Densification, grain growth and texturation in SPS nanoZnO ceramics

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Limoges
Motivation

ZnO:  
- Transparent oxide (Gap ~ 3.3 eV)
- Hexagonal structure
- Stability at high temperatures
- Biocompatible
- Multiple applications: Photovoltaics, varistors, medicine...

ZnO as thermoelectric material
- n-type TE oxide
- Abundant elements
- ZT ~ 0.6

Why SPS?
- High densities at low temperatures
- Small grain sizes $\rightarrow$ Low thermal conductivity ($\kappa$)
Controlled precipitation in aqueous solution

125 ml
4 M NaOH

100 ml
1 M Zn(NO$_3$)$_2$·6H$_2$O (+ 5 % AlCl$_3$)

Dropwise addition, stirring, 20°C
Centrifugation (4000 rpm-5 min)
Washing 4 times
Starting material
- Pure and Al doped (0.3%) ZnO powder prepared by co-precipitation
- No secondary phases
- Non-isotropic morphologies
Starting Powder:

- No secondary phases (Al doped 0.3%)
- Non-isotropic morphologies:
  - **Pure ZnO:**
    - platelets, flower-like structures (c-axis in plane)
  - **Al-doped ZnO:**
    - platelets, isolated (c-axis in the plane)
    - spherical small particles
    - needle like (along the c-axis)
SPS sintering Conditions

\[
\begin{align*}
\text{• } P &= 100 \text{ MPa} \\
\text{• } 500^\circ C < T < 1100^\circ C \\
\text{• } 100^\circ C/\text{min}, 5'
\end{align*}
\]

\[\text{Pure ZnO} \]
\[T < 800^\circ C \rightarrow \text{Low densities (<70%)} \]
\[T > 800^\circ C \rightarrow \text{High densities (>90%)} \]

\[\text{Al-doped ZnO} \]
\[T > 500^\circ C \rightarrow \text{High densities (>90%)} \]
Pure ZnO
- Low texturation degree
- Evolution of the 1 0 0 peak

Al doped ZnO
- High texturation degree
- Suppression of the 0 0 2 peak
- c-axis perpendicular to pressure

XRD on the surface

Intensity (arb. units)

θ

28 30 32 34 36 38 40

600°C
800°C
1000°C
1100°C

Intensity (arb. units)

θ

28 30 32 34 36 38 40

500°C
600°C
800°C
1000°C
Pure ZnO
- Low texturation degree
- Low T: (1 0 0)//pressure axis
- High T: (0 0 2)//pressure axis

Al doped ZnO
- High texturation degree
- (1 0 0)//pressure
- (0 0 2)⊥pressure ∀T
MORPHOLOGY: Isotropic grain

Al-doped ZnO
500°C

Cross Section

Surface

Mag = 10.00 K X 1 μm

EHT = 3.00 KV

WD = 2.3 mm

Signal A = InLens
Aperture Size = 30.00 μm
**MORPHOLOGY: Evolution of the grain size**

**Pure ZnO:**
- Isotrope grains at high temperatures
- Grain growth from $T > 800°C$

**Al doped ZnO:**
- Isotrope grains at all temperatures
- Grain growth from $T \sim 500°C$
DENSIFICATION MECHANISM

Pure ZnO

Al doped ZnO
Thermoelectric properties: influence of the texturation

- No influence of texturation on Seebeck and thermal conductivity
- Low influence of texturation on electrical resistivity
  - 100 direction more resistive at room temperature
  - No influence at high temperatures (T > 300°C)

- Perpendicular to pressure direction (c-axis randomly in plane)
- Parallel to pressure direction (100 direction)
Powder synthesis

Al doped ZnO
60°C

- Isotropic nanoparticles (< 50 nm)

Sintering

80% 800°C, 5 min
98% 850°C, 30 min
86% 900°C, 5 min
Effect of microstructure on thermal conductivity at 50°C

**Pure ZnO**
- Interconnected platelets
- 45 W/m K

**Al doped ZnO**
- Nanoparticles
- 35 W/m K
- Platelets + nanoparticles
- 34 W/m K
- 29 W/m K

**Nanoparticles**
- 12 W/m K
Conclusions

Starting powder:

- Synthesis by co-precipitation of pure and 0.3% Al-doped ZnO
- Non isotropic morphologies
  - Flower like structures in pure ZnO
  - Isolated platelets, nanoparticles and needles in doped ZnO
- Isotropic nanoparticles in doped ZnO

SPS:

- Dense ceramic at 500°C
- Differences in shrinkage due to different starting morphologies

TE properties (doped samples):

- No influence of texturation on Seebeck and thermal conductivity
- Influence of texturation on the electrical resistivity:
  - Higher resistivity along the 100 direction at low T (T < 300°C)
  - No influence at high temperatures (T > 300°C)
Thank you for your attention

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