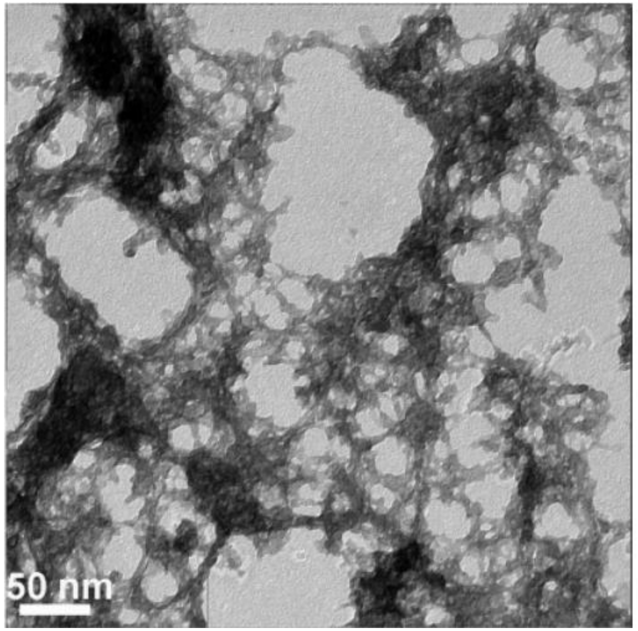

Conformal blankets & seals

Our Aims:
Reduce thermal conductivity
to improve performance.

Reduce mass/volume
to lower costs.

All images courtesy of NASA.

Aerogels are highly insulating and lightweight materials



High SSA: 200 to 1000 m^2/g

High Porosity: 90 to 99.9%

Low Density: 0.2 to 0.05 g/cm^3

Low thermal conductivity:
0.009 W/(m•K) in atmosphere
and 0.003 W/(m•K) under vacuum

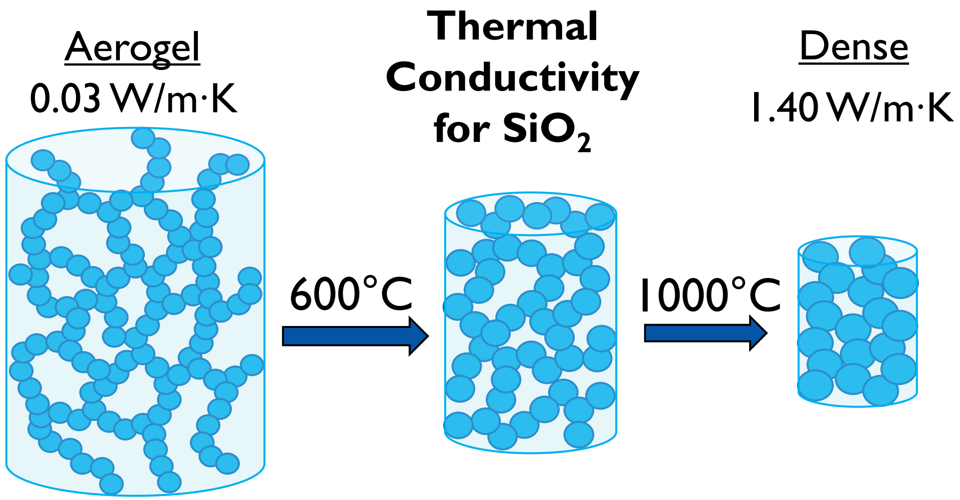
Highly porous structure of aerogel is responsible for its extremely low thermal conductivity.

Low density = Low solid conductivity

Pore sizes ≤ mean free path of gas
= Low gas convection

Cohen, E., and Glicksman, L. (2015). *Journal of Heat Transfer*,137(8), 81601.
Sun, H., et al. (2013). *Advanced Materials*, 25(18), 2554-2560.

Collapse of pore structure and loss of favorable properties occurs upon thermal exposure



Loss of SSA, porosity

↑ thermal conductivity, cracking, and shrinkage

Large SSA & porosity contribute to driving force for densification

Rapid densification & loss of porosity beyond…

- 500°C Polymeric
- 700°C Silica
- 750°C Undoped Zirconia
- 1000°C Alumina
- 1100°C Aluminosilicate

Develop aerogel to maintain **porosity** at high temperatures (≥**1200°C**) for use as insulation in next-gen aerospace applications

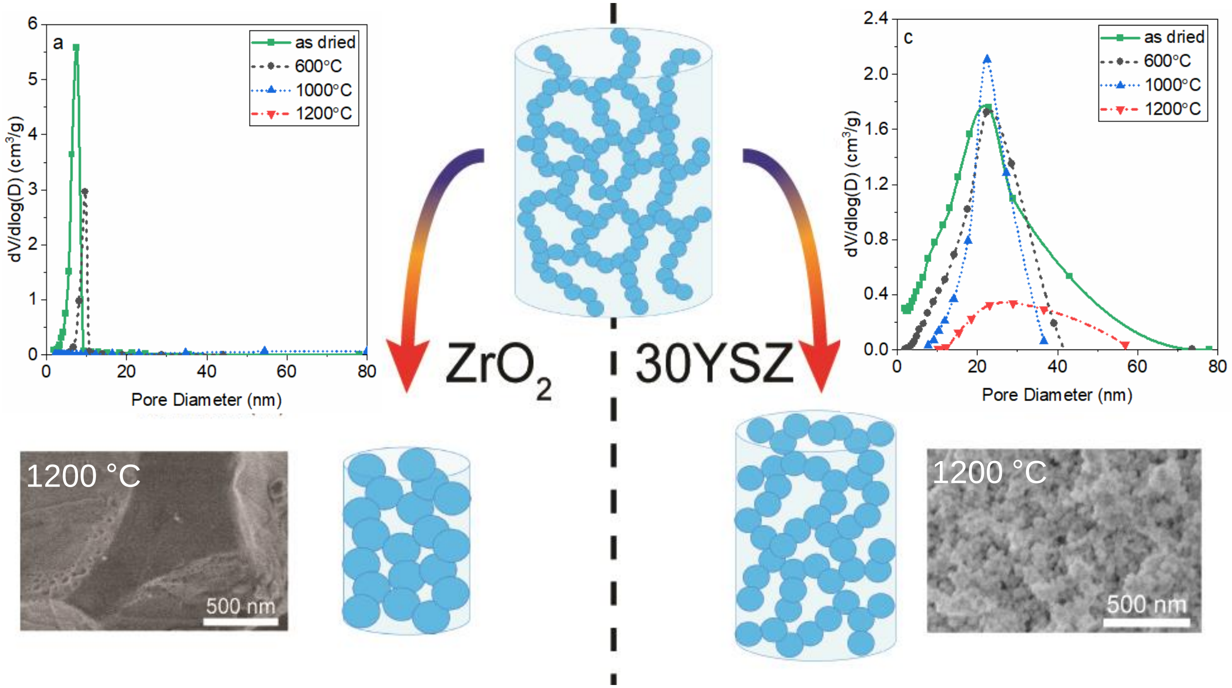
Powell, R.W., et al. (1966). NSRDS-NBS 8, 99.
Lide, D. R., ed; "Thermal conductivity", CRC Handbook of Chemistry and Physics (100th ed.).

Aegerter, M. (ed), (2011). *Aerogels Handbook*, Springer.

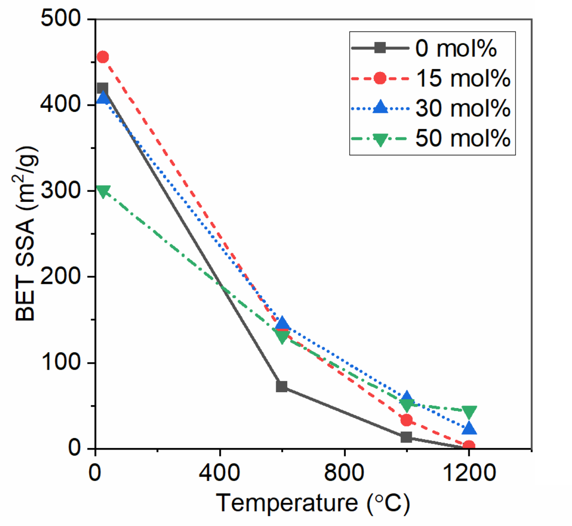
High yttria concentration improves thermal stability in yttria-stabilized zirconia (YSZ) aerogels

Mesoporosity eliminated at 1000 °C

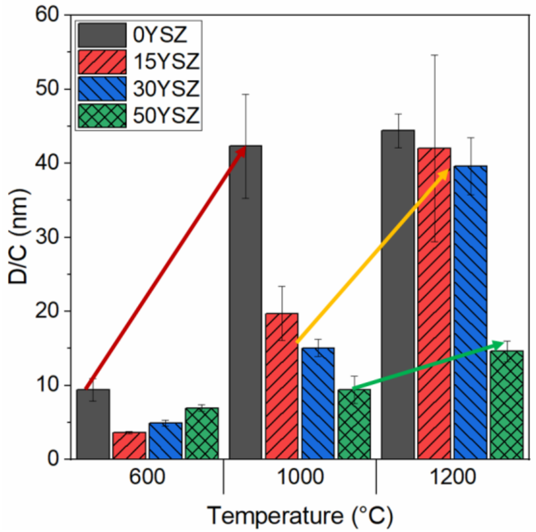
Mesoporosity remains to 1200 °C



Increases BET SSA at high temperatures



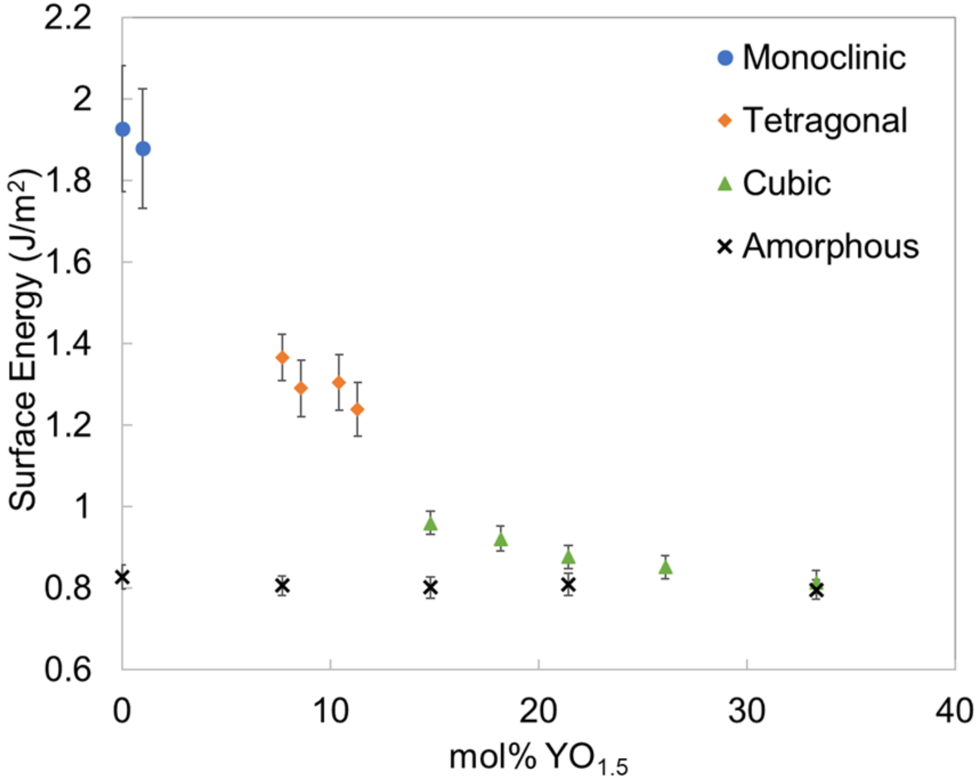
Inhibits crystallite growth

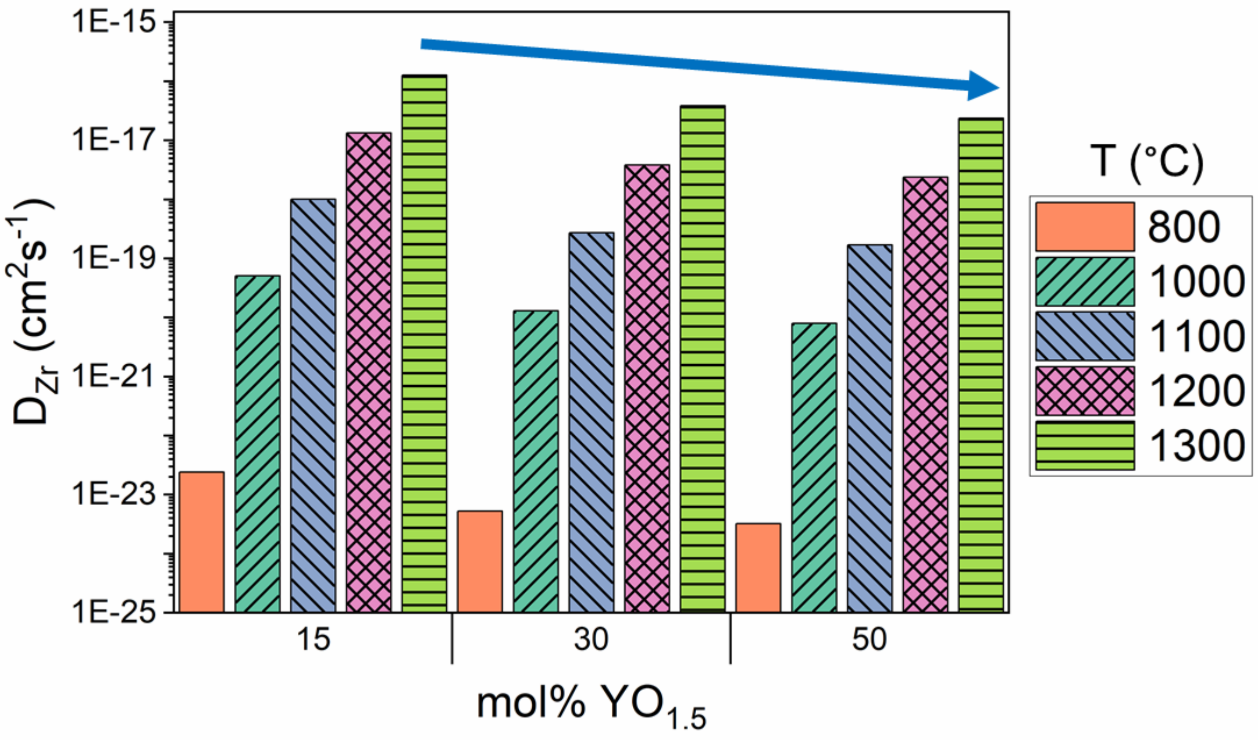


Doping ZrO_2 with > 30 mol% $YO_{1.5}$ improved the stability of the pore structure to 1200 °C.

Olson, N.S., et al. (2021). *Journal of the American Ceramic Society*, 104 (8), 4190-4202.

Improved thermal stability in context of thermodynamic (γ) and kinetic (D_{Zr}) factors





Reduced surface energy will reduce the driving force for elimination of surface area.[1]

Reduced diffusivity with increased yttria content may slow kinetics of densification & crystallite growth[2-4]

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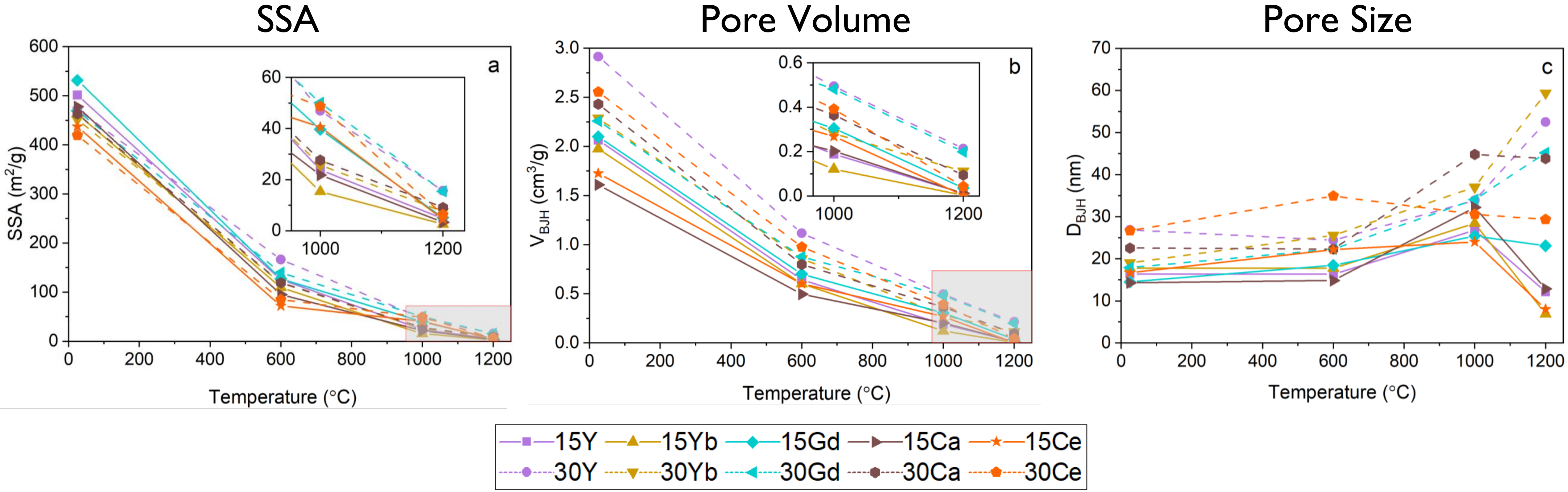
1. Drazin, J. W., & Castro, R. H. (2015). *Journal of the American Ceramic Society*, *98*(4), 1377-1384.
2. Kilo, M., et al. (2000). *Journal of the European Ceramic Society*, 20(12), 2069-2077.
3. Kilo, M., et al. (1997). *Berichte der Bunsen-Gesellschaft*, 101(9), 1361-1365.
4. Kilo, M., et al. (2003). *Journal of applied physics*, 94(12), 7547-7552.

Expanded dopant study (Y, Yb, Gd, Ca, Ce) didn't lead to improved stability



<u>Best Performers*</u>

1000 °C: 30Y, 30Gd, 30Ce

1200 °C: 30Y, 30Gd

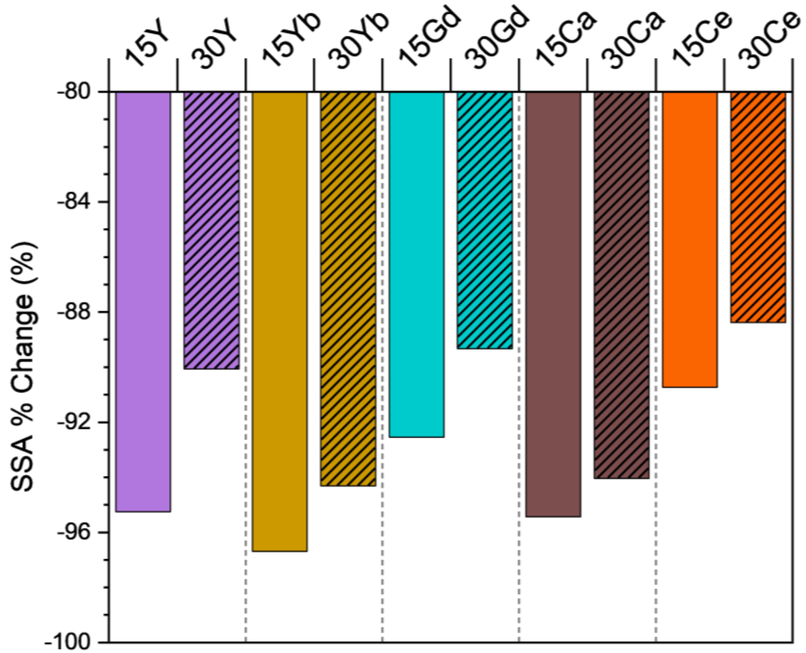
With 10 samples at 4 different conditions, becomes difficult to discern differences in behavior

*Best performance dictated by maximum SSA and pore volume at a given temperature

Olson, N.S., et al. (2023). *Journal of the American Ceramic Society*, in preparation.

With available material properties, difficult to establish new property-stability relationships

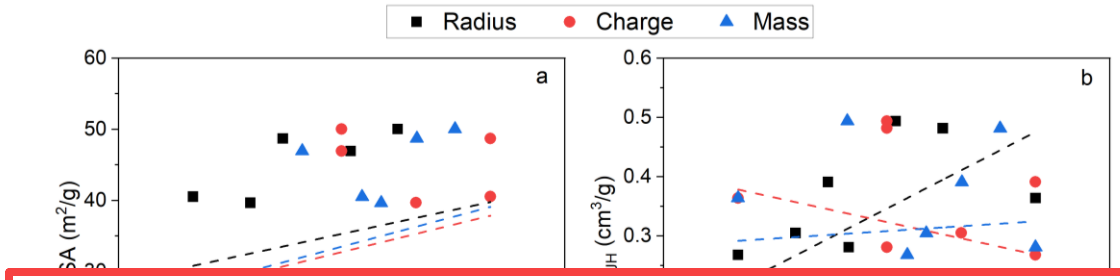
% Change in SSA from AD to 1000°C



$$\% \text{ Change} = \frac{\mathrm{SSA_f} - \mathrm{SSA_i}}{\mathrm{SSA_i}} \times 100\%$$

Increased dopant concentration leads to reduced densification.

How do weighted cation properties relate to **SSA** and **pore volume (V_{BJH})** at **1000 °C**?



Wider availability of material property data (such as surface energy, cation diffusivity, etc.) would enable more thorough analysis of property-stability relationships.

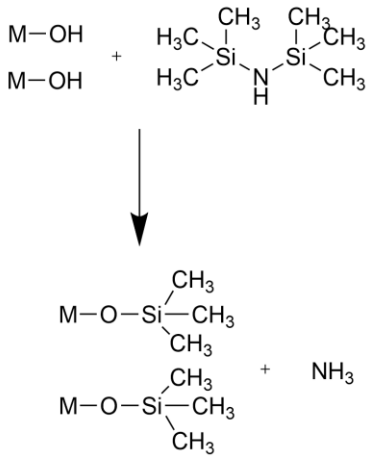
Radius	Specific Surface Area (SSA)	0.54
Charge		0.50
Mass		0.44
Radius	Pore Volume (V_{BJH})	**0.04**
Charge		0.47
Mass		0.8

In general, scatter predominates for these relationships and for others not depicted here.

Olson, N.S., et al. (2023). *Journal of the American Ceramic Society*, in preparation.

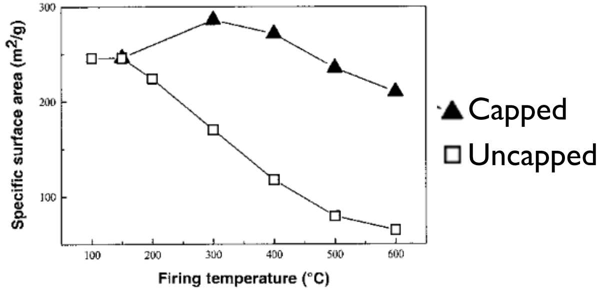
Surface modification of aerogels have shown promise in inhibiting coarsening & densification

Wu *et al.* Capping Approach

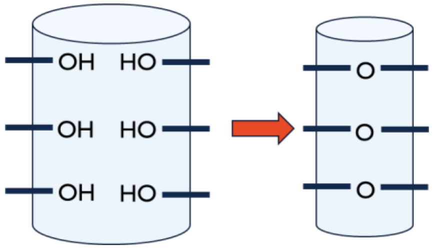


Capped surface hydroxyl groups with non-condensable group with hexamethyldisilane (HMDS)

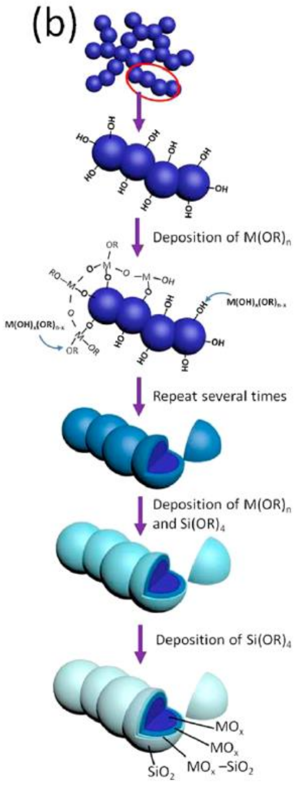
Applied to SnO_2, TiO_2, and ZrO_2 aerogels

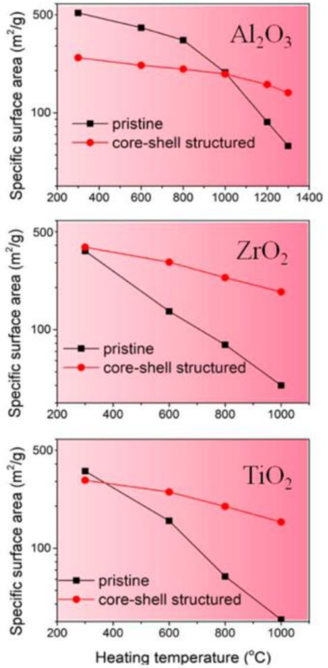


Capping surface hydroxyl groups with a non-condensable group prevents crystal growth & pore collapse



Zu *et al.* Coating Approach





Prepared MO_x/(MO_x-SiO_2)/SiO_2 core-shell metal oxide aerogels produced via alkoxide chemical liquid deposition

Applied to Al_2O_3, ZrO_2, and TiO_2 aerogels

Formation of SiO_2 particles on the aerogel surface prevent particle growth and phase transformation

Wu, N.L., et al. *Science*, 1999, 285(5432), 1375-1377.
Zu, H., et al. *Chemistry of Materials*, 2014, 26, 5761-5772.

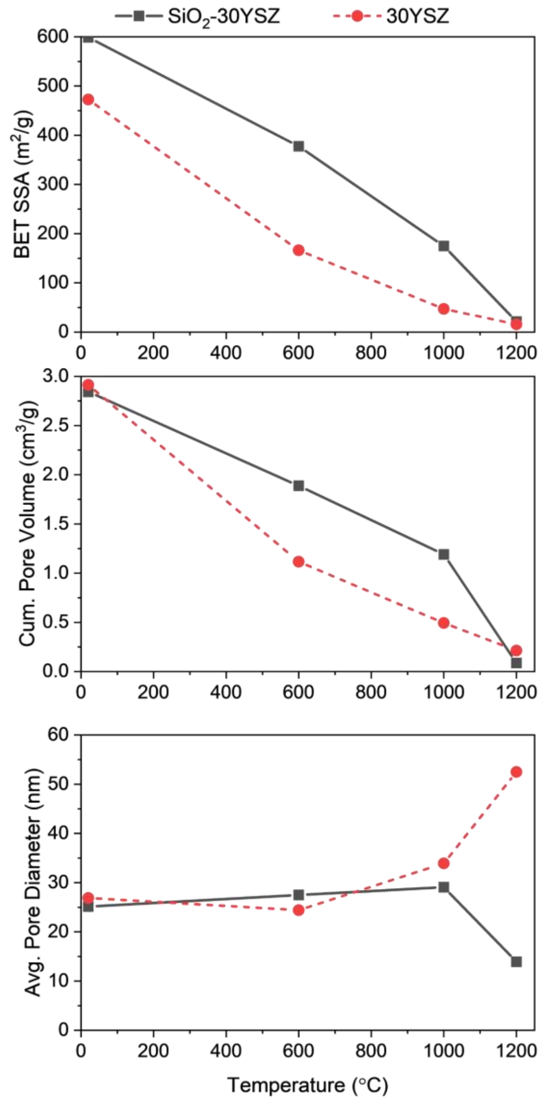
Application of SiO_2 coatings to best YSZ compositions show excellent stability to 1000 °C

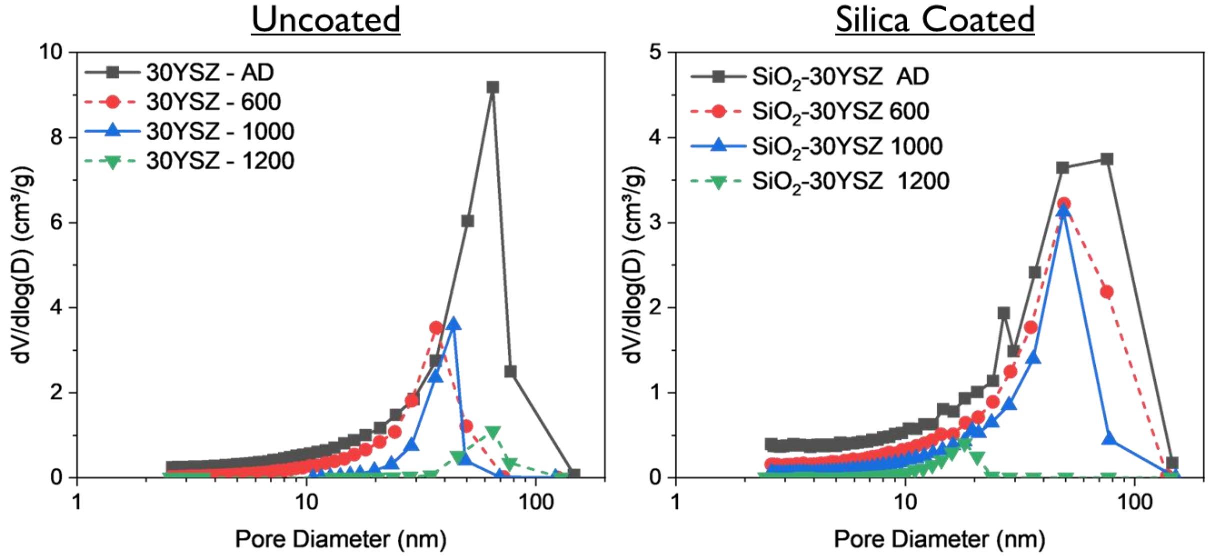
Apply simplified Zu coating approach to 0, 10 and 30 mol% $YO_{1.5}$ ZrO_2 aerogel

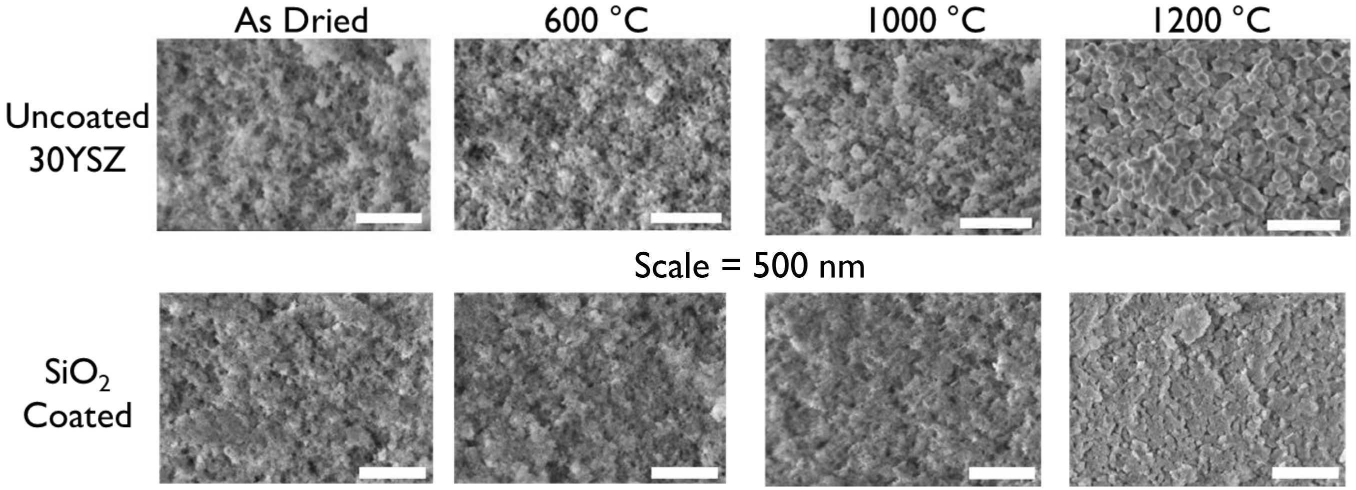
According to EDS, the molar ratio for 30YSZ is:

Zr	Y	Si
1.00	0.55	3.01

More Si than Zr and Y!

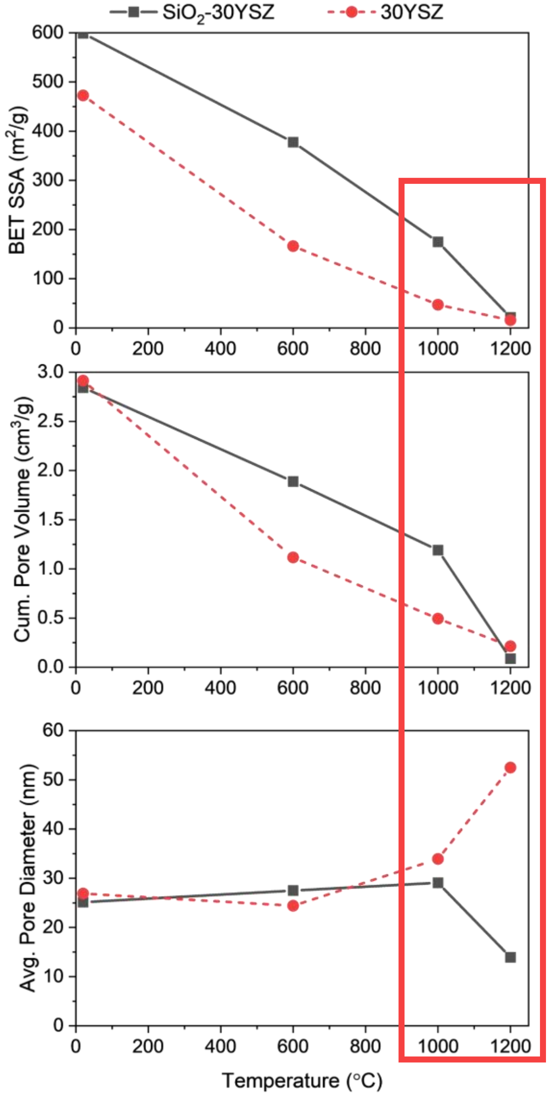


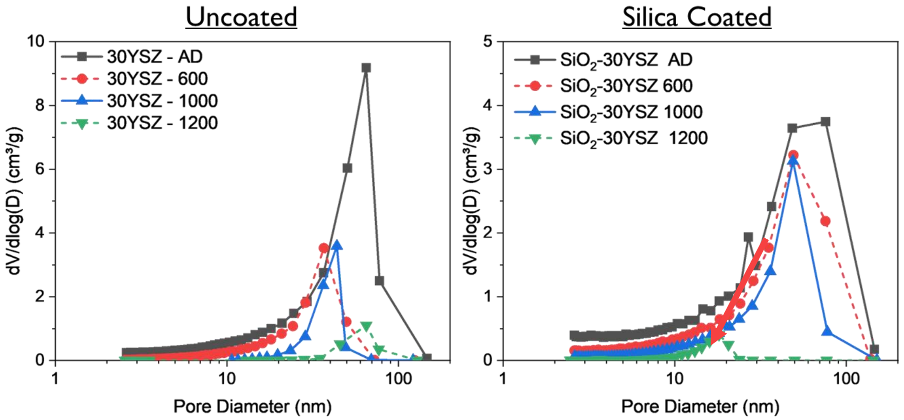


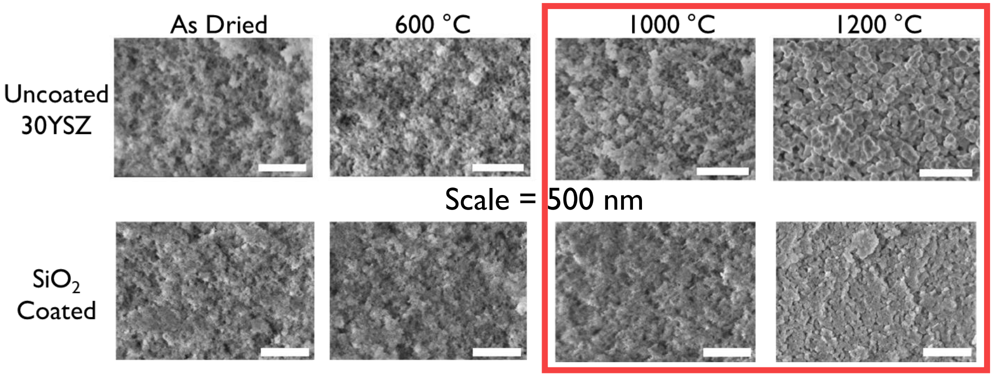


Olson, N.S., and Stokes, J.L., et al. (2023). *Journal of the American Ceramic Society*, in preparation.

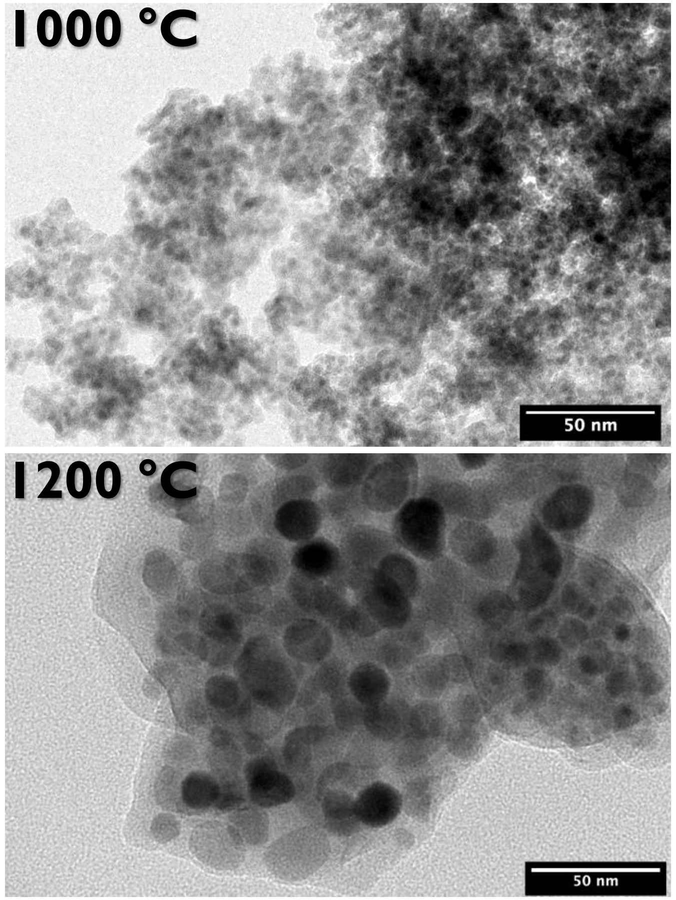
Application of SiO_2 coatings to best YSZ compositions show excellent stability to 1000 °C







SiO$_2$-coated 30YSZ

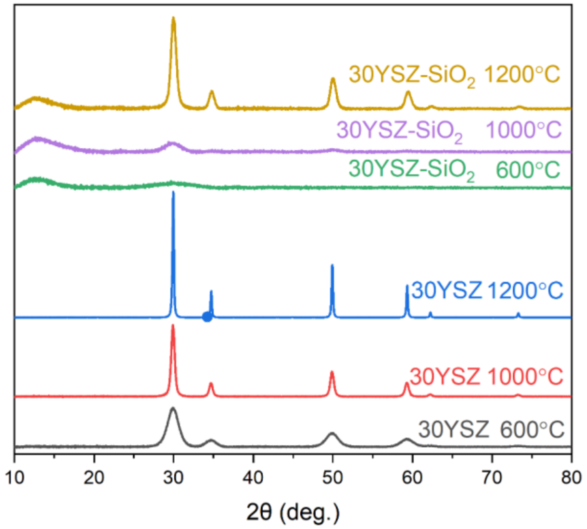


From 1000 to 1200 °C, SiO_2 coating enables viscous sintering and *enhances* densification.

Olson, N.S., and Stokes, J.L., et al. (2023). *Journal of the American Ceramic Society*, in preparation.

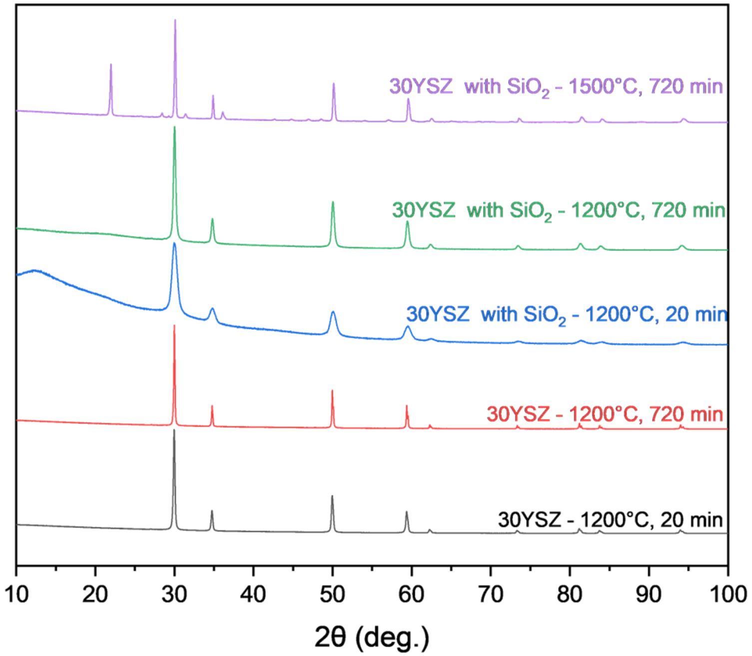
Thanks to Nachiket Shah (UIUC MatSE) for TEM of aerogel samples.

Application of SiO_2 coatings to best YSZ compositions show excellent stability to 1000 °C



SiO_2 coating delays crystallization of YSZ and strongly inhibits crystallite growth.

Sample	T (°C)	Crystallite Size (nm)	a (Å)
30YSZ	600	5.8	5.163
30YSZ-SiO_2	600	-	-
30YSZ	1000	21.7	5.163
30YSZ-SiO_2	1000	3.2	5.162
30YSZ	1200	55.3	5.163
30YSZ-SiO_2	1200	13.9	5.153



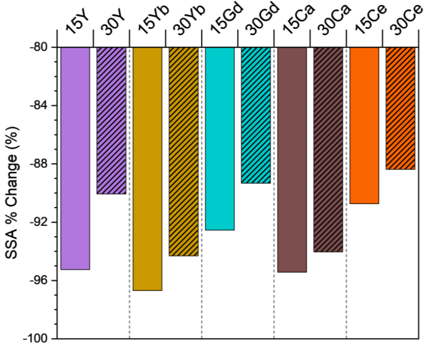
Temperatures > 1200 °C required for crystallization of silica

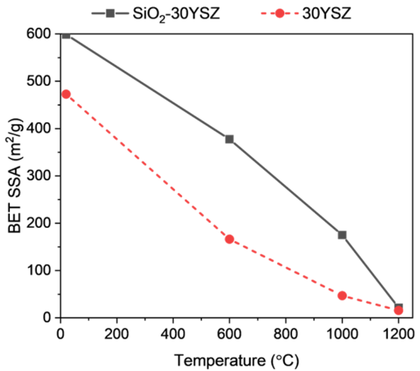
1. (1) Why does SiO_2 coating improve thermal stability to 1000 °C?
2. (2) Beyond 1000 °C, how is the SiO_2 coating evolving in relation to the YSZ aerogel?

Olson, N.S., and Stokes, J.L., et al. (2023). *Journal of the American Ceramic Society*, in preparation.

Summary

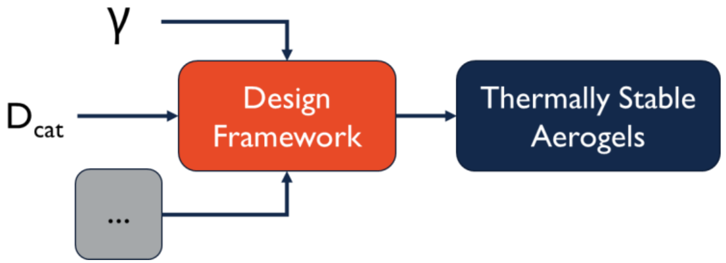
1. Aerogels are promising candidates for lightweight, highly insulating materials, but the pore structure must be preserved to $T \geq 1200$ °C
2. Reduced surface energy and cation diffusivity are hypothesized to improve aerogel thermal stability.
3. Increased dopant concentration from 15 to 30 mol% M/(M+Zr) reduces densification of the pore structure (Gd, Y perform best).
4. Post-synthetic modification of YSZ aerogels with SiO_2 coatings significantly improves thermal stability to 1000 °C but promotes viscous sintering beyond this temperature.





Looking Forward

1. Wider availability of <u>material property data</u> (surface energy, cation diffusivity, etc.) may help understand source(s) of variability in aerogel thermal stability.


γ

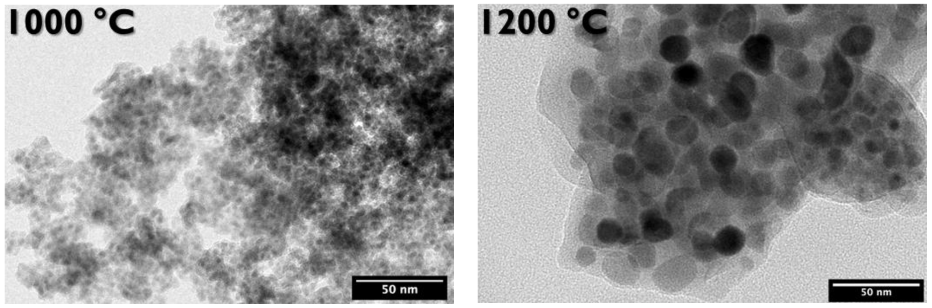
D_{cat}

...

Design Framework

Thermally Stable Aerogels

2. The source of thermal stability and instability in SiO_2-coated YSZ aerogels needs to be identified via evaluation of the chemistry and structure of the aerogel and coating.



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- Dr. Frances Hurwitz (NASA GRC, retired)
- Jordan Meyer (UIUC MatSE U-Grad)
- Krogstad Group members
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Engineering Ceramics Division
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- Materials Research Laboratory, UIUC
- SCS Microanalysis Laboratory, UIUC
- NASA Glenn Research Center

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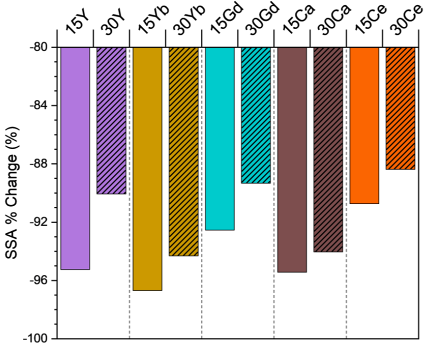

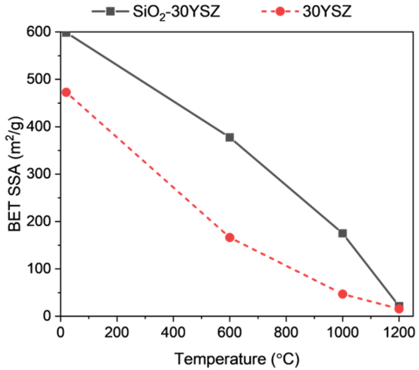

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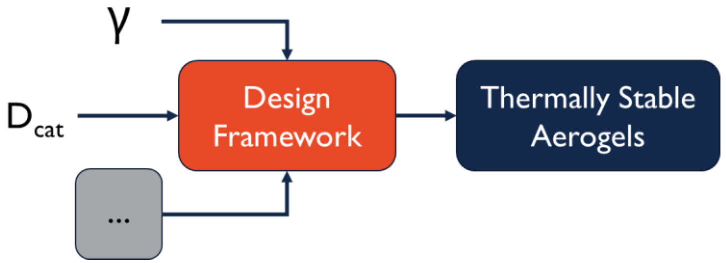

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