The Challenge and the Opportunity for Manufacture of Zinc Magnesium Oxide Ceramics

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SCI Engineered Materials, Inc
The Science of Engineered Materials™

History of SCI

- Founded in 1987 by Prof. Funk (Ohio State University) as Superconductive Components, Inc. in Columbus, OH. Changed name to SCI Engineered Materials, Inc. in 2007
- Initially focused on R&D with high temperature superconducting materials and devices
- Developed manufacturing capabilities to produce advanced ceramic compositions for sputtering targets
- Manufacture products for diverse global markets
- Continue to leverage manufacturing capabilities, intellectual property and proprietary knowledge into complementary growth markets

SCI Timeline

- **1987** – Superconductive Components (SCI) Formed
- **1989** – SCI becomes a publicly traded company
- **1991** – Formed Target Materials Corp.
- **1999** – Patent Fine Particle Bi-Sr-Ca-Cu-O
- **2001** – Patent, large strongly linked Monoliths
- **2003** – Began rebranding company as SCI Engineered Materials
- **2004** – Third Frontier Grant to commercialize Thin Film Battery materials
- **2006** – Commercialize & scale-up of products for automotive
- **2007** – Legally rename SCI Engineered Materials, Inc.
- **2008** – Receive 3rd Frontier Grant to Commercialize AZO & Rotatable Capacity
- **2014** – MgO development
- **2015** – TCO Development for Displays,
- **2015-2016** – **ZnO-MgO development**

❖ AZO – Aluminum Zinc Oxide Transparent Conductive Oxide
❖ NASA – National Association Space Agency
❖ NSF – National Science Foundation

Contents

- **Opportunities of (Zn,Mg)O**
- Ceramic sputtering targets manufacturing process
- Challenge of (Zn,Mg)O manufacture

Application of (Zn,Mg)O

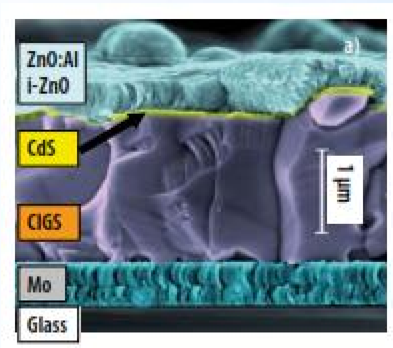
Transparent Conducting Thin Films

- Wide bandgap semiconductor (>3.3 eV)
    - Direct bandgap for up to 30% MgO
    - Wurtzite structure
    - Light emitting diodes
    - Photodetector
    - (Zn,Mg)O/ZnO multilayer → 2D gas for high frequency high powder devices
- Buffer/i layer for CIGS thin film solar cell

    Films with thickness of 10s of nanometer

Alternative buffer layer in thin film solar

- Buffer layer for CIGS thin film solar cell



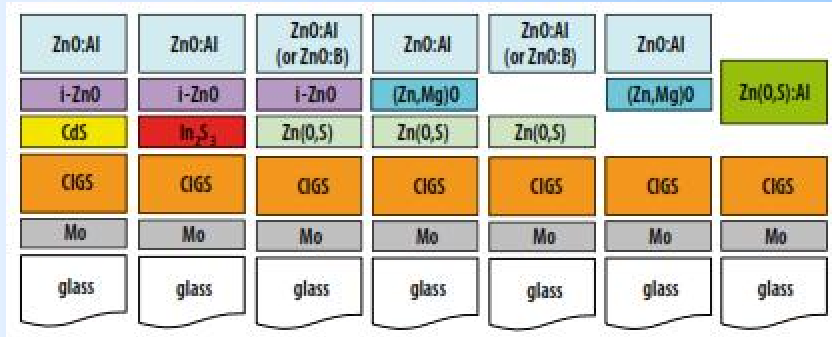
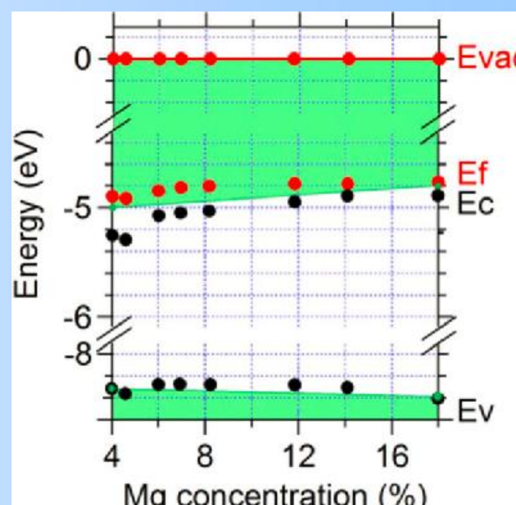


FIGURE 4: Scheme of different CIGS cell stacks on glass/Mo substrates with alternative buffer layer systems in comparison to the commonly used CdS/i-ZnO.

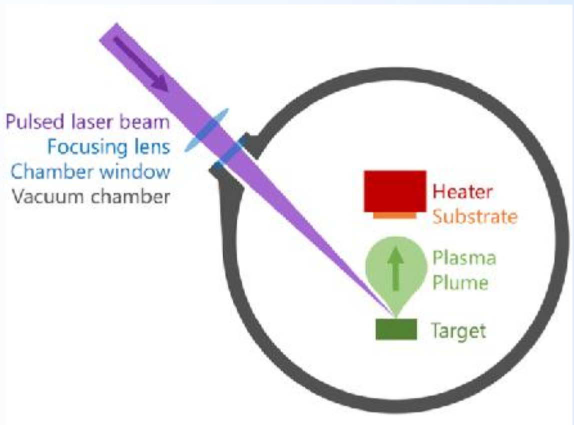
* W. Witte et al., Status of current research and record cell efficiencies

- Currently use CdS as the buffer layer
- Tunable bandgap for band alignment (~3.3eV – 3.6 eV)
- Tunable lattice parameter for lattice match



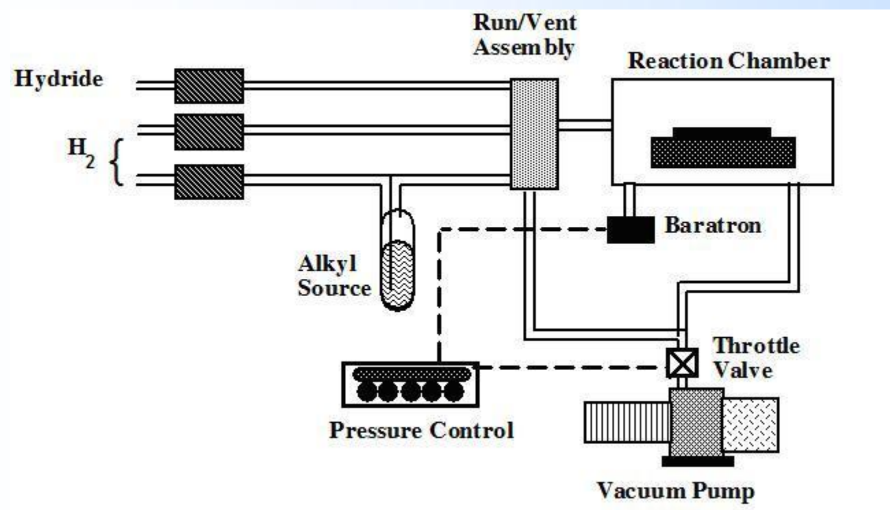
P. P. Rajbhandar et al., Solar Energy Materials & Solar Cells 159 (2017) 219

Methods for (Zn,Mg)O deposition



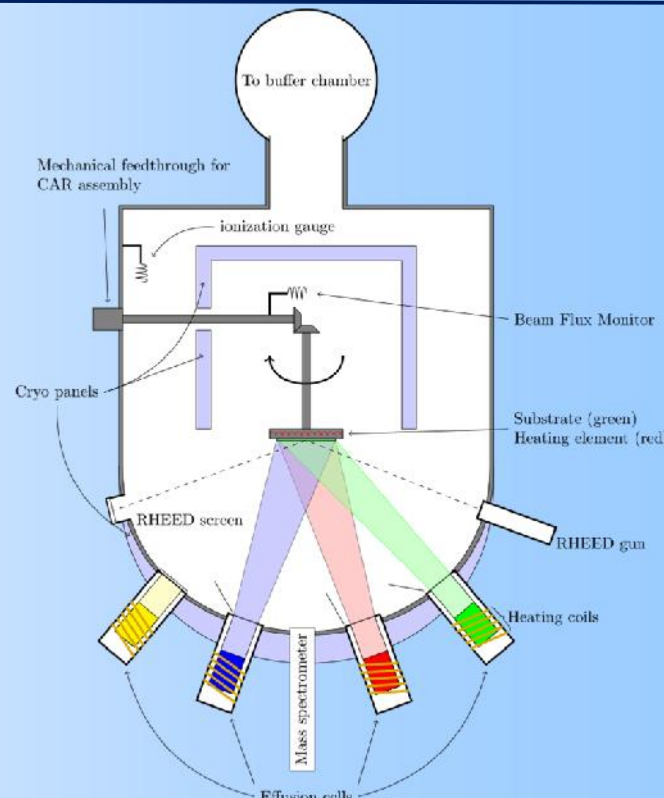
Pulse Laser Deposition

Credit by Ted Sanders



MOCVD

Credit by Author C. J. Pinzone



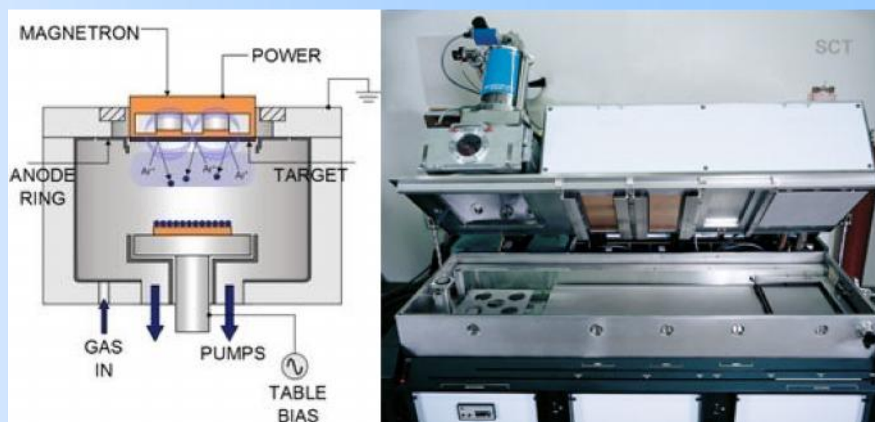
MBE

Credit by Vegar Ottesen

- Sputtering is preferred for manufacture efficiency and compatibility with CIGS process.

Introduction: scope of this work

Development of high density (greater than 90% of TD), low porosity, high uniform (Zn,Mg)O sputtering targets for thin film processing



- High density:

  Uniform sputtering deposition

- Low porosity:

  → High strength, hardness and other mechanical property

  → Low contamination from gas trapped inside the pores during sputtering

- High uniform (MgO has limited solid solubility in ZnO)
- Preferably conductive → DC sputterable
- *No (Zn,Mg)O ceramic targets are industrially produced so far*

Contents

- Opportunities of (Zn,Mg)O
- **Ceramic sputtering targets manufacturing process**
- Challenge of (Zn,Mg)O manufacture

Ceramic sputtering target manufacture process

Process Flow

Starting powders → Milling → Forming → Pressureless Sintering → Machining → Bonding

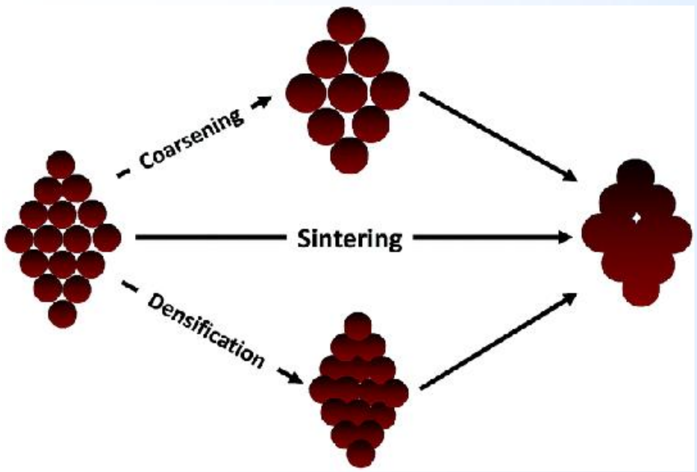
→ Hot Press; HIP; SPS and other Pressure-assisted sintering technology → Machining

- Milling: reduction of particle size to improve sintering and homogeneity
- Forming: shape small particle powders into a solid piece by applying pressure, e.g. uniaxial or cold isostatic pressing, or by casting (slip casting, gel casting, pressure filtration)
- Sintering/Hot Press/HIP: the process of heating with or without pressure to reach a high level of consolidation and desired microstructure.
- Forming and sintering routes are selected based on shape and size of components, available equipment, starting materials features and properties requirements

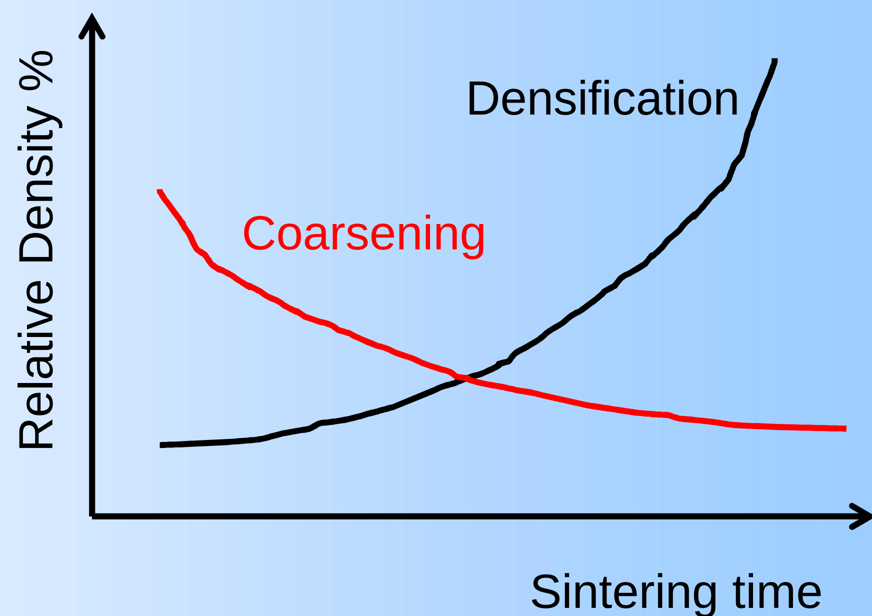
Ceramic sputtering target manufacture process

- Basic physics in sintering process:

Diffusion



Carrillo et. al., J. Matt. Chem. A, 2014



Densification is competing with coarsening (grain growth), thus there is a maximum sintering time to achieve a highest density at a certain sintering temperature.

Contents

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Challenge of (Zn,Mg)O manufacture process: general processing requirements

Necessity to reach high density and high electrical conductivity sputtering targets → to be able to use DC magnetron sputtering (industrial film technology)

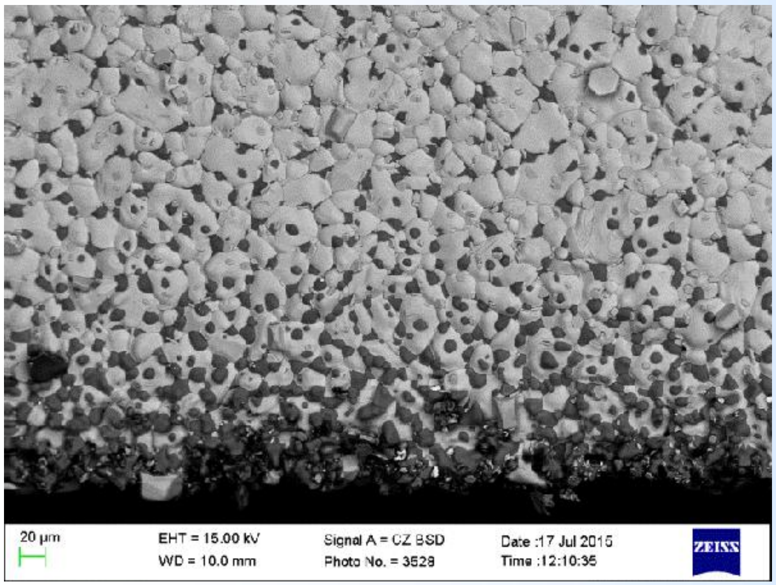
MgO content – up to 30 wt.%
- Low MgO content – 5-15%
- High MgO content – 20-25%

General processing route to produce sputtering targets
- Highly homogeneous powder from commercially produced powders
- Colloidal processing
- Forming for possibility to obtain
  planar targets (tiles of 600-1000 cm^2 and more)
  rotary targets (hollow cylindrical bodies)
- Pressureless sintering at rather low temperatures to use conventional electric kilns
- Grinding (machining)
- Bonding to metallic substrate

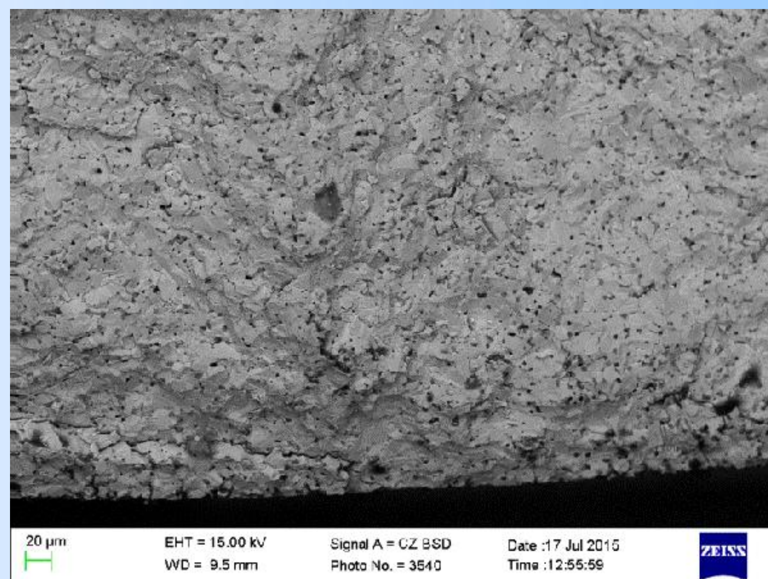
Challenge of (Zn,Mg)O manufacture process: mixing-milling

To reach high homogeneity and particle size well suitable for low-temperature sintering

- Different ball mill condition



Milled in water
4.68g/cm^3 (91.9%TD*)



Milled in IPA
4.75g/cm^3 (93.2%TD*)

* Estimated TD is a linear interpretation between two compound due to lack of literatures.

- Milled in water: MgO react with water, very high viscosity → inefficient milling
- Milled in IPA: better uniformity

Challenge of (Zn,Mg)O manufacture process: milling

- Challenge of milling in IPA:
  - Evaporation of IPA
    - Immediate "cake" formation
    - Strong smell of IPA
  - Enclosed production milling system needed
  - Non-compatibility with SCI's in house equipment
  - High in cost

❖ <u>Water based process is preferred</u>→ need to overcome interaction of MgO with water

(higher MgO contents → higher hydration)

Exploration of water based process

- (Zn,Mg)O calcination route – to “bond” ZnO-MgO and to reduce interaction with water

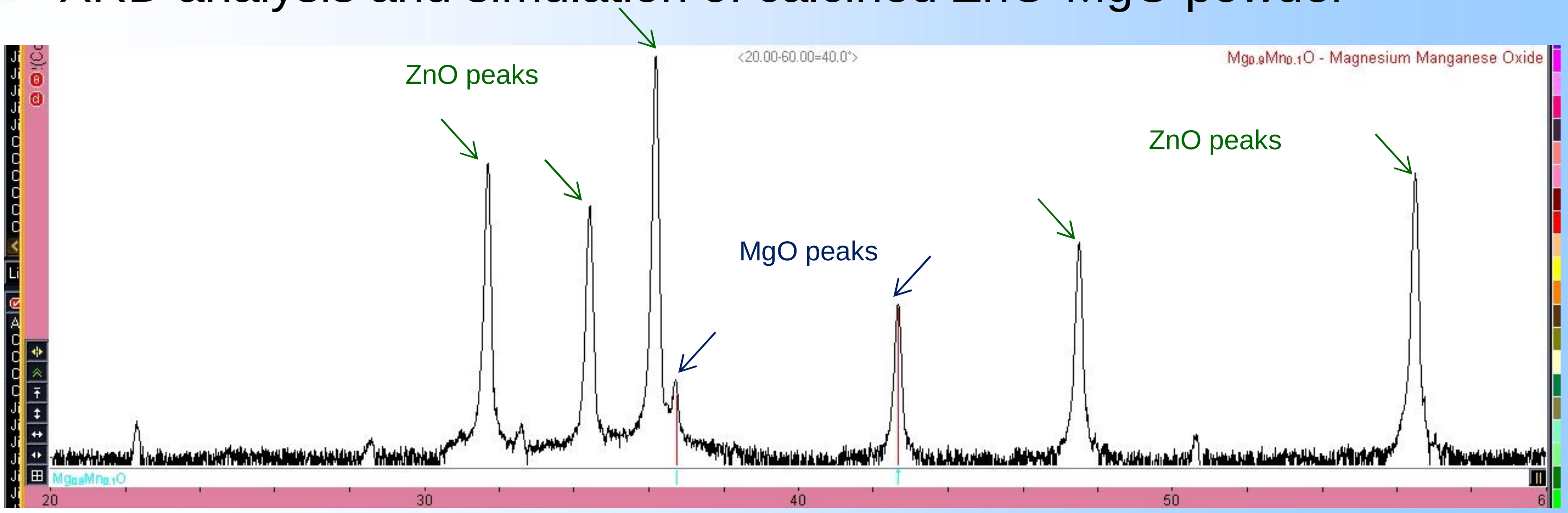
  - Mixing of ZnO and MgO powder for uniform distribution
  - Low temperature calcination (up to 1000^{o}C)
  - Ball milling in <u>water</u> for desired particle size distribution
  - High temperature (1000-1600^{o}C) sintering for densification

- As a reference, ball milling of the same amount of non-calcined ZnO-MgO mixed powder results in viscous “cake-like” slurry

- Calcination can be effective in reducing MgO hydration when using water-based colloidal processing

Exploration of water based process

- XRD analysis and simulation of calcined ZnO-MgO powder

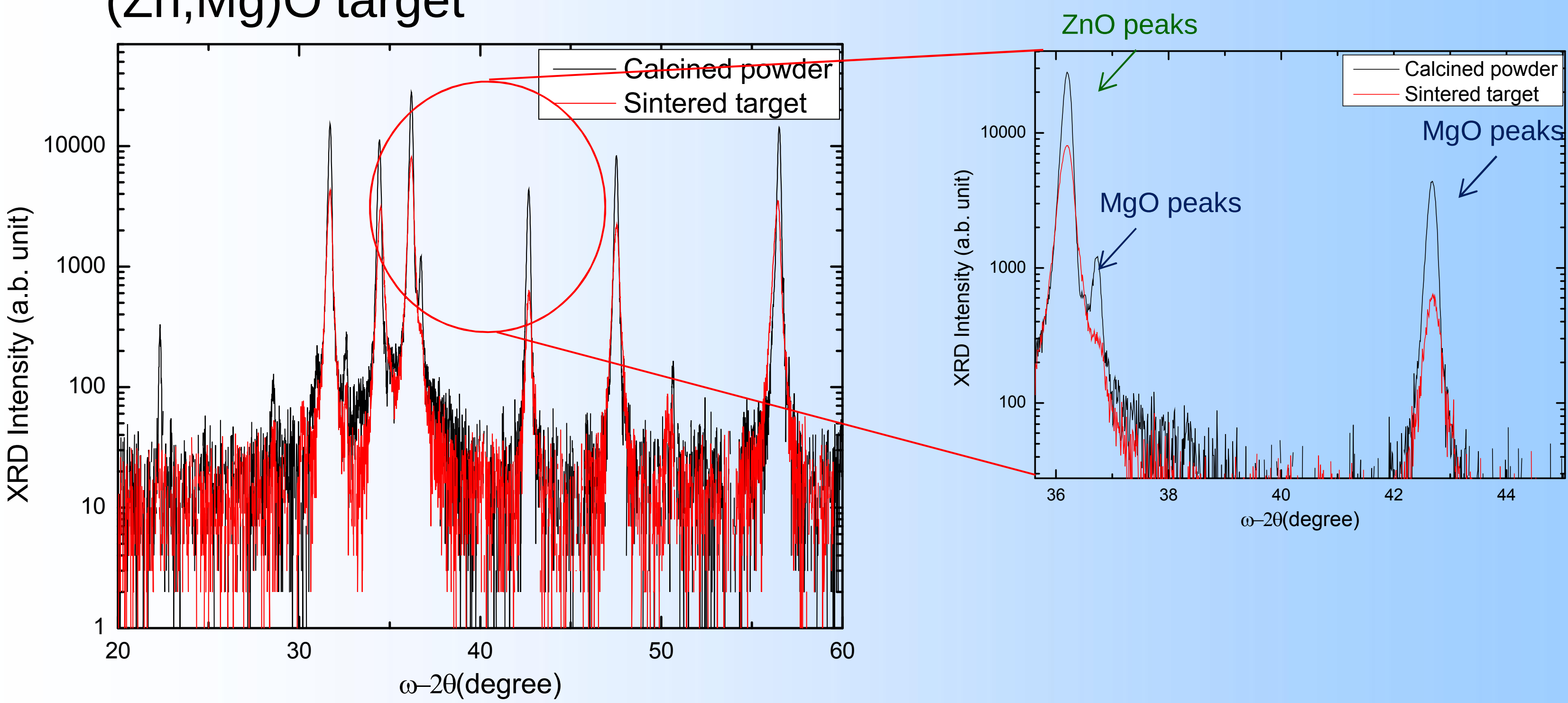


- The simulation indicates a larger lattice plane spacing compound.

- It's possible some weak ZnO-MgO bonds formed during calcination.

Exploration of water based process

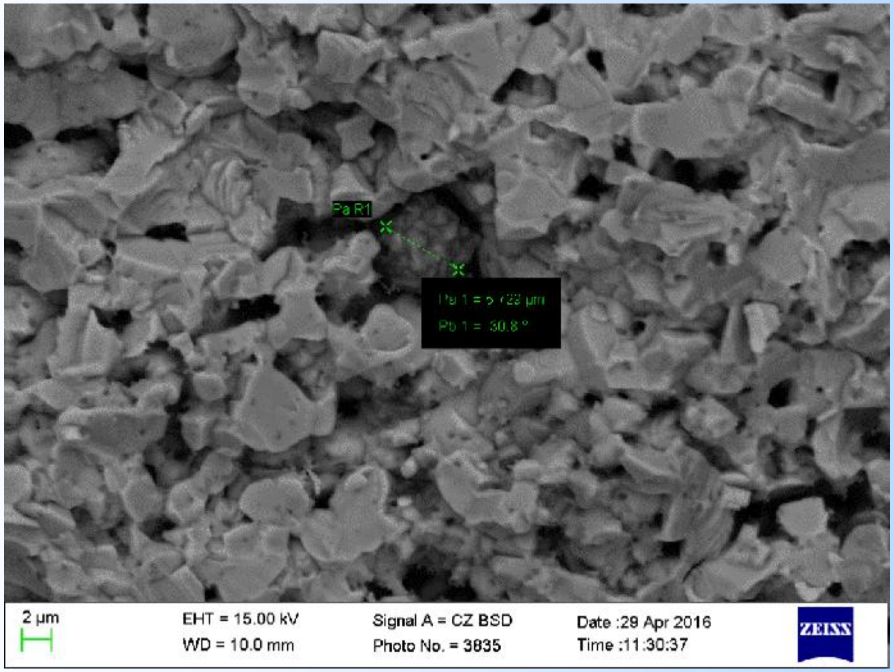
- XRD comparison of calcined ZnO-MgO powder and sintered (Zn,Mg)O target



- Comparing to calcined powder, the sintered (Zn,Mg)O target shows weaker MgO peaks.

Challenge of (Zn,Mg)O Densification

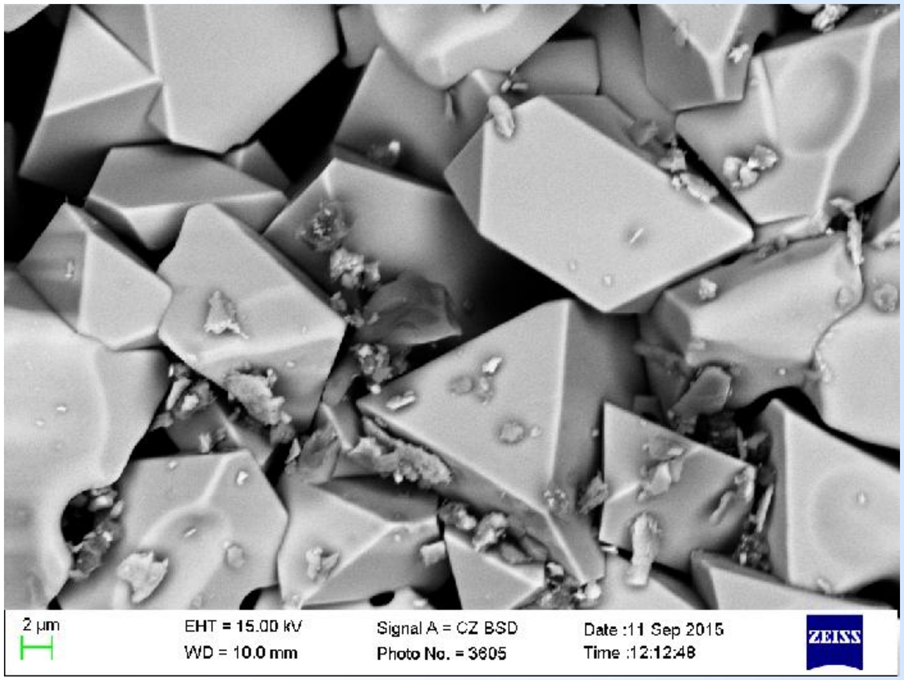
- Sinterability of ZnO-MgO mixture



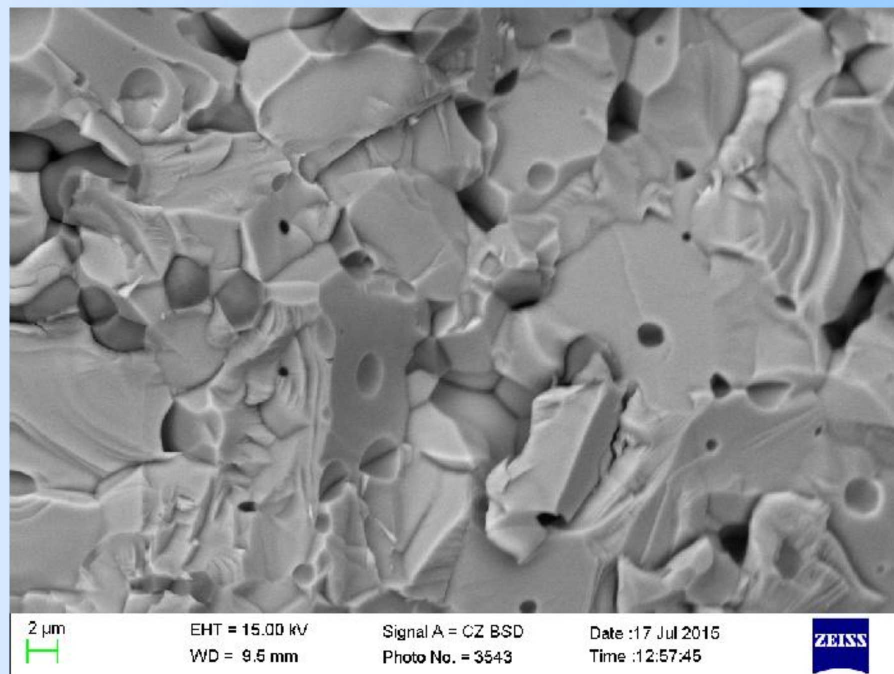
- High sintering T required to reach high density of (Zn,Mg)O
- Sintering aid can be considered for densification, e.g. Nb_2O_5
- Solid phase sintering through grain boundary diffusion
- Small amount of Nb_2O_5 has been selected as transition valence oxide. Formation of another phase at sintering should be eliminated

Challenge of (Zn,Mg)O Densification

- Nb_2O_5 doping for densification



With Nb_2O_5, 94%TD

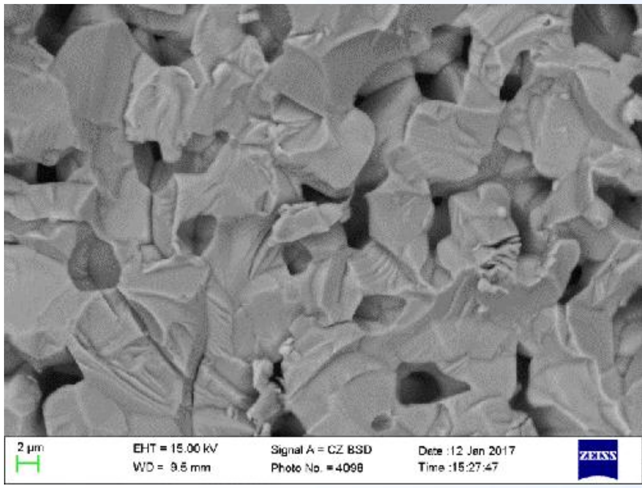


Without Nb_2O_5, 92%TD

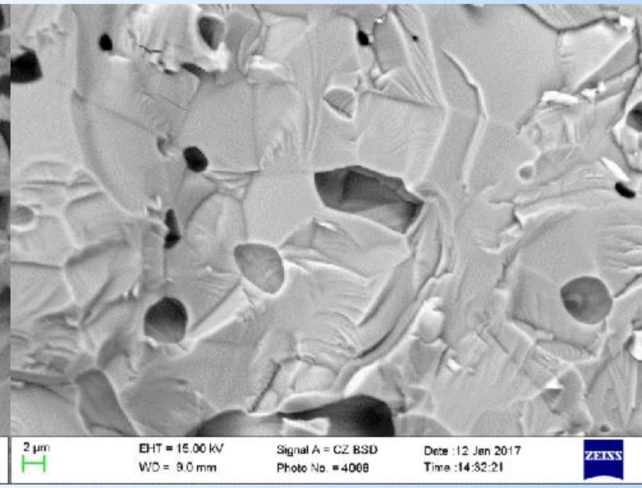
- Doping of Nb_2O_5 did increase the density under same sintering condition
- It also modified the microstructure of (Zn,Mg)O (wurtzite → rocksalt?)

Challenge of (Zn,Mg)O Densification: Different compositions

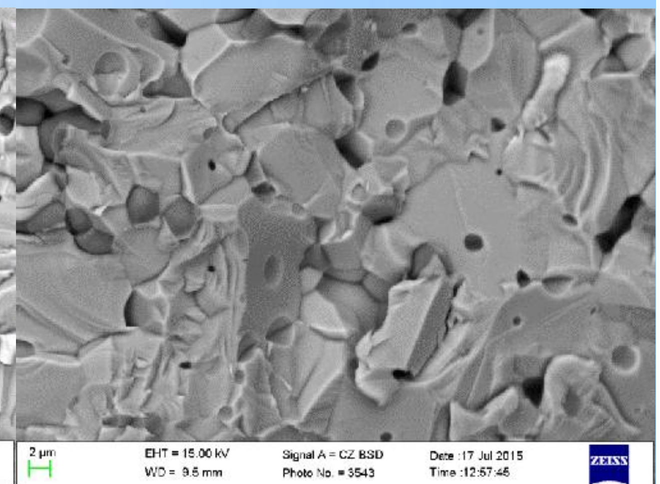
- SEM analysis on different MgO contents in ZnO matrix



5at% MgO



15at% MgO

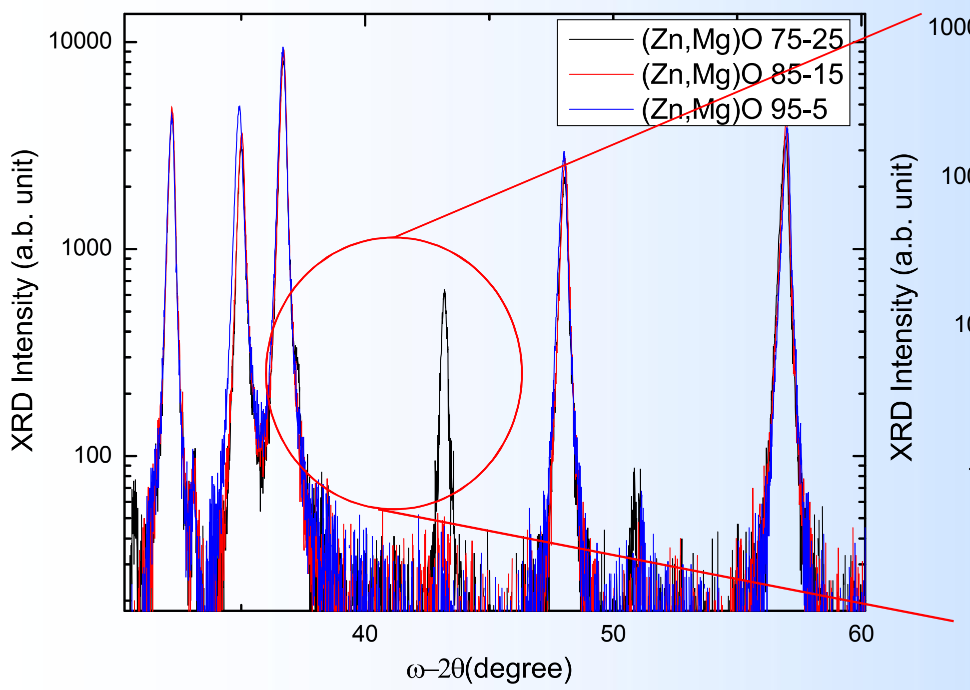


25at% MgO

- 5at%, 15at%, 25at% are nominal MgO contents in the composite.
- Sintering conditions were not optimized for each composition.
- Similar microstructure for the matrix composite
- 25at% shows MgO phase precipitation

Challenge of (Zn,Mg)O Densification: Different compositions

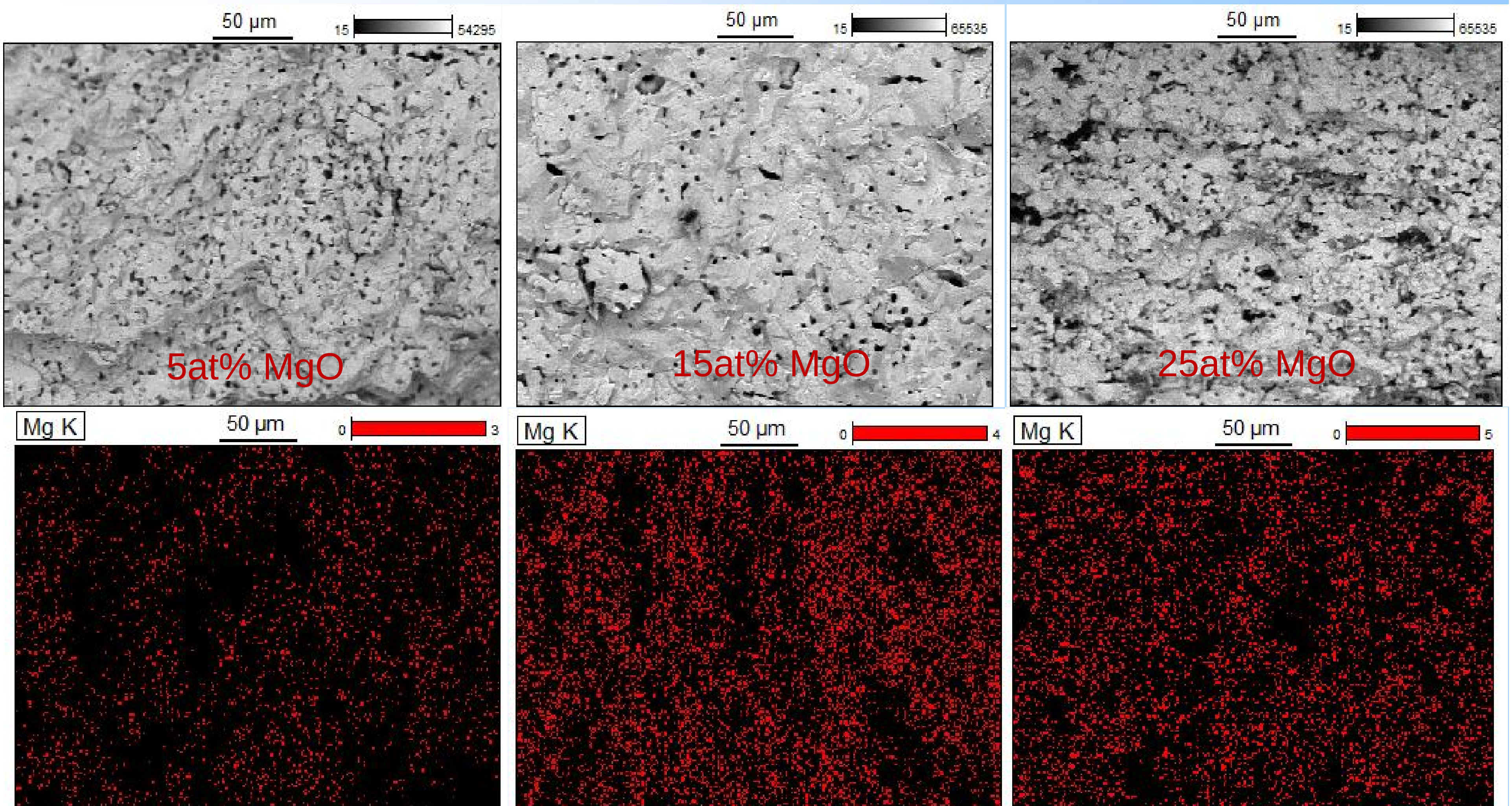
- XRD analysis on different MgO contents in (Zn,Mg)O



- XRD analysis of 25at% shows distinct MgO peaks.

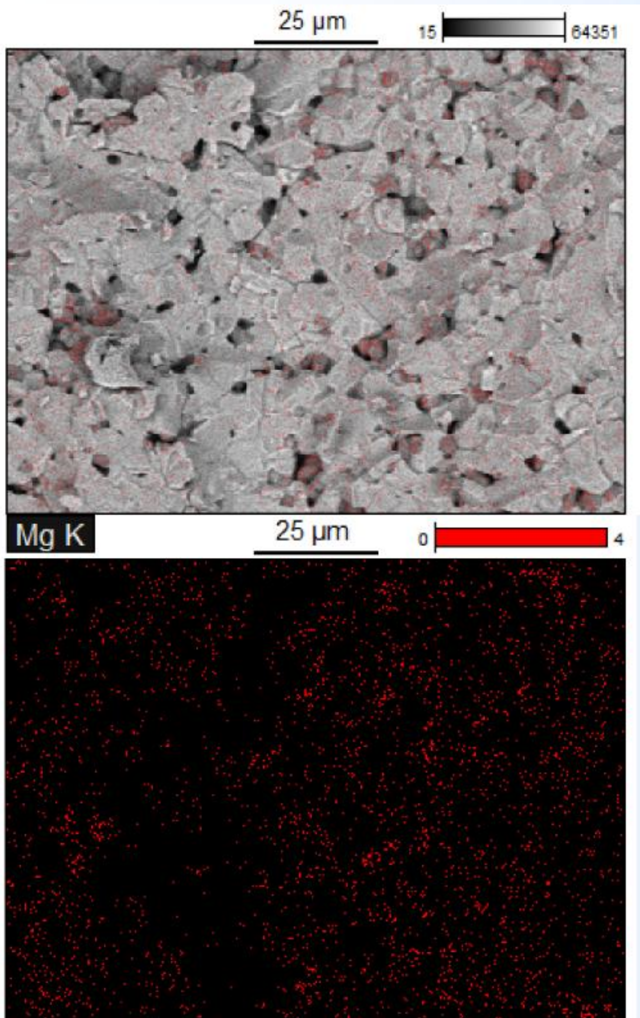
Challenge of (Zn,Mg)O Densification: Different compositions

- EDS analysis on different MgO contents in (Zn,Mg)O

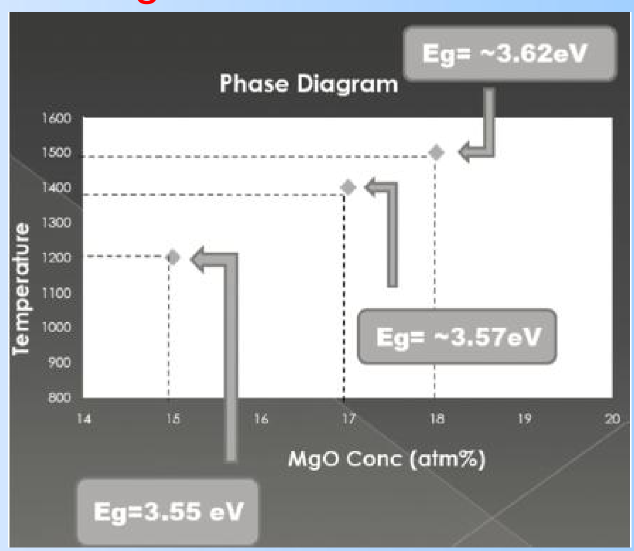


Challenge of (Zn,Mg)O Densification: Different compositions

- EDS analysis on different MgO contents in (Zn,Mg)O



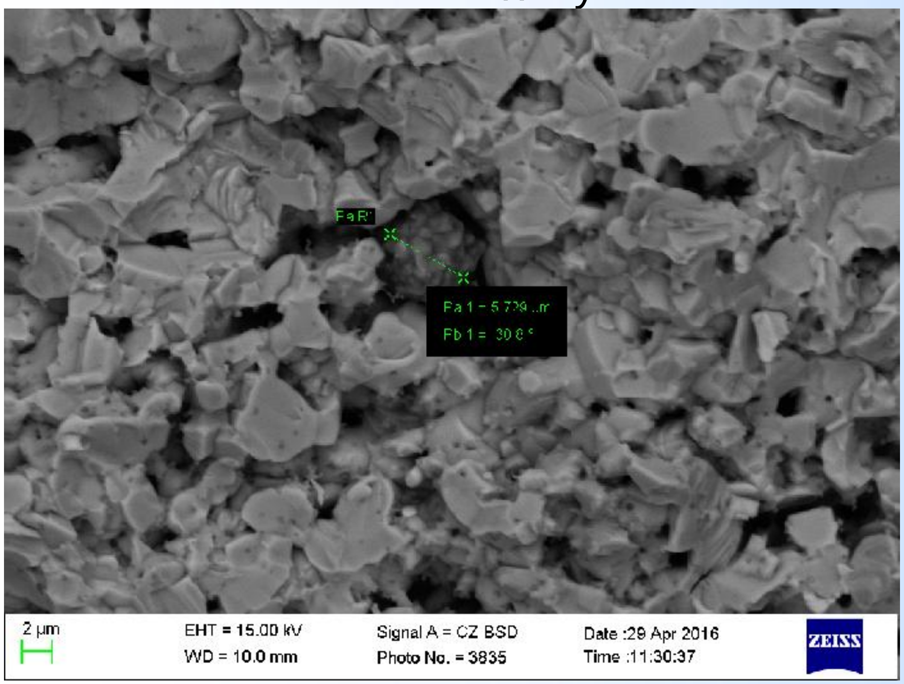
- Mg detected in 5at%, 15at%, 25at% composite matrix
- 25at% shows high Mg phase between (Zn,Mg)O matrix-- MgO precipitation
- MgO precipitation is due to 25at% exceeds the solid solubility in ZnO
- Precipitated MgO can be detected via XRD

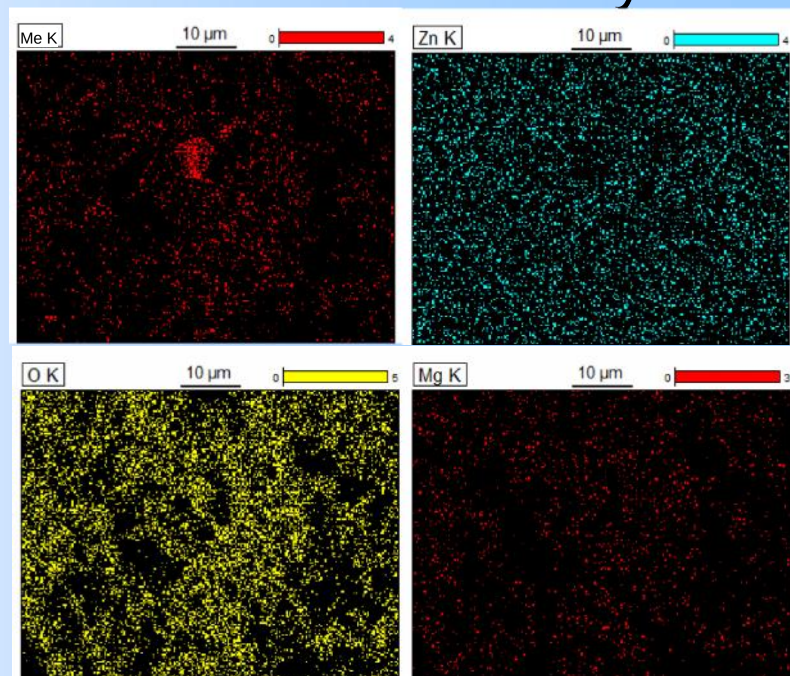


C. Bergstein, Clarification of Phase Diagram in a (Zn, Mg)O Pseudo Binary System by Using Ultra-Fine MgO Source Powder

Challenge of (Zn,Mg)O Sputterability

- Metal oxide (Me_xO_y) dopands for increase conductivity

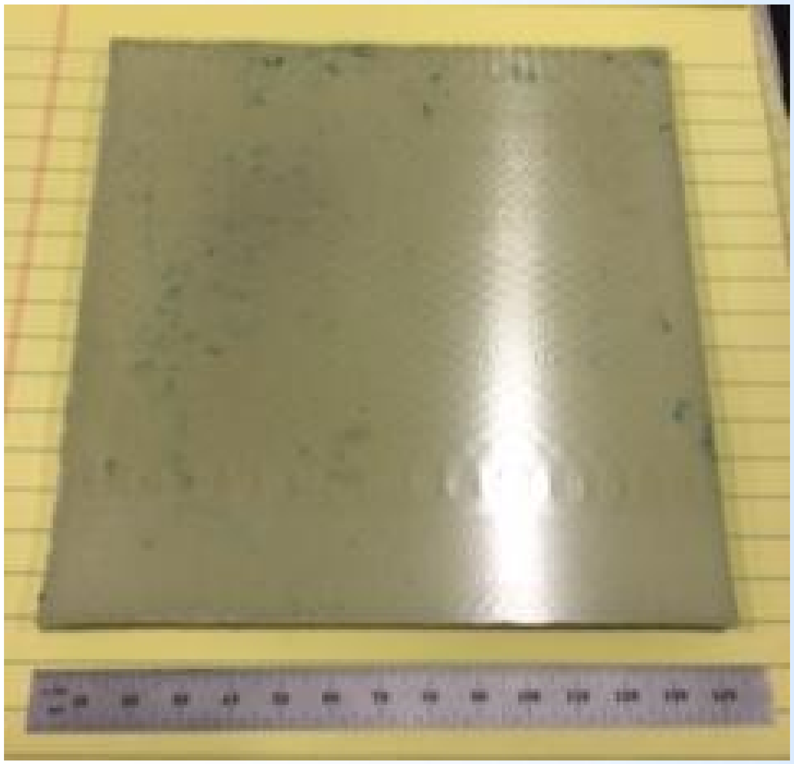


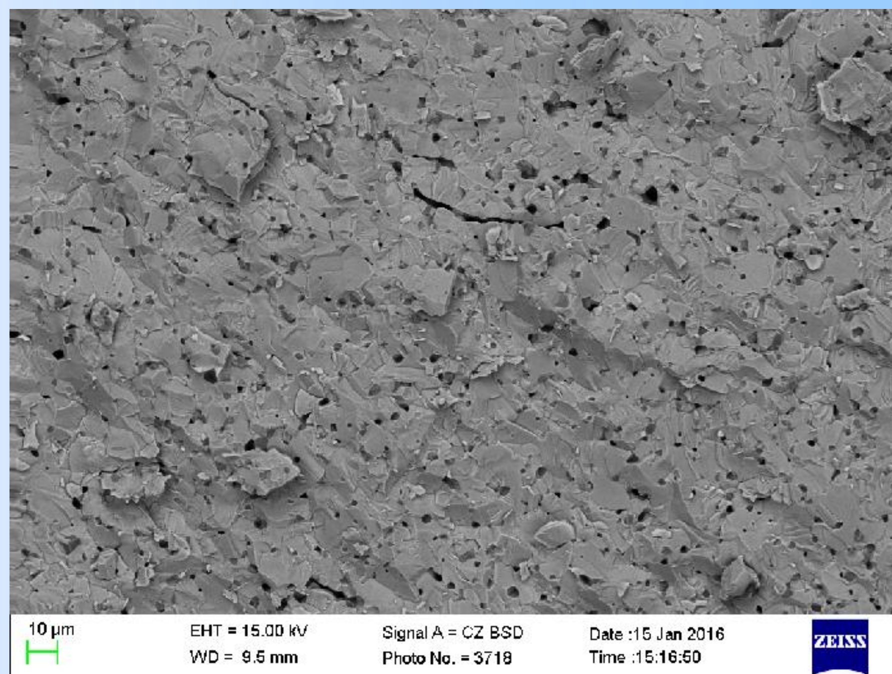


- Pressureless sintered, density up to 94% of TD
- Solid solution ZnO-MgO; no large MgO-Me_xO_y and ZnO-Me_xO_y spinel observed
- Doping Me_xO_y requires higher T to achieve similar density as the (Zn,Mg)O without dopants
- Conductive tile is preferred for DC-sputterable target
- The most conductive sample achieved: ~ 10^3 Ω.cm

Scale up process – on going

- ZnO-MgO large tile processing:





ZnO-MgO tiles, 94% of TD, area 161cm^2

Summary and Future Works

- ✓ ZnO-MgO ceramic sputtering targets with different MgO contents, density >90% of TD and high uniformity have been produced for the first time
- ✓ High electrical conductivity obtained allows DC sputtering process

- ➢ Further optimization of the ceramic processing: density increase
- ➢ Enlarge targets dimensions
- ➢ Rotary targets processing
- ➢ Sputtering process study and optimization; thin film evaluation

Thank you!