Exploration of rare earth doped zirconia aerogels for high temperature aerospace applications

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Developing lightweight, high performance insulation for aerospace applications

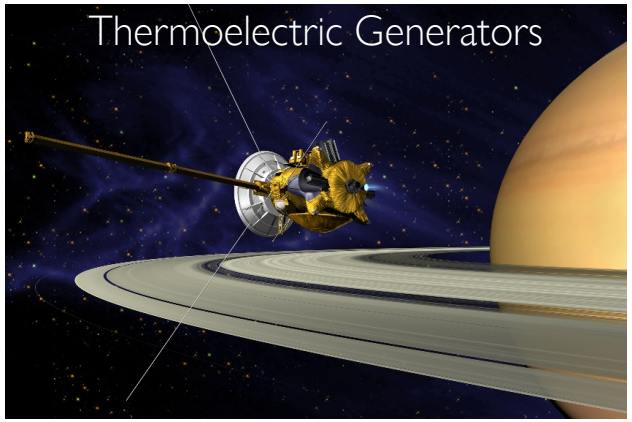
NASA's estimated cost to launch into low Earth orbit is approximately **$5000 per kilogram**

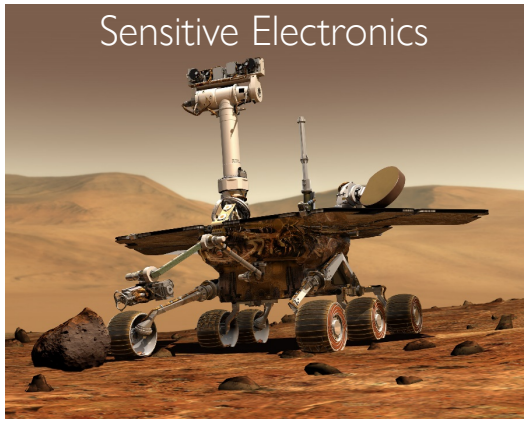
<u>For the Space Shuttle program</u>

10% reduction in mass of thermal protection system = $4,300,000 reduction in cost per launch

1) Lower thermal conductivity → improve insulative performance

2) Reduce mass and/or volume → reduce cost, improve payload capacity



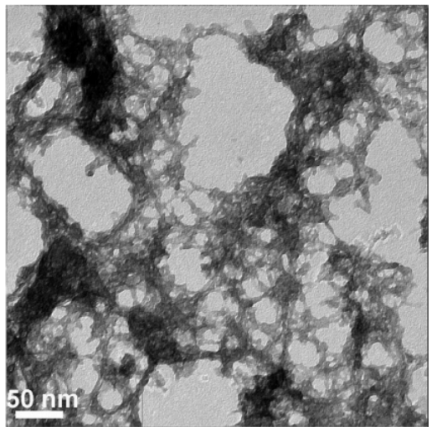


All images courtesy of NASA.

Aerogels are highly insulating and lightweight materials

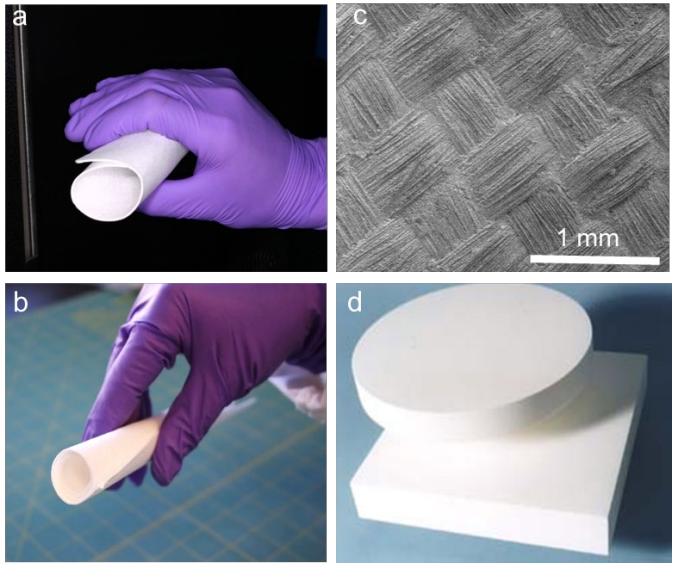
- High specific surface area (SSA), high porosity, and low density
  - **SSA**: 200 – 1000 m^2/g
  - **Porosity**: 90 – 99.9%
- Low thermal conductivity
  - Low as 0.009 W/(m•K) in atmosphere and 0.003 W/(m•K) under vacuum
  - Low density = Low solid conductivity
  - Pore sizes ≤ mean free path of gas = Low gas convection
- Versatile synthesis adaptable to a wide array of metal oxide compositions
- Incorporate ceramic fibers/felts/papers with aerogel to reinforce for insulation

Bunsen burner applied to aerogel (LANL)



Highly porous network of interconnected nanoparticles

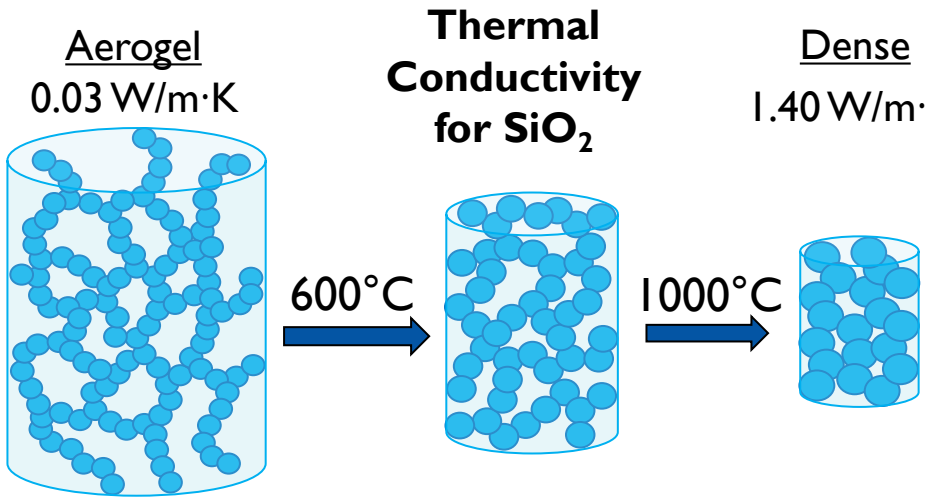
Highly porous structure of aerogel is responsible for its extremely low thermal conductivity.



Various aerogel composite materials using alumina or aluminosilicate reinforcements

Cohen, E., and Glicksman, L. (2015). *Journal of Heat Transfer*,137(8), 81601.
Sun, H., et al. (2013). *Advanced Materials*, 25(18), 2554-2560.
Gash, A.E., et al. (2001). *Journal of Non-Crystalline Solids*, 285(1-3): 22-28.

Collapse of pore structure and loss of favorable properties occurs upon exposure to high temperatures

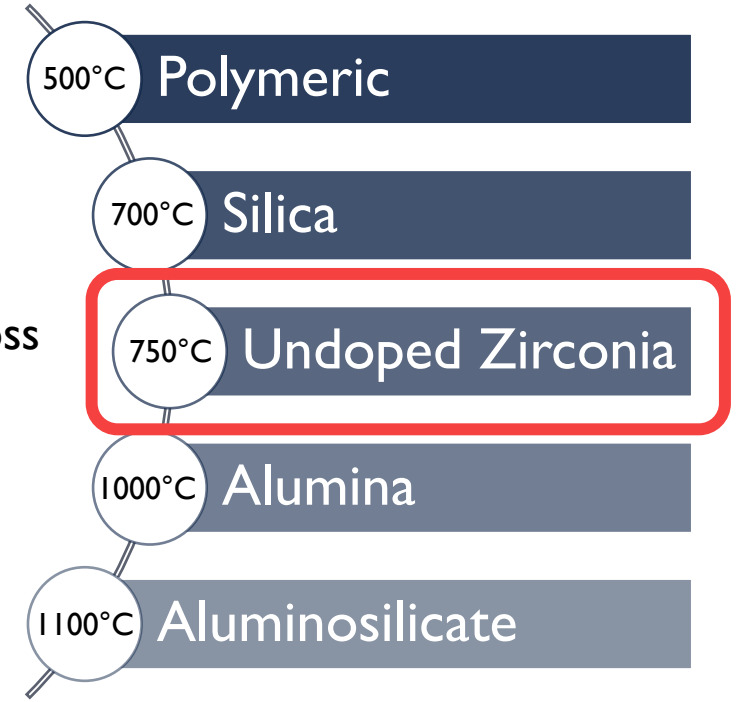


Loss of SSA, porosity

↑ thermal conductivity, cracking, and shrinkage

Large SSA & porosity contribute to driving force for densification

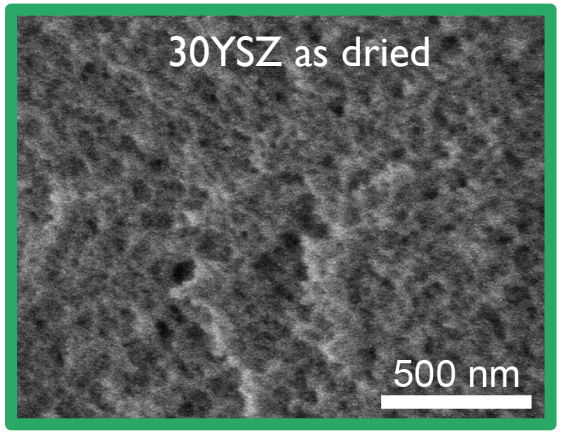
Rapid densification & loss of porosity beyond…

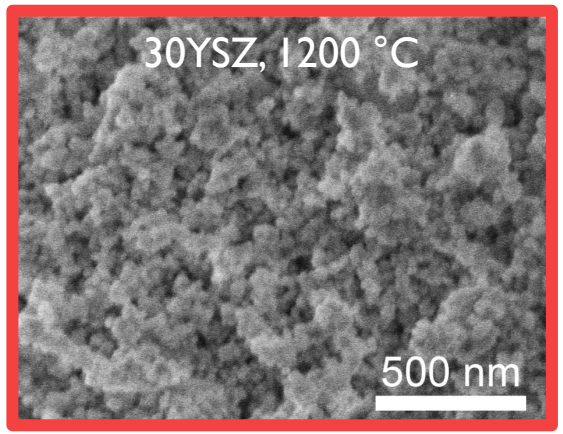


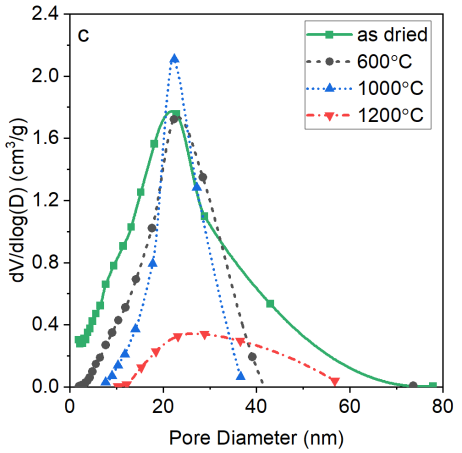
Powell, R.W., et al. (1966). NSRDS-NBS 8, 99.
Lide, D. R., ed; "Thermal conductivity", CRC Handbook of Chemistry and Physics (100th ed.).
Aegerter, M. (ed), (2011). *Aerogels Handbook*, Springer.

High yttria concentration improves thermal stability

1. **Reduces densification** of the pore structure (SEM, N_2 physisorption)

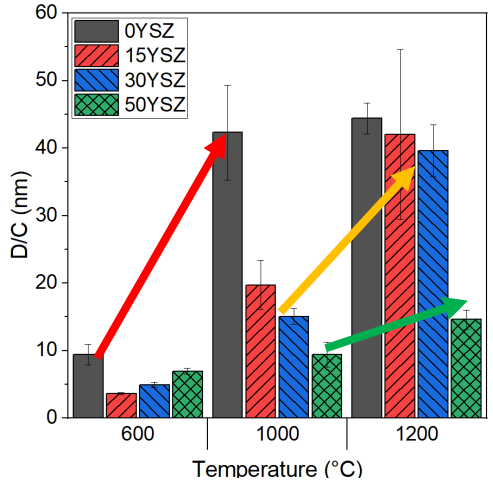






30YSZ pore size distribution

2. **Suppresses crystallite growth** to 1200 °C (XRD, TEM)



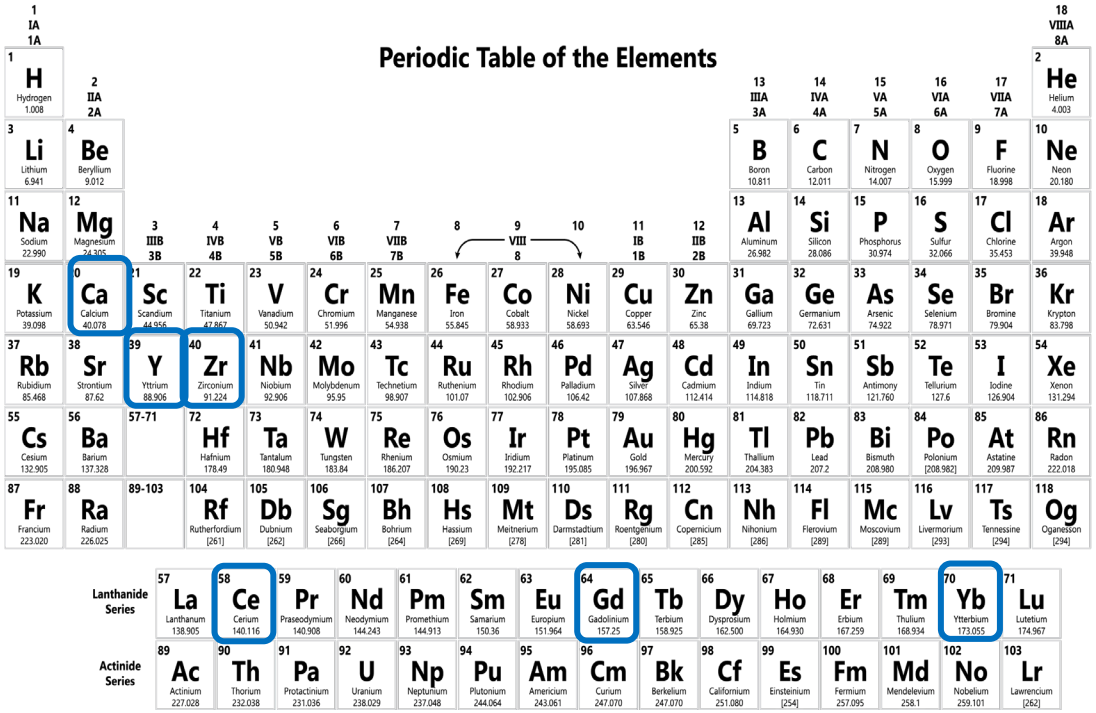
By what mechanism is yttria improving the thermal stability of the pore structure?

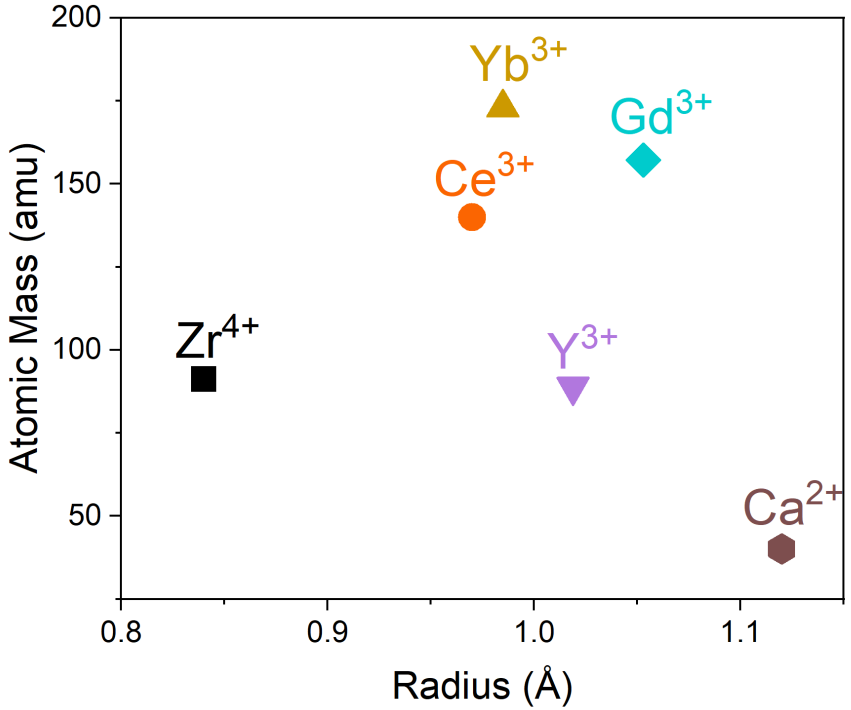
Thermodynamics
(Lower Surface Energy)

Kinetics
(Lower Cation Diffusivity)

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



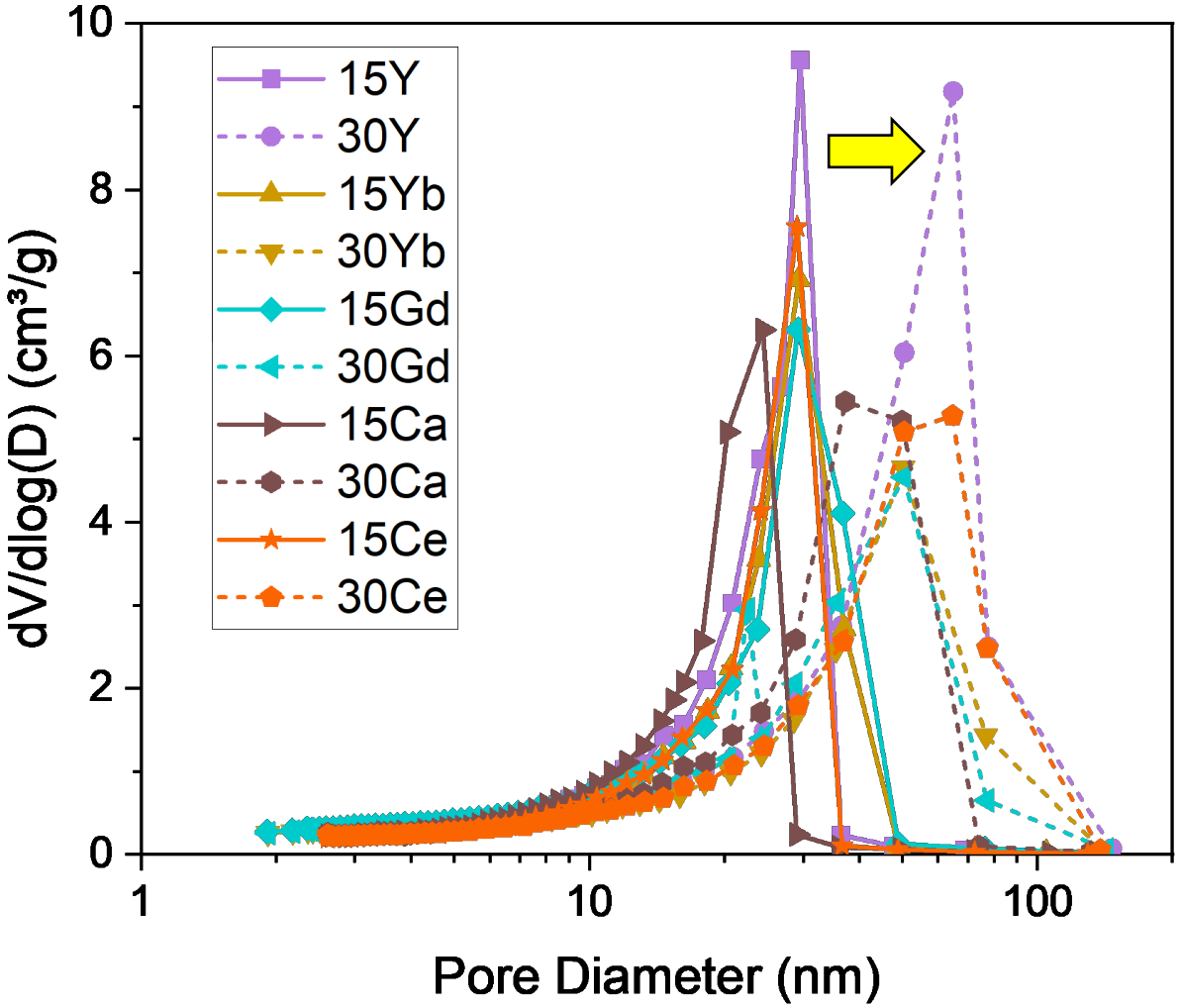


→ Modify thermal conductivity, surface energy and cation diffusivity

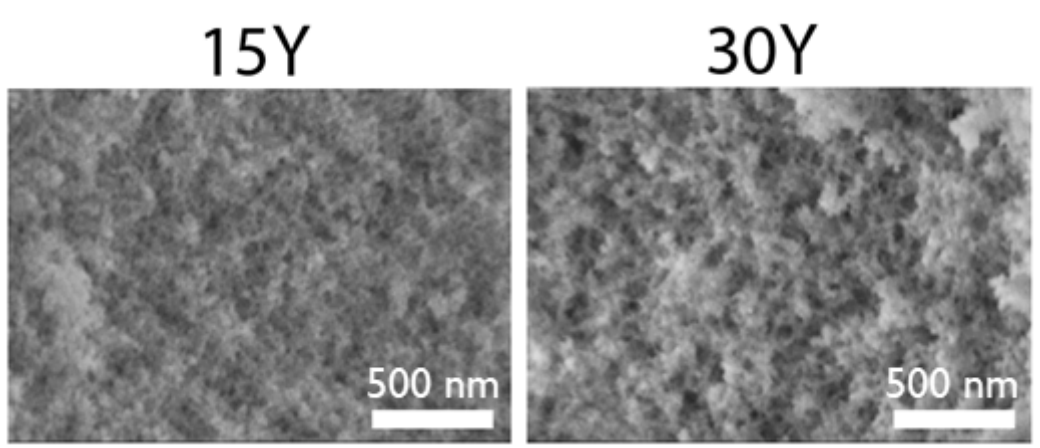
→ Connect **material properties** to changes in **structural evolution**

Atomic radii from http://www.mrl.ucsb.edu/~seshadri/Periodic/

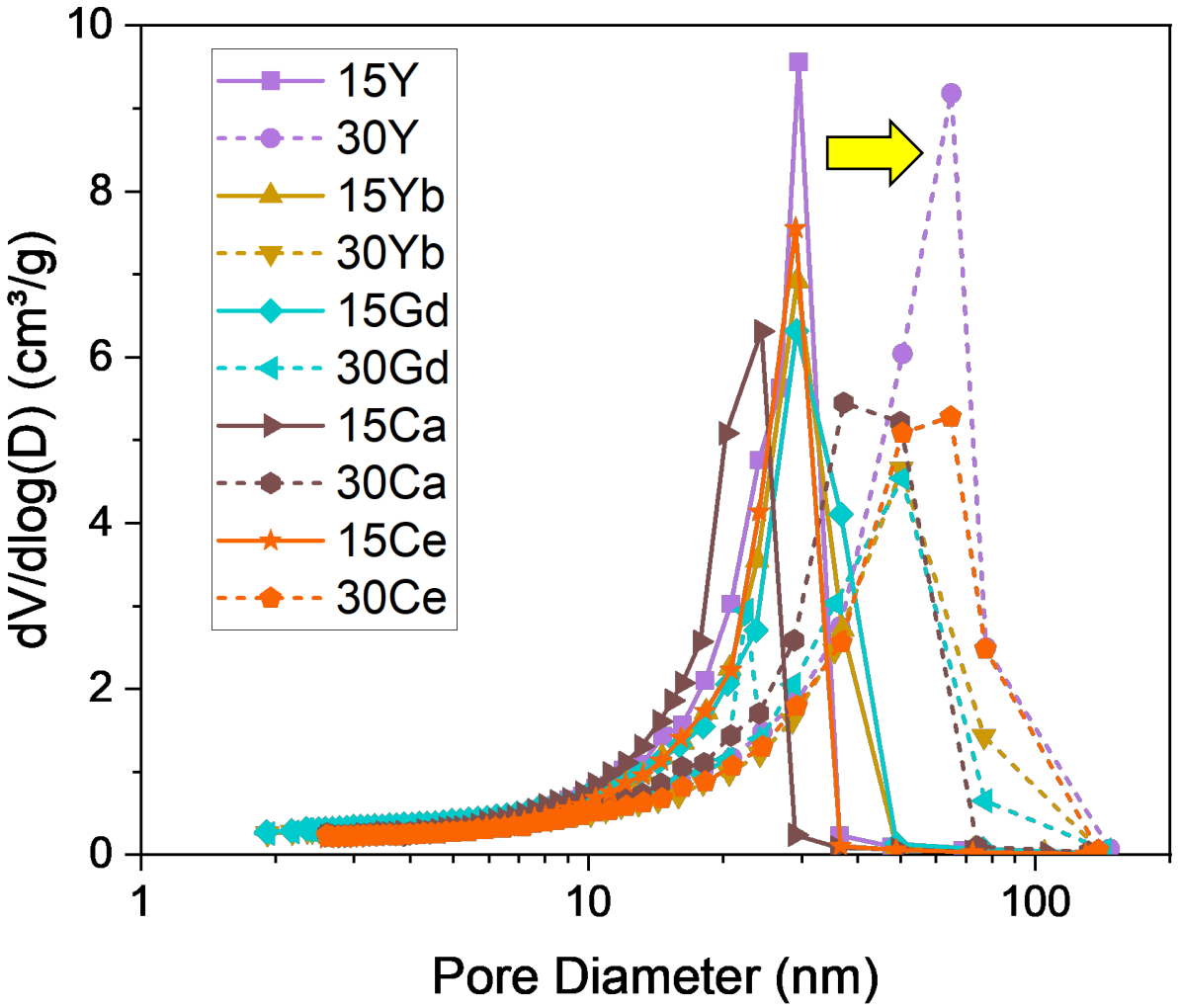
As dried structure characterized with nitrogen physisorption and SEM



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



Change in average metal oxidation state hypothesized to increase distribution breadth at 30 mol% dopant



From 15 to 30 mol% dopant we replace more Zr^{4+} with cations of lower charge

↓

Average metal oxidation state is decreased

↓

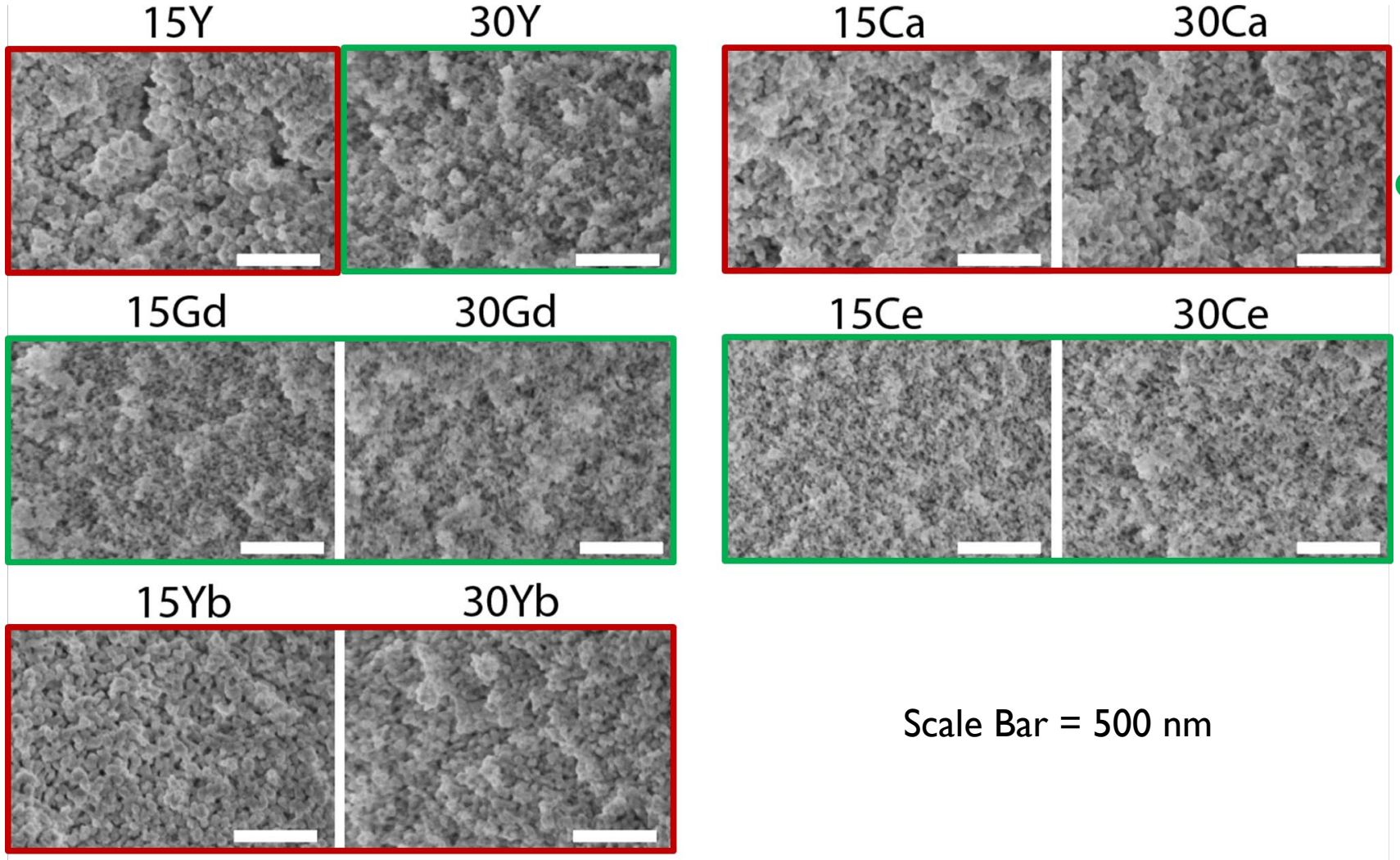
Average acidity of $[M(H_2O)_x]^{x+}$ is reduced

Reducing the acidity in turn slows down gel formation. This gives more time for nucleation and growth of particles in the sol.

Larger particles cannot pack as closely together, leading to broader pore size distributions with larger average pore size.

Clapsaddle, B., et al. (2004). *Journal of Non-Crystalline Solids*,350: 173-181.
Baes, C. and Mesmer, R. (1976). "The Hydrolysis of Cations", Wiley-Interscience.

Pore structure stability to 1000 °C appears to be dependent on dopant identity & amount



Scale Bar = 500 nm

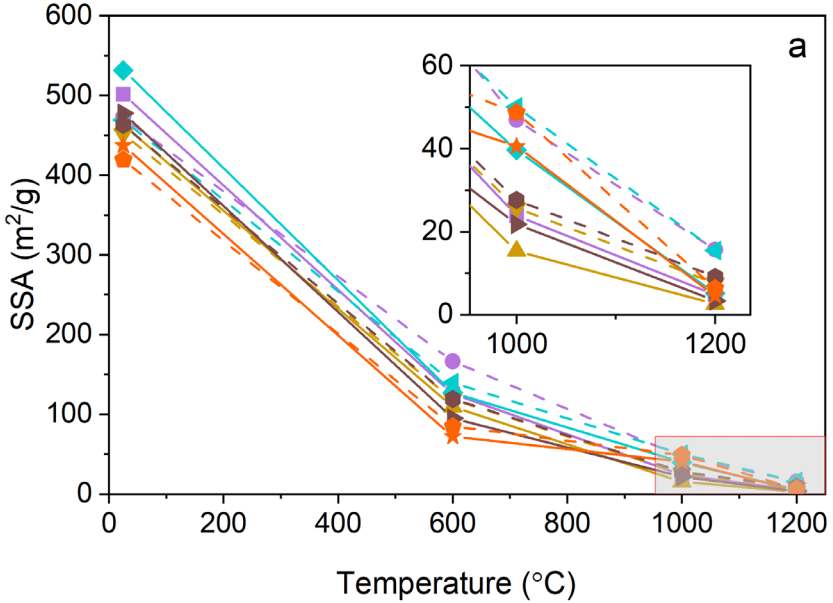
Red: increased particle size and reduction of mesoporosity.
Green: mesoporous structure maintained.

Larger set of samples & temperatures requires quantifiable criteria for "thermally stable" aerogels

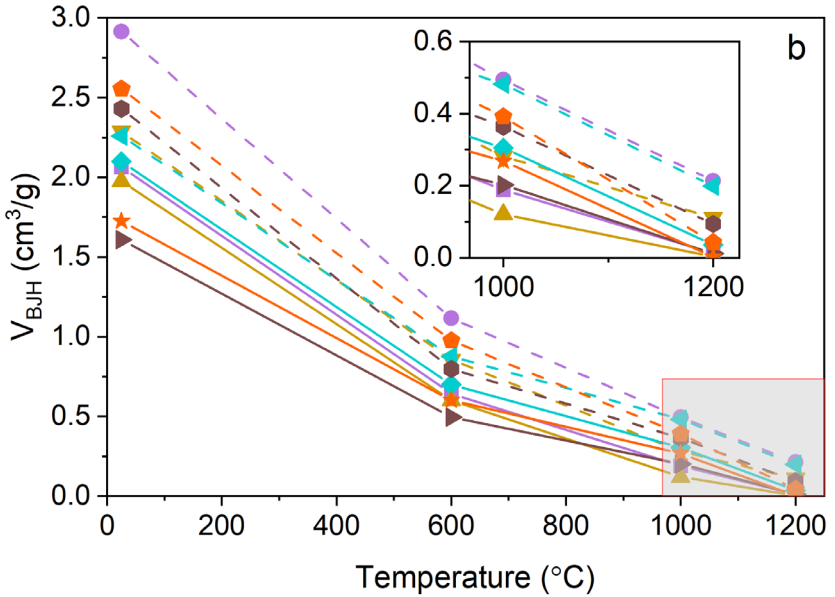
Bulk of the work on this study lies in developing these metrics of thermal stability

Evaluation of pore structure with nitrogen physisorption quantifies change in performance

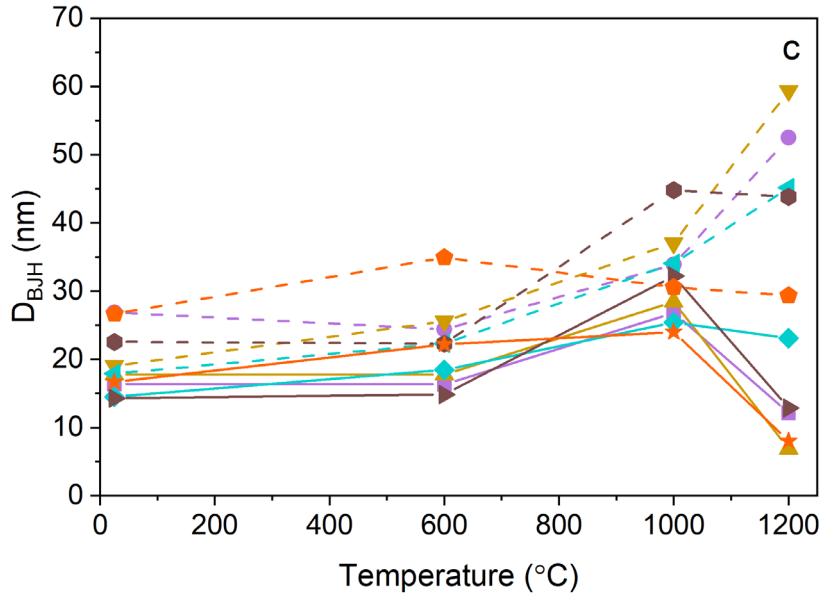
SSA

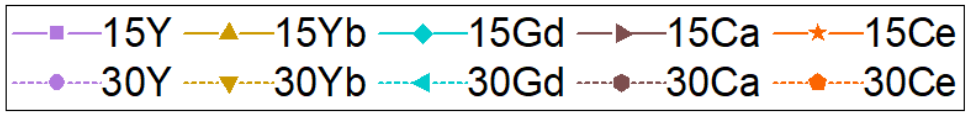


Pore Volume



Pore Size





<u>Best Performers*</u>

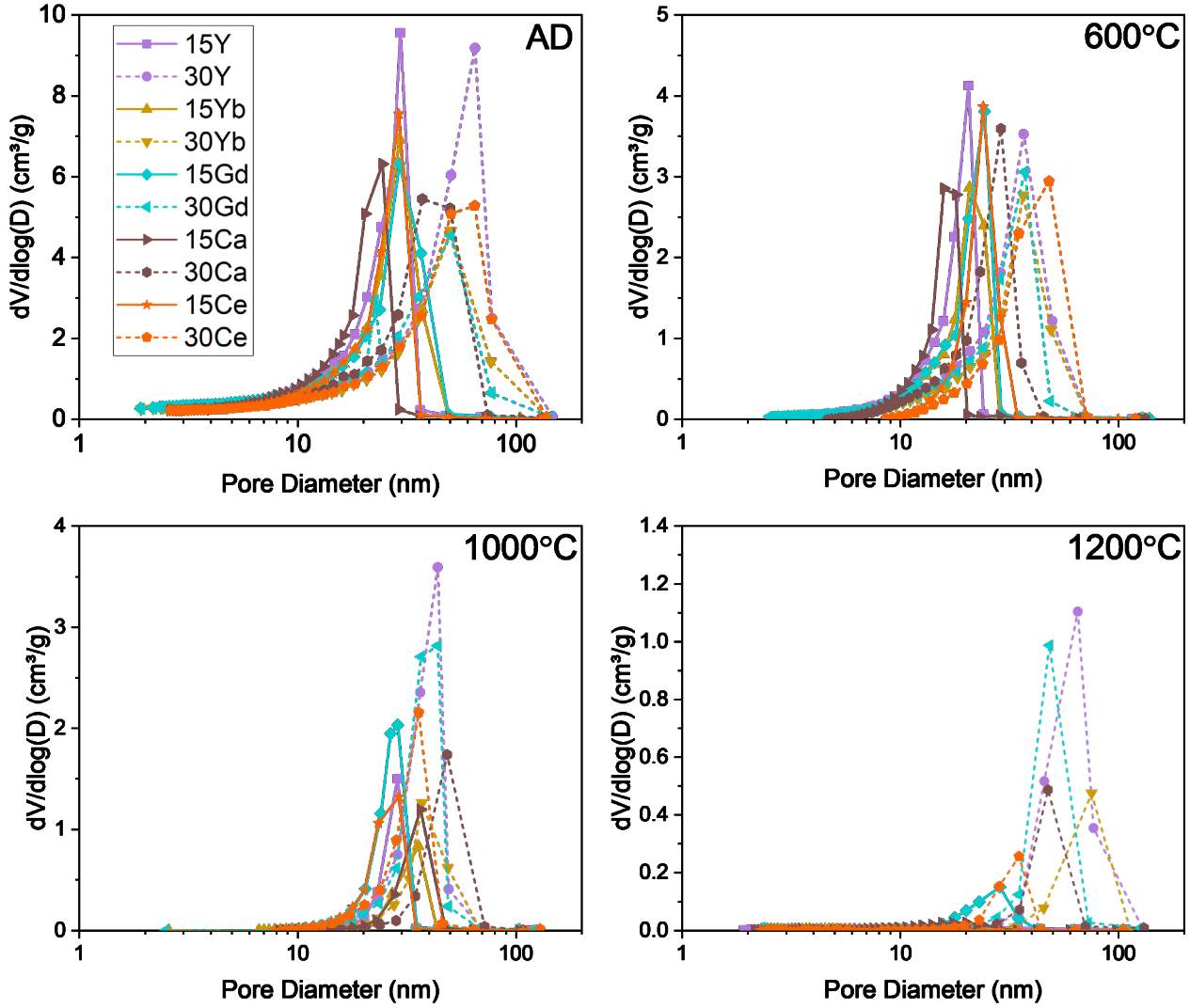
1000 °C: 30Y, 30Gd, 30Ce

1200 °C: 30Y, 30Gd

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

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



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

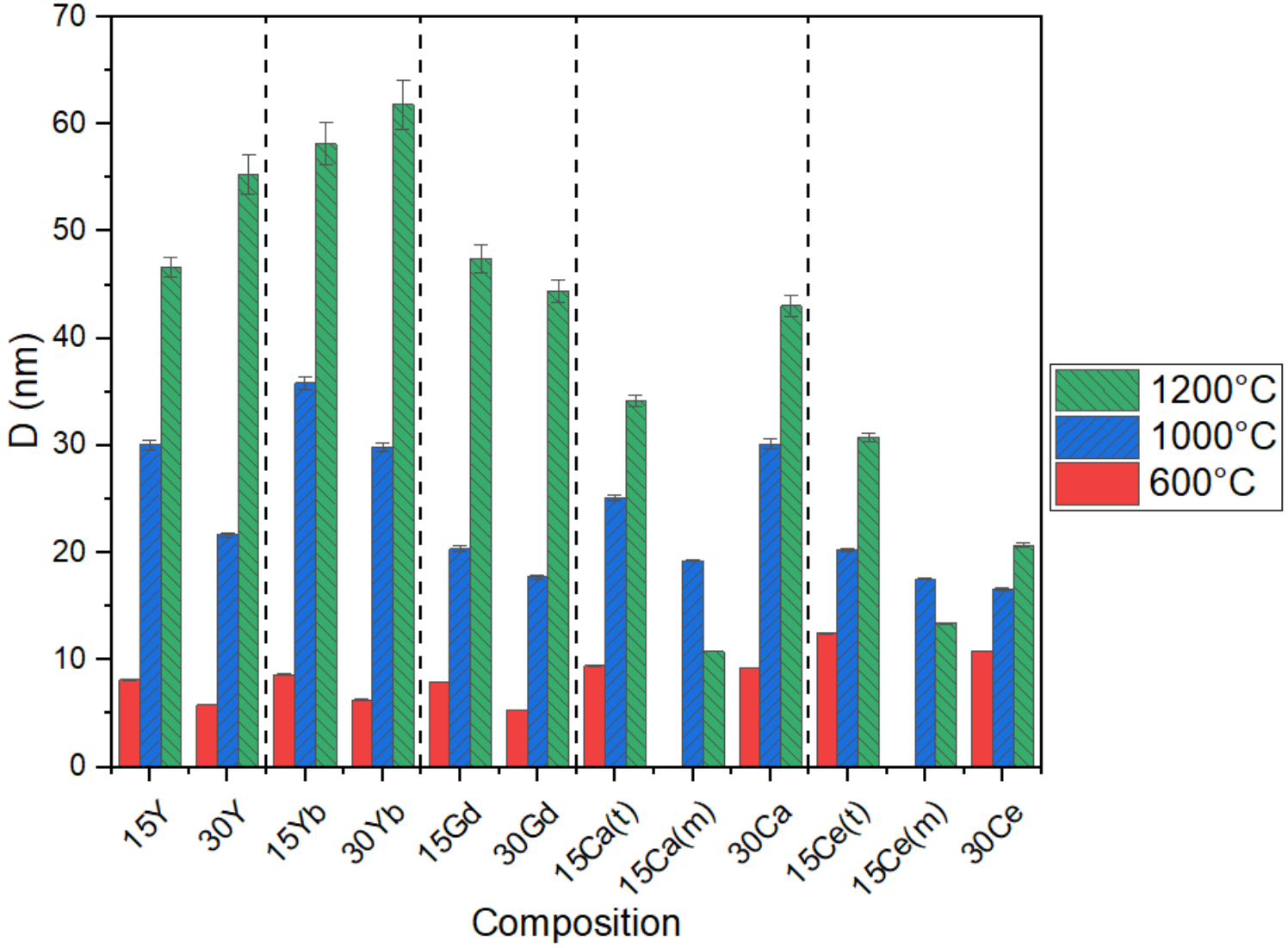
At 1000 and 1200 °C, it becomes apparent 30 mol% MO_x maintains more porosity. Gd and Y perform the best.

Crystallite growth quantified as a function of dopant identity and concentration

Trivalent dopants (Y, Yb, Gd) all maintain a single cubic phase at 15 and 30 mol%

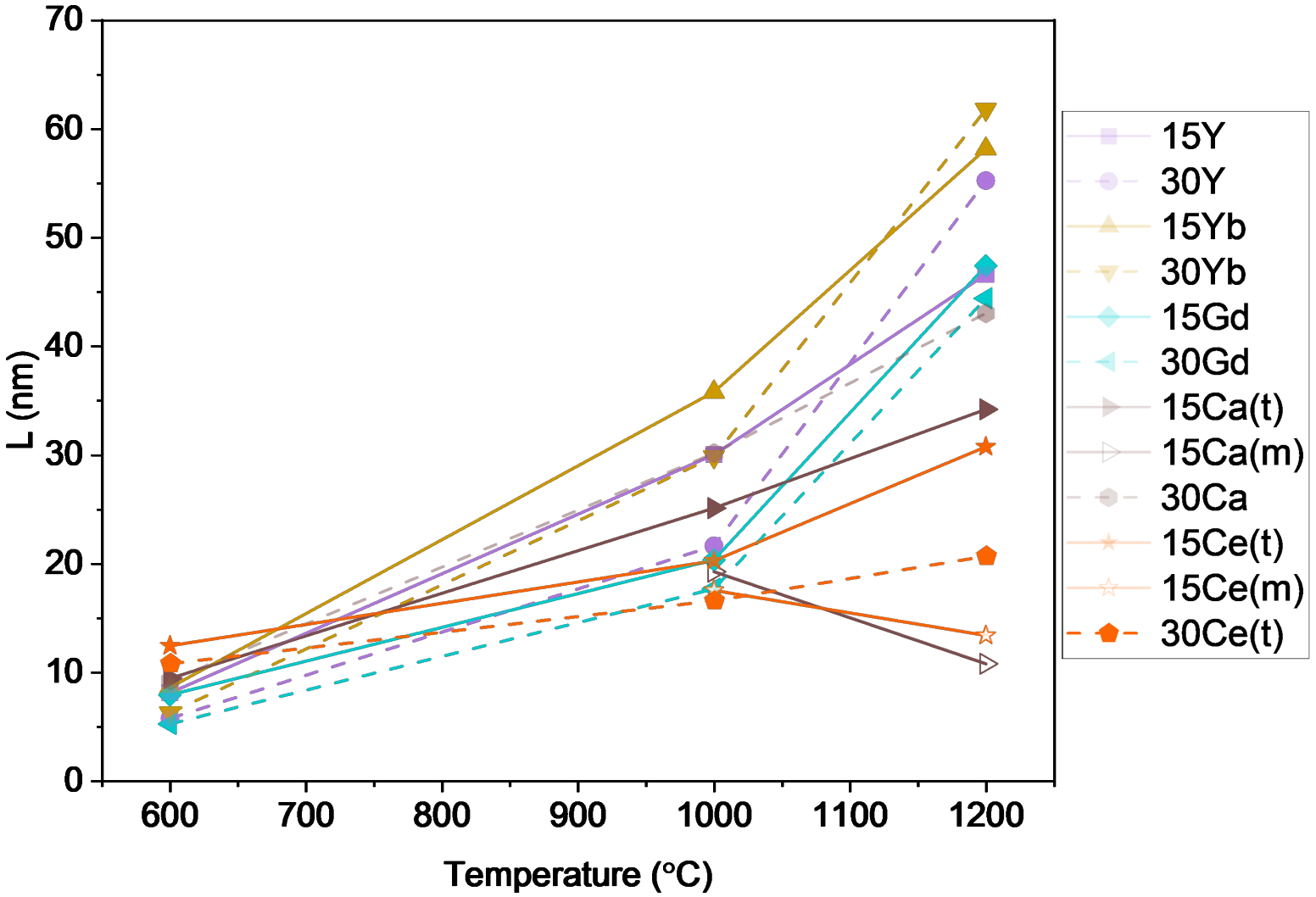
15Ca and 15Ce contain mixed tetragonal and monoclinic phases

30Ca is cubic and
30Ce is tetragonal



Rietveld refinement performed in GSASII. Phase assumed to be cubic unless otherwise indicated.

Crystallite growth quantified as a function of dopant identity and concentration



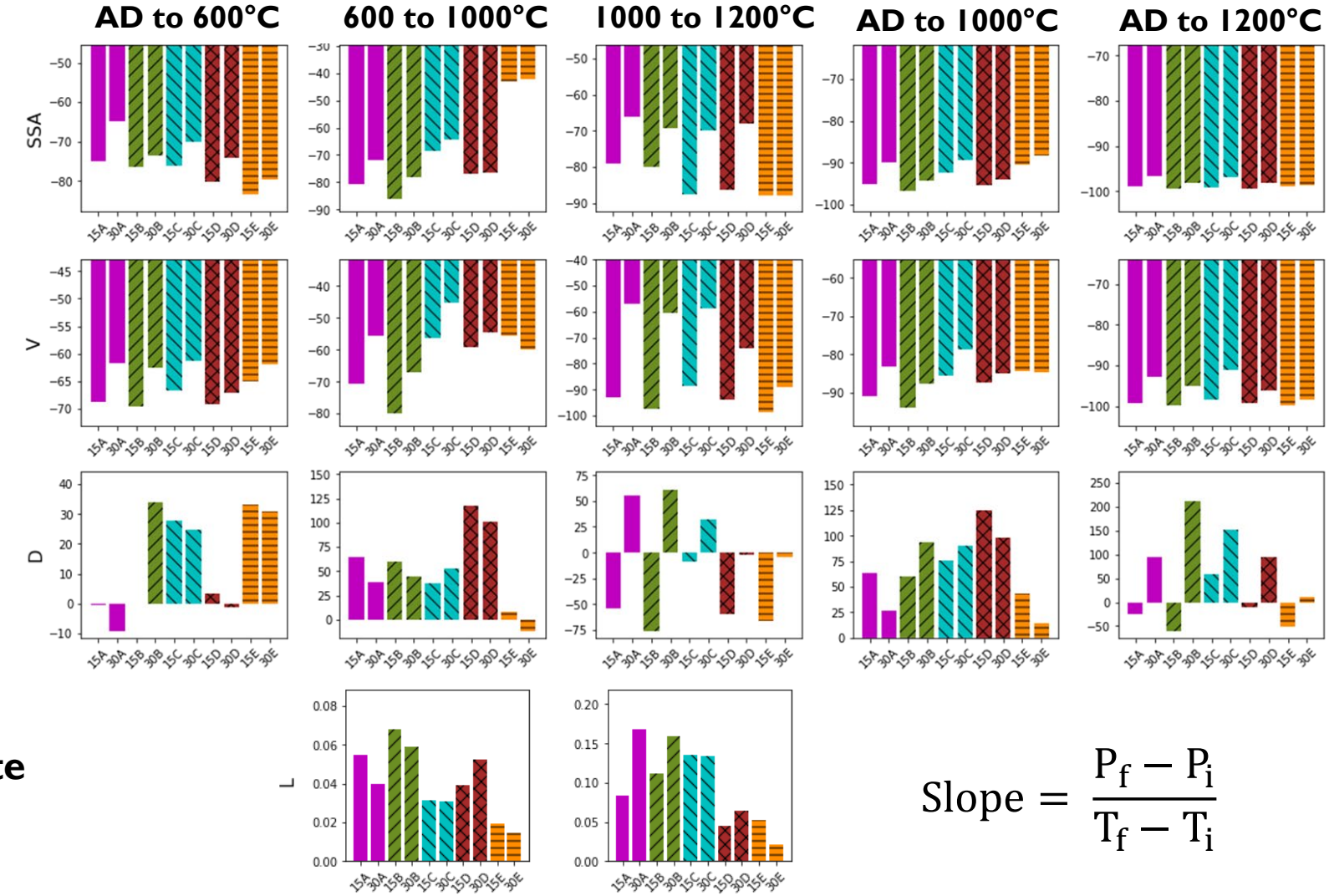
Notable similarity in all trivalent dopants (Y, Yb, Gd) at both 15 and 30 mol%

Gd < Y < Yb

Samples that form mixed tetragonal and monoclinic phases (15Ca, 15Ce) maintain small crystallite size, but have low phase stability, which can lead to structure collapse

30Ce maintains a single phase and the smallest crystallite size (by far!) to 1200 °C

Evaluation of relative stability via percent change and slope of properties as function of temperature



$$\% \text{ Change} = \frac{P_f - P_i}{P_i} \times 100\%$$

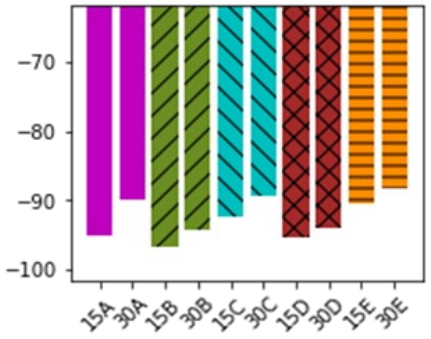
A = Y
B = Yb
C = Gd
D = Ca
E = Ce

$$\text{Slope} = \frac{P_f - P_i}{T_f - T_i}$$

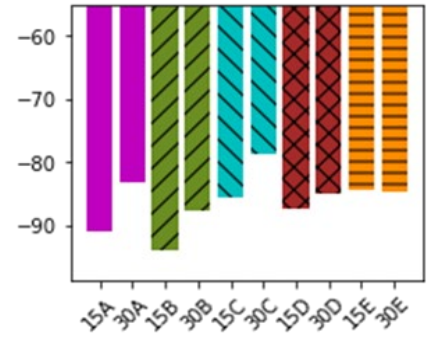
Evaluation of relative stability via percent change and slope of properties as function of temperature

AD to 1000°C

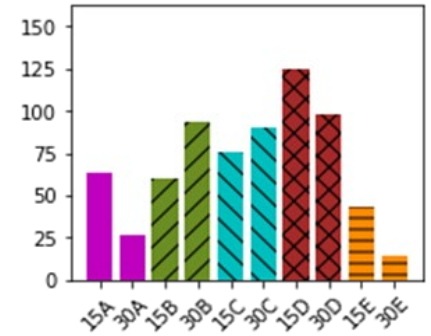
Specific Surface Area



Pore Volume



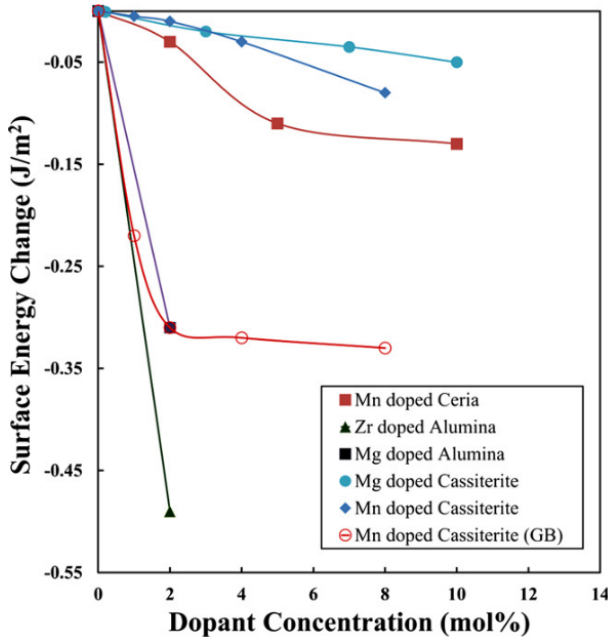
Pore Size

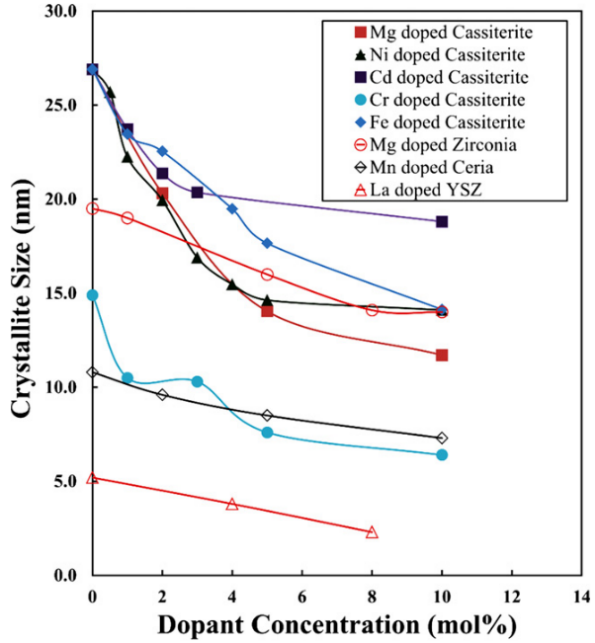


A = Y
B = Yb
C = Gd
D = Ca
E = Ce

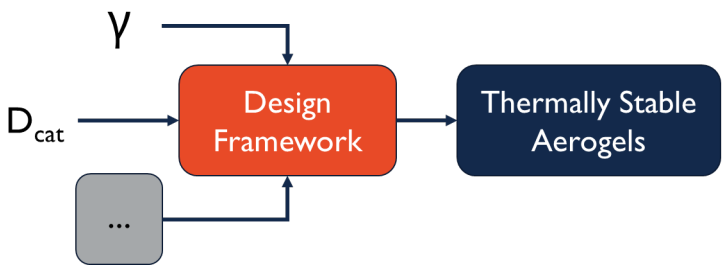
Increased dopant concentration leads to reduced densification.

Work in the field of nanocrystalline ceramics suggests dopants can segregate to surfaces, pinning grain boundaries and reducing surface energies and thereby reducing rates of sintering and densification.





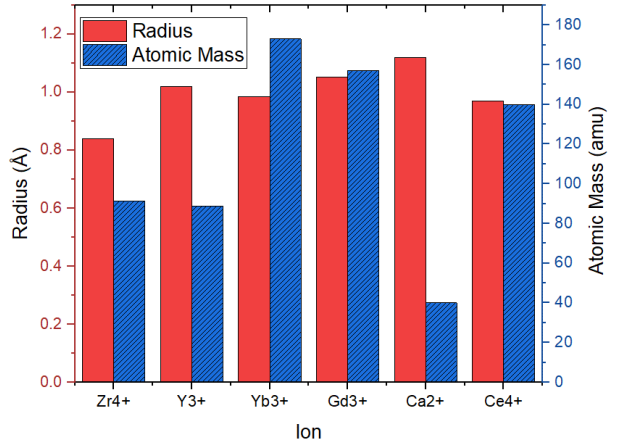
Connecting material properties to thermal stability



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

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



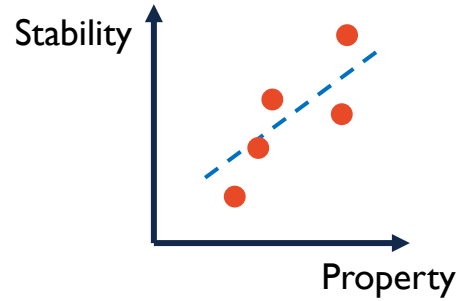
Next, we calculated a weighted average for each material

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

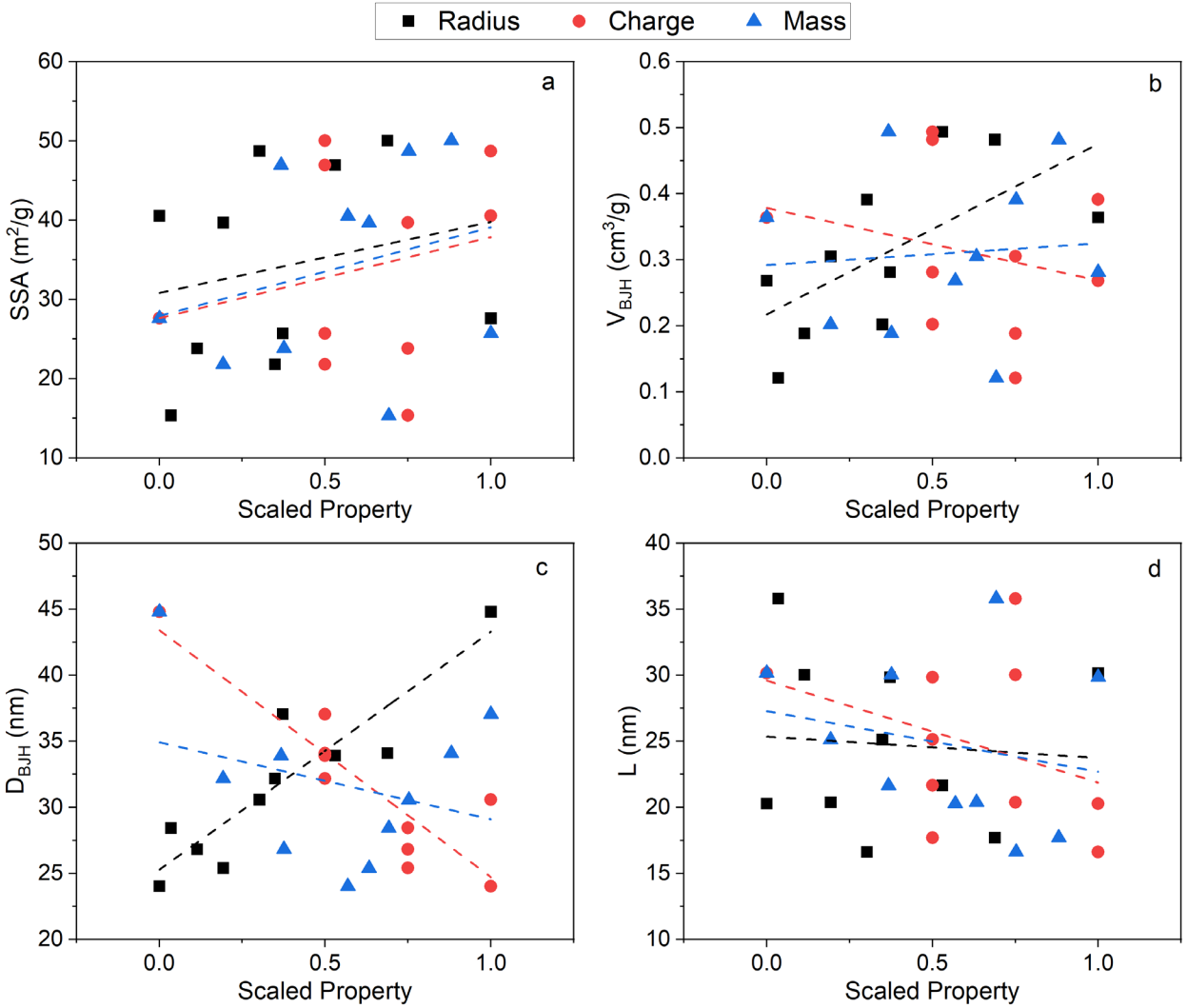
x_M = mole fraction MO_y

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

We then performed linear regression on the absolute (SSA, V, D, L at a given temperature) and relative (percent change) thermal stability.



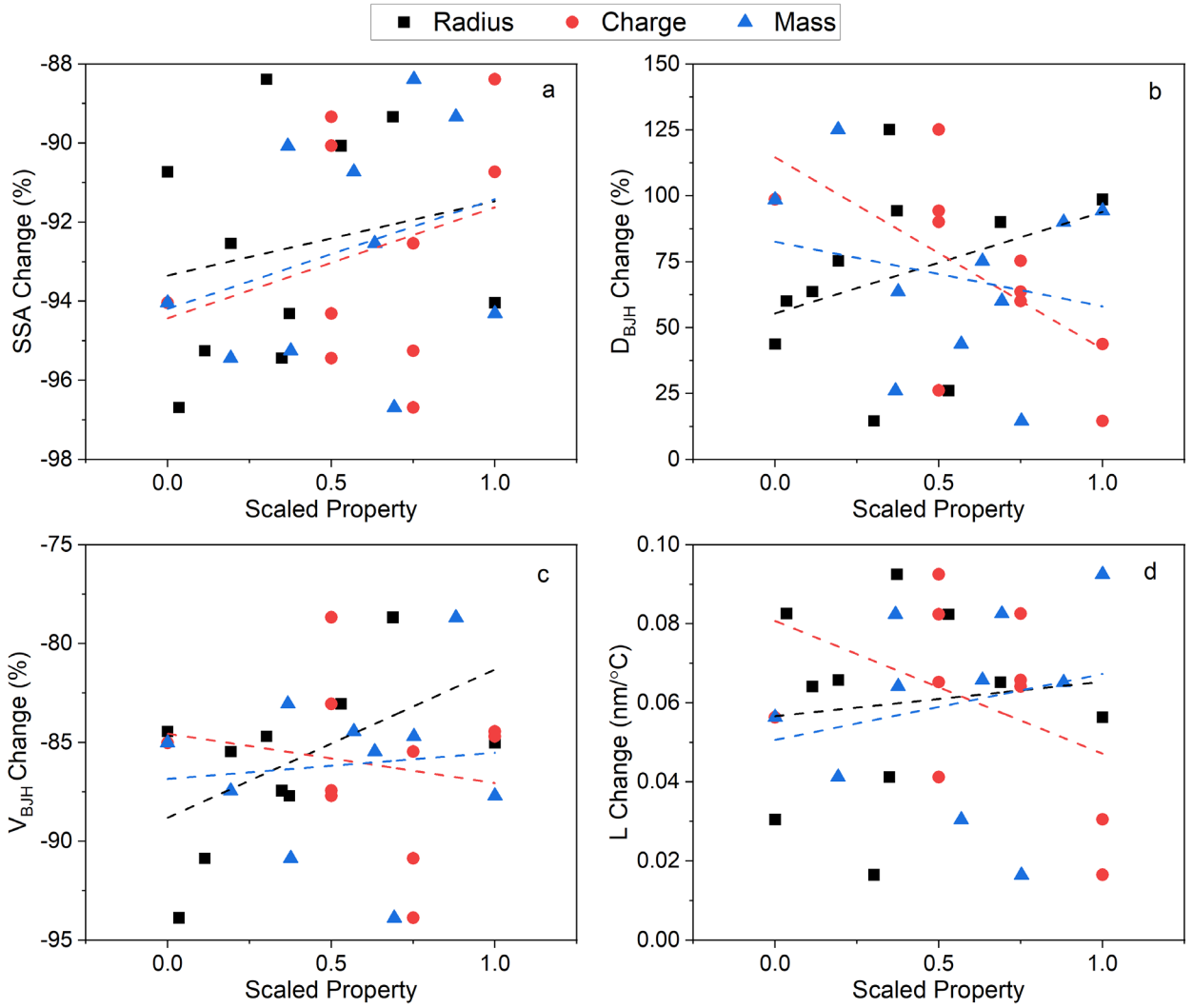
Cation properties are not clearly related to **absolute** or relative stability



Property	Response		p-value
Radius	SSA	1000	0.54
Charge			0.50
Mass			0.44
Radius	V	1000	0.04
Charge			0.47
Mass			0.8
Radius	D	1000	3.0E-04
Charge			5.9E-04
Mass			0.41
Radius	L	1000	0.83
Charge			0.31
Mass			0.54

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

Cation properties are not clearly related to absolute or **relative** stability

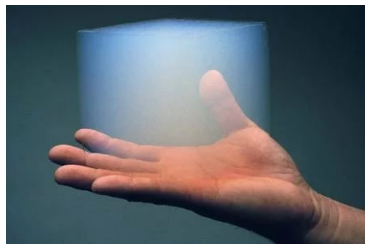


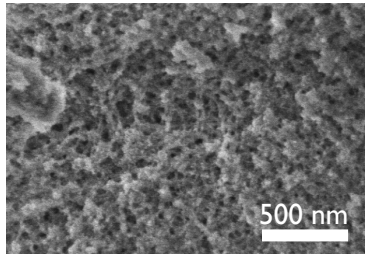
Property	Response		p-value
Radius	% SSA	AD to 1000	0.57
Charge			0.42
Mass			0.40
Radius	%V	AD to 1000	0.09
Charge			0.63
Mass			0.79
Radius	% D	AD to 1000	0.32
Charge			0.06
Mass			0.54
Radius	Slope L	600 to 1200	0.76
Charge			0.24
Mass			0.55

SSA, D, and V are percent change from AD to 1000 °C
L is slope from 600 to 1200 °C

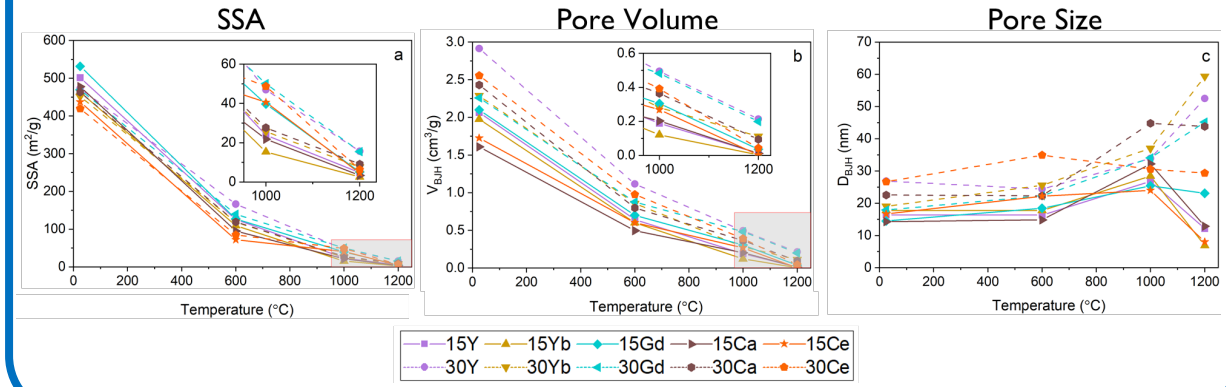
Summary

1. Aerogels are promising candidates for light weight, highly insulating materials in next-gen aerospace applications, but pore structure must be preserved to temperatures ≥ 1200 °C



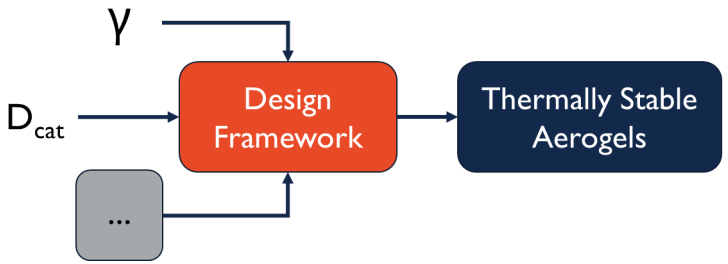


2. Increased dopant concentration from 15 to 30 mol% M/(M+Zr) reduces densification of the pore structure, with Gd and Y performing best.



Looking Forward

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



2. Considering the magnitude of improvements achieved by tuning composition, other routes beyond doping may be necessary to achieve thermal stability to temperatures ≥ 1200 °C

3. Evaluation of new synthetic routes to aerogels with dramatically different chemistries and structures that offer improved thermal stability.

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- Dr. Frances Hurwitz (NASA GRC, retired)
- Jordan Meyer (UIUC MatSE U-Grad)
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- SCS Microanalysis Laboratory, UIUC
- NASA Glenn Research Center

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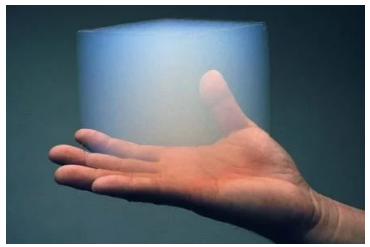
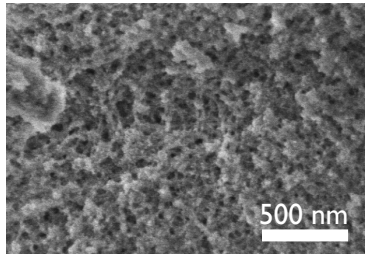
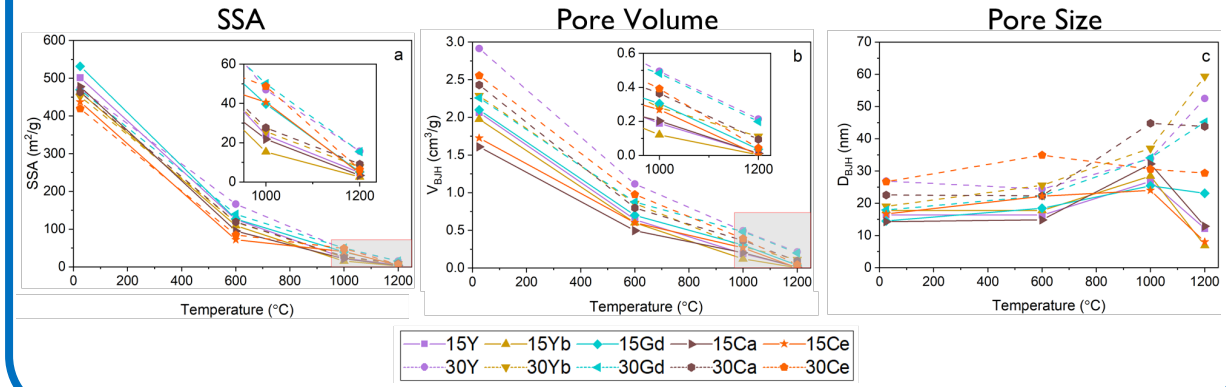
1. Aerogels are promising candidates for light weight, highly insulating materials in next-gen aerospace applications, but pore structure must be preserved to temperatures ≥ 1200 °C



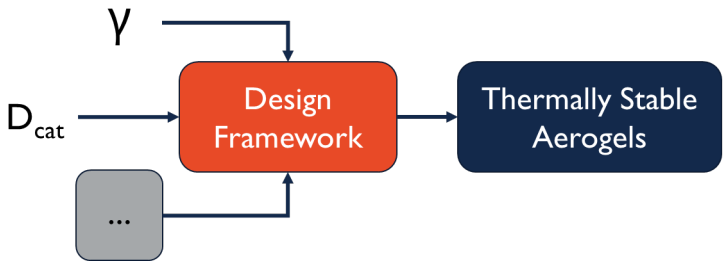


2. Increased dopant concentration from 15 to 30 mol% M/(M+Zr) reduces densification of the pore structure, with Gd and Y performing best.



Looking Forward

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



2. Considering the magnitude of improvements achieved by tuning composition, other routes beyond doping may be necessary to achieve thermal stability to temperatures ≥ 1200 °C

3. Evaluation of new synthetic routes to aerogels with dramatically different chemistries and structures that offer improved thermal stability.

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