Advanced Nanoporous Composite Materials for Industrial Heating Applications

Towards Low-Cost Nanostructured Refractories

Arlon J. Hunt

Michael R. Ayers

E.O. Lawrence Berkeley National Laboratory

IHEA Forum - ORNL

Industrial Needs for Insulation

- Industrial hearth, tank, and pot furnaces used by various IoF's (e.g. Glass) can benefit from improved insulations in critical areas
  - Regenerators, ports, crowns, forebay channel, etc.
- Current insulations used: firebricks, fiber bats, composite materials, microporous insulation
- Desired performance improvements:
  - Lower thermal conductivity
  - Space savings
  - Longer life times
  - Increased corrosion resistance
  - Lower cost

Aerogels: Background & Process

- Aerogels: Nanoporous, open-celled solids formed by controlled removal of the liquid phase from a gel.
  - First prepared by Samuel Kistler in 1931
- Typical preparation:
  - Sol-Gel formation of wet gel
    - Hydrolysis-condensation of Alkoxides
    - Organic polymerization
    - Other colloid-forming methods
  - Supercritical drying
    - Alcohol drying
    - CO_2 substitution-drying

Challenges for High Temperature Uses

- Must withstand temperatures of 700-1500 °C
  - Increase sintering resistance
- Must be chemically inert
- Must show reduced thermal conductivity
  - Target: 0.01-0.10 W/m-K
    - Block solid, gaseous, and ***Radiative*** heat transfer modes

- **$x(Al_2O_3)\bullet y(Cr_2O_3)$ or $x(0.94Al_2O_3/0.06SiO_2)\bullet y(Cr_2O_3)$**

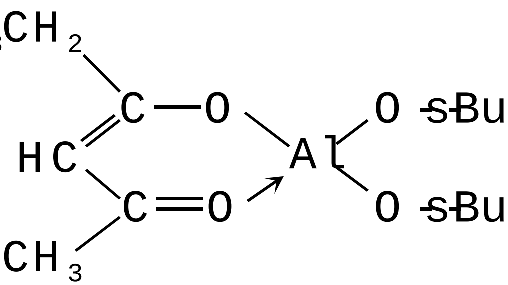
- Must be affordable
  - Target: $5-20 per board foot, Composition:

BERKELEY LAB

imf Industrial Materials for the Future

Two Routes to Al_2O_3-Cr_2O_3 Aerogels

- Aluminum alkoxide/CrO_3

2 

$+ \; CrO_3 \xrightarrow[\text{s.c. } CO_2,\ 1000\ °C]{H_2O,\ EtOH} 2\ Al_2O_3 \bullet Cr_2O_3$

- Acid-Base

$$xAl(OH)_3 + yCrO_3 \xrightarrow[x\ HNO_3]{H_2O} xAl^{3+} \bullet yCrO_4^{2-} \bullet xNO_3^-$$

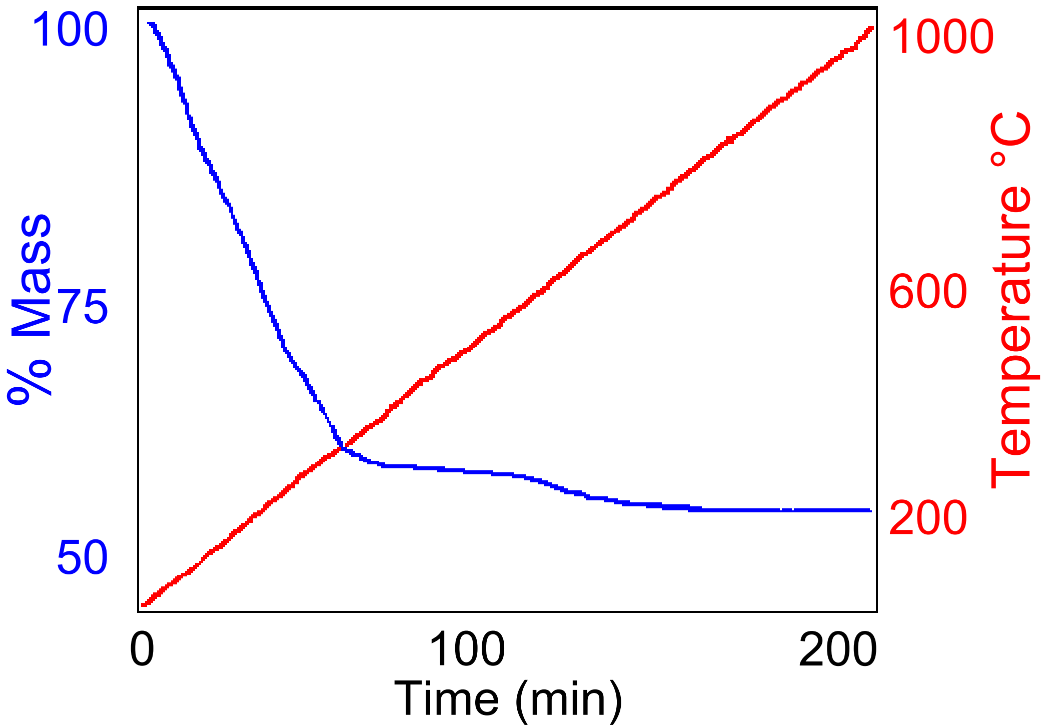
(aqueous)

$$xAl^{3+} \bullet yCrO_4^{2-} \bullet xNO_3^- \xrightarrow[\text{s.c. } CO_2]{\text{ethanol}} xAl(OH)_2NO_3 \bullet yCrO_2$$

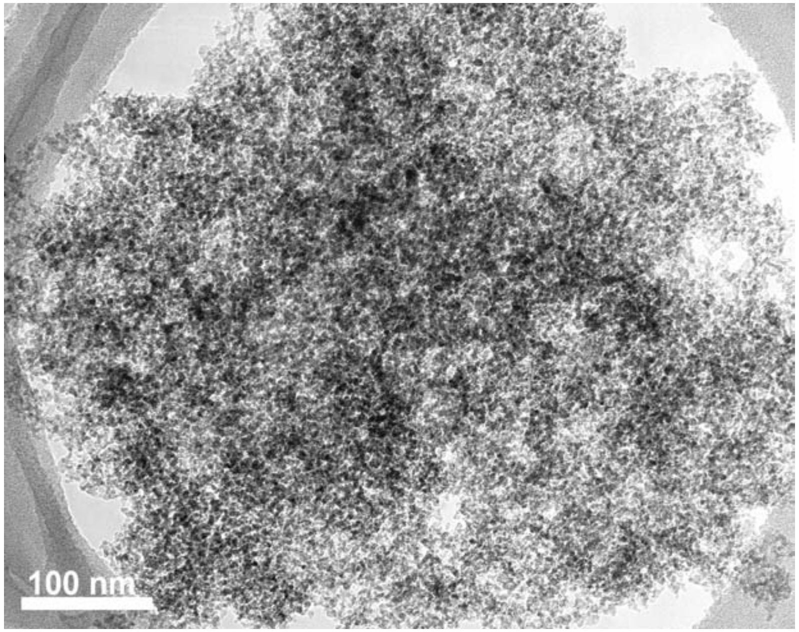
(solid)

$$xAl(OH)_2NO_3 \bullet yCrO_2 \xrightarrow{1000\ °C} xAl_2O_3 \bullet yCr_2O_3$$

Microstructure After Firing



TGA (air) plot of alkoxide-derived aerogel



TEM image of alkoxide-derived aerogel fired at 1000 °C

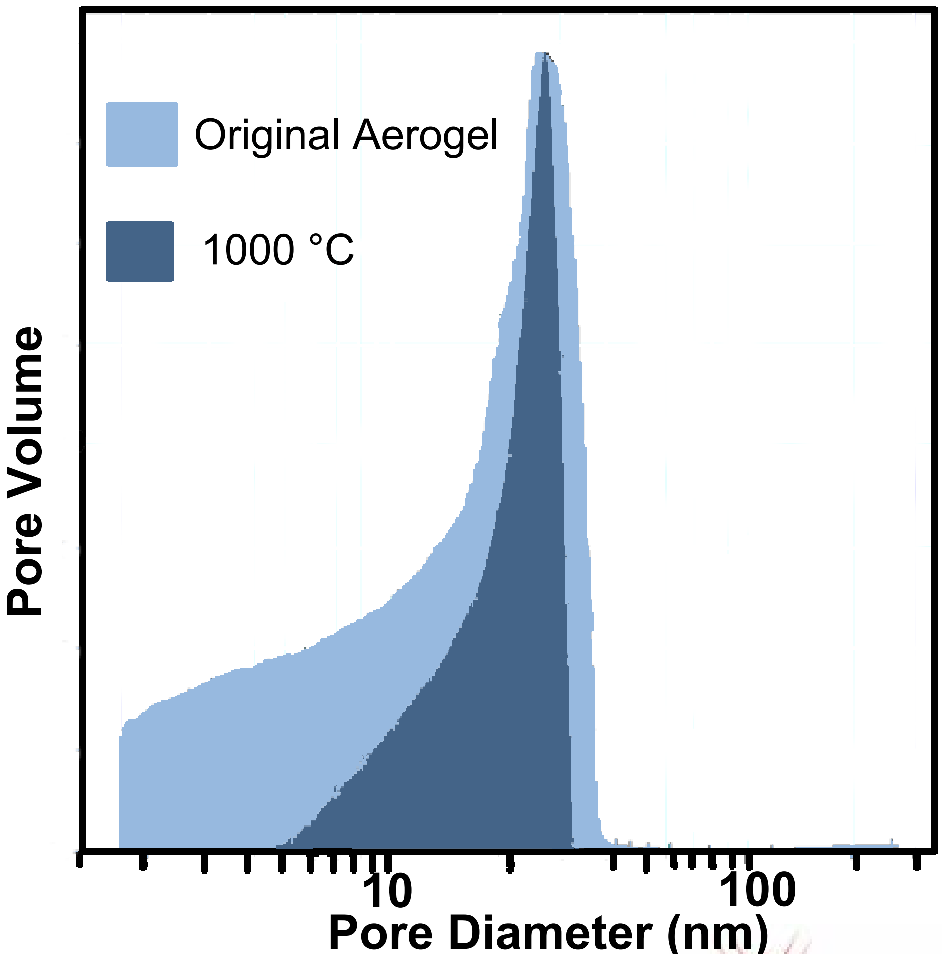
Effect of Temperature on Surface Area

- Surface areas (BET) of various compositions (acid-base route) before and after firing (m^2/g)

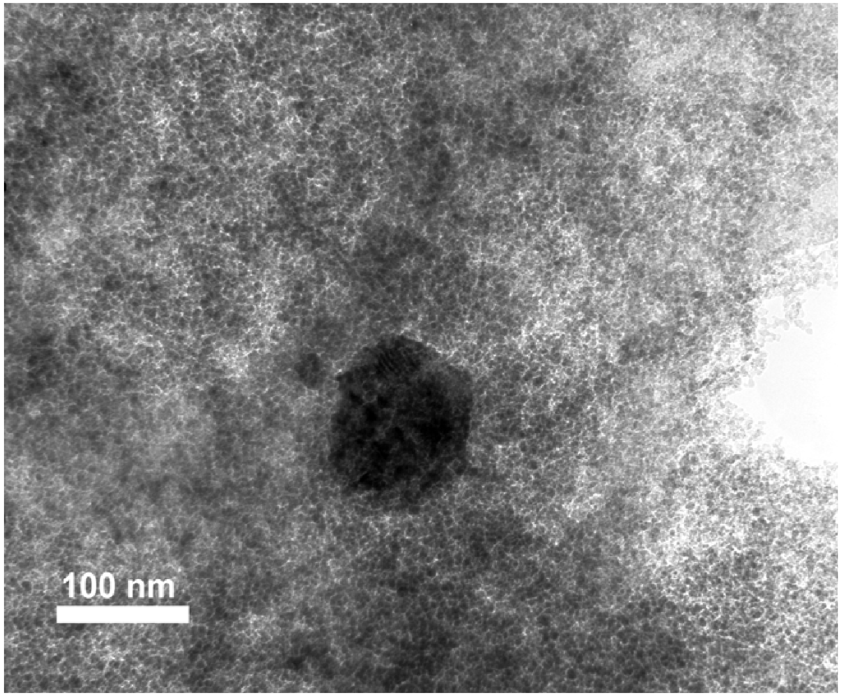
Compound	Neat aerogel	450 °C	1000 °C
Cr_2O_3	290	13	13
$Al_2O_3 \cdot 2Cr_2O_3$	270	180	41
$Al_2O_3 \cdot Cr_2O_3$	260	160	44
$2Al_2O_3 \cdot Cr_2O_3$	240	170	64
$2(0.94Al_2O_3 \cdot 0.06SiO_2) \cdot Cr_2O_3$	350	—	130

Porosity After Thermal Processing

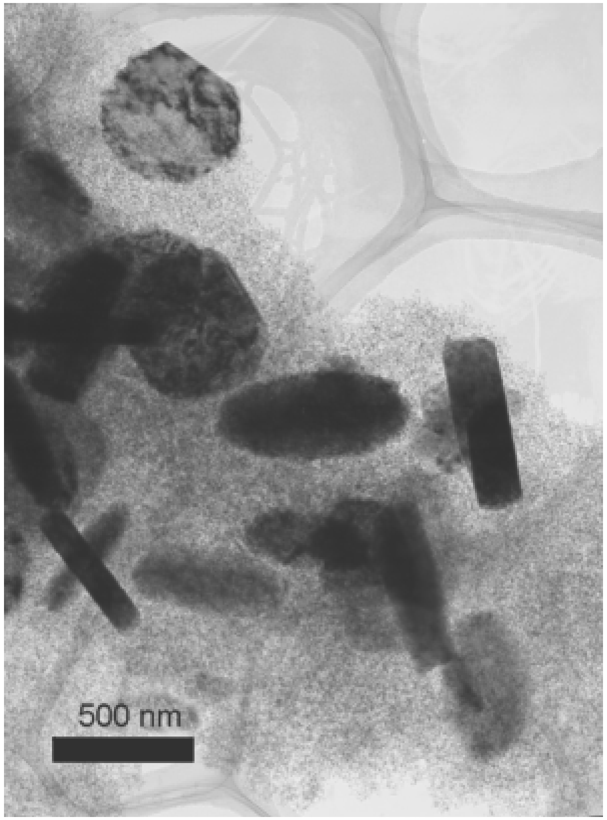
- Peak of Pore size distribution is ~ 26 nm
- Considerable pore volume between 2-10 nm
- Thermal treatment closes smaller pores
- Peak remains at ~26 nm



TEM Images of Al_2O_3-Cr_2O_3 Aerogels

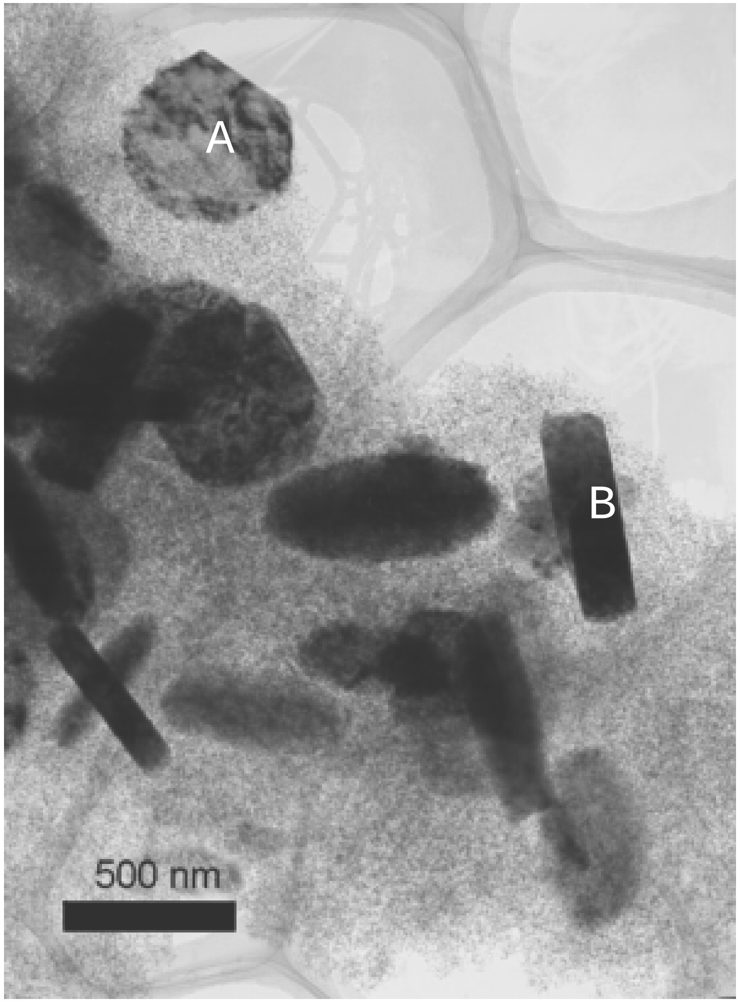


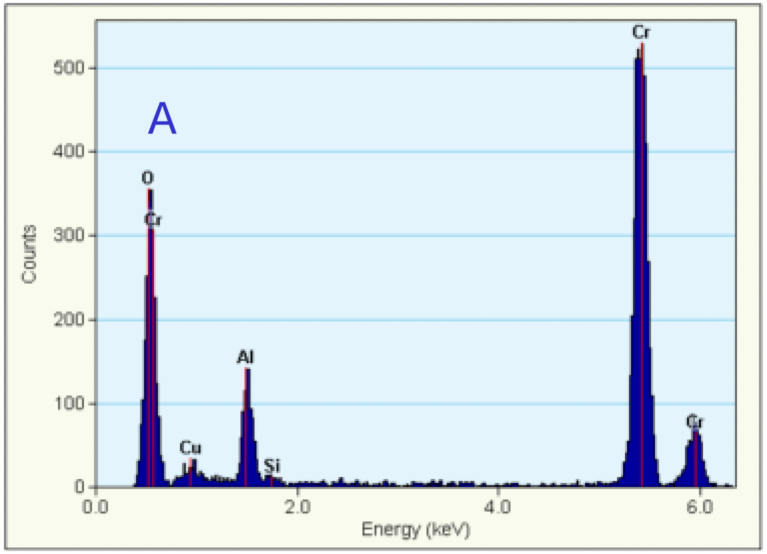
Alkoxide route

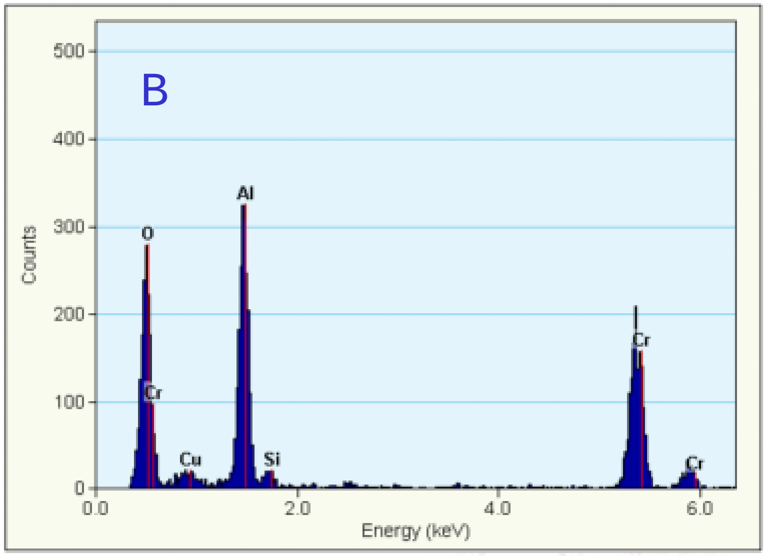


Acid- Base route

EDX Indicates Two Phases



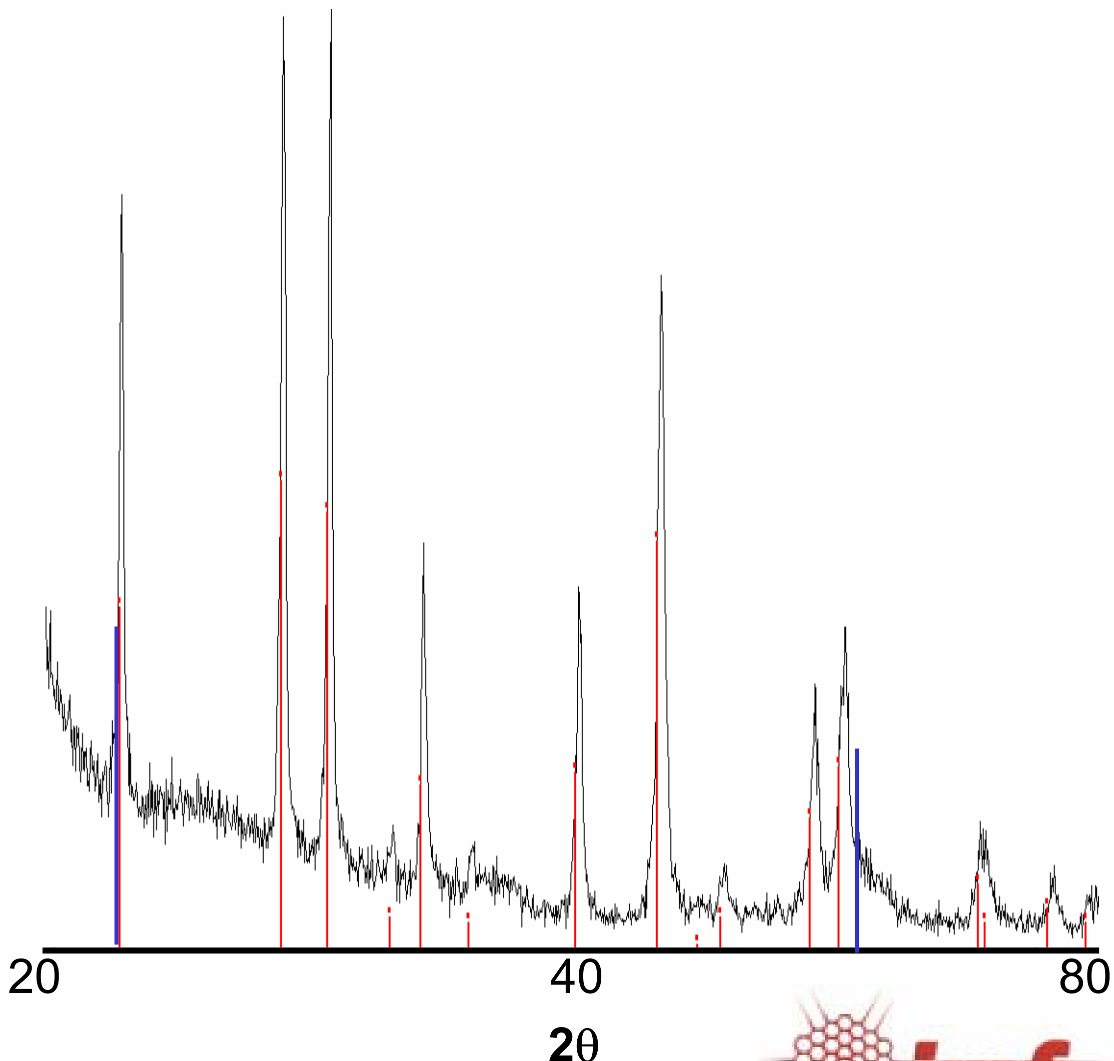




BERKELEY LAB

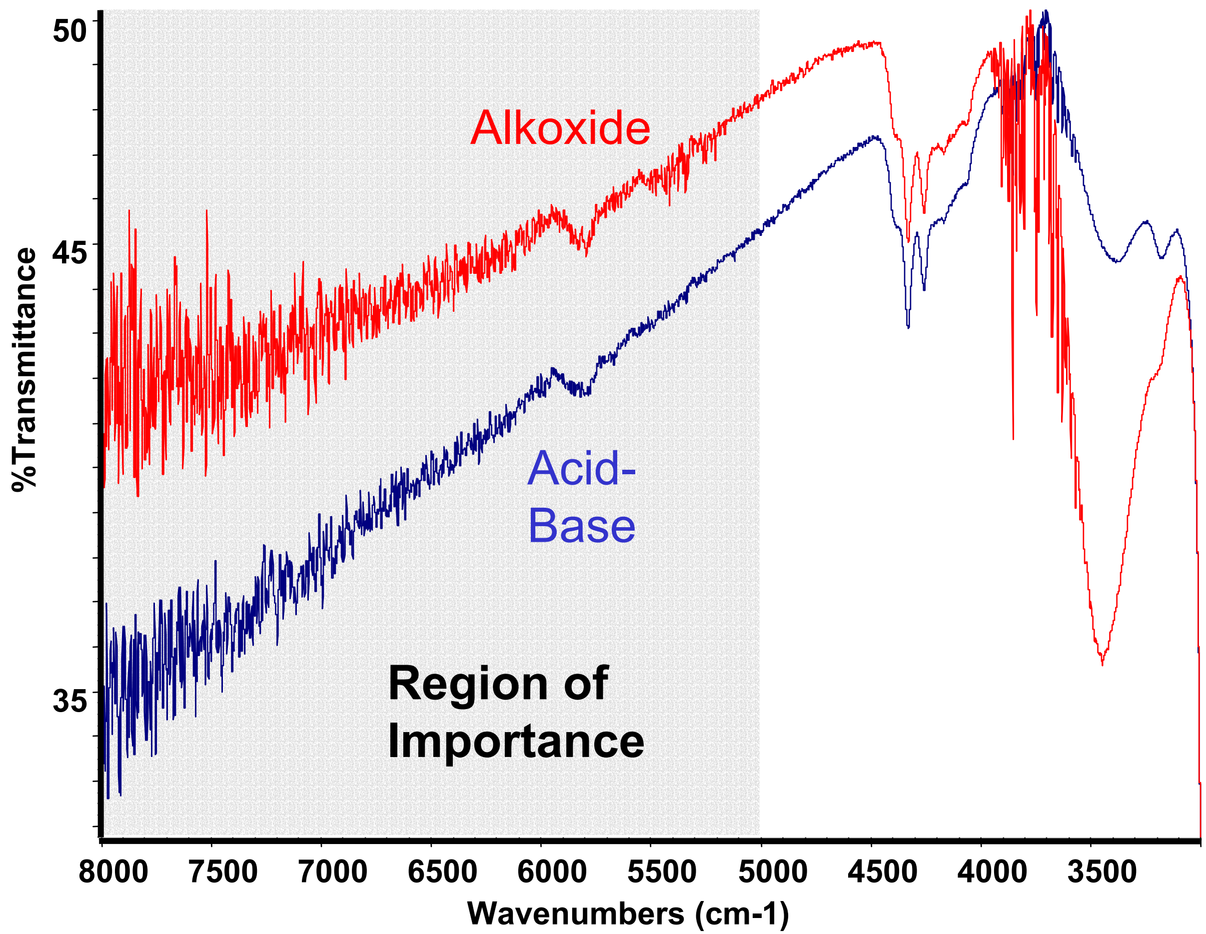
X-Ray Identification

- Acid-base derived aerogel shows one primary crystalline phase:
  - Eskolaite, Cr_2O_3
- Second phase may also be present;
  - $Al_{1.4}Si_{0.3}O_{2.7}$



Opacity of Al-Cr Aerogels

- 0.1-1.5 micron crystal inclusions scatter incident IR radiation
- Acid base route gives higher # density of crystals
- Shows lower transimittance in area of interest
- Material is largely self-opacified



Raw Materials Costs

For 1 board-foot @ 0.35 g/cm^3 (~8% solids); bulk or semi-bulk

Worst case:

Item	Cost/board-foot ($)
Aluminum alkoxide	58
CrO_3	1.36
Tetraethylorthosilicate	0.54
ZrO_2 fiber opacifant (1% v/v)	58

Total: $118.00

Best case:

Item	Cost/board foot ($)
Aluminum trihydroxide	0.23
CrO_3	1.36
Tetraethylorthosilicate	0.54

Total: $2.13

Future Work

- Continue compositional study and characterization of alumina-chromia aerogels to achieve lower density and better opacification
- Evaluate best approach for using this material in a commercial insulation product
  - Compacted Monoliths,
  - Additions to Composite products
- Cost estimates for physical processing
- Prototyping for glass furnace application
- Expand program to look at various other routes to nanostructured materials derived from commodity raw materials