Understanding thermal stability in zirconia-based aerogels

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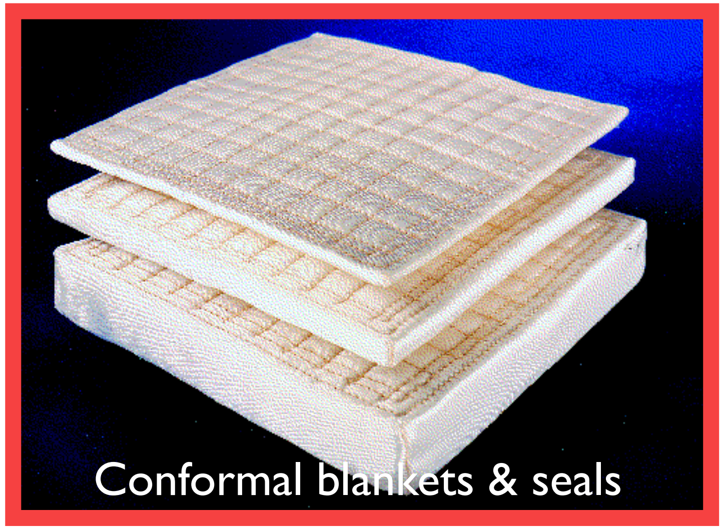
TMS2023: Advances in Powder and Ceramic Materials Science
22 March 2023
San Diego, CA
This work is supported by a NASA Space Technology Research Fellowship

Developing lightweight, high-performance aerospace thermal protection systems (TPS)

Advanced composites

Reusable ceramic tiles & coatings



Conformal blankets & seals

<u>TPS Needs:</u>

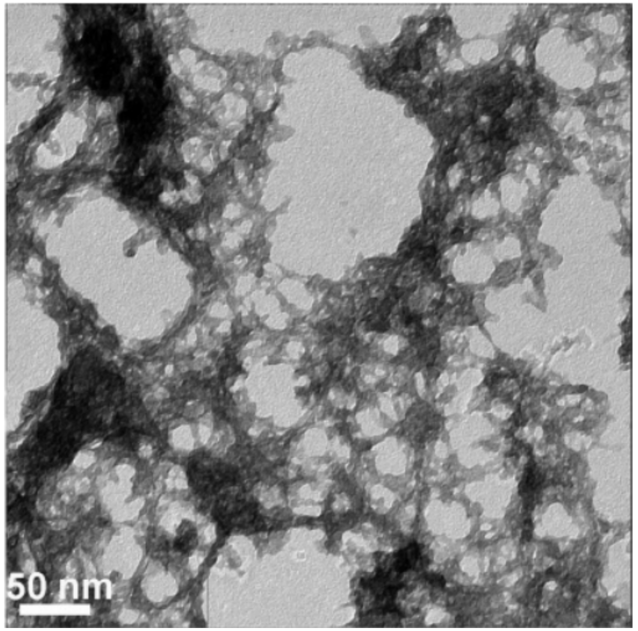
Manage heat loads
Withstand mechanical loads
Lightweight
Reusable when possible

<u>Our Aims:</u>

Reduce thermal conductivity to improve performance.

Reduce mass/volume to lower costs.

Aerogels are highly insulating and lightweight materials



High SSA: 200 to 1000 m²/g

High Porosity: 90 to 99.9%

Low Density: 0.2 to 0.05 g/cm³

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

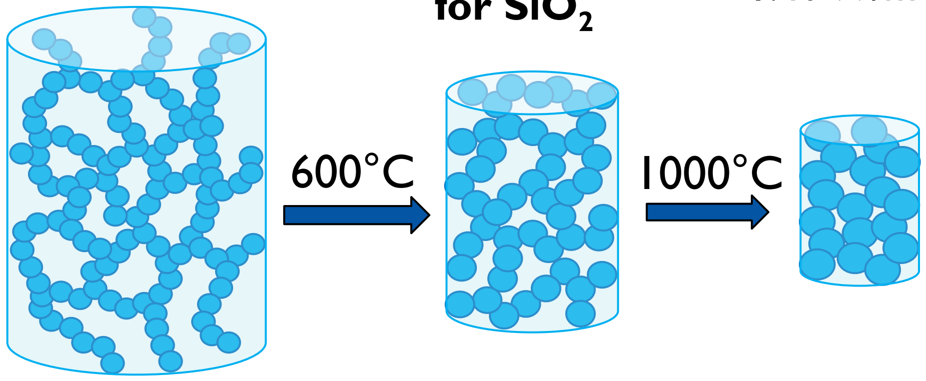
Cohen, E., and Glicksman, L. (2015). *Journal of Heat Transfer*, 137(8), 81601.
Sun, H., et al. (2013). *Advanced Materials*, 25(18), 2554-2560.

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

<u>Aerogel</u>
0.03 W/m·K

Thermal Conductivity for SiO_2

<u>Dense</u>
1.40 W/m·K

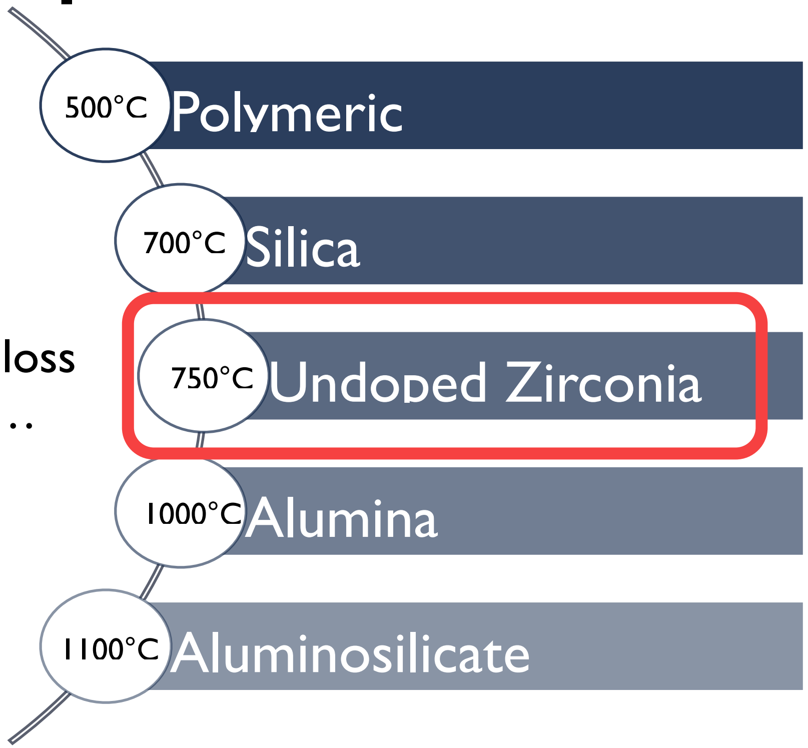


Loss of SSA, porosity

↑ thermal conductivity, cracking, and shrinkage

Large SSA & porosity contribute to driving force for densification

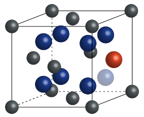
Rapid densification & loss of porosity beyond…



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.

Yttria-stabilized zirconia as a candidate composition for a thermally stable aerogel

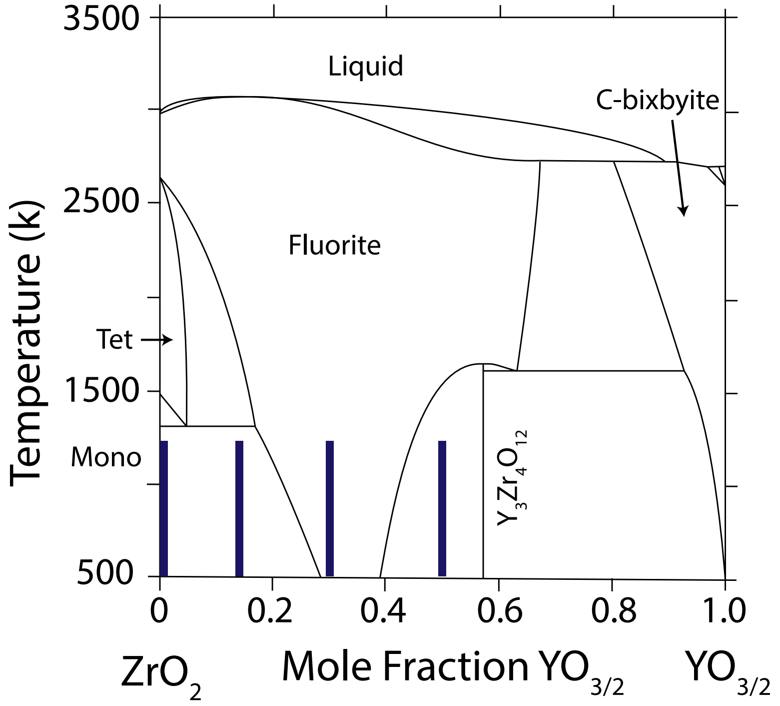


- YSZ well-known for use as a thermal barrier coating for superalloys in turbine engines
  - *Low thermal conductivity* of 0.8 to 2.9 W/(m•K)
  - Y_2O_3 doping *inhibits phase transformations*

(1) How/why does yttria change the **as-dried structure**?

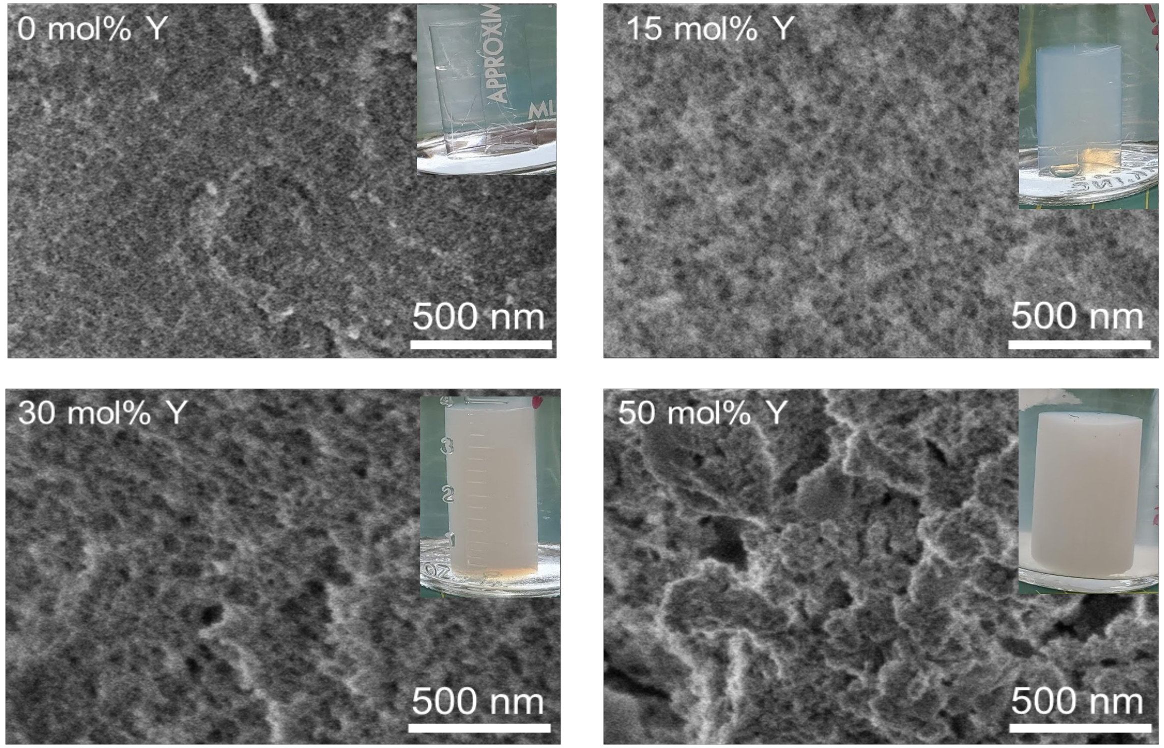
(2) How does yttria influence phase behavior & **structural evolution**?

(3) Does yttria improve the **thermal stability** of YSZ aerogels? If so, how?

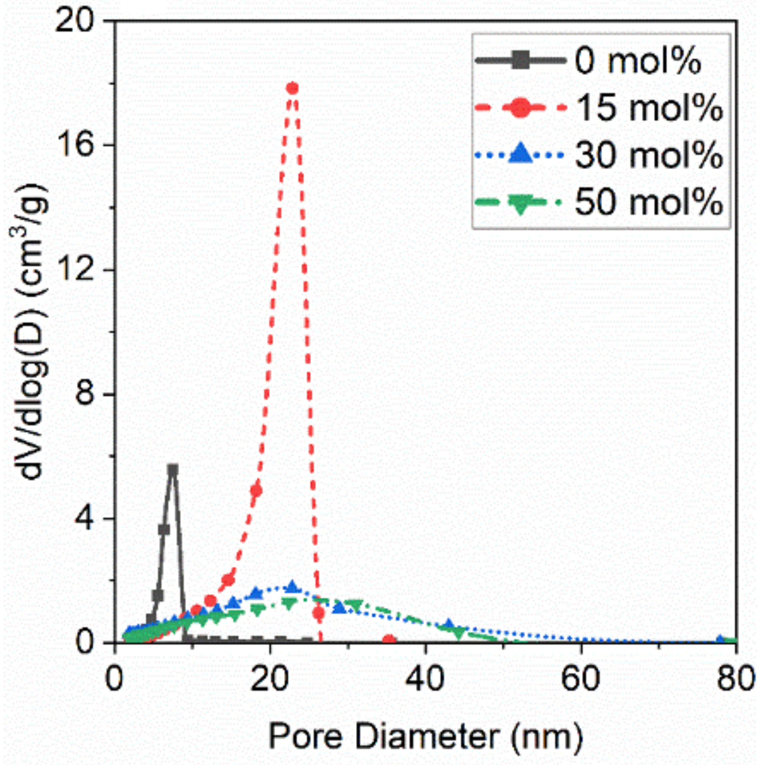


Selected compositions for study:
0, 15, 30, and 50 mol% $YO_{1.5}$

As dried aerogels: yttria increases pore size and distribution breadth

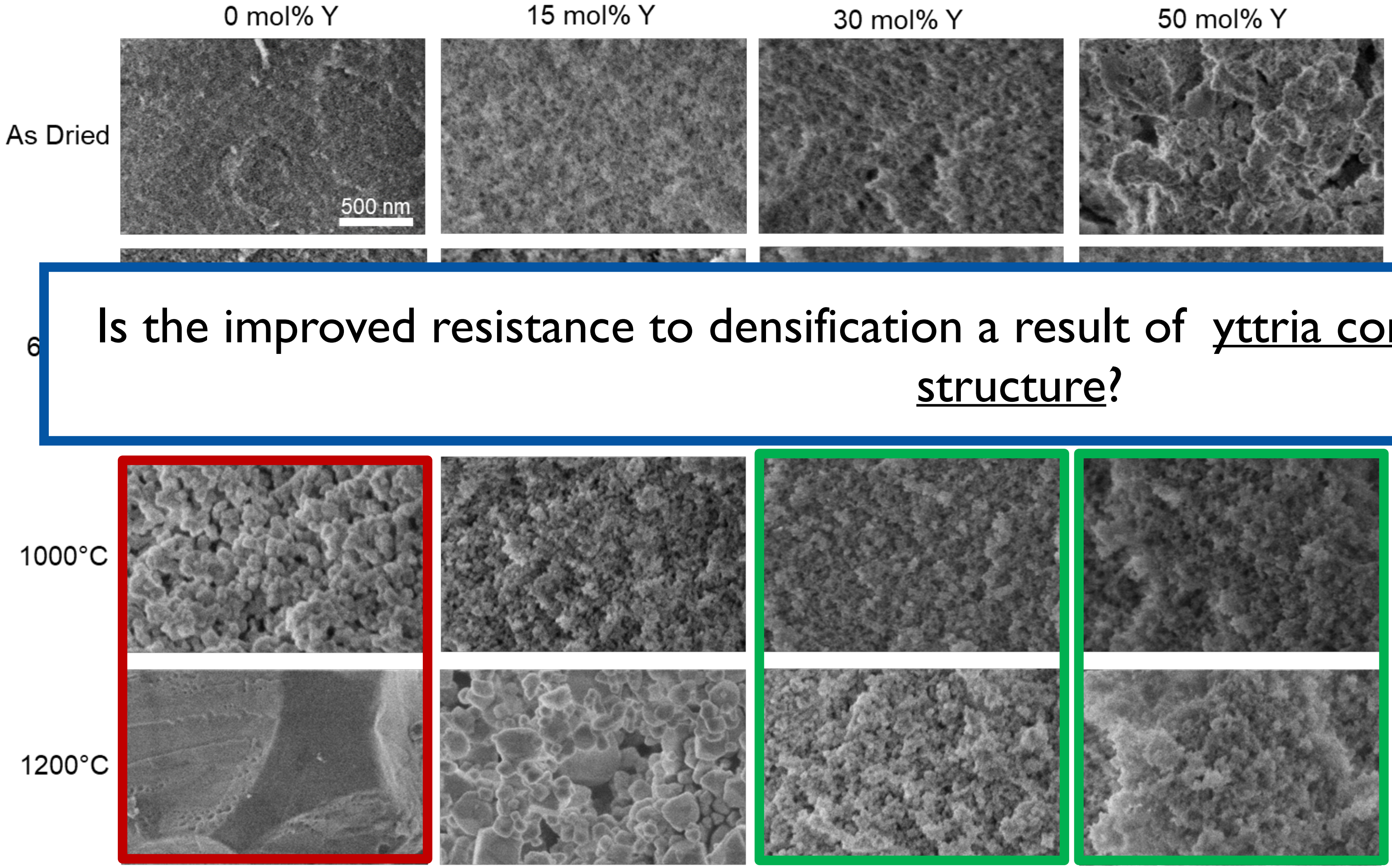


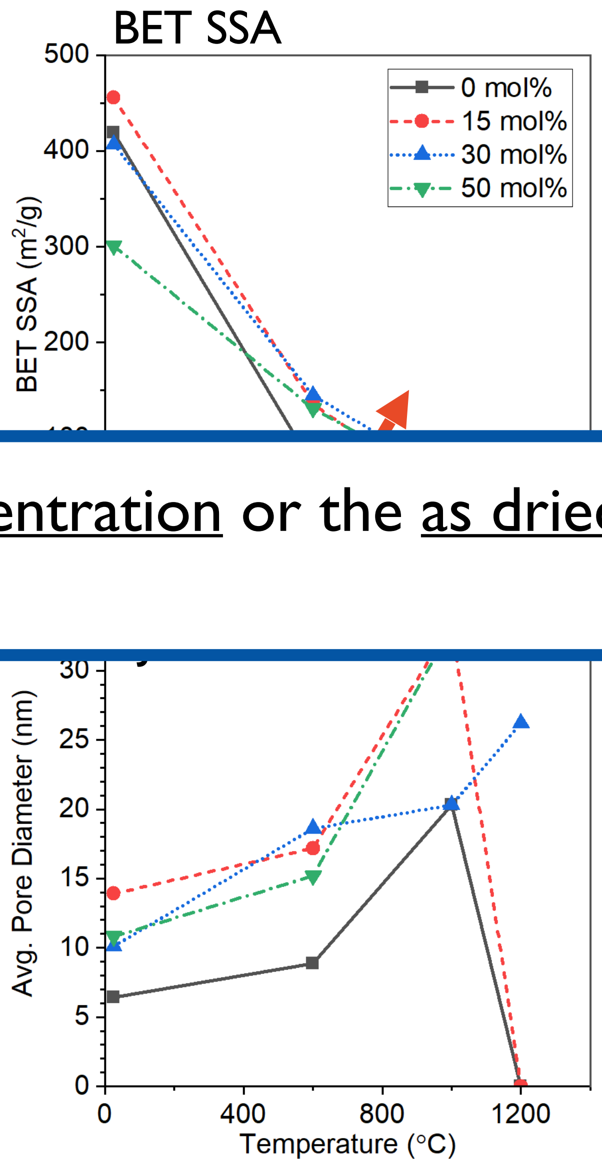
Pore Size Distributions



mol % $YO_{1.5}$	SSA (m^2/g)	Pore Volume (cm^3/g)	D_{peak} (nm)	Shrinkage (%)	Bulk Density (g/cm^3)
0	419	0.986	7.5	-25.6	0.292
15	456	1.950	22.9	-21.1	0.250
30	407	1.190	22.8	-13.2	0.193
50	301	0.997	28.5	-	-

Increased yttria content reduces densification & pore collapse upon heating to 1200°C





Is the improved resistance to densification a result of yttria concentration or the as dried structure?

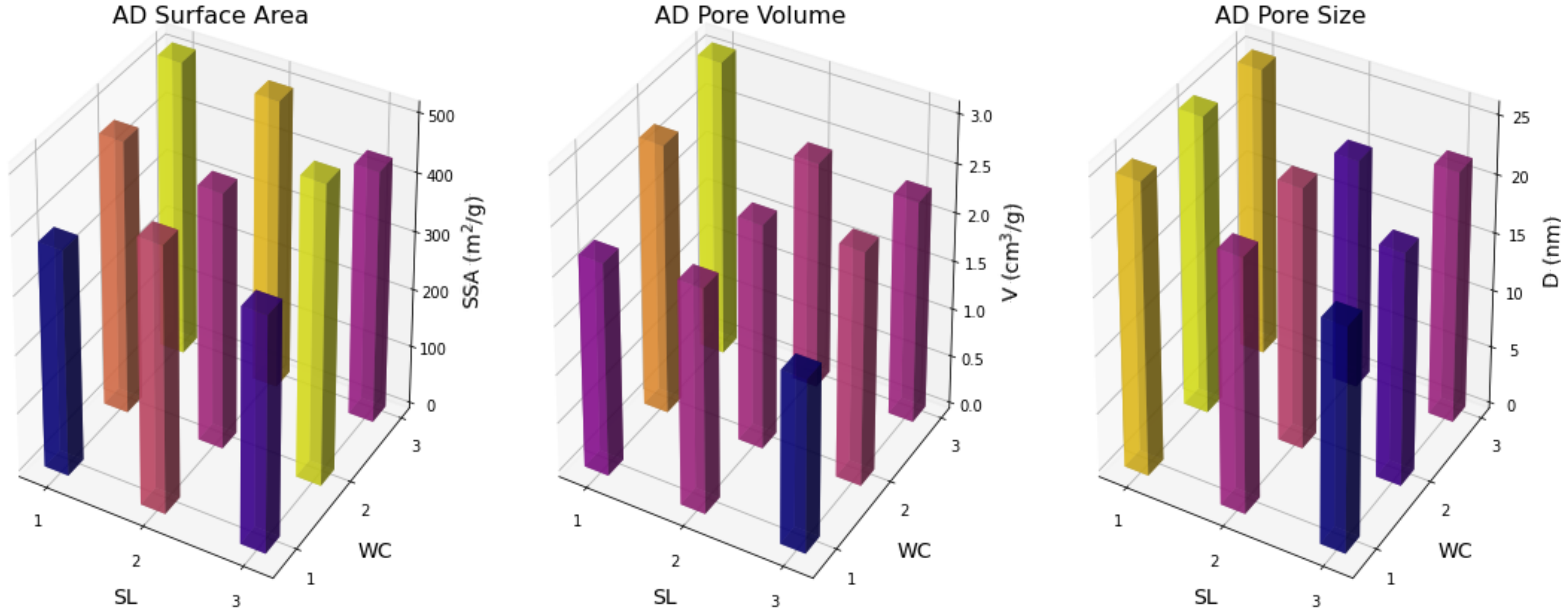
As dried structure is tunable via synthetic parameters of SL and WC

Finely adjust as dried structure independently of composition

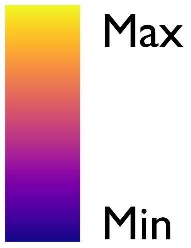
All 30 mol% $YO_{1.5}$ in ZrO_2

Water content = mmol water added / mmol metal
Solids loading = mmol metal / mL solvent

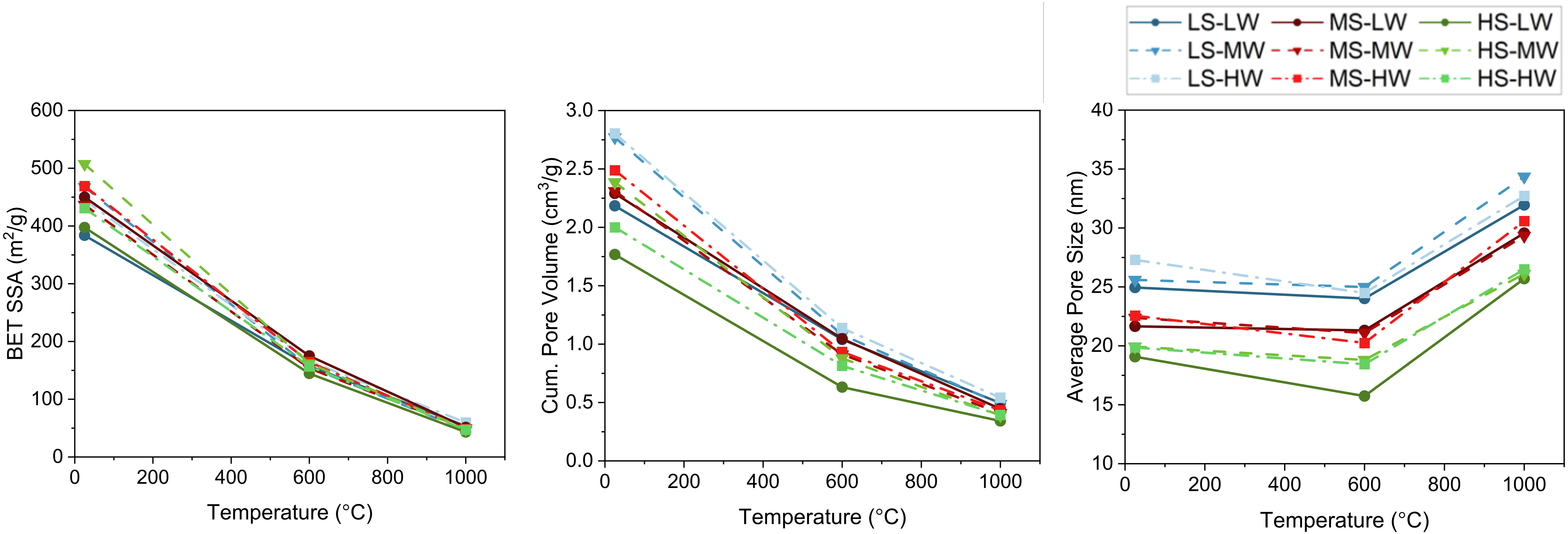
Solids Loading \ Water Content	L	M	H
L	LS-LW	LS-MW	LS-HW
M	MS-LW	MS-MW	MS-HW
H	HS-LW	HS-MW	HS-HW



In general, **smaller SSA, pore size and pore volume** with:
increased solids loading
and
decreased water content



Impact of starting structure on subsequent evolution at high temperatures



Same color = same solids loading
Same line style = same water content

Exploration of relationships between the as dried structure & thermal stability

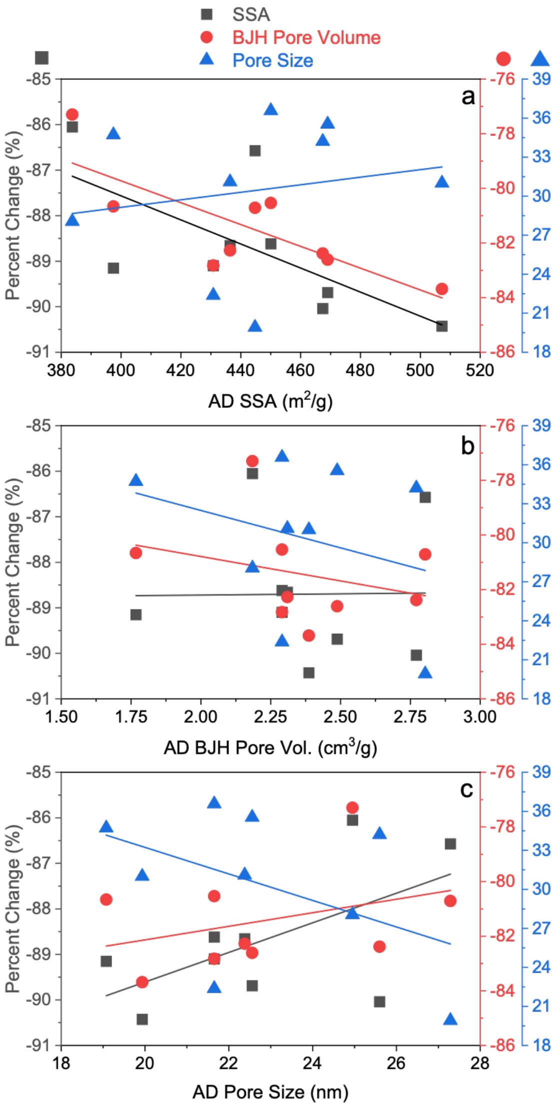
To evaluate thermal stability, we switch the **independent variable** to the as dried properties (starting structure).

Here, the **dependent variable** is the percent change in SSA, V_{BJH}, and D_{BJH} over various temperature ranges.

AD SSA

AD V_{BJH}

AD D_{BJH}

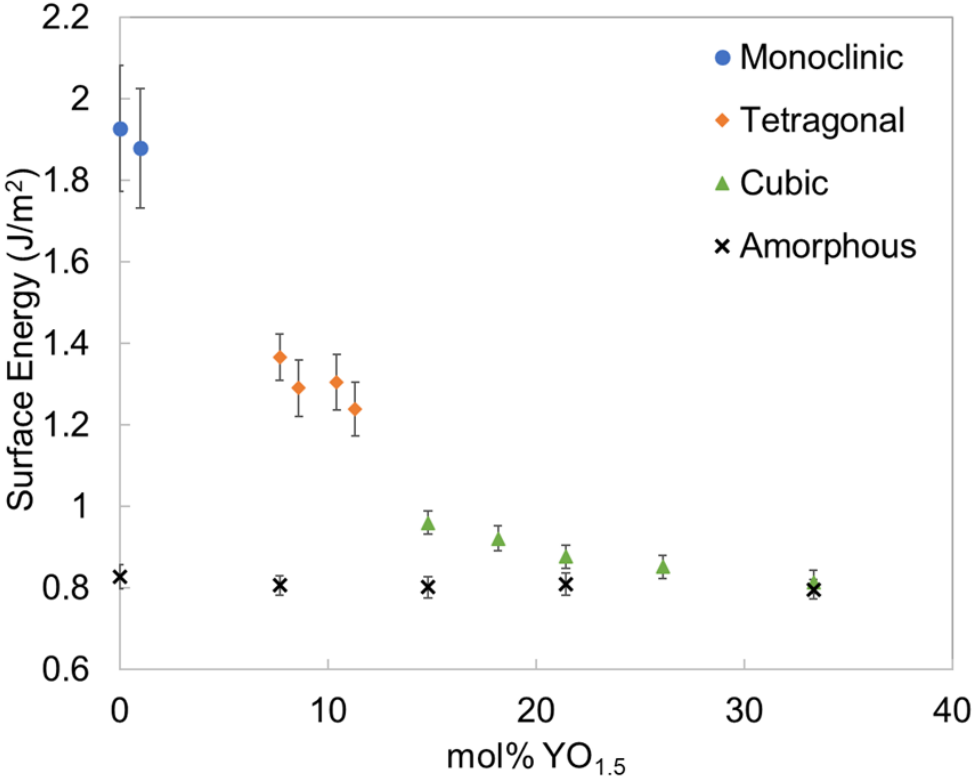


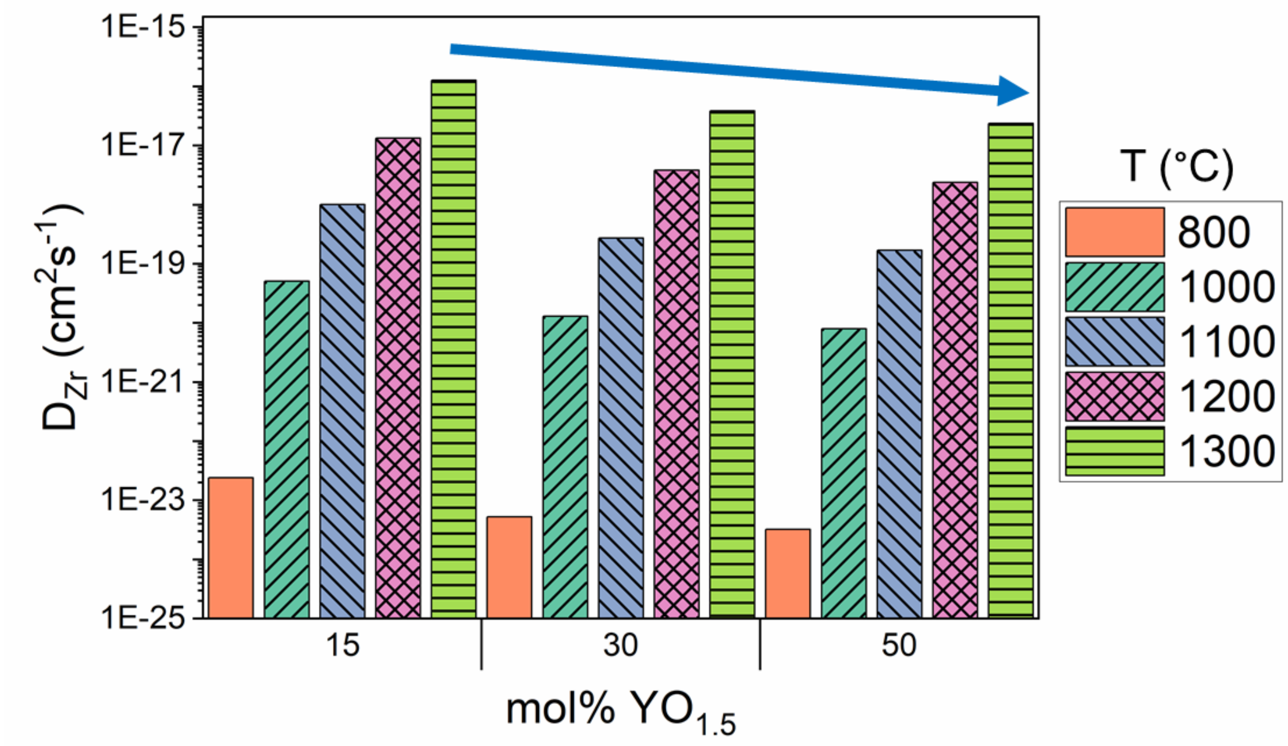
AD Property (x)	% Change - AD to 1000°C (y)	Slope	Intercept	p-value
SSA	SSA	-0.03	-77	0.049
SSA	V	-0.04	-64	0.012
SSA	D	0.03	18	0.635
D	SSA	0.33	-96	0.251
D	V	0.25	-87	0.357
D	D	-1.02	54	0.209
V	SSA	0.05	-89	0.977
V	V	-1.79	-77	0.446
V	D	-5.75	44	0.427

Coarser structures (lower SSA) sinter and densify less rapidly, as expected by thermodynamics.

Is the improved resistance to densification observed in the YSZ aerogels a result of yttria concentration or the as dried structure?

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





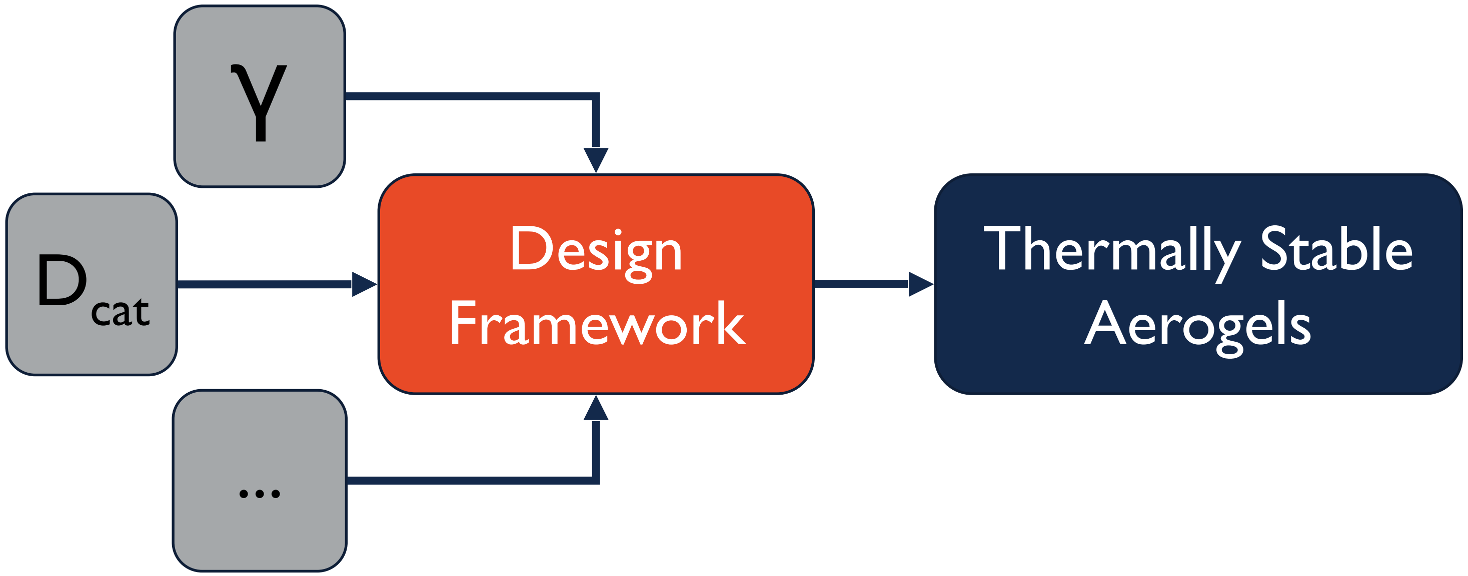
Reduced surface energy will reduce the driving force for elimination of surface area.[1]

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

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.

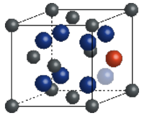
A design framework for thermally stable aerogels informed by kinetics and thermodynamics

1. **Decreased cation diffusivity** of Zr^{4+}, Y^{3+} in YSZ with increased Y_2O_3 doping responsible for decreased mass flow
    - *Less densification AND crystallite/grain growth* (reduced rate of mass flow)
2. **Lower surface energy** with increased yttria content ($\gamma_c < \gamma_t < \gamma_m$) leads to:
    - *Improved stability of pore structure* (lower driving force for densification)

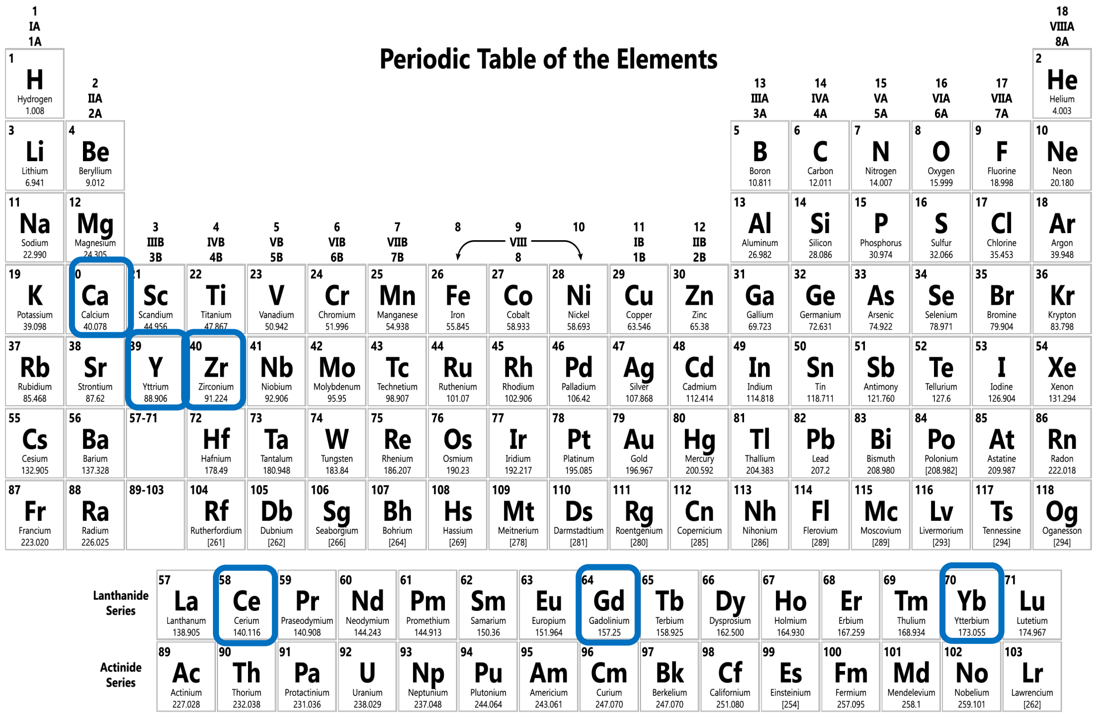


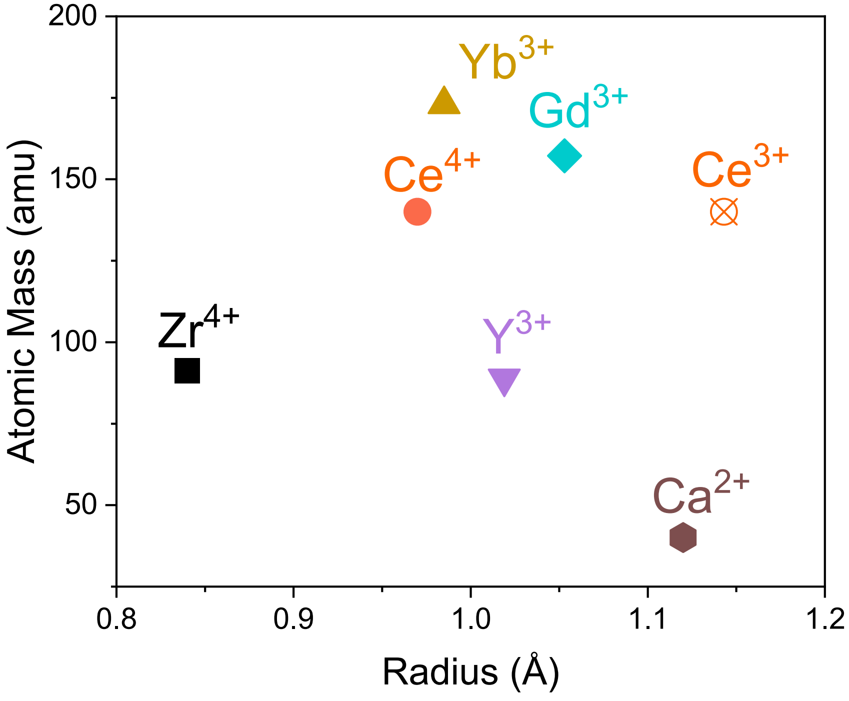
Olson, N.S., et al; *Journal of the American Ceramic Society*, 2021.

Study of other dopants (Y, Yb, Gd, Ca, Ce) in zirconia aerogels at 15 and 30 mol% M/(M+Zr)



Further exploration of dopant properties (size, mass, charge) on aerogel thermal stability

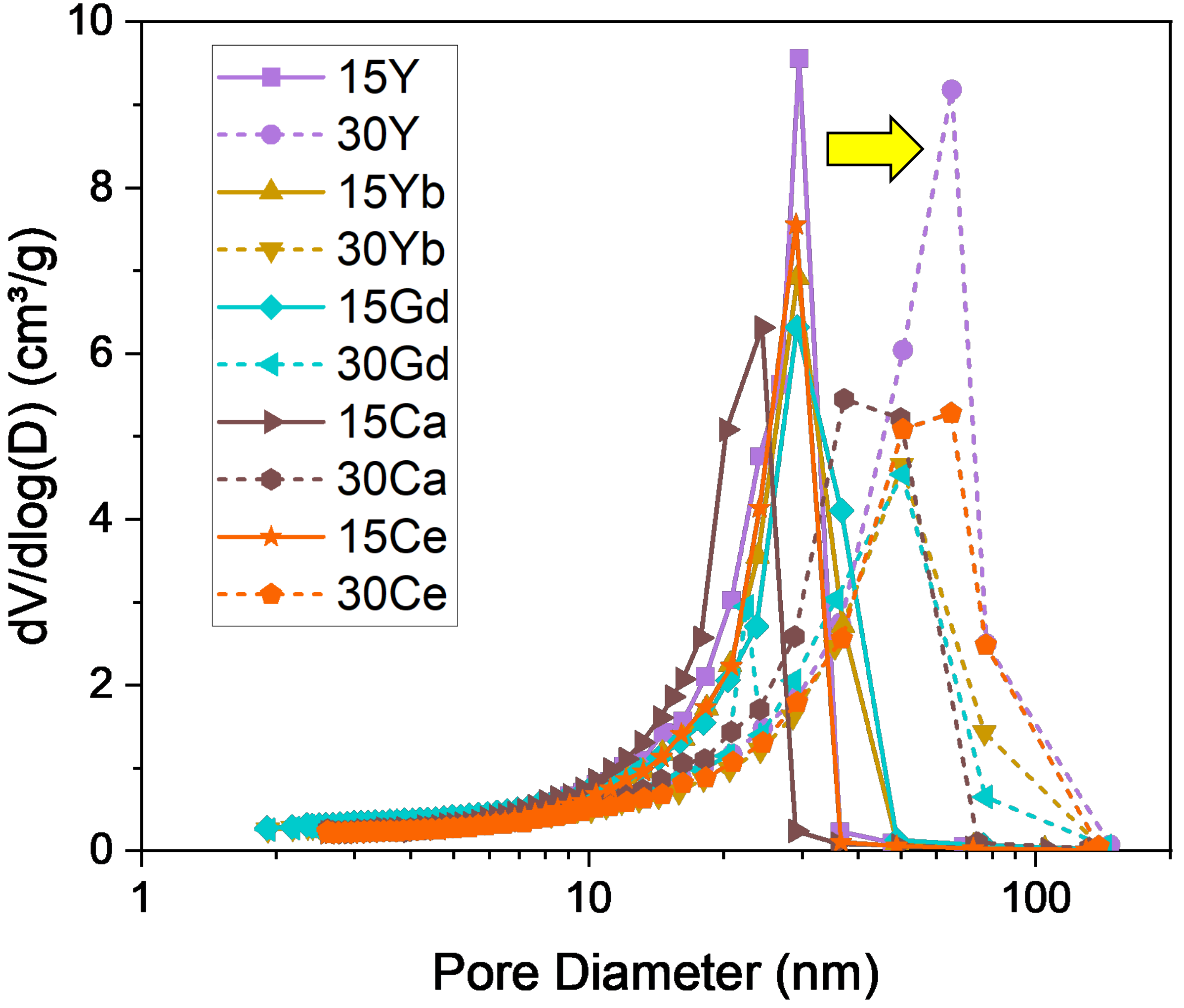




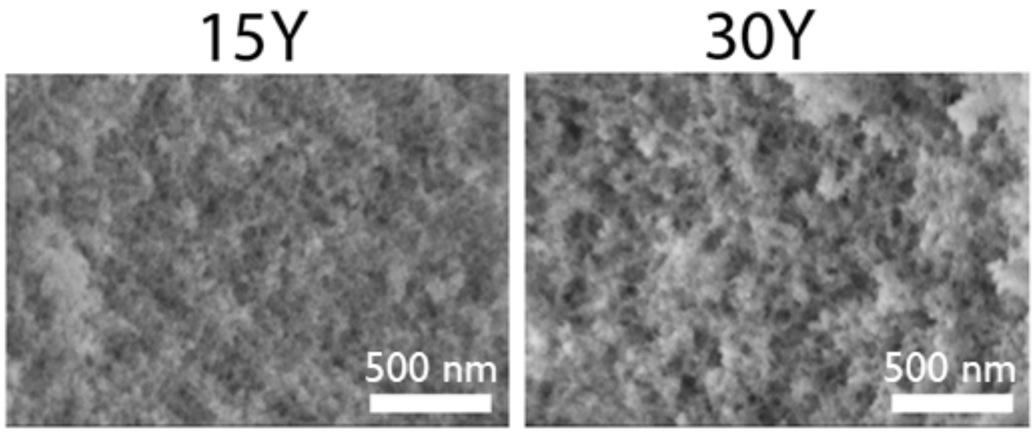
→ Modify thermal conductivity, surface energy and cation diffusivity

→ Connect **material properties** to changes in **structural evolution**

As dried structure characterized with nitrogen physisorption and SEM



Increased dopant concentration from 15 to 30 mol% increases average pore size and distribution breadth for *all* dopants.

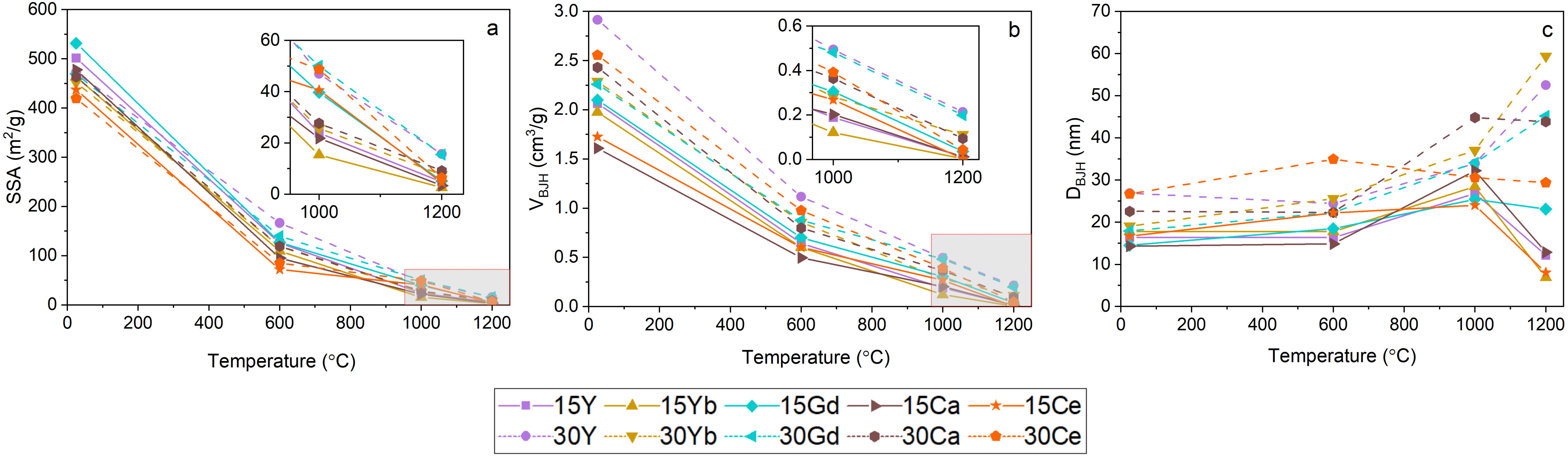


Evaluation of pore structure with nitrogen physisorption quantifies change in performance

SSA

Pore Volume

Pore Size



<u>Best Performers*</u>

1000 °C: 30Y, 30Gd, 30Ce

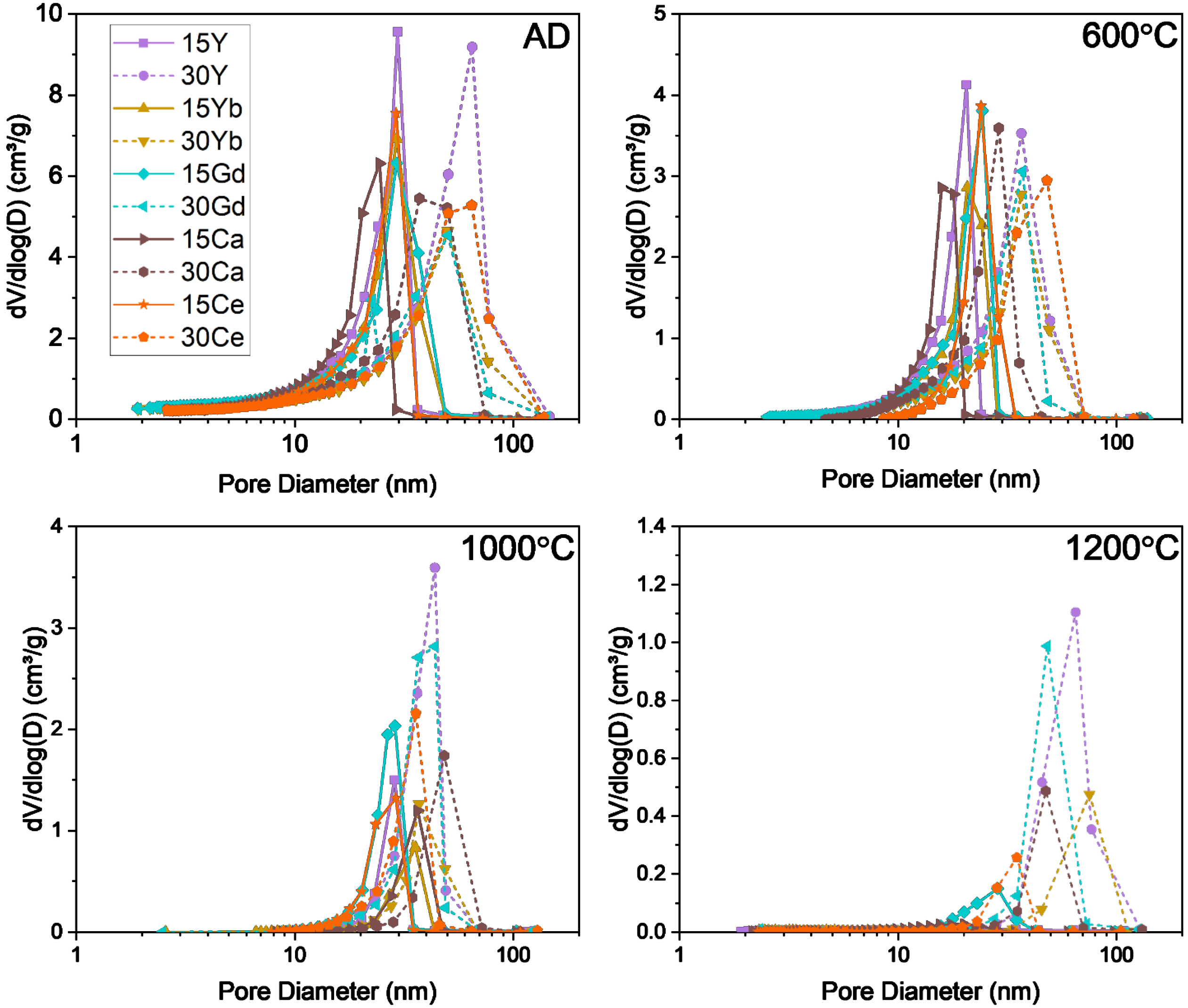
1200 °C: 30Y, 30Gd

Increased dopant concentration leads to reduced densification.

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

Olson, N.S., et al. (2023). Under review at *Journal of the American Ceramic Society*.

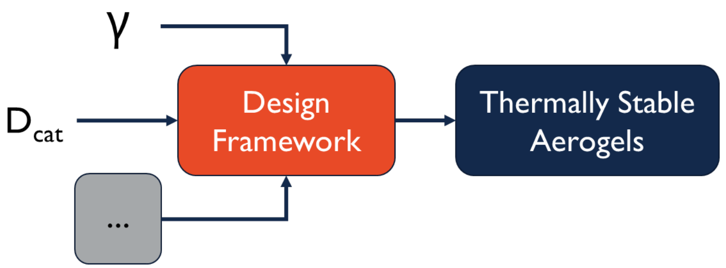
Increased dopant content improves stability of pore structure to 1200 °C



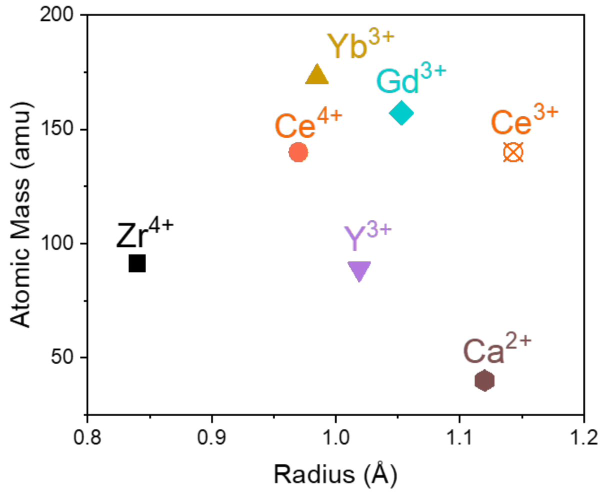
At 600 °C, no visible difference between 15 and 30 mol% MO_x

At 1000 and 1200 °C, it becomes apparent 30 mol% MO_x maintains more porosity. Gd and Y perform the best.

Connecting material properties to thermal stability



Given this absence, we turned to something readily available: cation properties (mass, radius, charge)



From our work on YSZ, we were able to connect our results to others' measurements of surface energy and cation diffusivity.

But… neither those properties nor others are available for wider ranges of dopants and concentrations

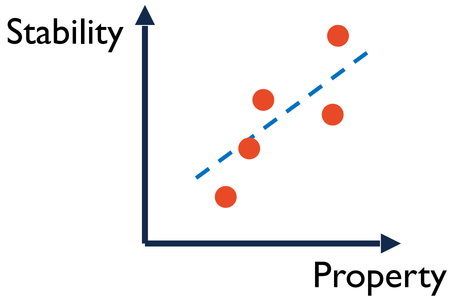
Next, we calculated a weighted average for each material

$$\text{Weighted Property} = x_{Zr}P_{Zr} + x_M P_M$$

x_M = mole fraction MO_y

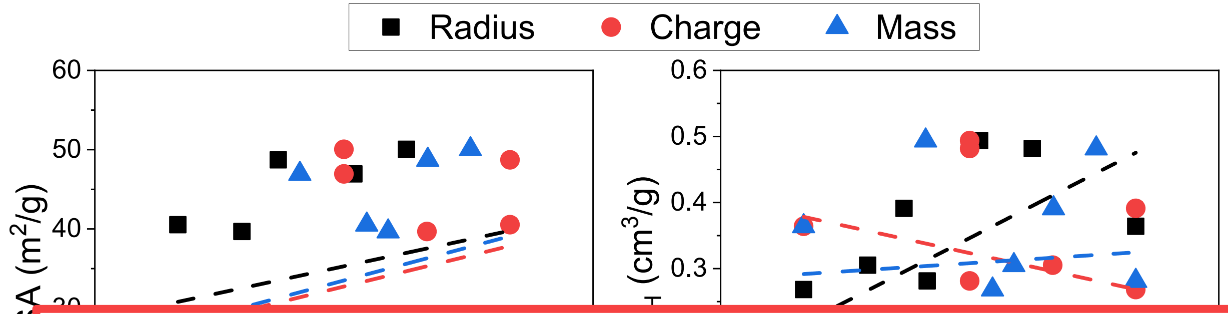
P_M = property of dopant M^{2y+}

We then performed linear regression on the **absolute** (property at a given temperature) and **relative** (percent change) thermal stability.

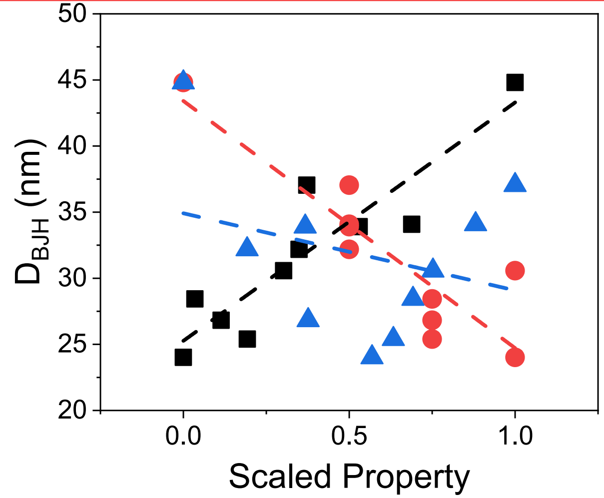


$$\% \text{ Change} = \frac{x_f - x_i}{x_i}$$

Cation properties are not clearly related to thermal stability (absolute or relative)



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



Property	Response		p-value
Radius			0.54
Charge	V_{BJH}	1000	0.47
Mass			0.8
Radius			3.0E-04
Charge	D_{BJH}	1000	5.9E-04
Mass			0.41

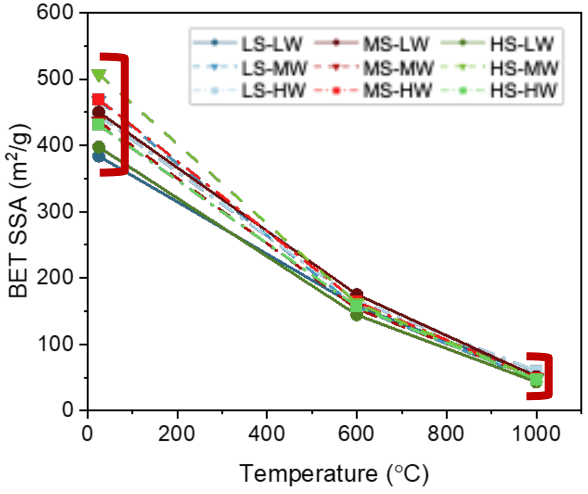
All properties are for samples after 1000 °C heat treatment.

Synthetic parameter study can serve as a "control" for studies on composition

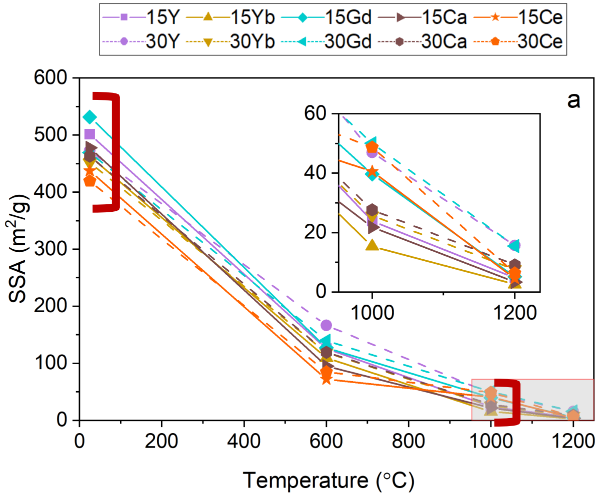
- For both YSZ and dopant study, the amount of dopant influenced the starting structure & thermal stability
- Presumably, lower starting SSA and coarser structure should densify less rapidly, but by how much?

Improvement in thermal stability likely result of <u>change in material properties</u> and *not* the change in as dried structure.

Synthetic Parameters



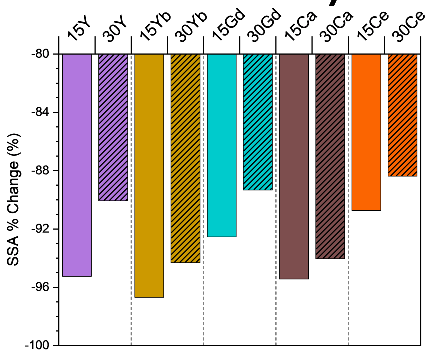
Dopants



Study	ΔSSA as dried
YSZ	118
Dopants	112
Synthetic Parameters	123

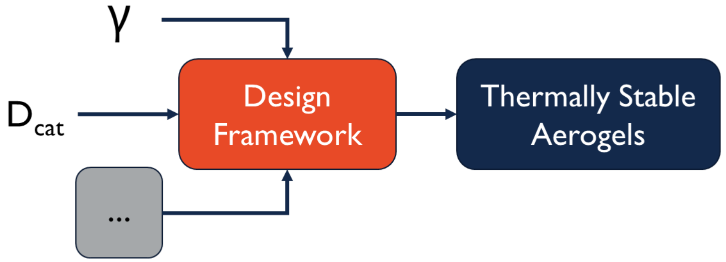
Summary

1. Aerogels are promising candidates for lightweight, highly insulating materials, but the pore structure must be preserved to T ≥ 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).



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.



2. Alternative strategies for zirconia-based aerogels synthesis need to be identified including the potential of nucleating agents and post-synthetic modifications such as surface capping strategies

Thank you for your attention! Special thanks to…

- <u>PhD Student</u>: Nathaniel Olson (UIUC, soon to be NASA JSC)
- <u>Technical Collaborator</u>: Dr. Jamesa Stokes (NASA GRC)
- Dr. Frances Hurwitz (NASA GRC, retired)
- Jordan Meyer (UIUC MatSE U-Grad)
- Krogstad Group members
- Others at NASA GRC: Dr. Haiquan (Heidi) Guo, Dr. Richard Rogers, Jessica Cashman

<u>Funding</u>:

- NASA Space Technology Research Fellowship (80NSSC18K1189)
- ACerS Engineering Ceramics Division Student Travel Grant

Engineering Ceramics Division
The American Ceramic Society

<u>Facilities</u>:

- Materials Research Laboratory, UIUC
- SCS Microanalysis Laboratory, UIUC
- NASA Glenn Research Center

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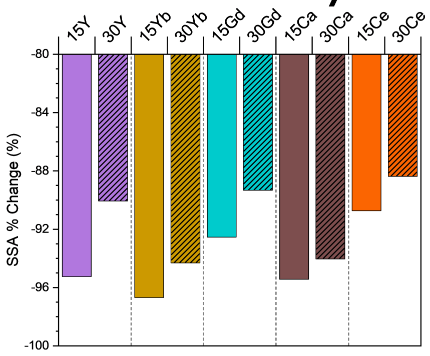

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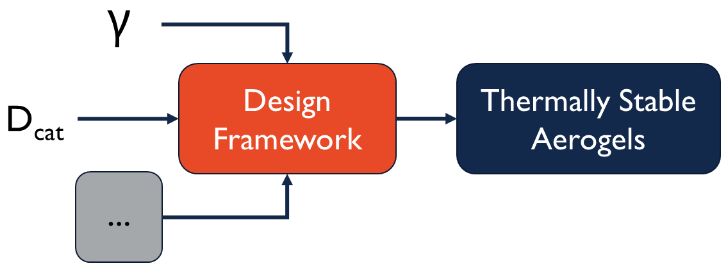

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