

The Influence of Yttria Content on the Thermal Stability of Yttria-Stabilized Zirconia Aerogels

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MS&T 2020: Synthesis, Characterization, Modeling, and Applications of Functional Porous Materials

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Development of lightweight, high performance insulation for aerospace applications



NASA's estimated cost to launch into low Earth orbit (LEO) is approximately **\$5000 per kilogram.**



For the Space Shuttle program

10% reduction in mass of thermal protection system =

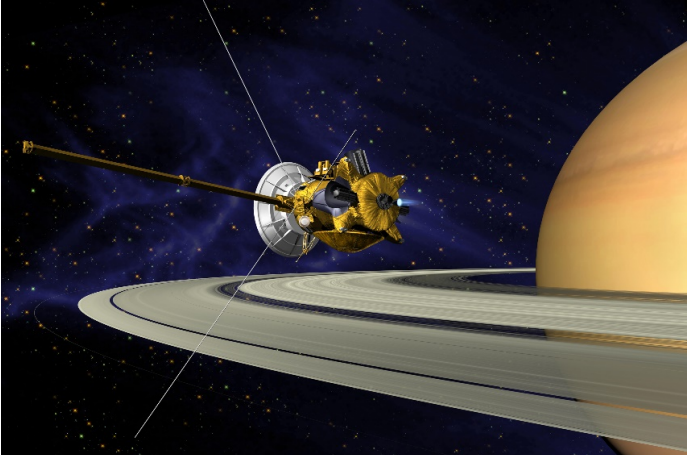
\$4,300,000 reduction in cost per launch

Aims for future:

- 1) Lower thermal conductivity → improve performance
- 2) Reduce mass and/or volume → reduce cost



Orion capsule: provide insulation for use in seals for doors & panels



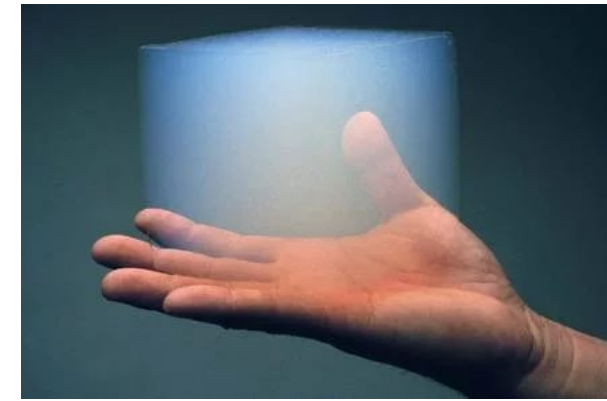
Deep space probes: thermoelectric generators insulated to prevent heat loss & sublimation



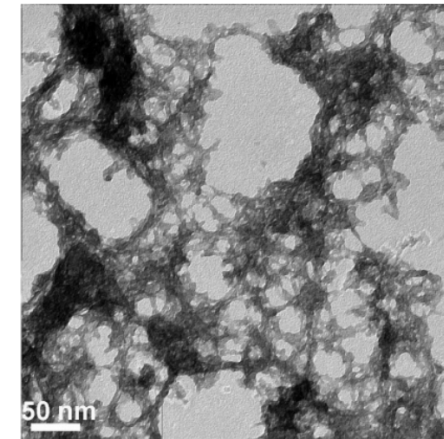
Missions to the Moon & Mars: lightweight insulation to reduce cost and increase payload capability

Aerogels are highly insulating and lightweight materials

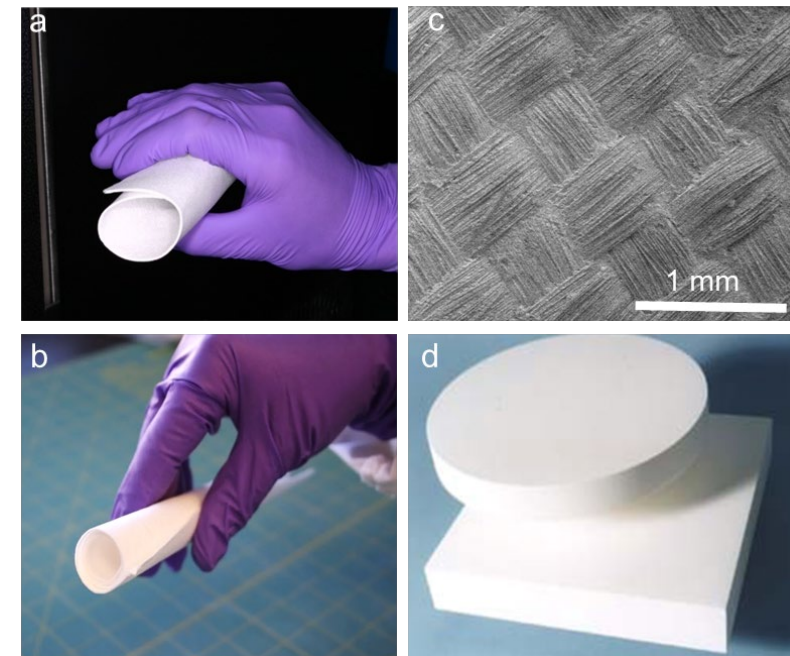
- Low thermal conductivity
 - Low as 0.009 W/(m•K) in atmosphere and 0.003 W/(m•K) under vacuum
- High specific surface area (SSA), high porosity, and low density
 - SSA:** 200 – 1000 m²/g
 - Porosity:** 90 – 99.9%
 - Density:** As low as 0.00016 g/cm³
- Versatile synthesis adaptable to a wide array of metal oxide compositions
 - Metal salts & epoxide gelation agent
- Incorporate ceramic fibers/felts/papers with aerogel to reinforce for insulation



Silica aerogel block (NASA JPL)



Highly porous network of interconnected nanoparticles



Various aerogel composite materials using alumina or aluminosilicate reinforcements

Cohen, E., and Glicksman, L. *Journal of Heat Transfer*, **2015**, 137(8), 81601.

Sun, H., et al. *Advanced Materials*, **2013**, 25(18), 2554-2560.

Gash, A.E., et al. *Journal of Non-Crystalline Solids*, **2001**, 285(1-3): 22-28.

Low thermal conductivity arises from the highly porous aerogel structure

- Heat Transfer =
 - Solid Conductivity
 - + Gas Convection
 - + Radiative Transmission
- Low density = **Low solid conductivity**
 - Complex solid network creates a tortuous path for heat transfer and decreases sectional area
 - Also controlled by composition
- Pore sizes \leq mean free path of gas = **Low gas convection**
 - Prevents transport of gas molecules through aerogel
- Opacifier (e.g. TiO_2) can lower radiative transmission if desired



Bunsen burner applied to aerogel (LANL)

Low thermal conductivity arises from the highly porous aerogel structure

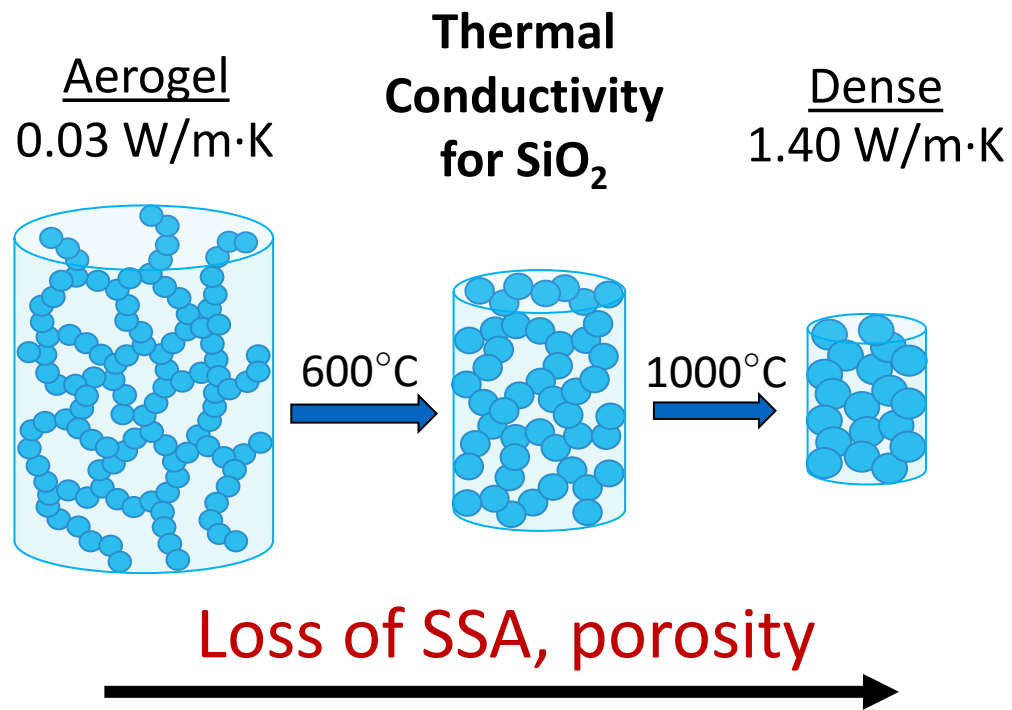
- Heat Transfer =
 - Solid Conductivity
 - + Gas Convection
 - + Radiative Transmission
- Low density = **Low solid conductivity**
 - Complete a tortuous path and de
 - Also controlled by composition
- Pore sizes \leq mean free path of gas = **Low gas convection**
 - Prevents transport of gas molecules through aerogel
- Opacifier (e.g. TiO_2) can lower radiative transmission if desired

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



Bunsen burner applied to aerogel (LANL)

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



- Extremely high surface areas as synthesized
- High surface energy provides large driving force for sintering & densification
- Detrimental to favorable aerogel properties

Composition	Sufficient porosity to... (°C)
SiO ₂	700
Al ₂ O ₃	900
Al ₂ O ₃ -Y ₂ O ₃	1000
Al ₂ O ₃ -SiO ₂	1100

Project Objective

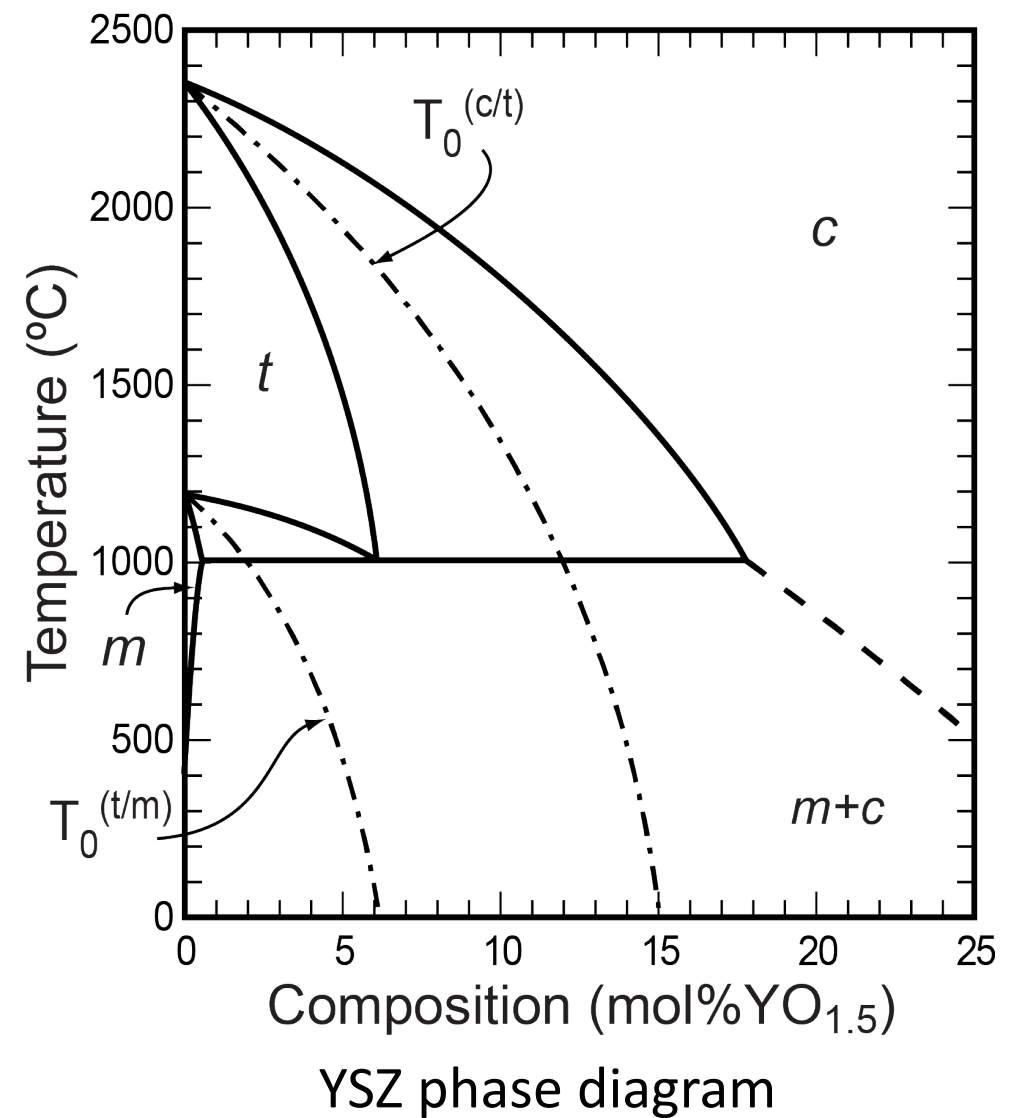
Develop aerogel to maintain **porosity** and **surface area** at high temperatures ($\geq 1200^\circ\text{C}$) for use as insulation in next-gen aerospace applications

Yttria-Stabilized Zirconia (YSZ) as a candidate composition for a thermally stable aerogel

- **Thermal barrier coatings** → YSZ is a ceramic used in thermal insulating layers on super alloys in aircraft engines → $\text{ZrO}_2\text{-Y}_2\text{O}_3$
- **Low thermal conductivity** → 0.8-2.9 W/(m·K)
- Inhibit zirconia phase transformations by substitution of Zr^{4+} with Y^{3+}
- Questions to answer: how does yttria content affect as-dried structure, phase behavior, and structural evolution?

Selected compositions for study:

0, 15, 30, and 50 mol% $\text{YO}_{1.5}$



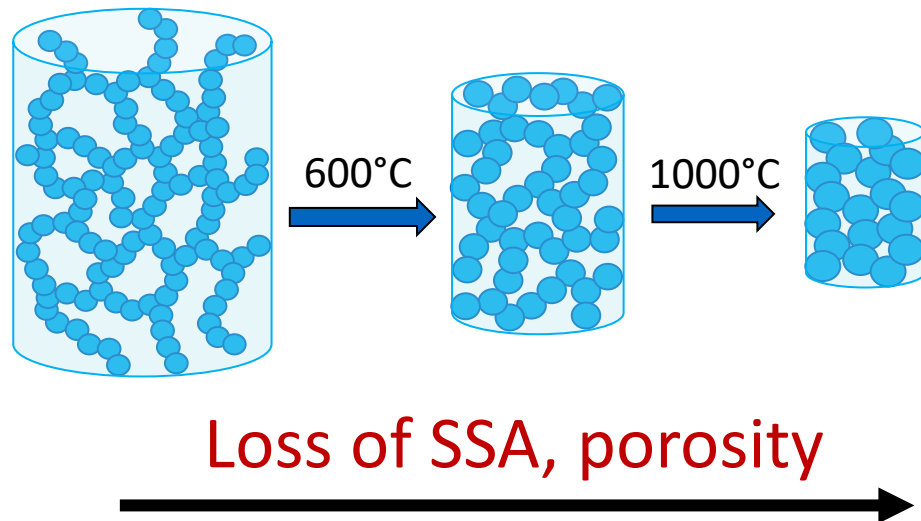
Hurwitz, F.I., *et al*; *J. Am. Cer. Soc.*, **2020**, accepted. →

Yb_2O_3 and Y_2O_3 below 20 mol% $\text{MO}_{1.5}$

Measuring an aerogel's performance in extreme environments

Properties measured as dried and following heat treatments at **600, 1000, or 1200 °C** (1112, 1832, or 2192 °F) with an 18-minute hold for each temperature

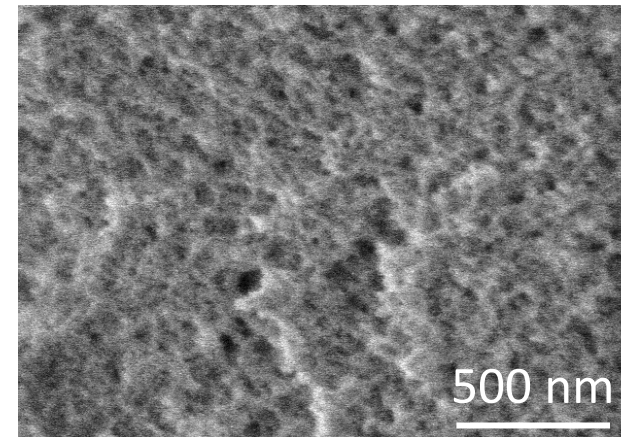
Specific Surface Areas & Pore Size Distribution



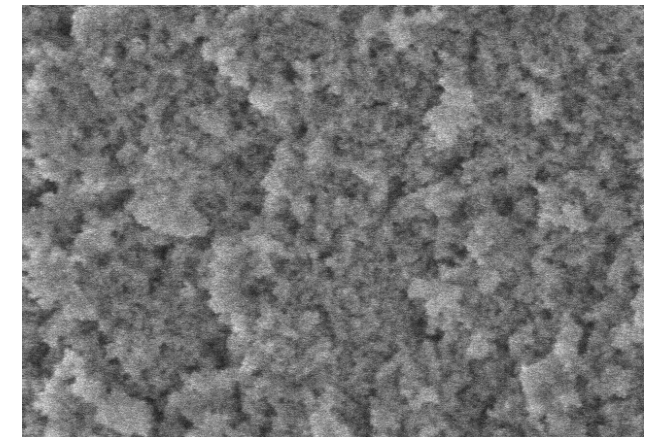
- Combat shrinkage & densification
- Maintain high SSA at high temperatures
- Maintain constant pore size distribution
- Measure with N₂ physisorption

Microstructural Evolution

As Synthesized

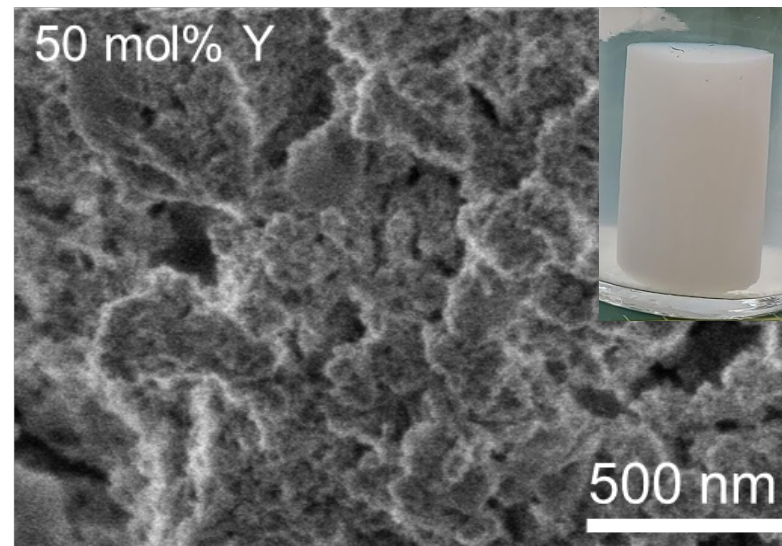
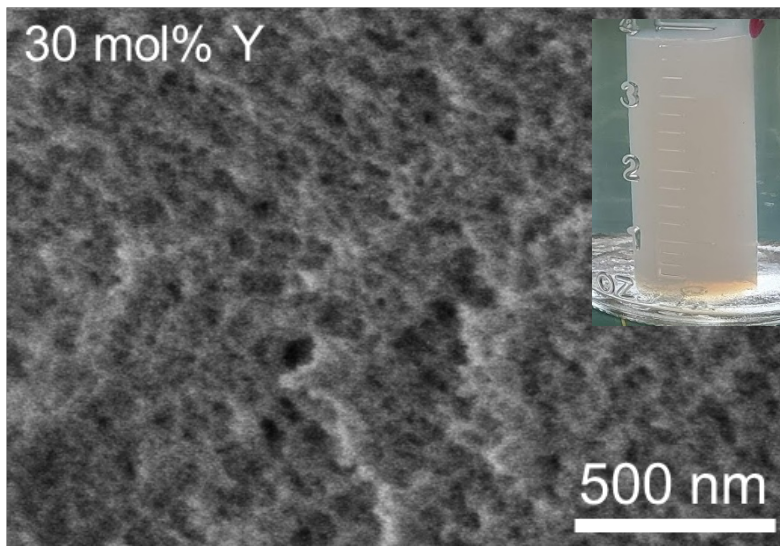
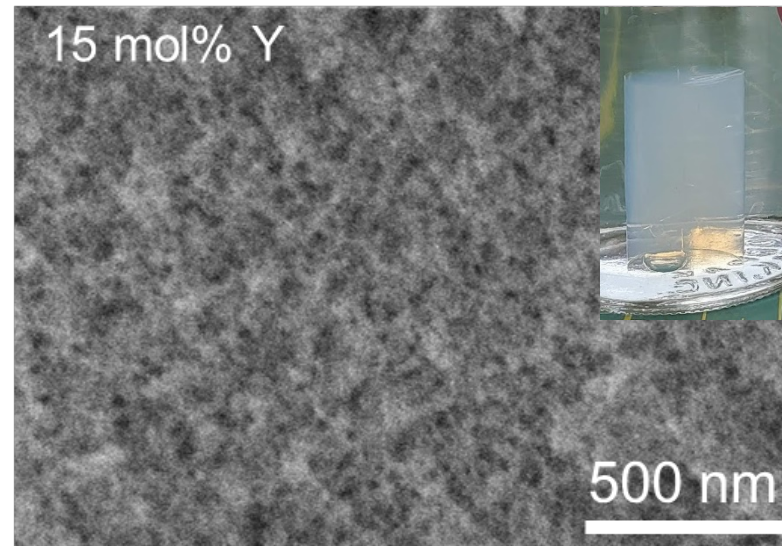
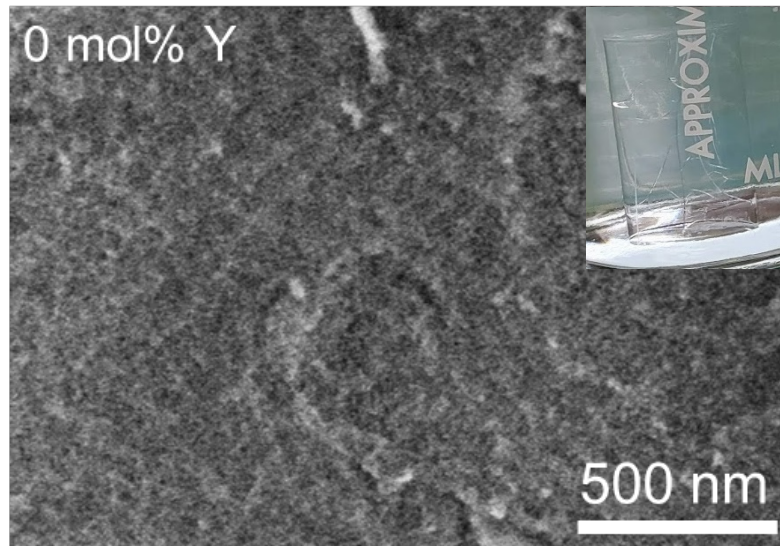


1000°C (18 min)

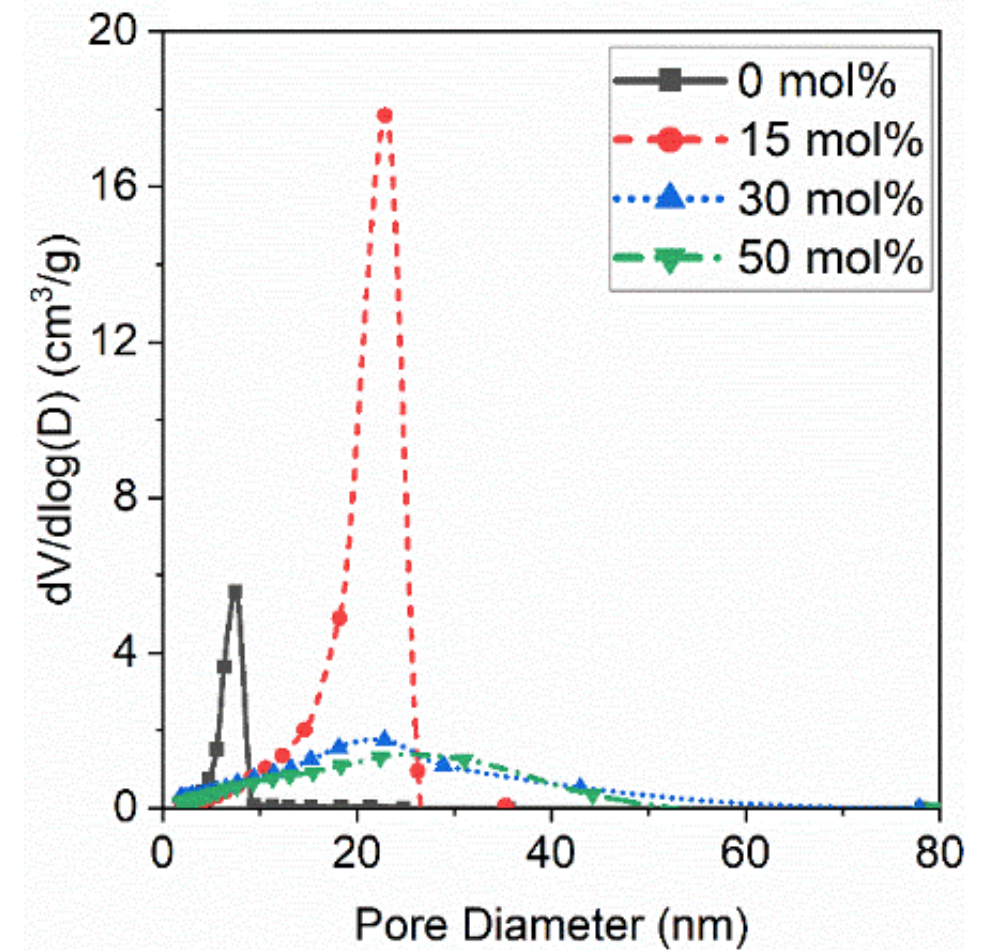


- Inspect pore structure and evolution after heat treatment
- Visualize with SEM & TEM
- Phase, crystallite size, and lattice parameters with XRD

As dried aerogels: yttria increases the pore size and distribution breadth

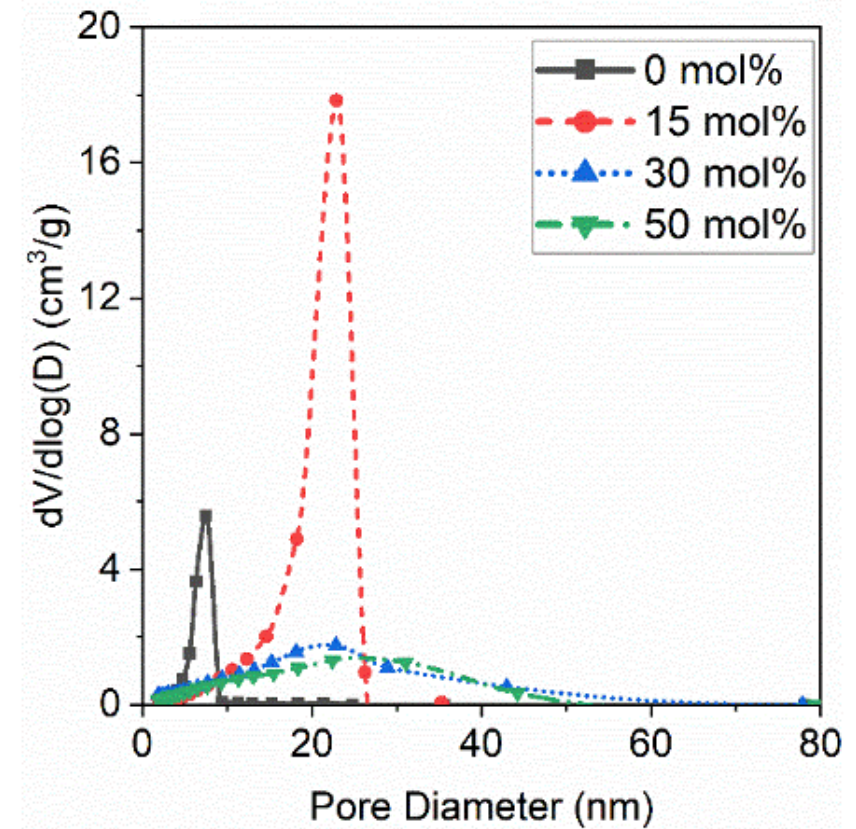
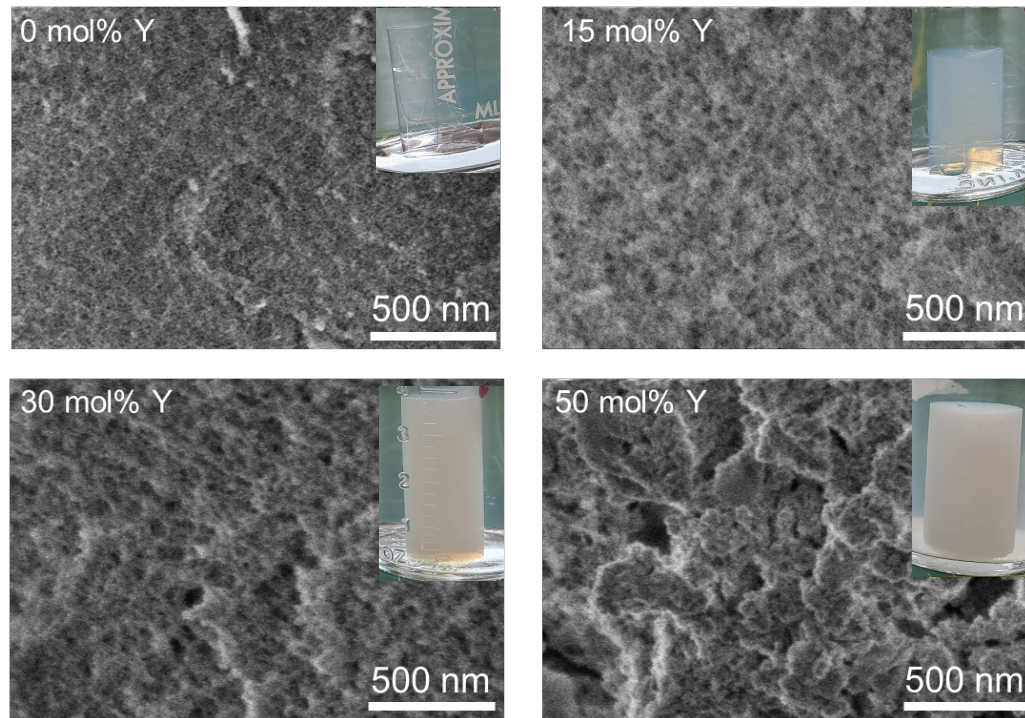


Pore Size Distributions

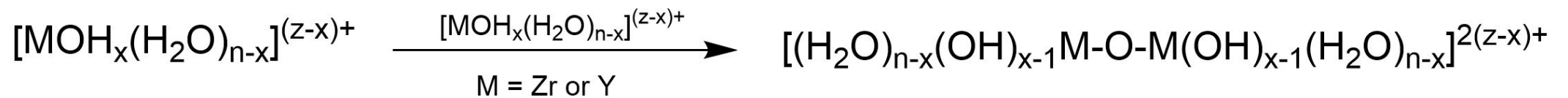


mol % $YO_{1.5}$	SSA (m^2/g)	Pore Volume (cm^3/g)	D_{peak} (nm)	Shrinkage (%)	Bulk Density (g/cm^3)
0	419	0.986	7.5	-25.6	0.292
15	456	1.950	22.9	-21.1	0.250
30	407	1.190	22.8	-13.2	0.193
50	301	0.997	28.5	-	-

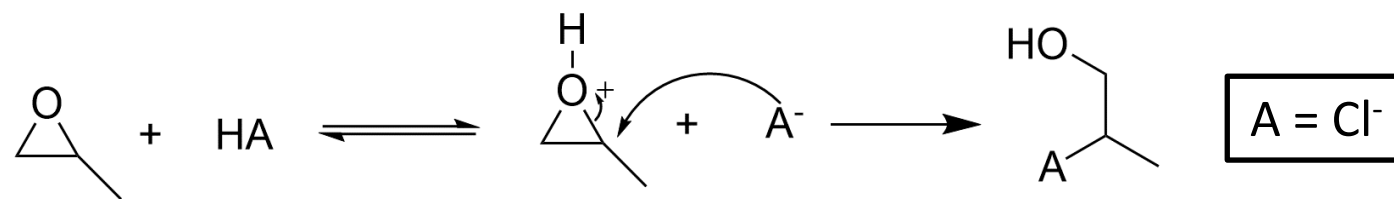
Increased rate of reaction with increased [Cl⁻] tends towards precipitation over homogeneous gelation



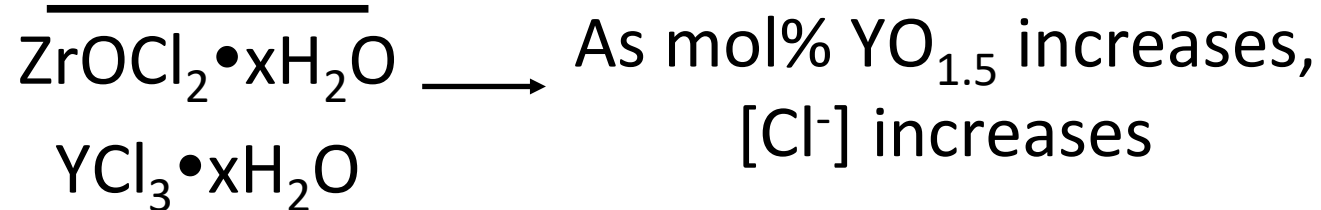
Condensation Reaction



Irreversible ring opening

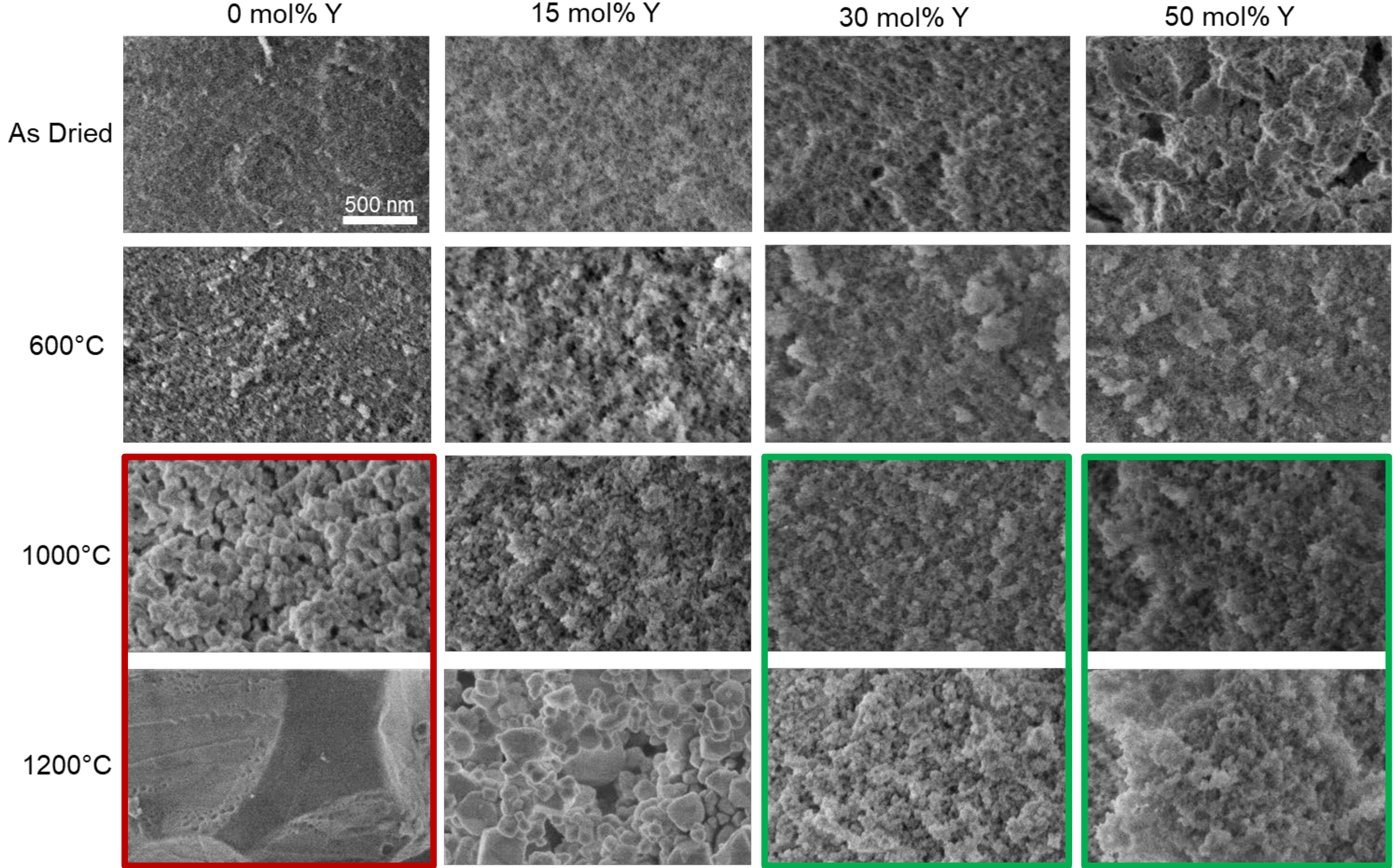



Precursors



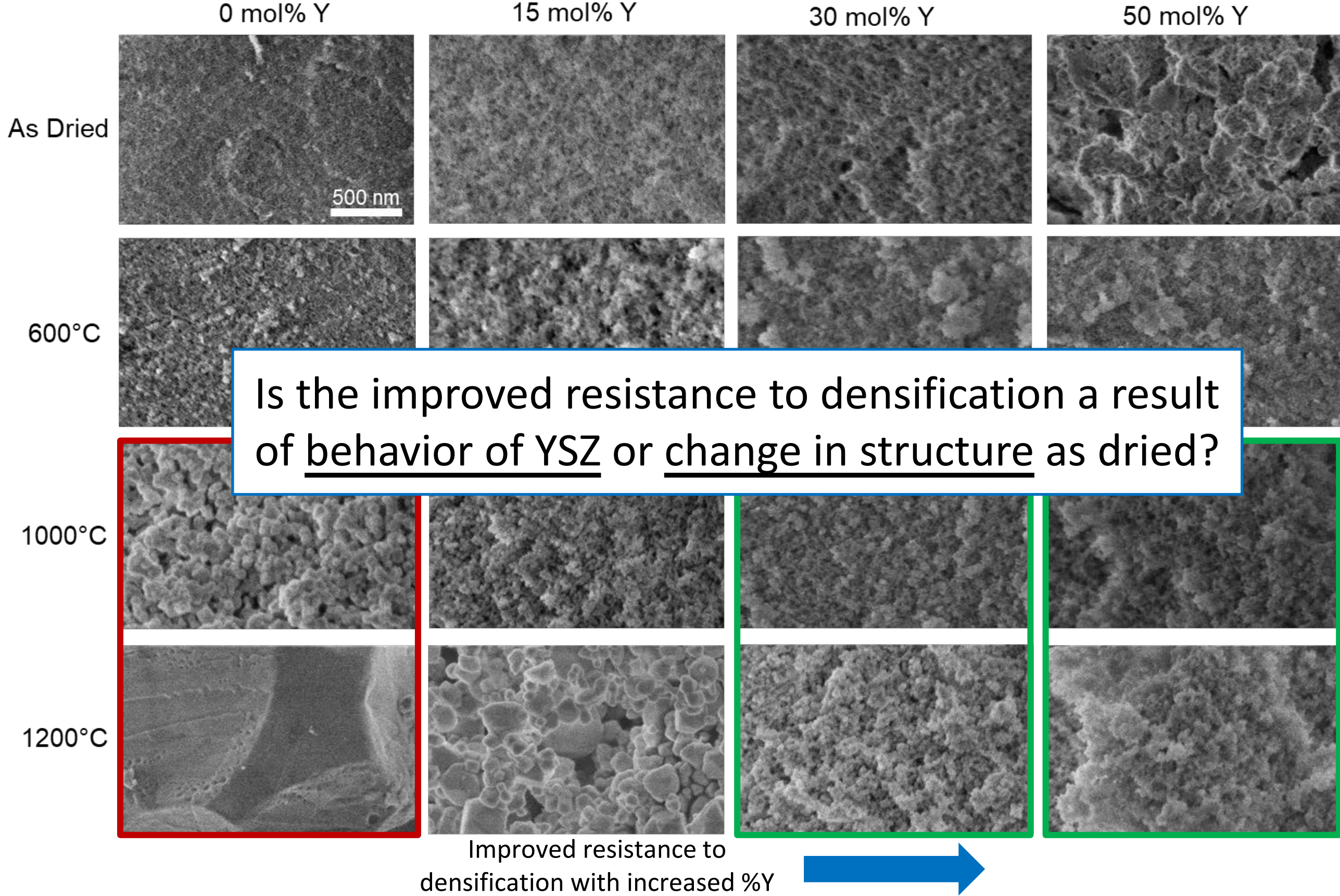
With more Cl⁻ in solution, faster irreversible ring opening and **faster deprotonation/condensation**

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



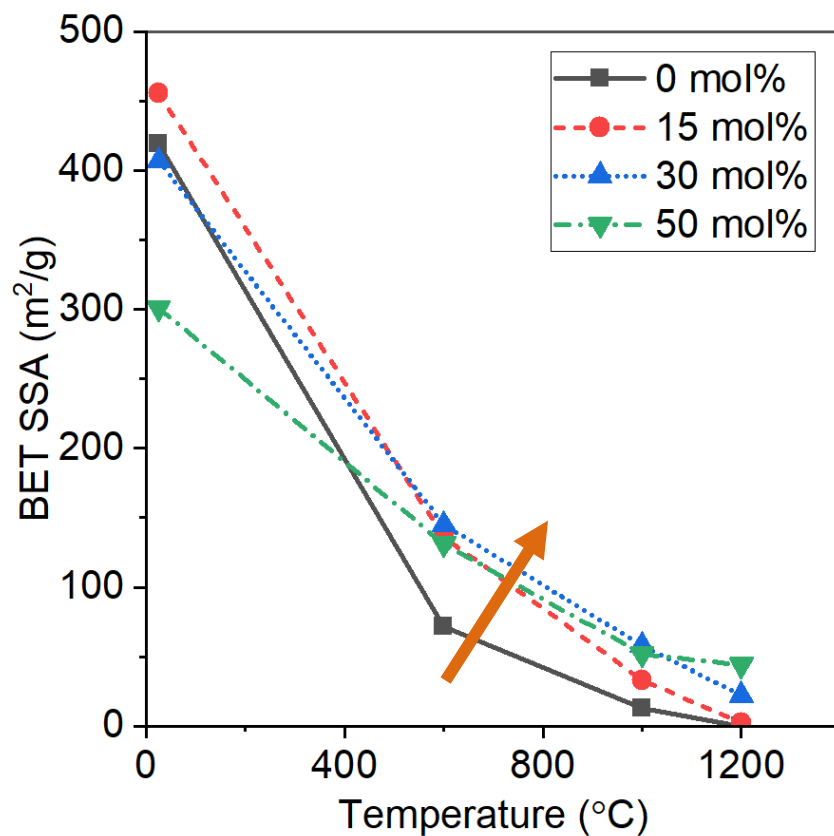
Improved resistance to densification with increased %Y 

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

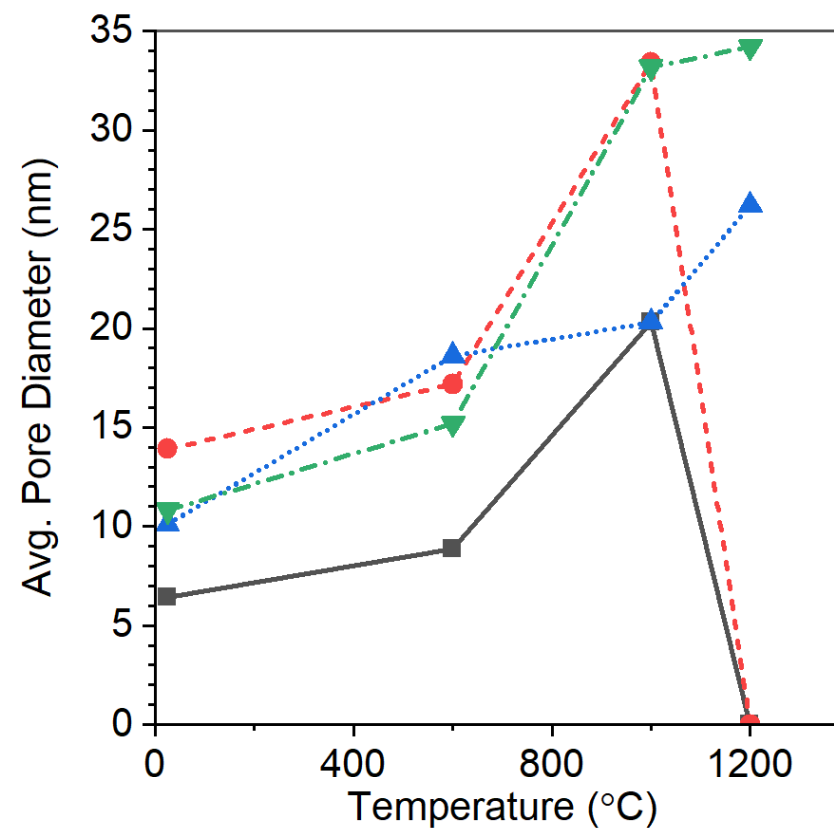


Nitrogen physisorption quantifies improvement in thermal stability with increased yttria content

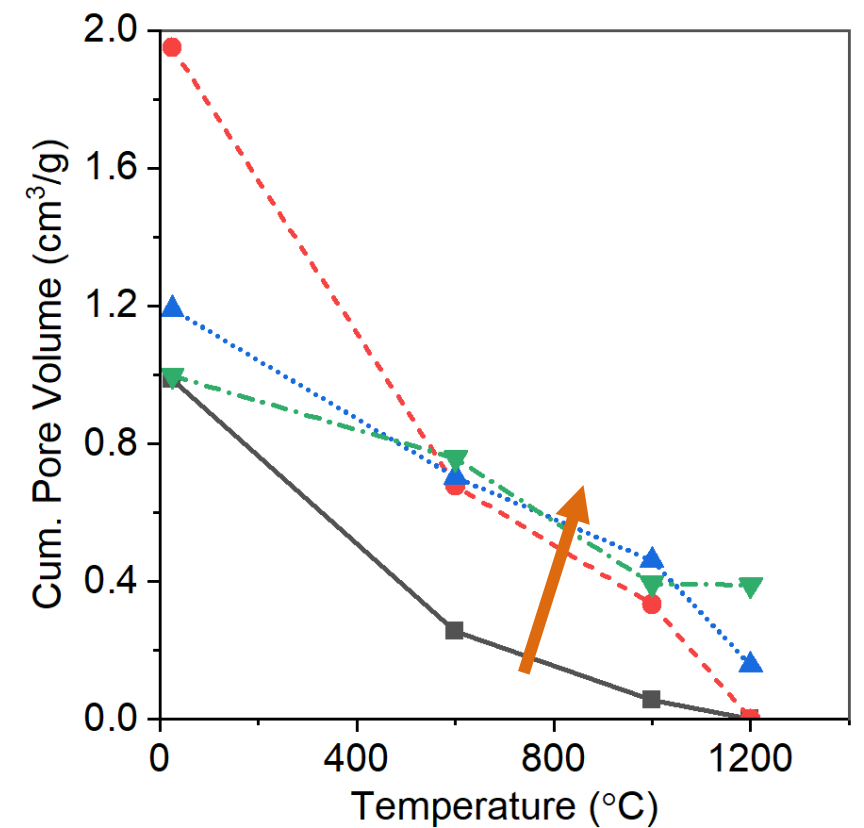
BET SSA



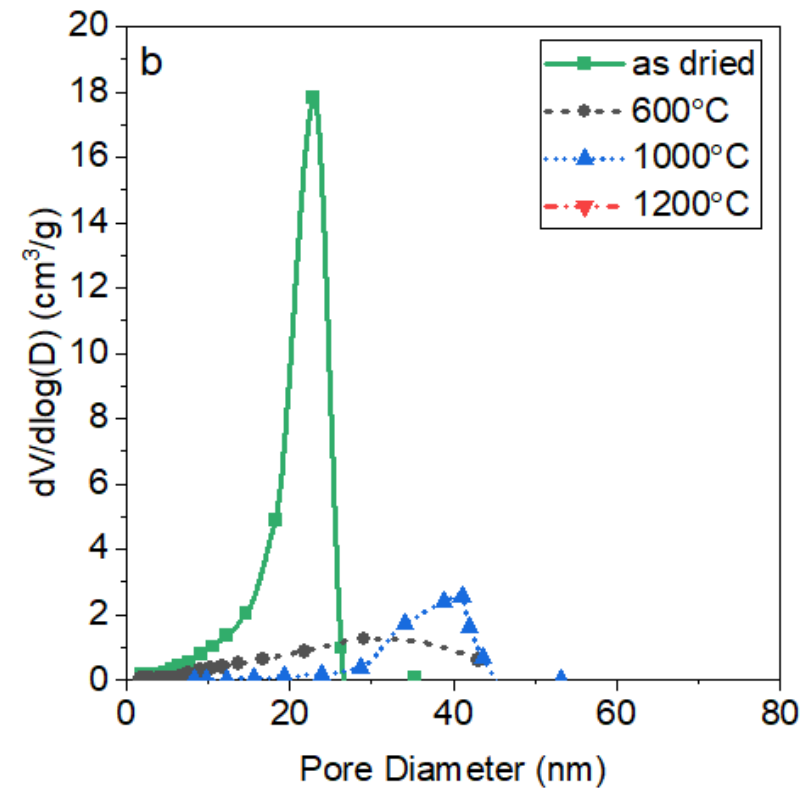
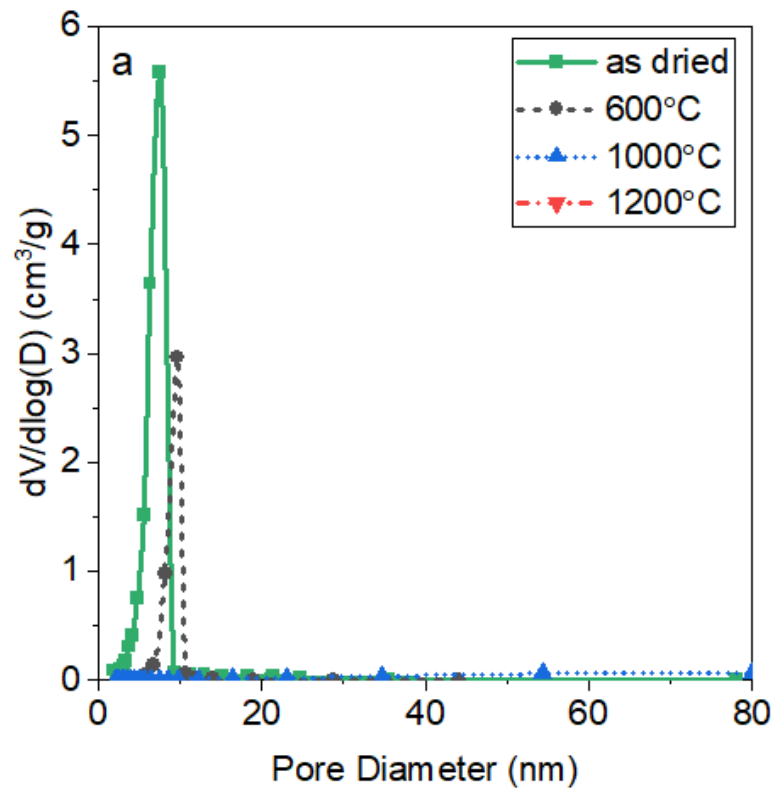
BJH Desorp. Pore Size



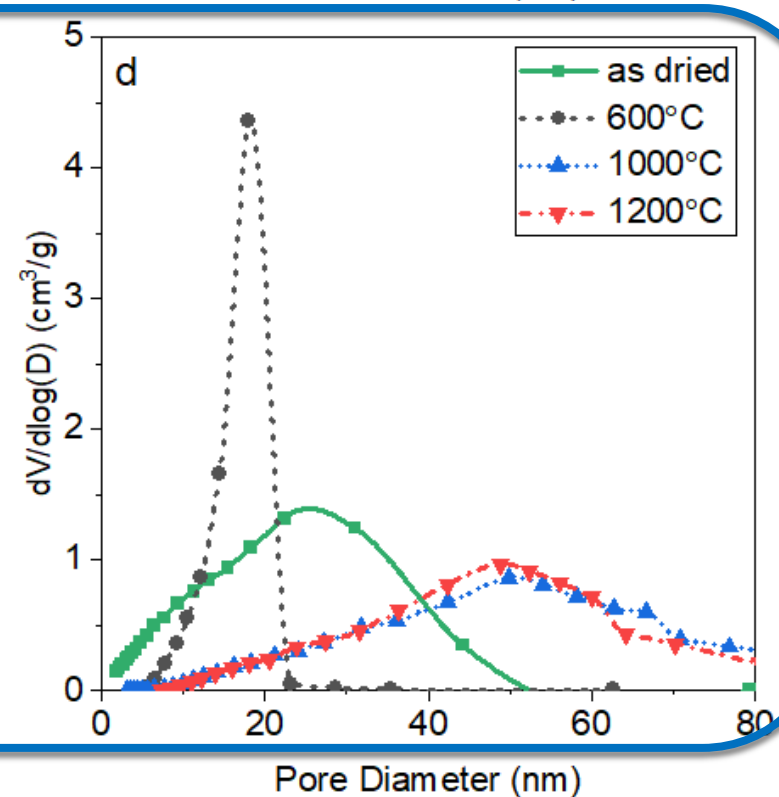
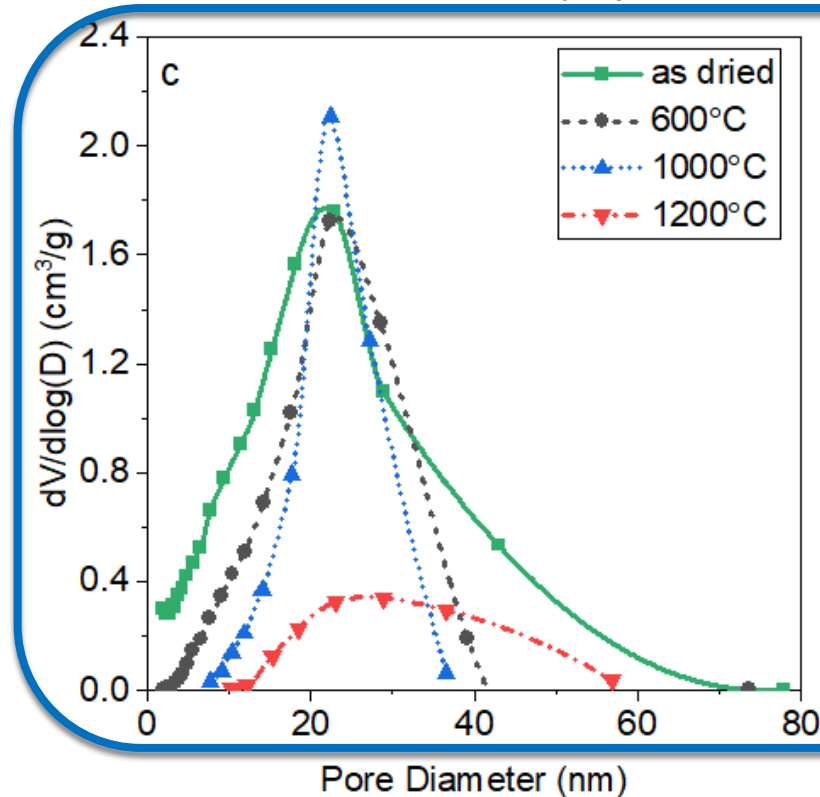
BJH Desorp. Pore Volume



Nitrogen physisorption demonstrates porosity maintained to 1200 °C in 30 and 50YSZ



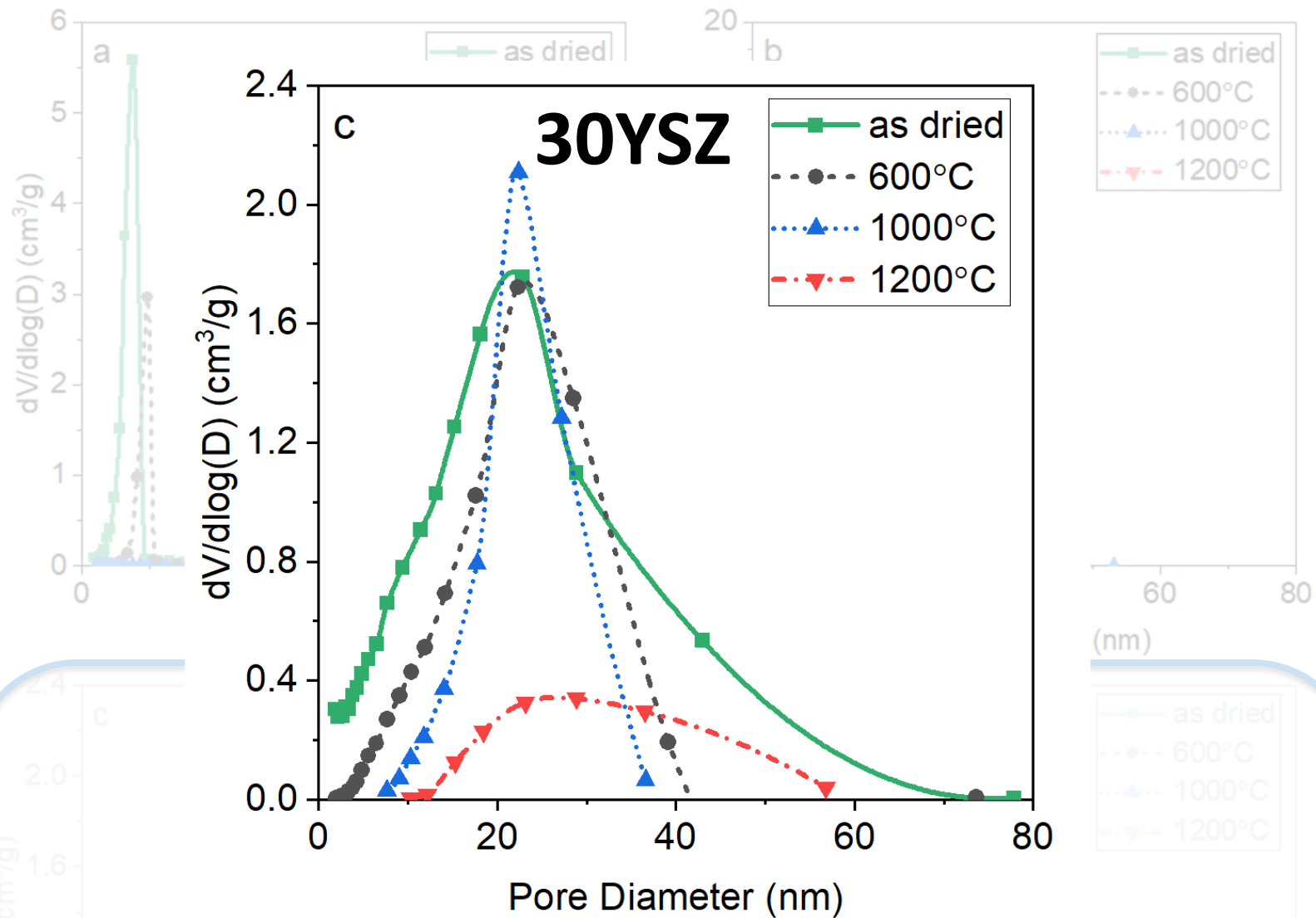
BJH Pore Size Distributions



(a) 0YSZ (b) 15YSZ

(c) 30YSZ (d) 50YSZ

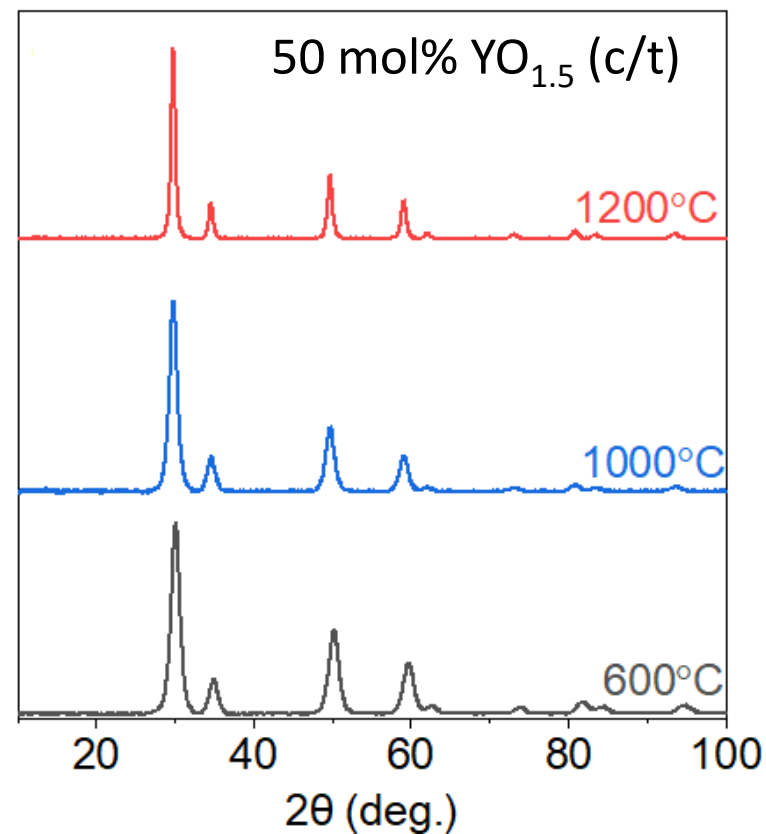
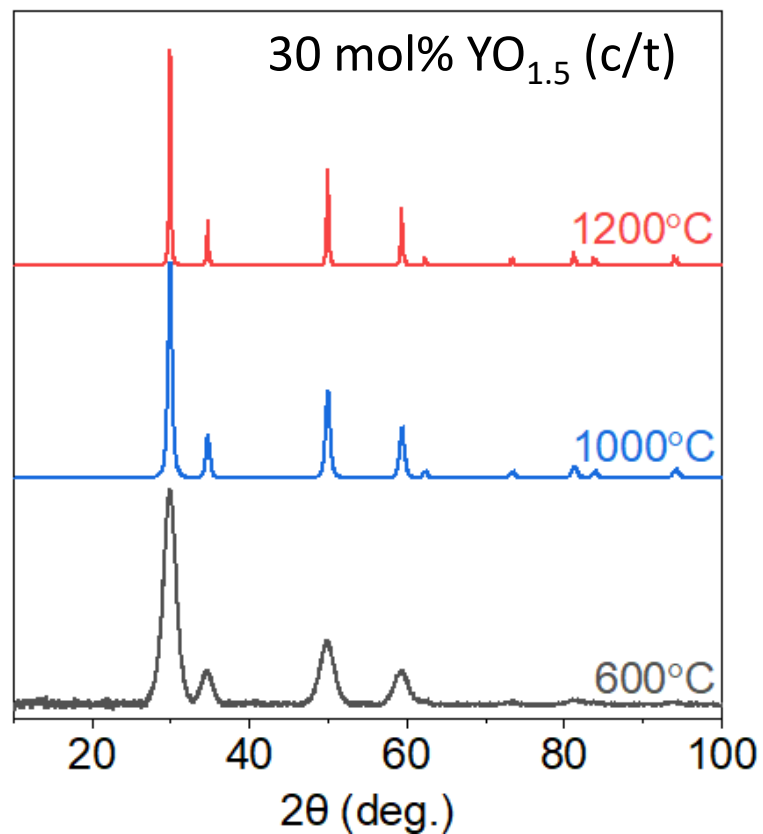
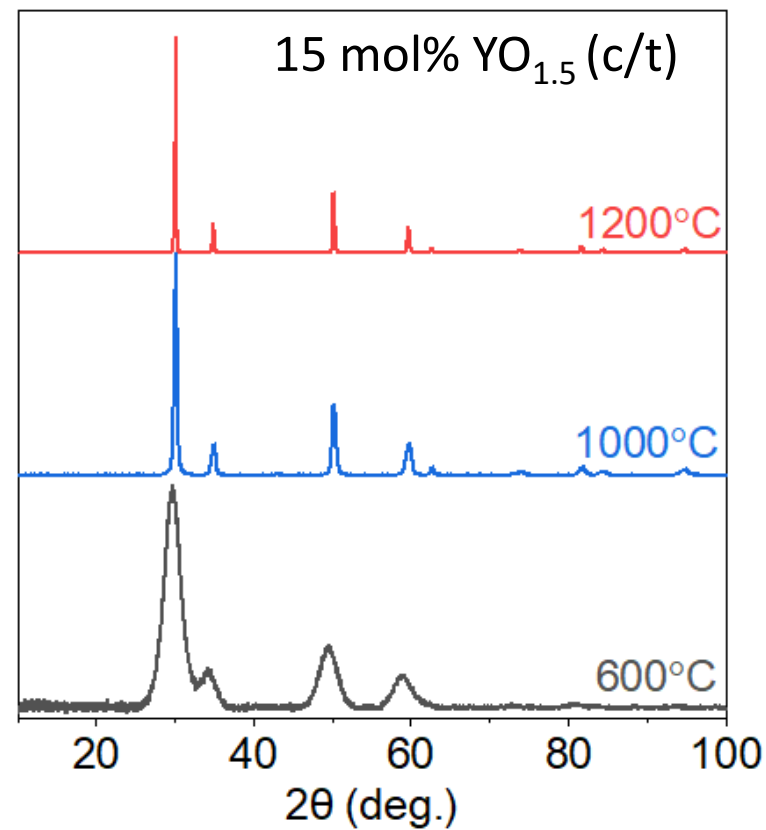
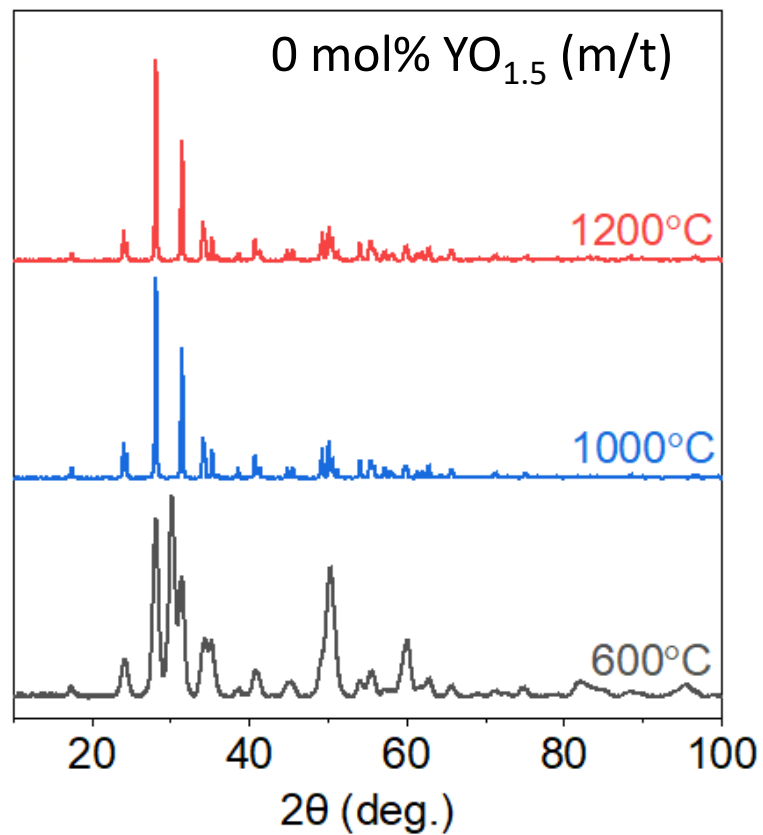
Nitrogen physisorption demonstrates porosity maintained to 1200 °C in 30 and 50YSZ



Although SSA significantly decreased, maintenance of nearly constant pore size is promising in 30YSZ!

(a) 0YSZ (b) 15YSZ
(c) 30YSZ (d) 50YSZ

No unexpected phase transformations or separations as observed with x-ray diffraction (XRD)



0YSZ crystallizes into
monoclinic with
some tetragonal

15, 30, and 50YSZ
crystallize into cubic
(though tetragonal
cannot be ruled out)

Crystallite growth is suppressed with increased yttria content (Scherrer method)

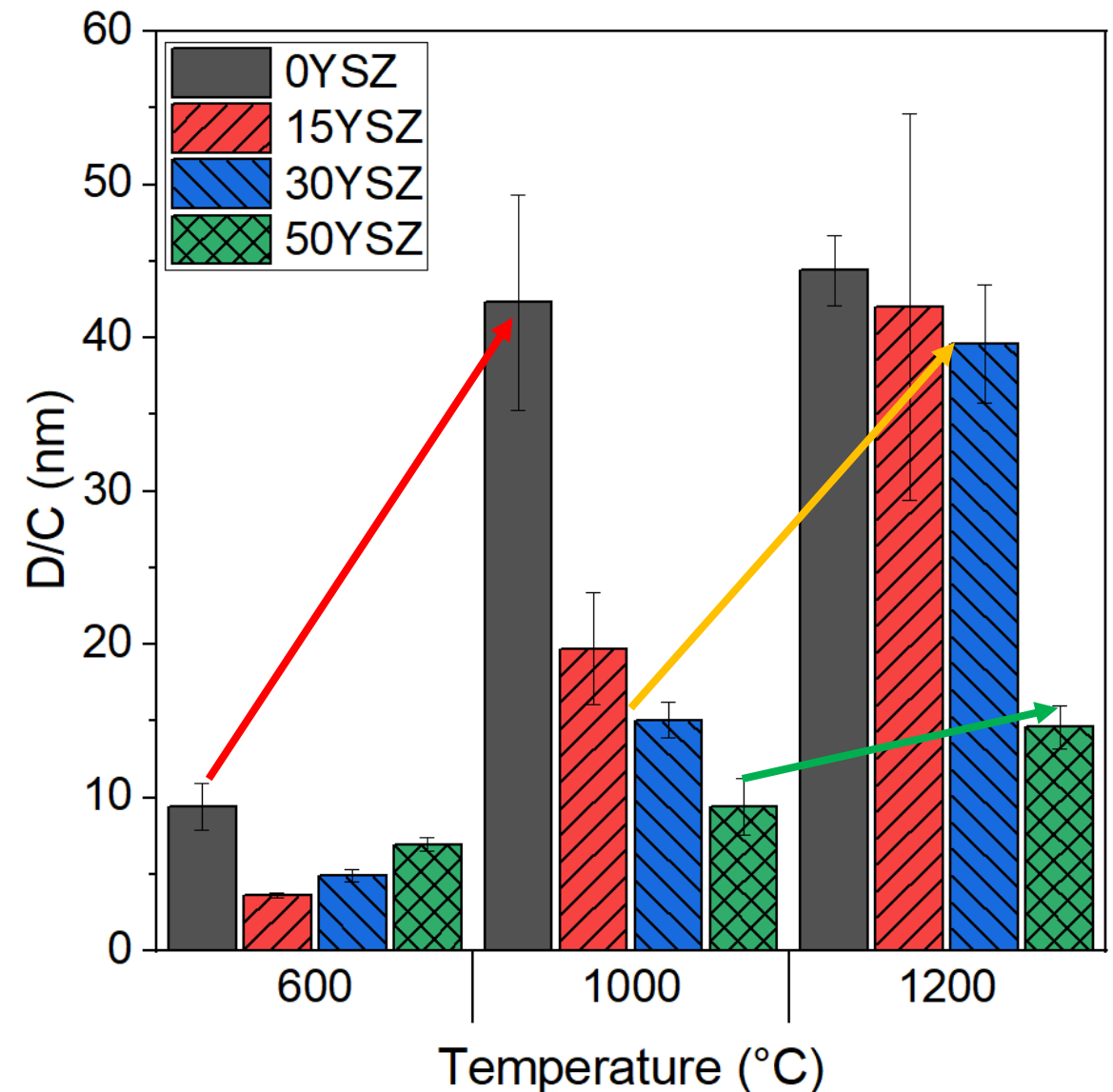
- Took peak position (θ) & FWHM (β) and calculated D/C from Scherrer equation

$$\frac{D}{C} = \frac{\lambda}{\beta \cos\theta}$$

- Allows for comparison between samples
 - Avoids having to choose C value and subtract instrument broadening
 - Does NOT provide absolute values
- Large variation in 15 mol% explained by abnormal grain growth observed in SEM and quantified in ImageJ

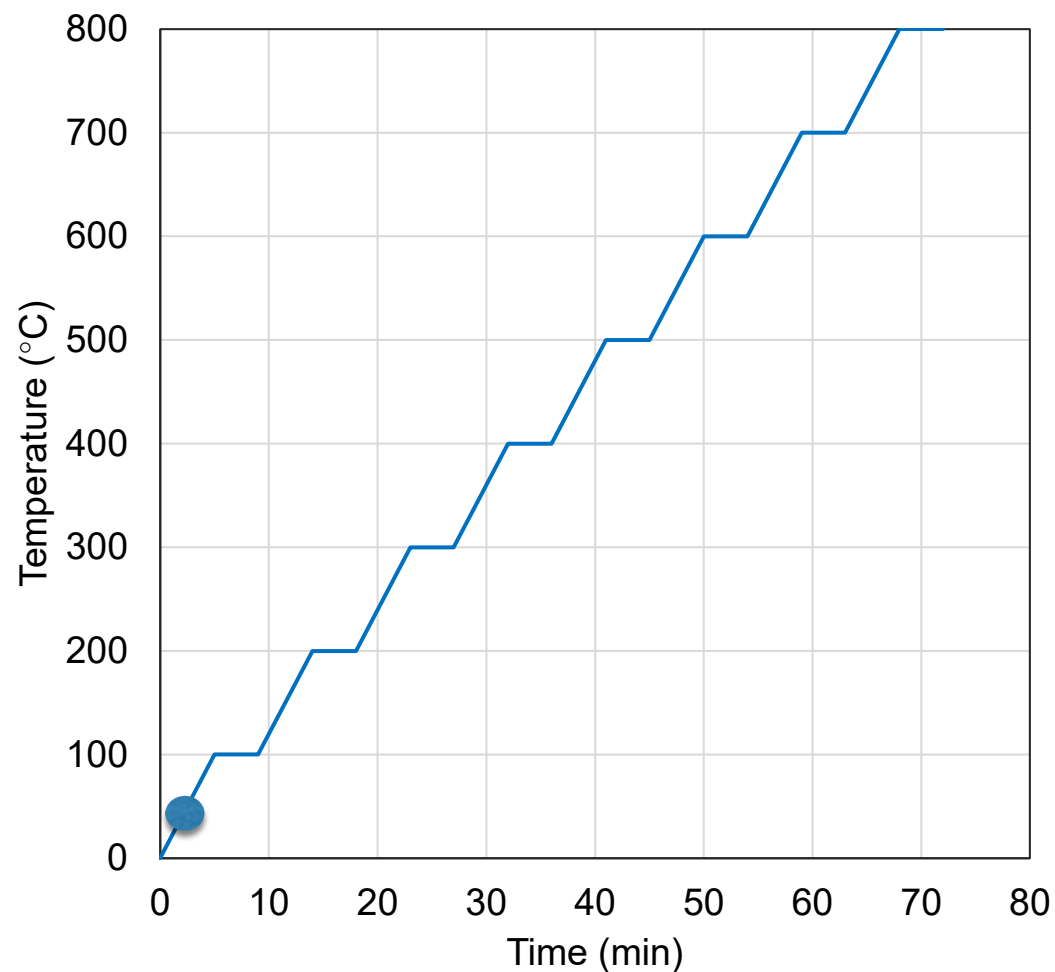
0 mol%: Stable to 600 °C
15, 30 mol%: Stable to 1000 °C
50 mol%: Stable to 1200 °C

Crystallite Size, Scherrer Method

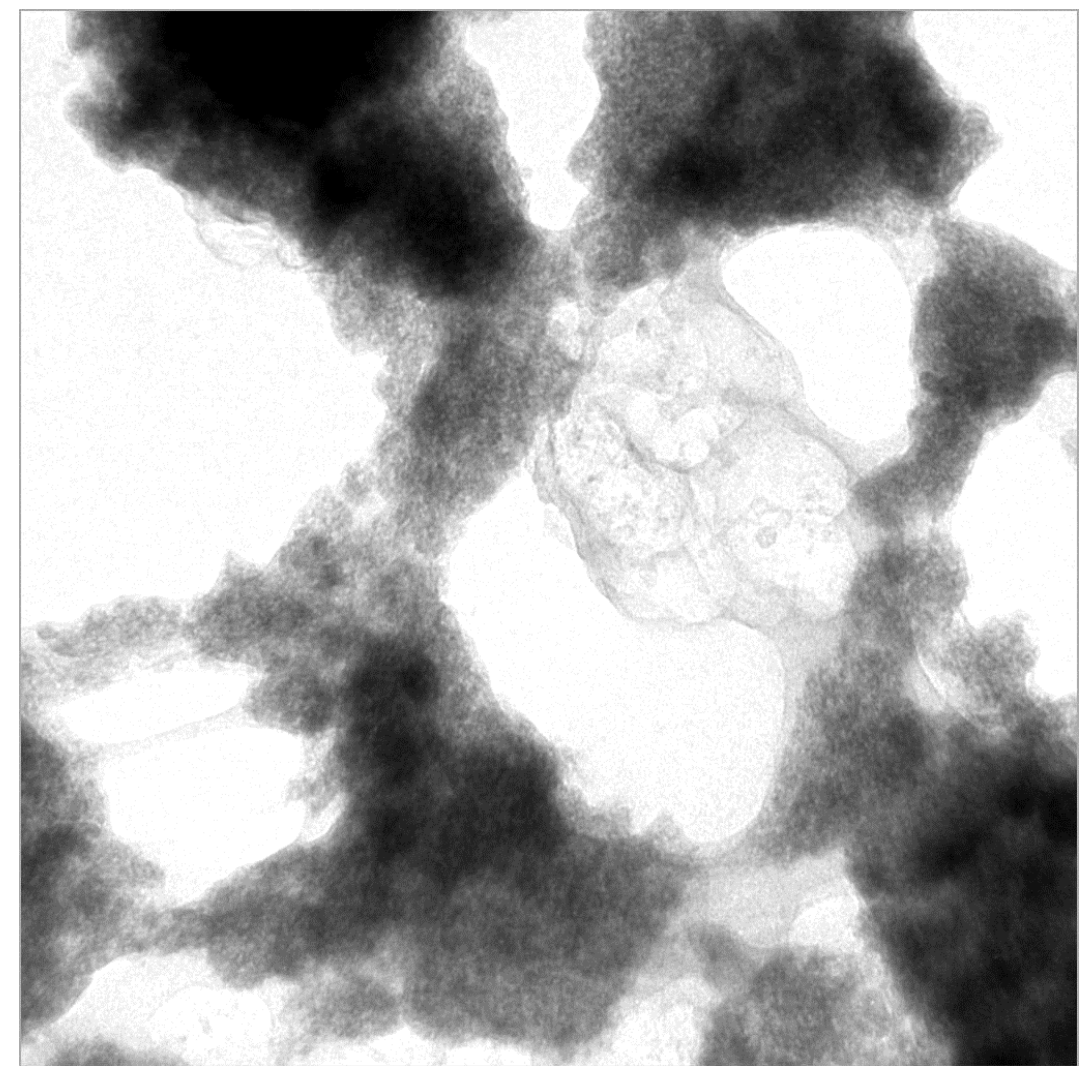


Activation energy barrier for densification & crystallite growth between 1000 and 1200 °C. Increased Y content increases this E_a barrier for mass flow.

Furthering our understanding of crystallite growth with in-situ dark field transmission electron microscopy



Special thanks to Nathan Madden & Charles Smith (SMEE, UIUC) for TEM data



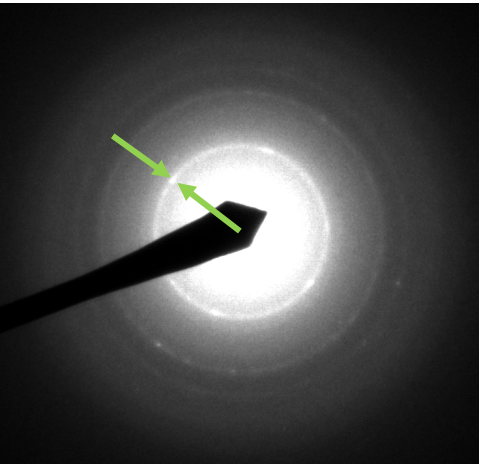
150 nm

- Dip grids into aerogel/ethanol dispersion and allow to dry
- Ramp of 20 °C / min
- Hold of 4 min every 100 °C
- **Diffraction patterns & dark field images** taken during each hold

In situ video available: <https://youtu.be/HGt6vPIIwDs>

Dark field TEM corroborates XRD: yttria suppresses crystallite growth upon heating

Bright regions are crystallites that contribute to this spot

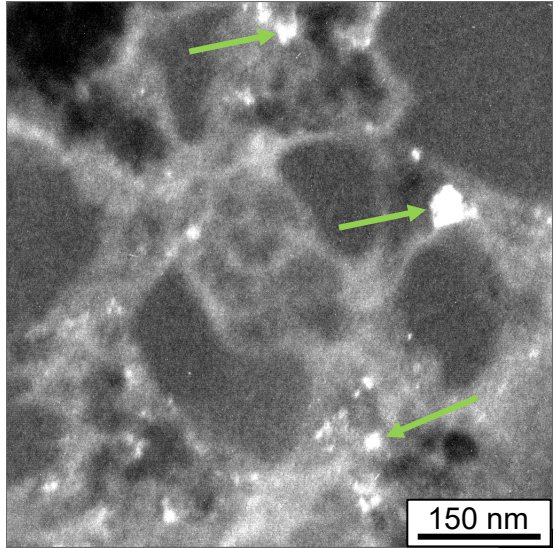


15 mol% Y ED pattern

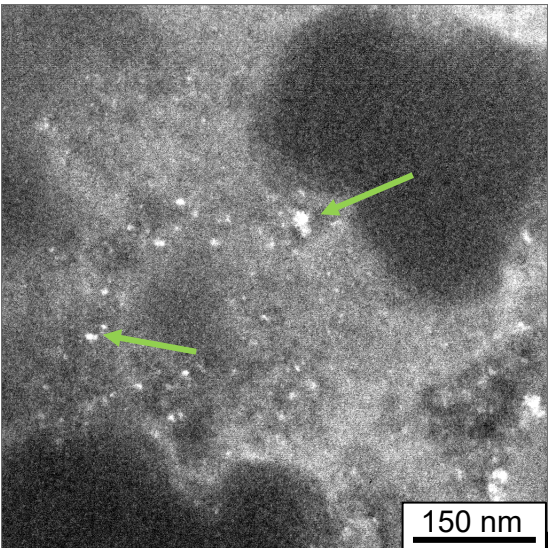
Dark field at 800°C



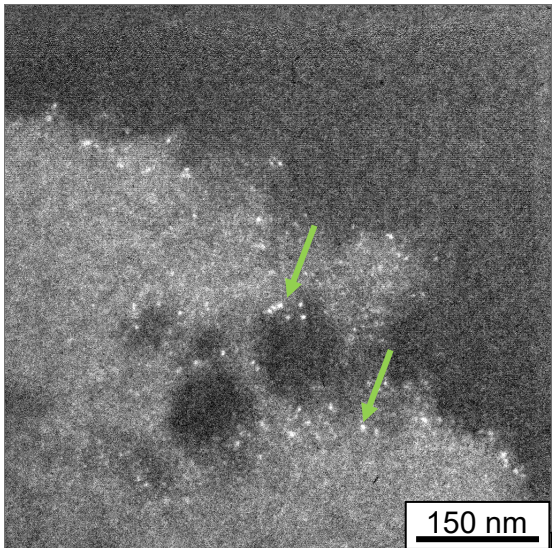
Select spot on ring from electron diffraction pattern



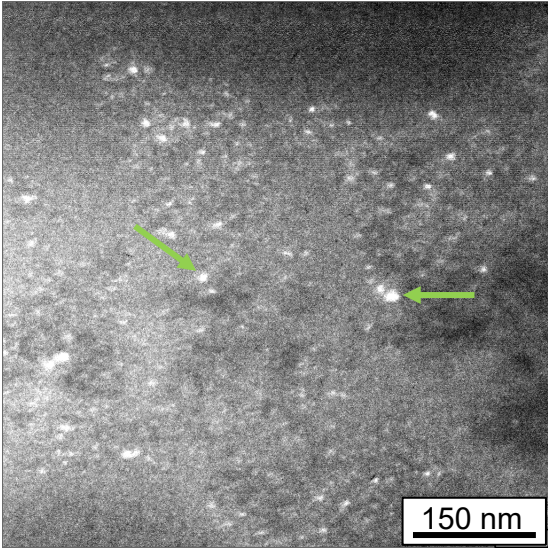
0 mol% Y



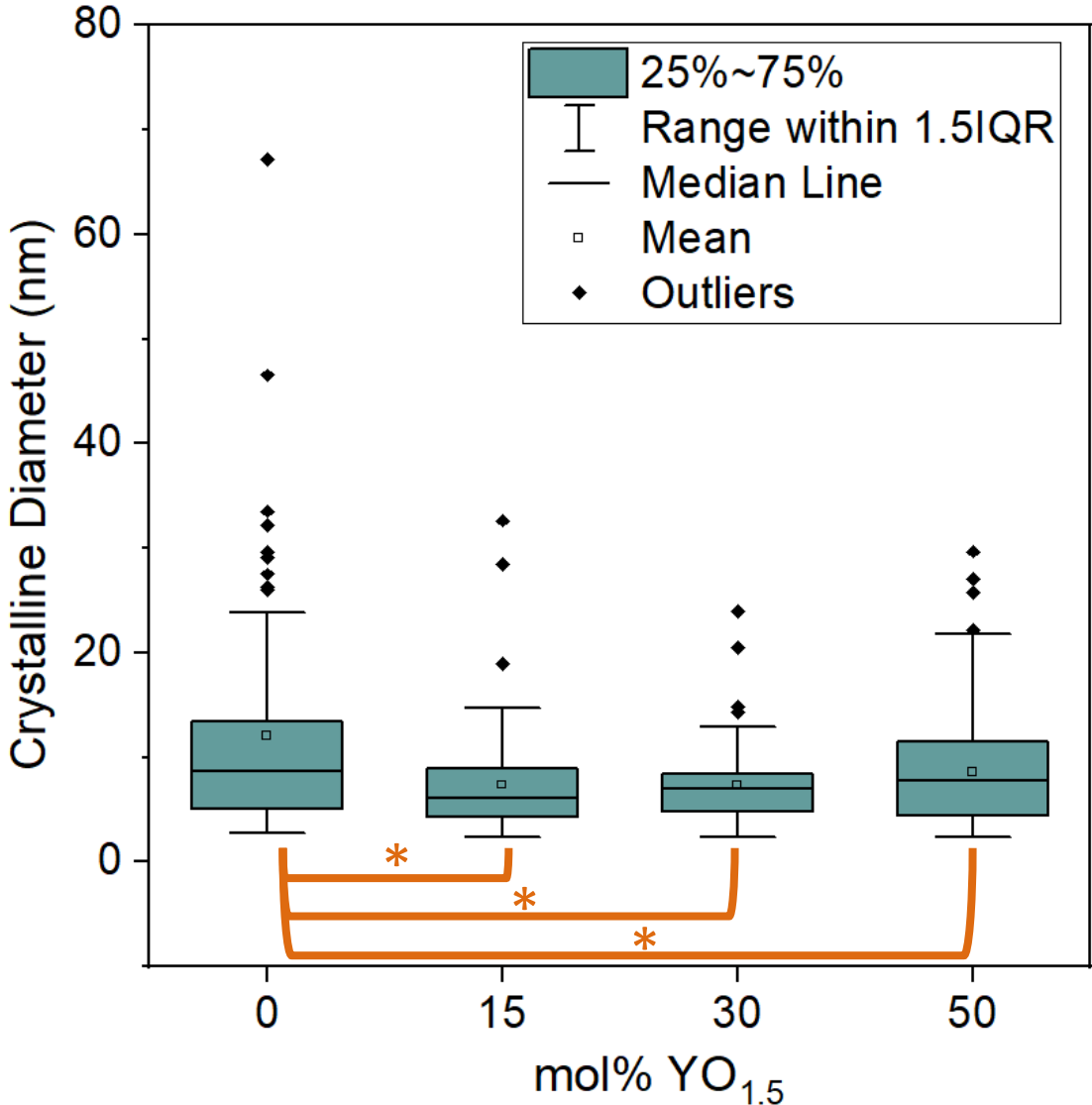
15 mol% Y



30 mol% Y



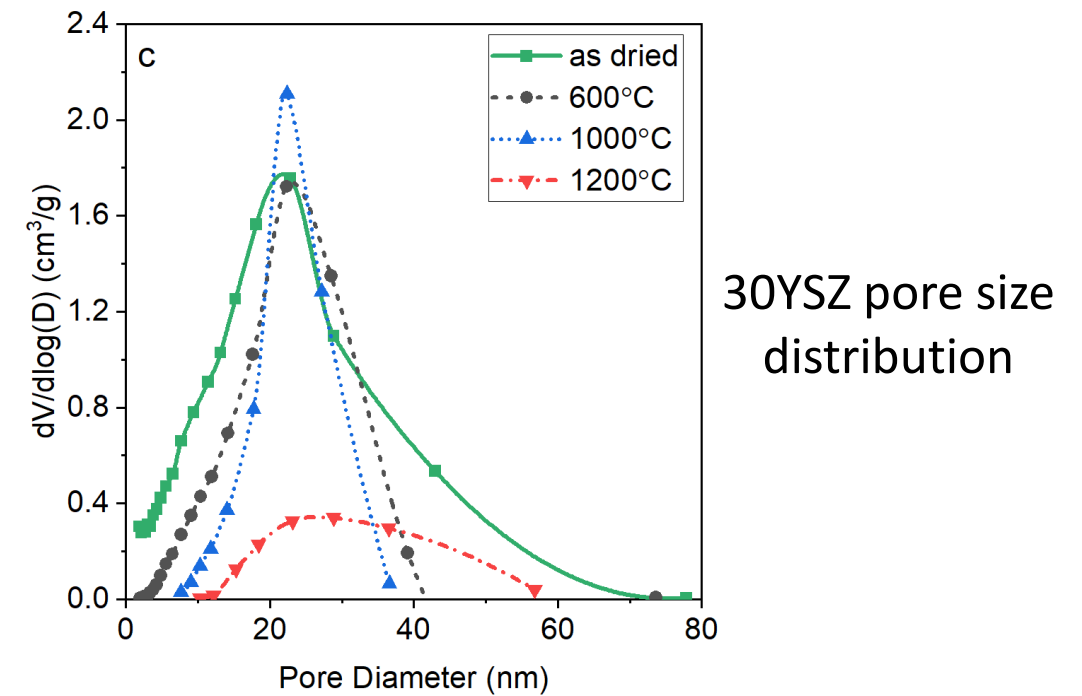
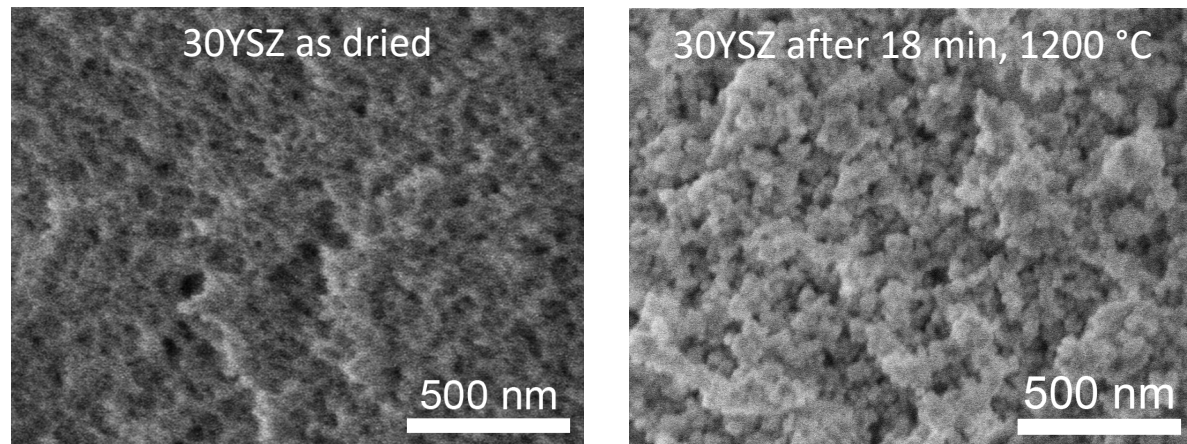
50 mol% Y



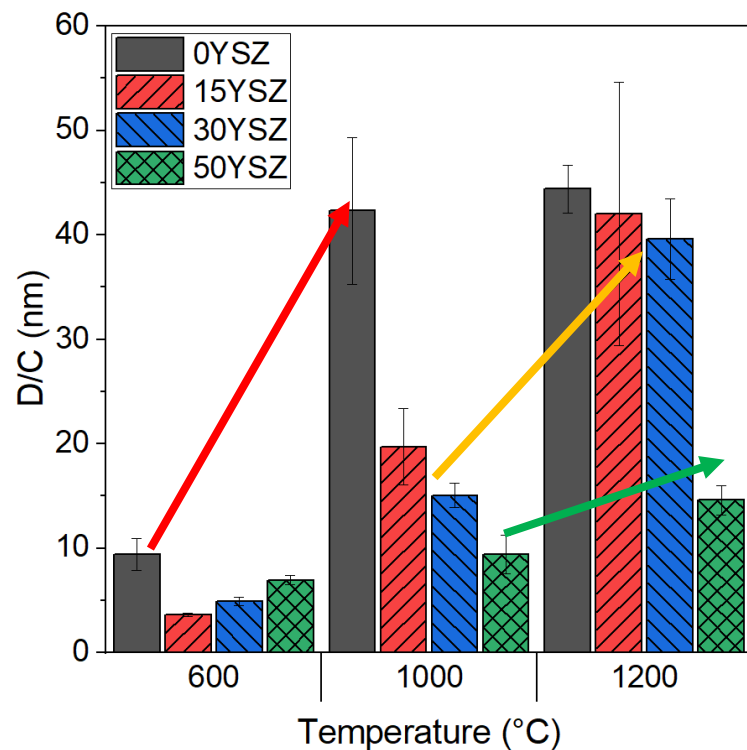
* = Significantly different at $\alpha = 0.05$

Increased yttria content in YSZ aerogels improves thermal stability

1. Reduces densification of the pore structure



2. Suppresses crystallite growth to 1200 °C

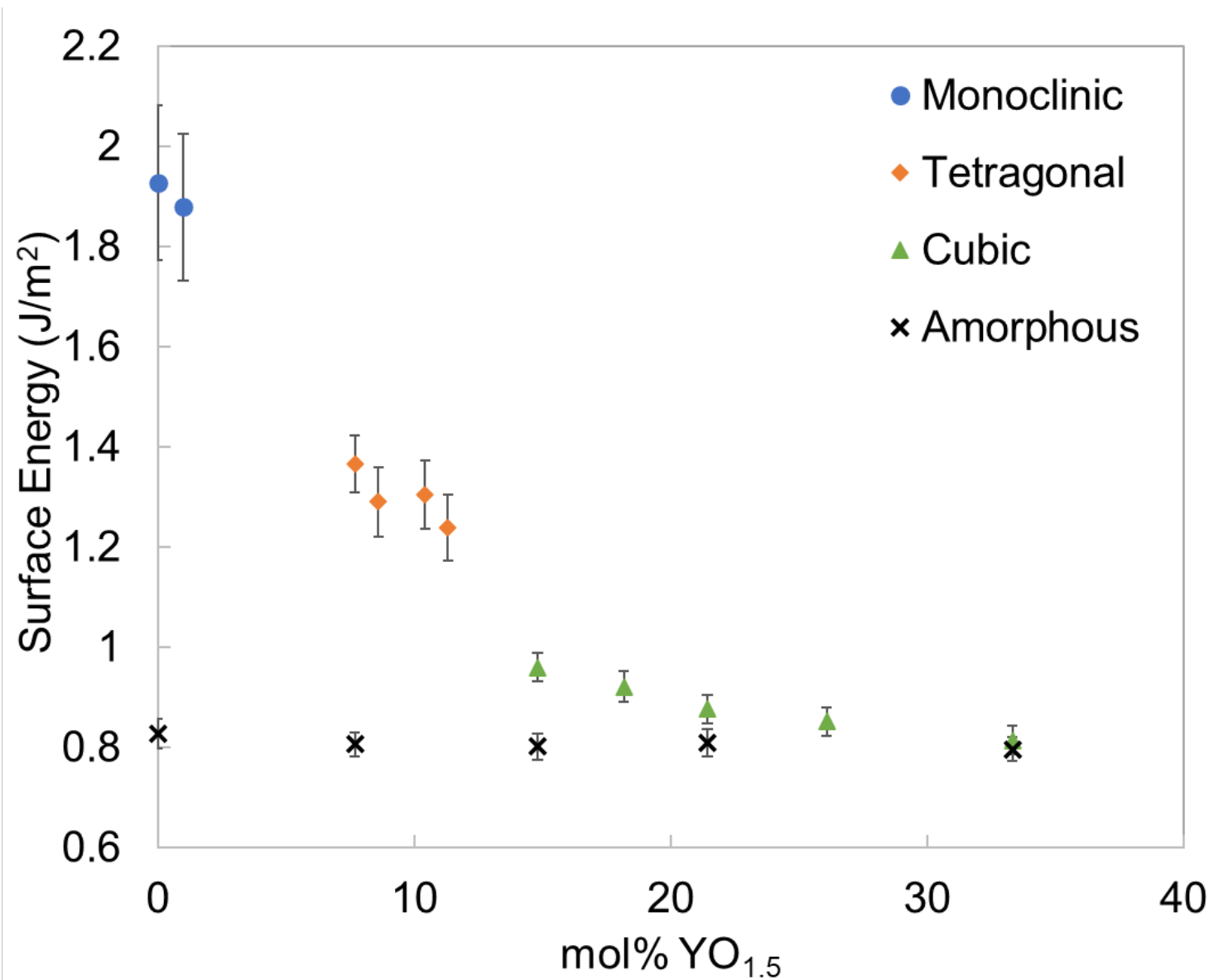


By what mechanism is yttria improving the thermal stability of the pore structure?

Thermodynamics
(Surface Energy)

Kinetics
(Cation Diffusivity)

Understanding the effect of yttria on structural evolution: **thermodynamics** (surface energy)

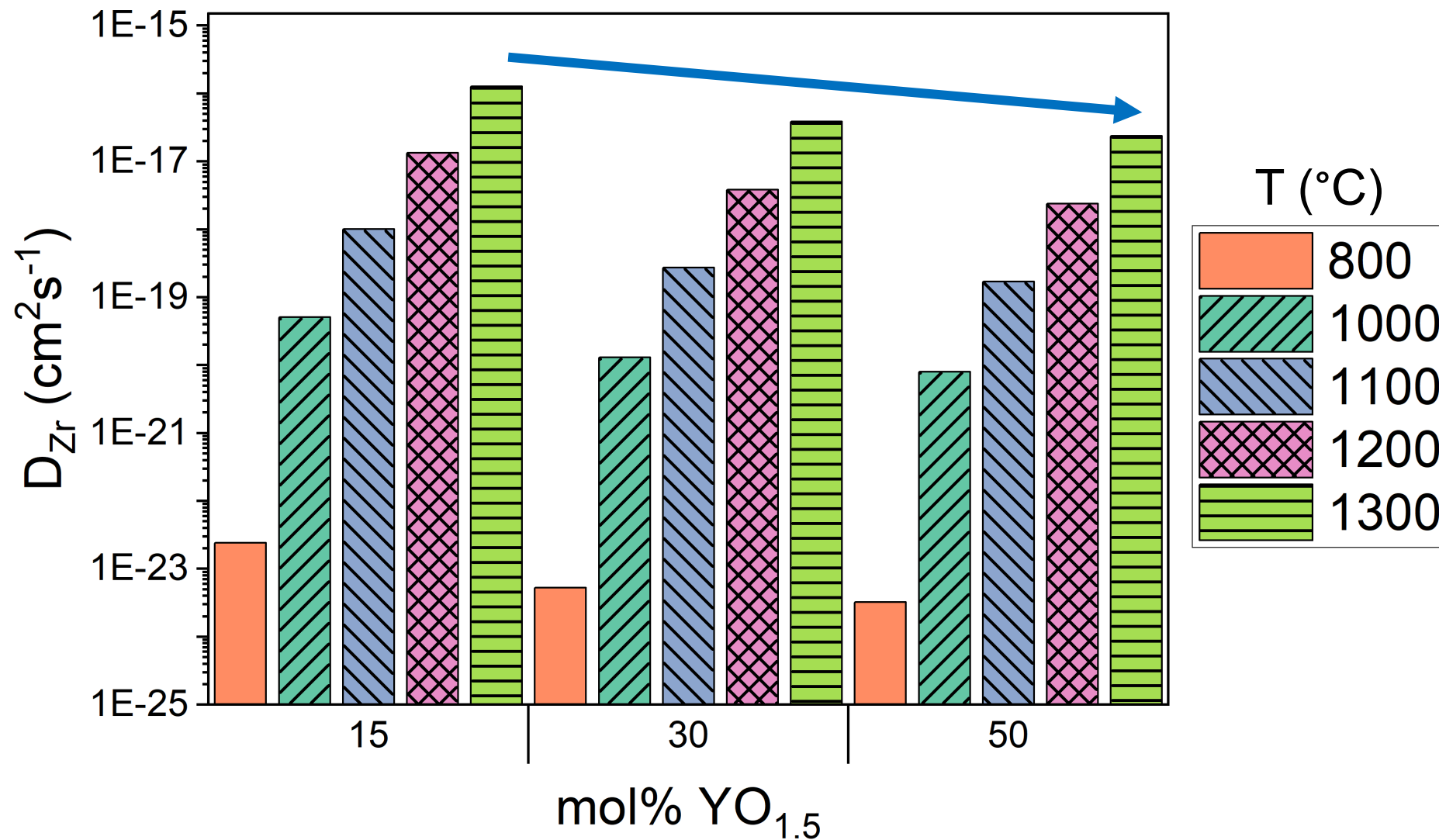


According to Drazin & Castro, significant decrease in surface energy with increased yttria content via water adsorption microcalorimetry

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

With SSAs of 300 to 500 m²/g, *surface energy has massive impact!*

Understanding the effect of yttria on structural evolution: **kinetics** (cation diffusivity)

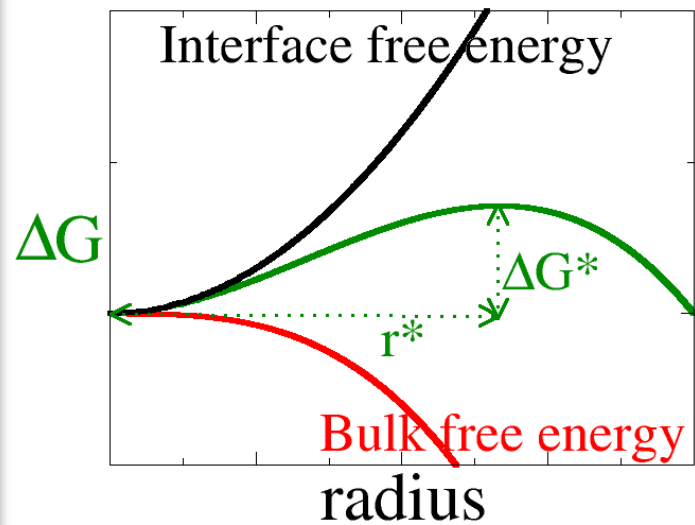


Cation diffusivity controls mass transport in YSZ (e.g. densification processes and crystallite growth)

Reduced diffusivity with increased yttria content may slow densification & crystallite growth

1. Kilo, M., Borchardt, G., Lesage, B., Kaitasov, O., Weber, S., & Scherrer, S. (2000). Cation transport in yttria stabilized cubic zirconia: ^{96}Zr tracer diffusion in $(\text{Zr}_x\text{Y}_{1-x})\text{O}_{2-x/2}$ single crystals with $0.15 \leq x \leq 0.48$. *Journal of the European Ceramic Society*, 20(12), 2069-2077.
2. Kilo, M., Borchardt, G., Weber, S., Scherrer, S., & Tinschert, K. (1997). Zirconium and calcium tracer diffusion in stabilized cubic zirconia. *Berichte der Bunsen-Gesellschaft*, 101(9), 1361-1365.
3. Kilo, M., Taylor, M. A., Argiris, C., Borchardt, G., Lesage, B., Weber, S., ... & Martin, M. (2003). Cation self-diffusion of ^{44}Ca , ^{88}Y , and ^{96}Zr in single-crystalline calcia- and yttria-doped zirconia. *Journal of applied physics*, 94(12), 7547-7552.

Increased yttria content is hypothesized to **reduce the energy barrier to crystallization**



$$\Delta G = \frac{4}{3} \pi r^3 \Delta g + 4\pi r^2 \gamma$$

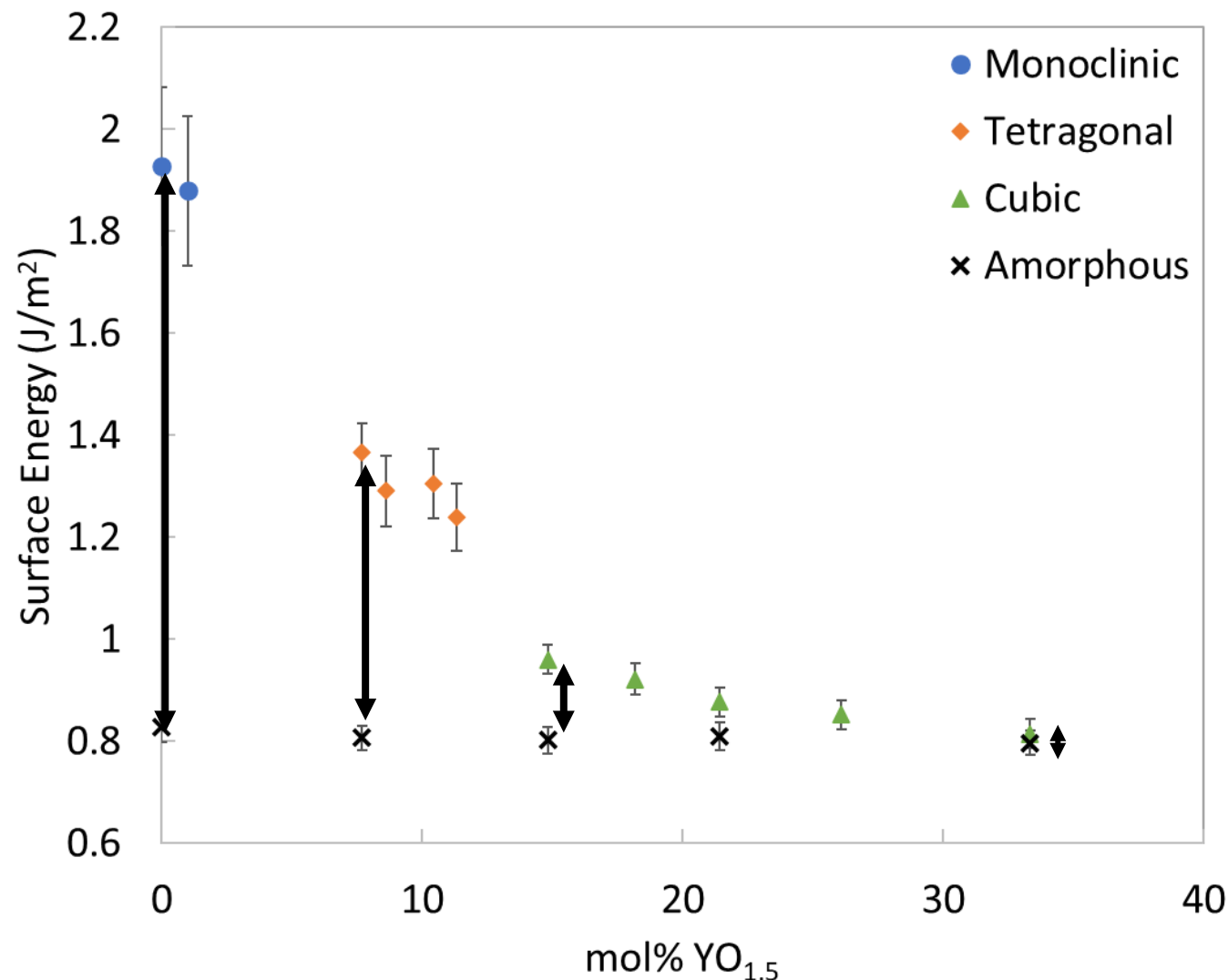
r = particle radius (m)

Δg = change in bulk free energy (J/m³)

γ = interfacial specific energy (J/m²)

The difference between amorphous phase and crystalline phase at any given mol% YO_{1.5} can give an approximation to the energy barrier.

This barrier decreases with increasing yttria content!

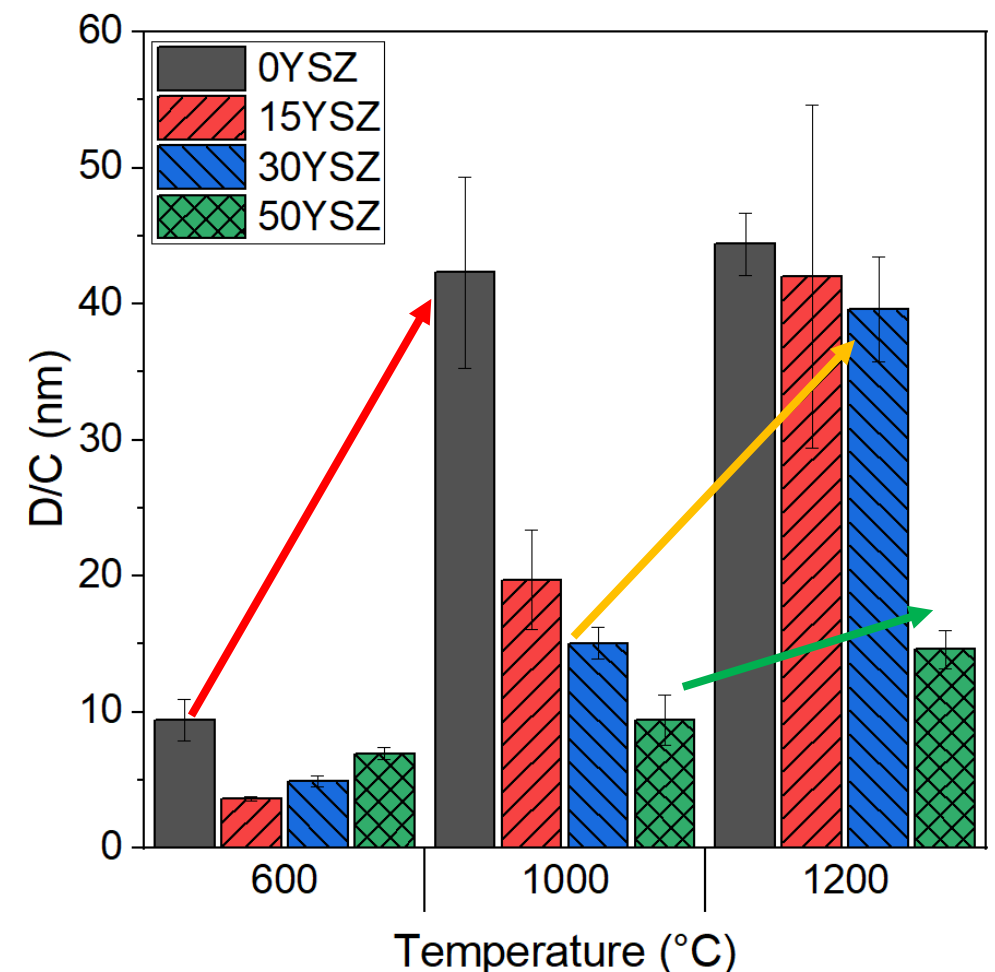
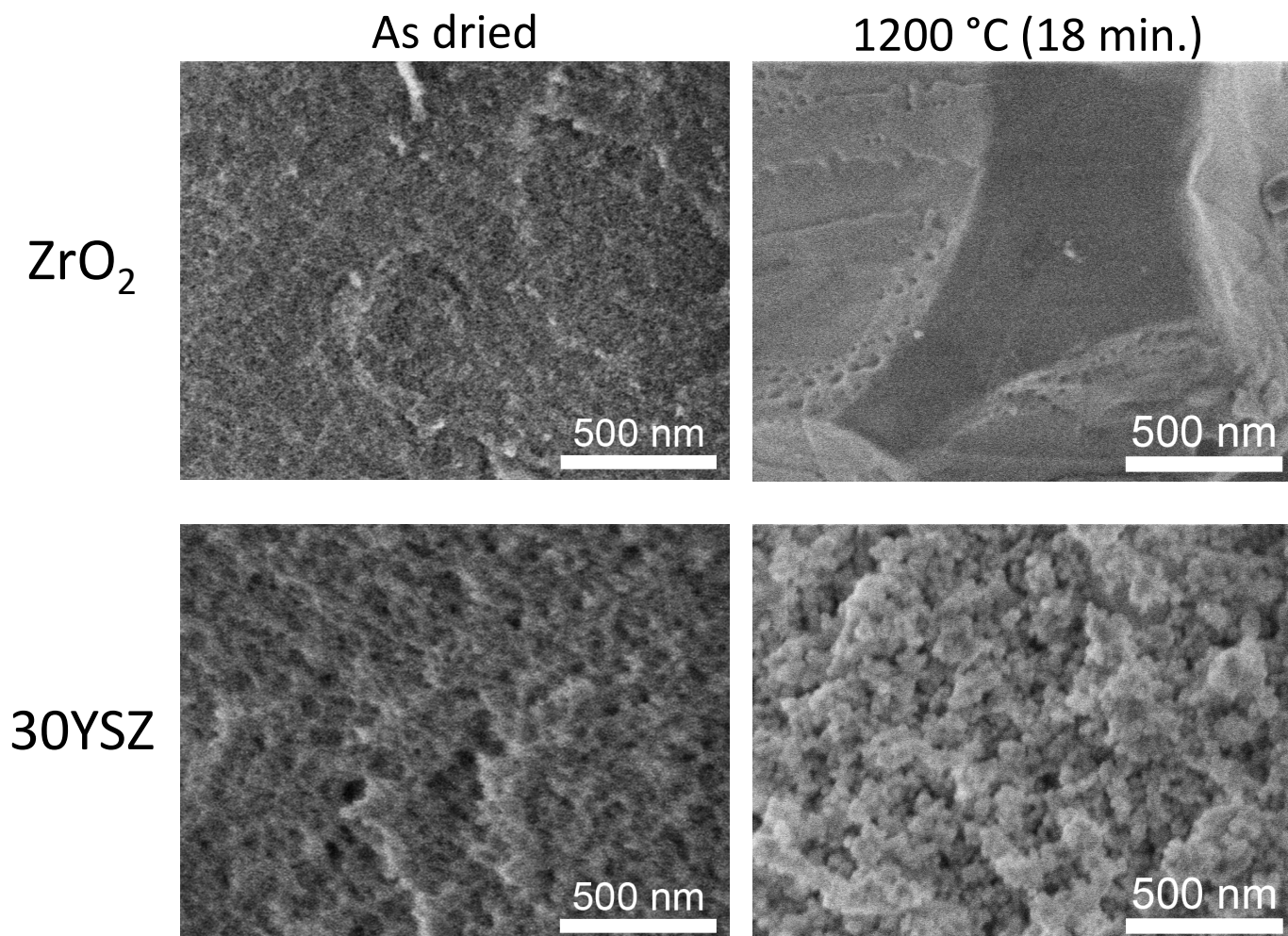


Lower barrier = smaller nuclei = **smaller crystallites to begin with**

Lower diffusivity **prevents their growth** until activation energy surmounted

Both kinetic and thermodynamic factors contribute to increased thermal stability with increased yttria content

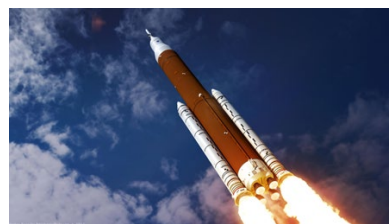
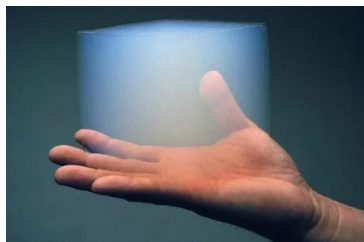
- **Decreased diffusivity** of Zr^{4+} , Y^{3+} in YSZ with increased Y_2O_3 doping responsible for decreased mass flow
 - *Less densification AND crystallite/grain growth* in 50YSZ relative to 30, 15, 0YSZ
- **Lower surface energy** with increased yttria content ($\gamma_c < \gamma_t < \gamma_m$) leads to:
 - *Improved stability of pore structure* (lower driving force for densification)
 - *Smaller crystallites* (lower barrier to nucleation)



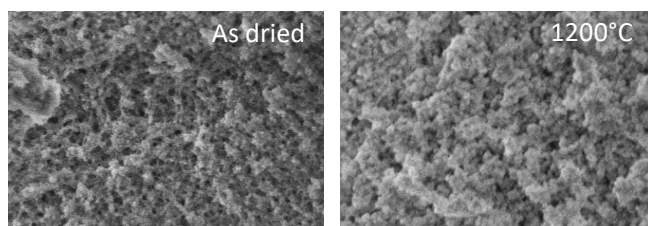
Summary

1. Aerogels are a promising candidate for lightweight, highly insulating materials in next-gen aerospace applications.

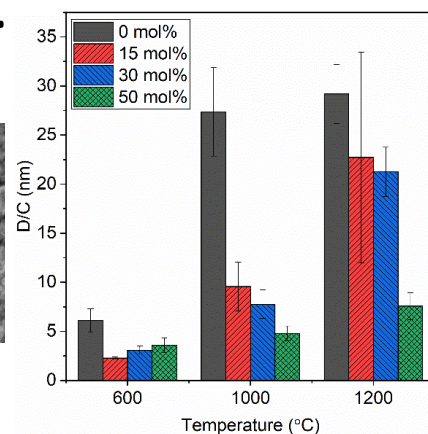
Pore structure must be preserved to temperatures $\geq 1200\text{ }^\circ\text{C}$



2. Introduction of yttria into zirconia aerogels reduces densification of pore structure and **crystallite growth** to $1200\text{ }^\circ\text{C}$.



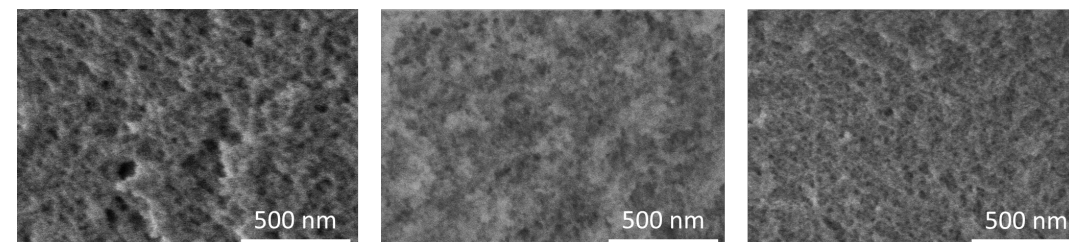
30 mol% $\text{YO}_{1.5}$
pore structure
evolution



3. Increased yttria content improves stability of YSZ aerogels as a result of **lower cation diffusivity** (mass flow) and **lower surface energy** (driving force for densification).

Future Work

1. Study of effect of **starting structure** on structural evolution by tuning synthetic parameters independent of composition.



1.263 mmol M / mL EtOH

1.895 mmol M / mL EtOH

2.526 mmol M / mL EtOH

2. Characterization of **doped metal oxides** beyond YSZ to study effect of dopant charge, mass, and size (D_{cation} , γ)
15, 30 mol% M/(M+Zr) for Yb, Gd, Ce, Ca, Y

3. Leverage lessons learned from YSZ in **development of framework to select favorable compositions & synthetic routes** for porous materials with improved thermal stability.

Primary Contact:

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Thank you for your attention!



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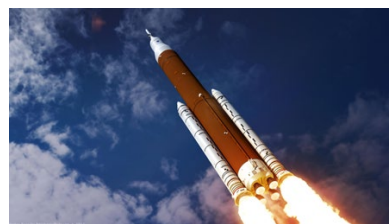
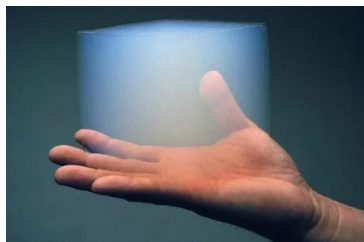
- Materials Research Laboratory, UIUC
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Summary

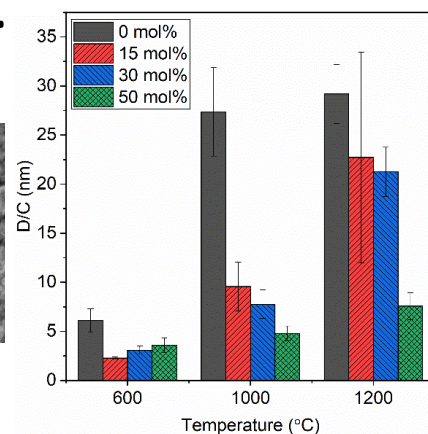
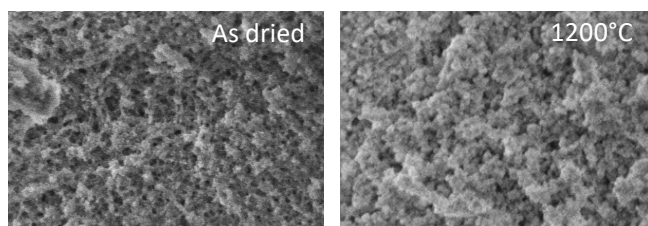
1. Aerogels are a promising candidate for lightweight, highly insulating materials in next-gen aerospace applications.

Pore structure must be preserved to temperatures $\geq 1200\text{ }^{\circ}\text{C}$



2. Introduction of yttria into zirconia aerogels reduces densification of pore structure and crystallite growth to $1200\text{ }^{\circ}\text{C}$.

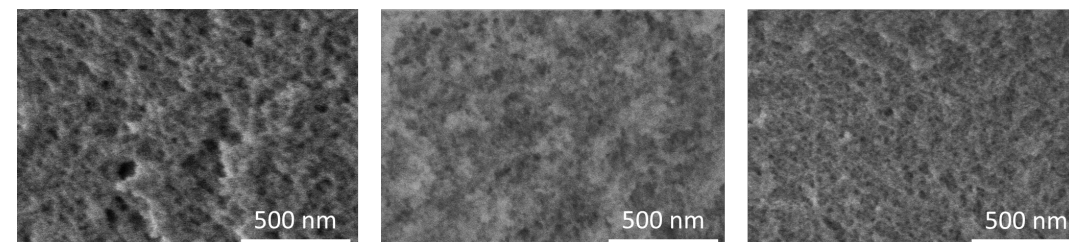
30 mol% $\text{YO}_{1.5}$ pore structure evolution



3. Increased yttria content improves stability of YSZ aerogels as a result of **lower cation diffusivity** (mass flow) and **lower surface energy** (driving force for densification).

Future Work

1. Study of effect of **starting structure** on structural evolution by tuning synthetic parameters independent of composition.



1.263 mmol M / mL EtOH

1.895 mmol M / mL EtOH

2.526 mmol M / mL EtOH

2. Characterization of **doped metal oxides** beyond YSZ to study effect of dopant charge, mass, and size ($D_{\text{cation}}, \gamma$)
15, 30 mol% M/(M+Zr) for Yb, Gd, Ce, Ca, Y

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