Enhanced thermal stability of high yttria concentration YSZ aerogels

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TMS 2021: Advances in Powder and Ceramic Materials Science Structure Design & Processing

March 15th, 2021

This work is supported by a NASA Space Technology Research Fellowship

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

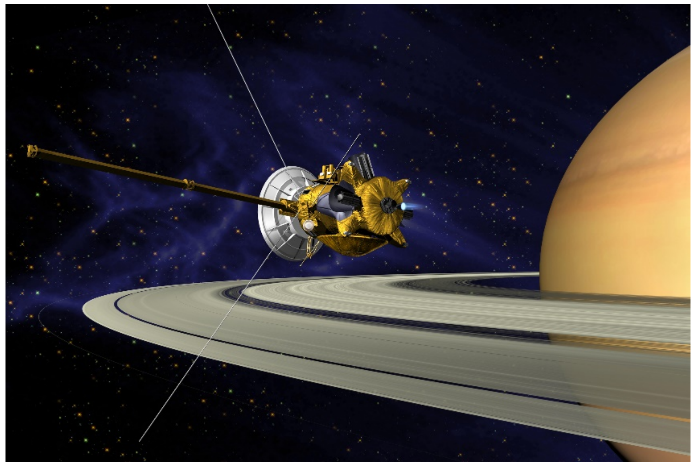
10% reduction in mass of thermal protection system → = $4,300,000 reduction in cost per launch

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

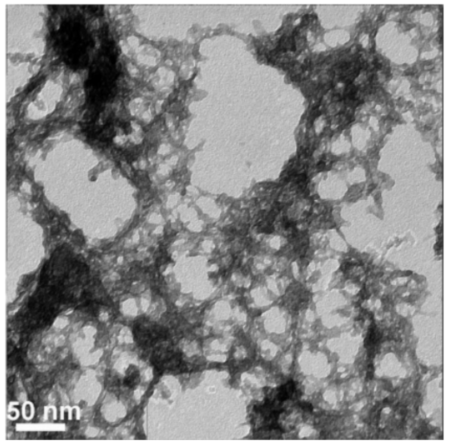
Missions to the Moon & Mars: lightweight insulation to reduce cost and increase payload capability

All images courtesy of NASA

Aerogels are highly insulating and lightweight materials

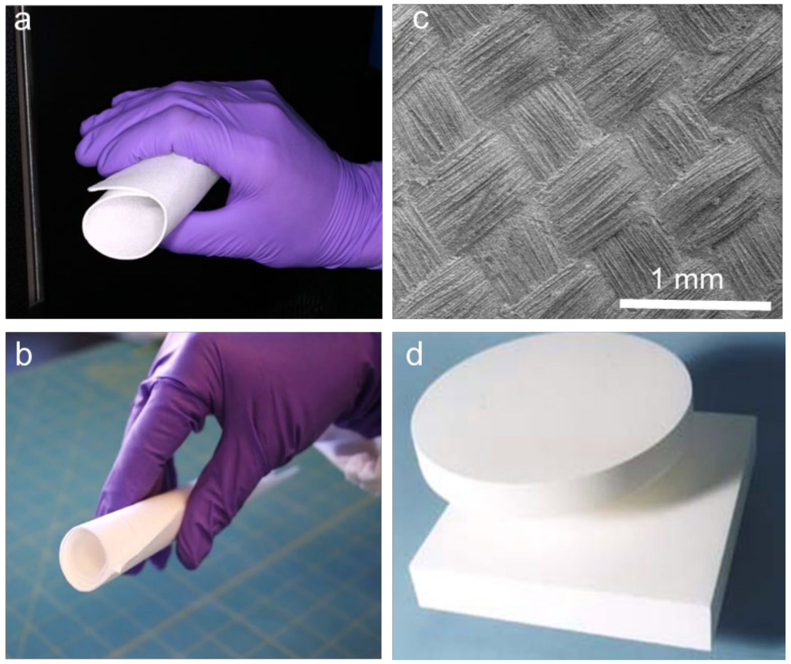
- High specific surface area (SSA), high porosity, and low density
  - **SSA**: 200 – 1000 m^2/g
  - **Porosity**: 90 – 99.9%
- Low thermal conductivity
  - Low as 0.009 W/(m•K) in atmosphere and 0.003 W/(m•K) under vacuum
  - Low density = Low solid conductivity
  - Pore sizes ≤ mean free path of gas = 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

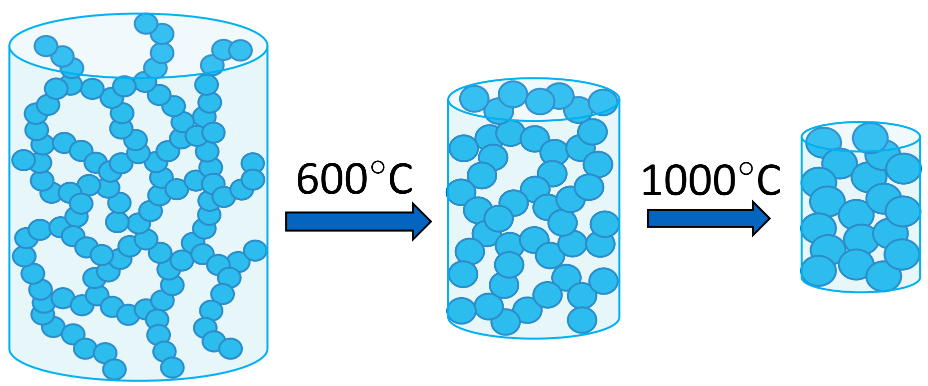
Cohen, E., and Glicksman, L. *Journal of Heat Transfer*, **2015**, 137(8), 81601.
Sun, H., et al. *Advanced Materials,* **2013**, 25(18), 2554-2560.
Gash, A.E., et al. *Journal of Non-Crystalline Solids,* **2001**, 285(1-3): 22-28.

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

Thermal Conductivity for SiO_2

Aerogel
0.03 W/m·K

Dense
1.40 W/m·K

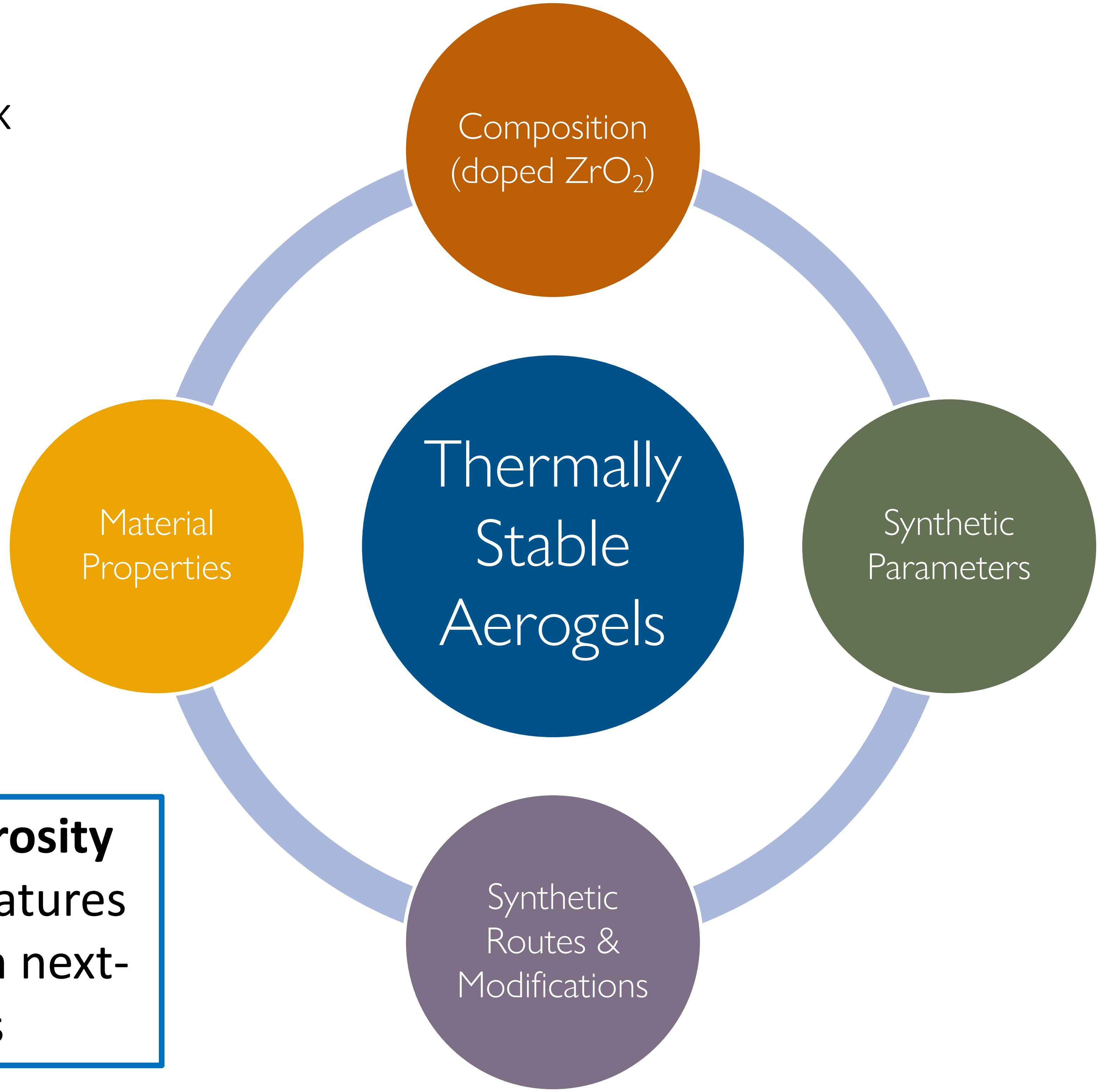


Loss of SSA, porosity →

Large SSA = large driving force
↑ thermal conductivity

Project Objective

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



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

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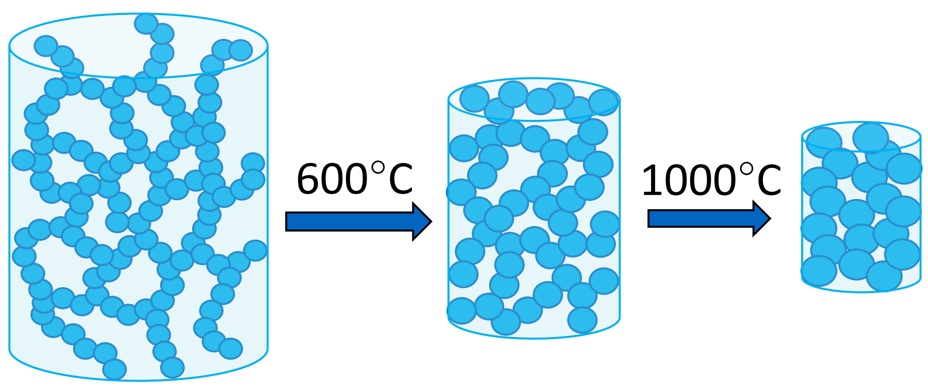

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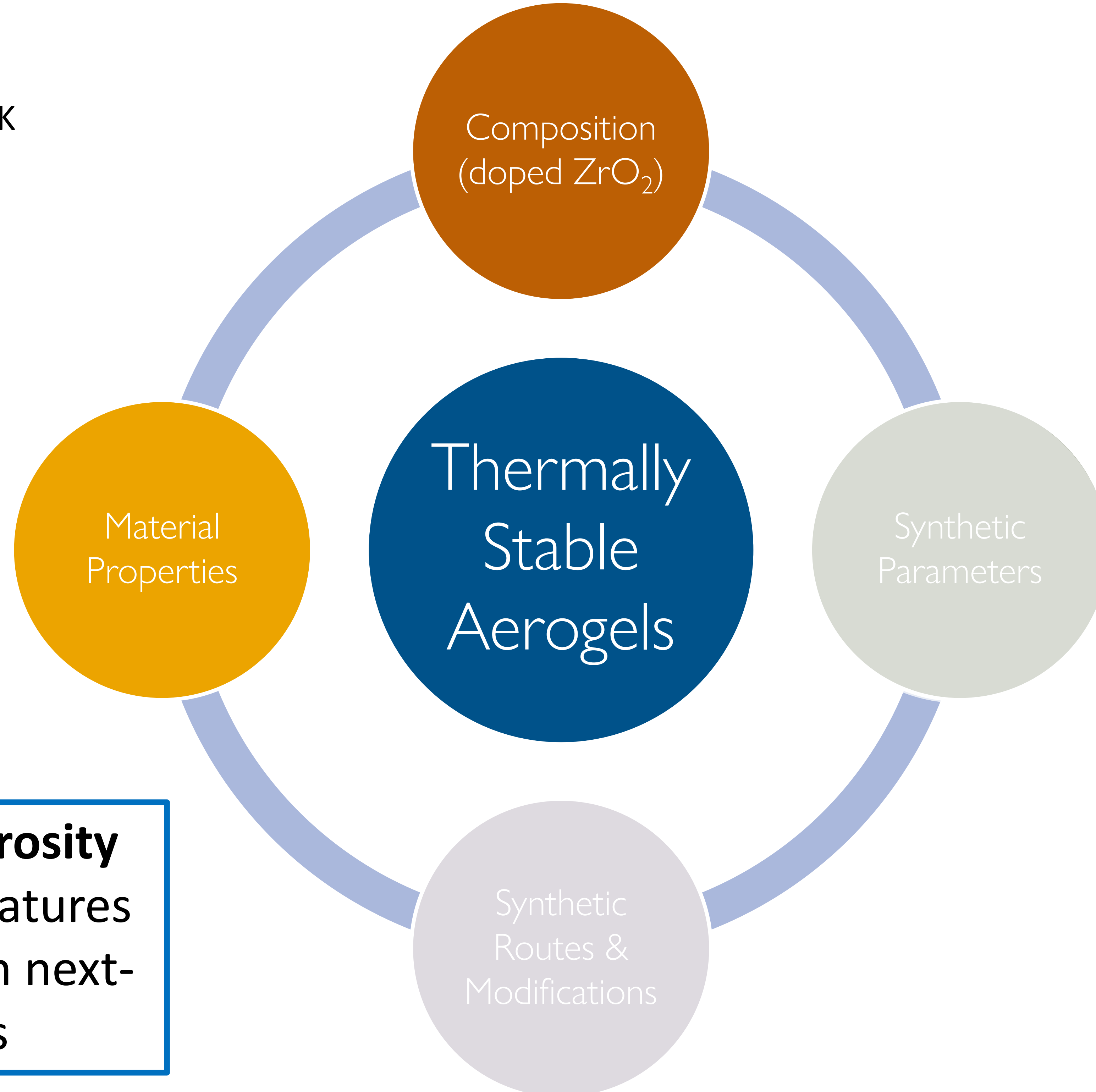
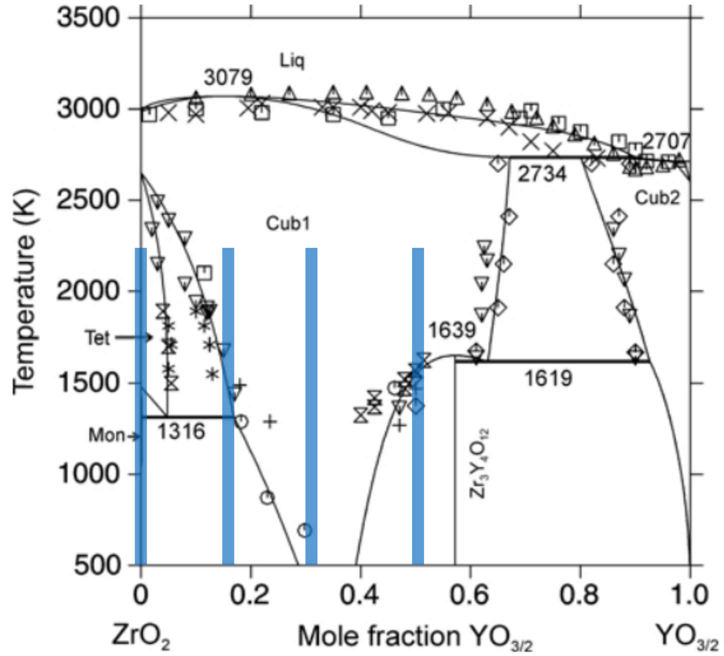


Powell, R.W., et al; NSRDS-NBS 8, **1966**, 99.
Lide, D. R., ed; "Thermal conductivity", CRC Handbook of Chemistry and Physics (100th ed.).

Improving aerogel stability in extreme environments

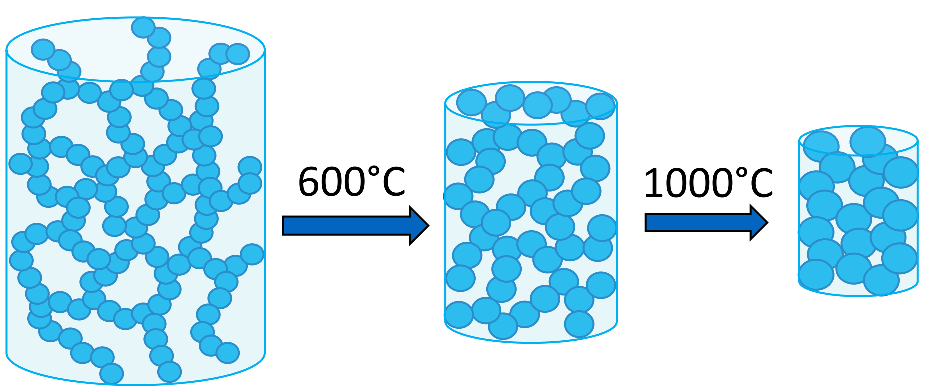
- **Yttria stabilized zirconia** (YSZ) as a candidate composition for a thermally stable aerogel
- YSZ is a ceramic used as thermal barrier coating on super alloys in aircraft engines
  - → Low thermal conductivity of 0.8-2.9 W/(m·K)
  - → Y_2O_3 doping inhibits phase transformation



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

Properties (as function of yttria content) 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

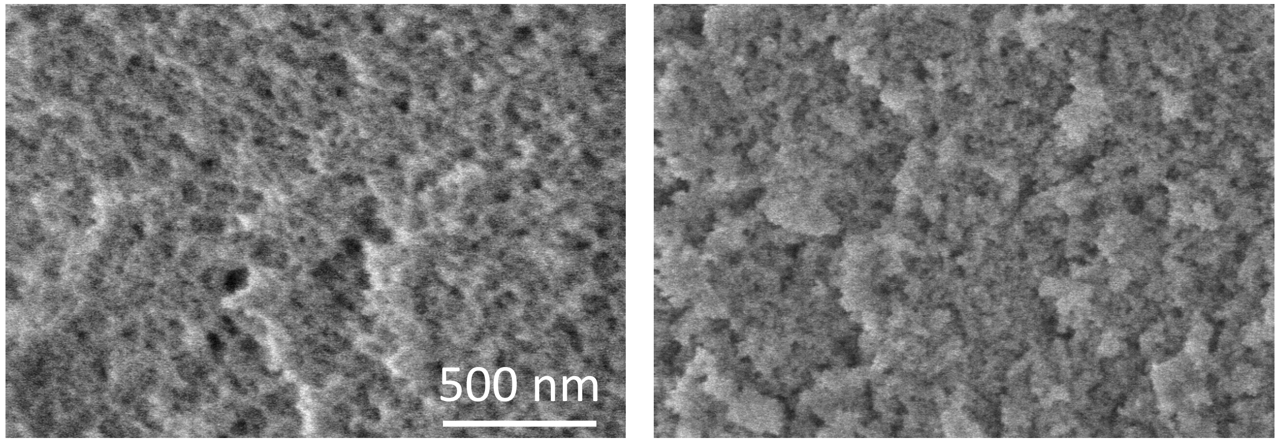


→Measure SSA and pore size distributions with N_2 physisorption

→Maintain high SSA, constant size distribution

Microstructural Evolution

As Synthesized 1000°C (18 min)

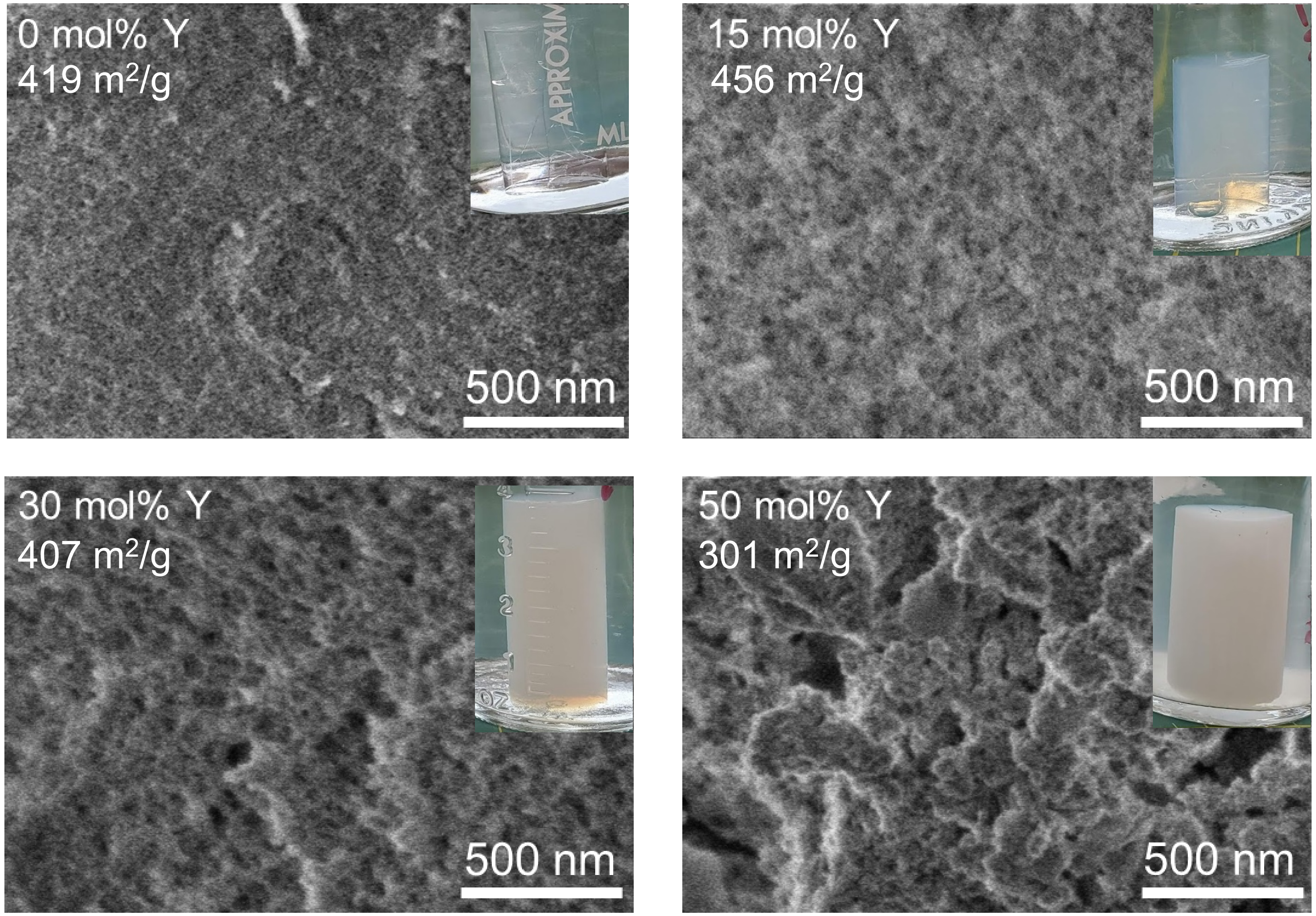


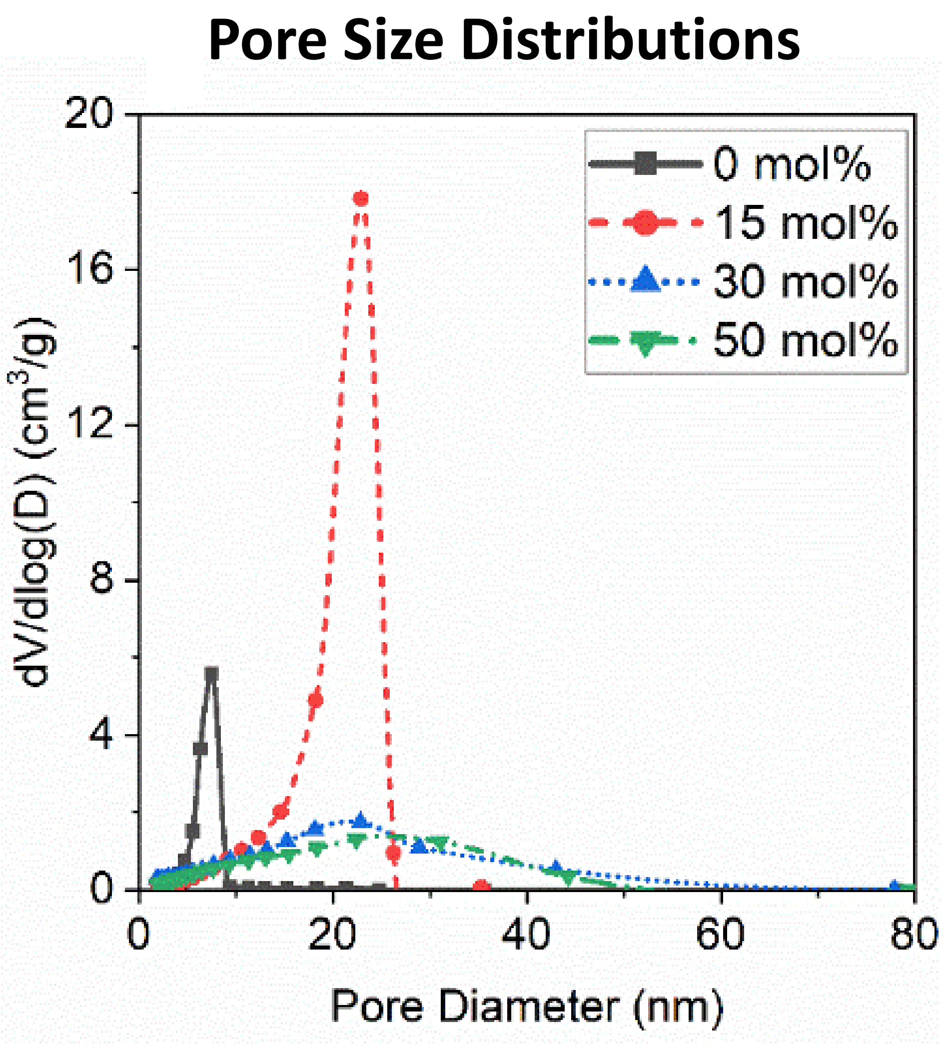
→Pore morphology with SEM & TEM

→Phase & crystallite size with XRD

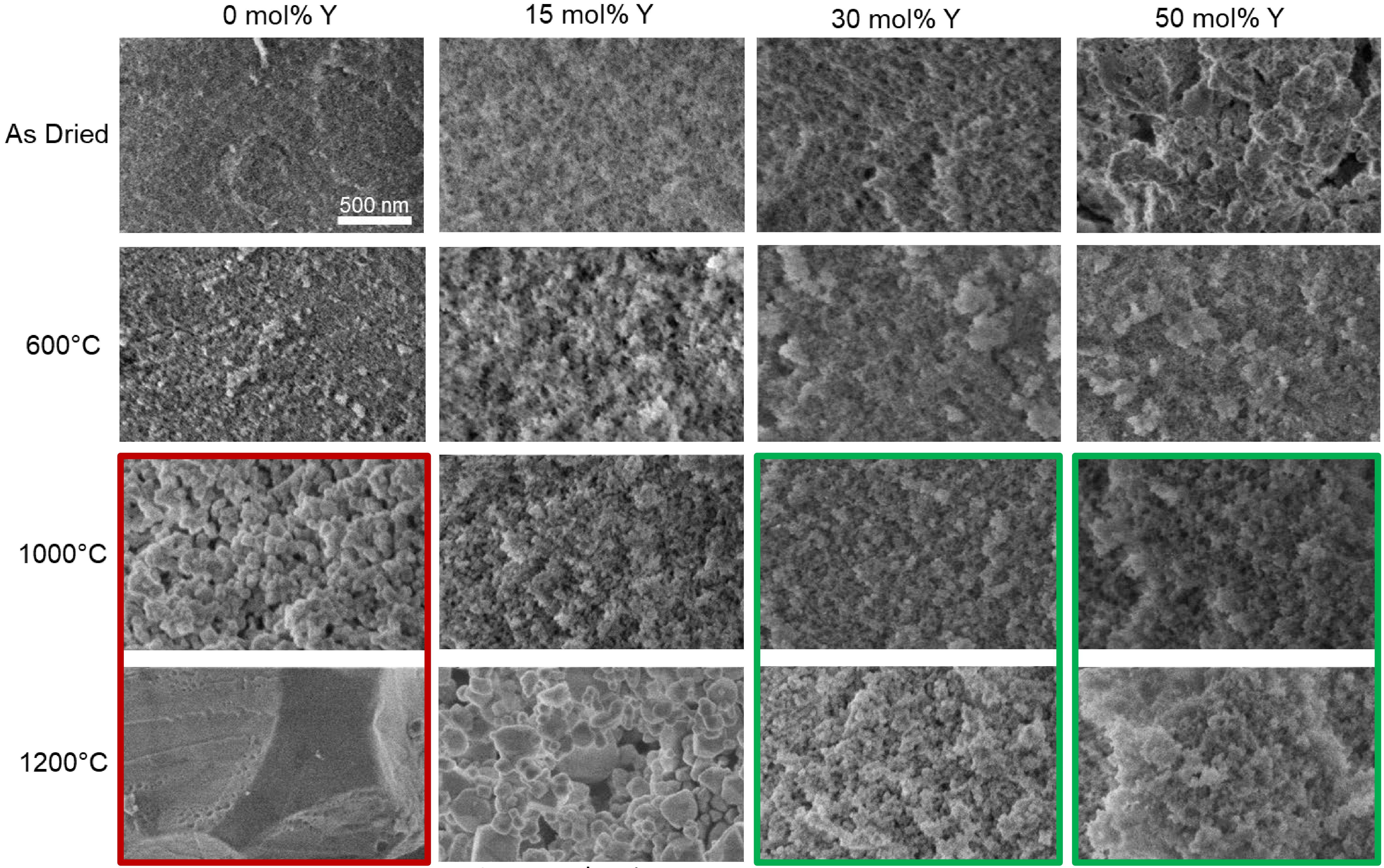
Schlichting, K.W., *et al*; *J. Mater. Sci.*, **2001**, 36, 3003-10. Fabrichnaya, O., *et al*; *Zeitschrift füür Metallkunde.*, **2004**, 95(1), 27-39.

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



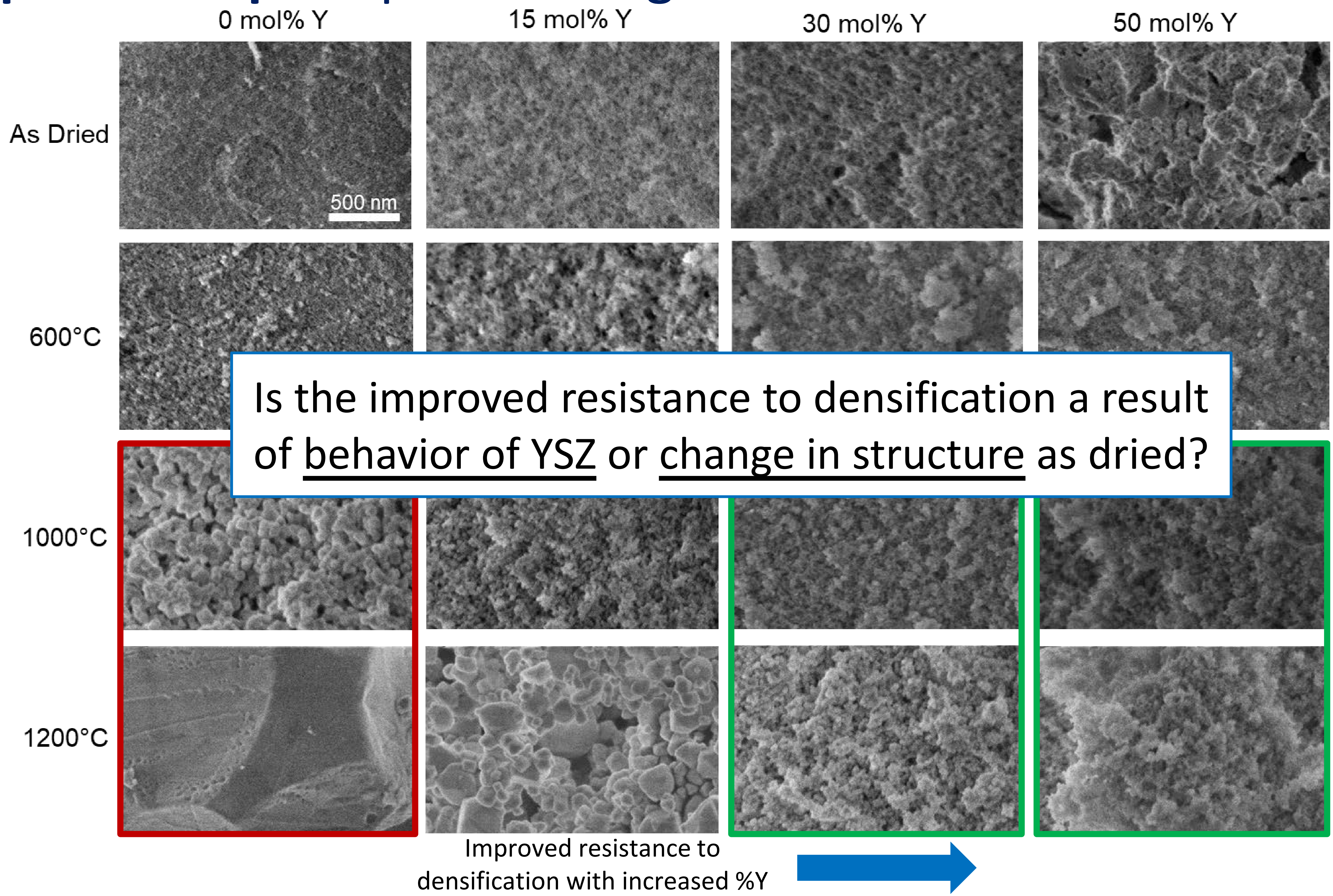


Increased yttria content **reduces densification and pore collapse** upon heating to 1200 °C



Improved resistance to densification with increased %Y

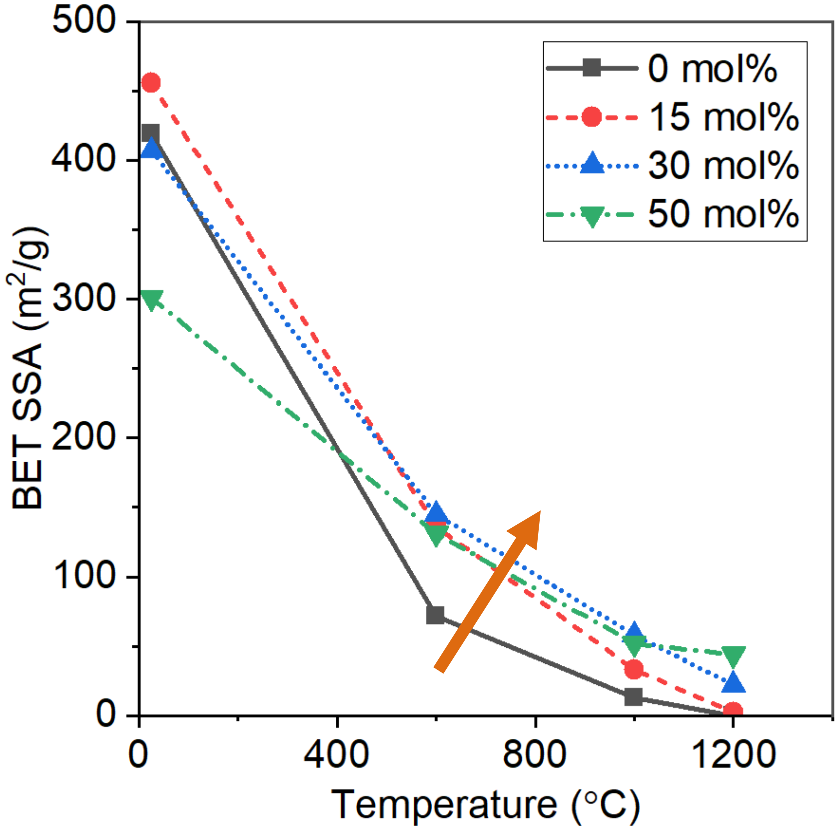
Increased yttria content **reduces densification and pore collapse** upon heating to 1200 °C



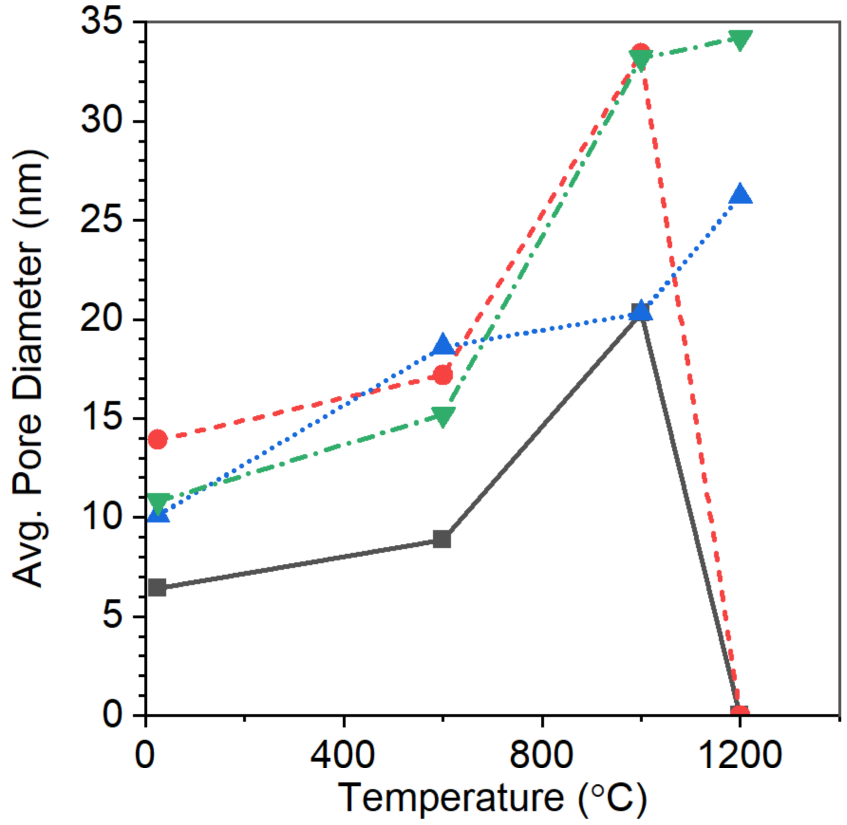
Is the improved resistance to densification a result of behavior of YSZ or change in structure as dried?

Nitrogen physisorption quantifies improvement in thermal stability with increased yttria content

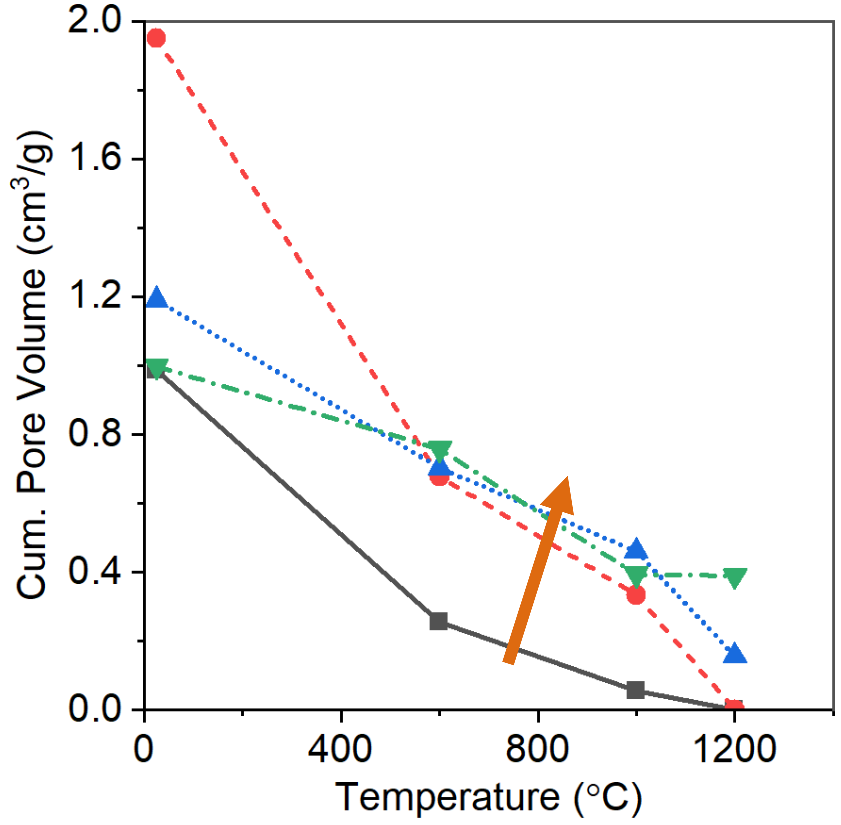
BET SSA



BJH Desorp. Pore Size

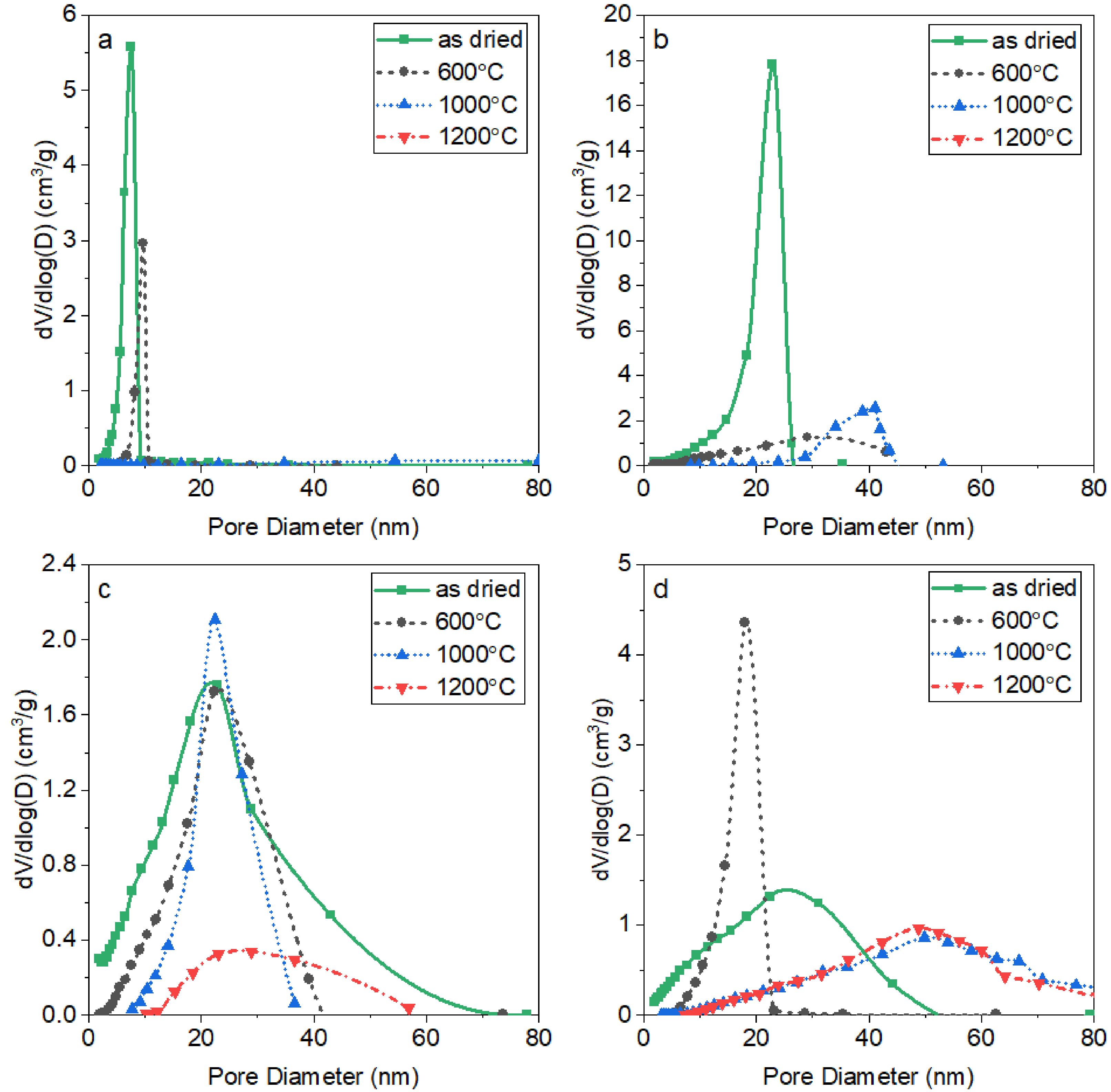


BJH Desorp. Pore Volume



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

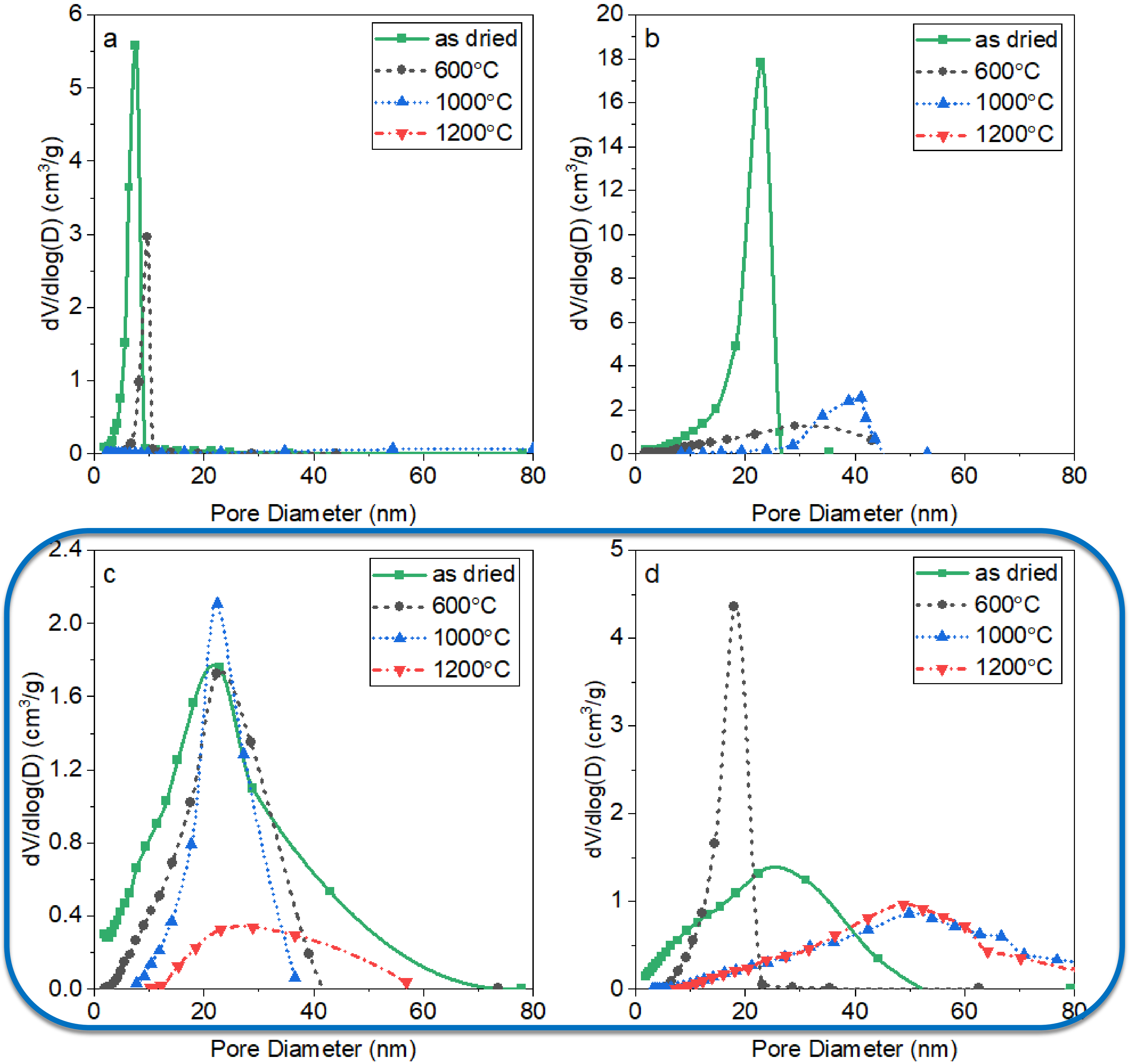
BJH Pore Size Distributions



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

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

BJH Pore Size Distributions



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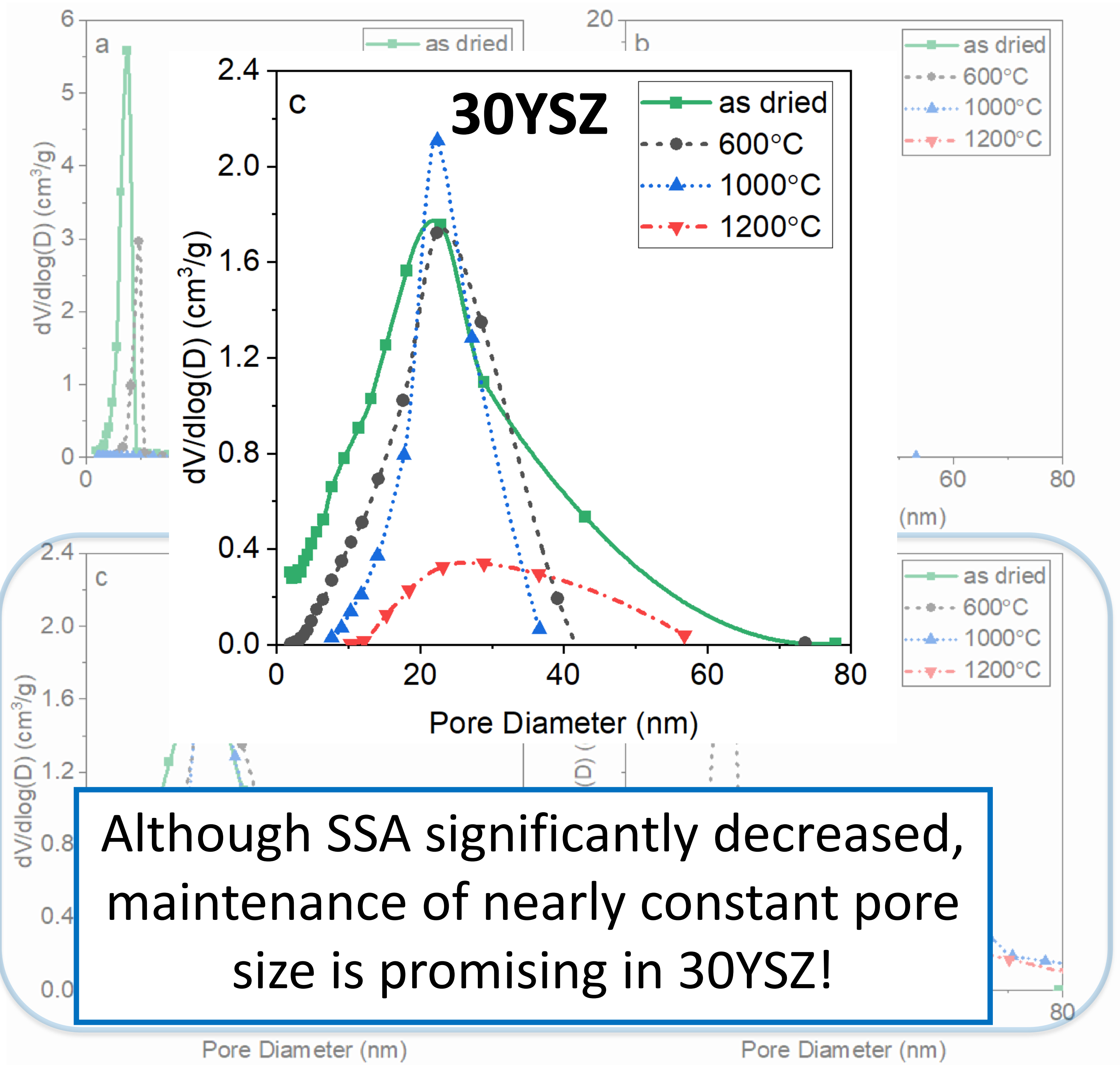
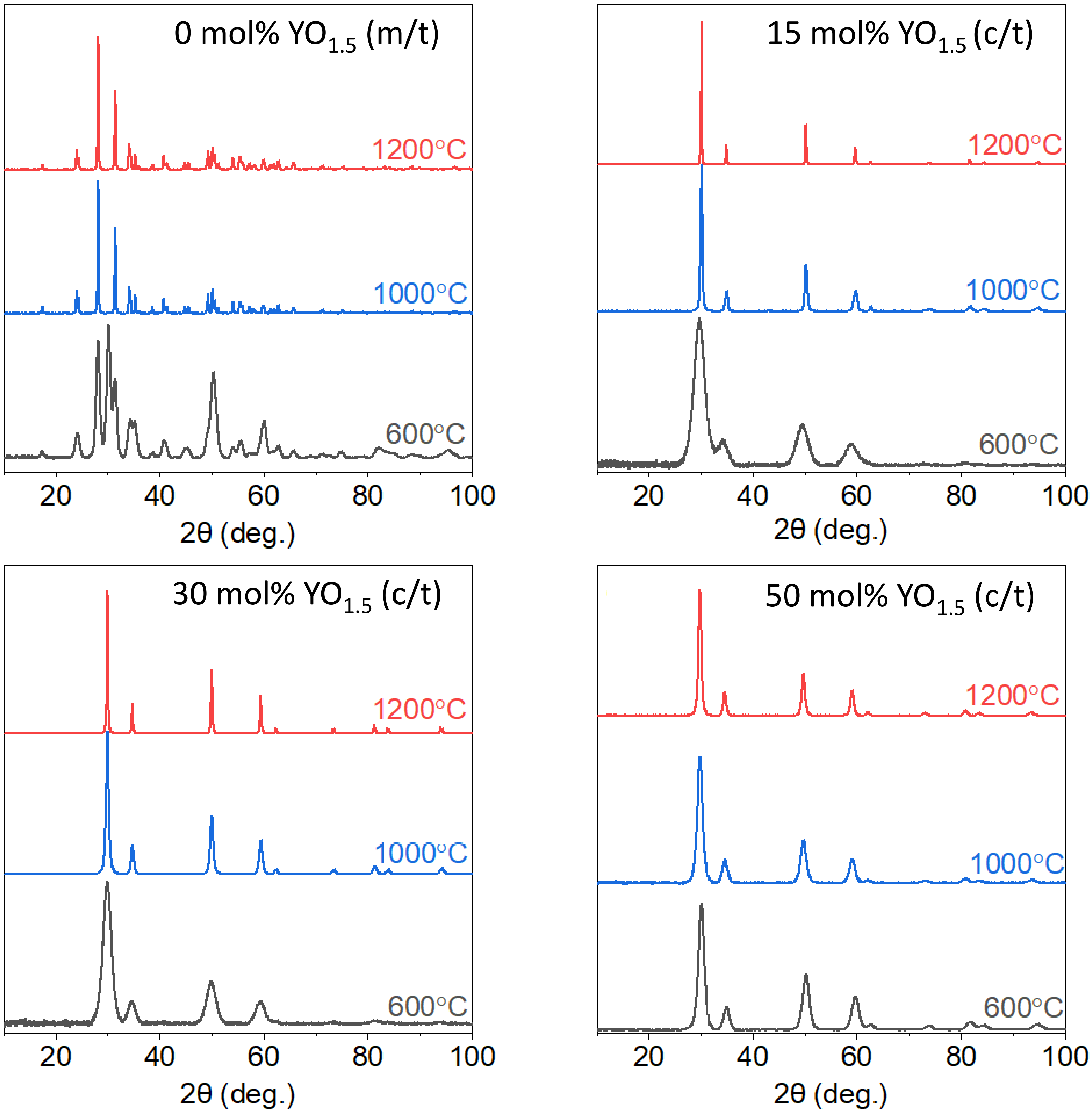


Although SSA significantly decreased, maintenance of nearly constant pore size is promising in 30YSZ!

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

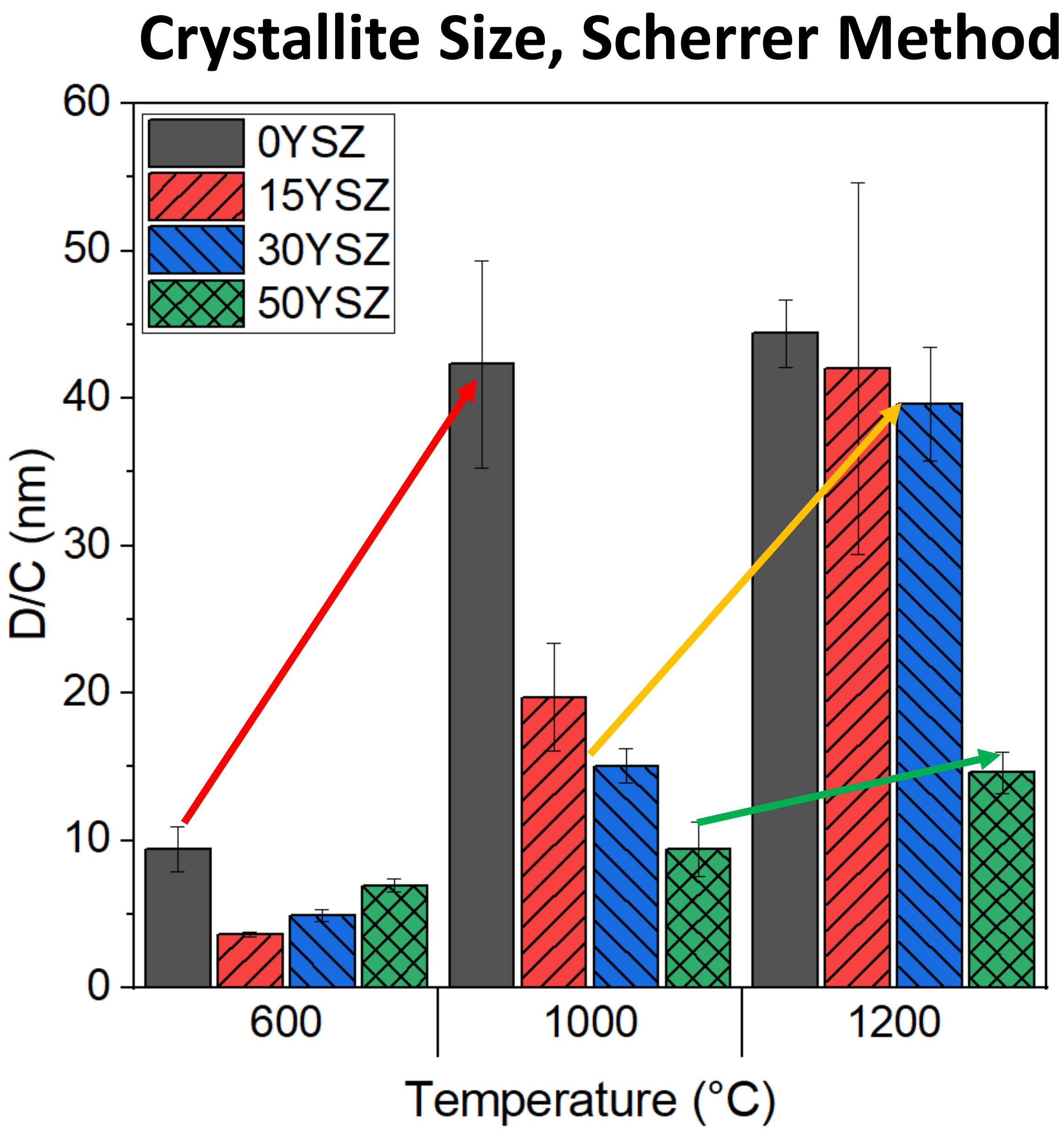
No unexpected phase transformations or separations as observed with x-ray diffraction (XRD)



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)



0 mol%: Stable to 600 °C

15, 30 mol%: Stable to 1000 °C

50 mol%: Stable to 1200 °C

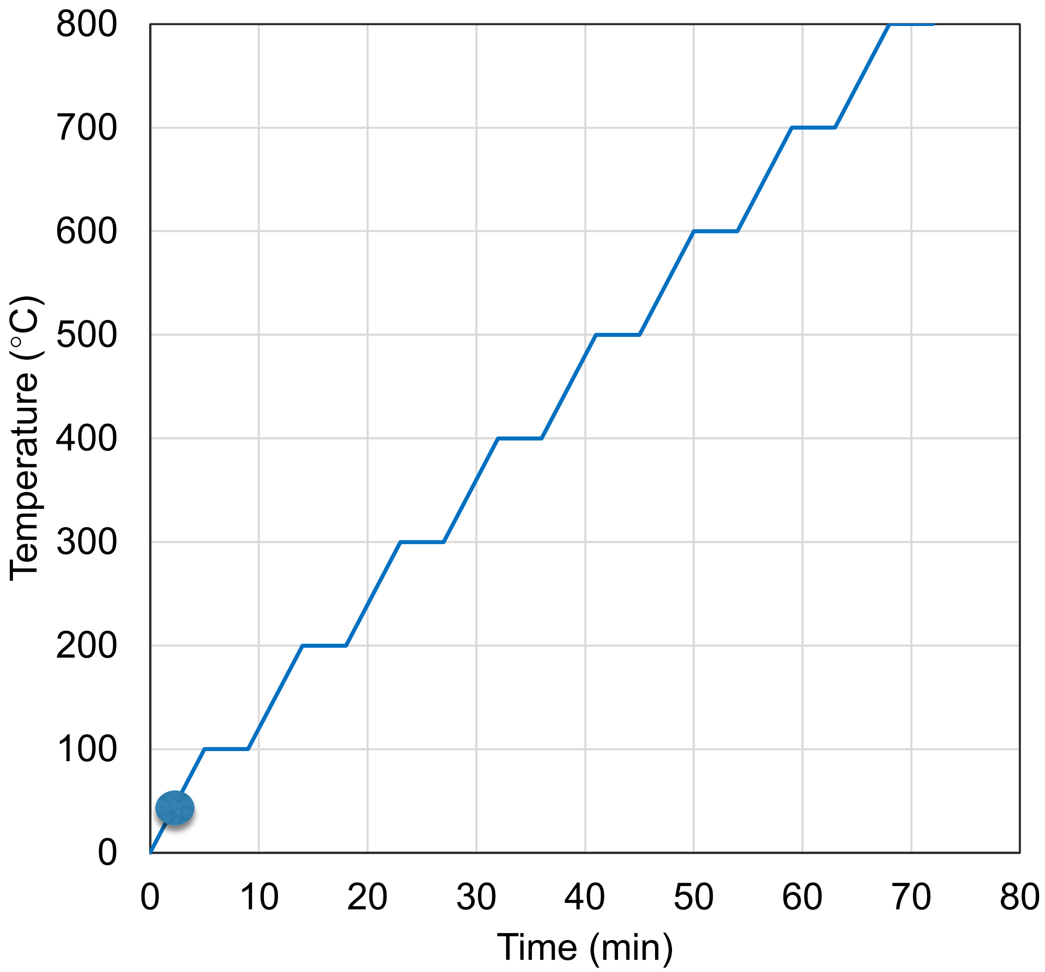
- Took peak position (θ) & FWHM (β) and calculated D/C from Scherrer equation

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

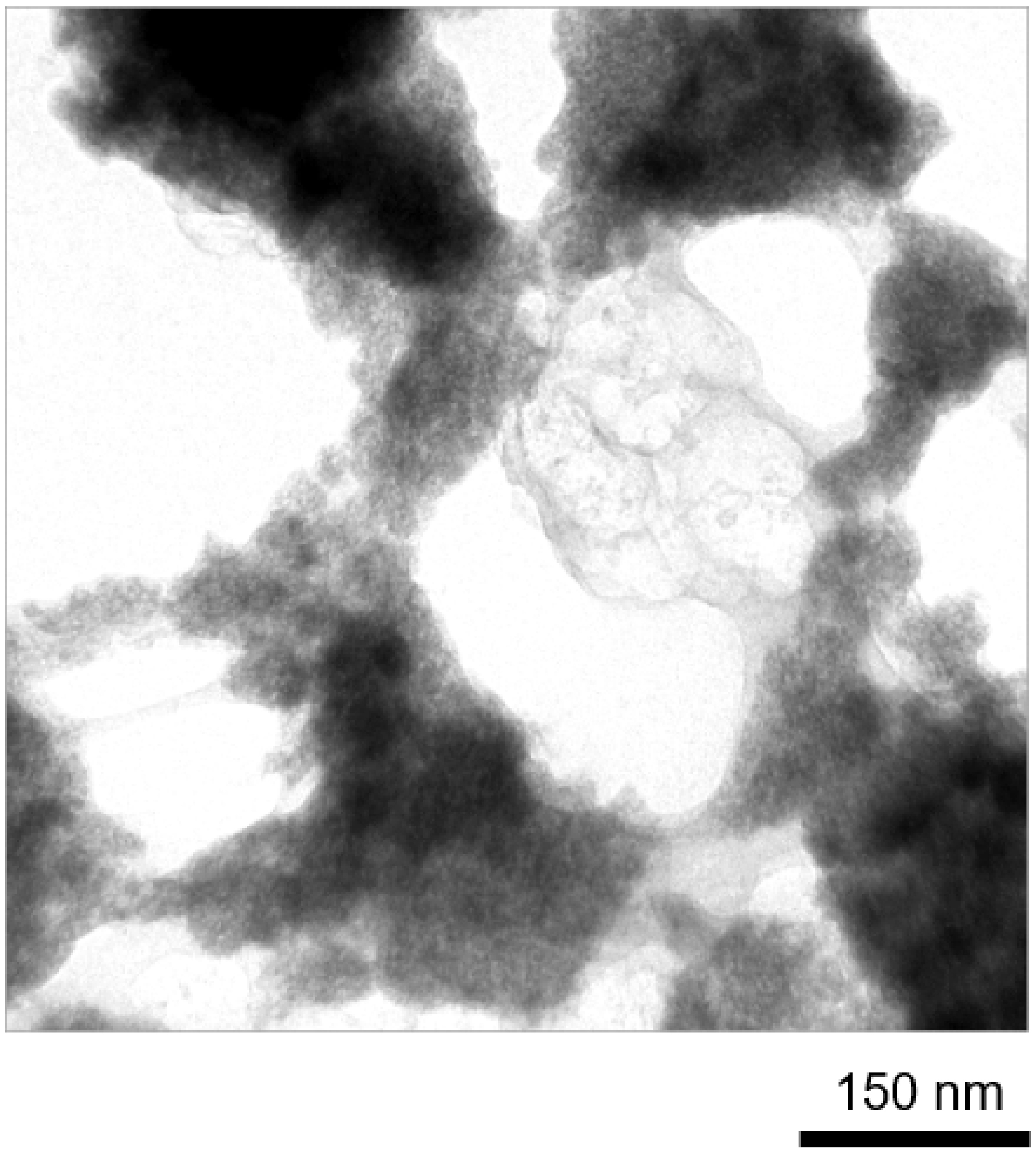
- Averaged over all peaks to provide a mean and standard deviation
- Large variation in 15 mol% may be explained by abnormal grain growth observed in SEM

Increased yttria content seems to **inhibit** both **densification** & **crystallite growth** to 1200 °C.

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



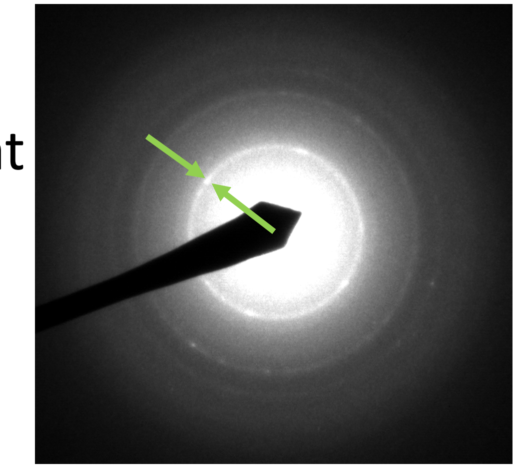
Special thanks to Nathan Madden & Charles Smith (SMEE, UIUC) for TEM data



- 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

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

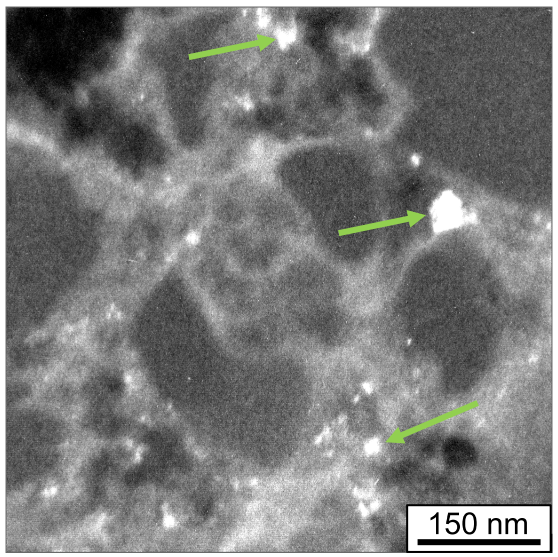
Bright regions are crystallites that contribute to this spot



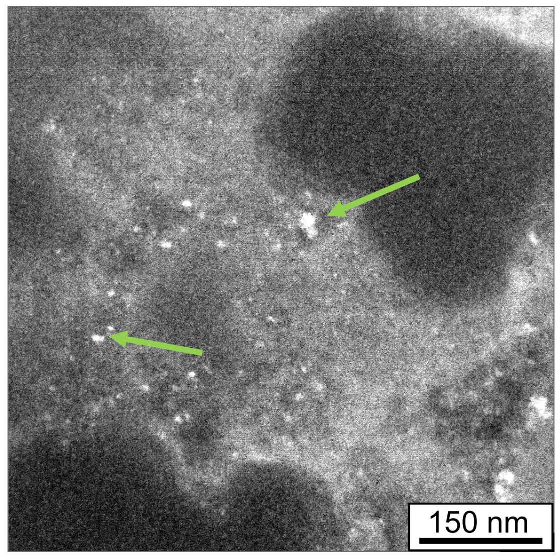
15 mol% Y
ED pattern

Select spot on ring from electron diffraction pattern

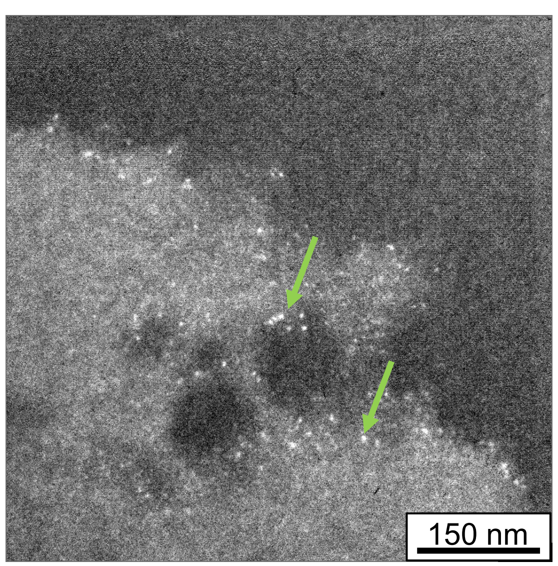
Dark field at 800°C



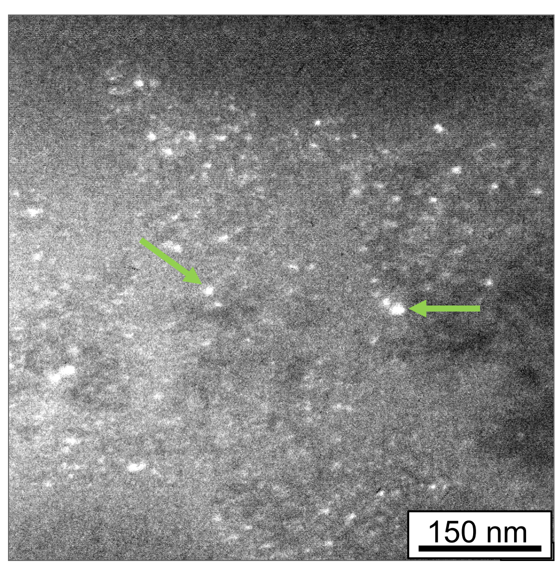
0 mol% Y



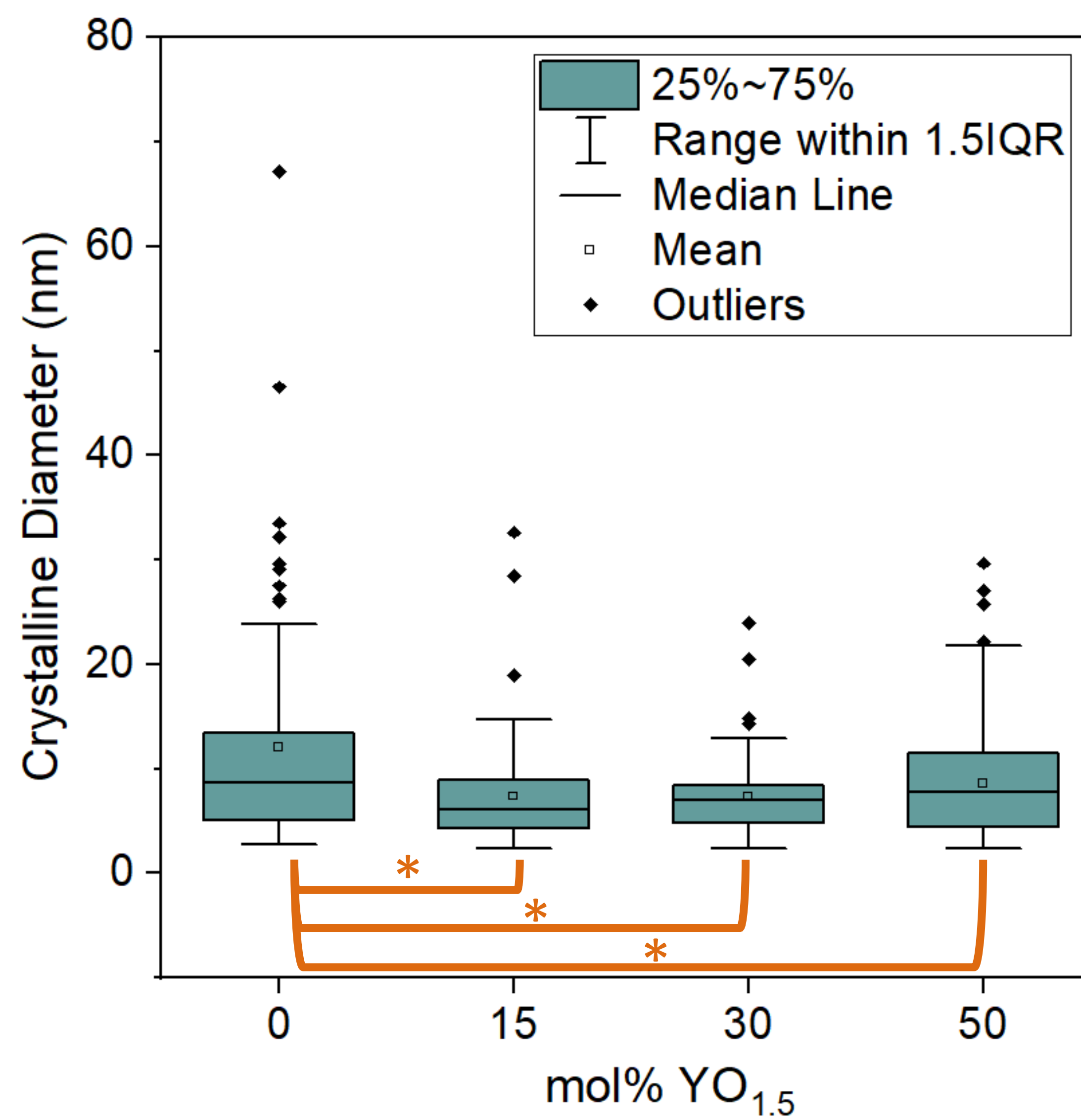
15 mol% Y



30 mol% Y



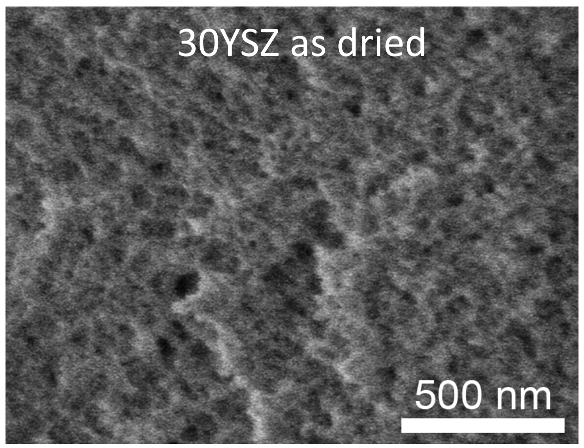
50 mol% Y

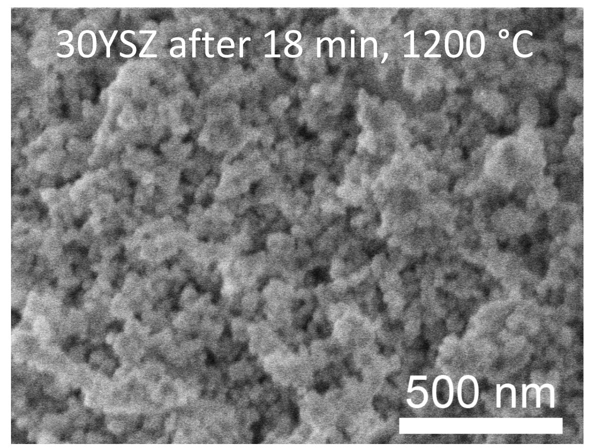


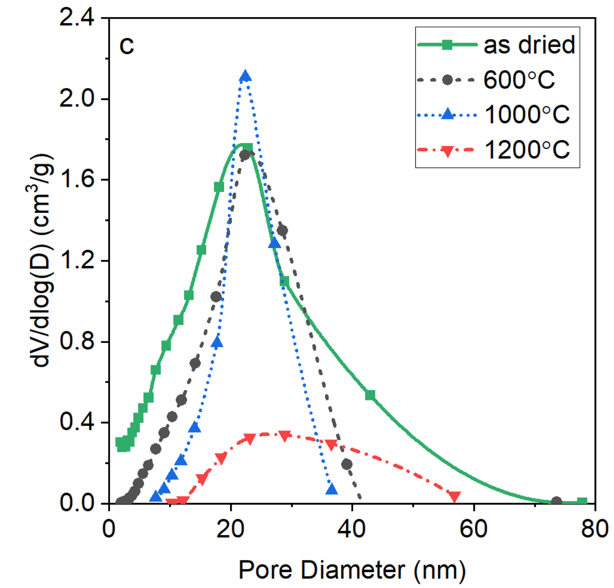
* = Significantly different at α = 0.05

Increased yttria content in YSZ aerogels improves thermal stability

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

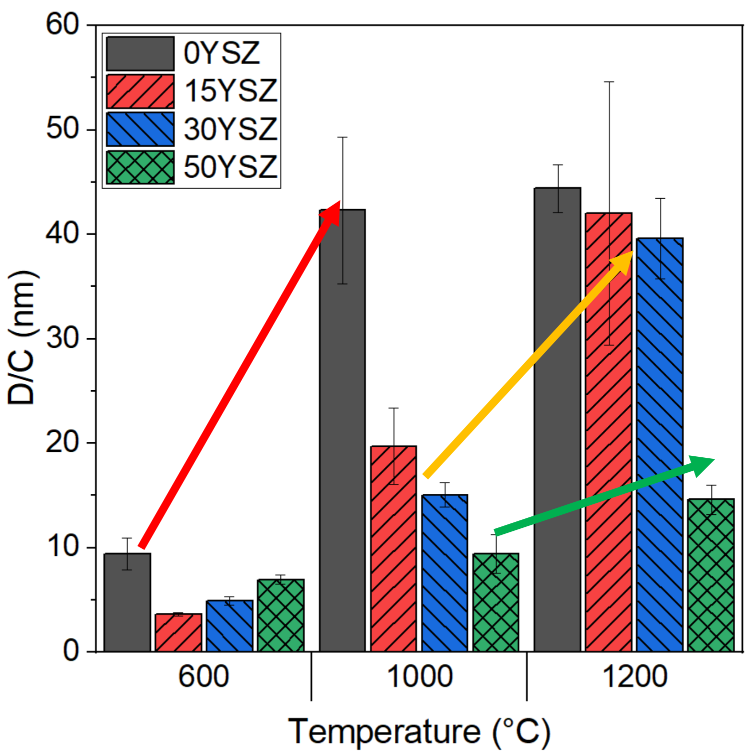






30YSZ pore size distribution

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

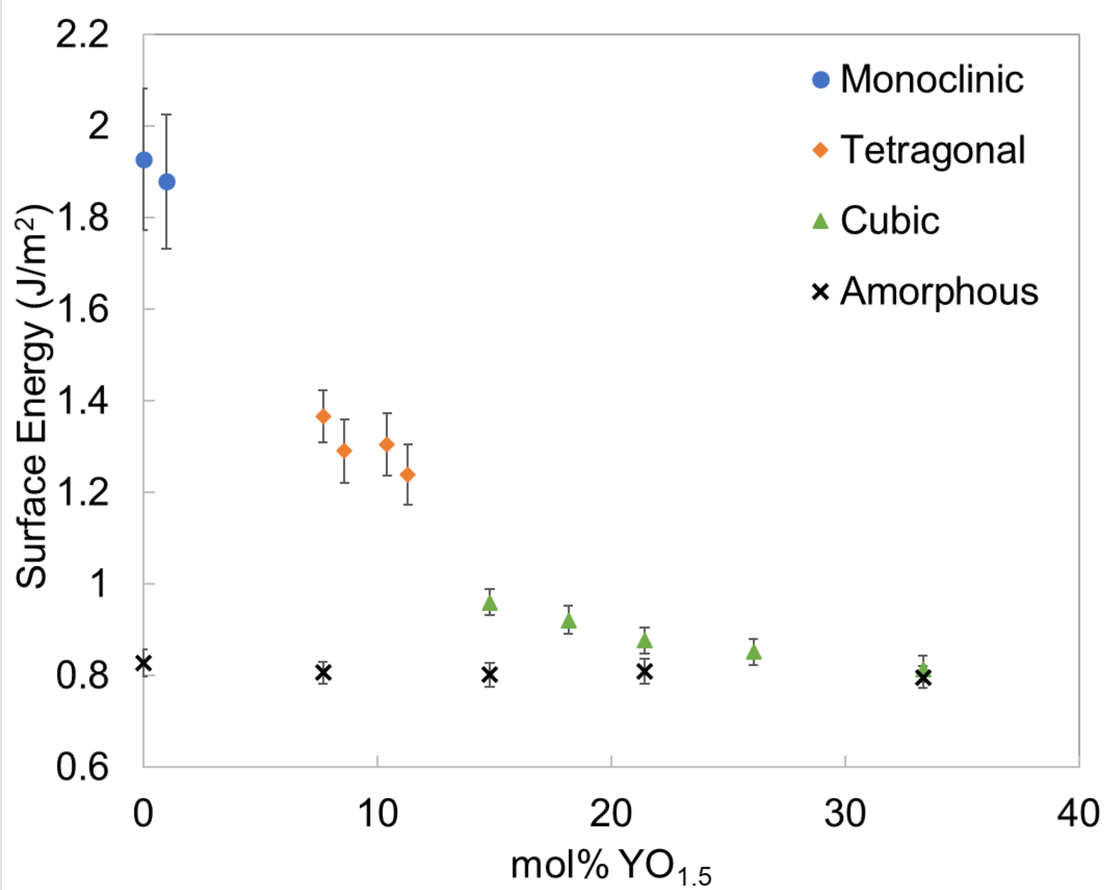


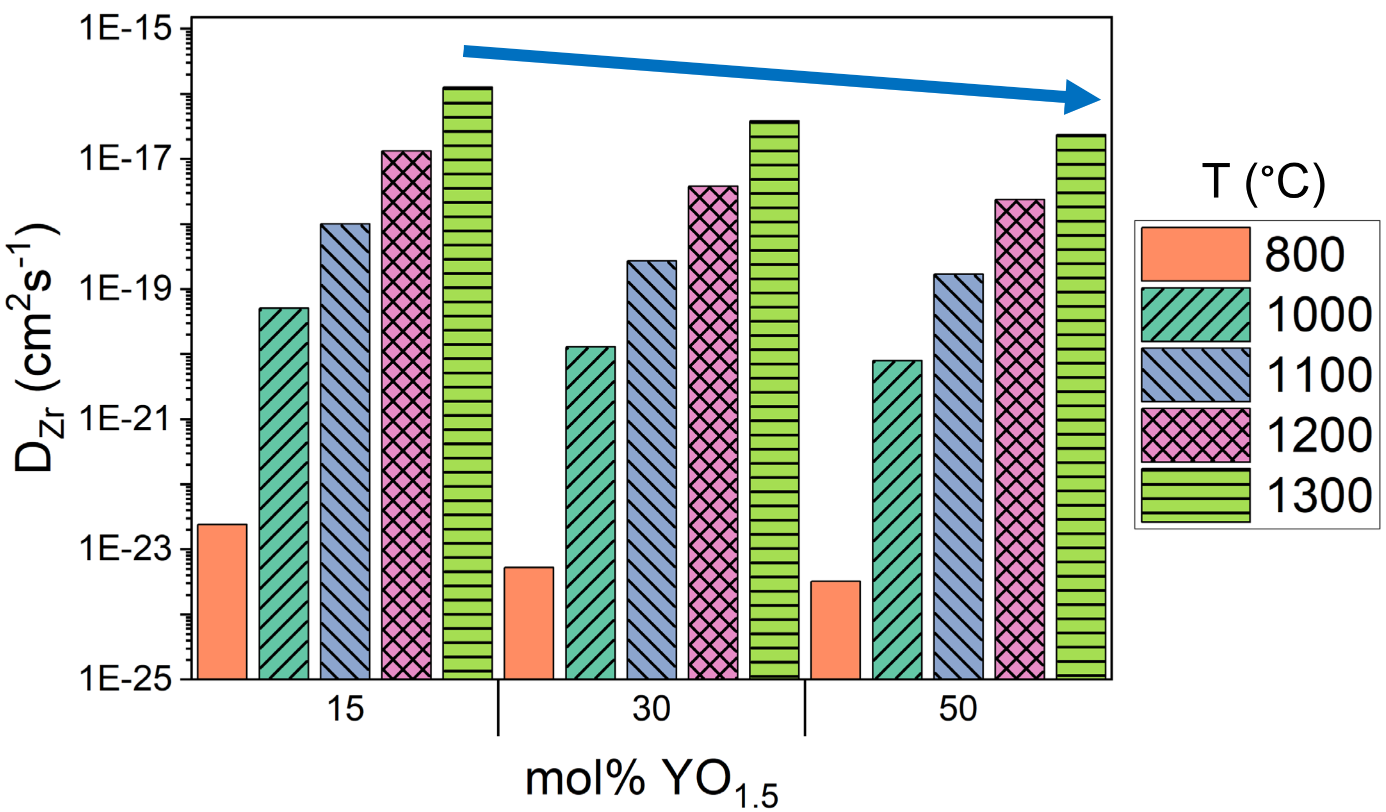
By what mechanism is yttria improving the thermal stability of the pore structure?

Thermodynamics
(Surface Energy)

Kinetics
(Cation Diffusivity)

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





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

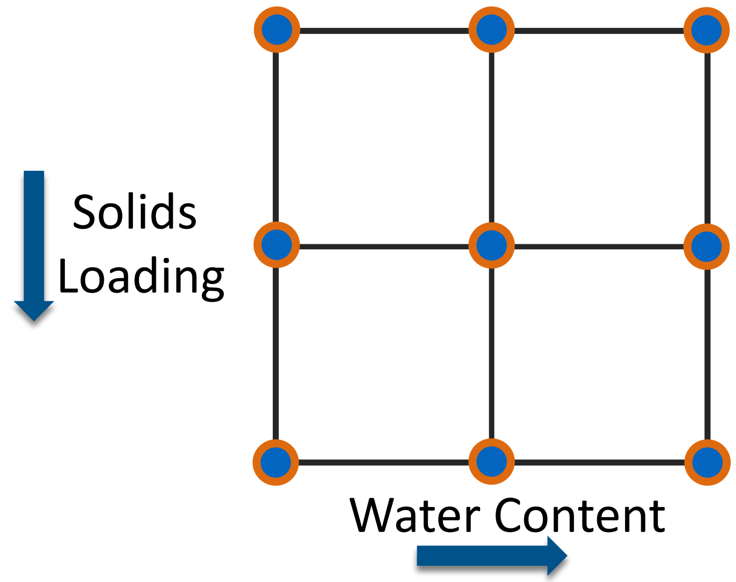
With SSAs of 300 to 500 m^2/g, surface energy has massive impact!

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

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

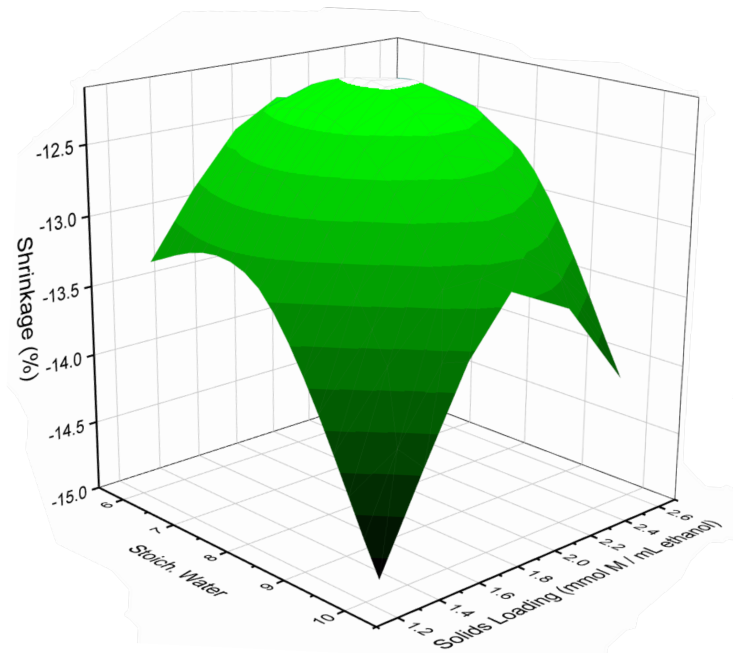
1. Drazin, J. W., & Castro, R. H. (2015). *Journal of the American Ceramic Society*, *98*(4), 1377-1384.
2. Kilo, M., et al. (2000). *Journal of the European Ceramic Society*, *20*(12), 2069-2077.
3. Kilo, M., et al. (1997). *Berichte der Bunsen-Gesellschaft*, *101*(9), 1361-1365.
4. Kilo, M., et al.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

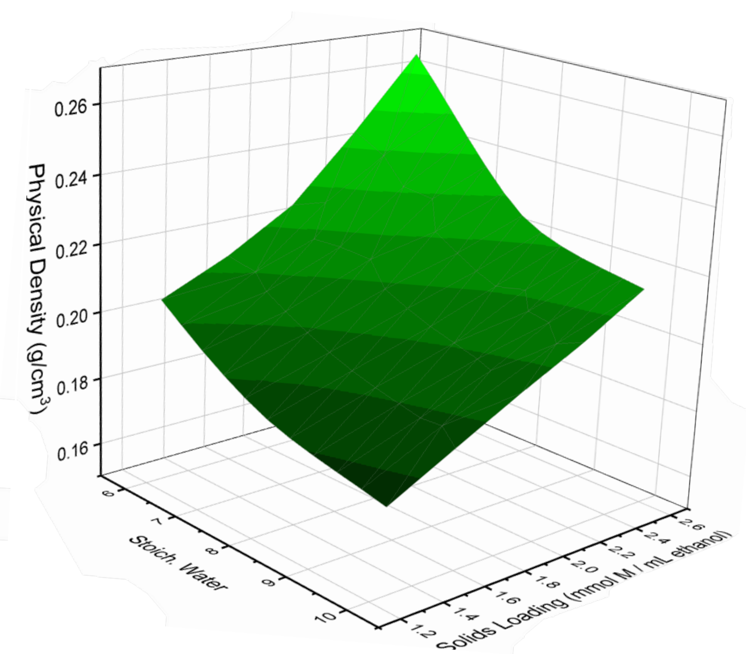
Tuning aerogel structure & structural evolution via **synthetic parameters**



Finely adjust as dried structure independently of composition

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

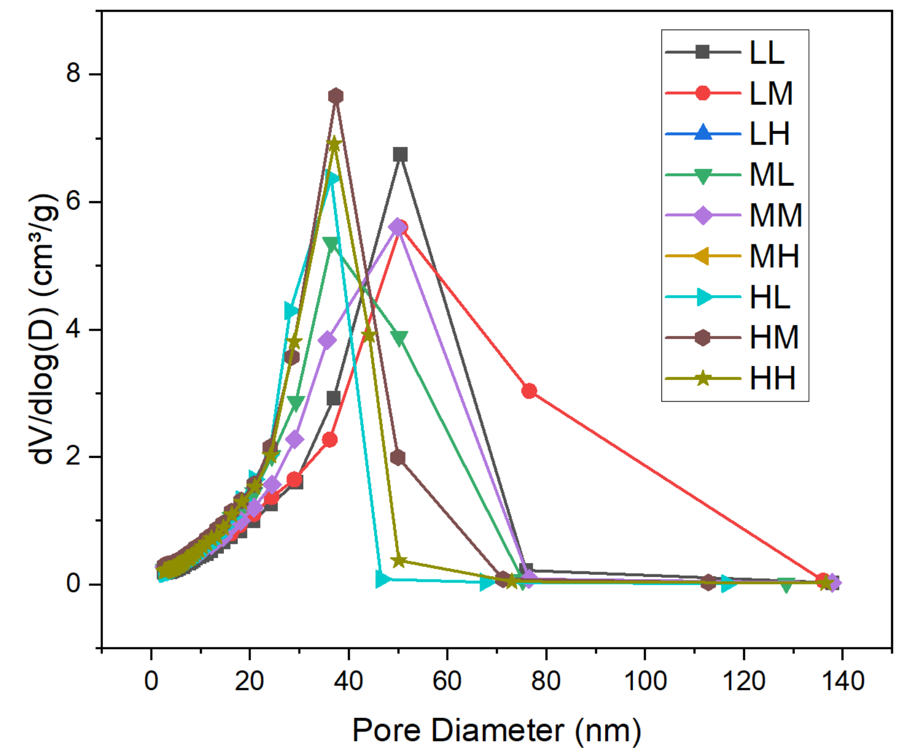




$$\text{Shrinkage} = \beta_o + \beta_1 w_s + \beta_2 w_s^2 + \beta_3 s_e^2$$

$$\text{Phys. Density} = \gamma_o + \gamma_1 w_s + \gamma_2 s_e$$

Shrinkage & physical density impacted by synthetic parameters.

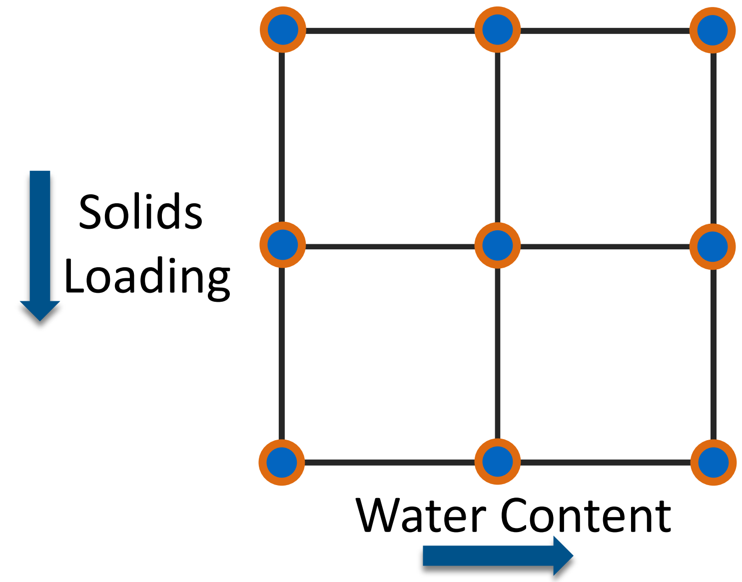


BJH Desorption Pore Size Distribution

Pore size distribution can be tuned by solids loading & water content.

Work performed by Jordan Meyer (UIUC MatSE U-Grad)

Tuning aerogel structure & structural evolution via **synthetic parameters**



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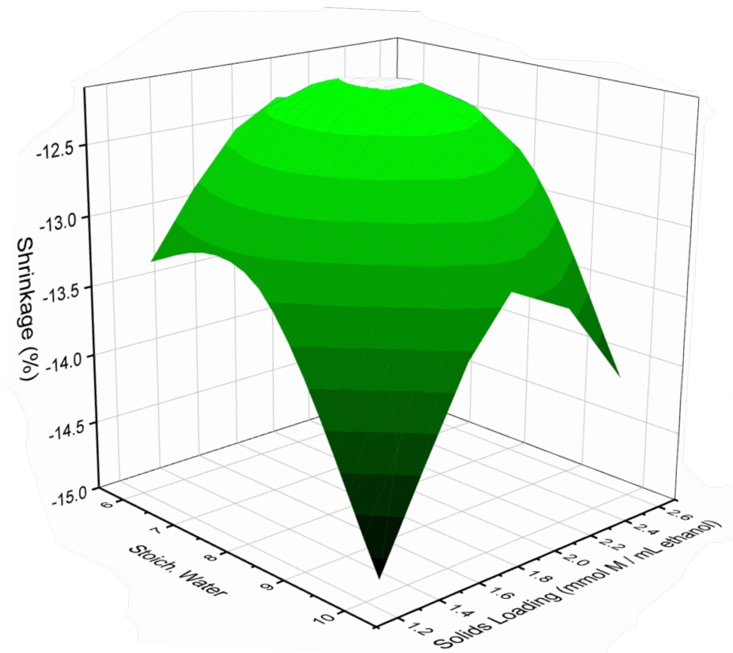

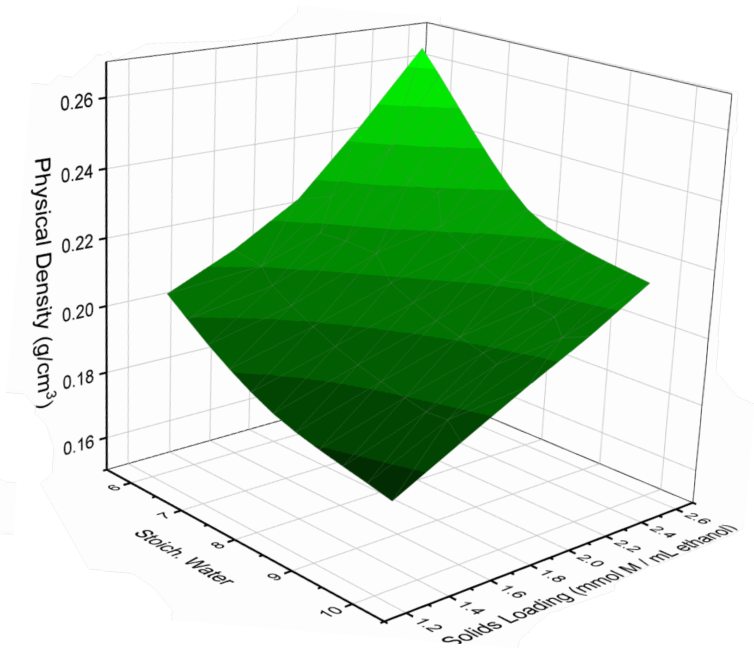

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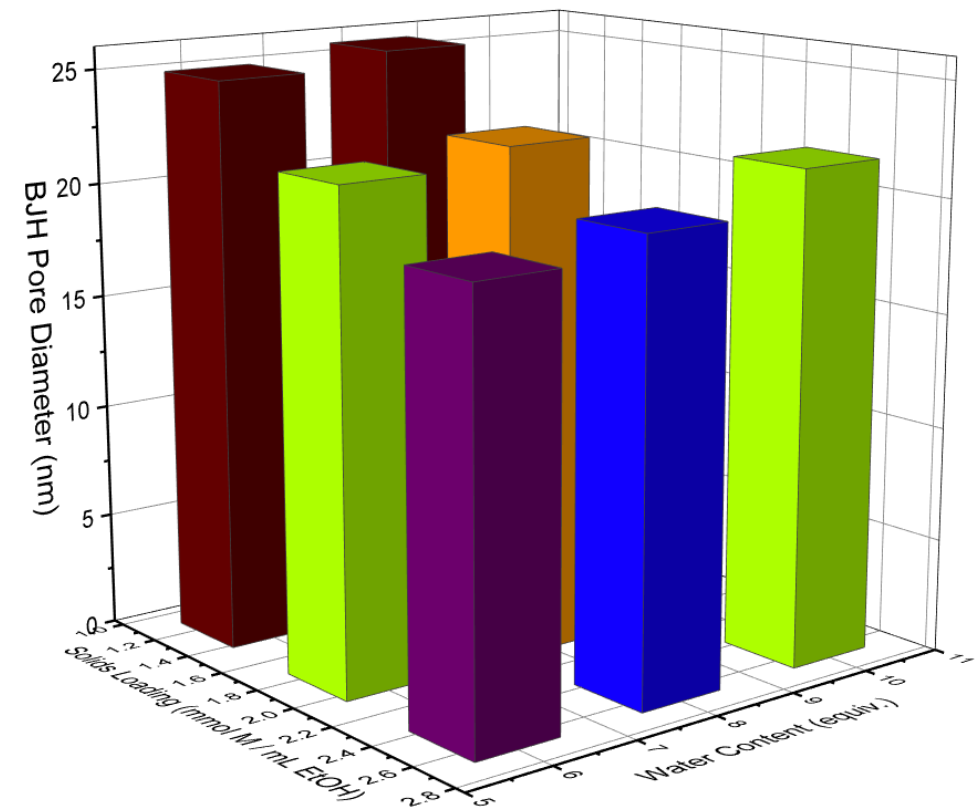
Shrinkage & physical density impacted by synthetic parameters.

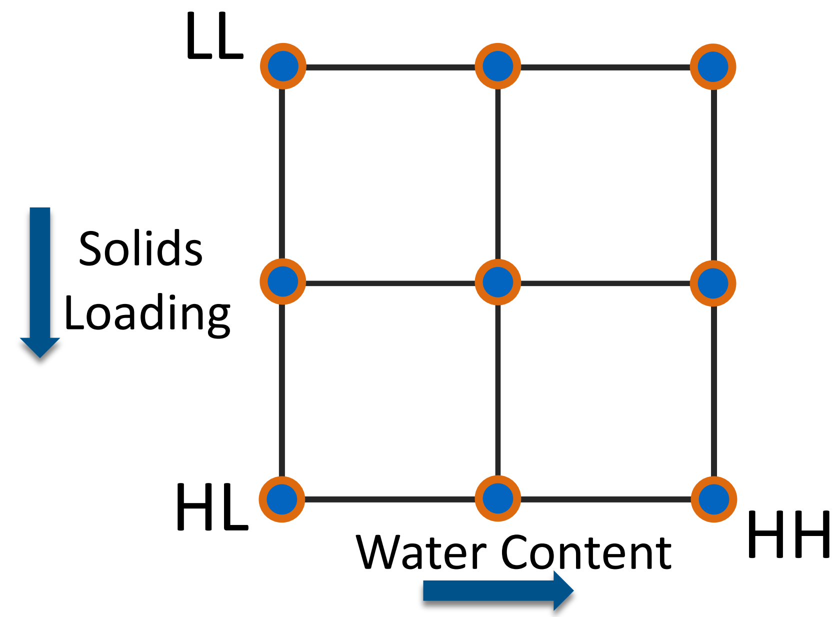


BJH Average Pore Size

Pore size distribution can be tuned by solids loading & water content.

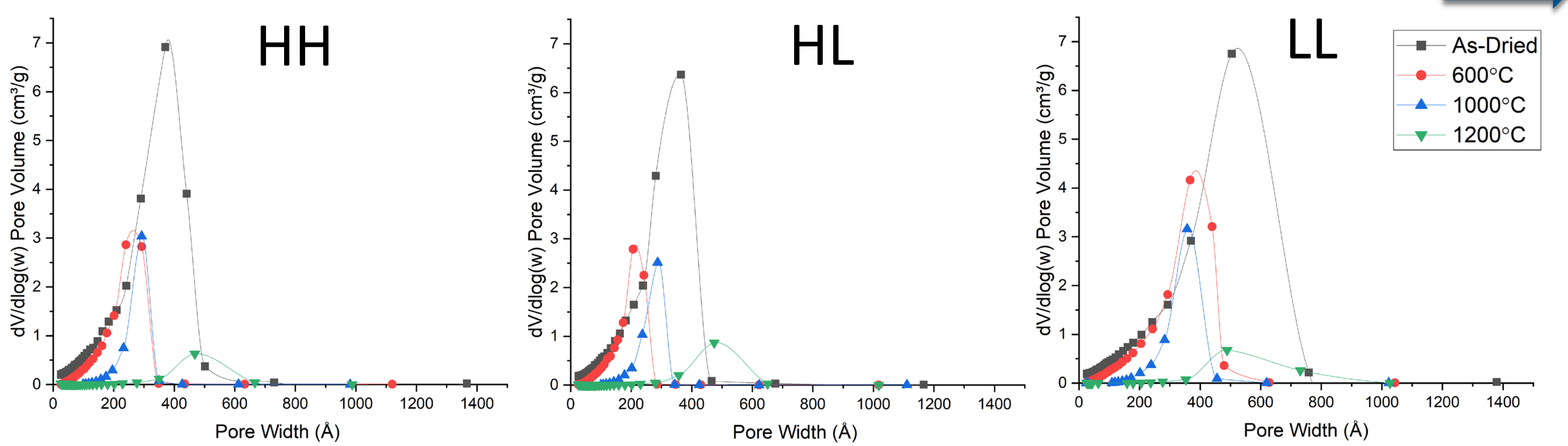
Work performed by Jordan Meyer (UIUC MatSE U-Grad)

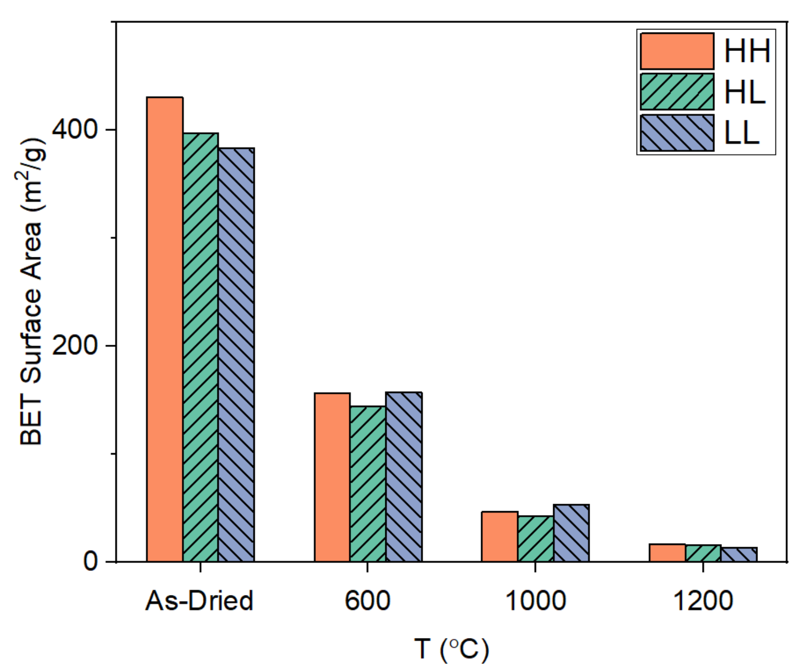
Tuning aerogel structure & structural evolution via **synthetic parameters**

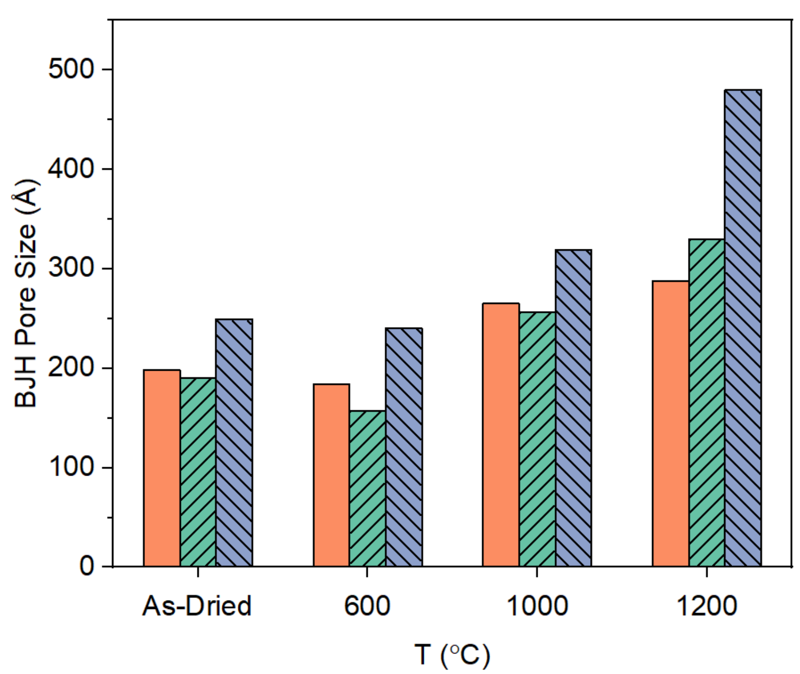


How does the as dried structure impact evolution upon heating?

Naming convention: **XY** where X = solids loading
Y = water content



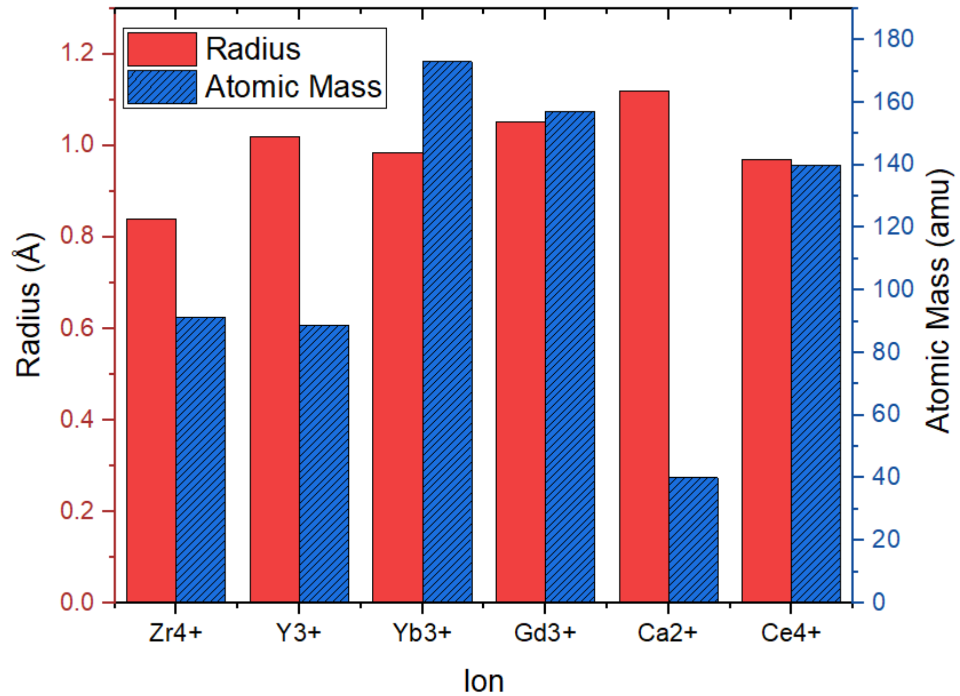




Work performed by Jordan Meyer (UIUC MatSE U-Grad)

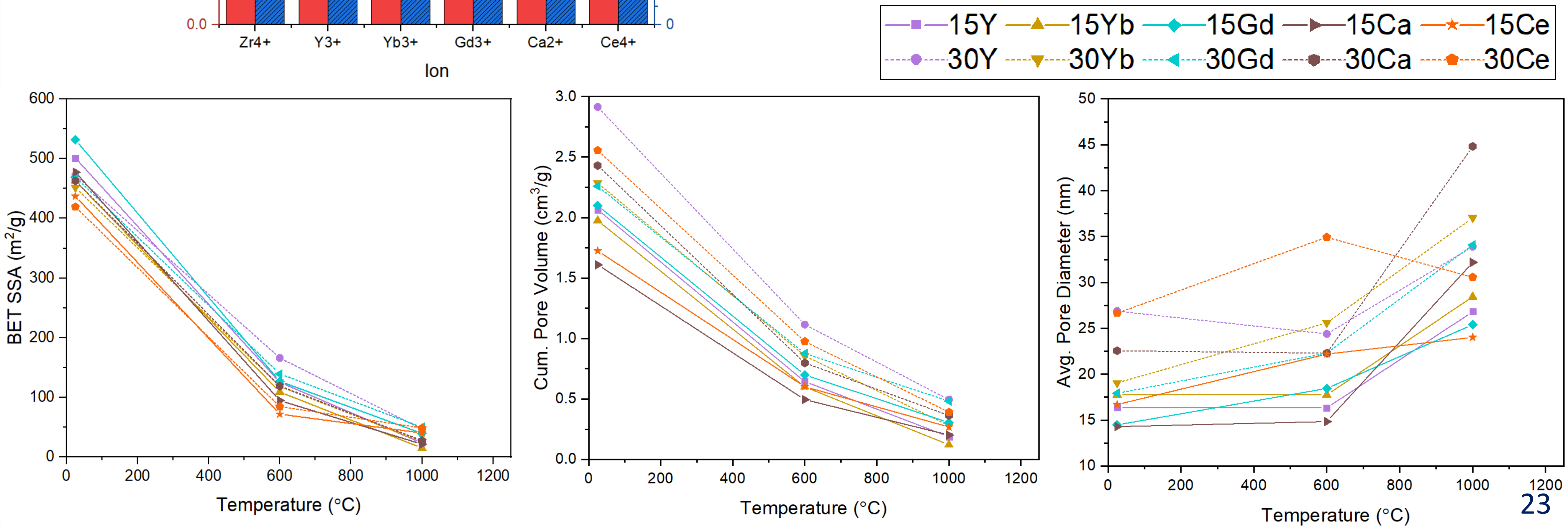
Study of other dopants (Yb, Gd, Ca, Ce) in zirconia aerogels at 15 and 30 mol% M/(M+Zr)

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

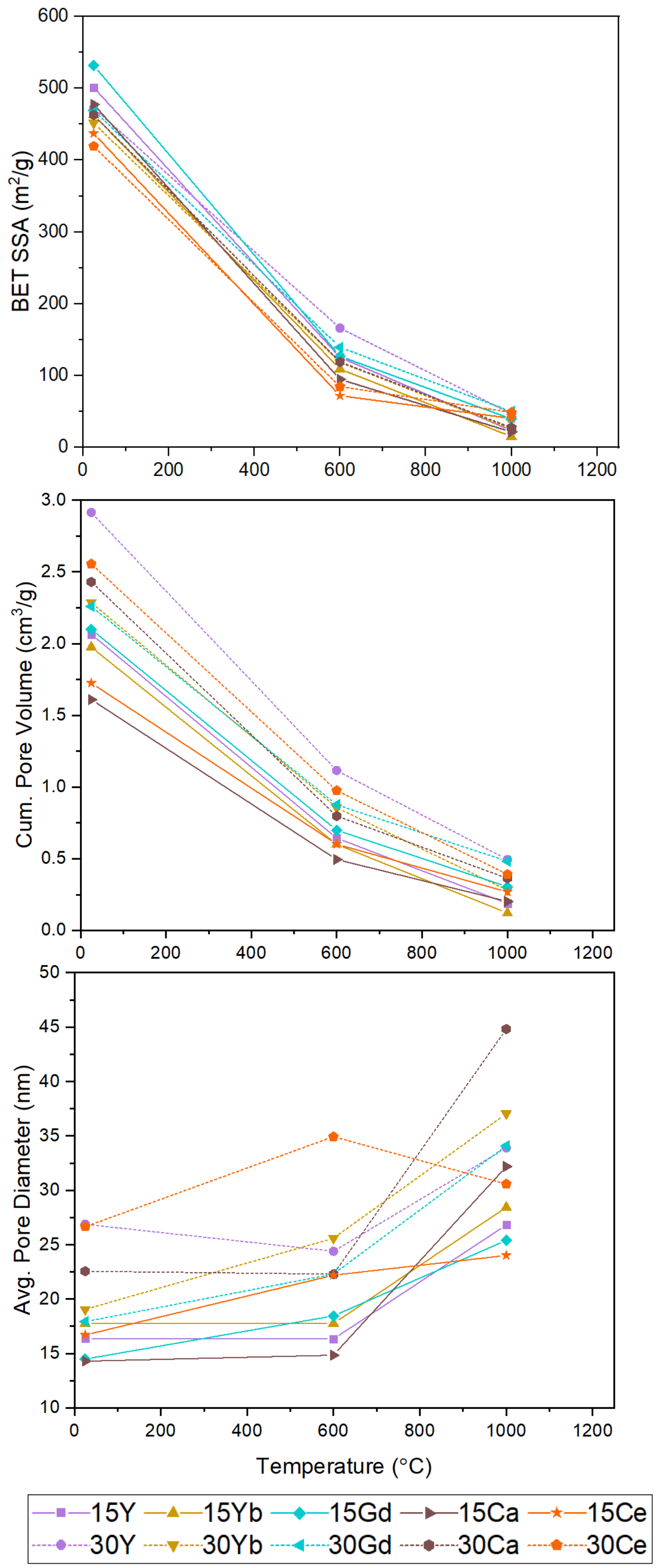


→ Modify thermal conductivity, surface energy and cation diffusivity

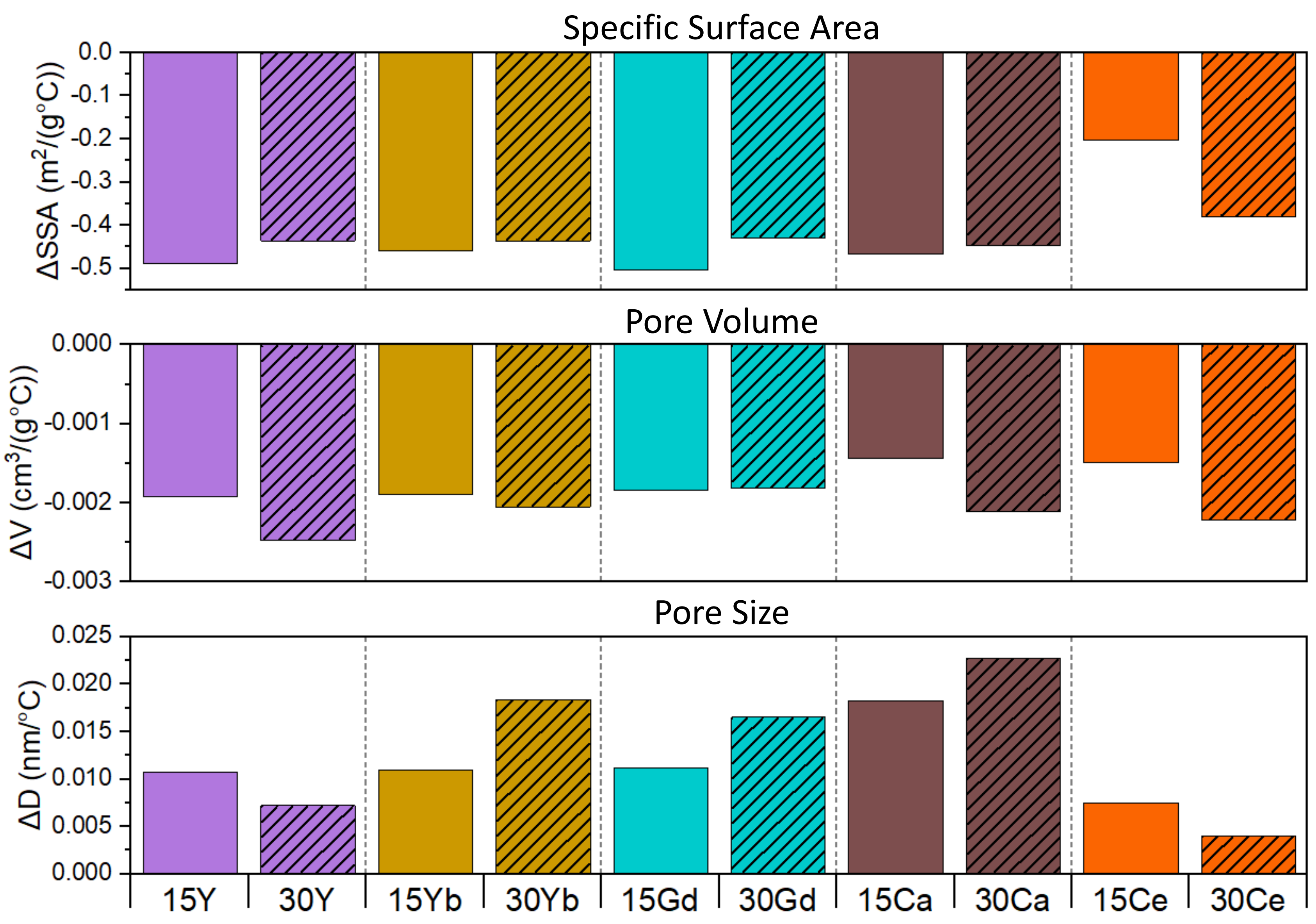
→ Connect material properties to changes in structural evolution



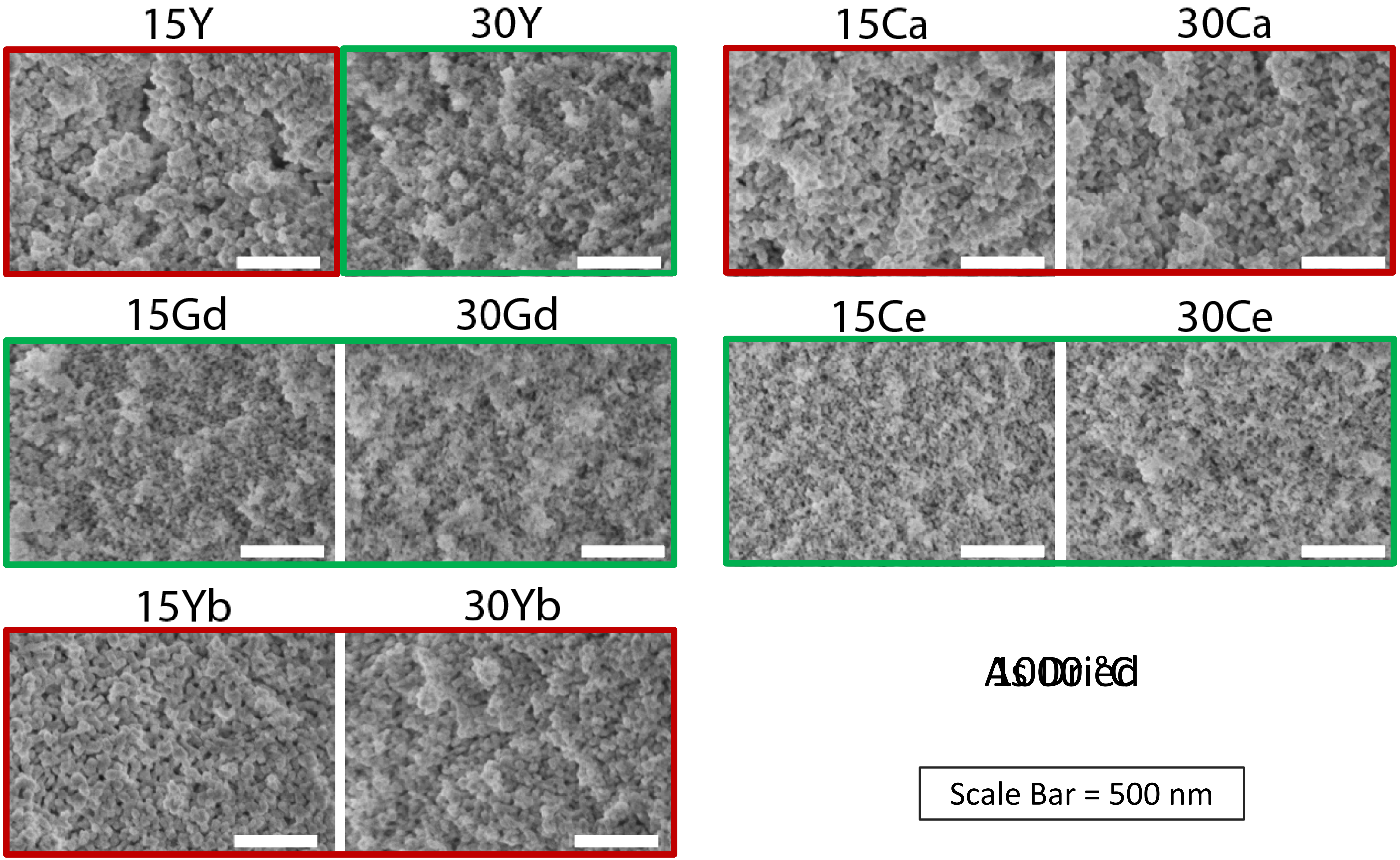
Work underway to develop quantifiable criteria for “thermally stable” aerogels via N_2 physisorption



Slope between as-dried and 1000 °C heat-treated aerogels



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



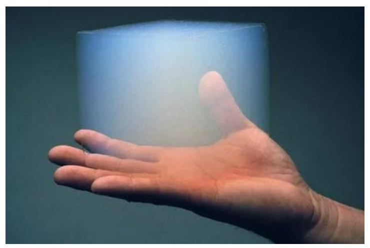
As Dried

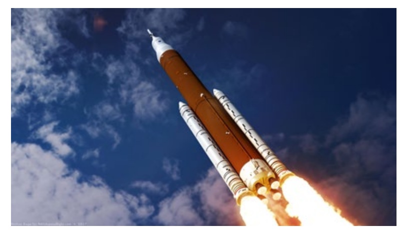
1000 °C

Scale Bar = 500 nm

Summary

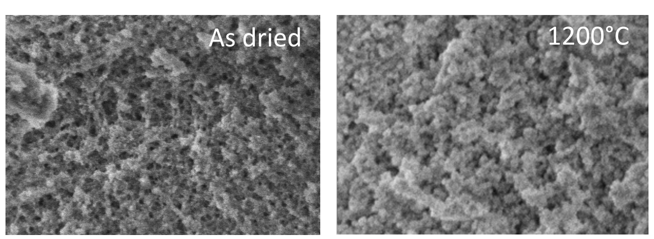
1. Aerogels are a promising candidate for lightweight, highly insulating materials in next-gen aerospace applications.
   Pore structure must be preserved to temperatures ≥ 1200 °C

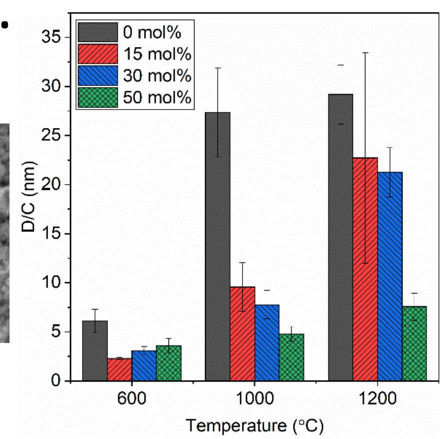




2. Introduction of yttria into zirconia aerogels <u>reduces</u> **densification** of pore structure and **crystallite growth** to 1200 °C.

30 mol% $YO_{1.5}$ pore structure evolution

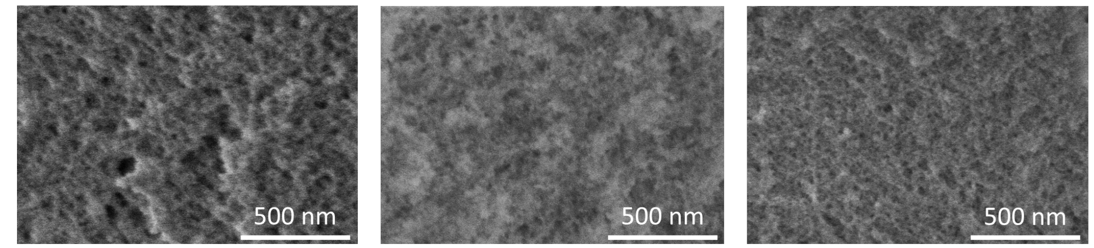




3. Increased yttria content improves stability of YSZ aerogels as a result of **lower cation diffusivity** (mass flow) and **lower surface energy** (driving force for densification).

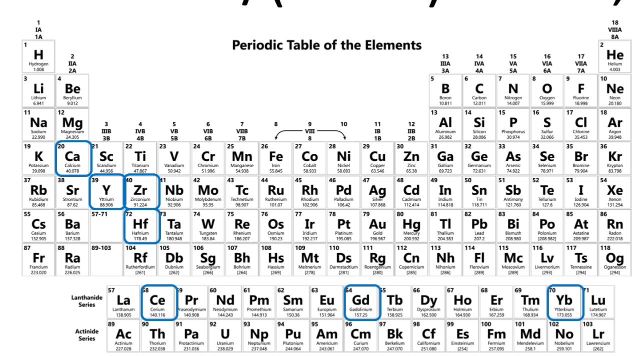
Future Work

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.

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Thank you for your attention!

Special thanks to:

- Advisor: **Dr. Jessica Krogstad** (UIUC)
- Technical Collaborator: **Dr. Jamesa Stokes** (NASA GRC)
- **Dr. Frances Hurwitz** (NASA GRC, retired)
- **Jordan Meyer** (UIUC MatSE U-Grad)
- Krogstad Group Members
- At NASA GRC: Dr. Haiquan (Heidi) Guo, Jessica Cashman, Dr. Richard Rogers

Funding:

- NASA Space Technology Research Fellowship (80NSSC18K1189)

Facilities:

- Materials Research Laboratory, UIUC
- NASA Glenn Research Center

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