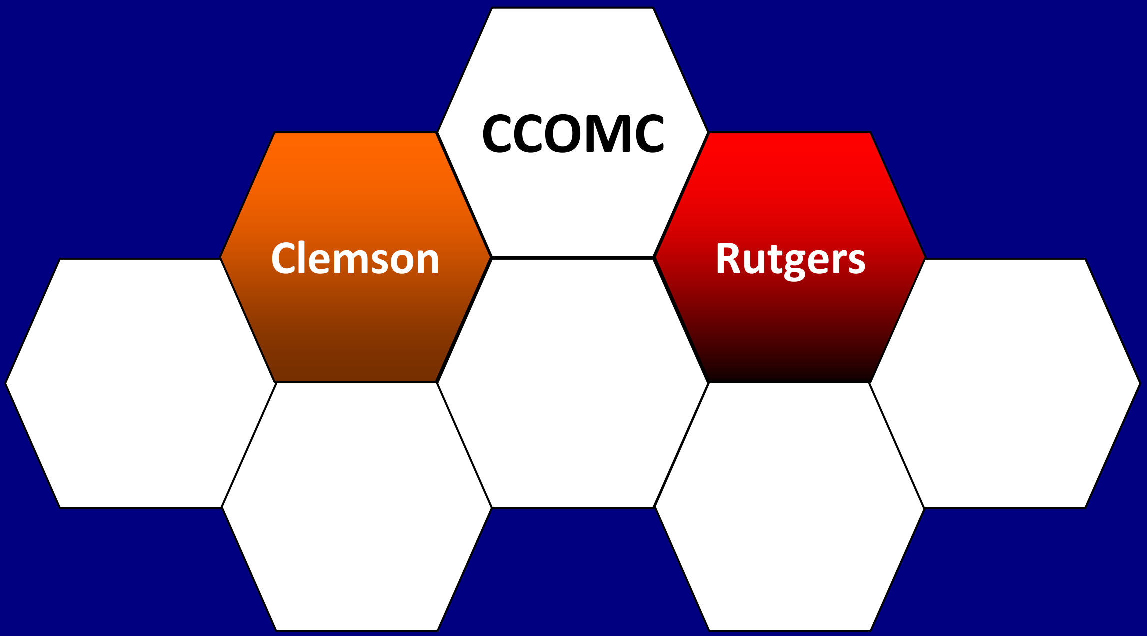
Solution Synthesis of Spinel



Ceramic, Composite and Optical Materials Center
Rutgers, The State University of New Jersey

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Background

- Spinel ($MgAl_2O_4$) is a very attractive material for the preparation of IR-transparent windows that have excellent ballistic protection properties.

- Current approaches for commercially producing spinel use high temperature (600 to 1000ºC) solid-state reaction methods along with subsequent milling, leading to reduced purity and high energy costs.

- Only one manufacturer of high-quality spinel powder in the USA, Baikowski and the cost is high ($60/kg).*

- There is an opportunity to research, develop and commercialize low-energy hydrothermal technology that can produce low-cost spinel.

Overall Goals

- Find the mildest reaction conditions and shortest reaction times to prepare $MgAl_2O_4$ spinel powder direct from solution (with no high temperature treatment).
- Study the crystallization and reaction kinetics for particle formation to understand how to control the physical and chemical characteristics of the spinel powder.
- Develop a thermodynamic and kinetic model to predict the behavior of the particle formation and subsequent physical and chemical characteristics of the spinel as a function of the processing variables.

Hydrothermal Synthesis

- Chemical precursors are heterogeneous slurries, gel and or homogeneous solutions, acid or base mineralizer required
- Aqueous, mixed solvent or solvothermal solution medium
- Mild to severe reaction conditions (T=25-600^{o}C, p=1-4110 atm)
- Anhydrous oxides form in a single process step
- P-T-H_2O interaction => unique phase equilibria
- Solution-mediated reaction => labile reaction kinetics relative to solid state reaction
- Controlled nucleation, growth and aging => controlled size and morphology
- Process can be inexpensive

Mechanochemical and M-H Synthesis

- Mechanical forces generate stresses that induce chemical reactions
- Inexpensive milling equipment
- Inexpensive starting materials
- Well suited for scale up (air, atomspheric pressure, room temperature)
- Solid-solid reactions
- Reactions between solid and aqueous solution (M-H synthesis)

Conventional- and Mechanochemical-Hydrothermal Methods

C-H method

P = 5-20 bars

T = 50-200^{o}C

RPM = 0, 100-1400

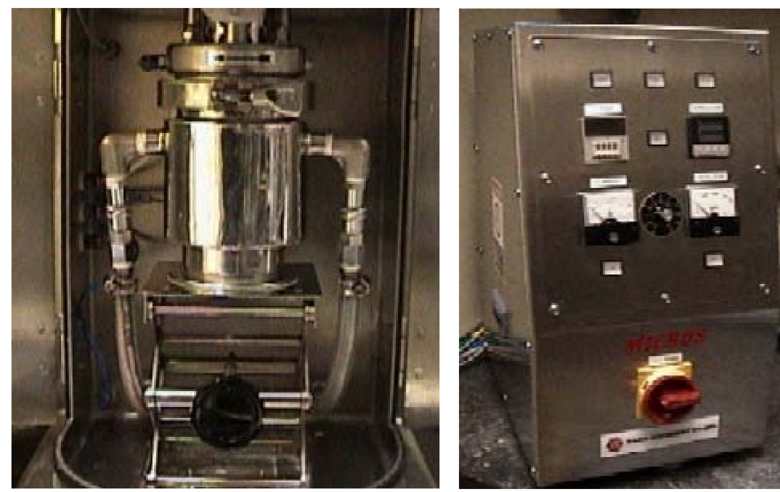
M-H method

P = 1 atm

T = 25-32^{o}C

RPM = 800-2000

Parr Autoclaves: Model 4530



Nara Micros: MIC-0

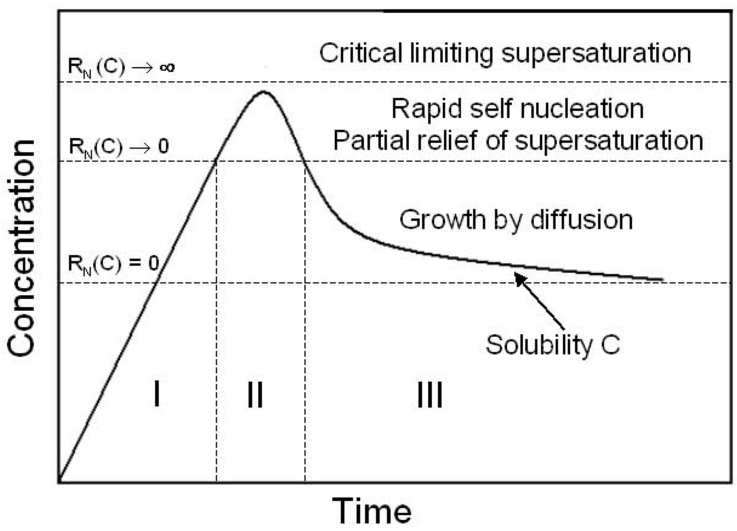
Rational Approach to Direct Crystallization of Oxides

- Compute thermodynamic equilibria as a function of the processing variables for phase of interest
- Generate equilibrium diagrams to map processing variable space for phase of interest
- Design hydrothermal experiments to test and validate computed diagrams
- Utilize processing variable space maps to explore opportunities for control of reaction and crystallization kinetics

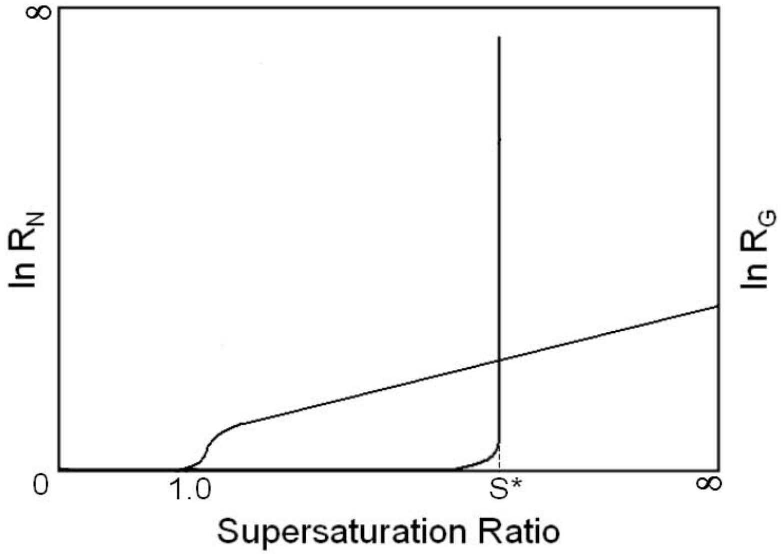
Baseline Knowledge

- Thermodynamics
- Reaction Kinetics
- Crystallization Kinetics
- Reactor know-how

Principles Governing Crystal Growth



(after La Mer and Dinegar, 1950))



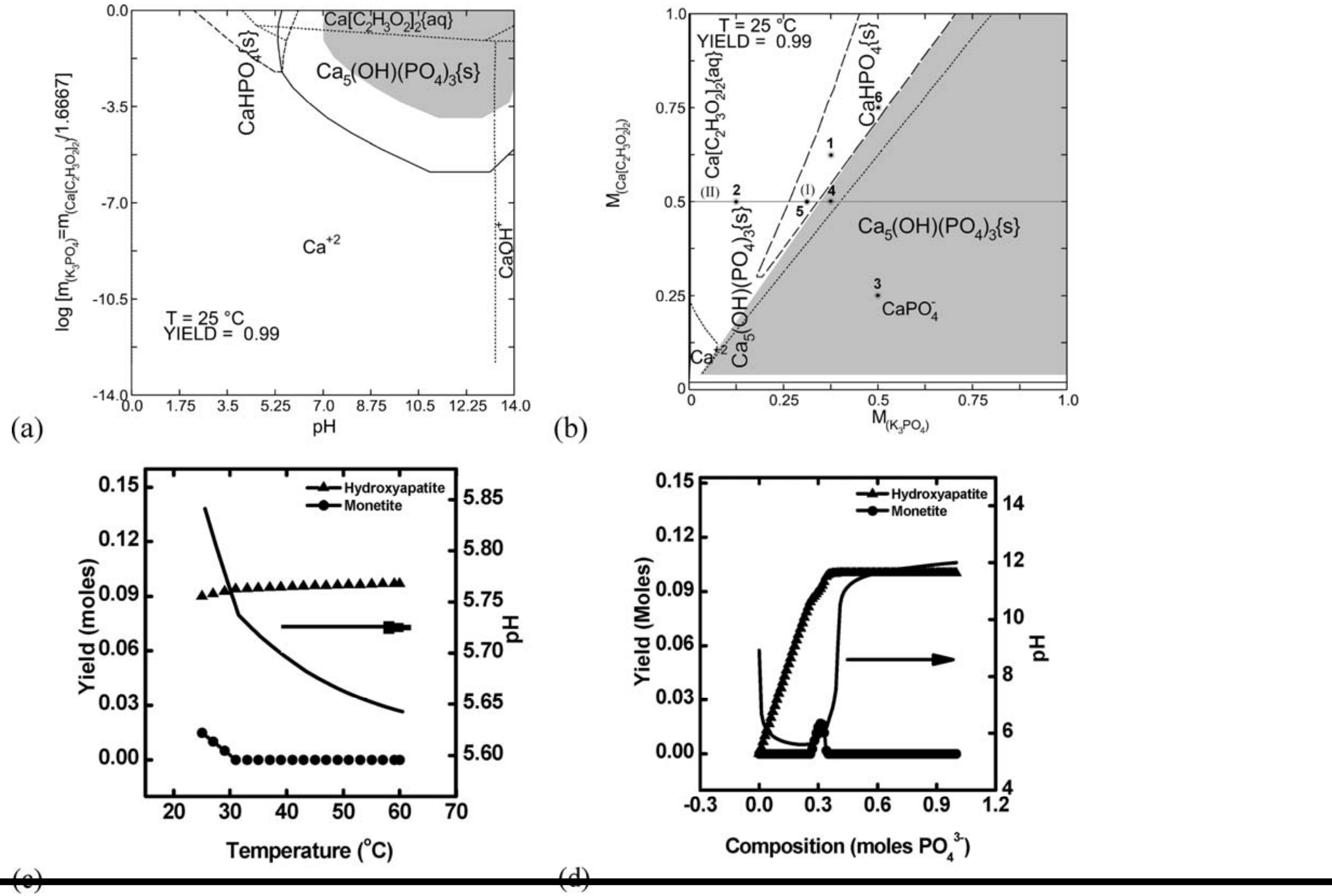
(Modified after Walton (1967)

- Uniformity creates nucleation, growth, and ageing regimes
- Nucleation is an on/off function
- Growth is a continuous function once solubility (S>1) is exceeded in the slightest fashion
- Ageing is dominant after S approaches one (saturated solution)

Equilibria of $Ca(OH)_2$-H_3PO_4-NH_4OH-HNO_3-H_2O System

1. $H_2O = H^{+1} + OH^{-1}$
2. $HP_2O_7^{-3} = H^{+1} + P_2O_7^{-4}$
3. $H_2P_2O_7^{-2} = H^{+1} + HP_2O_7^{-3}$
4. $H_3P_2O_7^{-1} = H^{+1} + H_2P_2O_7^{-2}$
5. $H_4P_2O_7$ (aq) $= H^{+1} + H_3P_2O_7^{-1}$
6. $HPO_4^{-2} = H^{+1} + PO_4^{-3}$
7. $H_2PO_4^{-1} = H^{+1} + HPO_4^{-2}$
8. $2\ H_2PO_4^{-1} = (H_2PO_4)_2^{-2}$
9. H_3PO_4 (aq) $= H^{+1} + H_2PO_4^{-1}$
10. HNO_3 (aq) $= H^{+1} + NO_3^{-1}$
11. NH_3 (aq) $+ H_2O = NH_4^{+1} + OH^{-1}$
12. NH_4NO_3 (aq) $= NH_4^{+1} + NO_3^{-1}$
13. $CaH_2PO_4^{+1} = Ca^{+2} + H_2PO_4^{-1}$
14. $CaNO_3^{+1} = Ca^{+2} + NO_3^{-1}$
15. $CaOH^{+1} = Ca^{+2} + OH^{-1}$
16. $CaPO_4^{-1} = Ca^{+2} + PO_4^{-3}$
17. $CaHPO_4$ (aq) $= Ca^{+2} + HPO_4^{-2}$
18. $Ca(OH)_2$ (aq) $= Ca^{+2} + 2OH^{-1}$
19. $Ca(NO_3)_2$ (aq) $= Ca^{+2} + 2NO_3^{-1}$
20. $Ca_5(OH)(PO_4)_3$ s $= 5Ca^{+2} + OH^{-1} + 3PO_4^{-3}$
21. $CaHPO_4$ (s) $= Ca^{+2} + HPO_4^{-2}$
22. $CaHPO_{4.2}{\bullet}H_2O$ (s) $= Ca^{+2} + HPO_4^{-2} + 2H_2O$
23. $Ca_3(PO_4)_2$ (s) $= 3Ca^{+2} + 2PO_4^{-3}$
24. $Ca(H_2PO_4)_2 \bullet H_2O$ (s) $= Ca^{+2} + 2H_2PO_4^{-1} + H_2O$
25. $Ca(H_2PO_4)_2$ (s) $= Ca^{+2} + 2H_2PO_4^{-1}$
26. $Ca_4O(PO_4)_2$ (s) $+ H_2O = 4Ca^{+2} + 2OH^{-1} + 2PO_4^{-3}$
27. $Ca_{10}O(PO_4)_6$ (s) $+ H_2O = 10Ca^{+2} + 2OH^{-1} + 6PO_4^{-3}$
28. $Ca_4H(PO_4)_3$ (s) $= 4Ca^{+2} + HPO_4^{-2} + 2PO_4^{-3}$
29. $Ca_8H_2(PO_4)_{6.5} \bullet H_2O$ (s) $= 8Ca^{+2} + 2HPO_4^{-2} + 4PO_4^{-3} + 5H_2O$
30. $Ca(NO_3)_{2.3}\ H_2O$ (s) $= Ca^{+2} + 2NO_3^{-1} + 3H_2O$
31. $Ca(NO_3)_{2.4}\ H_2O$ (s) $= Ca^{+2} + 2NO_3^{-1} + 4H_2O$
32. $Ca(NO_3)_2$ (s) $= Ca^{+2} + 2NO_3^{-1}$
33. $Ca(OH)_2$ (s) $= Ca^{+2} + 2OH^{-1}$
34. $(NH_4)_2HPO_4.2H_2O$ (s) $= 2NH_4^{+1} + HPO_4^{-2} + 2H_2O$
35. $(NH_4)_2HPO_4$ (s) $= 2NH_4^{+1} + HPO_4^{-2}$
36. $(NH_4)_3PO_{4.3} \bullet 3H_2O$ (s) $= 3NH_4^{+1} + PO_4^{-3} + 3H_2O$
37. $(NH_4)H_2PO_4$ (s) $= NH_4^{+1} + H_2PO_4^{-1}$
38. $(NH_4)NO_3$ (s) $= NH_4^{+1} + NO_3^{-1}$
39. H_2O (v) $= H_2O$
40. NH_3 (v) $= NH_3$ (aq)
41. HNO_3 (v) $= HNO_3$ (aq)

$Ca(CH_3COO)_2$-K_3PO_4-H_2O System

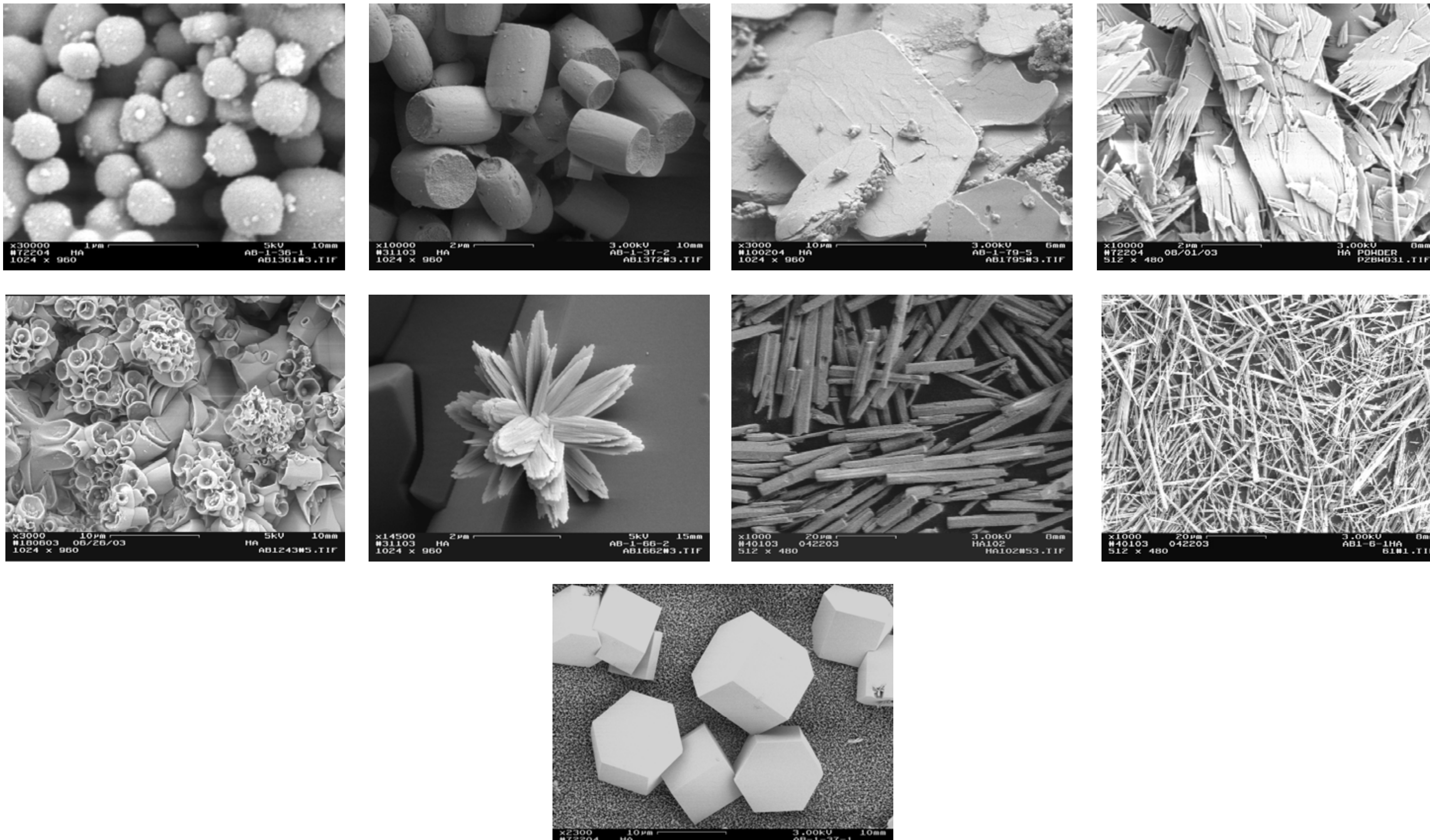


Reaction Conditions

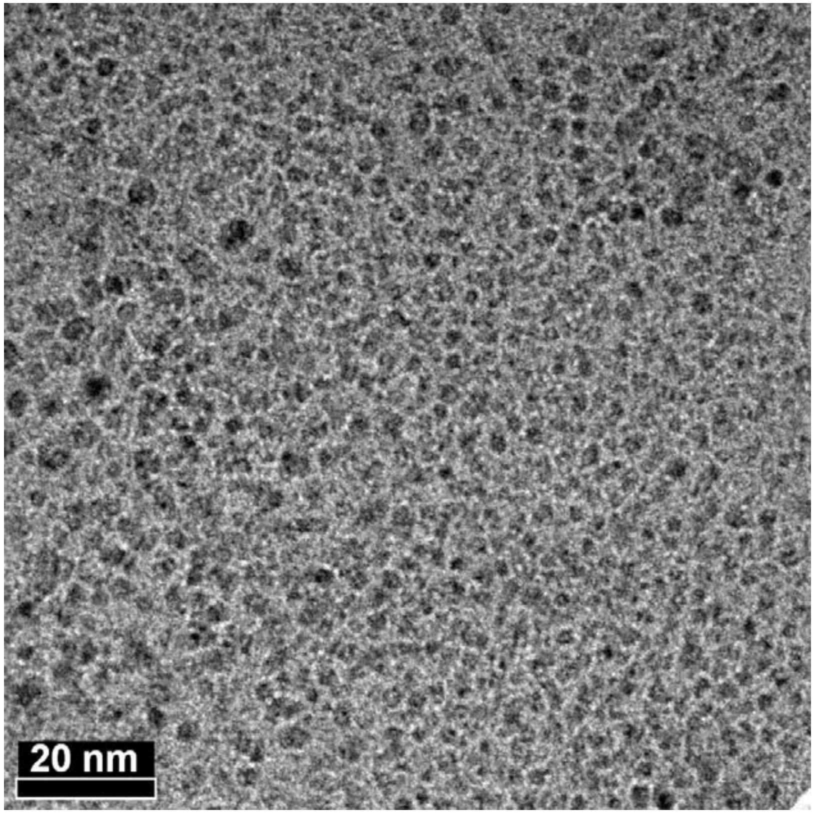
Morphology	Ca/P	NH_3/KOH	EDTA/Ca	Time (h)	Temp (˚C)	Stirring Rate (rpm)
Plates	2	NH_3	0	8	180	300 (High Shear)
Needles	2	None	0	24	200	0
Equiaxed Spheres	2	NH_3	0	24	200	1700
Equiaxed Hexagons	1.24	KOH	1	24	200	0
Barrels	1.24	KOH	1	1	200-230	5375 (High Shear)
Dendrites	1.24	KOH	1	25	192	0
Coral	2	KOH	0	24	180	0
Leaves*	1.67	NH_3	0.93	24	120	0

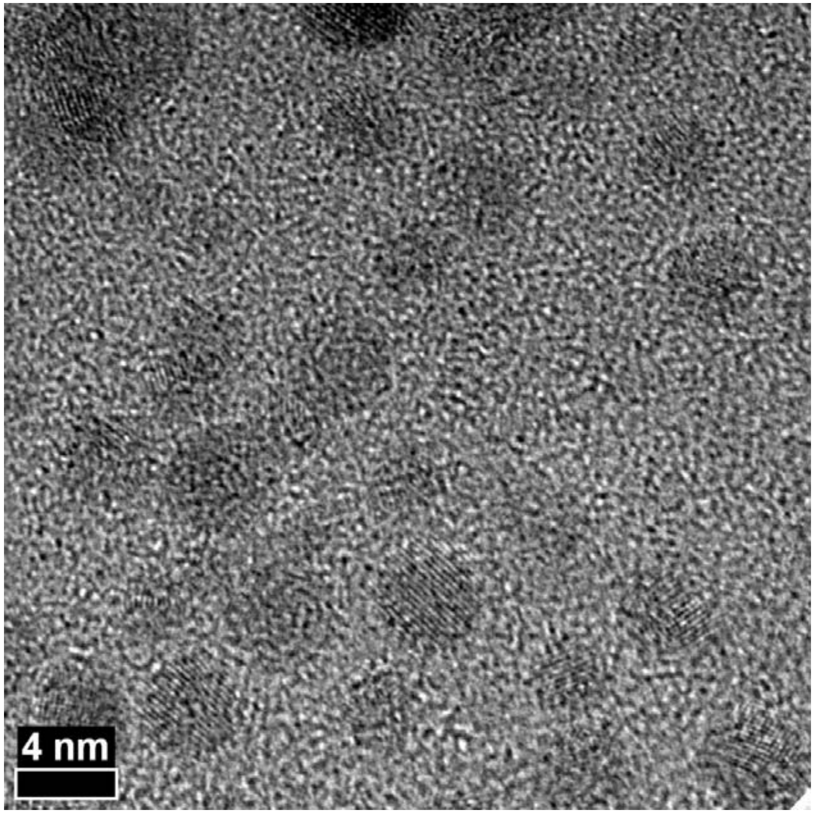
*solvothermal: 1,4-butandiol/H_2O=30/10 (v/v)

Gallery of Morphologies with Solution Crystallization of HA



TEM – Very Small Nanoparticles! Very Difficult to Isolate.



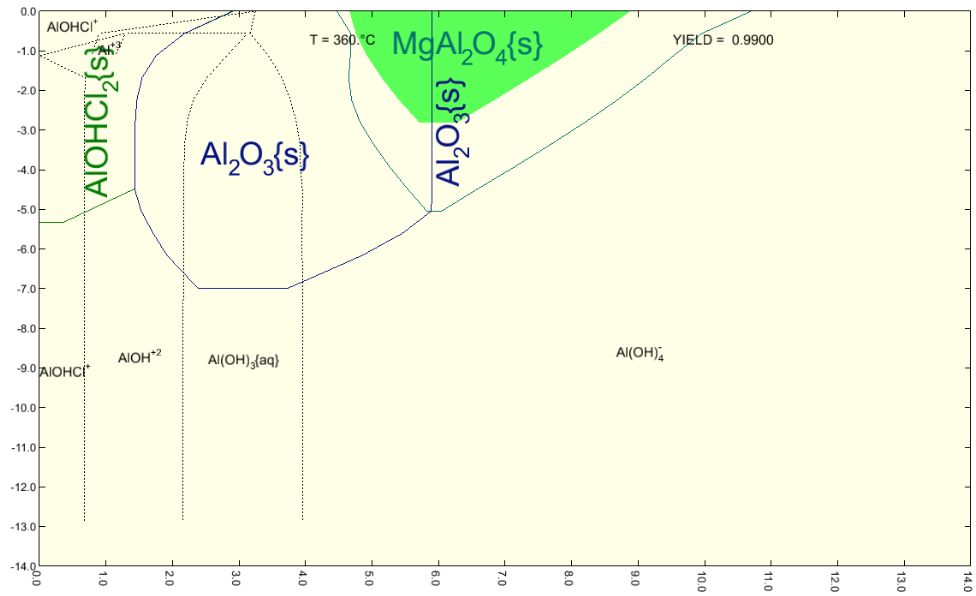


Method of Attack

- Daniel Kopp (1st year graduate student)
  - BS Materials Science and Engineering, Rutgers University
- Thermodynamic modeling
  - Precursor selection
  - Reaction conditions
- Down-select Synthesis Approach
  - Hydrothermal synthesis
    - Conventional Reactors
    - Microwave reactors (largest one in the USA in a university)
  - Mechanochemical synthesis
    - Unique Micros 0 system at RU (only 2 in the USA)
  - Mechanochemical-hydrothermal
- Develop *in situ* characterization methods
  - FT-IR spectroscopy
  - XRD
- Study reaction and crystallization kinetics to control physical and chemical characteristics.
- Develop kinetic model to semi-quantitatively predict the physical and chemical characteristics of the spinel powder.
- Supply powder to Haber group in 20-50 g quantities for processing studies

Prior work - Atakan and Riman 2007

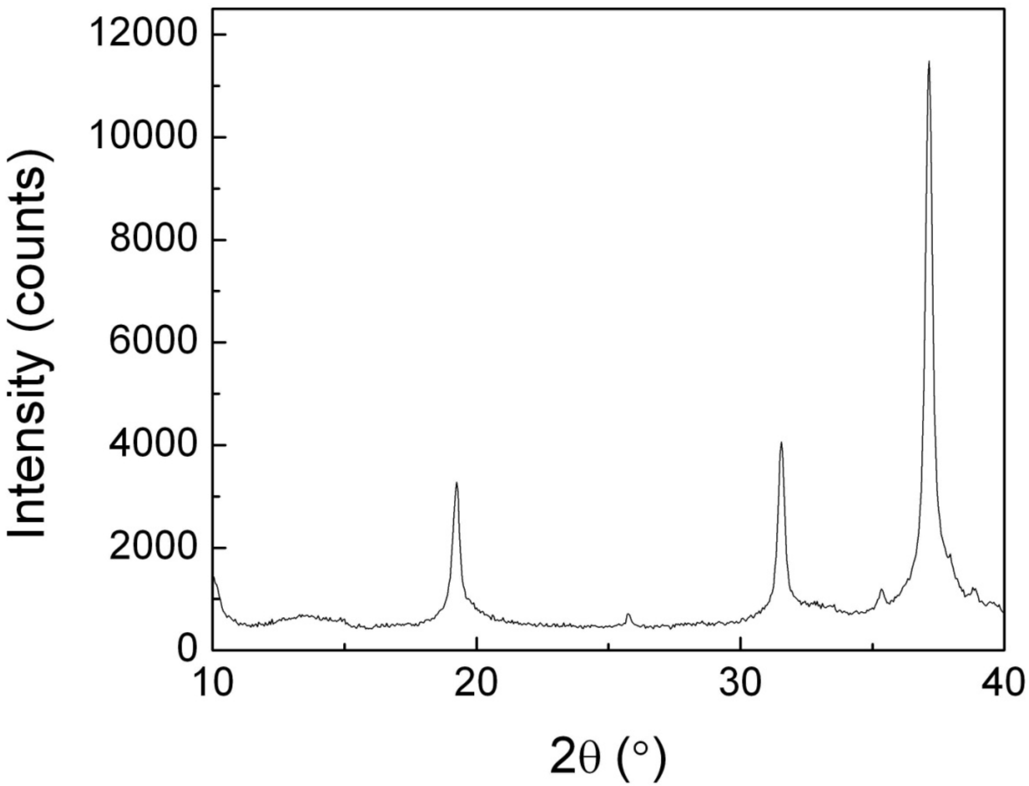
- Recommended precursors:
  MgO and Al_2O_3
- T = 360 °C
- P = 2828 psi
- pH = 5.8
- Advantages:
  - Does not require mineralizer to control pH
  - No by-product
  - Minimal corrosion
  - Precursors available within the desired purity level



- Are synthesis routes with cheaper precursors such as bauxite compounds feasible?

Prior work – Atakan and Riman 2007

- Spinel hydrothermally synthesized from steam-based reactions of MgO and Al_2O_3 at 400 °C, 2680 psi and washed in 1 M HCl
- Simple separation technology!



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Mechanochemical Synthesis

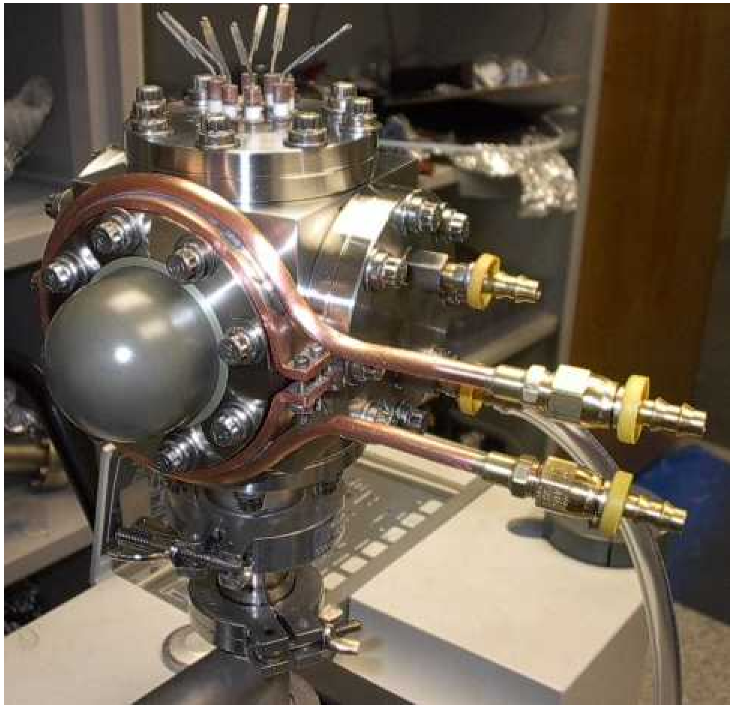
- Domanski et. al.[1] synthesized spinel from MgO and Alumina at room temperature by ball milling in 140 h.
- Contamination due to milling media equipment.
- Suchanek et. al.[2] synthesized hydroxyapatite at room temperature using stabilized zirconia media and liners in a *mechanochemical-hydrothermal (M-H) reactor*.
- Can *M-H* be used to synthesize spinel, with or without hydrothermal solutions?


Nara Machinery Co.'s MIC 0 zirconia ring/zirconia-lined wet milling machine from the Riman laboratory.

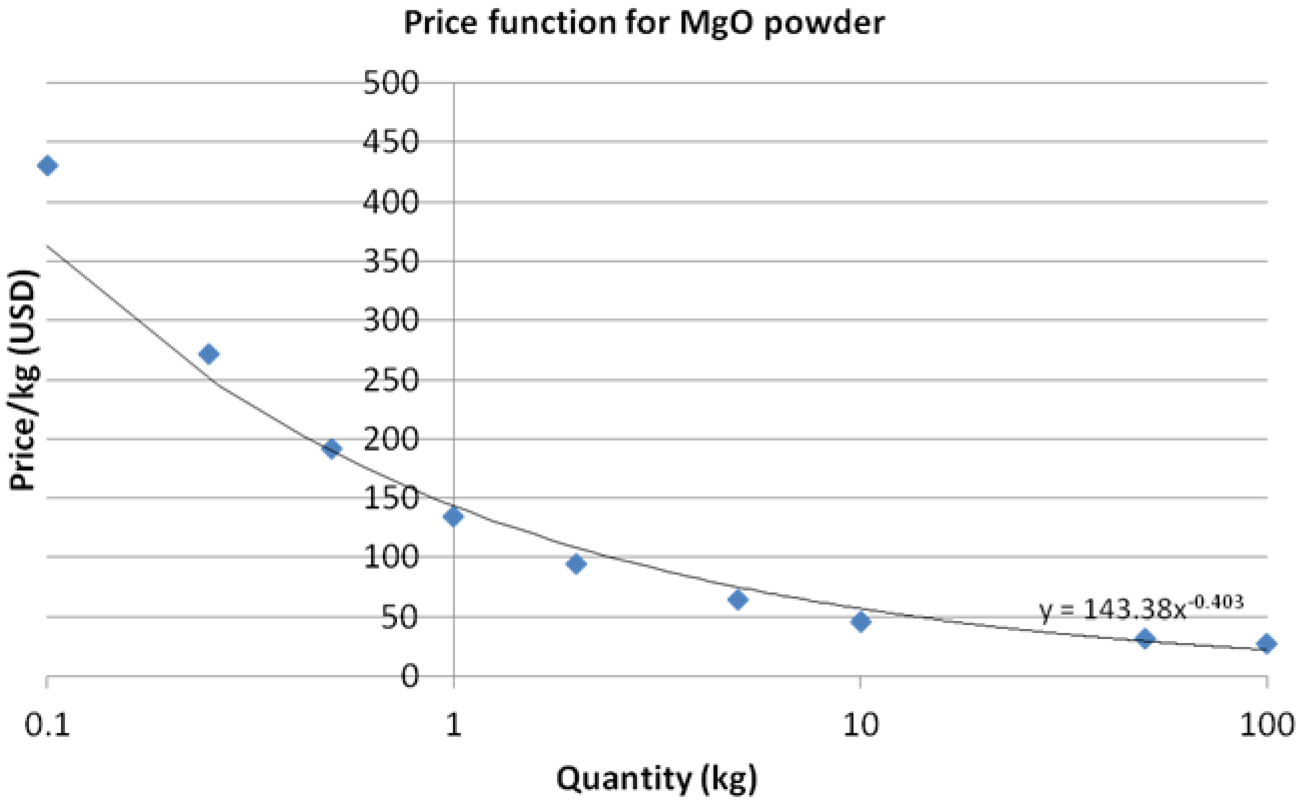
1. *J. Am. Ceram. Soc., 87 (11): 2020-2024 2004*
2. *Biomaterials, 25(19): 4647-4657 2004.*

In situ characterization

- ATR-FTIR spectroscopy reaction probe technology under development in the Riman laboratory for hydrothermal processes.
- Use of beryllium cell-based X-ray diffraction at PNNL, BNL and eventually at Rutgers.



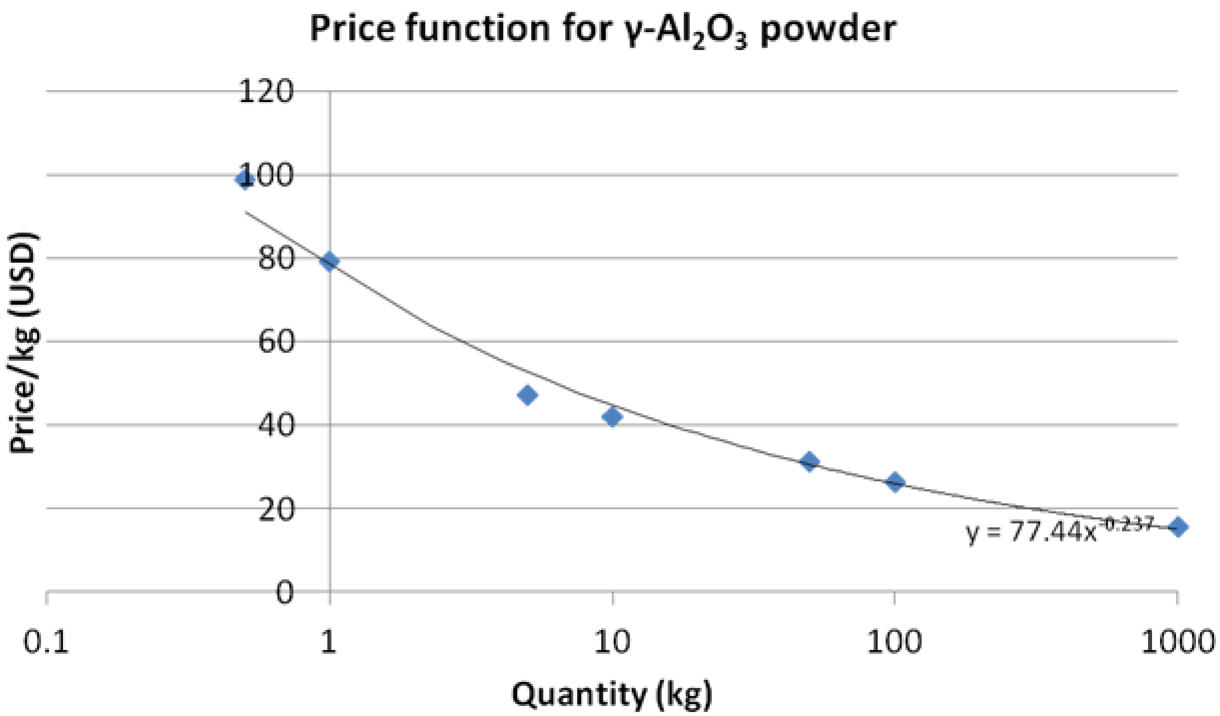
Cost Function for MgO Powder



$3/tonne at >15 tonne

99.9% pure, average particle size, surface area >20 m^2/g

Cost Function for γ-Al_2O_3 Powder



$8/tonne at >15 tonne

99.99% pure, surface area 70-100 m^2/g

Project Benefits

- Economic
  - Capital equipment, energy and raw materials costs (< $20/ton) are kept low because of minimal drying and elimination of milling, separation and high temperature processing steps.
  - New source of $MgAl_2O_4$ spinel powder.
  - Opportunity for commercialization
- Academic
  - First low temperature spinel synthesis method that also offers control particle size and morphology.
  - First fundamental study on solution spinel crystallization thermodynamics and kinetics.
  - Method may be applicable to other ceramic chemistries

Next Steps

- Complete literature review of spinel synthesis literature and write a review paper.
- Prepare and characterize initial spinel samples using the Atakan and Riman approach.
- Research *in situ* and *ex situ* characterization techniques.
- Run and validate thermodynamic models for different precursors.
- Get training on hydrothermal reactor and chemical and physical characterization instrumentation