SYNTHESIS OF BULK FULLY DENSE NANOCRYSTALLINE FUNCTIONAL OXIDES WITH GRAIN SIZE APPROACHING 10 nm

U. Anselmi-Tamburini

Department of Chemistry
University of Pavia
Italy
Physical properties of materials change with grain size

- **Trivial effects**
  Due only to increase of the density of interfaces and grain boundaries

- **Real effects**
  Due to a change in local properties

  Example: confinement effect in semiconductors – quantum dots

Grain boundaries collect impurities and defects but have also an intrinsic effect

**Space Charge effect**

Effect of nanostructure and space charge effect on the electrical properties of ionic materials
SYNTHESIS OF BULK OXIDES WITH GRAIN SIZE APPROACHING 10 nm

It is one of the biggest challenges that materials scientists are facing.

In principle there are two possible routes:

• **Densification of nanopowders**
  • General applicability
  • Grain growth difficult to control
  • Very sensitive to the characteristics of the nanopowders

• **Controlled crystallization of amorphous precursors**
  • Applicable only to few systems
  • Single phase samples are difficult to obtain
HIGH-PRESSURE FIELD ASSISTED SINTERING (HP-FAST)

EXAMPLES OF THE PECULIAR PROPERTIES OBSERVED IN FUNCTIONAL NANOCRYSTALLINE OXIDES OBTAINED BY HP-FAST

**YSZ** – high proton conductivity

**CGO** – disappearance of the grain boundary resistivity in fully ionic conduction regime

**ZrO$_2$** – bulk undoped tetragonal zirconia


EXAMPLE #1

INFLUENCE OF GRAIN SIZE ON THE ELECTRICAL PROPERTIES OF \((\text{Ce}_{0.7}\text{Sm}_{0.3})\text{O}_2\)

INFLUENCE OF GRAIN SIZE ON (Ce$_{0.7}$Sm$_{0.3}$)O$_2$


$d_r > 98\%$
INFLUENCE OF GRAIN SIZE ON (Ce$_{0.7}$Sm$_{0.3}$)O$_2$

Grain size
16.5 nm

INFLUENCE OF GRAIN SIZE ON THE PROPERTIES OF 
\((\text{Ce}_{0.7}\text{Sm}_{0.3})\text{O}_2\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_a) (eV)</th>
<th>(\varepsilon_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 nm</td>
<td>0.98</td>
<td>58.8</td>
</tr>
<tr>
<td>16.5 nm</td>
<td>0.99</td>
<td>60.0</td>
</tr>
<tr>
<td>Microcryst</td>
<td>1.053</td>
<td>25.0</td>
</tr>
</tbody>
</table>


Synthesis of fully dense functional oxides with grain size approaching 10 nm
Possible interpretation:
accumulation of free $e^-$ in the Space Charge region
It is possible only if mixed
INFLUENCE OF GRAIN SIZE ON (Ce$_{0.7}$Sm$_{0.3}$)O$_2$

No dependence from \( p(O_2) \)

Purely ionic

Cerium Oxide (Ce$_{0.7}$Sm$_{0.3}$O$_2$)

Other Possible interpretations:

1) Overlap of space charge regions with disappearance of distinction between bulk and grain boundary

\[
\frac{\sigma_{bulk}}{\sigma_{gb}} = \frac{\exp\left(\frac{2e\Delta\varphi(0)}{kT}\right)}{4e\Delta\varphi(0)/kT}
\]
EXAMPLE #2

PROTONIC CONDUCTIVITY IN NANOCRYSTALLINE YSZ

Very large apparent grain boundary resistance

The difference between $\sigma_{gb}$ and $\sigma_{bulk}$ reduces with grain size

INFLUENCE OF GRAIN SIZE ON YSZ

Composition 8% mol Y2O3
Grain size 15.5 nm
\( d_r > 98\% \)
If exposed to air saturated with water, the conductivity increases almost 2 orders of magnitude.

The change involves both bulk and grain boundaries.

It is totally reversible.

It is observed only in samples with grain size below 50 nm.

Dehydration at 200°C for (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 80 min

INTERACTION OF NANOCRYSTALLINE YSZ WITH WATER

• Results suggest protonic conductivity

• Protonic conductivity in YSZ has been proposed before but never observed

• Nanostructure can enhance the localization of protons at the grain boundary

\[ H_2O + V_0^{\cdot\cdot} + O^X_o \rightarrow 2(OH)_o^{\cdot} \]

EXAMPLE #3

SYNTHESIS OF BULK, FULLY DENSE UNDOPED TETRAGONAL ZIRCONIA

ZIRCONIA PHASE STABILITY

Monoclinic  Tetragonal  Cubic
Effect of nanostructure

- In nanocrystals of undoped zirconia the tetragonal phase can be stabilized at room temperature
- It is generally recognized that there is a critical dimension \(< D_c >\)

<table>
<thead>
<tr>
<th>Author</th>
<th>(&lt; D_c &gt; ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garvie R.C. et al., Nature 258 (1975) 703–4</td>
<td>10</td>
</tr>
<tr>
<td>Clearfield A. Inorg. Chem. 3 (1964) 146–8.</td>
<td>12</td>
</tr>
</tbody>
</table>
Effect of nanostructure

The stabilization of the tetragonal structure in nanocrystals of pure zirconia is a complex phenomena that is influenced by several factors:

- Surface energy
- Interfacial energy
- Strain energy
- External pressure
- Presence of water vapour
- Presence of contaminant anions
- Oxygen vacancies concentration
Effect of nanostructure

The stabilization of tetragonal structure in pure zirconia has been realized only in nanopowders and thin films.

No attempt to produce bulk materials has ever been reported.

This will allow the investigation of bulk properties of undoped tetragonal zirconia:

- Mechanical properties
- Nature and concentration of point defects
- Transport properties
SYNTHESIS OF UNDOPED ZIRCONIA NANOPOWDERS

We tested few synthesis routes

Main objectives:

• Minimum amount of monoclinic phase
• Small grain size (< 10 nm) to enhance stabilization of monoclinic phase
• Minimum agglomeration to enhance densification
• Minimum amount of organic impurities to enhance densification
## Synthesis of Undoped Zirconia Nanopowders

### Synthesis methods investigated

<table>
<thead>
<tr>
<th>Route</th>
<th>Precursors</th>
<th>Method</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pechini</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO(NO₃)₂</td>
<td>polymerization @ 80°C</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Alkoxides hydrolysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr Isoproxide</td>
<td>acidic hydrolysis</td>
<td>isopropanol</td>
<td></td>
</tr>
<tr>
<td>Zr Propoxide</td>
<td>acidic hydrolysis</td>
<td>propanol</td>
<td></td>
</tr>
<tr>
<td>Zr Propoxide</td>
<td>acidic hydrolysis – inverted addition</td>
<td>propanol</td>
<td></td>
</tr>
<tr>
<td><strong>Solvothermal treatment of gels precipitated at basic pH</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO(NO₃)₂</td>
<td>treatment @ 130°C, 10-72 h</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>ZrOCl₂</td>
<td>treatment @ 130°C, 10 h</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>ZrO(NO₃)₂</td>
<td>treatment @ 160°C, 20 h</td>
<td>methanol</td>
<td></td>
</tr>
<tr>
<td>ZrO(NO₃)₂</td>
<td>treatment @ 160°C, 20 h</td>
<td>isopropanol/methanol 90/10</td>
<td></td>
</tr>
</tbody>
</table>
PHASE STABILITY IN UNDOPED NANOPOWDERS

Annealing time 20 min

Sintering temperature cannot exceed 850-900°C

DENSIFICATION OF UNDOPED ZIRCONIA NANOPOWDERS

Typical sintering conditions

Sintering pressure 700-800 MPa

\[ T \]  \quad \text{5 min} \quad 900^\circ \text{C} \quad 200^\circ \text{C/min} \]
Best result

Relative density 95%

densified

powder