Liquid-Feed Flame Spray Pyrolysis. Conquering the Tyranny of Thermodynamics Synthesis of Mixed-Metal Oxide Nanoparticles

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Funding:

AFOSR Contract No. F49620-03-1-0389, NSF (IGERT), Maxit Group, Defense Sciences National Labs, Singapore

June, 2004

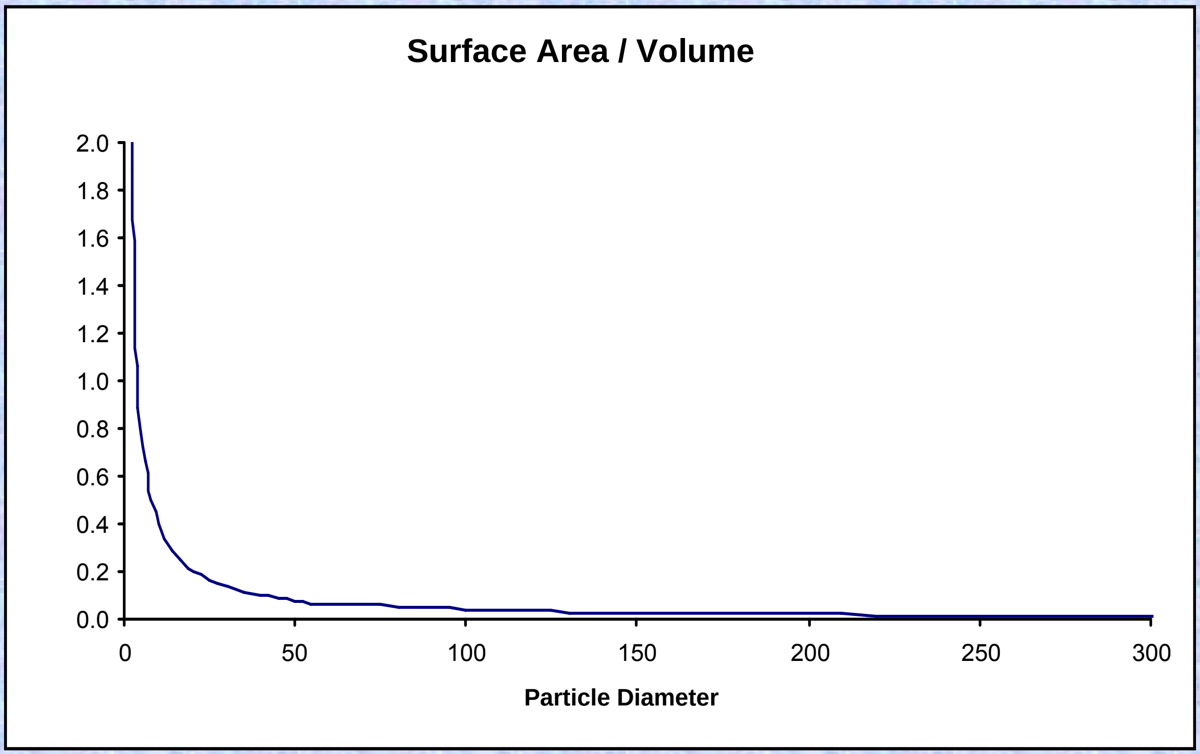
Outline

- What do nanopowders offer?
- A brief history of FSP
- Key problems in nanopowder synthesis
- Liquid-feed FSP (LF-FSP)
  - Combustion of low-cost, alcohol soluble precursors
  - Nanopowder formation mechanism(s)
- Mixed-metal oxide nanopowders for
  - Catalysts
  - *Photonics*
- Conclusions

1. What do nanopowders offer?

What are nanopowders?

< 100 nm



2. What do nanopowders offer?

Passive Physical Size Applications

- Finer powder sizes
  - Little or no grinding
    - Avoids impurities and costs
- Transparency for films and coatings
  - Abrasion resistant floor coatings
    - Nanophase
  - Higher gloss inks
  - Finer grain size in sintered ceramics
    - Better mechanical properties
    - Smaller flaw sizes, therefore more robust

Inkjet Printed Nanophosphors

G. Jabbour U. Arizona

3. What do nanopowders offer?

New Science Through New Materials

Novel phases with unexpected:

- Conductivity
  Thermal, electrical
- Catalytic properties
  Unusual combinations of phases
- Photonic properties

Brief History of FSP

- **One of oldest materials processing methods**
- **Used to make lamp black, carbon soot**

  reductive flames

- **Gaseous feed FSP**

- $SiCl_4 + H_2 + O_2 \text{ ---> } SiO_2 + 4HCl + H_2O$

- **Currently used to make kilotons of nano TiO_2 & SiO_2, some Al_2O_3**

Brief History of FSP

Some interesting quotes:

- *"As a general rule, flame-generated particulate materials require expensive raw materials"*

- *"Mixed-oxides comprise a relatively undeveloped avenue of flame technology"*

  G. Ulrich, C&EN News, April, 1984, pp. 25-

- ***Disadvantages include difficulties in producing multi-component materials, low production rates …and hazardous gaseous reactants and by products,"***

- *Another major disadvantage is formation of hard agglomerates in the gas phase leads to difficulties in producing high-quality bulk materials,"*

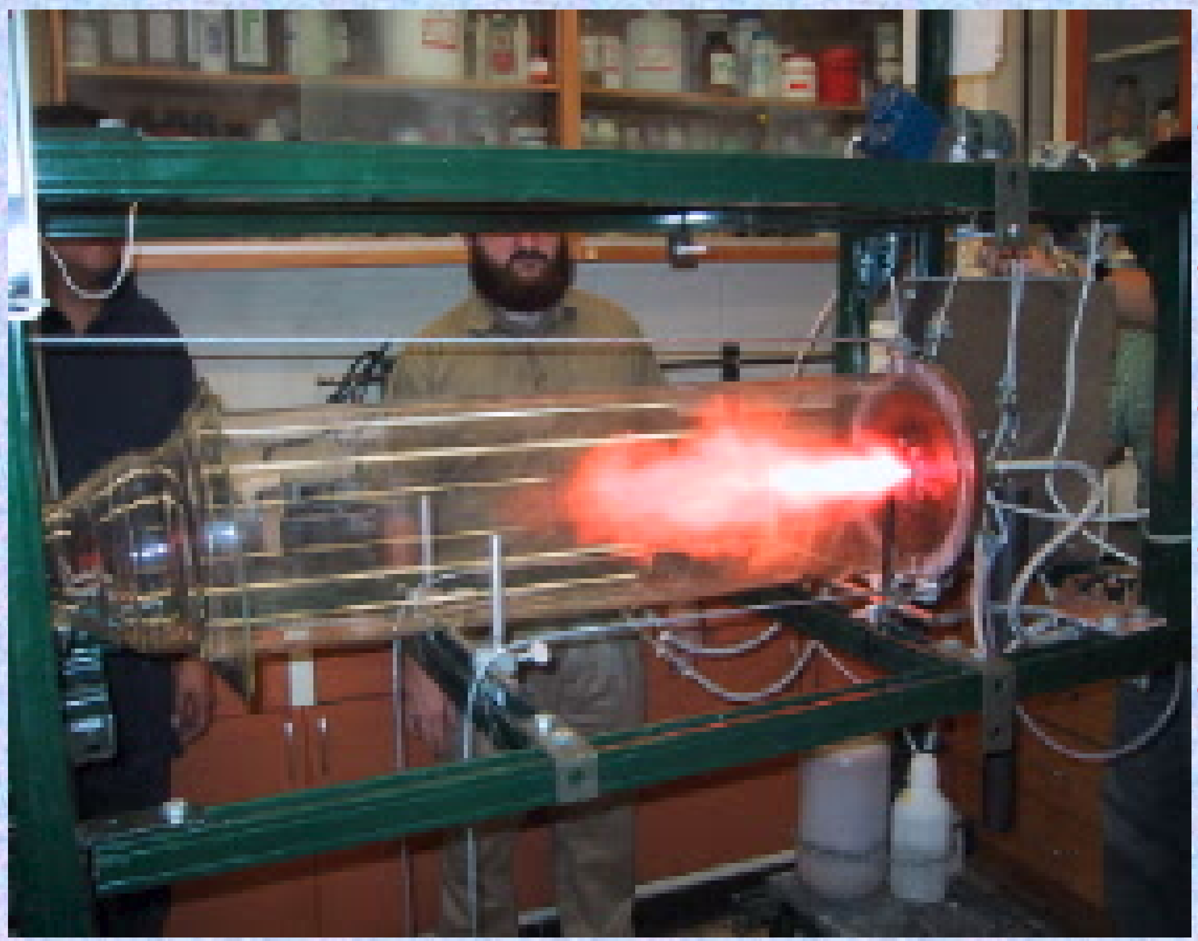
  T. Kodas , "Aerosol Processing of Materials," Aerosol. Sci. and Tech. 19, 411-52 (1993)

Key problems in nanopowder synthesis

- *No very general ways of making large quantities of mixed-metal oxides*
- *Difficult to control particle sizes and distributions*
- *Difficult to tailor compositions and surface chemistries*
- *Can be hard to control degree of agglomeration*
  And therefore processability of as-produced powders
- *Liquid-feed flame spray pyrolysis (LF-FSP) offers a solution to many of these problems*

What is LF-flame spray pyrolysis?

Fafnir



- Low cost precursors
- Dissolved in alcohol
- Aerosolized with O_2
- Combusted ≤1500°C
- Quenched rapidly
- Limited agglomeration
- **What you shoot is what you get!**

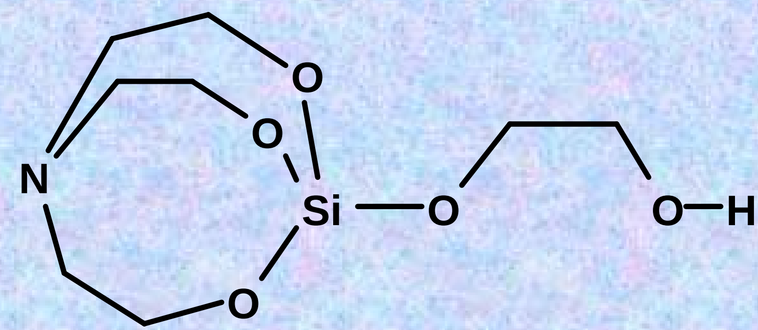
Commercial Scale Production

Tal

- 1- 3 kg/h
- Continuous operation
- Same quality
- Or better

Low cost metalloorganic precursors

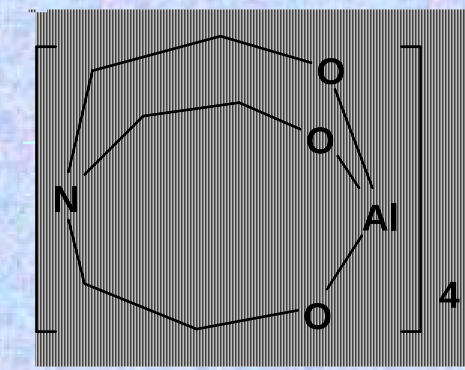
- **SiO_2 (TiO_2) + $N(CH_2CH_2OH)_3$ $\xrightarrow{200°C/-H_2O}$**



Silatrane (titanatrane) glycol

  - **Water soluble and stable**

- **$Al(OH)_3$ + $N(CH_2CH_2OH)_3$ $\xrightarrow{200°C/-H_2O}$**



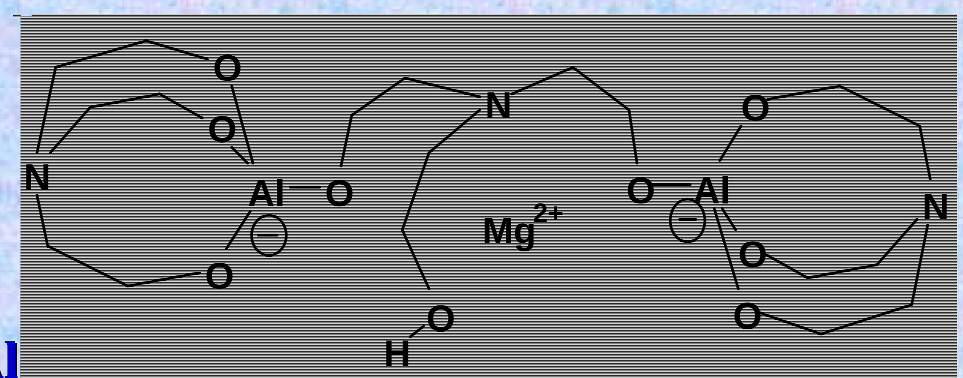
Alumatrane

  - **Air and moisture stable**

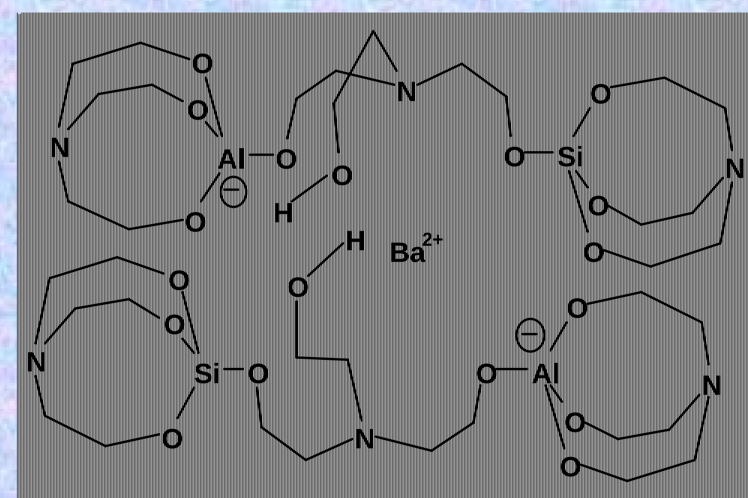
Low cost, mixed-metal precursors

- **Spinel-$MgO \cdot Al_2O_3$**

$MgO + 2Al(OH)_3 + 3TEA \xrightarrow{200°C/-H_2O}$

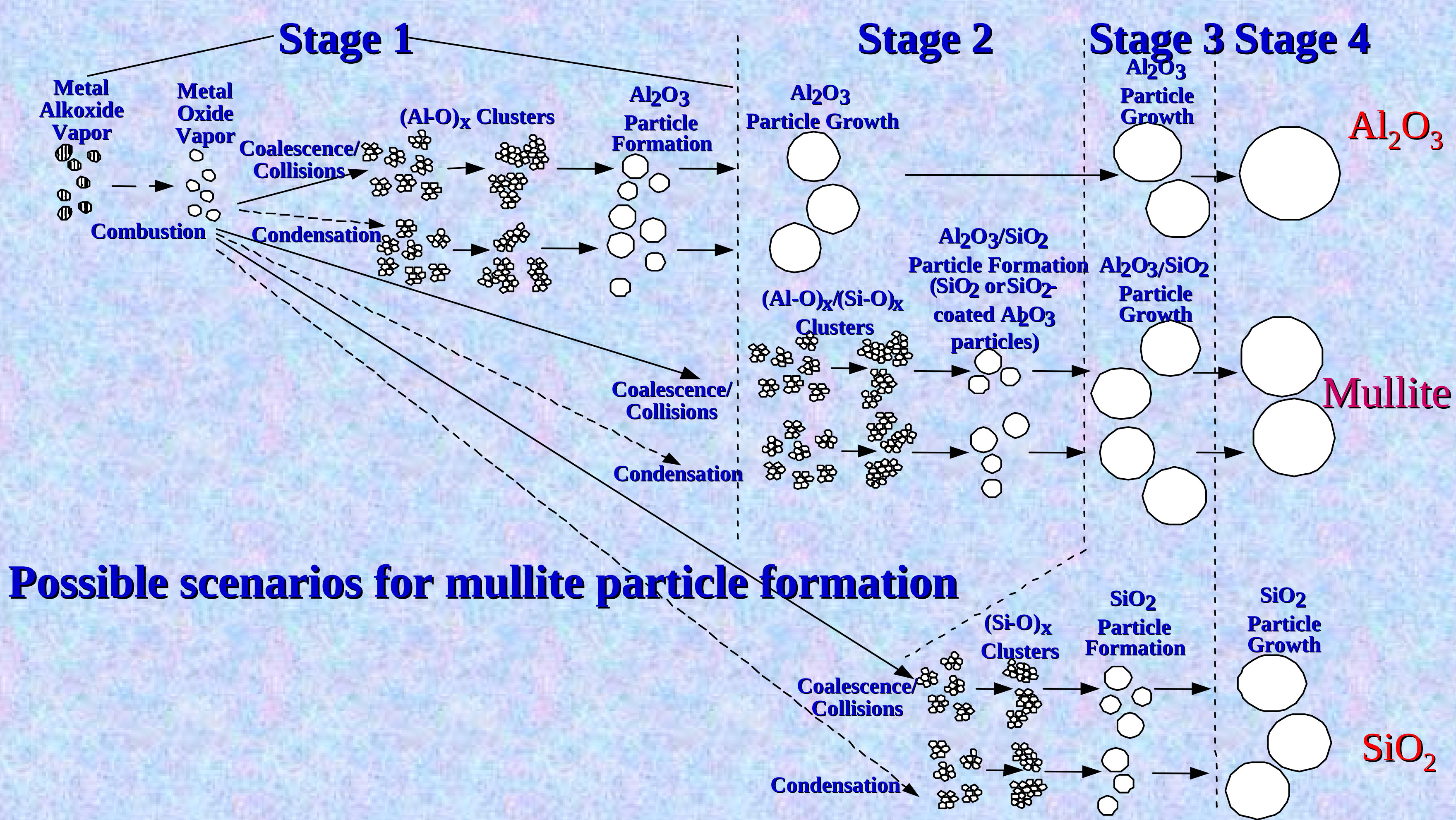


- **BAS (SAS) $BaO(SrO) \cdot 2SiO_2 \cdot Al_2O_3$**



- ***The art is in the chemistry***

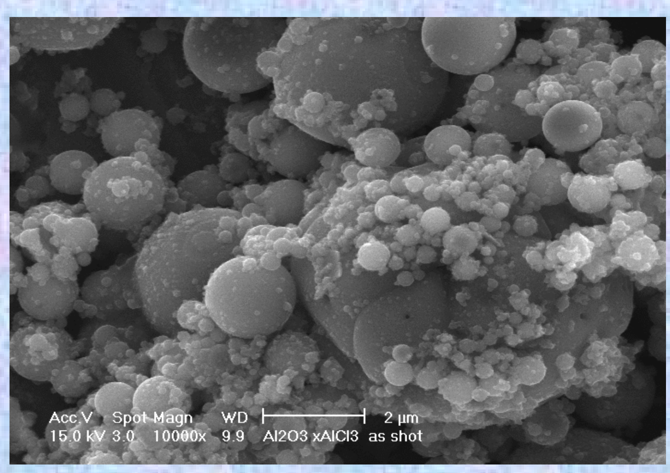
Powder Formation Process



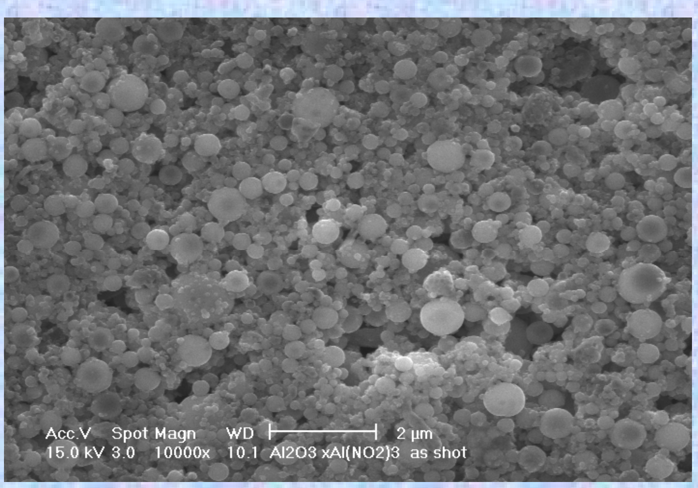
What you shoot is what you get

Single-Metal Oxide Nanopowders

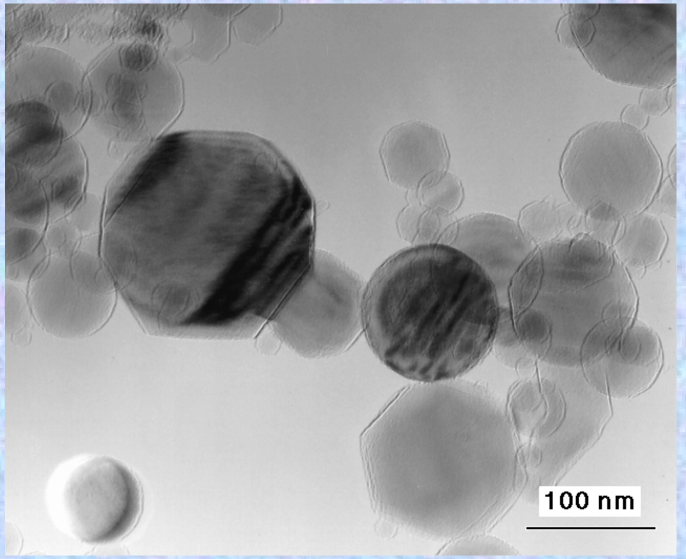
δ–Al_2O_3



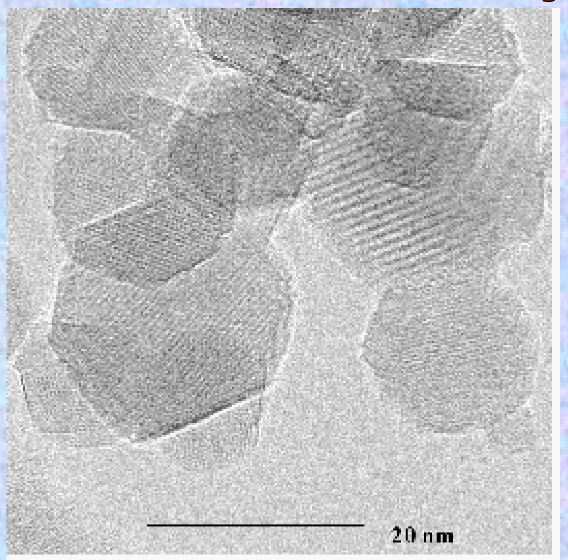
LF-FSP of $AlCl_3$



LF-FSP of $Al(NO_3)_3$

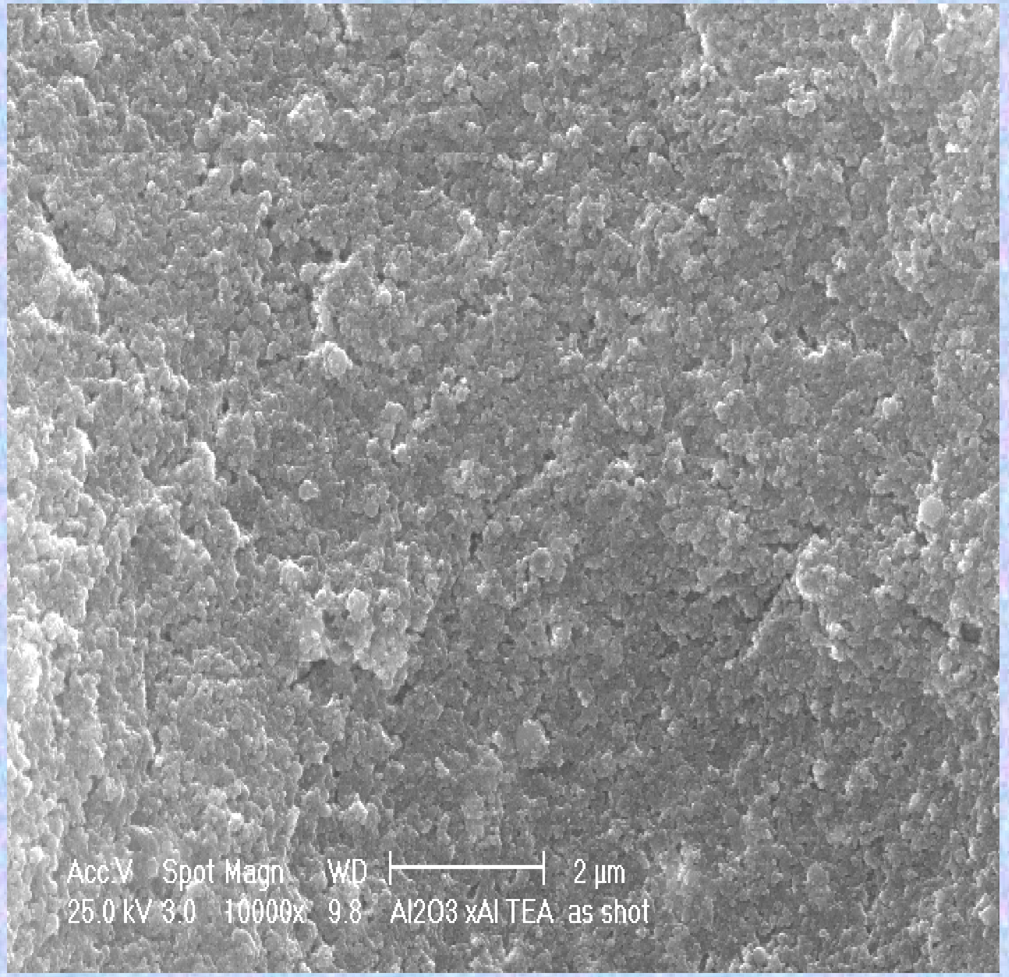


LF-FSP of $Al(OCH_2CH_2)_3N$



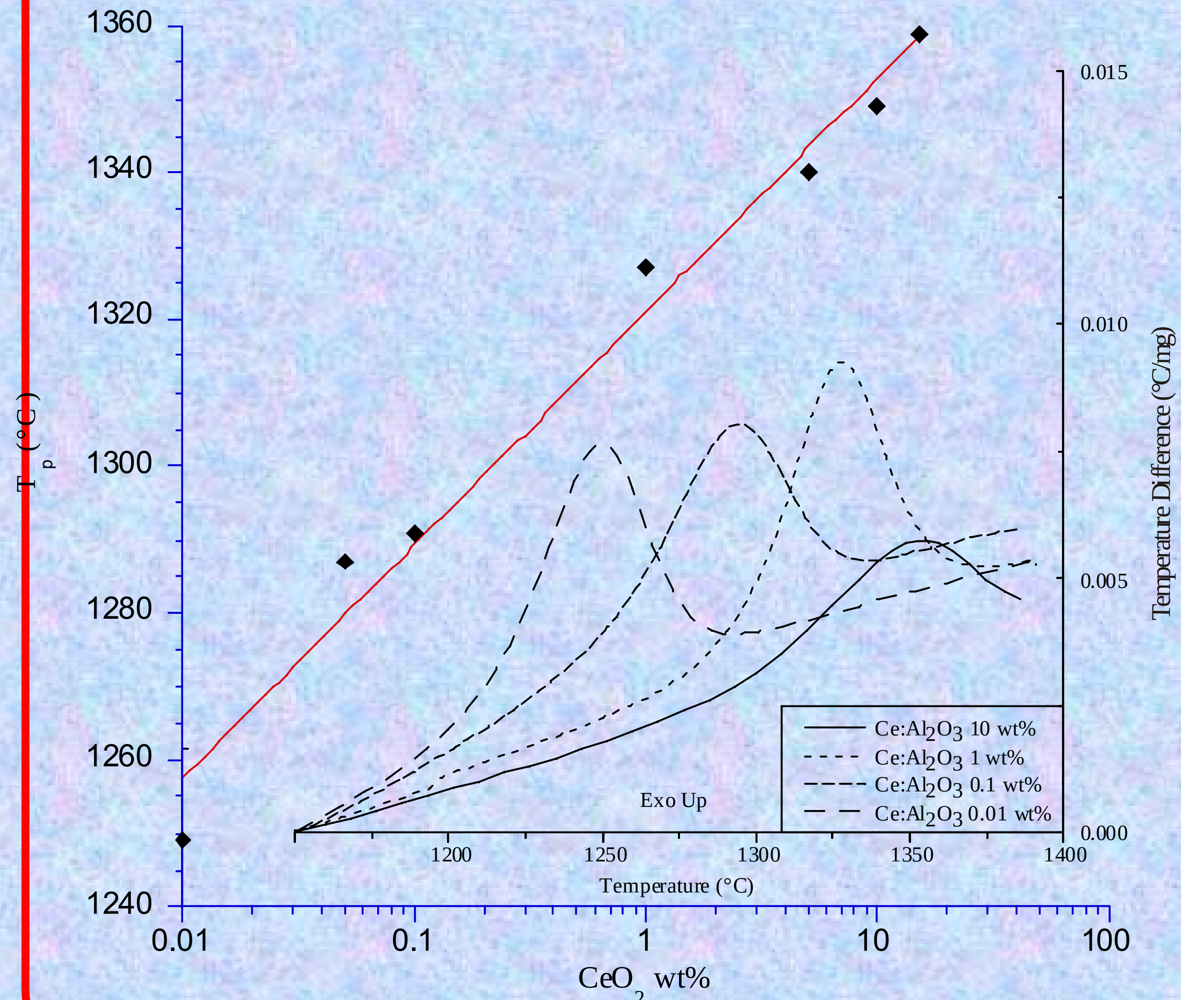
LF-FSP of $Al(OCH_2CH_2)_3N$

Single-Metal Oxide Nanopowders
Al_2O_3



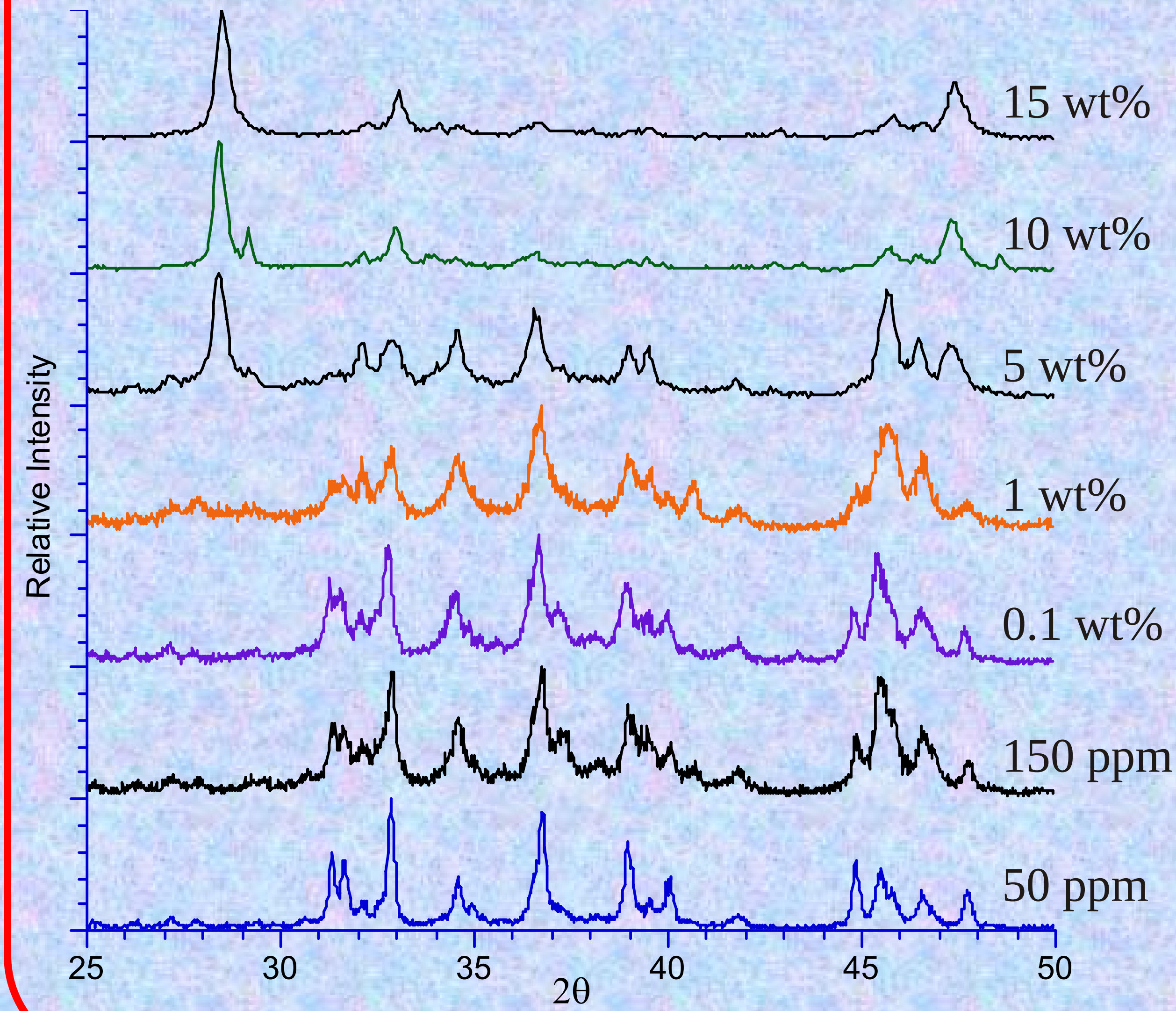
- δ-alumina
  - Novel phase
  - 3.5 g/cc
- Log normal size distribution
  - $\phi \approx 30$ nm
- Unaggregated,
  - self-disperse in water,
  - polar polymers
- Can dope to 10 ppth with rare earth ions

2. Thermal Behavior of Ce^{3+} Doping



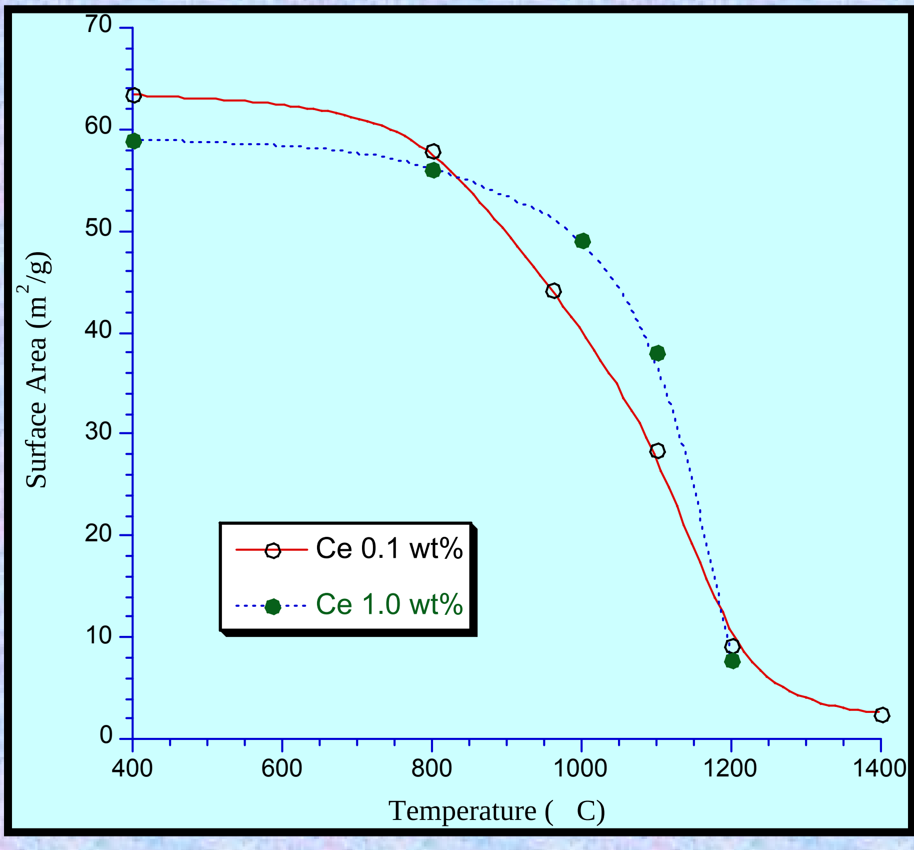
- δ- to α transformation
  - Inhibited by increases in [RE]
  - Can inhibit to ≈ 1400 °C
- Sintering behavior?
- Catalyst support?

Ceria doped δ-alumina

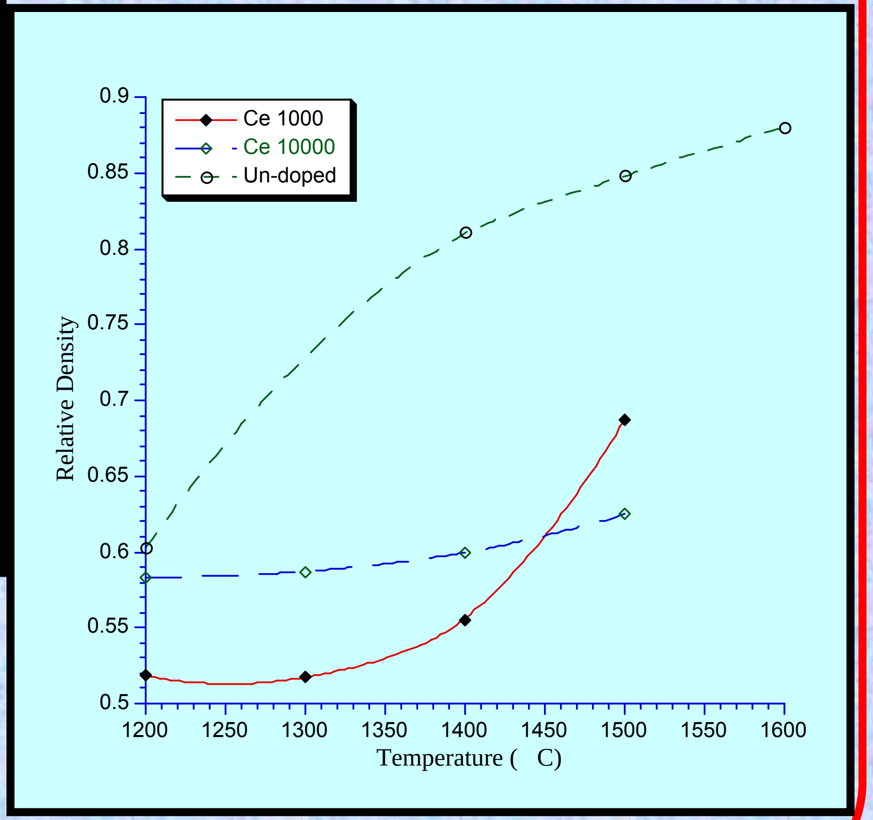


- Above 1 wt. % CeO_2 phase segregates
- Sintering and phase transformation inhibition still observed

Stability of Ce:δ-Al_2O_3



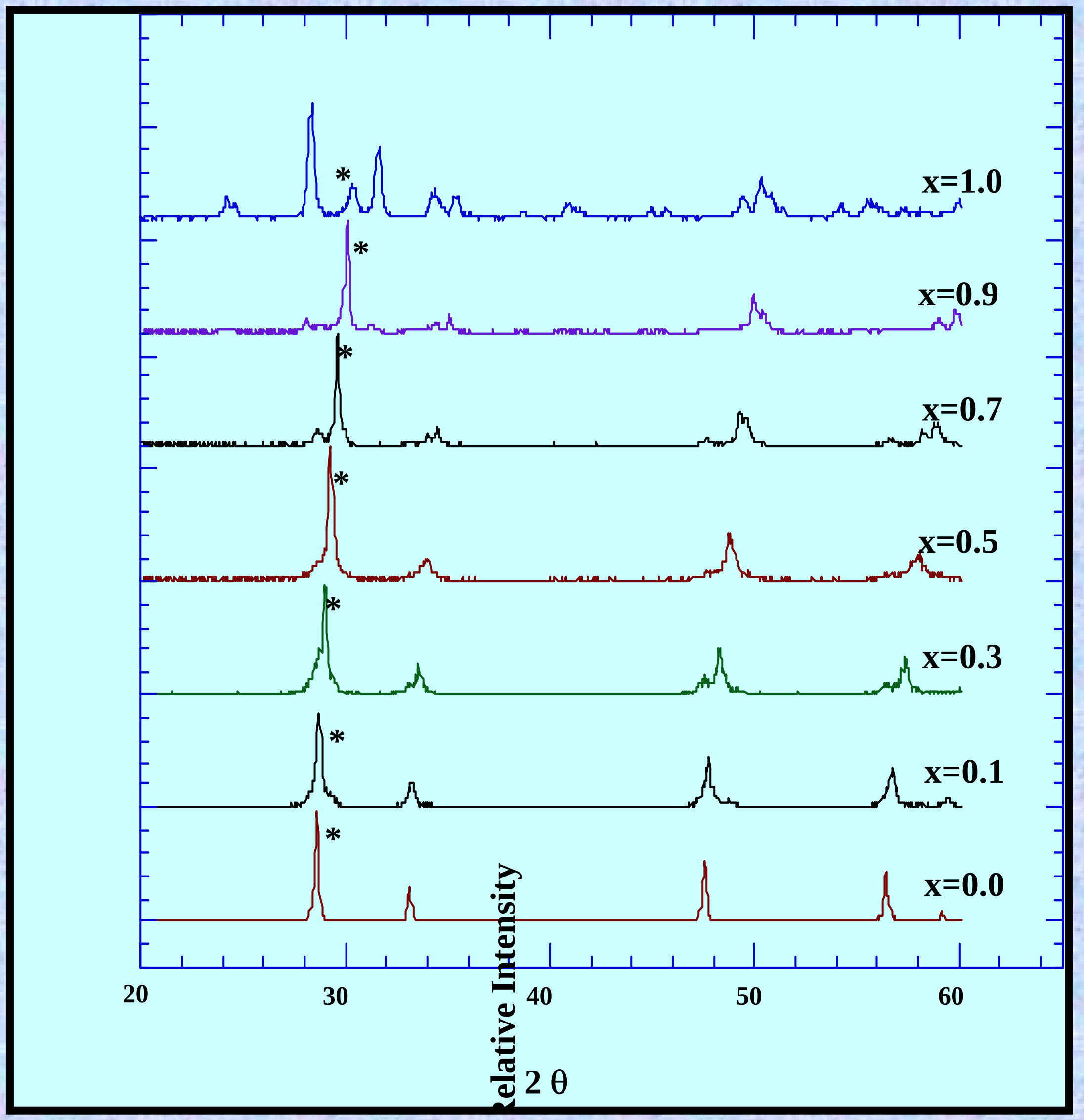
Implications for catalyst support materials



10°C/min 2 h hold

Ce^{3+} addition significantly inhibits surface diffusion and ∴sintering

Ceria/Zirconia Solid Solutions



Selected XRDs

- *100% (111) line for cubic phase
- Note shift as smaller Zr substituted for Ce
  Proof of solid solution
- At x = 0.7, tetragonal
- Φ ≈ 40 nm
- Surface area ≈ 30 m^2/g
- Powders dispersible

Nanostructured Cerium Oxide "Ecocatalysts,"

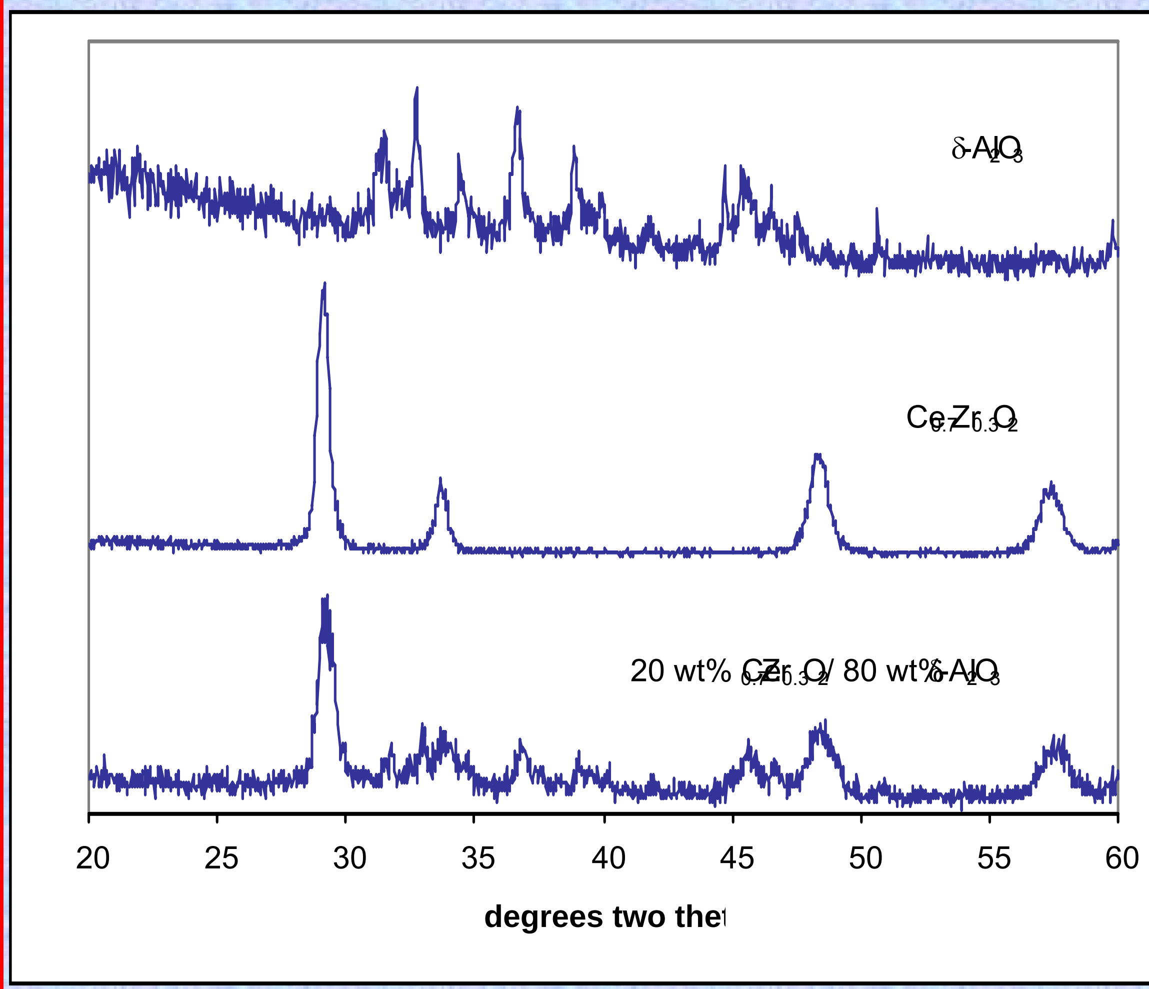
Various techniques can be used to prepare nanocrystalline cerium oxide. For large-scale production, several precipitation and gelation techniques are suitable. Ceria doped with rare-earth oxides or zirconia can be easily prepared by a coprecipitation (CP) method using ammonium carbonate as the precipitant. This involves mixing an **(1)** aqueous solution of cerium(III) nitrate and other metal nitrates in desired proportions with $(NH_4)_2CO_3$ at 60–70°C, keeping a constant pH value of 8, and aging the precipitate at 60–70°C for 1 h. After aging, the precipitate is filtered and washed with **(2 & 3)** distilled water several times, then it is dried at 100–120°C and calcined in air at **(4 & 5)** several hundred degrees Celsius for 10 h at a heating rate of 2°C/min. This method

Easily prepared

- 5 steps shown plus
- Product is 150 m^2/g solid solution
- Annealed at > 500°C to remove micropores gives final SSA of 50 m^2/g
- Product is then ground
- Mixed with sol-gel alumina precursor and coated on TWC monolith
- Then Pd is added
- Total of about 10 steps

M. Flytzani-Stephanopoulos, Mater. Res. Soc. Bulletin, Nov. 2001, pp. 885-9

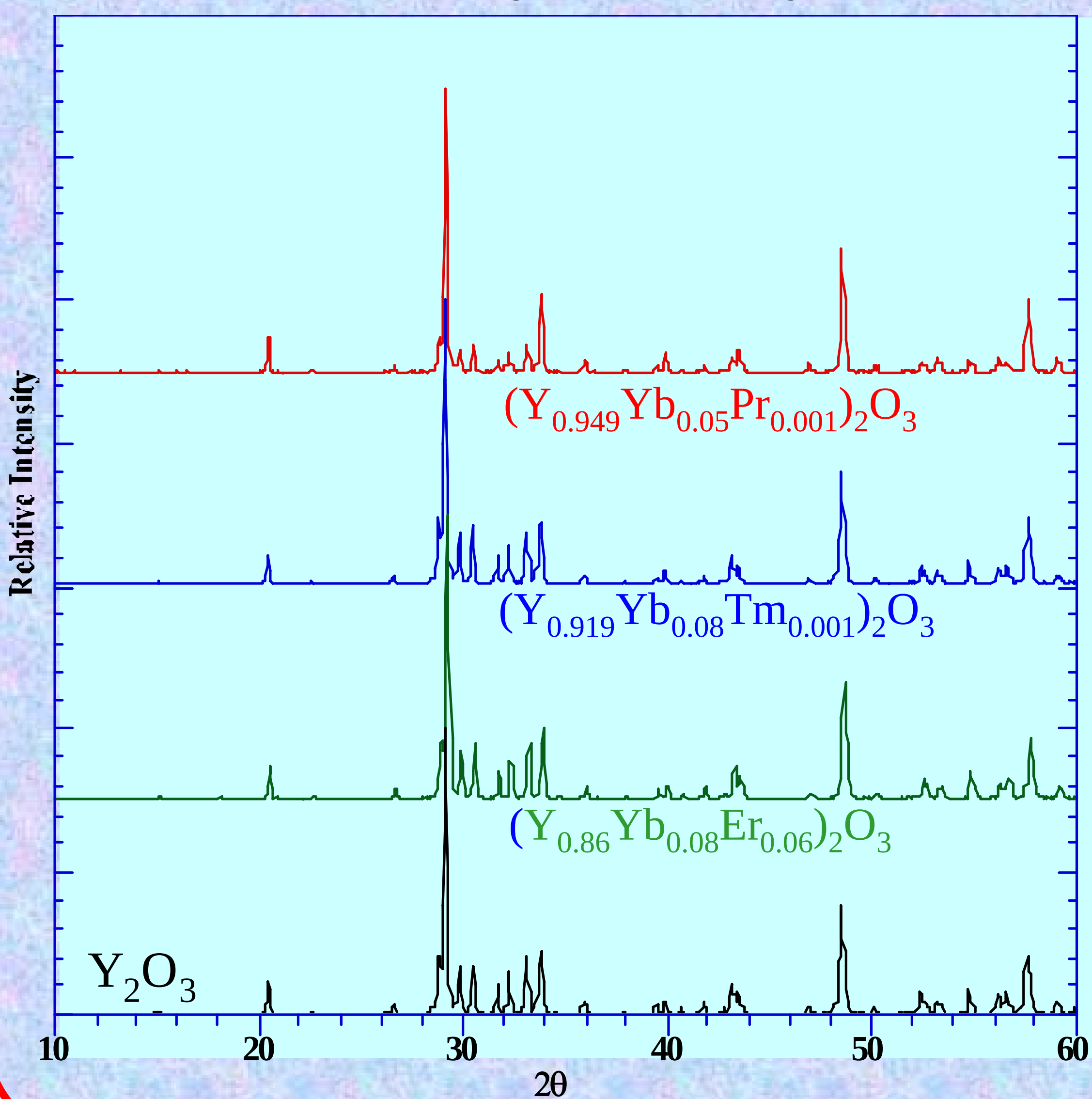
$Ce_{0.7}Zr_{0.3}O_2$ on Al_2O_3



- δ-Al_2O_3 = 60 m^2/g
- $Ce_{0.7}Zr_{0.3}O_2$ = 16 m^2/g
  Now at 30 m^2/g
- 20 wt. % $Ce_{0.7}Zr_{0.3}O_2$:

  80 wt. % δ-Al_2O_3
  30 m^2/g
- IDENTICAL ACTIVITY TO COMMERCIAL TWC WASHCOAT MADE IN > 8 PROCESS STEPS
- Green process

$(Y_{0.999-x-y}Yb_xRE_y)_2O_3$ Solid Solutions



Selected XRDs

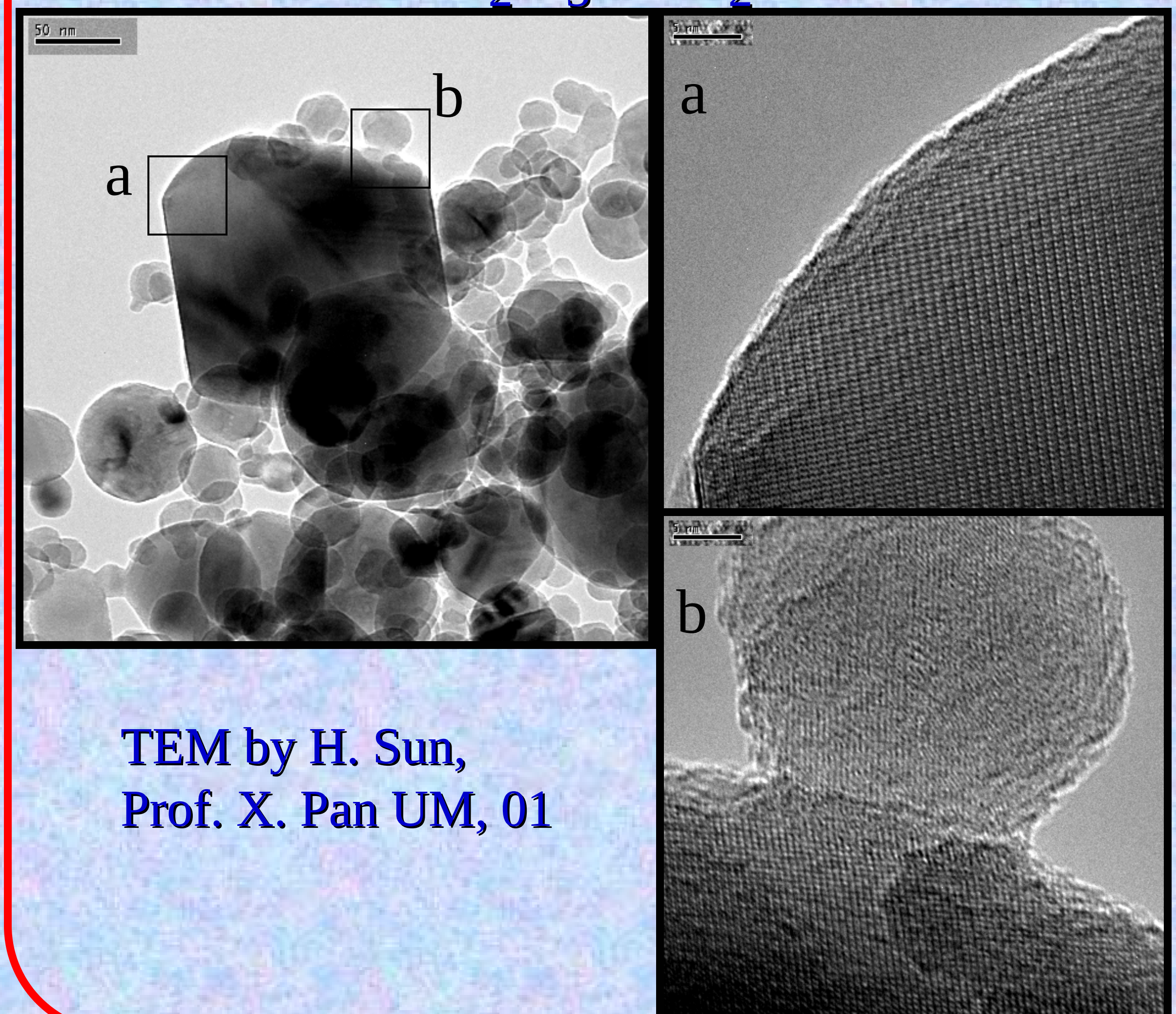
- Cubic + some monoclinic
  Proof of solid solution
- Upconvert 980 nm IR light to red, green, blue
- Orasure.com
  drug bioassays/picogram/g quantities

  No biologicals upconvert
- Taggants for counterfeit deterrence
- Nanomark has embedded them in molten Al

Conquering the Tyranny of Thermodynamics with LF-FSP

Ti:Al Oxide Nanopowders

δ-Al_2O_3:TiO_2 87:13



TEM by H. Sun,
Prof. X. Pan UM, 01

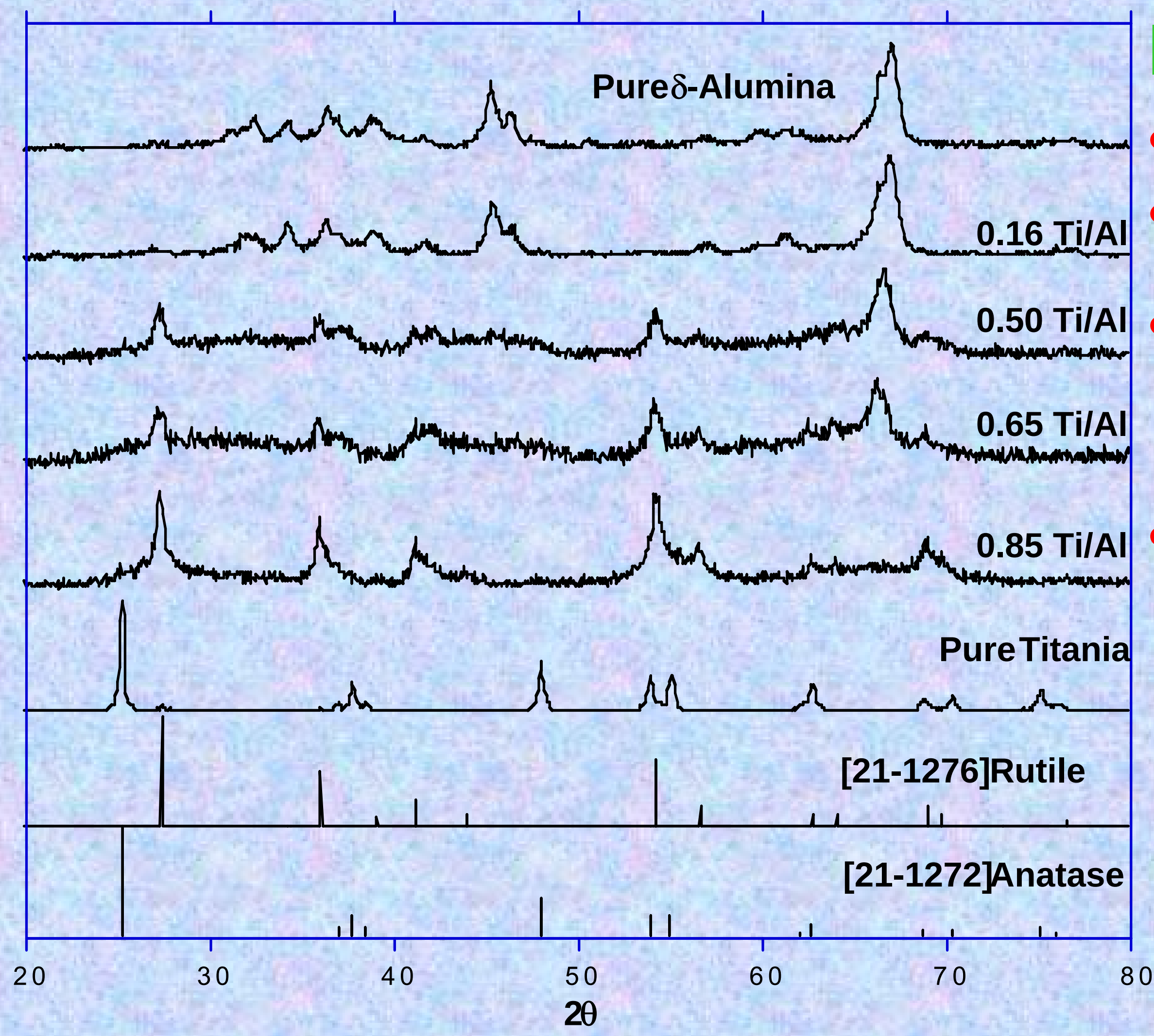
FSP Particles:

- Φ = 90, 50, 15 nm
- δ-alumina XRD
- Disperses like δ-Al_2O_3
- Photoactive catalyst

  Self-disinfecting Self-cleaning surfaces

  Visible light??
- Epoxidation catalysts

Ti:Al Oxide Nanopowders

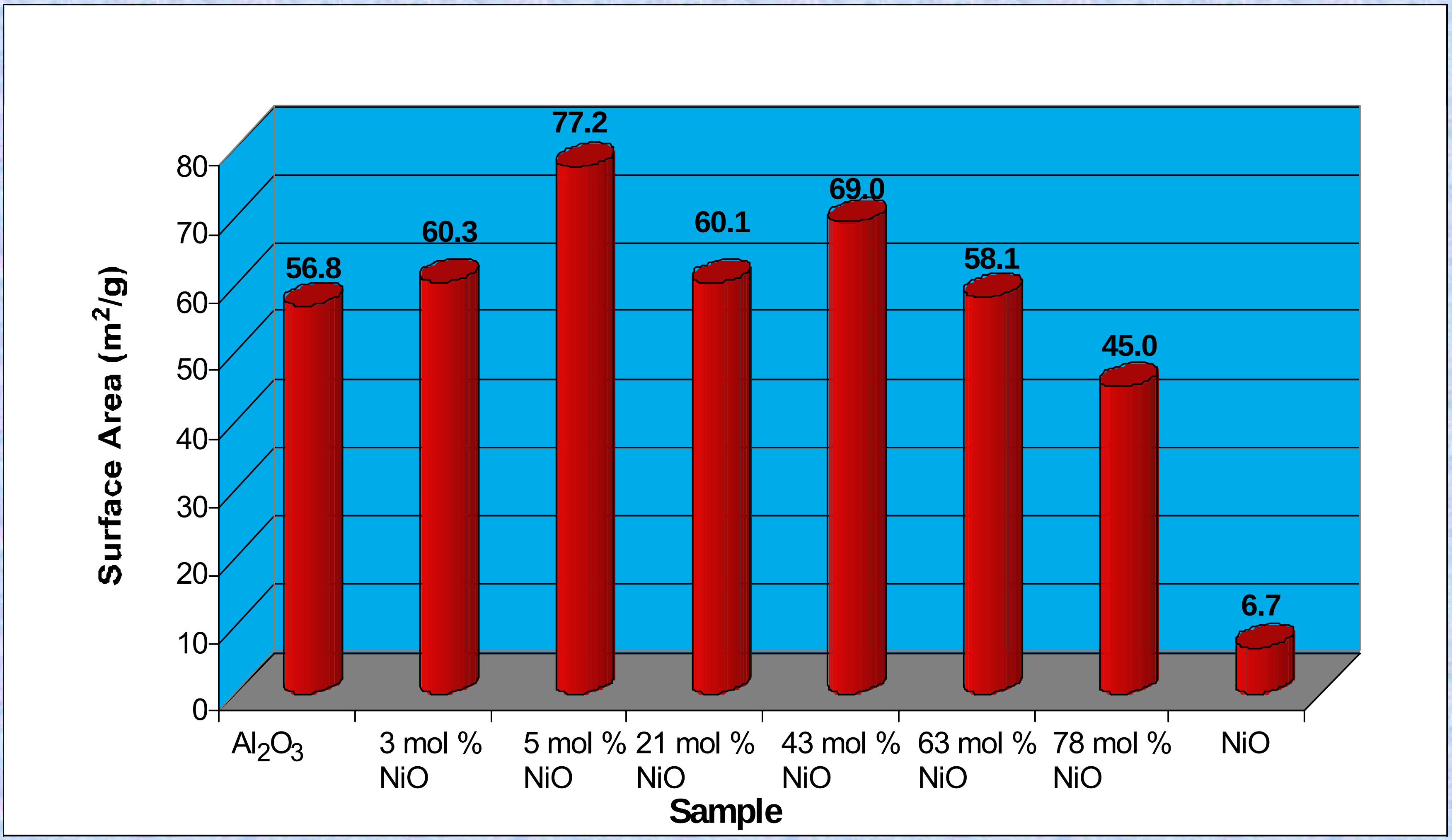


FSP Particles:

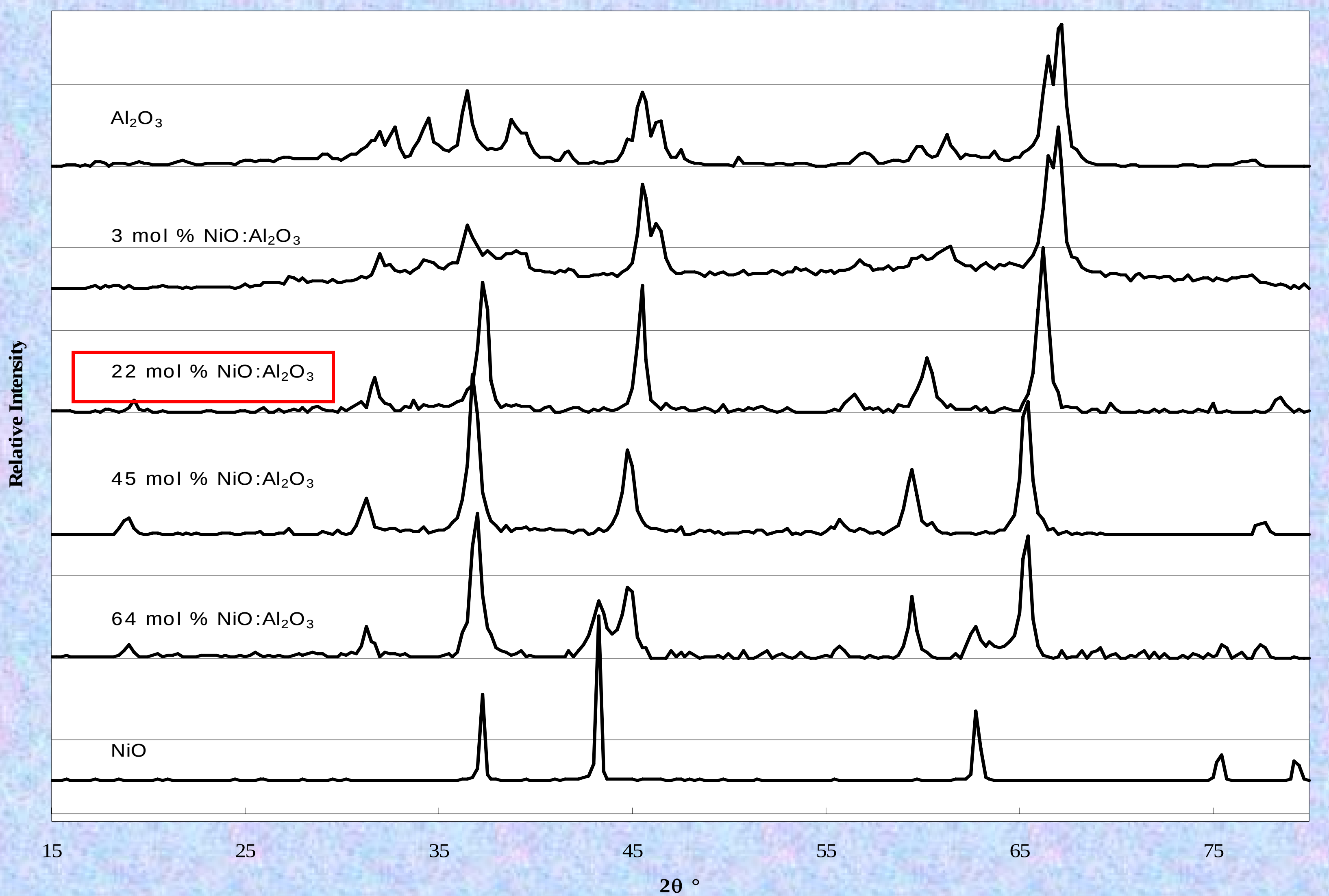
- Φ = 30 nm
- All disperse easily
- Pure TiO_2 90 mol % anatase
- Add 15 wt % Al_2O_3, See only rutile

S. Kim

NiO·Al_2O_3 compositions

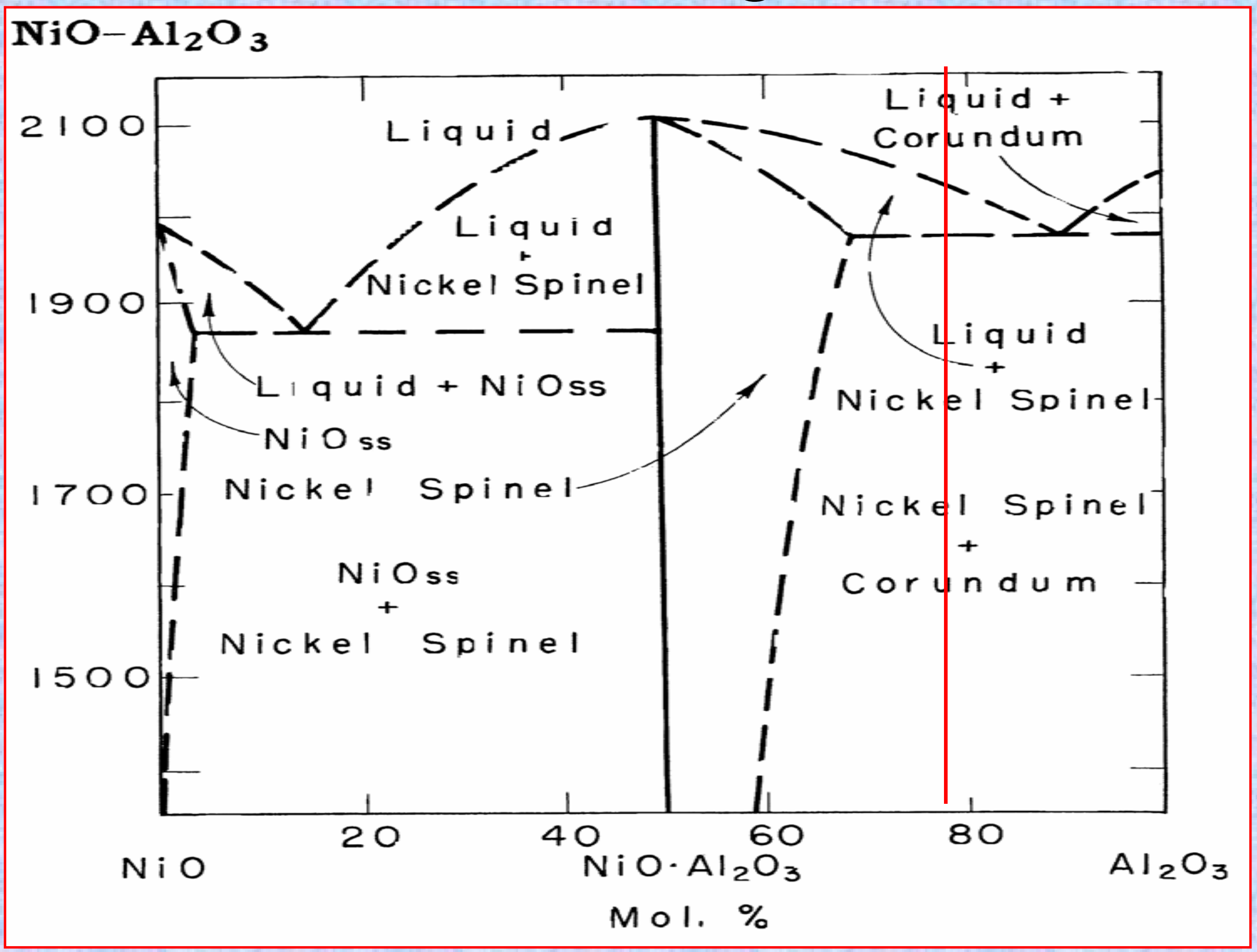


$NiO \cdot Al_2O_3$ compositions

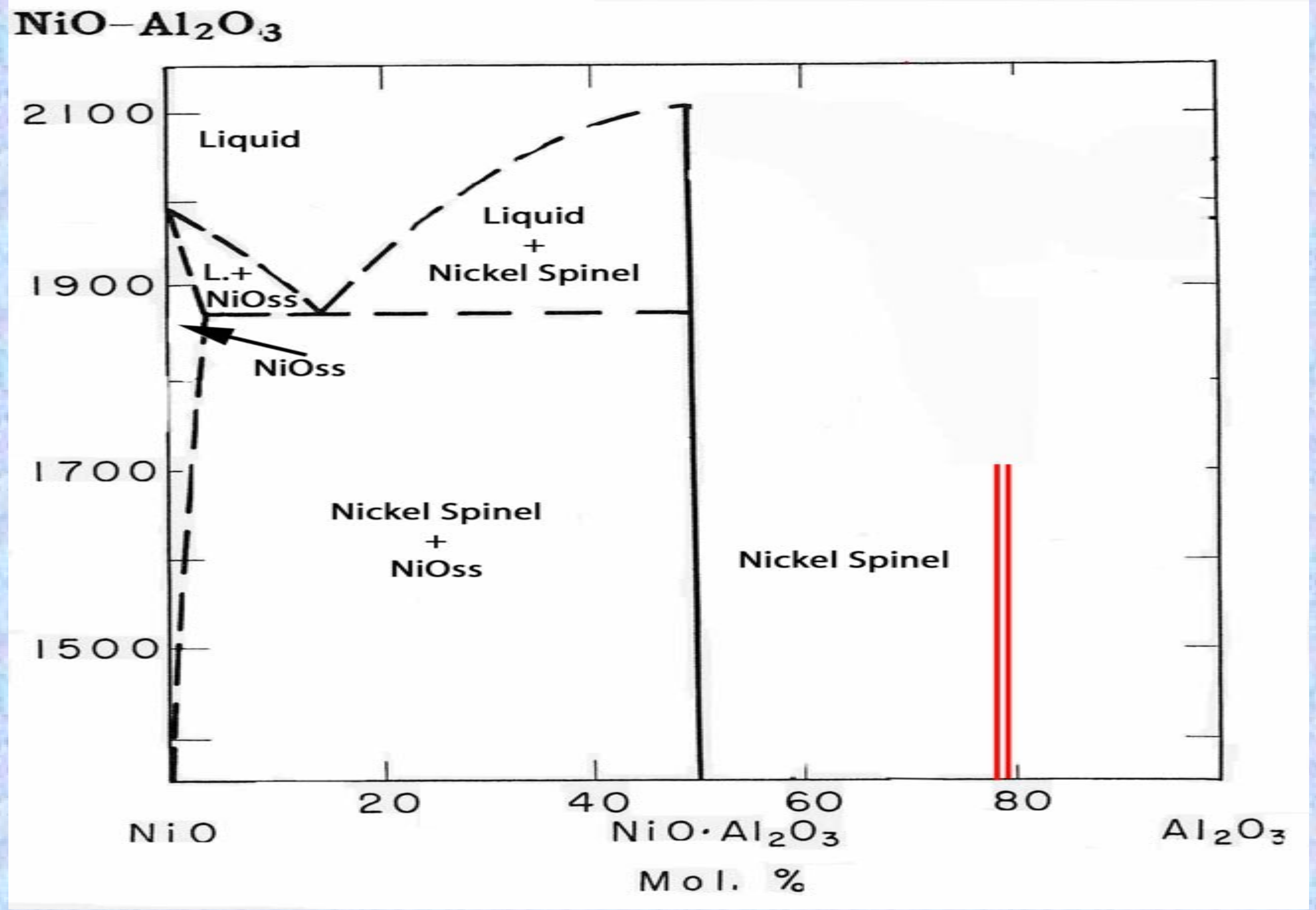


$(Ni^{2+})_{1-x}(Ni^{3+})_x O_{1-x}[]_x Al_2O_3$?

$NiO \cdot Al_2O_3$ Thermodynamic Phase Diagram



NiO·Al_2O_3 Kinetic Phase Diagram

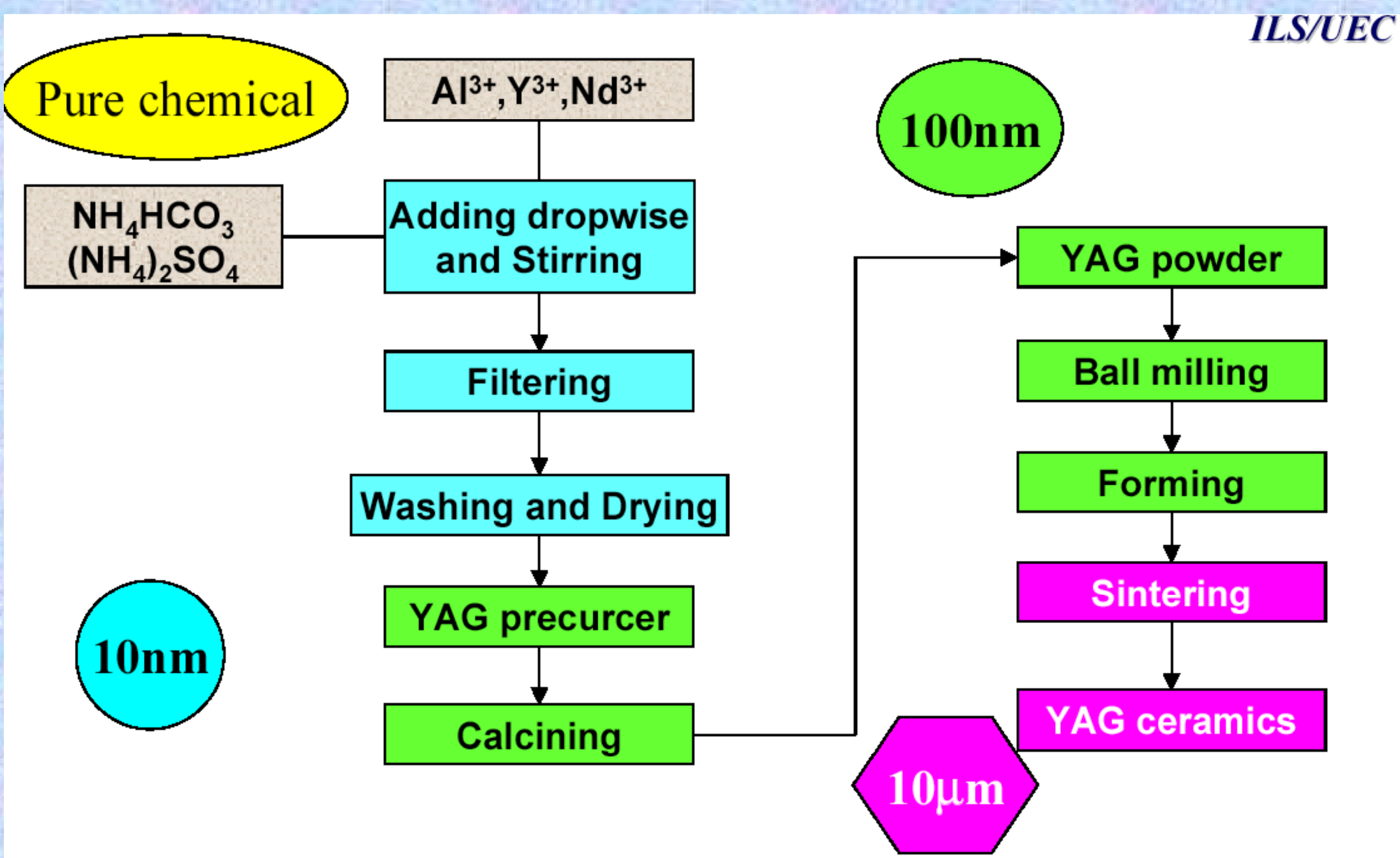


TGA shows phase stable to 1500 °C

Transparent YAG?

K-I. Ueda, "High Power Laser Materials based on Ceramic Materials," CLEO 2002, Long Beach, CA May 20, 2002

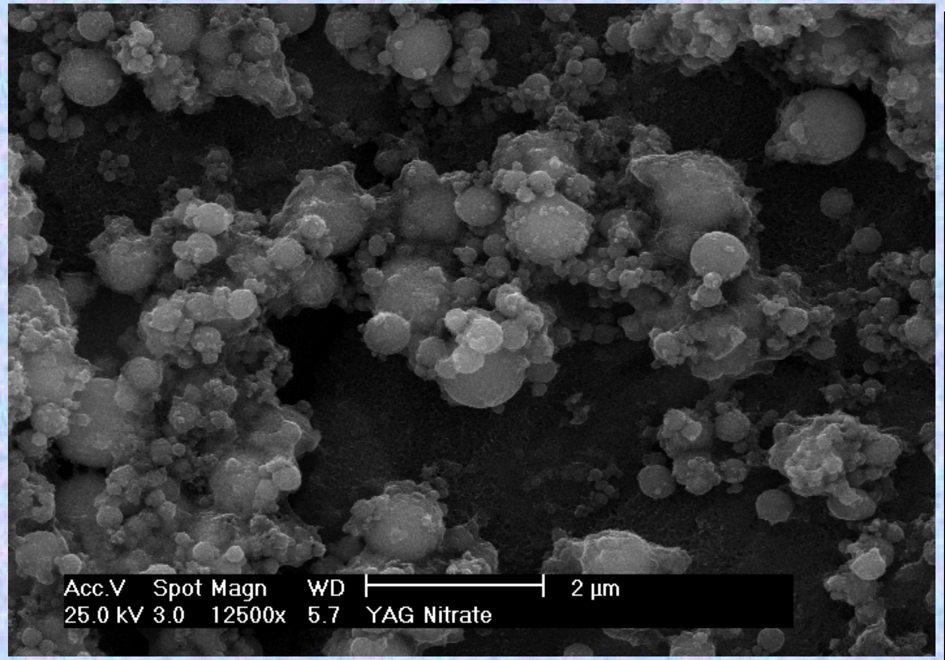
Transparent YAG?



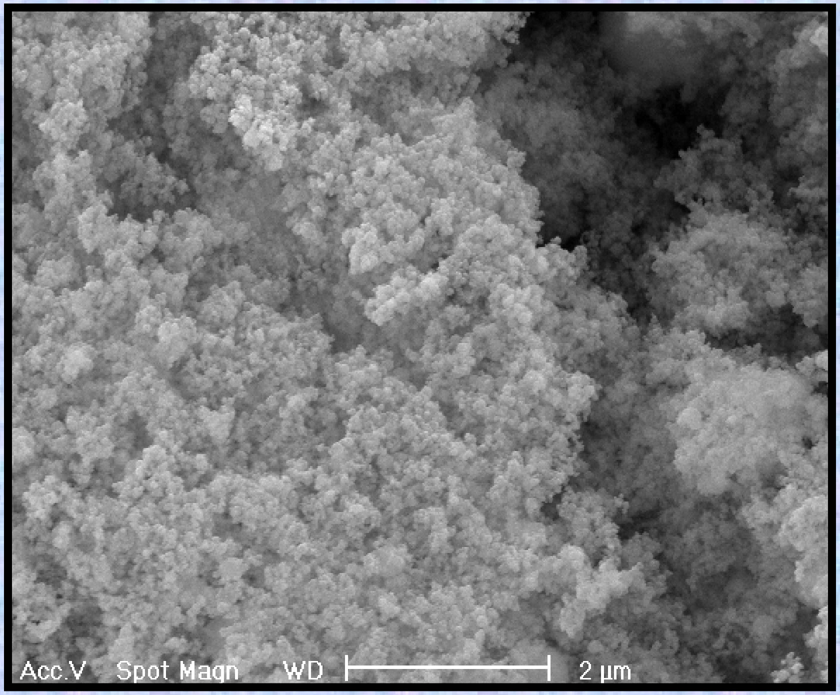
Ueda needs 5 steps to get to 100 nm, 7 steps to compacts!

YAG Composition Nanopowders

Wrong



Right



Y_3/Al_5 Nitrates

Y_3/Al_5 carboxylates

The Art is in the Chemistry

YAG Composition Nanopowders

SEM

- ϕ < 20 BET, SSA ≈ 90 m^2/g
- ϕ = 16 by XRD
- ϕ ≈ 18 lineal analysis
- *New Phase?*
- Still dispersible

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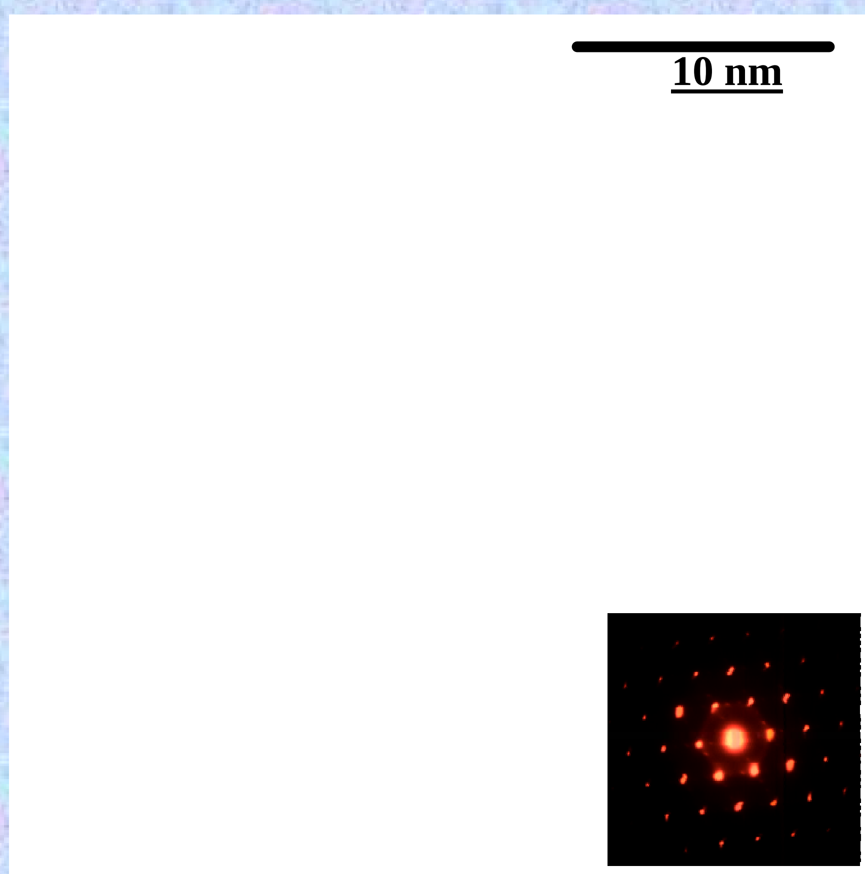
TEM



- Unusual phase formed
- XRD Shows new peak at 8.4 °2Θ

- Transforms to YAG phase with
  - E_a = 100 Kj/mol

- Transparent polycrystalline lasers with Nd^{3+}?

$Y_3Al_5O_{12}$ But Not YAG

Salient Features

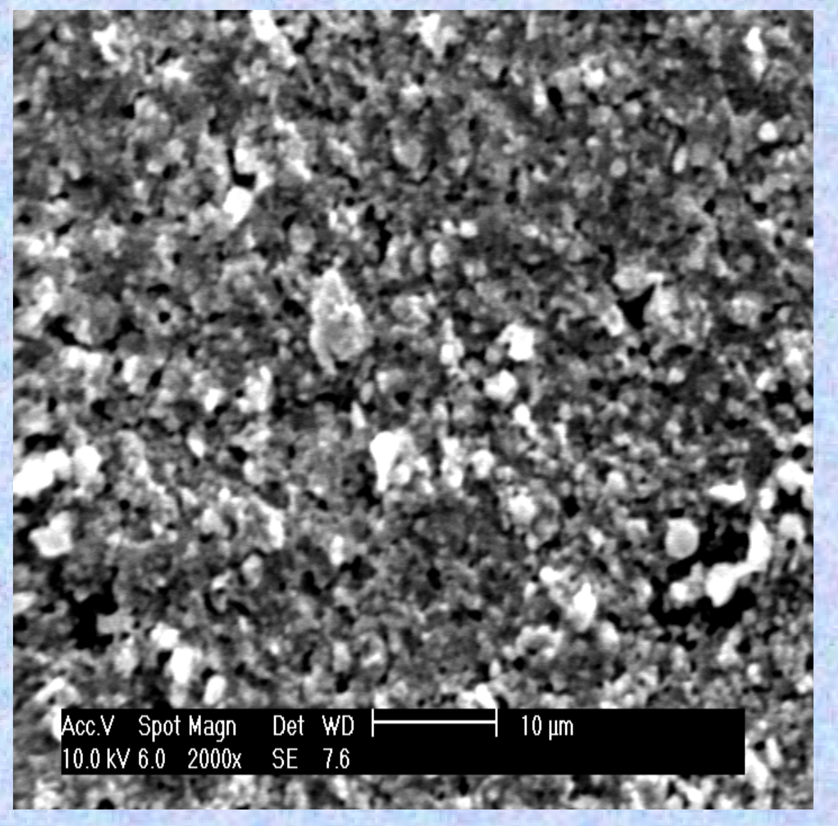
- Same structure as hexagonal $YAlO_4$
- Double cell length

- Red: O^{2-}
- Blue: Al^{3+}
- Grey: Y^{3+}

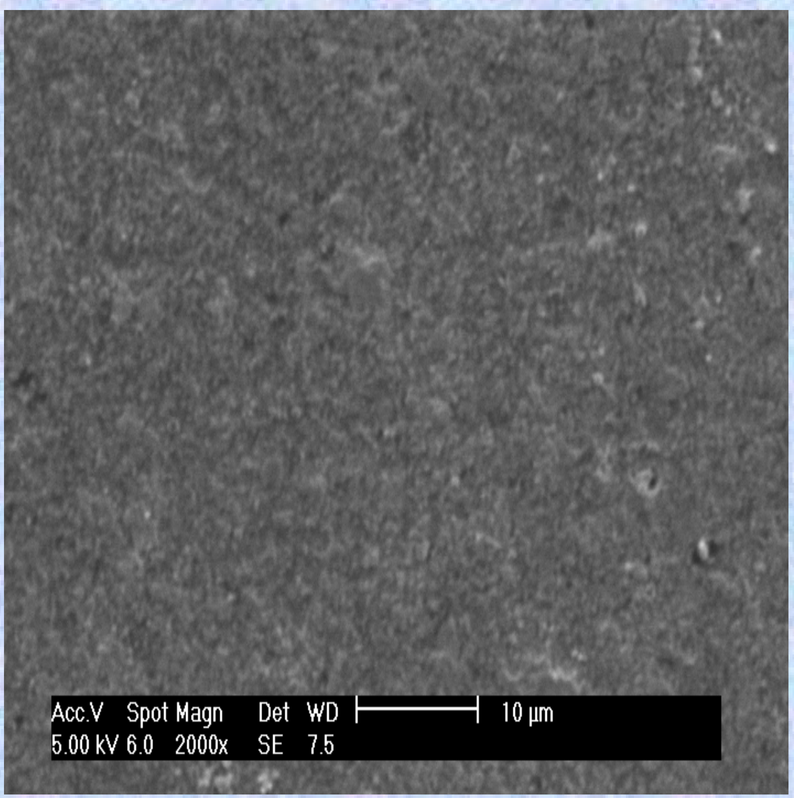
- Denser than YAG!
- New Phase?

Sintering YAG Nanopowders to Full Density

a. 10°C/min 800°C/O_2, 10°C/min 1400°C for 6h,
b. 10°C/min 800°C/O_2, 10°C/min vacuum 1000°C/2h, 10°C/min 1400 for 2 h



a. Cut, polished surface



b. Cut, polished surface

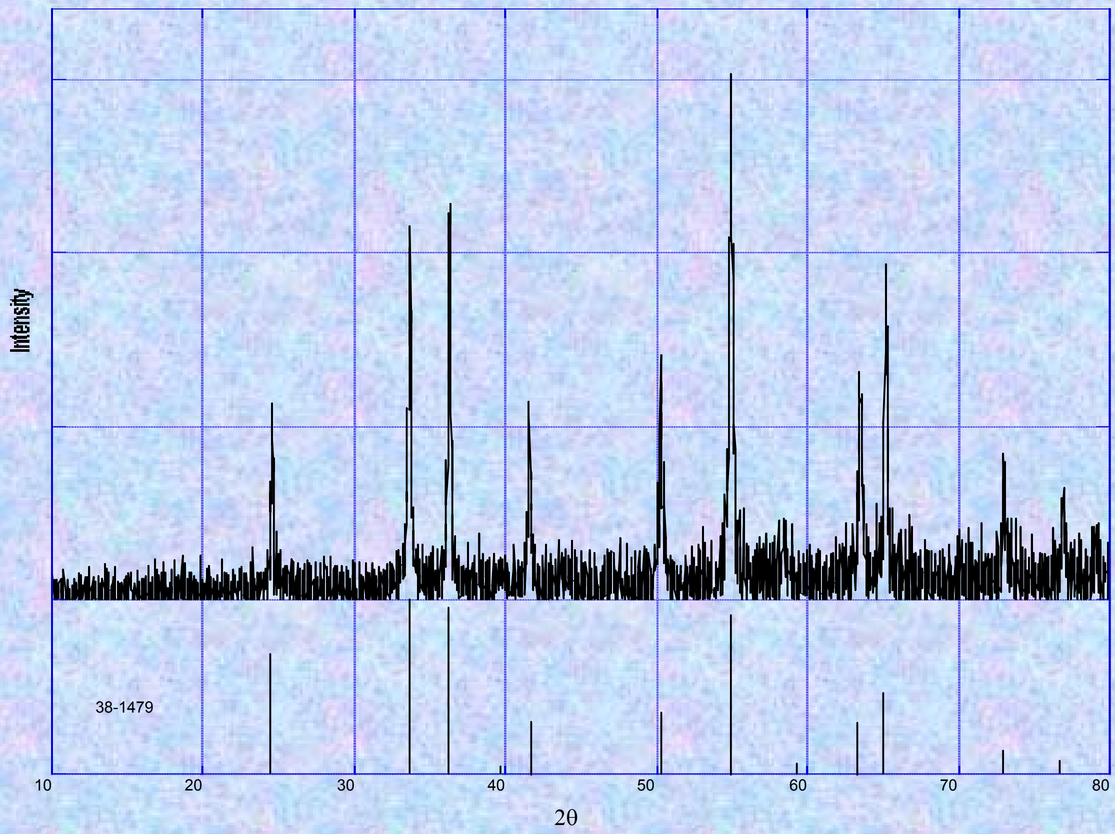
Novel Nano Processing

- LF-FSP with nanoparticle feeds
- Combinations of nanoparticles
- LF-FSP with nanoparticle and precursor feeds

- Why?
  - Coatings
  - Mixed phases
  - Particle nucleated growth

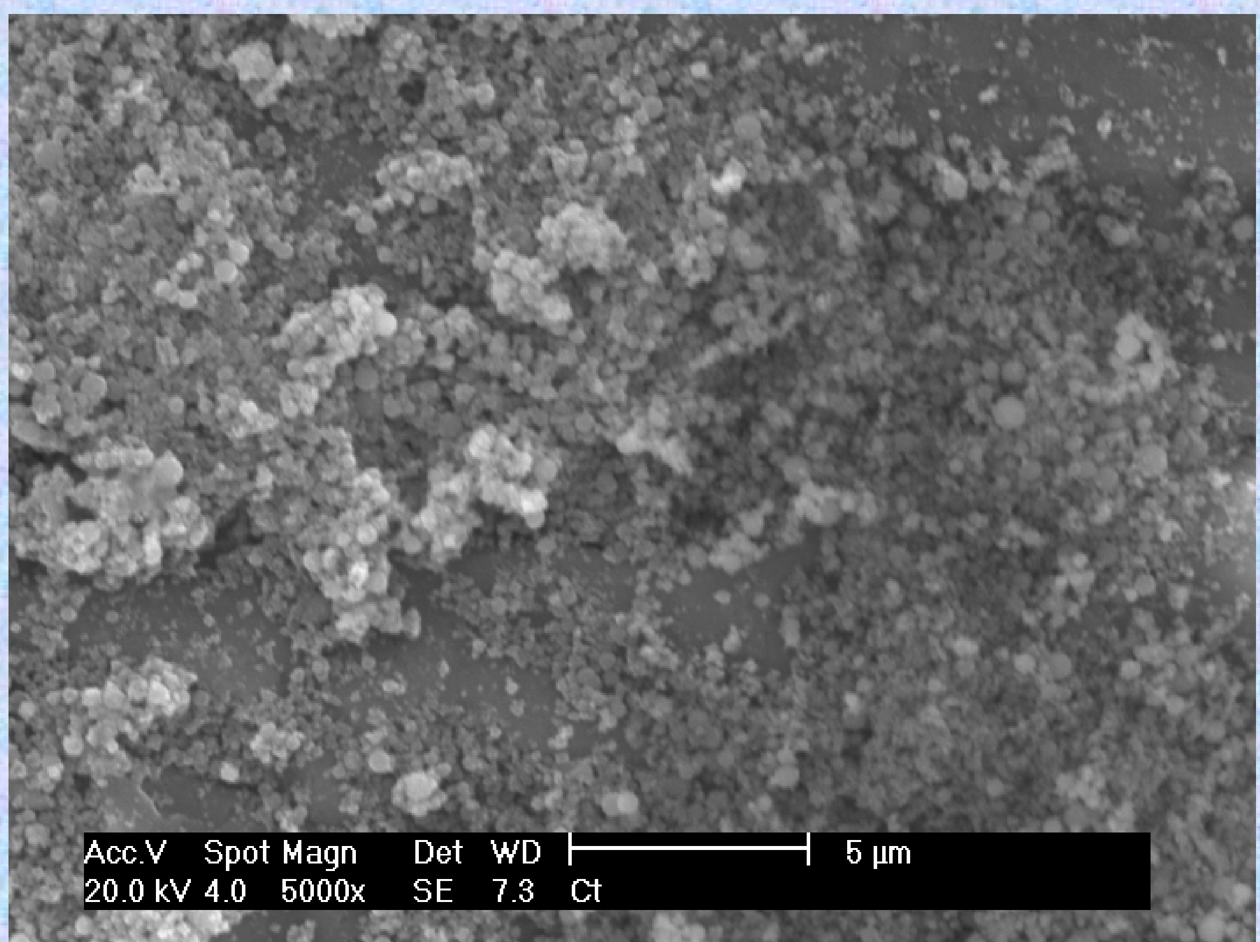
Novel Nano Processing

- LF-FSP with nanoparticle feeds
- Chromia coated alumina
- $Cr(O_2CEt)_3$
- ICDD 38-1479,
  α-phase Green
- Cr_2O_3



Novel Nano Processing

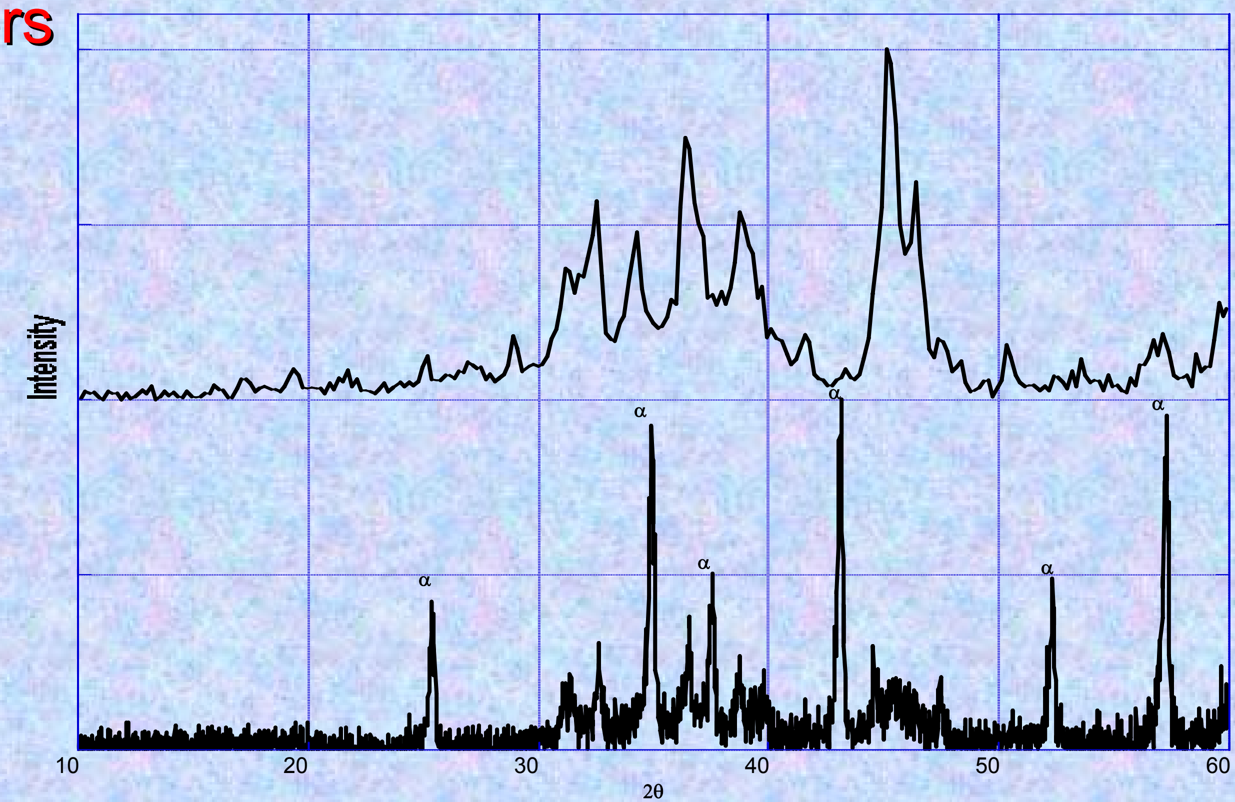
- LF-FSP with nanoparticle feeds
- 8 $Cr(O_2CEt)_3$: 92 δ-Al_2O_3
- $\phi \approx 60$ nm



Novel Nano Processing

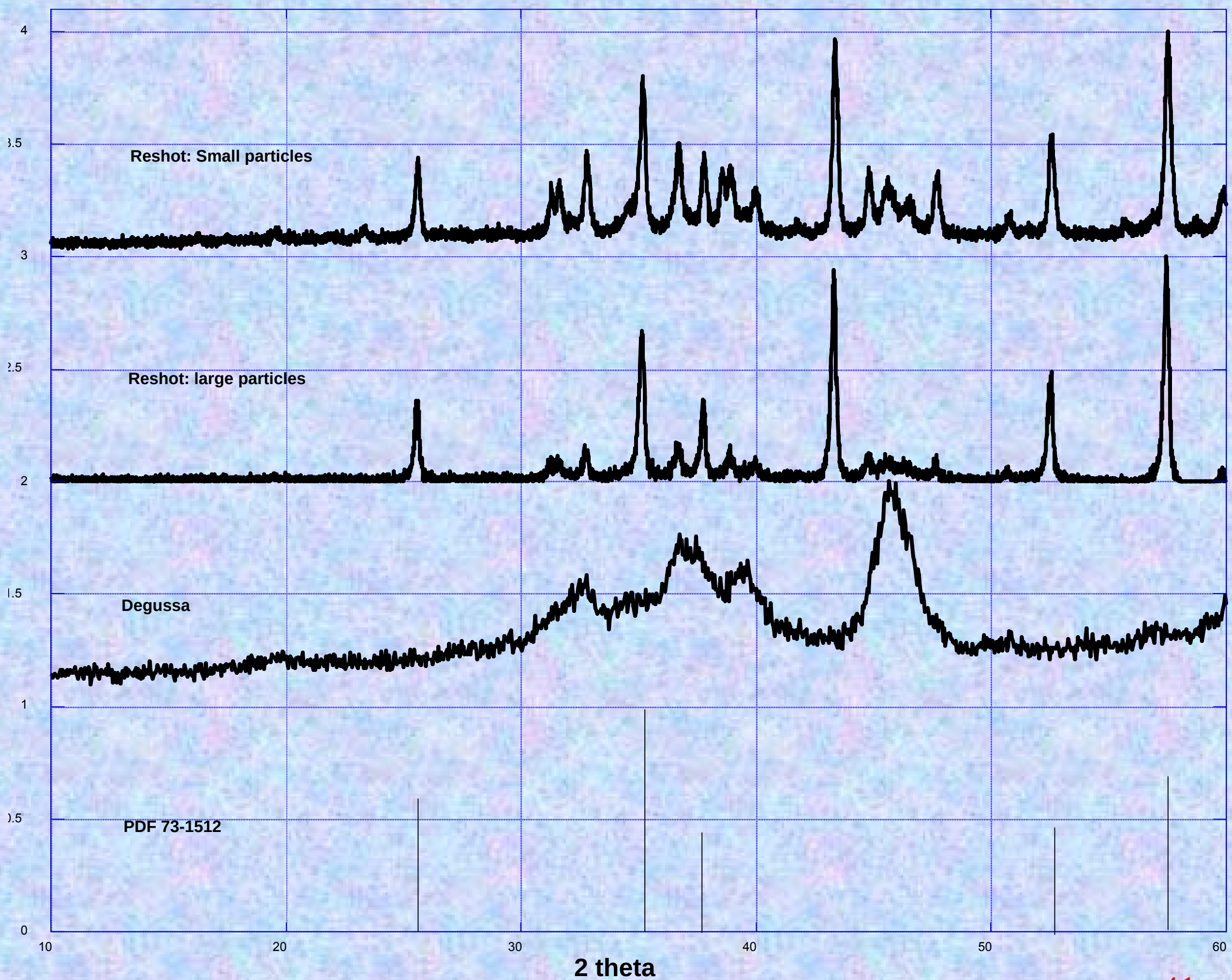
- 8:92 feed
- No chromia in XRD
- Off-white powders
- α-Al_2O_3
- After sonication
- Color red/green
  Cr^{3+}/Cr^{2+}

- It's RUBY



Novel Nano Processing

- α-Al_2O_3 product
- 40-60 nm



Novel Nano Processing

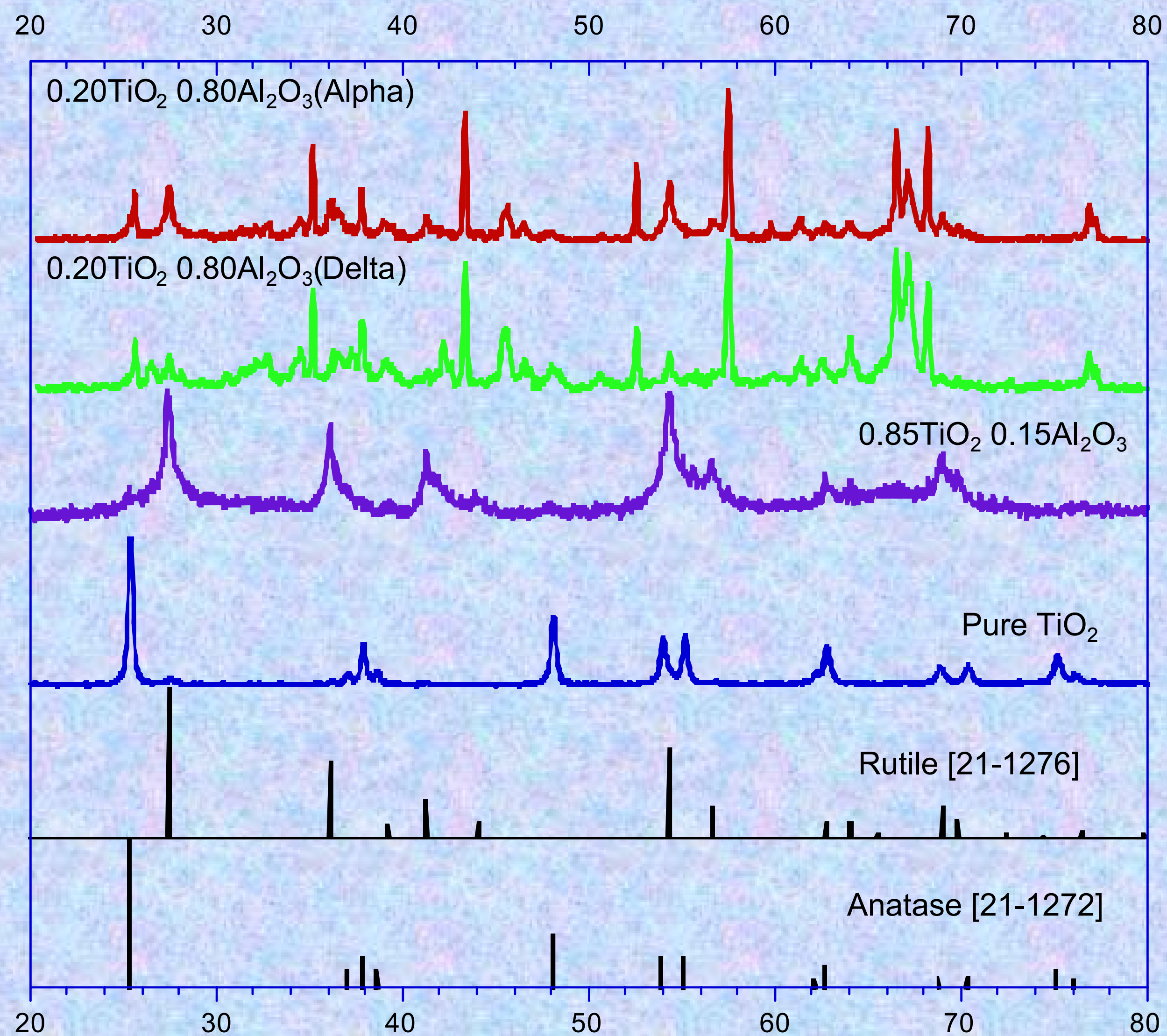
- Pure α-Al_2O_3
- Less water by FTIR

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Novel Nano Processing

- LF-FSP with Nano δ-Al_2O_3 or α-Al_2O_3
- 20 titanatrane: 80 δ-Al_2O_3
- Product depends on substrate

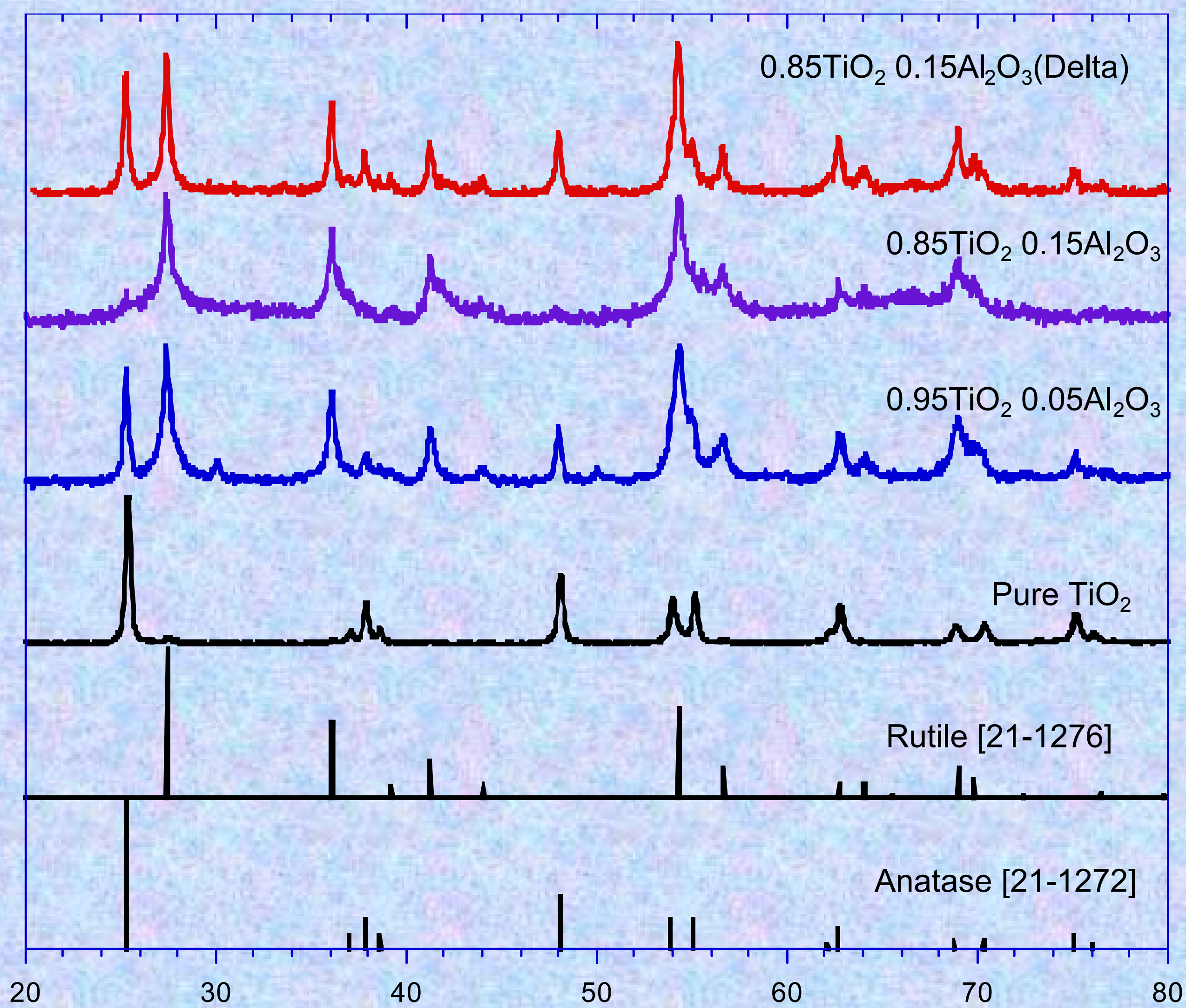
Materials with different band gaps Photocatalysts



Novel Nano Processing

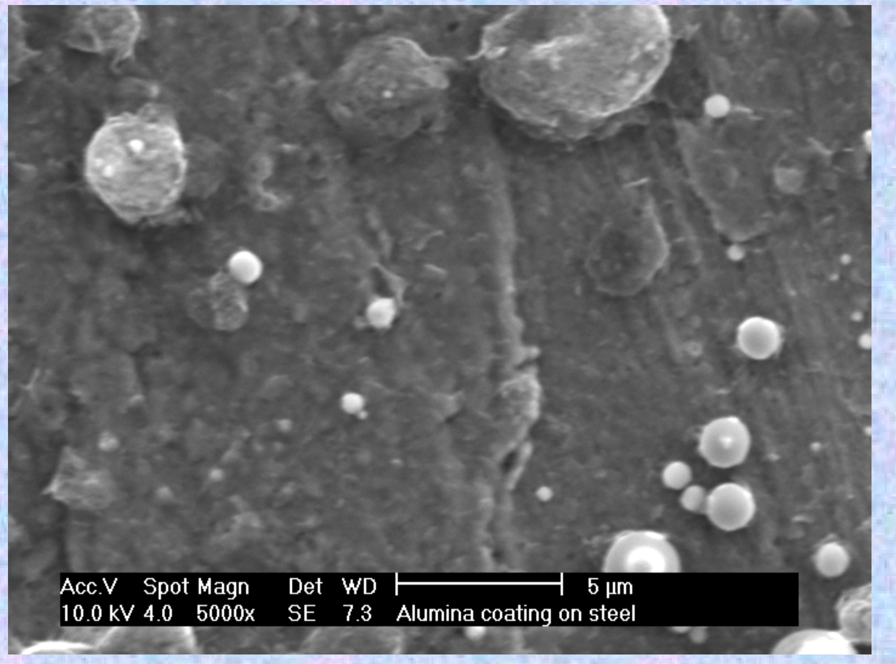
- LF-FSP with Nano δ-Al_2O_3 or α-Al_2O_3
- 85 titanatrane to 15 δ-Al_2O_3
- Get chemically graded coatings

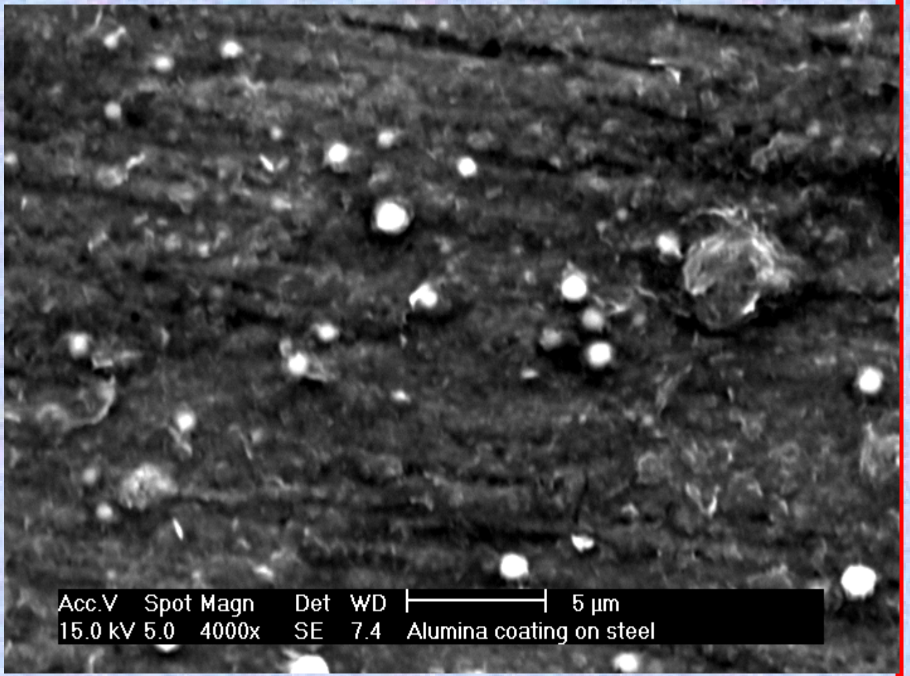
- Novel band gap
- Photocatalysts



Novel Nano Processing

- LF-FSP with Nano δ-Al_2O_3
- Coatings?
- Stainless steel in particle flame





- *Iridescent adherent 1-2 µm* α-Al_2O_3 *coatings*

Novel Nano Processing

- Pure nano α-Al_2O_3
- Abrasives
  - Chemical mechanical polishing
- Transparent ceramics
  - Sodium vapor lamps
  - Ti:Sapphire lasers among other things.
- Coatings
- High strength monoliths
  - Ceramic prosthetics for example
- Catalyst supports that do not sinter
- Catalysts