Synthesis of Nanosize Powders by Molecular Decomposition

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Project Title: A Low-Cost Process for the Synthesis of Nanosize Yttria-Stabilized Zirconia (YSZ) by Molecular Decomposition

Technical Issues Addressed:

1) Synthesis of nanosize, sinterable YSZ powders.
2) Synthesis of highly active, electrode powders.
3) Development of low-cost processes for SOFC materials.

R & D Objectives and Approach

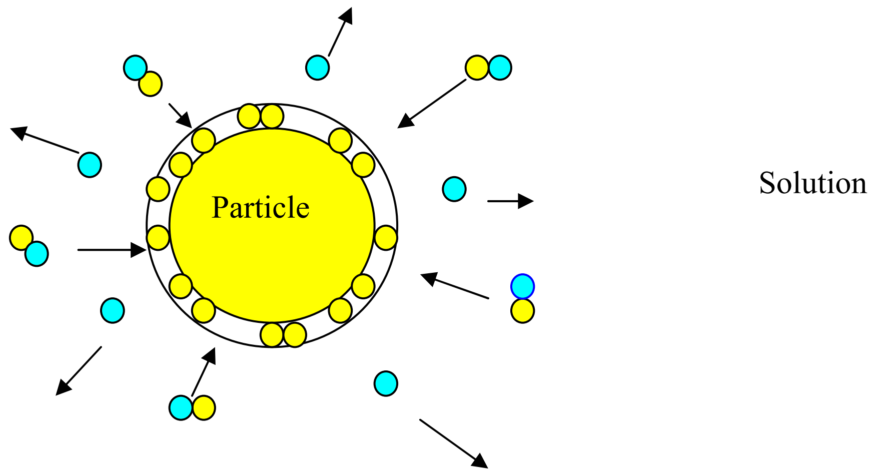
- To synthesize Y-$BaZrO_3$, Y-Na_2ZrO_3, and Y-$CaZrO_3$ starting with commercial grade powders of precursors.
- To synthesize and characterize the nanosize YSZ formed. Characterization includes: (a) Surface area, (b) Particle size, (c) Agglomerate size, and (d) Composition.
- To sinter YSZ discs and bars made from the nanosize YSZ powder, and characterize the sintered samples. Characterization includes: (a) Density, (b) Grain size, and (c) Conductivity.
- To conduct a preliminary design of a process for the synthesis of nanosize YSZ powder.

Results to Date

Introduction

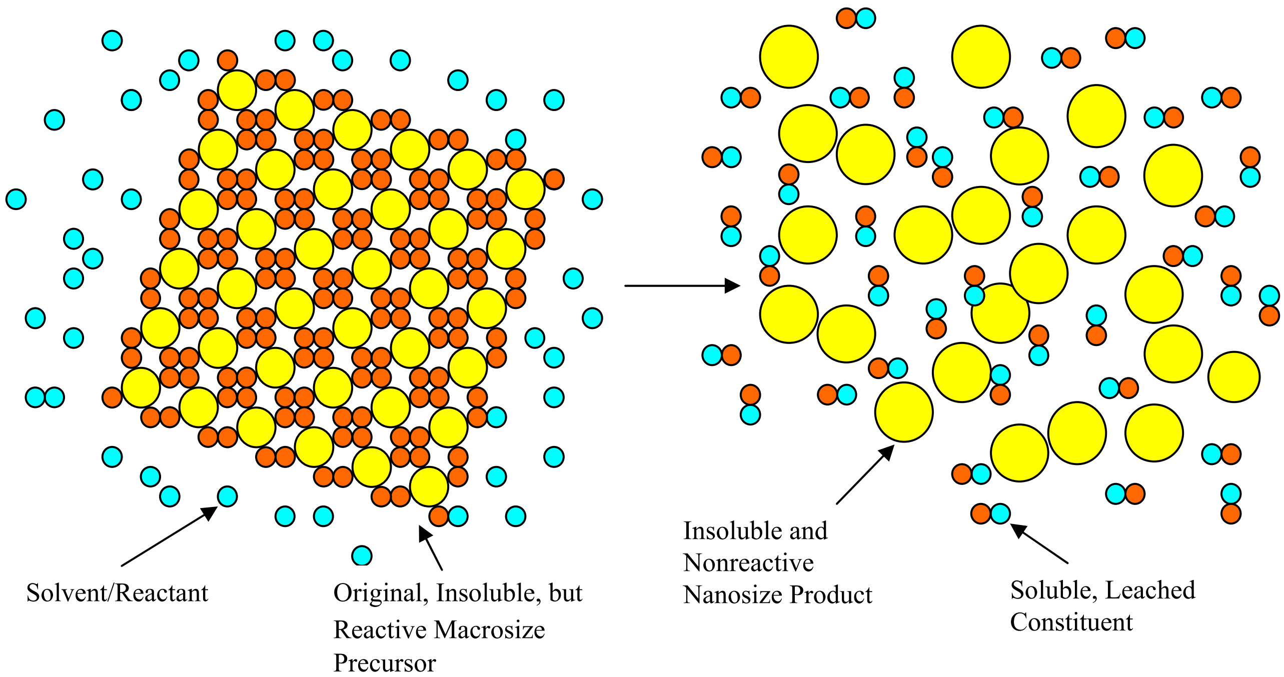
1) Nanosize powders have numerous applications such as electrolyte, catalysts, electrodes, active powders for the fabrication of dense bodies.
2) Synthesis processes include Gas-phase condensation, Chemical precipitation, Sol-gel process, Aerosol spray pyrolysis, Combustion synthesis, etc.
3) Problem with many nanosize synthesis methods: Particle growth is inevitable because of dissolution and re-precipitation process.
4) A new approach for nanosize powder synthesis is based on molecular decomposition.

Conventional, Precipitation-Based Process for Nanosize Powders



Particles precipitate from solution (or the gas phase), and continue to grow. Thus, particle growth is inevitable. Control of process parameters (temperature, pH, time) is necessary to prevent excessive growth.

Synthesis by Molecular Decomposition



Negligible particle coarsening occurs, as neither the precursor, nor the product is soluble in the liquid. Only the precursor reacts with the liquid. Fugitive constituent is leached out.

Advantages of the Process over Conventional Processes

1) Insoluble precursors and products, no dissolution-re-precipitation. Thus, particle coarsening is prevented.

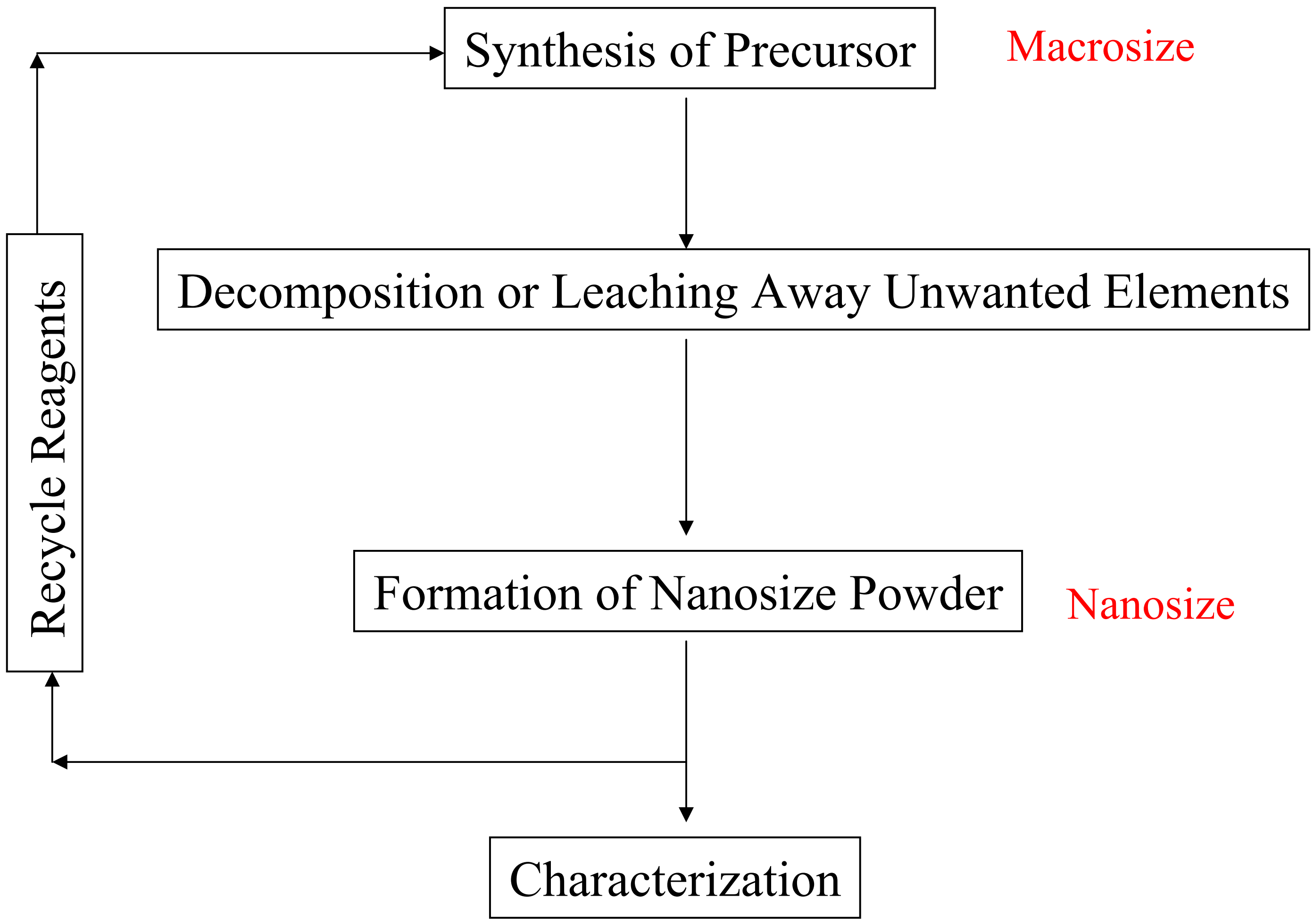
2) Homogeneous powder compositions, containing multiple ions.

3) Neither exotic equipment nor exotic chemistry required.

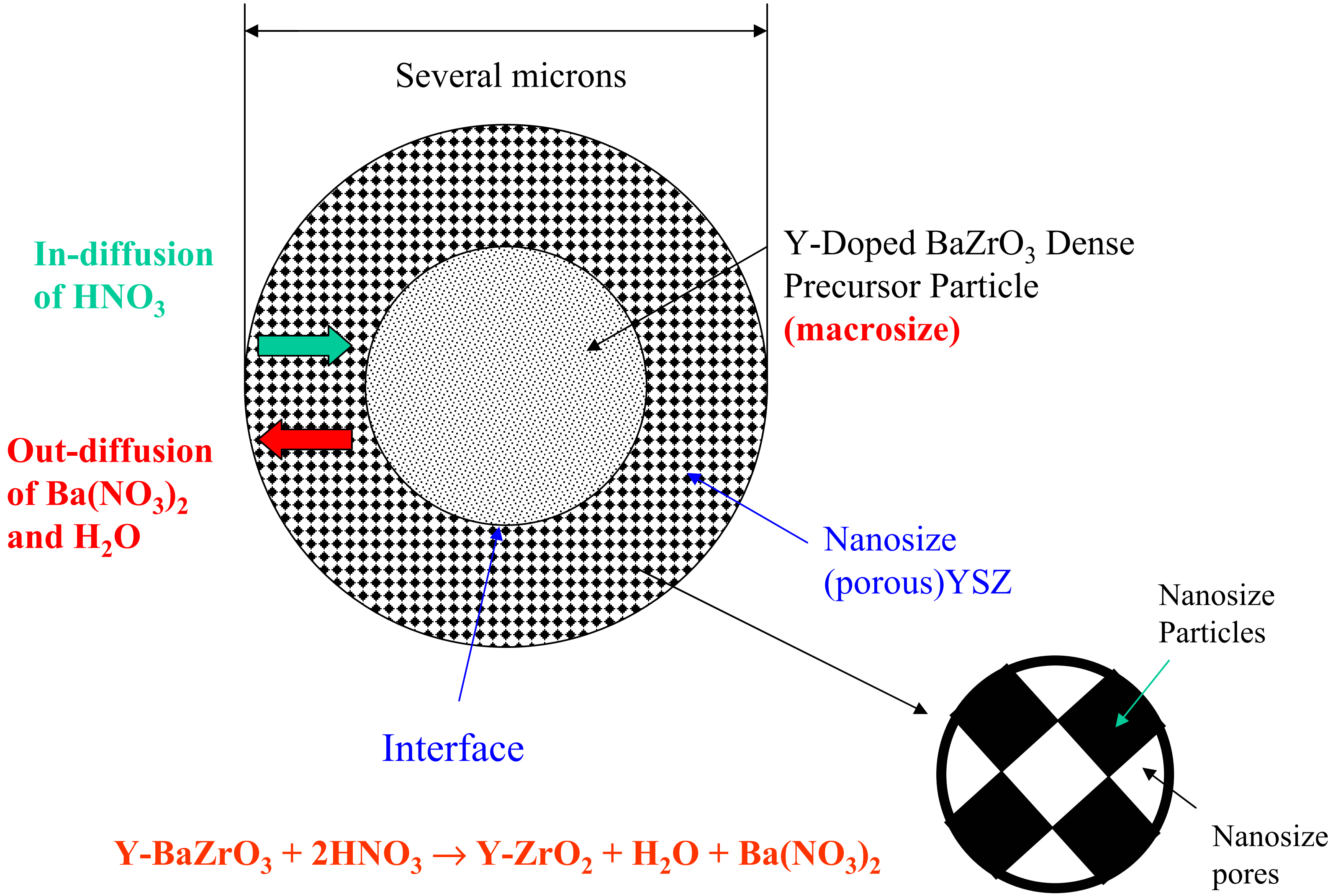
4) Ease of scale up production.

5) Reagent can be recycled – cost implications.

Procedure for the Synthesis of Nanosize Powders



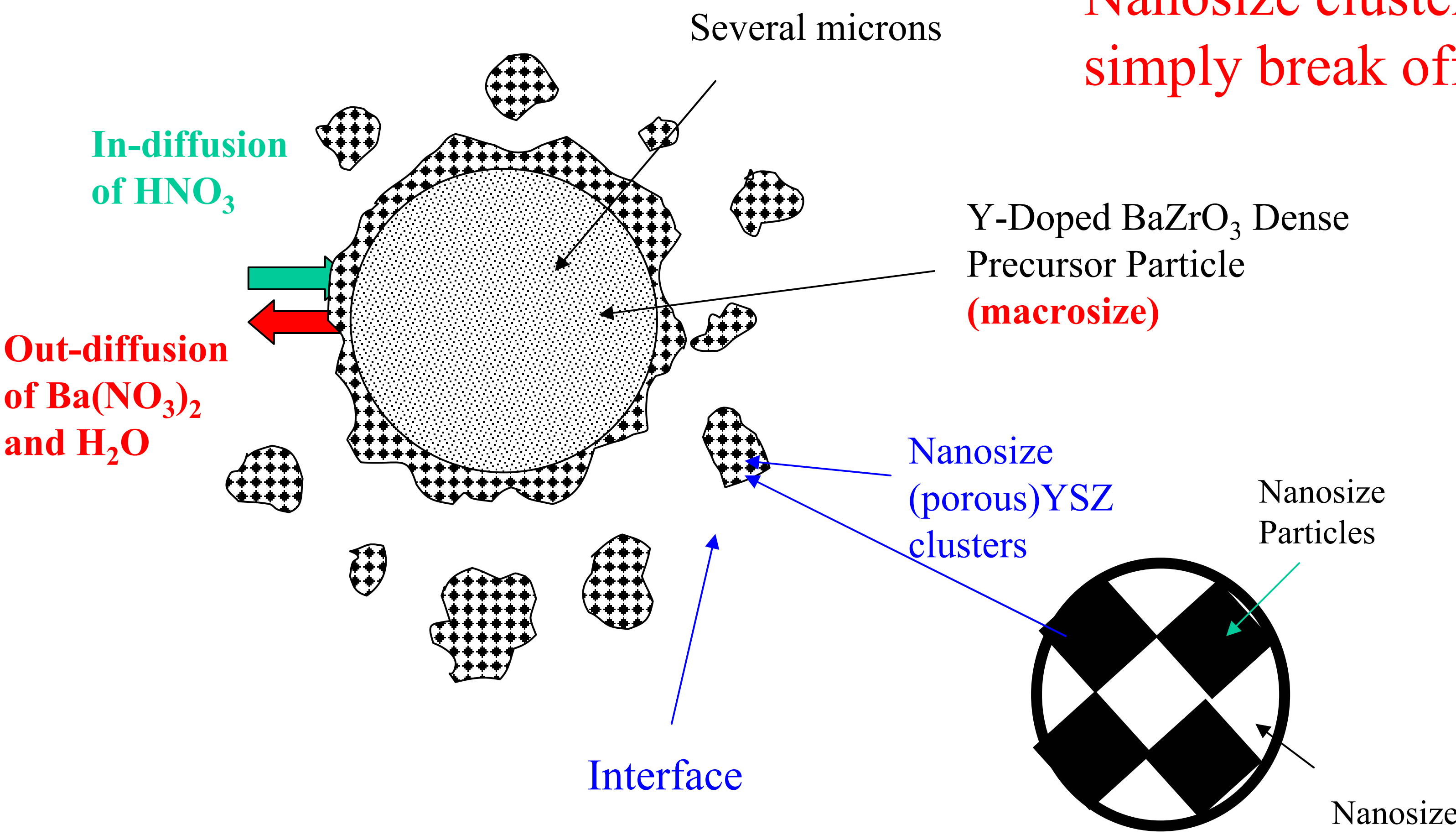
Mechanism of Nanosize Powder Formation



$$Y\text{-}BaZrO_3 + 2HNO_3 \rightarrow Y\text{-}ZrO_2 + H_2O + Ba(NO_3)_2$$

Mechanism of Nanosize Powder Formation

Nanosize clusters may simply break off



$$Y\text{-}BaZrO_3 + 2HNO_3 \rightarrow Y\text{-}ZrO_2 + H_2O + Ba(NO_3)_2$$

Thermodynamic and Kinetic Considerations

1) The precursor must not dissolve in the liquid, but must react with it.
2) The product must not dissolve in the liquid, and must not react with the liquid.
3) The fugitive compound must be soluble in the liquid.
4) There must be large volume change (decrease) for the reaction precursor → product.
5) Transport of the leaching agent in the liquid and the fugitive compound formed must be sufficiently rapid.

Some Examples

Precursor | Liquid Reagent | Product

1) $BaZrO_3$ (reacts with HNO_3, negligible solubility in HNO_3); ZrO_2 (does not readily react with HNO_3, negligible solubility in HNO_3); $BaNO_3$ (soluble in water).
2) $BaCeO_3$ (reacts with H_2O, negligible solubility in H_2O); CeO_2 (does not react with H_2O, negligible solubility in H_2O); $Ba(OH)_2$ (has some solubility in H_2O).
3) Ba_2TiO_4 (reacts with H_2O, negligible solubility in H_2O); $BaTiO_3$ (does not react with H_2O, negligible solubility in H_2O); $Ba(OH)_2$ (has some solubility in H_2O).
4) $BaTiO_3$ (reacts with HNO_3, negligible solubility in HNO_3); TiO_2 (does not react with HNO_3, small solubility in HNO_3); $Ba(NO_3)_2$ (soluble in water).

Some Reactions and Thermodynamics

- $Ba_2TiO_4 + H_2O \rightarrow$ n-$BaTiO_3 + Ba(OH)_2$
  ΔG^o = - 61.9 kJ/mol. at 25°C. Thus, $BaTiO_3$ can form.

- $BaTiO_3 + H_2O \rightarrow$ n-$TiO_2 + Ba(OH)_2$
  ΔG^o = + 60.3 kJ/mol. at 25°C. Thus, TiO_2 should not form.

- $BaTiO_3 + 2HNO_3 \rightarrow$ n-$TiO_2 + Ba(NO_3)_2 + H_2O$
  ΔG^o = -202.7 kJ/mol. at 25°C. Thus, TiO_2 can form.

- Y-$BaZrO_3 + 2HNO_3 \rightarrow$ n-Y-$ZrO_2 + Ba(NO_3)_2 + H_2O$
  ΔG^o = -258.6 kJ/mol. at 25°C. Thus, Y-ZrO_2 can form

Volume Change

Volume change for $BaZrO_3 \rightarrow ZrO_2$

$$\frac{(73.72 - 33.93)}{73.72} \times 100 \approx 54\%$$

That is, a volume decrease of over 54%.

Precursors for Doped Materials

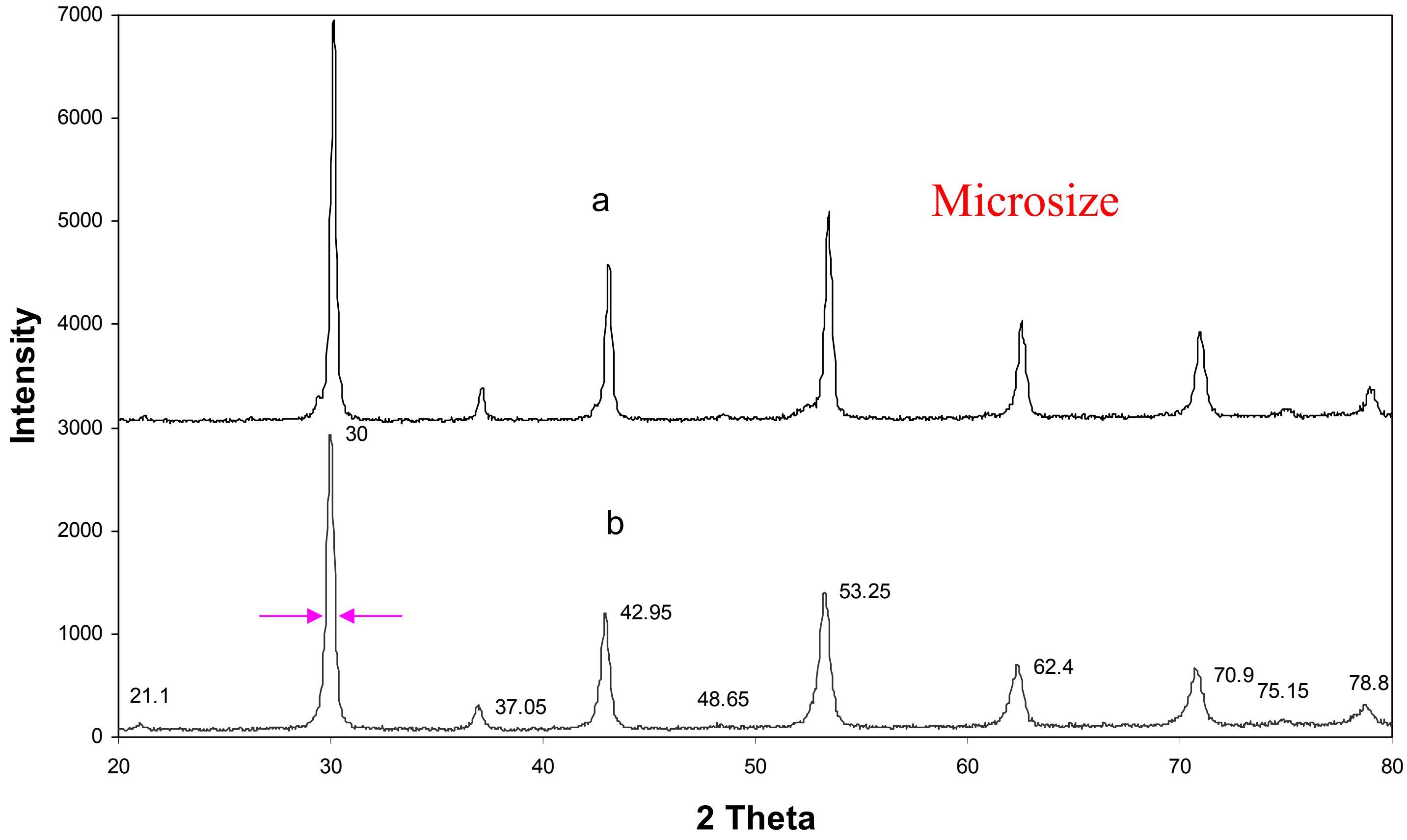
For Y_2O_3-stabilized ZrO_2, $Y_xZr_{(1-x)}O_{(2-\delta)}$ (YSZ):
Precursors are: $BaY_xZr_{(1-x)}O_{(3-\delta)}$
$Na_2Y_xZr_{(1-x)}O_{(3-\delta)}$

For Gd-doped CeO_2 (GDC):
Precursor is: $Gd_xCe_{(1-x)}O_{(3-\delta)}$

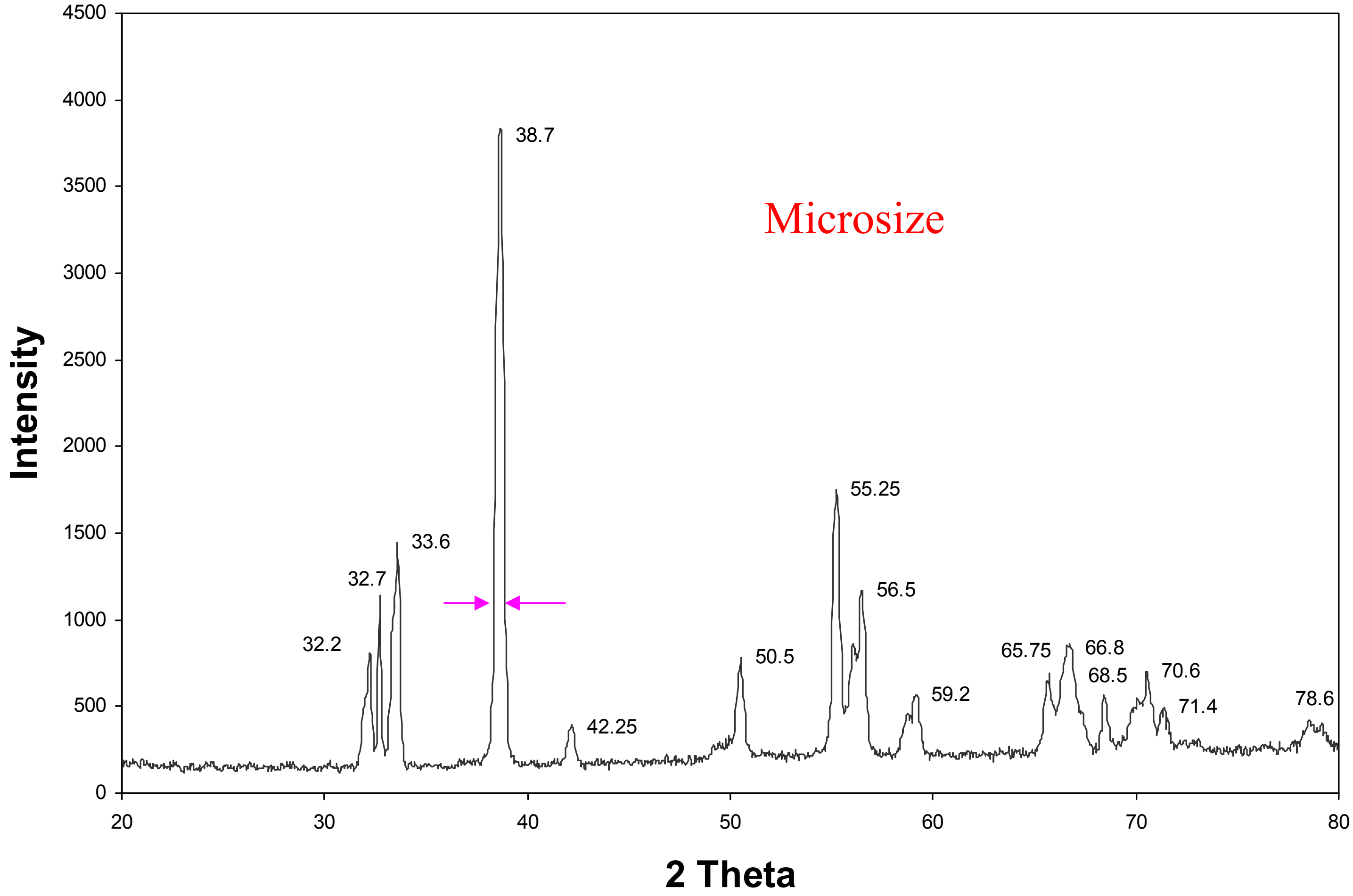
Precursors, Leaching Agents, and Nanosize Products Synthesized

Precursor	Leaching Agent	Nanosize Product
$BaZrO_3$ (Y-doped)	HNO_3	Y-ZrO_2
$BaCeO_3$ (Rare RE earth doped)	H_2O	RE-CeO_2
Y-Na_2ZrO_3	H_2O	Y-ZrO_2
$MgTiO_3$	HNO_3	TiO_2
Ba_2TiO_4	H_2O	$BaTiO_3$
$BaTiO_3$	HNO_3	TiO_2

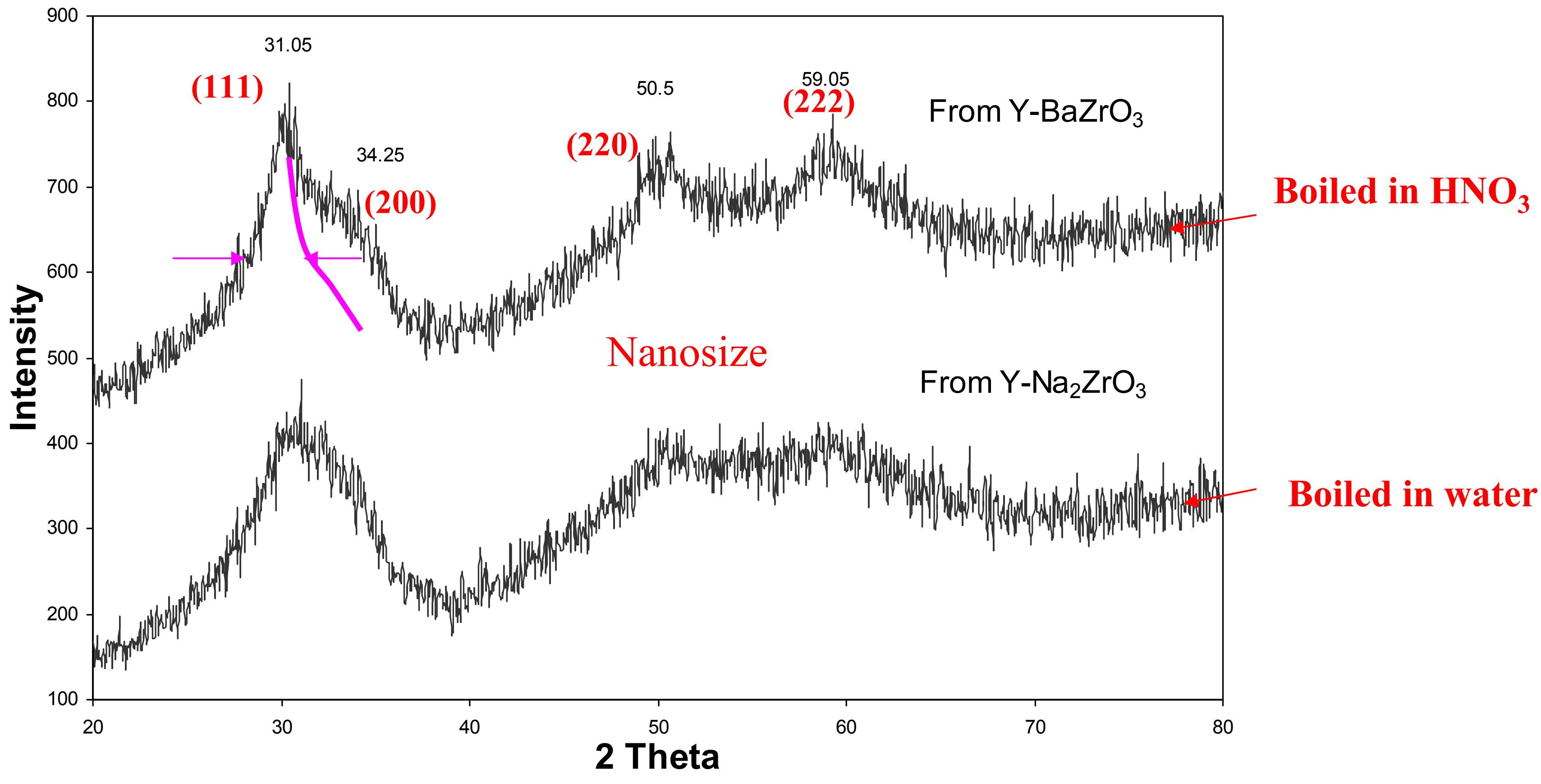
X-ray Diffraction Patterns of Y-$BaZrO_3$ Microsize Precursor



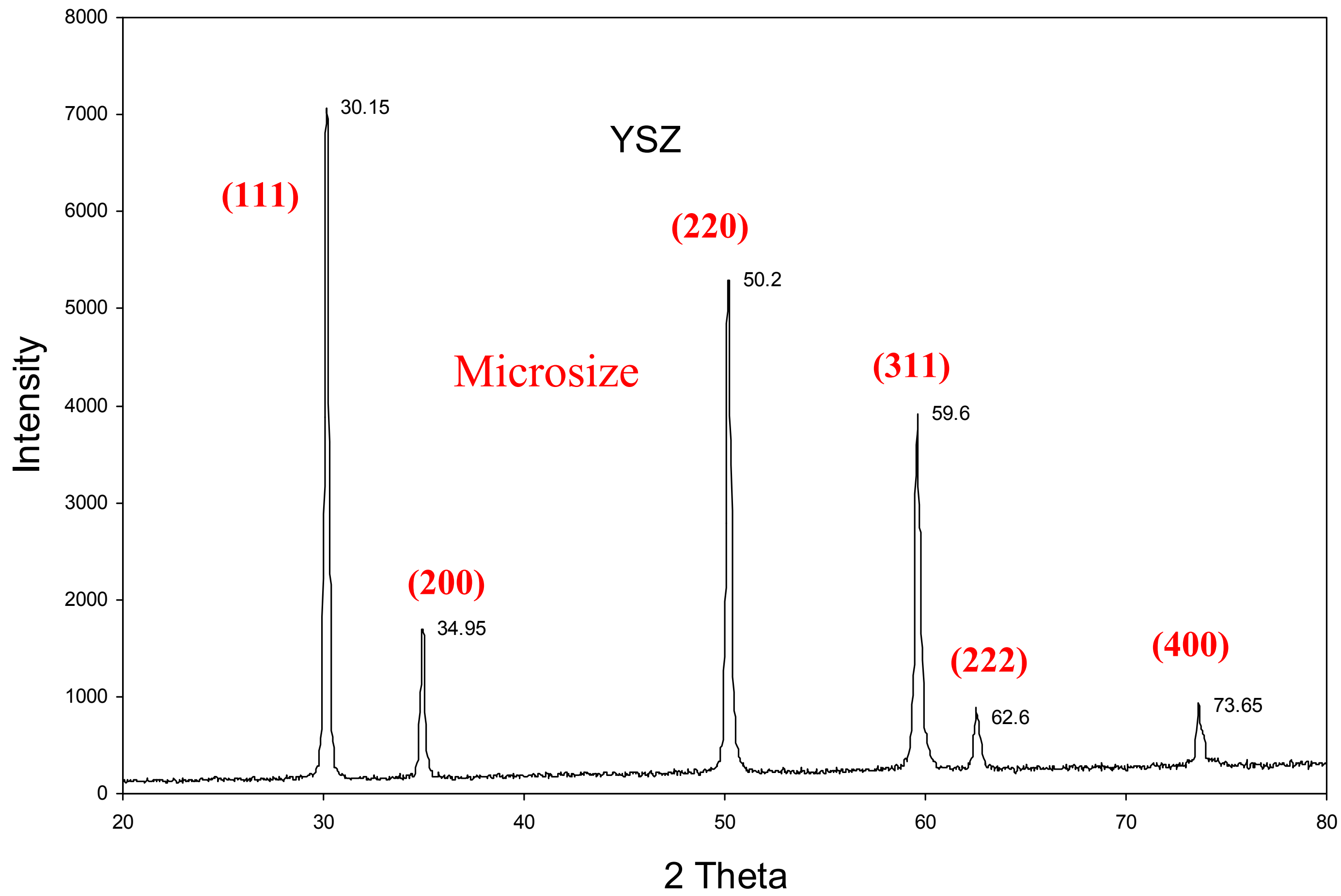
X-ray Diffraction Patterns of Y-Na_2ZrO_3 Microsize Precursor



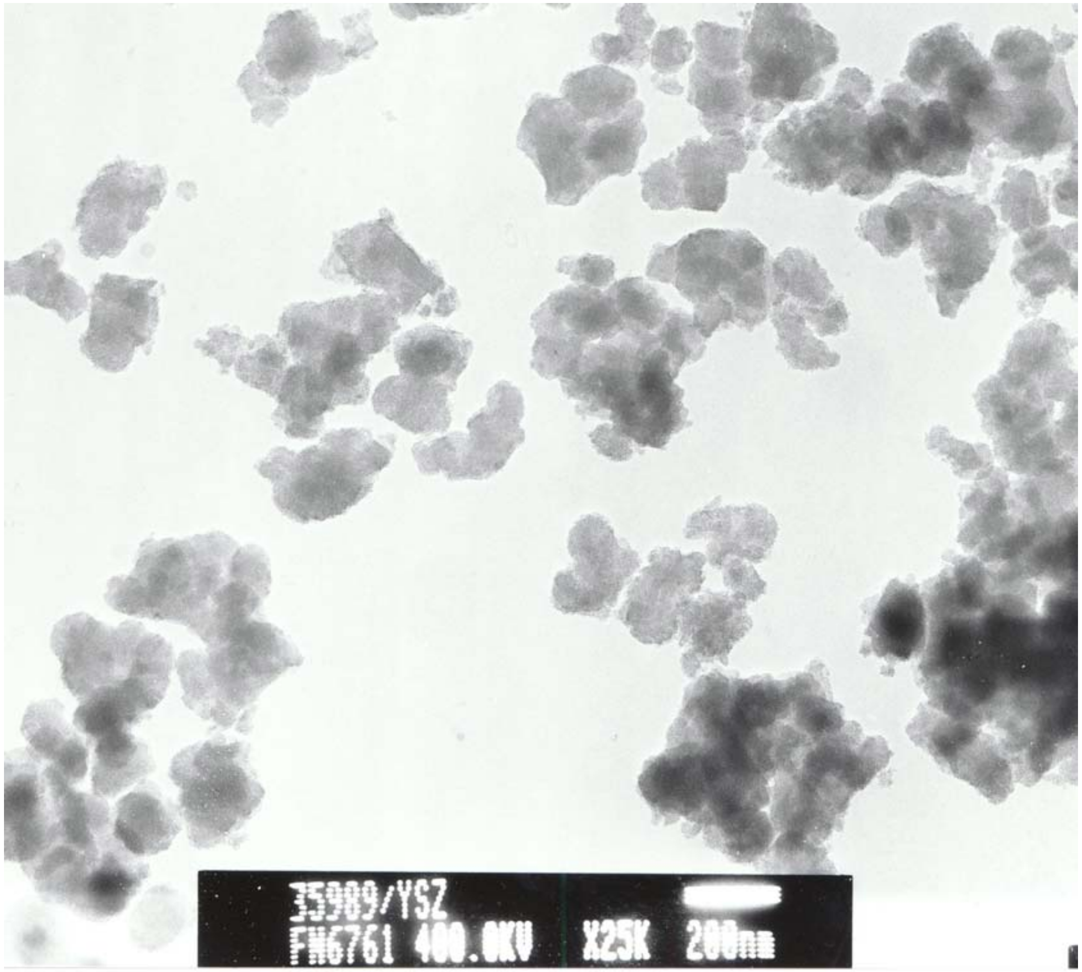
Nanosize YSZ Powders Synthesized from Two Different Precursors



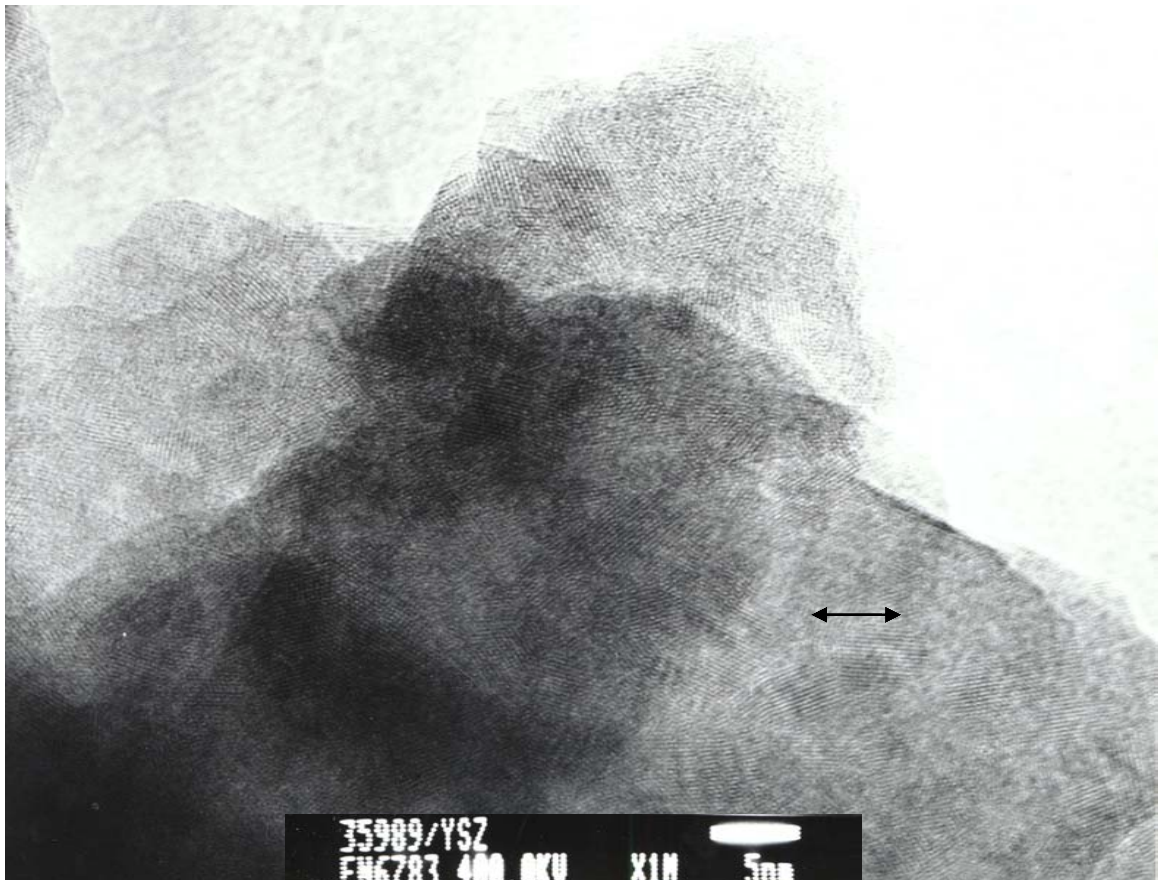
X-ray Diffraction Patterns of A Commercial YSZ Powder for Comparison



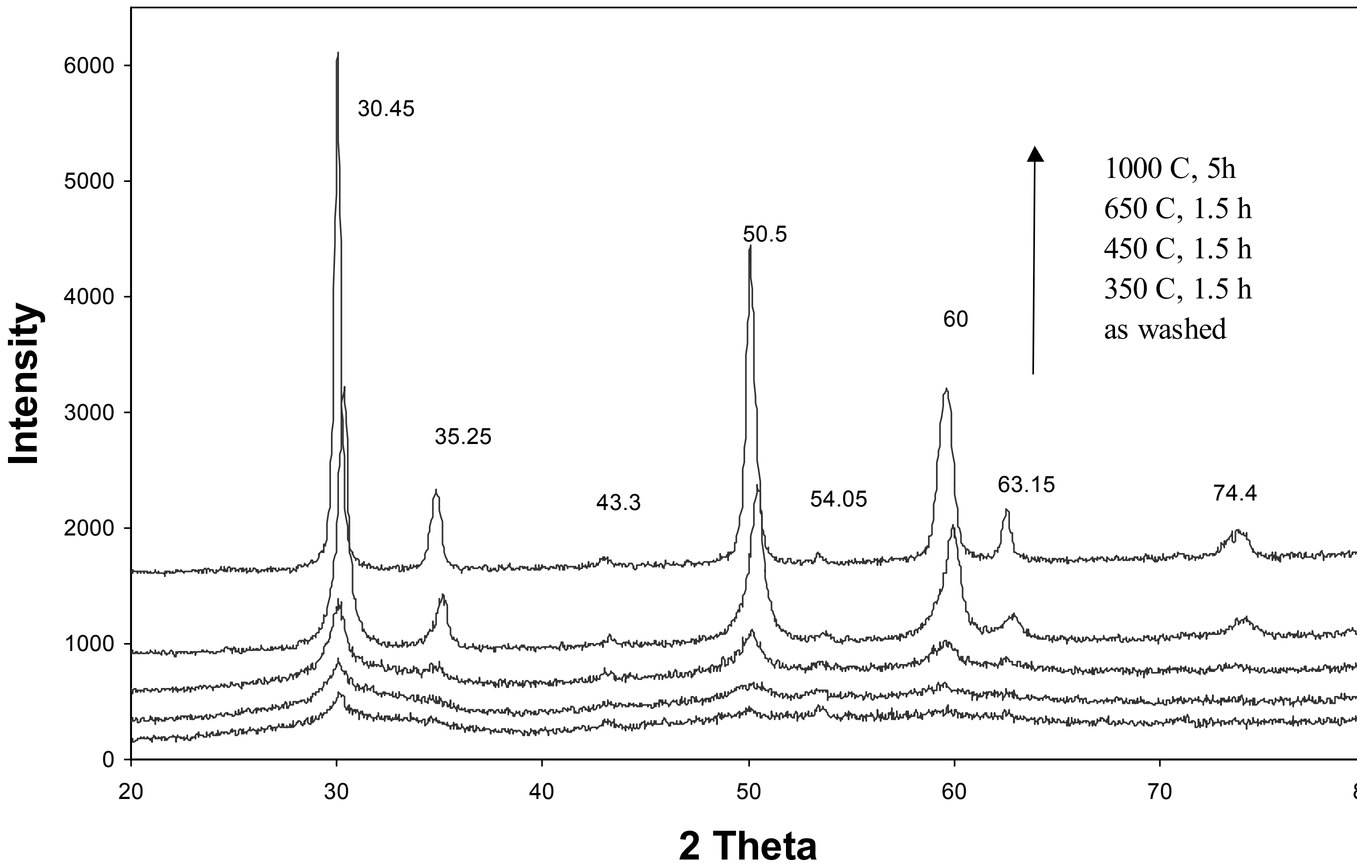
A TEM Micrograph of n-YSZ Powder (Agglomerate size ~50-100 nm)



High Resolution TEM Micrograph of n-YSZ Powder
(Individual crystallite size ~5 nm)



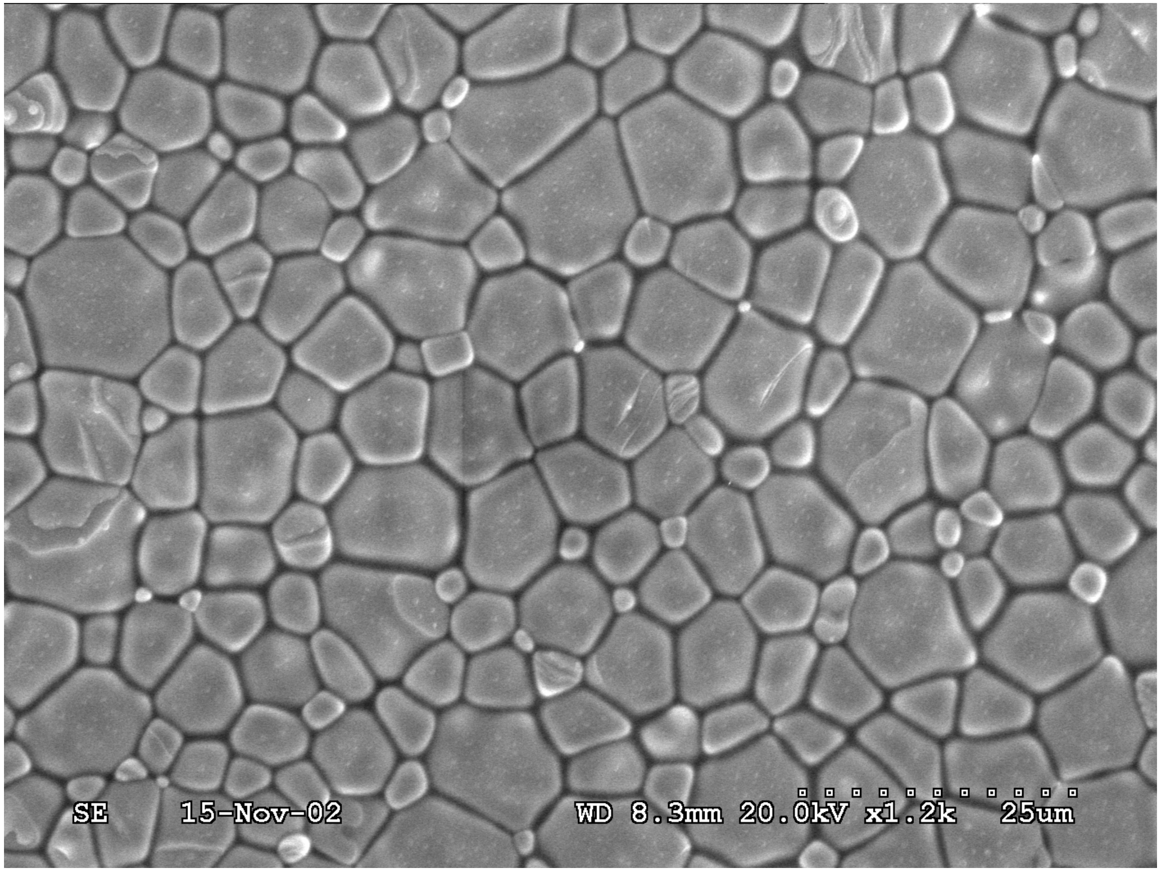
X-ray Diffraction Patterns of Nanosize YSZ Powder after Subsequent Heat Treatments



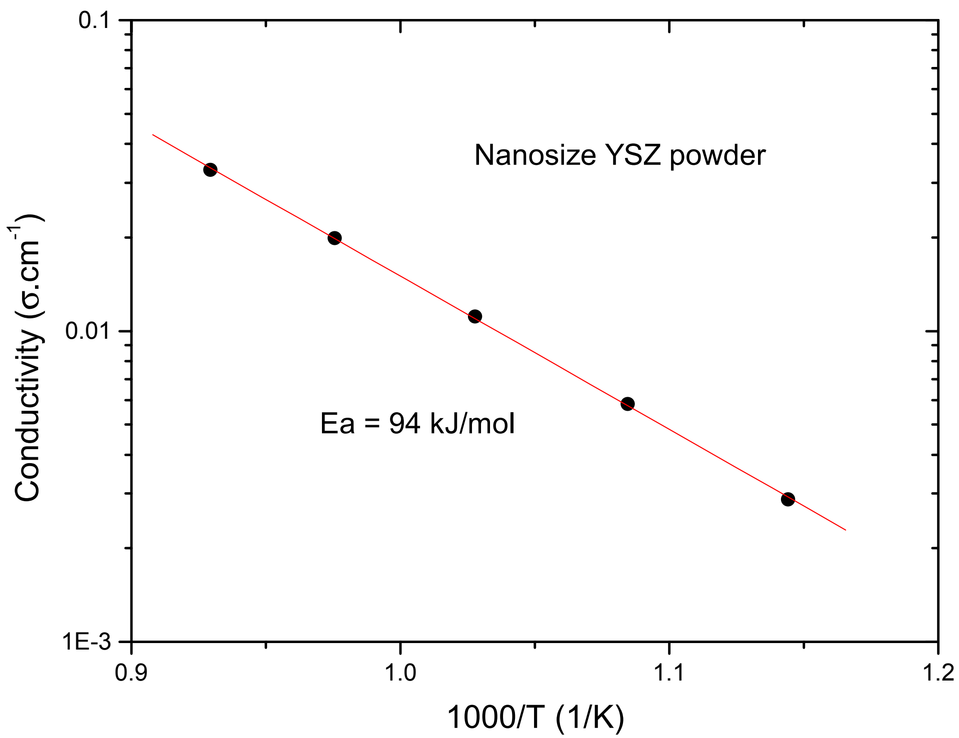
Particle size (nm) of as-synthesized nanosize YSZ powder and after heating in air at various temperatures.

Thermal treatment conditions	YSZ from Y-$BaZrO_3$ *d* in nm	Thermal treatment conditions	YSZ from Y-Na_2ZrO_3 *d* in nm
As-washed	2.4	As-washed	2.4
350^{o}C/1.5 h	8.0	300^{o}C/1.5 h	4.8
450^{o}C/1.5 h	10	350^{o}C/1.5 h	17
650^{o}C/1.5 h	23	650^{o}C/1.5 h	18
1000^{o}C/5 h	37	1000^{o}C/5 h	31

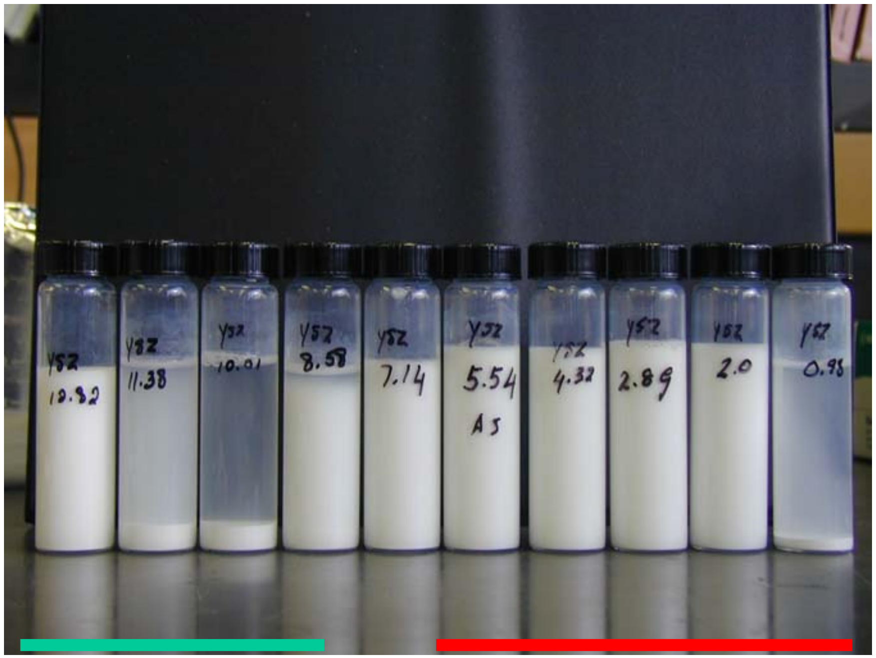
SEM of a Sintered Sample made with n-YSZ



Conductivity as a function of temperature



pH and the State of Agglomeration



Alkaline **Acidic**

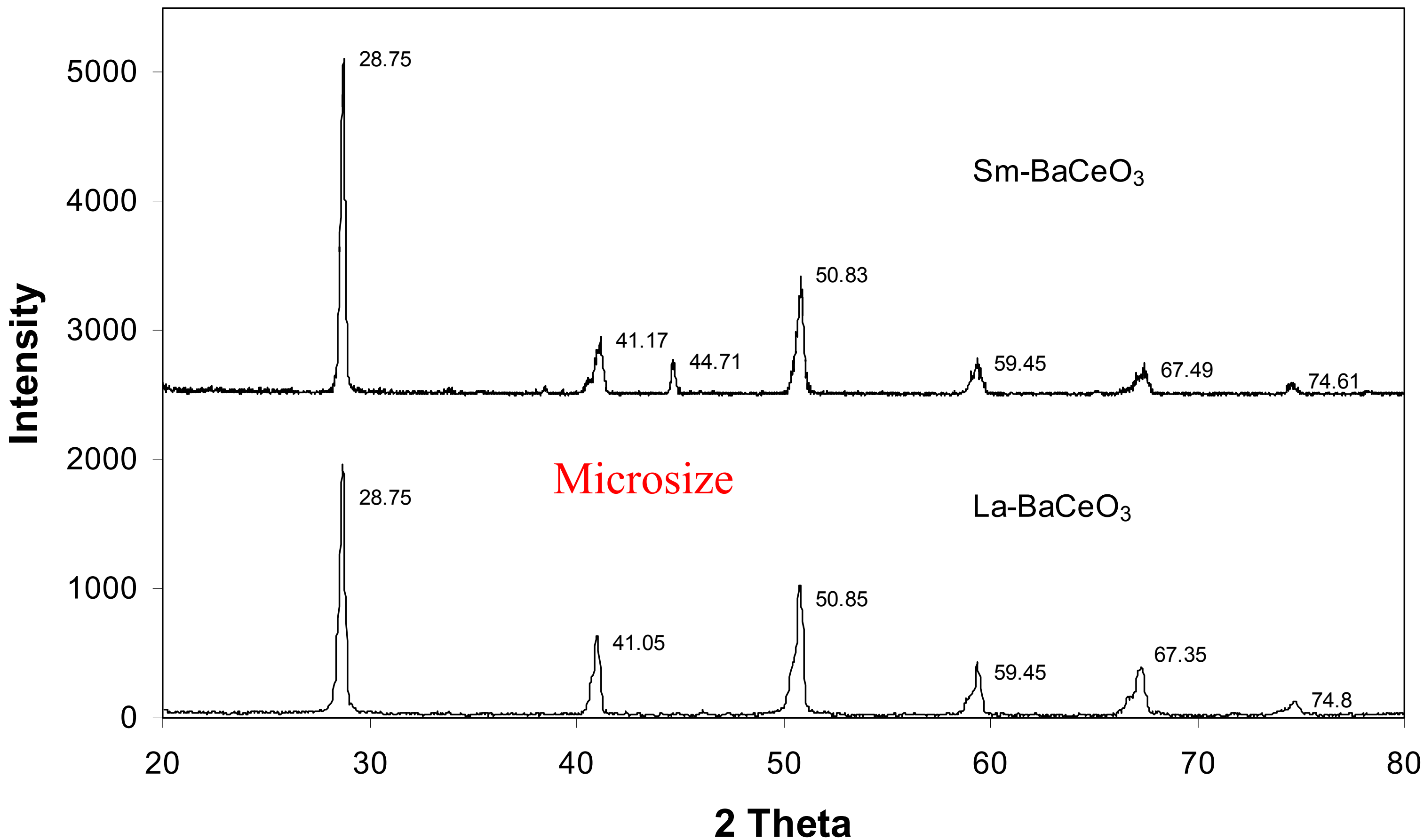
(a)

Alkaline **Acidic**

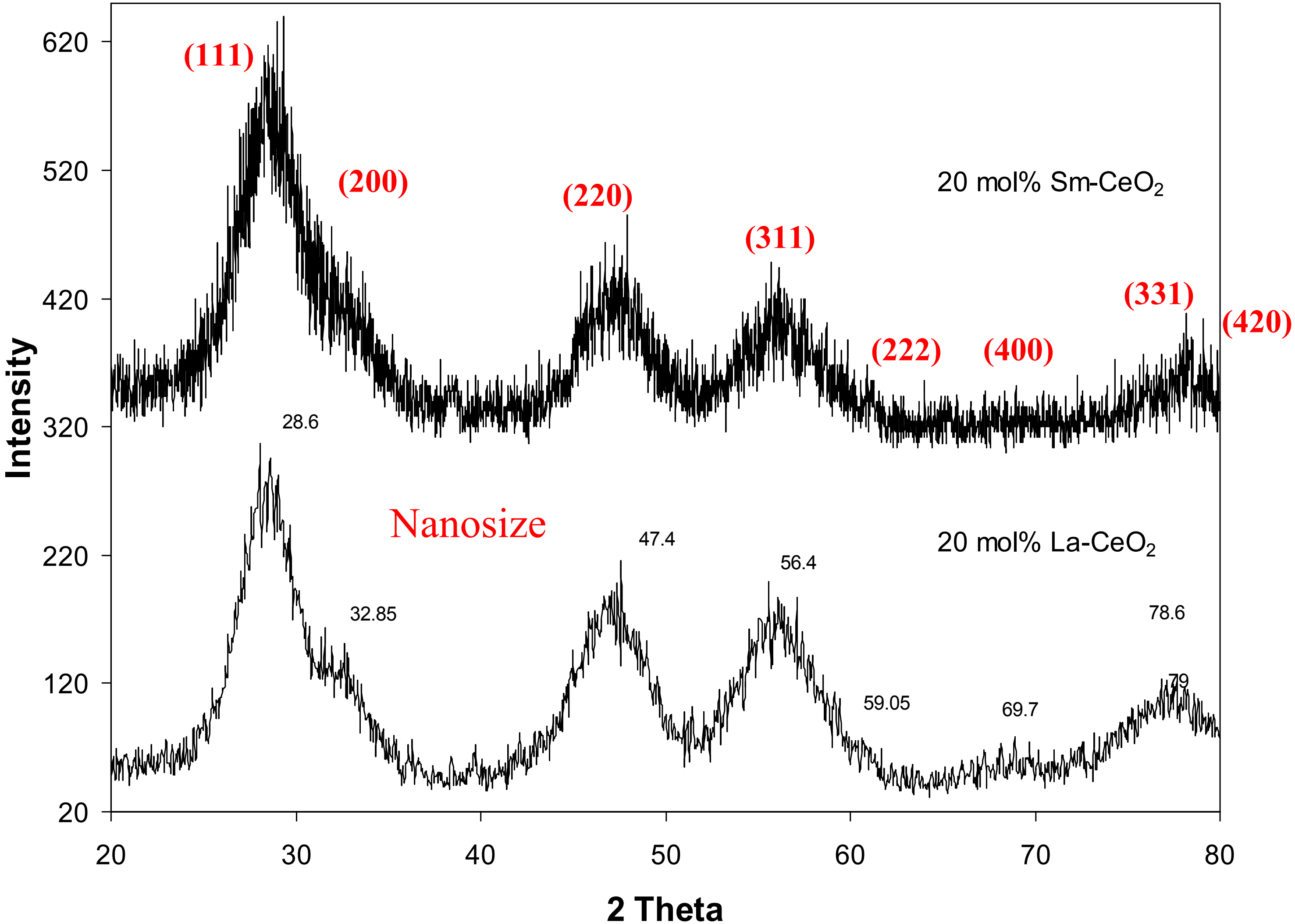
(b)

Suspensions of nanosize YSZ powder: (a) After 30 minutes, (b) After 48 hours

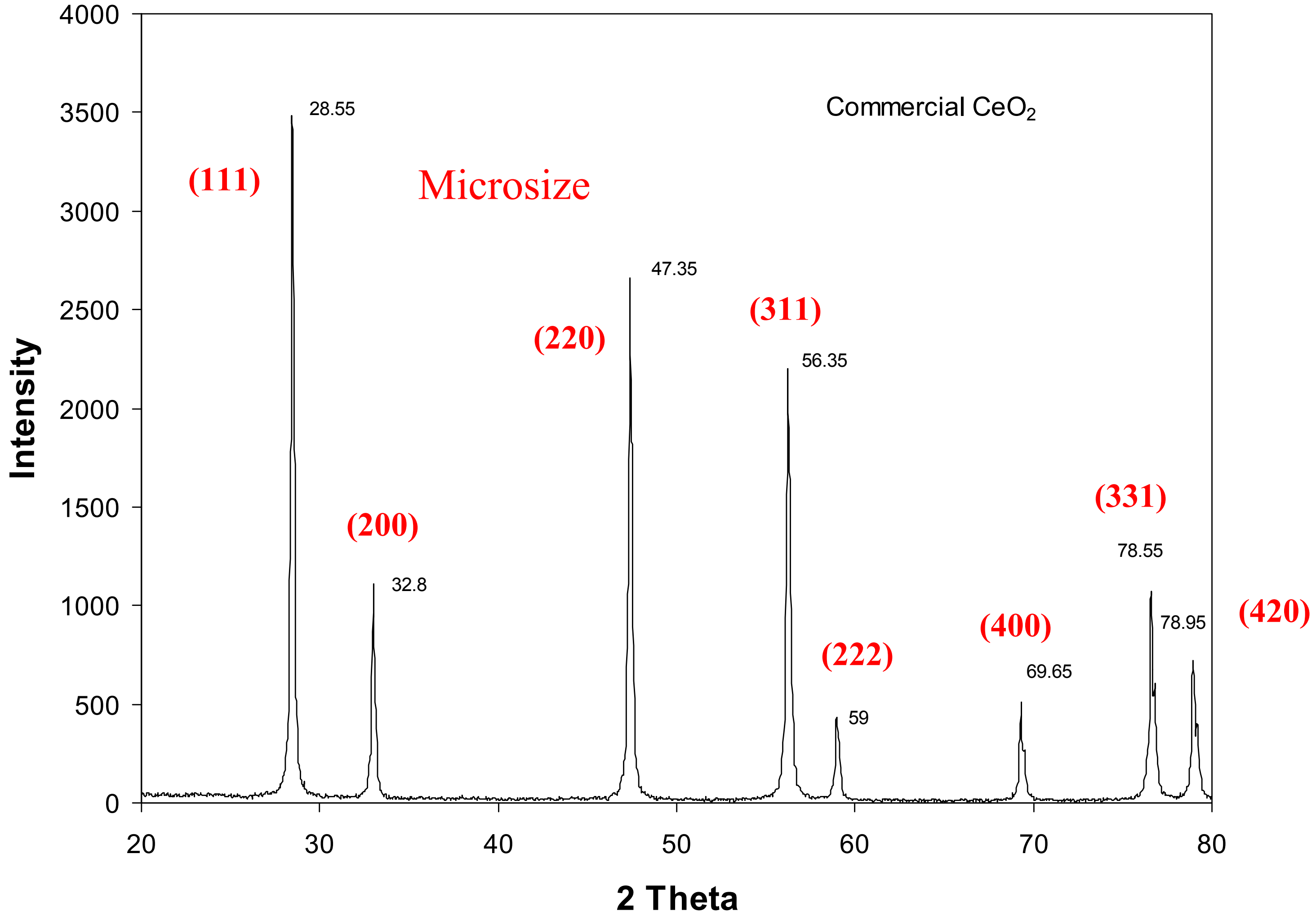
Synthesis of ceria: X-ray Diffraction Patterns of Sm- and La-Doped $BaCeO_3$ Precursors



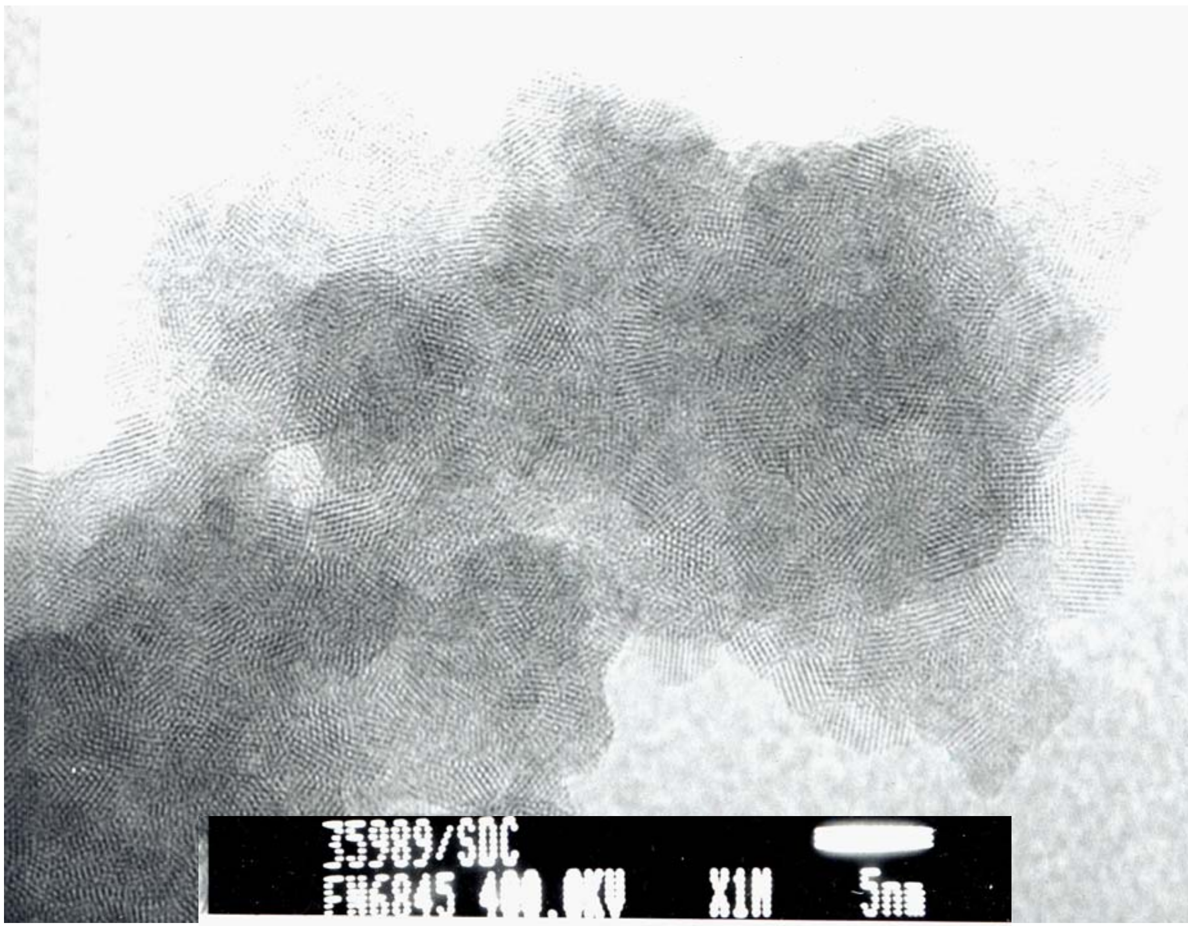
X-ray Diffraction Patterns of As Synthesized Doped CeO_2 Powders



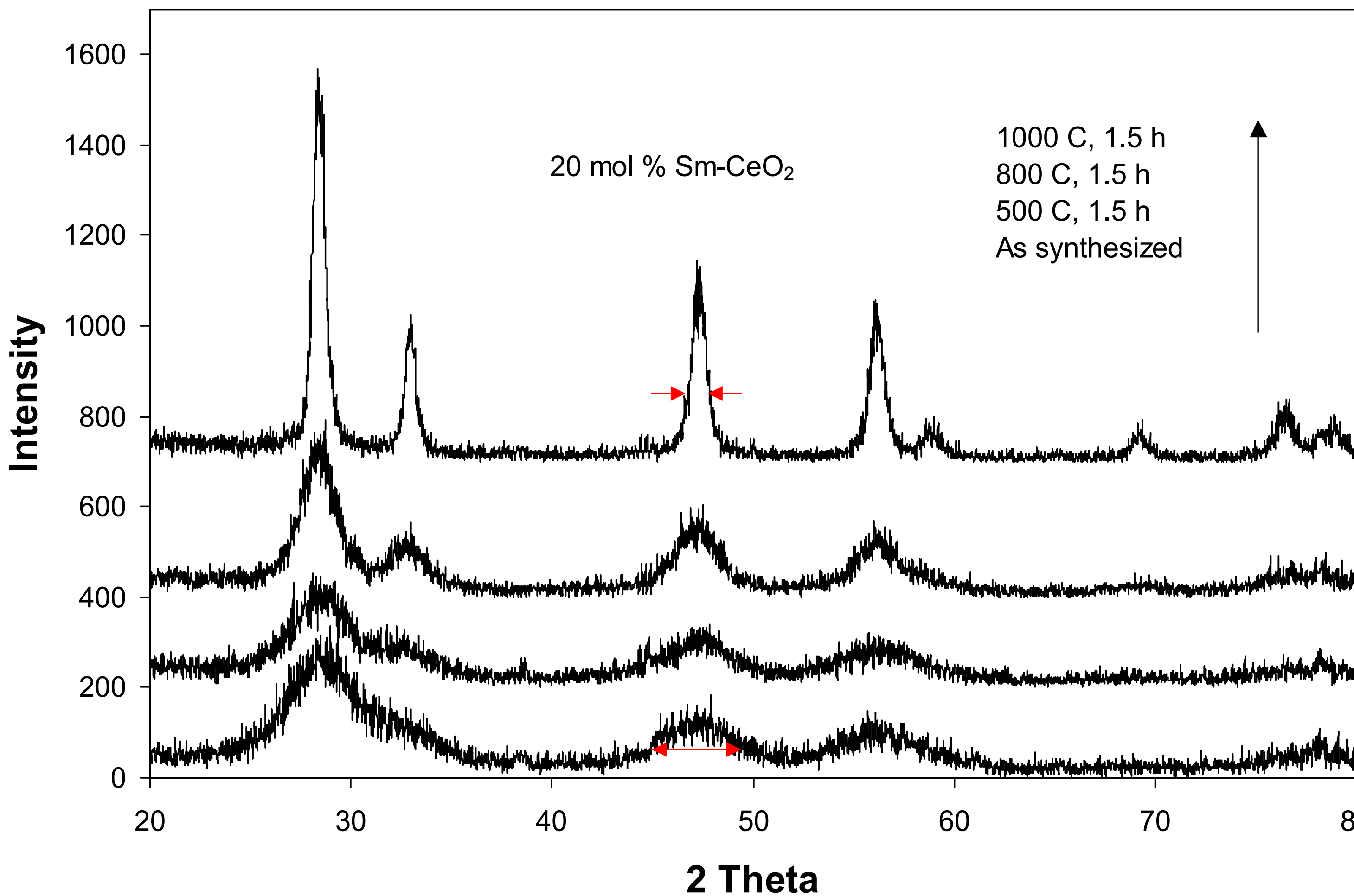
X-ray Diffraction Patterns of A Commercial CeO_2 Powder for Comparison



High Resolution TEM Image of Nanosize Doped CeO_2
Agglomerate size ~50 nm; crystallite size ~5 nm



X-ray Diffraction Patterns of Nanosize Sm-Doped CeO_2 Powder after Various Heat Treatments



Average particle size (nm) of as-synthesized nanosize doped CeO_2 powders and after heat treatment in air at various temperatures for 1.5 h.

Temperature (°C)	La-CeO_2 *d* in nm	Temperature (°C)	Sm-CeO_2 *d* in nm
as washed	2.0	As-washed	2.2
330	2.4	500	2.9
550	3.0	800	4.3
780	5.3	1000	13
950	13		
1050	21		

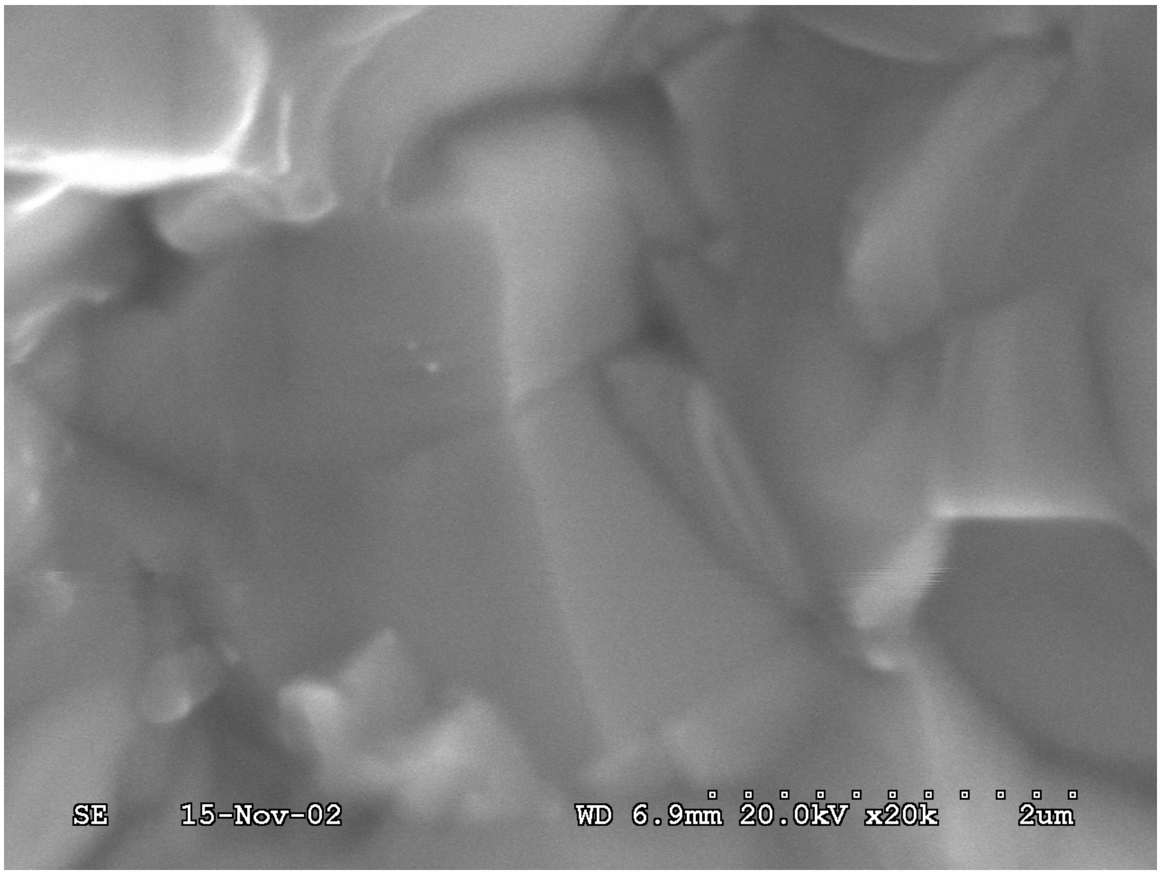
Important for cathode

Surface areas of as-calcined precursors, as-synthesized nanosize powders, and after heating treatment.

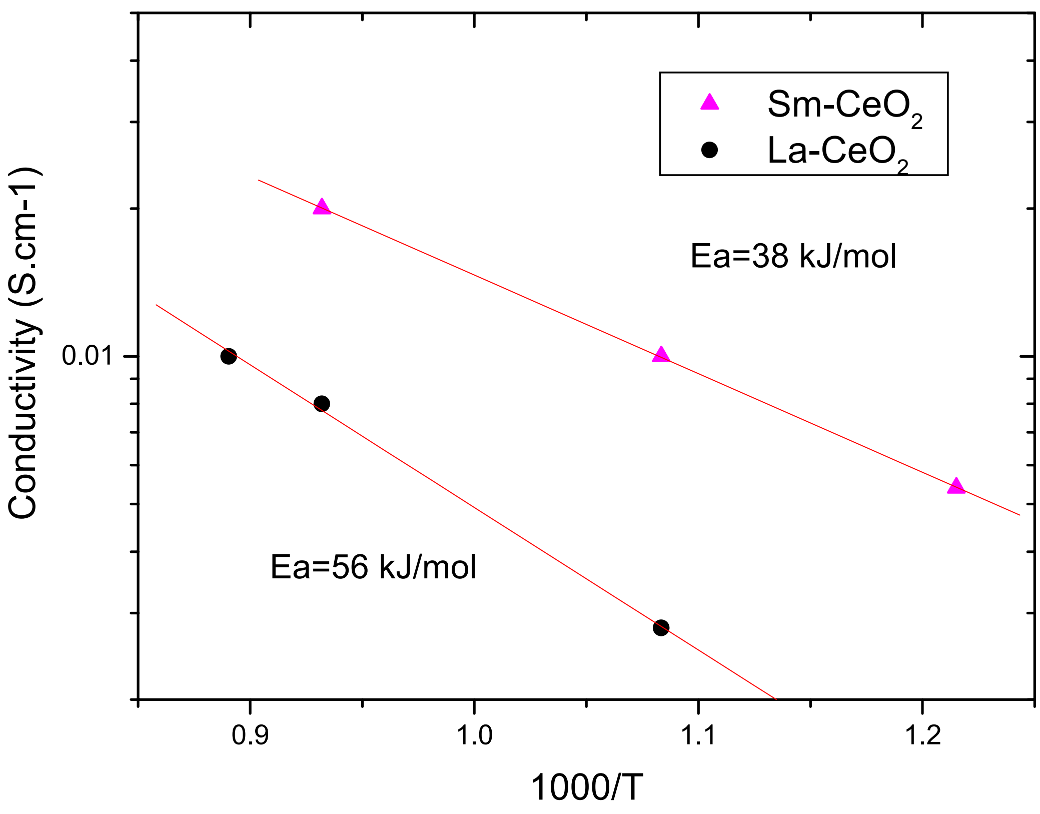
Sample	Y-$BaZrO_3$	Y-Na_2ZrO_3	As-synthesized YSZ	Nanosize YSZ after 5 hrs. at 1000°C
Surface Area (m^2/g)	3.5	2.7	66.6	13.6

Sample	La-$BaCeO_3$	As-synthesized Nanosize La-CeO_2	Nanosize La-CeO_2 after 1.5 hrs. at 1000°C
Surface Area (m^2/g)	0.7	73	1.4 Agglomerated

SEM of sintered Sm-doped ceria

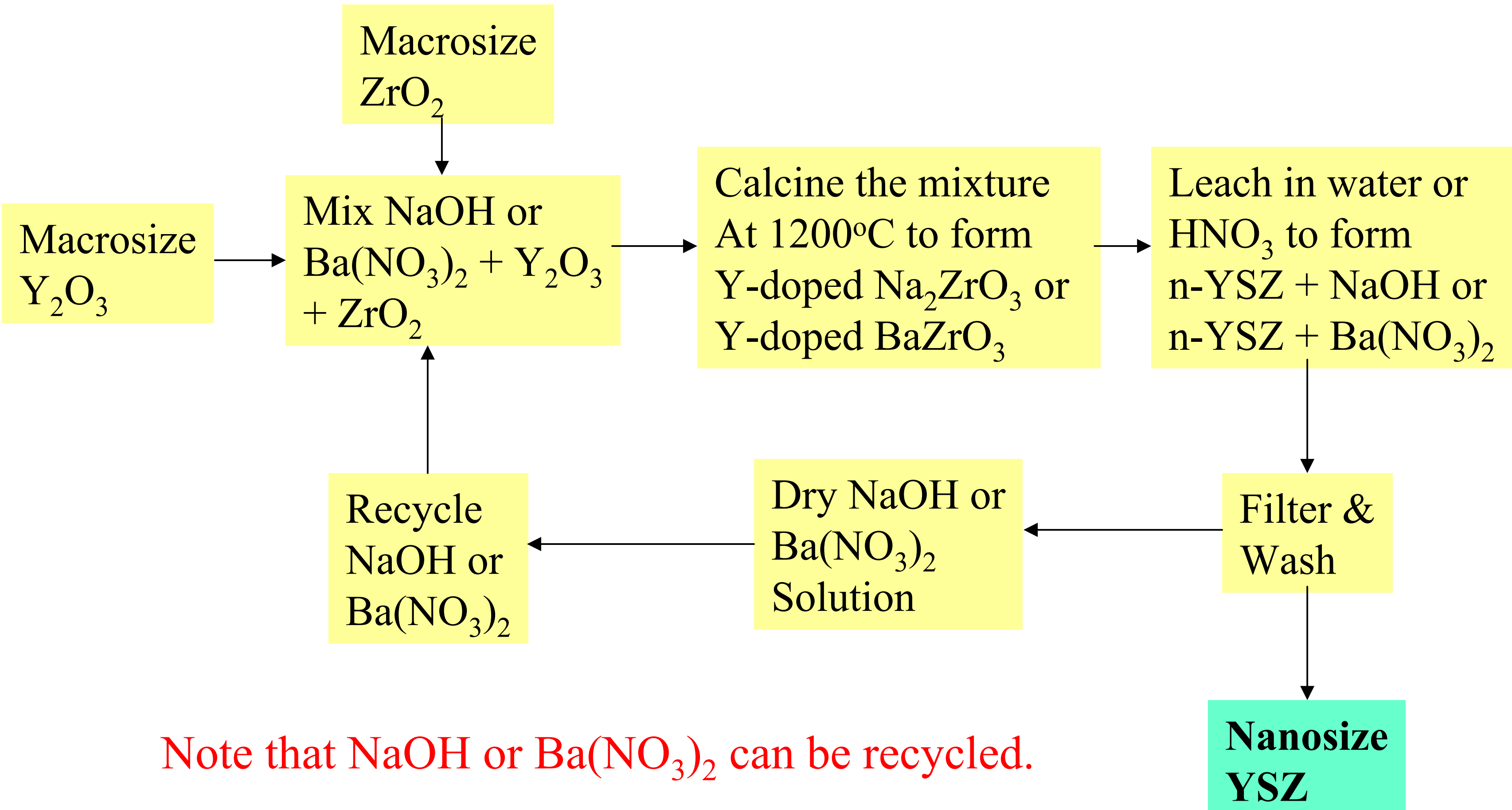


Conductivity of La- and Sm-doped CeO_2



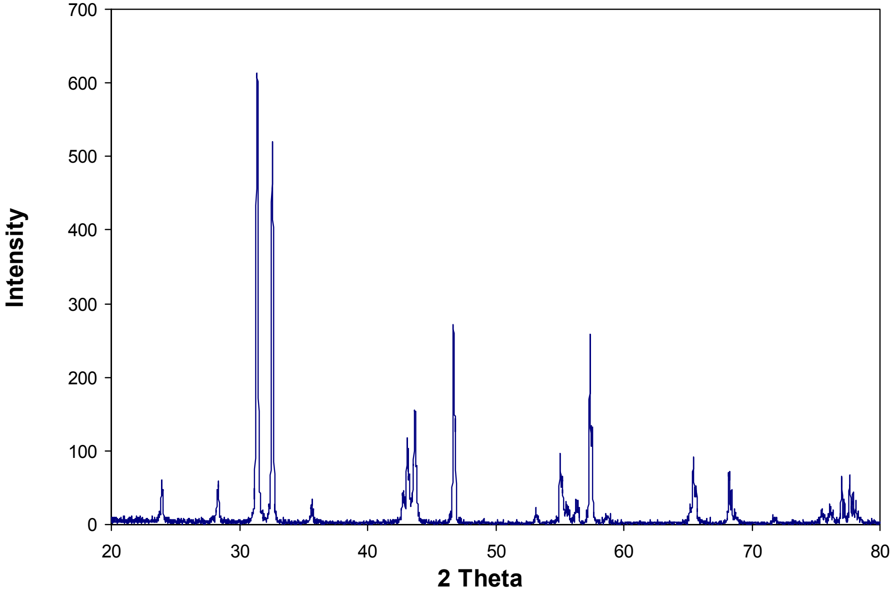
Four probe DC

A Process Flow Diagram for Zirconia

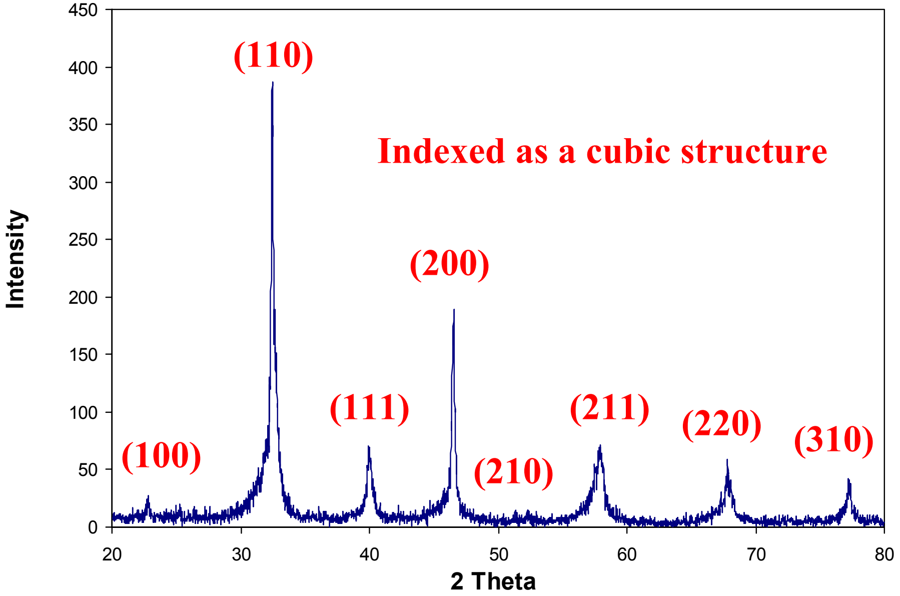


Note that NaOH or $Ba(NO_3)_2$ can be recycled.

Synthesis of $SrTiO_3$ using Sr_2TiO_4



X-ray Diffraction Pattern of Sr_2TiO_4 Precursor



X-ray Diffraction Pattern of as Synthesized n-$SrTiO_3$ Powder

Nanosize $BaTiO_3$ and $SrTiO_3$

Method	Particle Size (nm) As-synthesized n-$BaTiO_3$ (nm)	Particle Size (nm) As-synthesized n-$SrTiO_3$ (nm)
XRD Peak Broadening	~ 20	~ 19
BET Surface Area	~ 14	~ 20

Powders Made to Date

Nano powder	Precursor	Nano S. Area (m^2/g)	Size (nm) By XRD	Size (nm) By BET	Structure	Amount (g)
YSZ	Y-$BaZrO_3$ Y-Na_2ZrO_3	~66	~3	~15	Cubic	50
CeO_2	$BaCeO_3$	~70	~2	~15	Cubic	100
La-CeO_2	La-$BaCeO_3$	~73	~2	~12	Cubic	100
Sm-CeO_2	Sm-$BaCeO_3$	~70	~2	~15	Cubic	50
Gd-CeO_2	Gd-$BaCeO_3$	~70	~2	~15	Cubic	100
Sc-CeO_2	Sc-$BaCeO_3$	~70	~2	~15	Cubic	100

Summary

1) Various nanosize oxide powders from electrolytes to dielectric materials can be successfully synthesized using this new technique.
2) Nanosize powders with well defined crystalline structure can be formed at a low temperature (~100^{o}C).
3) Particle sizes of powders are typically in the range from a few nanometers to tens of nanometers.
4) The particle sizes of precursors have no bearing on final nanosize powders.
5) Homogeneous nanosize powders of various compositions can be formed.
6) The process in principle is easily scalable, and is expected to be inexpensive – since reagents can be recycled.

Applicability to SOFC Commercialization

Identification/development of low-cost processes for the synthesis of SOFC electrolyte and electrode materials will facilitate SOFC commercialization by

- Lowering the cost of highly sinterable and active materials.
- Facilitating the fabrication of cells in a single step, without compromising performance.

Cost Comparison

The following is a comparison of RELATIVE cost of raw materials for processes based on using nitrates or chlorides, vs. the present process based on using oxides as raw materials. The source is Alfa Aesar. Thus, the cost is only relative, and for small quantities. In large quantities, the cost should be lower for all materials.

Material	Cost	Cost per Unit Oxide
ZrO_2 (MW 123.2) 99+%	$51.2/kg	$51.2/kg.
$ZrCl_4$ (MW 233.03) 99.5+%	$103.5/kg	$103.03/kg.
Y_2O_3 (MW 225.81) 99.9%	$133.00/kg.	$133.00/kg
$Y(NO_3)_3.6H_2O$ 99.9% (MW 383.01)	$278.00/kg	$556.00/kg

Activities for the next 6-12 Months

- Development of processes for minimizing agglomeration.
- Development of processes for fabricating cells using highly active powders.
- Development of a preliminary design of a continuous process for the synthesis of n-YSZ and n-ceria.
- Development of a single step firing process.
- Preliminary cost analysis.