Development of Aerogel Composites for Multilayer Insulation, Thermoelectric Applications and High Temperature Thermal Protection Systems

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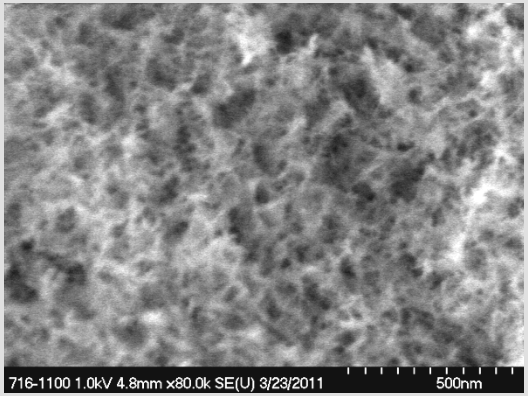
Aerogel-Impregnated Ceramic Papers as Lightweight, High Temperature Insulation: GRAAFiTI (**G**lenn **R**esearch **C**enter **A**luminosilicate **A**erogel **F**iber-reinforced **T**hermal **I**nsulation)

- Use temperatures to >1100˚C
- Aerogel is reinforced with non-woven ceramic fiber papers felts.
- Can be opacified to reduce radiation heat transfer.



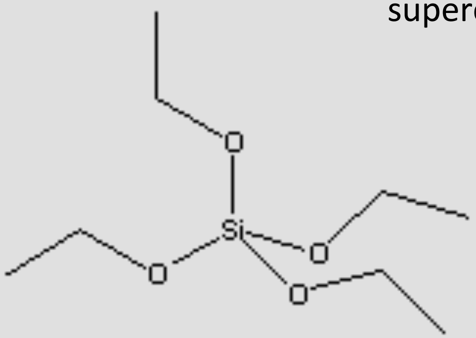
Aerogel maintains high surface area after exposure at 1100˚C

Aerogel synthesis approach:

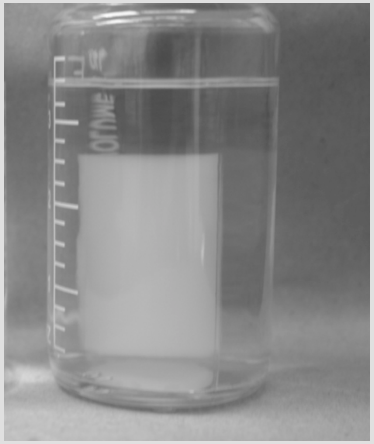
Boehmite [AlO(OH)]+ TEOS

→ hydrogel → aerogel

supercritical CO_2



TEOS

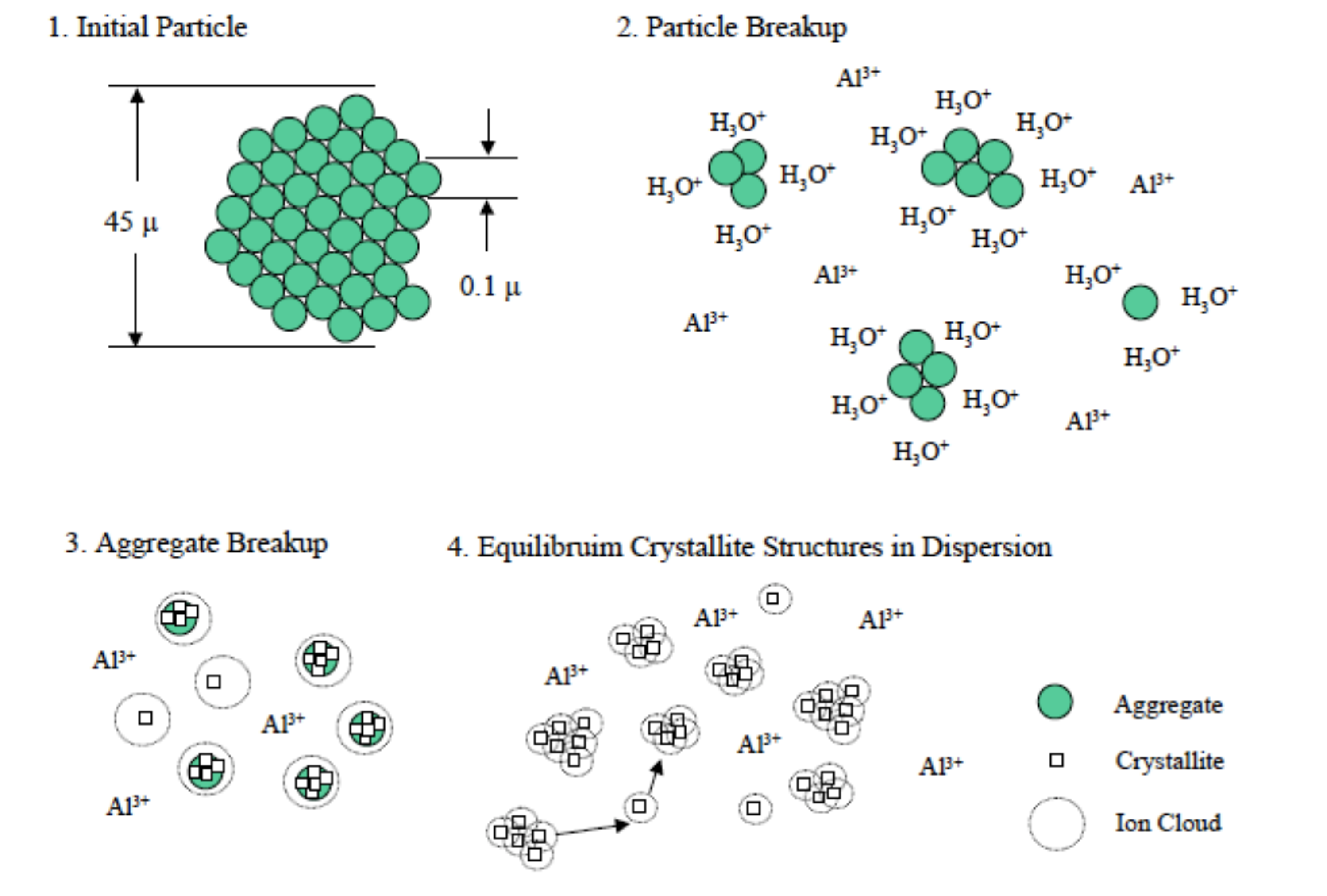


AlOOH powders (Sasol, NA)

- Boehmite powder dispersed in water with sonication
- TEOS hydrolyzed with nitric acid catalyst in ethanol
- TEOS solution combined with AlOOH dispersion
- Al:Si ratio can be tailored
- Opacifier can be added prior to gelation

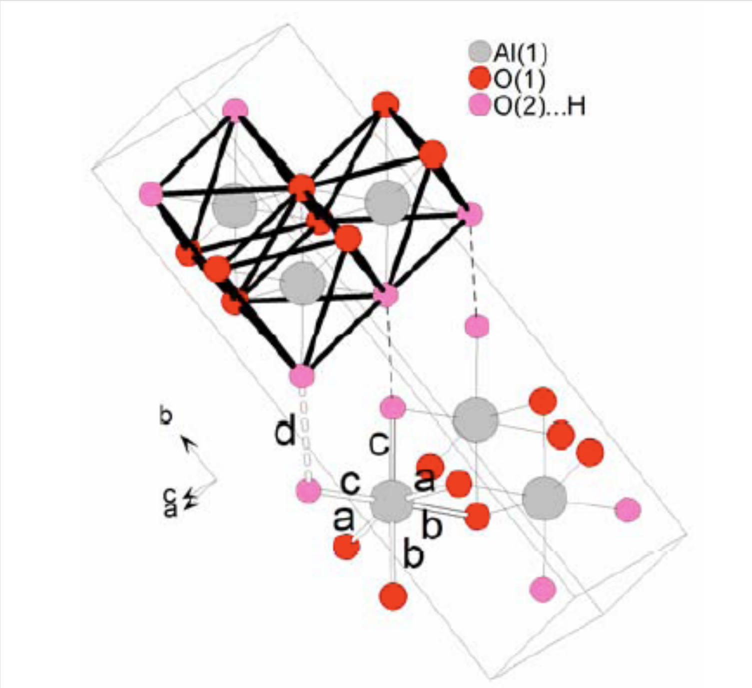
P. R. Aravind, *et al* Microporous and Mesoporous Materials 96 (2006) 14–20.

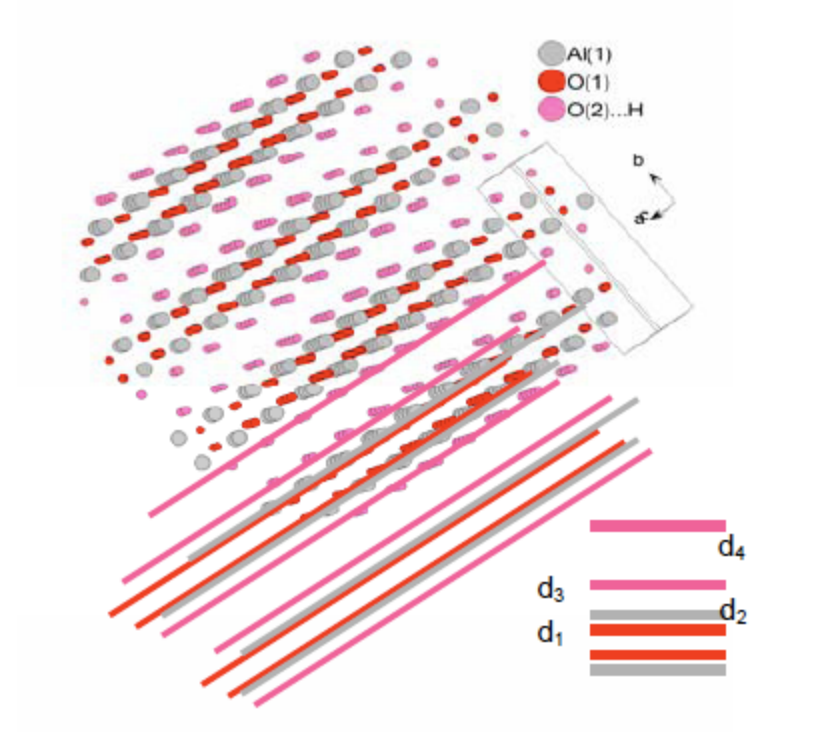
Aerogels synthesized from Boehmite + TEOS: Dispersion of Boehmite



Courtesy Sasol, NA

Boehmite [AlO(OH)] structure:





AlO_6 octahedra

Sheet spacing varies with crystallite size.

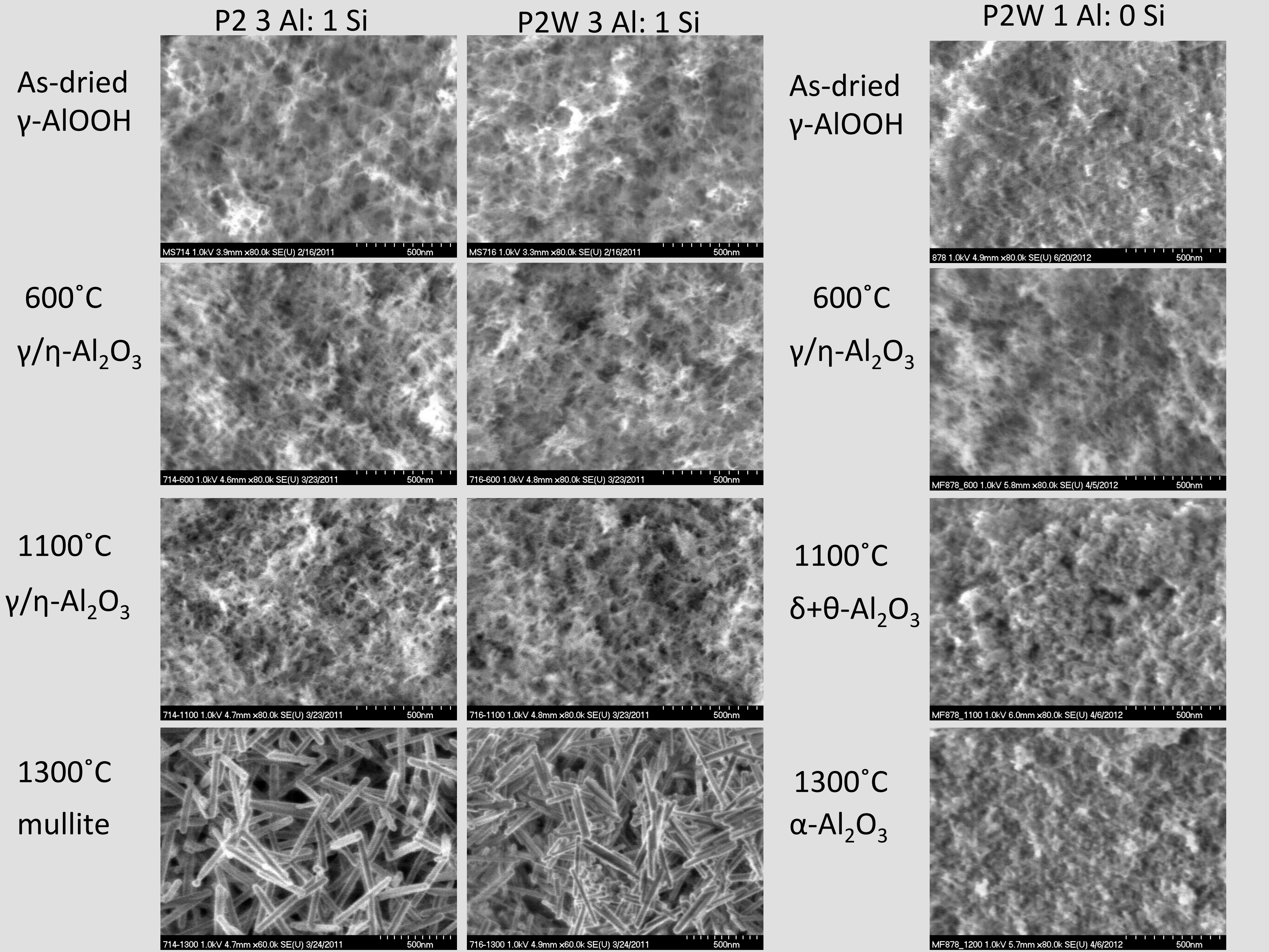
S. Bruhne, Cryst. Growth Des., 2008, 8 (2), pp 489–493n

Precursor powder:

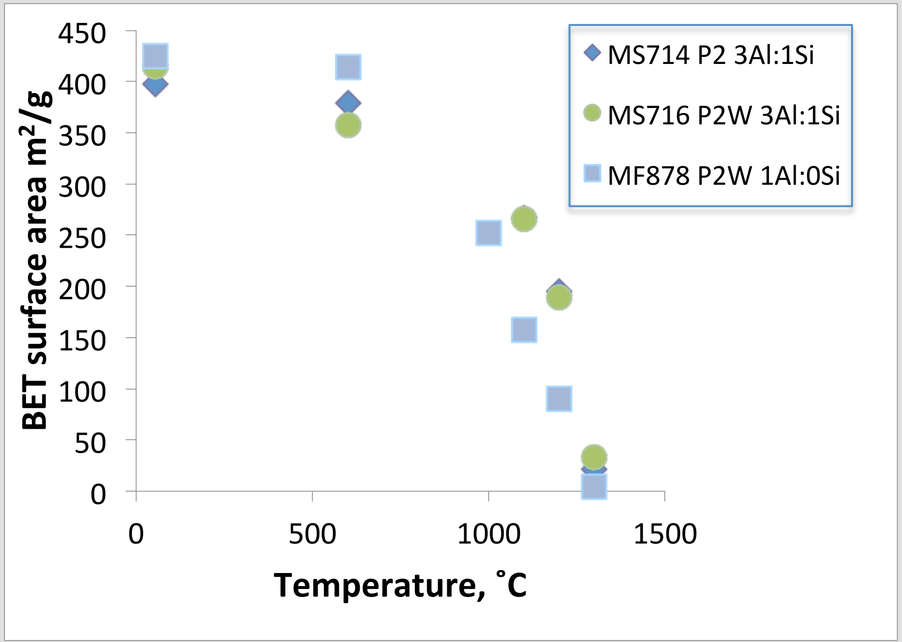
Precursor powder	2theta (deg)	d (Å)	b (meas.)	b (PDF)	crystallite size
P2	14.074	6.287	12.575	12.240	4.9+/- 0.2nm
P2W	14.094	6.279	12.558	12.227	2.6+/- 0.1nm

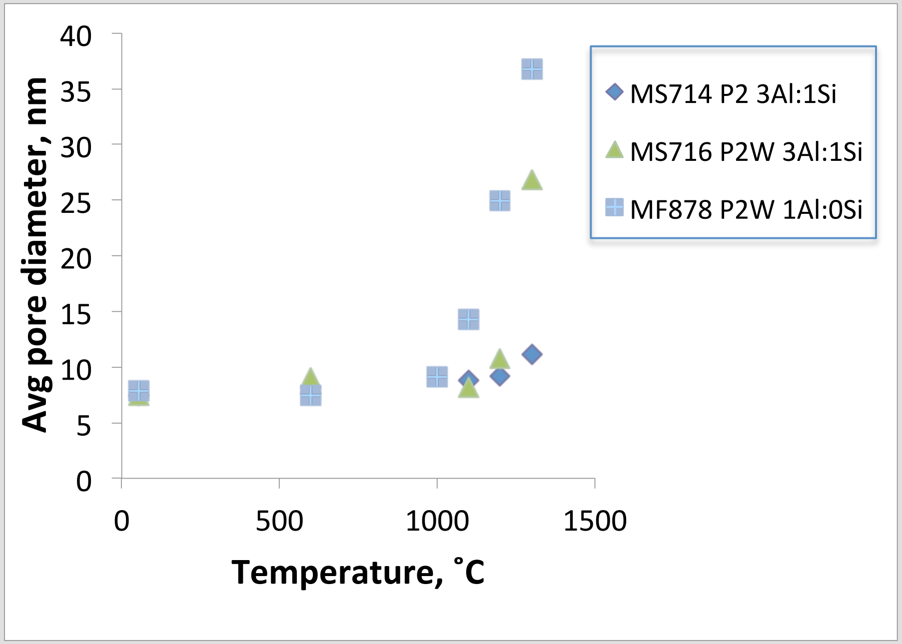
Phase Transformations

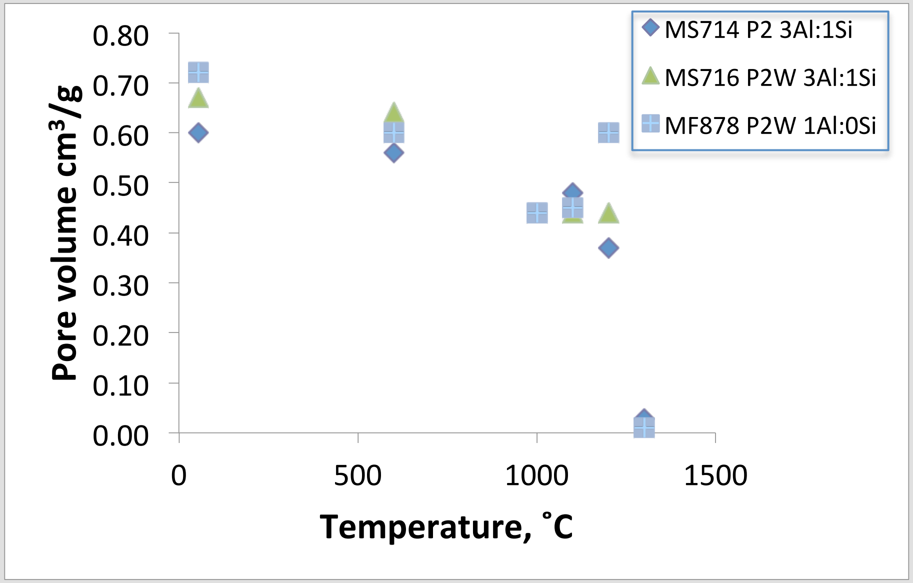
	Temp (°C)	RT	600	1000	1100	1200	1300	1400
	Sample							
P2 3Al:1Si	MS714	boehmite + gibbsite (minor)	γ/η alumina	γ/η alumina	γ/η alumina	γ/η alumina + δ/θ-alumina	mullite	mullite
P2W 3Al:1Si	MS716	boehmite	γ/η alumina	γ/η alumina	γ/η alumina	γ/η alumina + δ/θ-alumina	mullite	mullite
P2W 1Al:0Si	MF878	no XRD	γ/η alumina	γ/η alumina + δ/θ-alumina	δ-alumina + θ-alumina	δ-alumina + θ-alumina	α-alumina	no XRD



P2 3 Al: 1 Si
P2W 3 Al: 1 Si
P2W 1 Al: 0 Si
As-dried γ-AlOOH
As-dried γ-AlOOH
600˚C γ/η-Al_2O_3
600˚C γ/η-Al_2O_3
1100˚C γ/η-Al_2O_3
1100˚C δ+θ-Al_2O_3
1300˚C mullite
1300˚C α-Al_2O_3
MS714 1.0kV 3.9mm x80.0k SE(U) 2/16/2011 500nm
MS716 1.0kV 3.3mm x80.0k SE(U) 2/16/2011 500nm
878 1.0kV 4.9mm x80.0k SE(U) 6/20/2012 500nm
714-600 1.0kV 4.6mm x80.0k SE(U) 3/23/2011 500nm
716-600 1.0kV 4.8mm x80.0k SE(U) 3/23/2011 500nm
MF878_600 1.0kV 5.8mm x80.0k SE(U) 4/5/2012 500nm
714-1100 1.0kV 4.7mm x80.0k SE(U) 3/23/2011 500nm
716-1100 1.0kV 4.8mm x80.0k SE(U) 3/23/2011 500nm
MF878_1100 1.0kV 6.0mm x80.0k SE(U) 4/6/2012 500nm
714-1300 1.0kV 4.7mm x60.0k SE(U) 3/24/2011 500nm
716-1300 1.0kV 4.9mm x60.0k SE(U) 3/24/2011 500nm
MF878_1200 1.0kV 5.7mm x80.0k SE(U) 4/6/2012 500nm

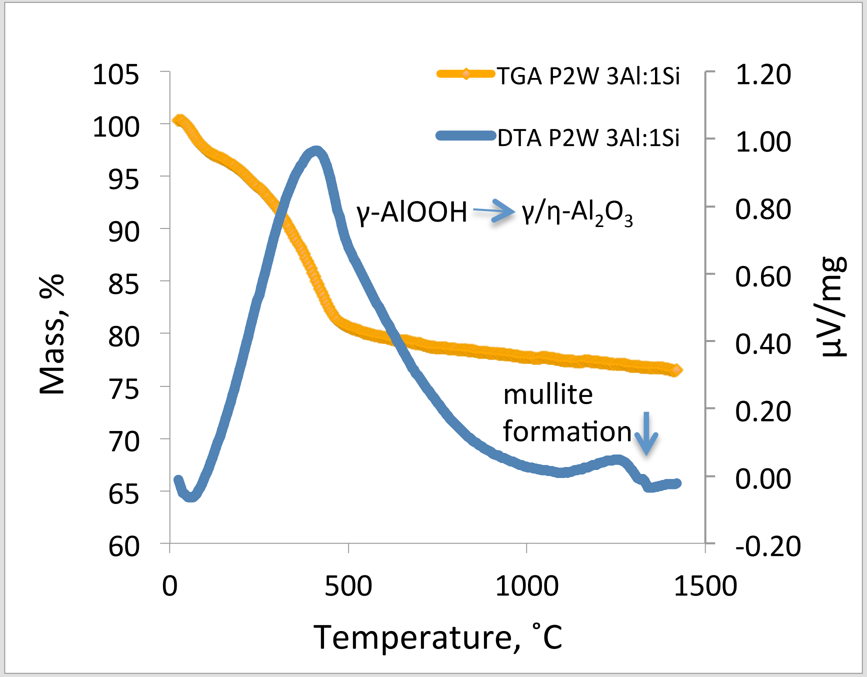


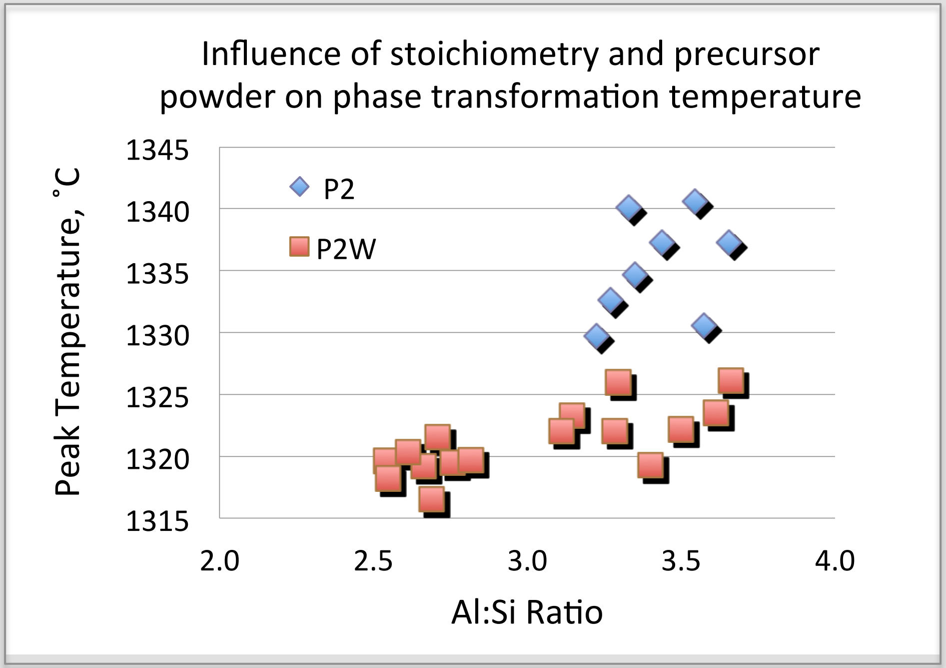




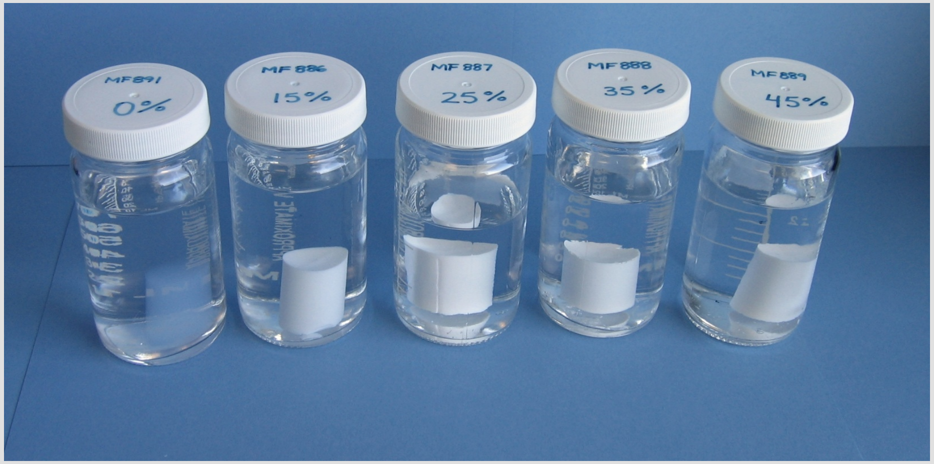
- Mesoporous structure is maintained to 1100˚C.
- High surface area is lost earlier in all alumina aerogels than in aluminosilicate systems

- Phase transformation to mullite shifts to higher temperature in Al-rich formulations
- Smaller crystallite size precursor transforms at lower temperatures than larger crystallite size boehmite powder

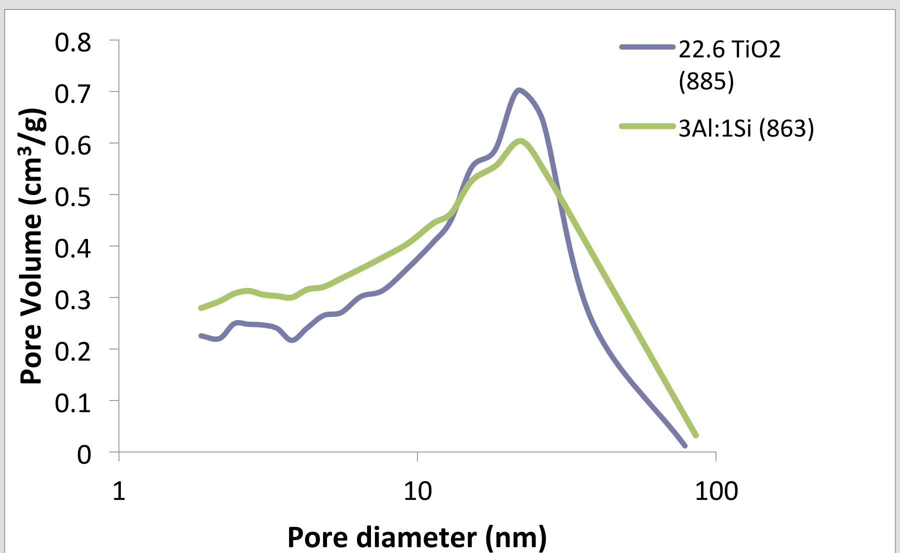


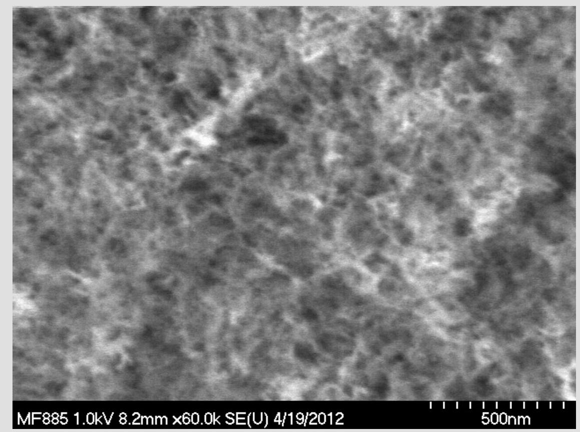


TiO_2 can be incorporated as an opacifier



Hydrogels with varying levels of TiO_2 incorporation

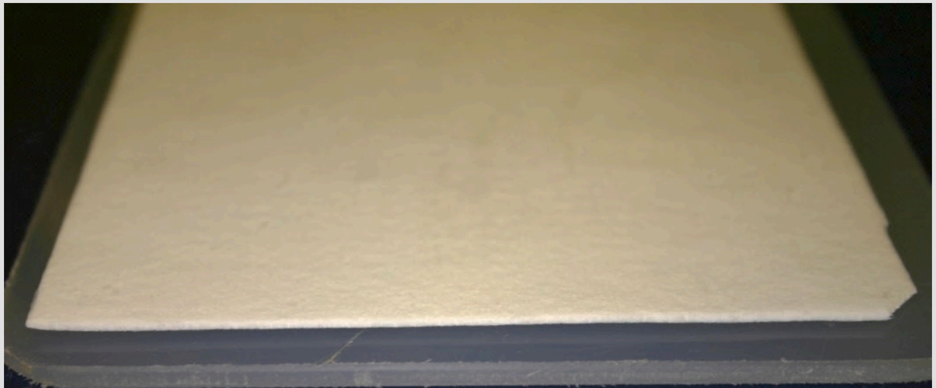




Arrow shows TiO_2 particles.
Pore structure is unchanged by TiO_2 addition

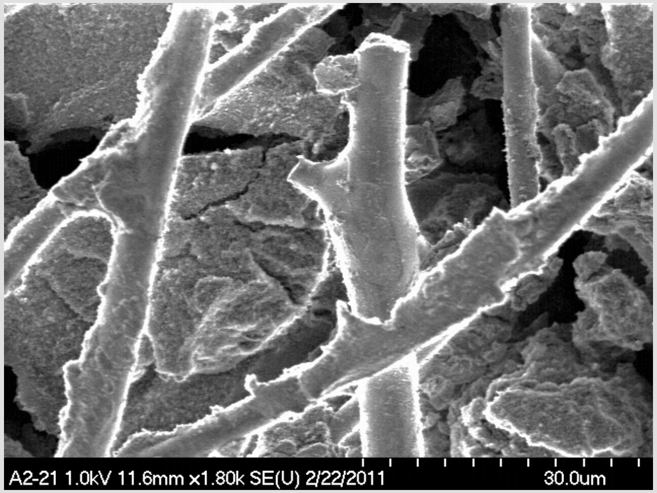
Aerogel-Impregnated Paper Composites

- Layers of aerogel impregnated papers can act as thermal insulators on their own or as separators in MLI.
- Paper reinforcement provides dimensional stability and mechanical reinforcement.
- Aerogel-impregnated paper remains flexible.
- Aerogel formulations adhere well to fibers, eliminating dust formation.
- Density of 0.15 g/cm^3 compared with Microtherm HT (0.3428 g/cm^3)



Alumina paper impregnated with aluminosilicate aerogel

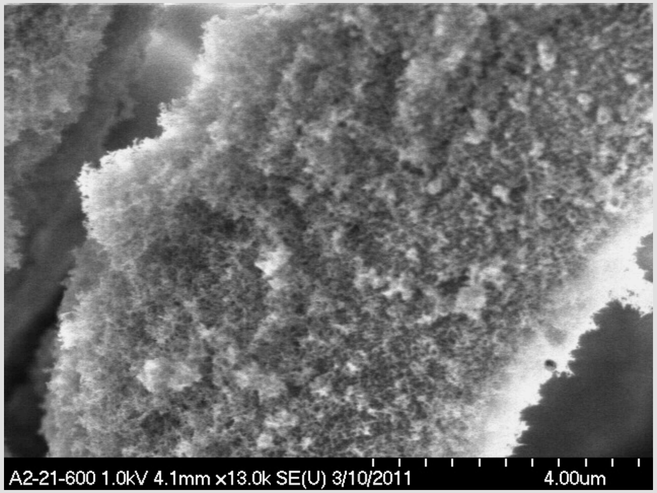
APA-2



P2W 3Al:1Si APA-2 paper composite, as fabricated

Microstructure of alumina paper (above), and felt aerogel composites (right)

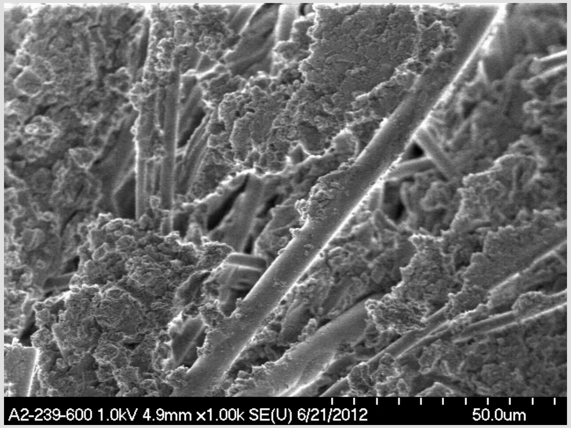
Aerogel well bonded to fiber—does not “flake”

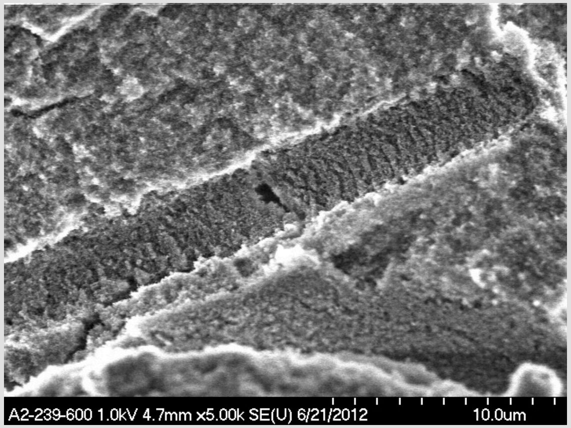


P2W 3Al:1Si APA-2 paper composite, post 600˚C exposure, air

APA-2/Aerogel Composite Formulations

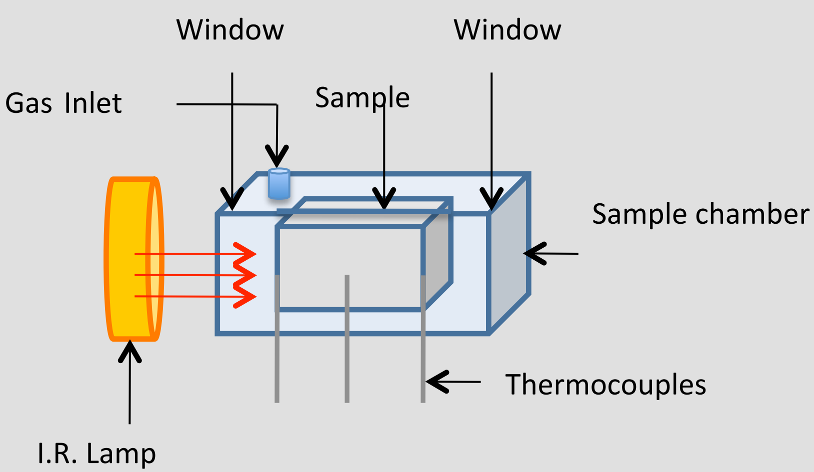
Sample ID	% paper by mass	% aerogel by mass	Aerogel Composition $Al_2O_3:SiO_2:TiO_2$ (moles)	Density g/cm^3
A2-170 (716)	65.8	34.2	1.6:1:0	0.148
A2-169 (749)	66.7	33.3	1.36:1:0	0.152
A2-238/239	70.6	29.4	1:0:0	0.161
A2-254	60.4	39.6	1.6:1:1.28	0.169





Stepped Heating Method for measuring thermal diffusivity

J. Gembarovic, R. E. Taylor, *Int. J. Thermophys.*(2007) 28:2164-2175.



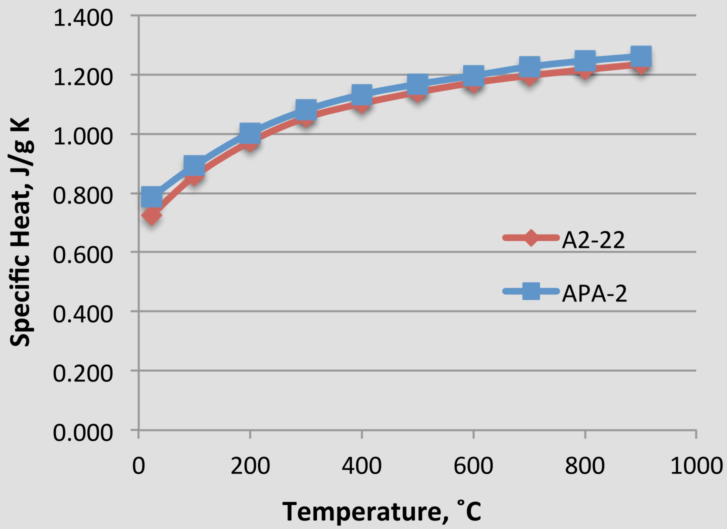
Calculation of thermal conductivity:

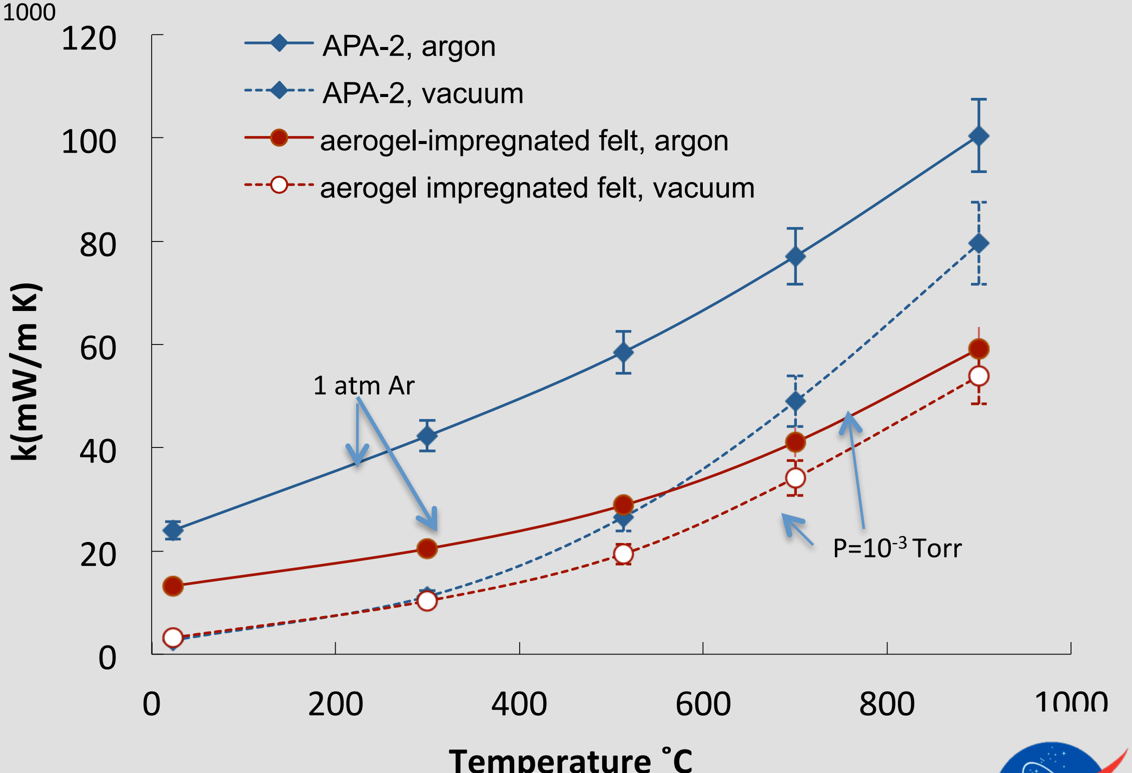
$\kappa = \alpha * C_p * \rho$

where:

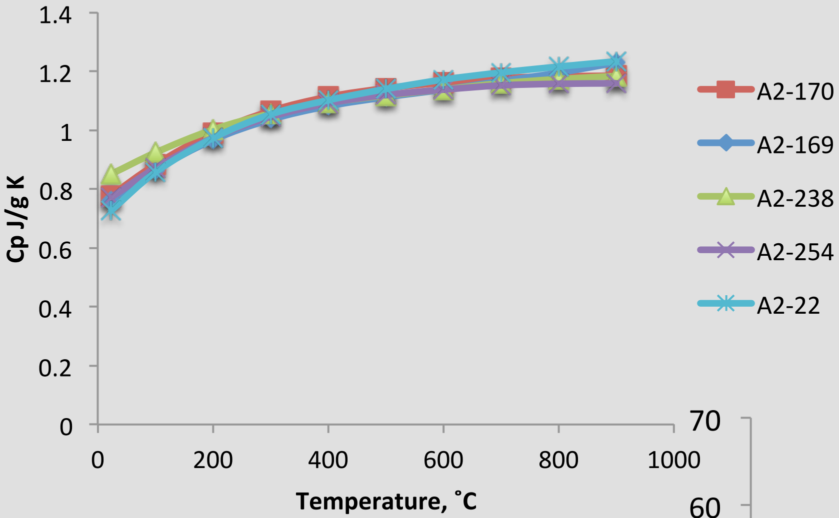
κ : thermal conductivity (SI units: W/(m·K))
α: thermal diffusivity (cm^2/s)
ρ : density (kg/m^3)
C_p: specific heat capacity (J/(kg·K))

Thermal Conductivity Determination of APA-2/Aerogel Composites

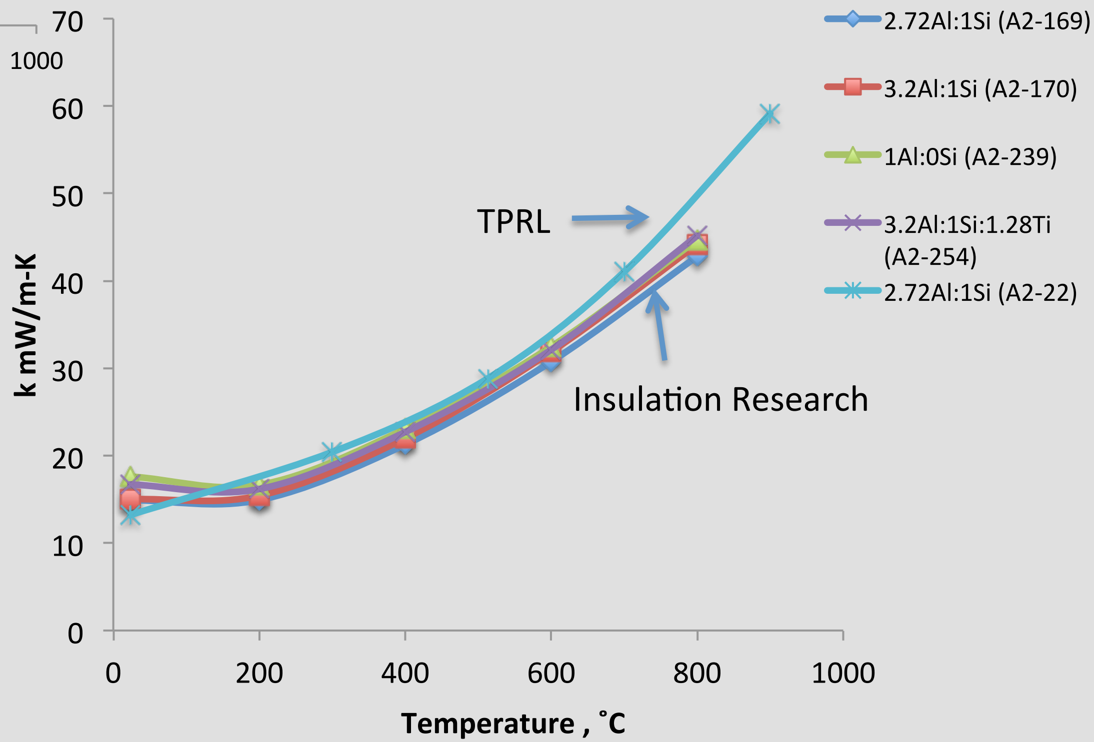




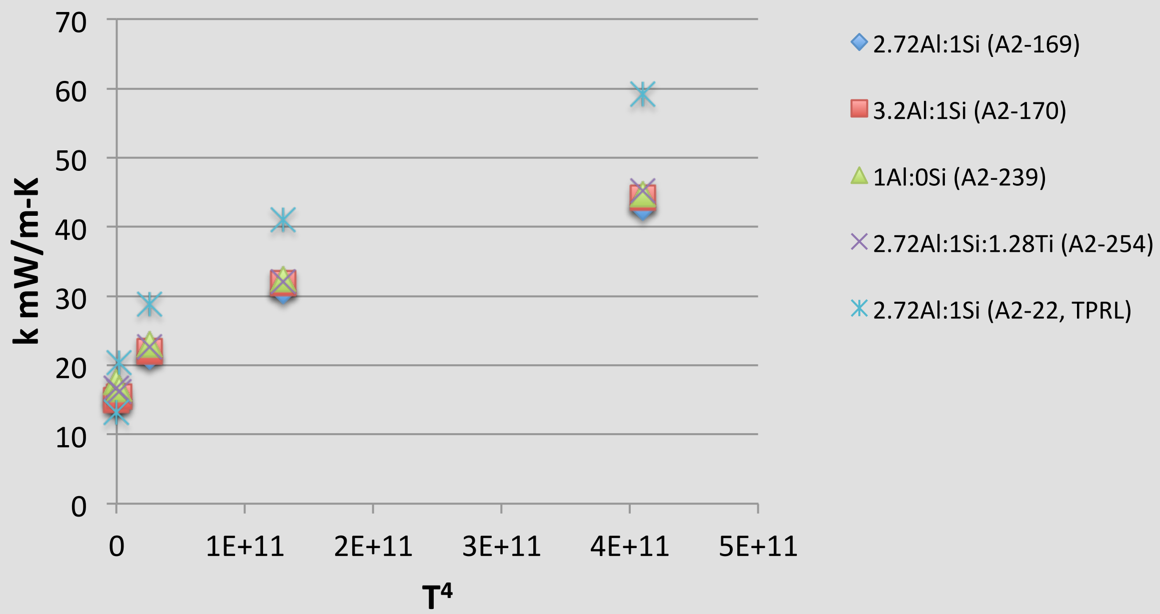
Thermal Conductivity Determination of APA-2/aerogel Composites



Specific heat, A2-22 measured, other values calculated based on rule-of-mixtures composition determined by Inductively coupled plasma (ICP)



Thermal conductivity, 1 atm argon

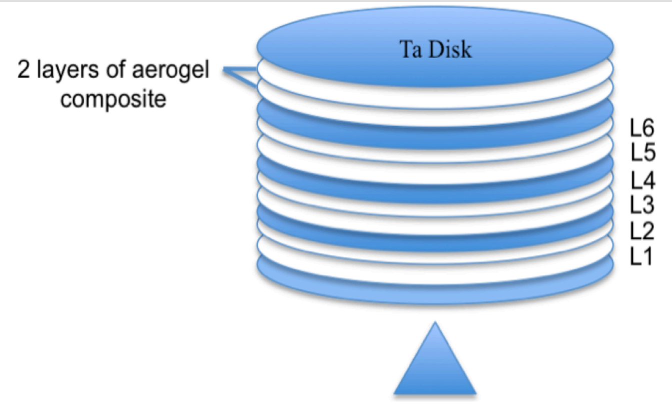


In 1 atm argon, and at $P=10^{-3}$ Torr (not shown), T^4 behavior is non-linear, indicating that radiation is not the primary component of thermal conductivity. Therefore, effects of TiO_2 addition cannot be evaluated from this data.

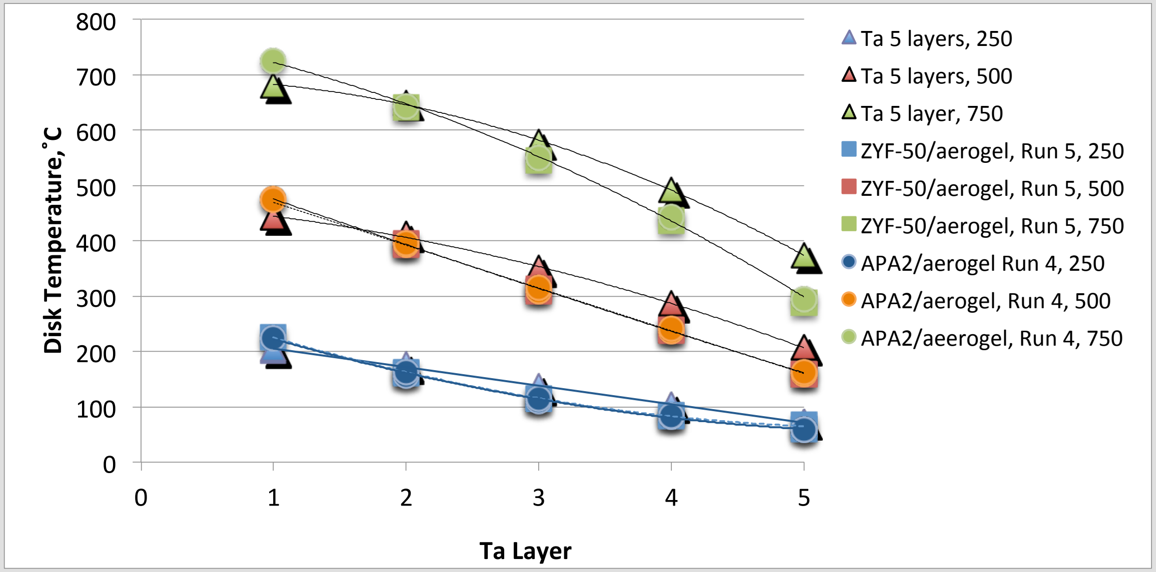
NASA GRC MLI Test Rig

- Operates at 10^{-6}-10^{-7} Torr at temperatures to 750˚C (should be radiation dominated)
- Thermal conductivity
- Allows easy stacking of samples of various compositions

MLI (Multi-Layer Insulation)



- Use of aerogel composite separators between layers reduces heat transfer from foil to foil, resulting in hotter foil temperature at first layer, but temperature reduction in subsequent layers.
- The largest effect is seen at the highest temperature, with an 86˚C reduction at the fifth layer when aerogel composites are used.
- ΔT between baseline foils alone and foils with aerogel separators appears to be increasing with number of layers.

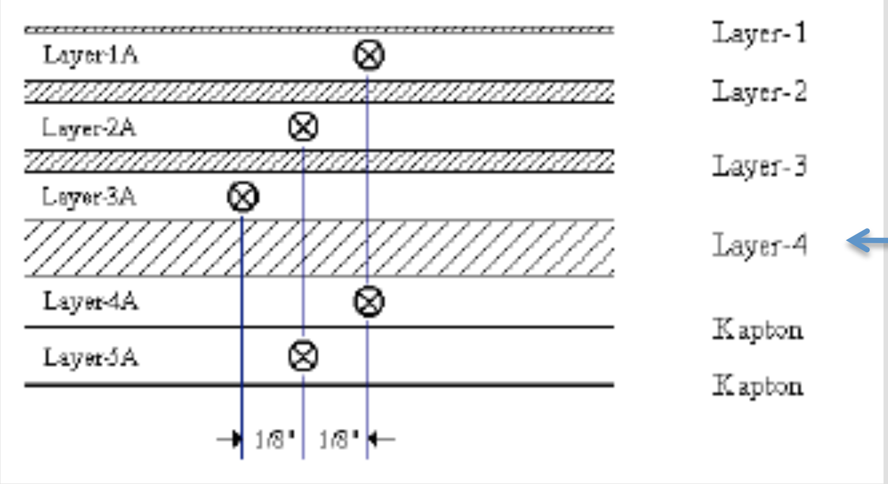


Measurements at 10^{-6}-10^{-7} Torr. (Data points obtained at thermal equilibrium).

Rig test did not differentiate between APA-2 paper alone and APA-2 composite separators. Modeling showed alumina tube to be providing thermal short. Rig is undergoing re-design.

Applications: Inflatable Decelerators

Flexible felt-aerogel composites can be used as layers in inflatable decelerators.

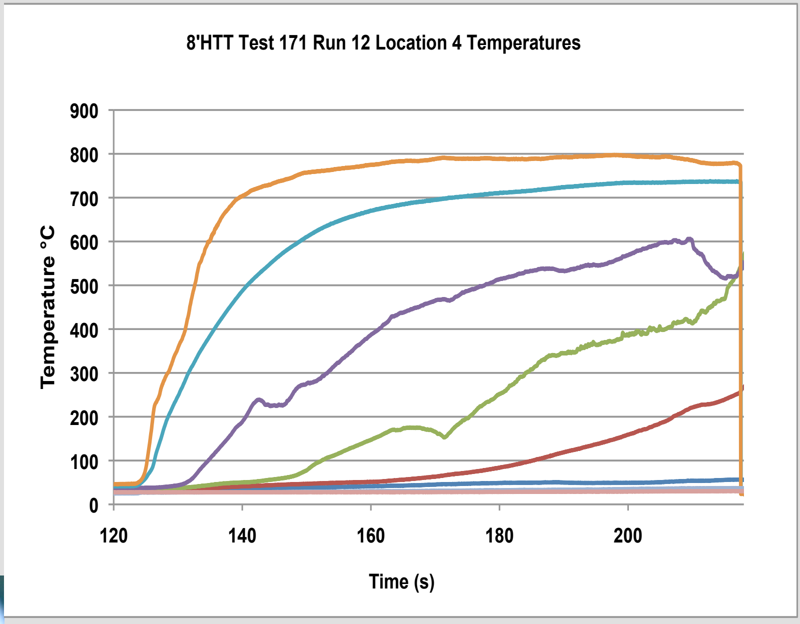


Aerogels being incorporated here.

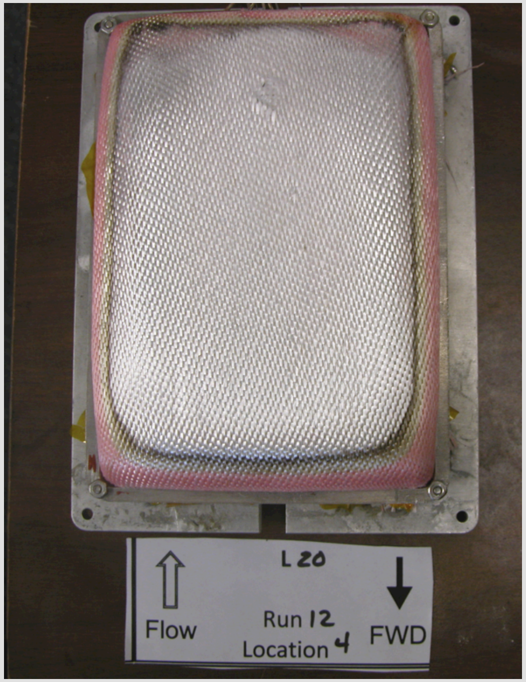
AIAA-2006-1698 J. P. Masciarelli et al

High Temperature Aluminosilicate Aerogel-Composite Tested in LaRC 8'HTT (to evaluate for EDL):

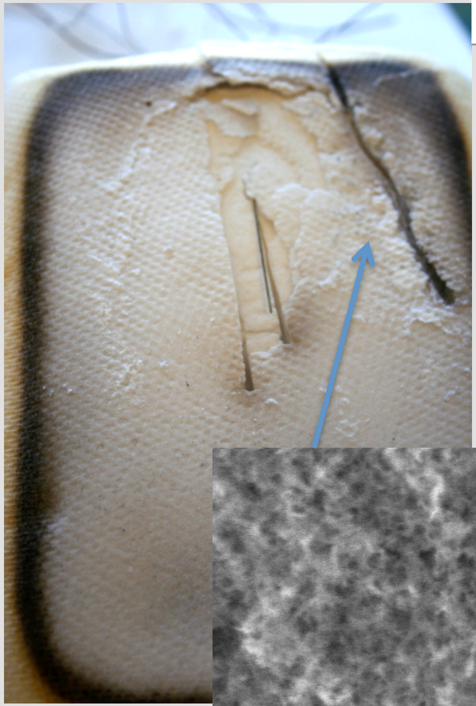
- 2 BF-20/7 AS-APA-2/Aluminized Kapton
- 17W/cm^2 flux; 1435 psi @3300˚R combustor pressure
- Temperature between aerogel composite and Kapton nominally 50˚C, a drop of 700˚C across 7 layers)

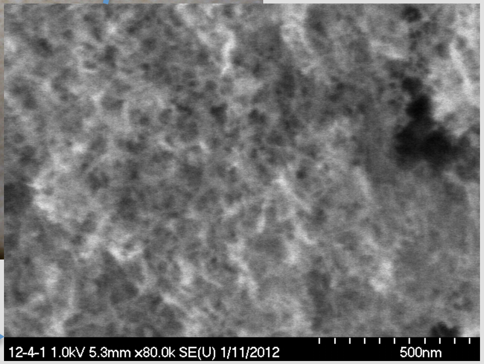


Post-test Run 12 Loc 4



Post-test BF-20 layers removed





Aerogel microstructure is maintained

Underside, APA-2/aerogel layer 7

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Conclusions:

- Flexible, alumina paper reinforced aerogel composites were fabricated with a density of 0.15 g/cm^3, nominally 43% the density of Microtherm HT.
- Aerogel adheres well to fiber (no " flaking" or spalling).
- Aerogels maintain mesoporous structure beyond 1100˚C, > 400˚C above use temperature of SiO_2 aerogels .
- Aerogel composition can be used to tailor surface area and pore size distribution, but variation in the range seen here has little effect on thermal conductivity in 1 atm argon.
- Composition does influence crystalline phases formed and phase transformation temperature, with higher alumina content in aluminosilicates shifting phase transformation to mullite to higher temperatures, thereby increasing upper use temperature. Surface area maintained to higher temperatures in aluminosilicates Compared with all alumina aerogel.
- Smaller crystallite boehmite powder transforms to mullite at lower temperature than slightly larger crystallite powder.
- Thermal conductivities of < 60 mW/m-K at 900˚C in argon have been achieved.
- Aerogel composites out-performed ZrO_2 spacers in MLI testing at 10^{-6}-10^{-7} Torr.

- Opacification of aluminosilicate aerogels with TiO_2 has been demonstrated at levels up to 45 mole % Ti in an Al-Si-Ti system. However, due to thermal short issues in NASA GRC MLI rig, the effect of TiO_2 opacification under radiation dominated heat transfer conditions could not be ascertained at this time, but will be evaluated after re-design of test rig.
- Composites performed well in 8'HTT test at NASA LaRC at 17W/cm^2 flux; 1435 psi @3300˚R combustor pressure. A 700˚C temperature drop was achieved across seven 1.25mm composite layers. Mesoporous aerogel structure maintained post-test in all layers.

Acknowlegments:

- Thermal Materials Team: Peggy Cornell, David Ellis, Paul Schmitz, Katie Shaw
- Jessica Panella, NASA LERCIP Intern
- Carrie Rhoades, LaRC

- NASA ARMD Hypersonics Project
- NASA RPS Program