# Fabrication of Magnesium Oxide Ceramics with Density Close to Theoretical Using Nanopowders

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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

Superconductive Components (SCI) Formed
**1987**

SCI becomes a publicly traded company
**1989**

Formed Target Materials Corp.
**1991**

Patent Fine Particle Bi-Sr-Ca-Cu-O
**1999**

Patent, large strongly linked Monoliths
**2001**

Began rebranding company as SCI Engineered Materials
**2003**

Third Frontier Grant to commercialize Thin Film Battery materials
**2004**

Commercialize & scale-up of products for automotive
**2006**

Legally rename SCI Engineered Materials, Inc.
**2007**

Receive 3rd Frontier Grant to Commercialize AZO & Rotatable Capacity
**2008**

MgO development
**2014**

TCO Development for Displays
**2015**

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

# Contents

- **Introduction to Magnesium Oxide**
- Ceramic sputtering targets manufacturing process
- Nano-powder for MgO manufacture
- High density MgO manufacture

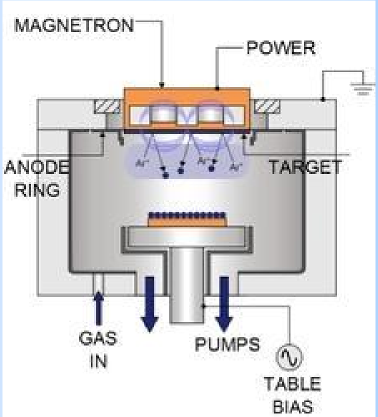
# Introduction to MgO

- Properties
  - Very stable physically – ionic bond
  - Not electrically conductive
  - Chemically inert
  - Dissolves in water and slightly basic
  - High strength
  - Stable at very high temperature
  - High thermal conductivity

- Application
  - Electrical insulator
  - Anti-corrosion coating
  - Heart burn relief
  - Desiccant
  - Refractory
  - Sputtering targets for thin films for special electronic applications

# Introduction: scope of this work

- Developing high density, low porosity and high purity MgO 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 thermal conductivity → low chance of cracking during sputtering

  - High purity → particular thin film properties and consistency

  - Particular microstructure: a) fully dense, no restriction for grain size

    b) structure with small grain size

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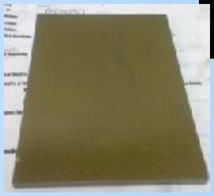
# Ceramic sputtering target manufacture process

## Process Flow

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

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

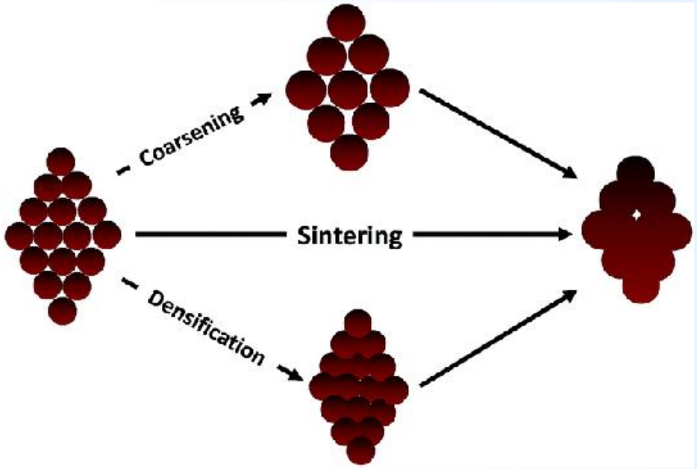


- Milling: reduction of particle size to improve sintering and homogeneity
- Forming: shape small particle powders into a solid piece by applying pressure, e.g. uniaxial or cold isostatic pressing, or by casting (slip casting, gel casting, pressure filtration)
- Sintering/Hot Press/HIP: the process of 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

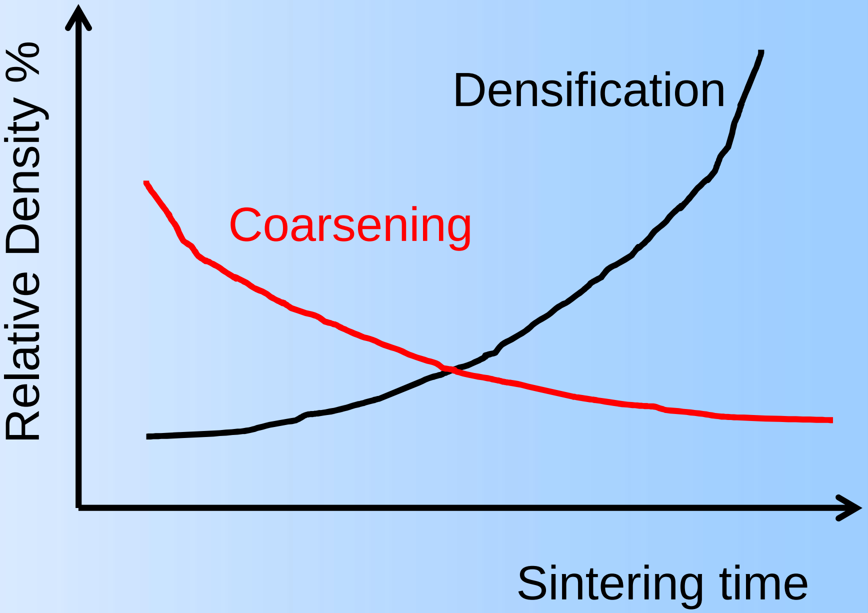
# Ceramic sputtering target manufacture process

- 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.

# Ceramic sputtering target manufacture process

- Hot pressing process:
  - Pressure-assisted process for metallic or ceramic powders to form a high density, solid pieces most likely in disk or plate shape.
  - Controllable variables including temperature; soak time and pressure; the rate pressure is applied; atmosphere, etc.

I. Pressure applied in hot pressing increases the driving force (diffusion) of densification thus requiring lower temperature and shorter soak time.

II. Control and adjustment of grain size and microstructure for hot pressing parameters.

$$\rho = \rho_{*} + k\ln(t); \quad G = G_0 + Kt; \; dG/dt = (G.K)/[G_j(1-\rho)]$$ *(P – density; G – grain size; t- time)*

III. Part size by hot pressing process is more limited by the equipment.

IV. Hot pressing is more expensive than pressureless sintering in general.

# Ceramic sputtering target manufacture process

- Challenge of manufacturing high density MgO:
  - Demands of high density – 99.5% or higher, high structure uniformity
  - Particular grain size depending on application and film processing features
  - High purity – greater than 99.9% (3N+)
  - High reactivity of MgO powder with water restricts the manufacturing capability
  - Industrial equipment limits, e.g. for rather large size targets (up to 12” dia.)

How to overcome these issues?

- ➢ High activity of starting materials, e.g. nano-size powders
- ➢ High purity of starting materials (99.99%); commercial powders
- ➢ No sintering aids
- ➢ Available production equipment
- ➢ Technology to reach almost 100% of TD with controllable grain size

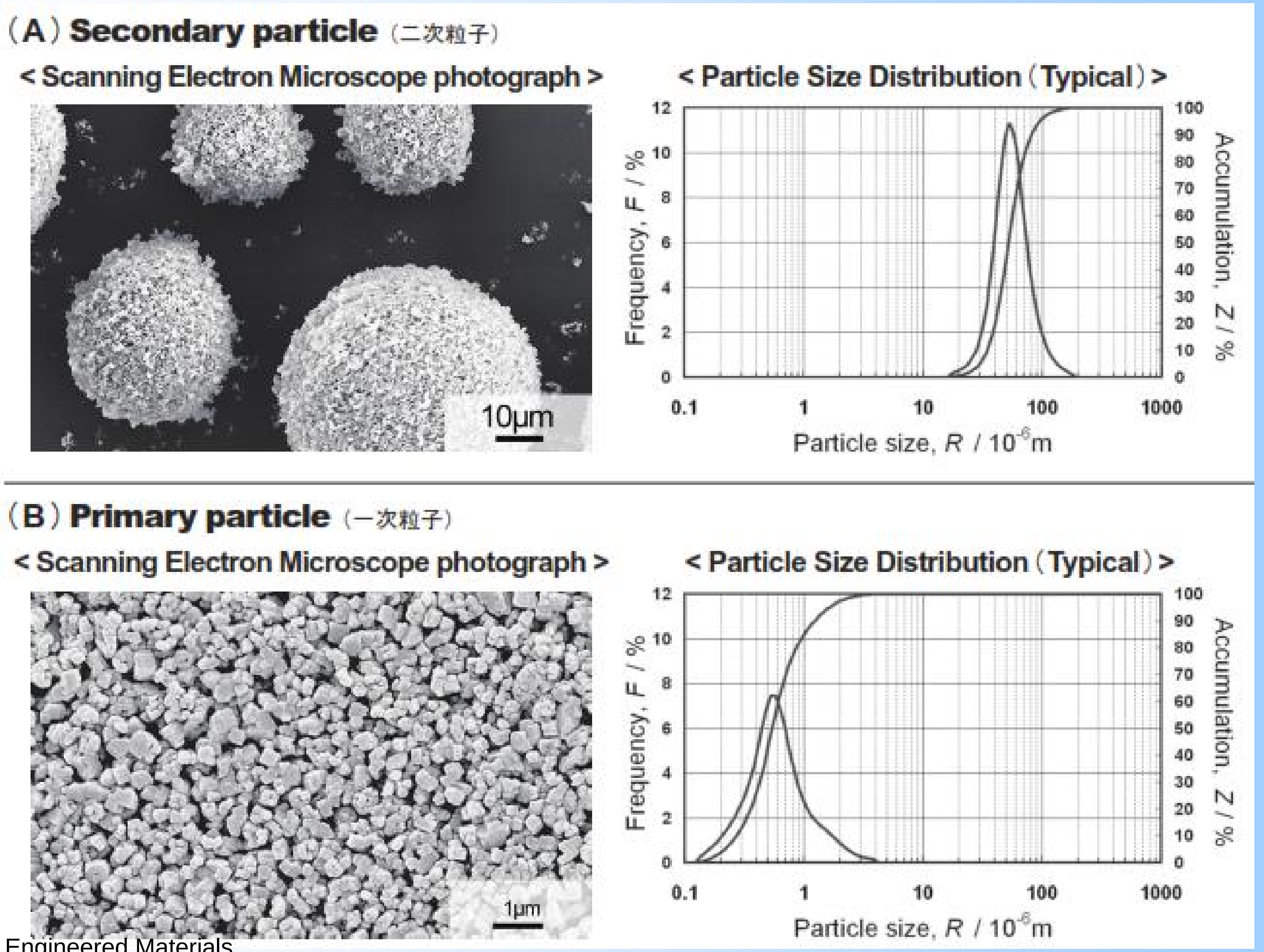
# Ceramic sputtering target manufacture process

- Manufacturing route selection:
  - Nano-size, high purity (4N) starting MgO powders, commercially available
  - Hot pressing technology (hot press available in-house)
  - Post-HP annealing
  - Grinding (machining)
  - Bonding to metallic substrate
  - QC at each processing step

# Contents

# Nano-powder for MgO manufacture

- Specification from vendor:



**(A) Secondary particle** (二次粒子)

< Scanning Electron Microscope photograph >

< Particle Size Distribution (Typical) >

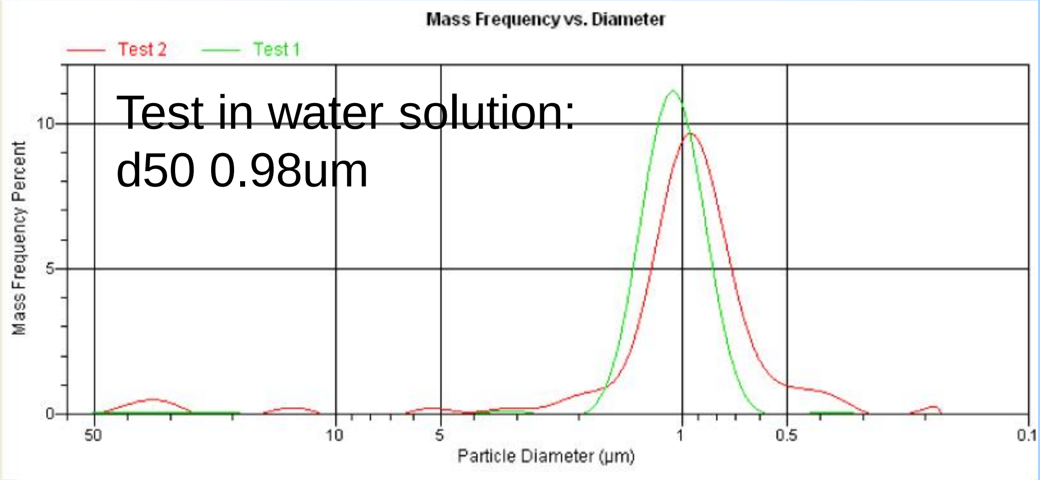
**(B) Primary particle** (一次粒子)

< Scanning Electron Microscope photograph >

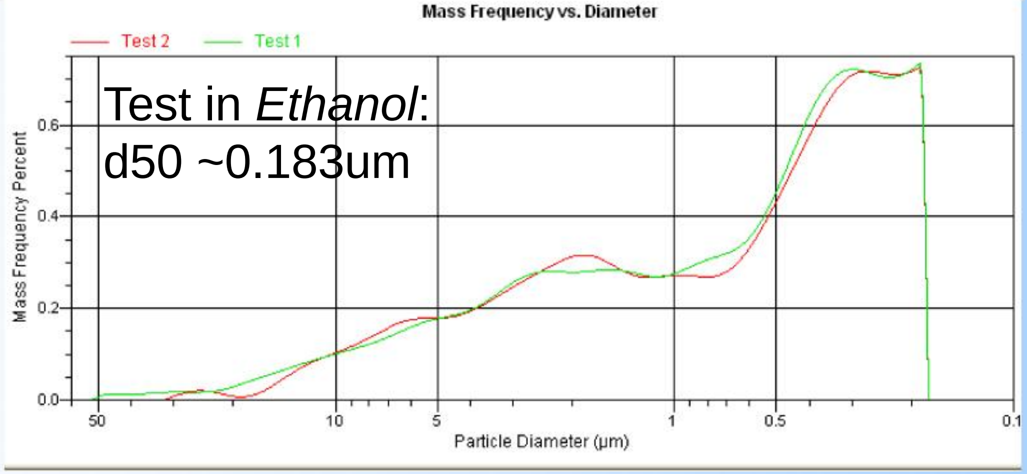
< Particle Size Distribution (Typical) >

# Nano-powder for MgO manufacture

- Sedigraph test:



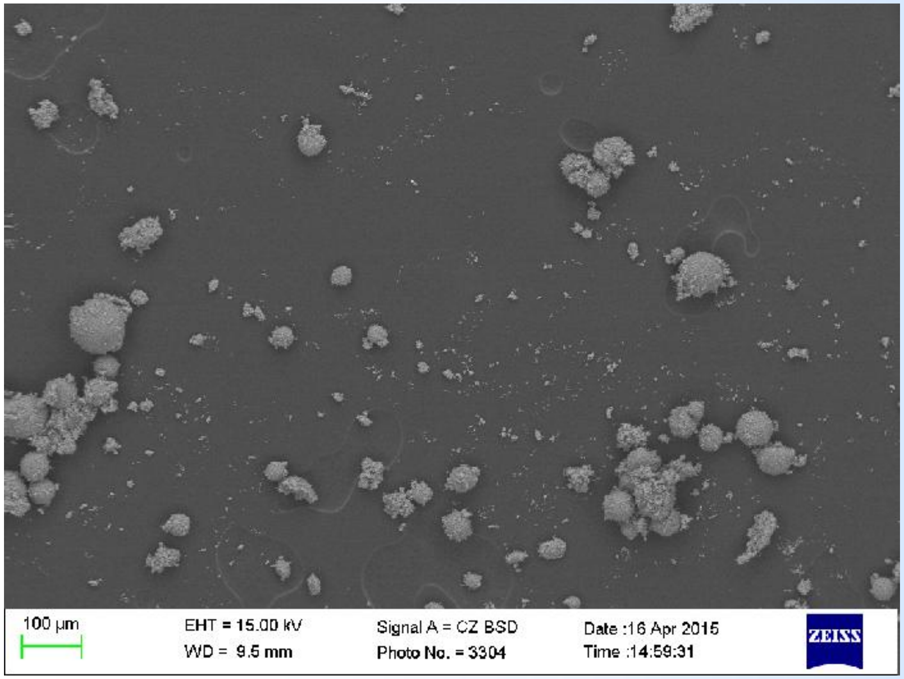
Test in water solution:
d50 0.98um

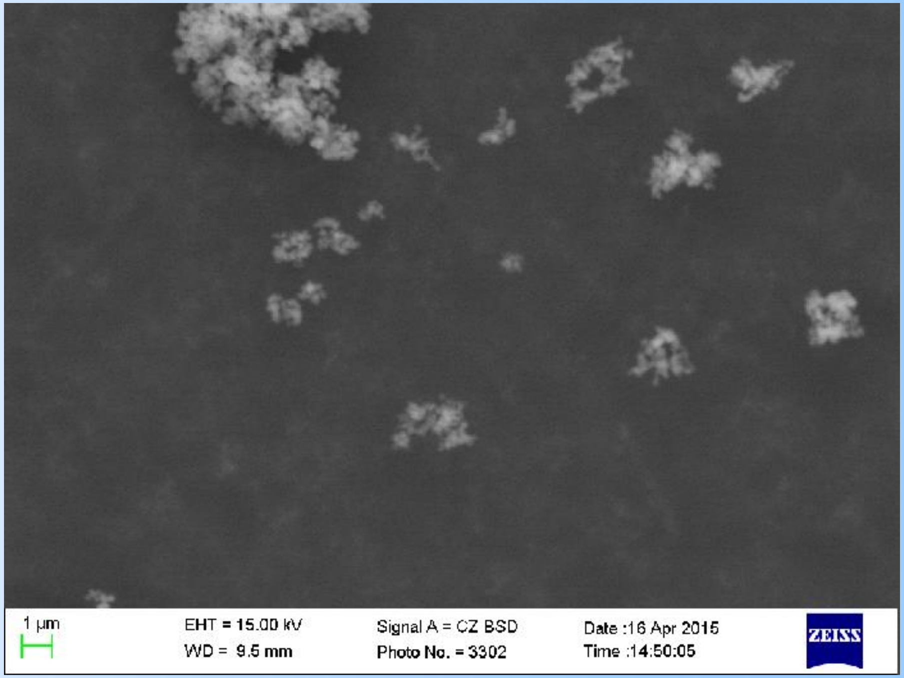


Test in *Ethanol*:
d50 ~0.183um

# Nano-powder for MgO manufacture

- SEM in house:





- The high purity MgO powder is commercially available.
- Particle size d50 ~0.18 µm

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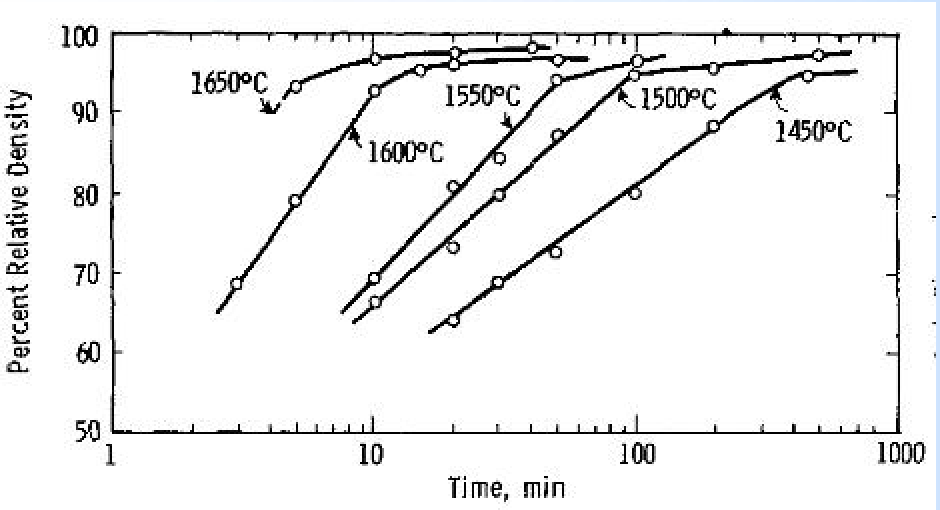
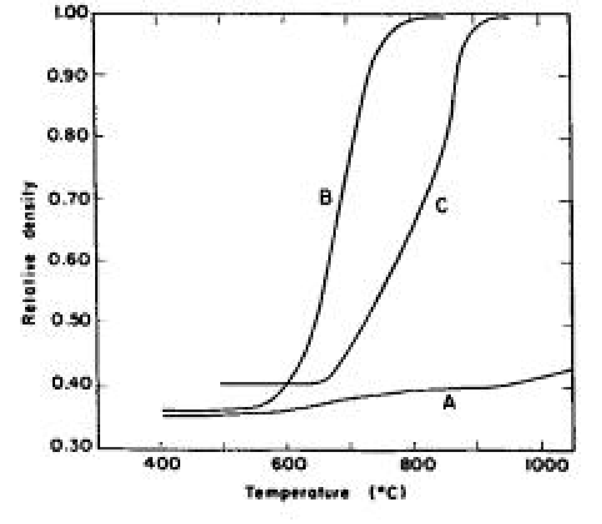
- **High density MgO manufacture**

# High density MgO manufacture

- Literature data:
  - Requires very high temperature >1500C to get close to TD with pressureless sintering
  - With pressure-assisted sintering, additive such as LiF was often added for liquid phase sintering; Mg(OH)2, MgCO3 etc. can be added without the introduce of impurities.
  - An example of the process to reach close to 100% TD: pressureless sintering (1400C)→hot pressing (1500C)→HIP(1400-1600C)→Annealing(1550C) (US patent: 8,454,933,B2)



Gupta, J. Matt. Sci. 1971



Beneche et. al., *JACerS*

# High density MgO manufacture

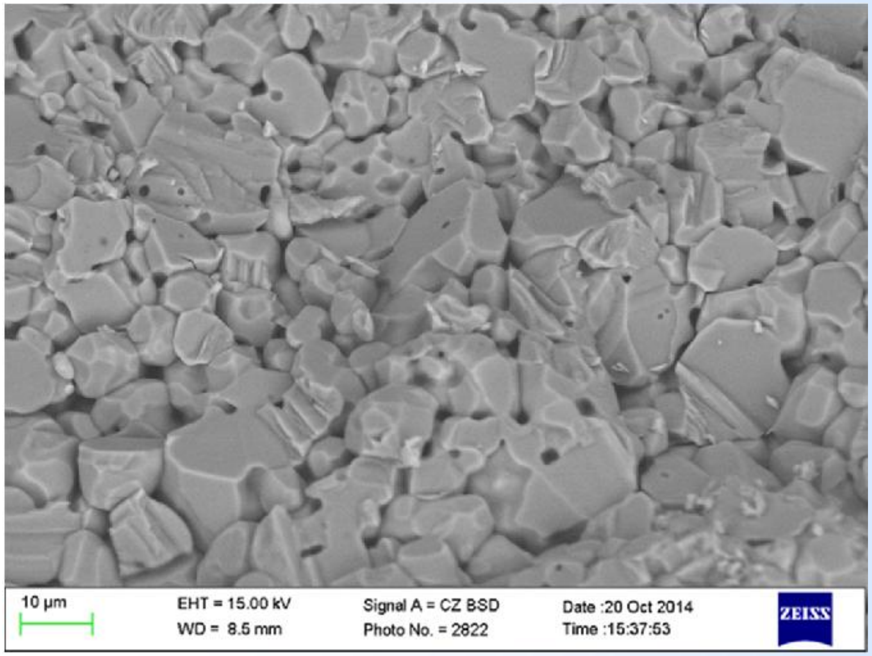
- Manufacture process:
  - Low temperature (0-1000°C) *starting powders calcination*
  - High temperature (1000-1600°C) sintering for densification *(hot pressing)*
  - Post HP annealing (0-1600°C) for reaching 100% of TD and to remove C diffused from the die *(conventional furnace)*

Experimental works focused on:

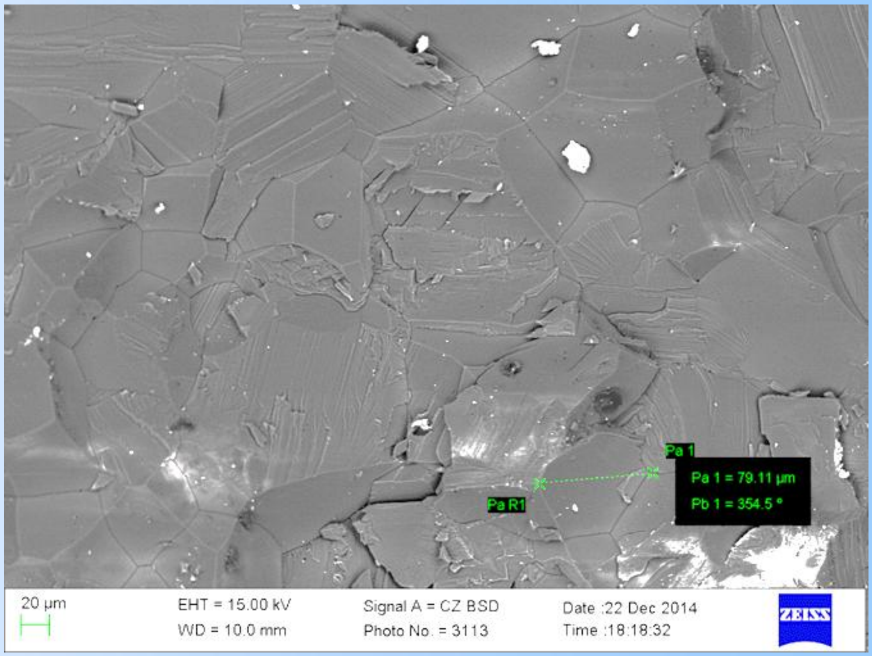
- Optimization of starting material (MgO) transformation
- Optimization of pressure – temperature – soak time during hot pressing
- Optimization of temperature – soak time during annealing in conventional furnace
- Optimization of structure, uniformity and grain size

# High density MgO manufacture

- Optimization of pressure – temperature – soak time to achieve higher density MgO:



95% TD →

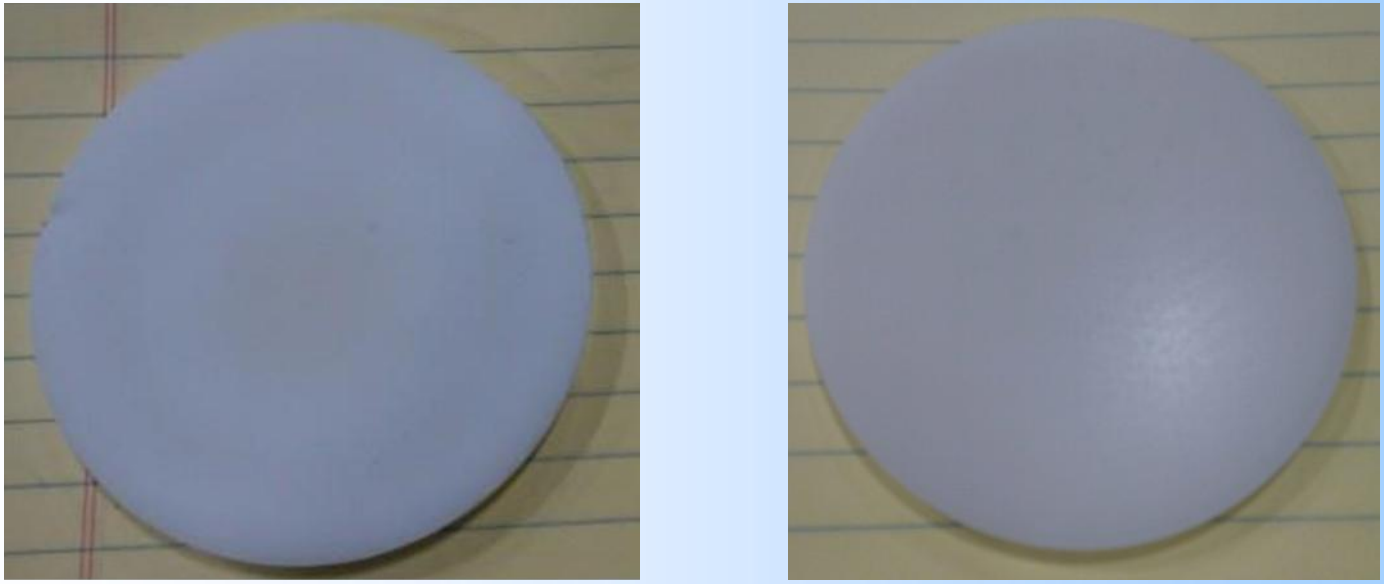


>99.5% TD

- Increase the density

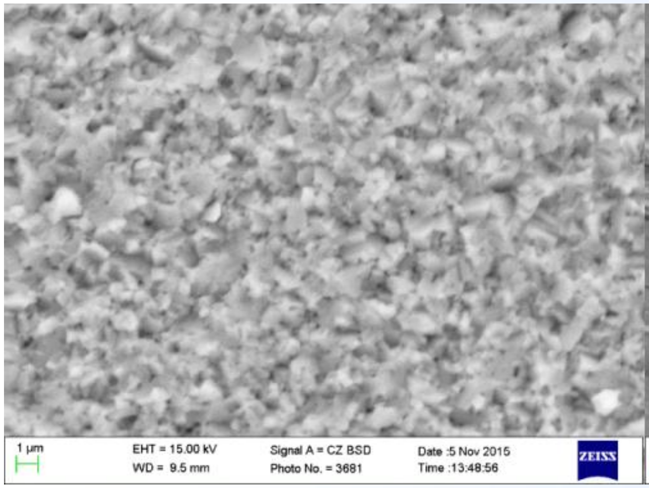
# High density MgO manufacture

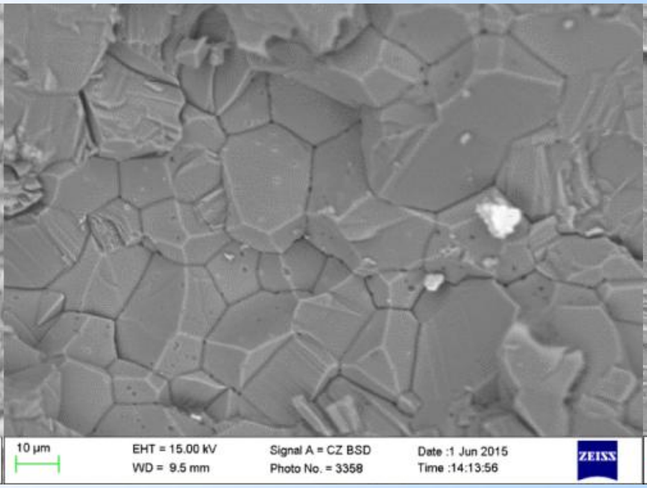
- Optimization of pressure – temperature – soak time to achieve uniformity of the body:

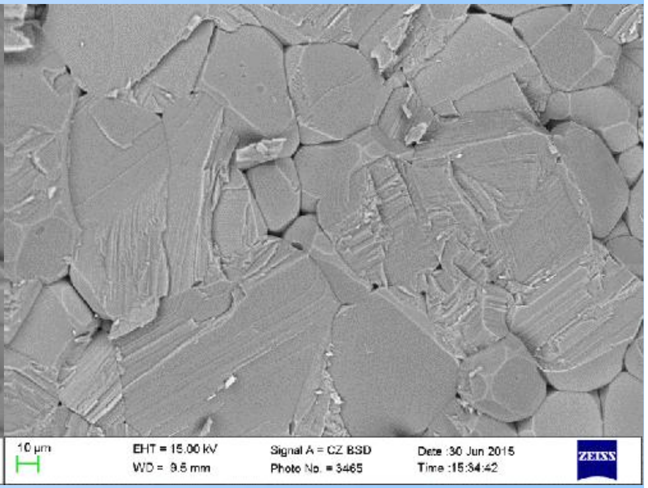


# High density MgO manufacture

- Optimization of pressure – temperature – soak time to achieve different grain size:





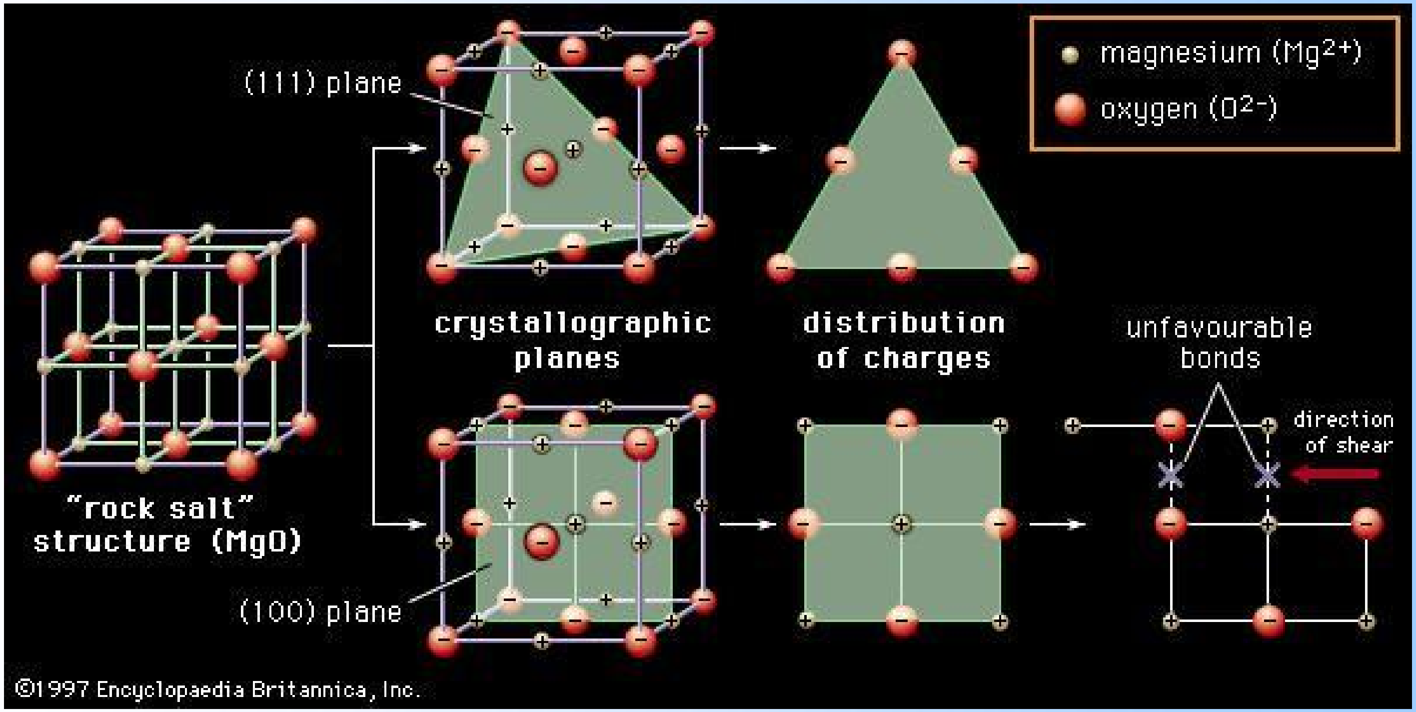


Grain size: <5µm ~ 20µm ~ 50µm

- < 1% of porosity → <0.5% of porosity

# High density MgO manufacture

- Anisotropy analysis of high density MgO



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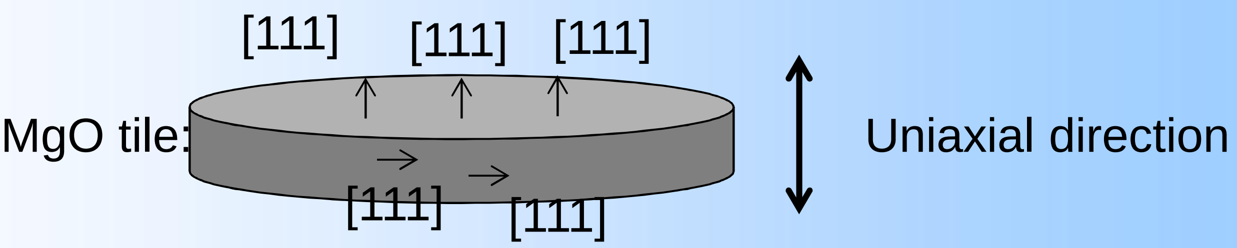


[111] [111] [111]

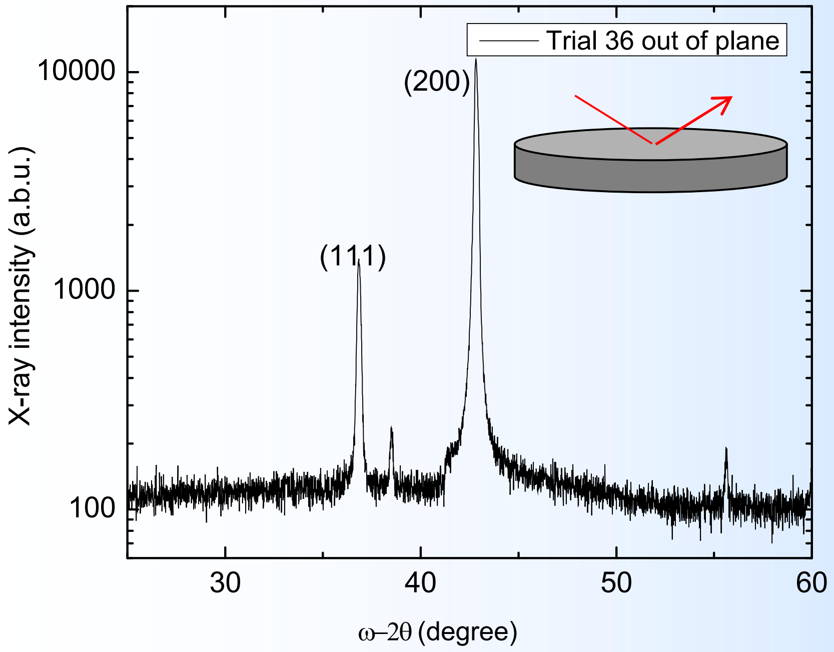
MgO tile:

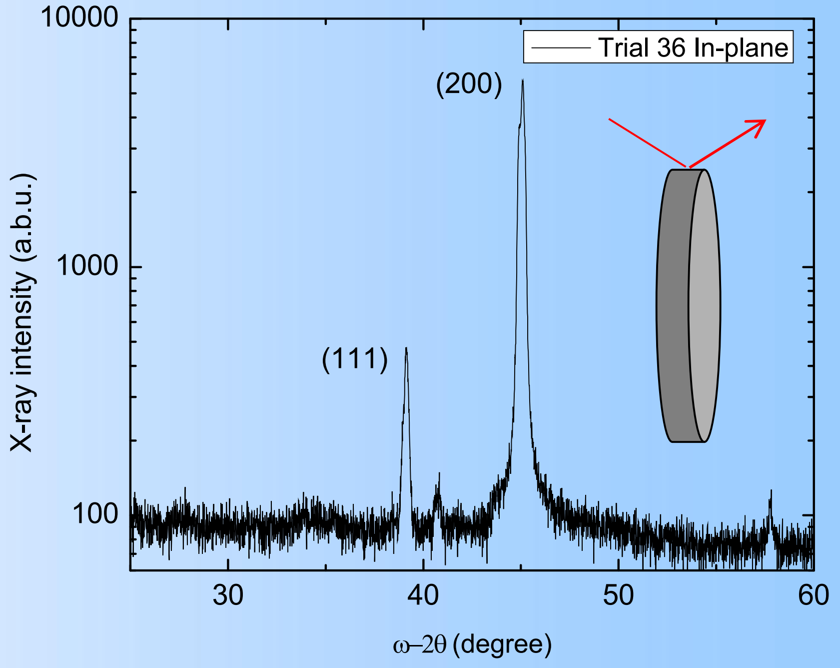
[111] [111]

Uniaxial direction

# High density MgO manufacture

- Anisotropy analysis of high density MgO

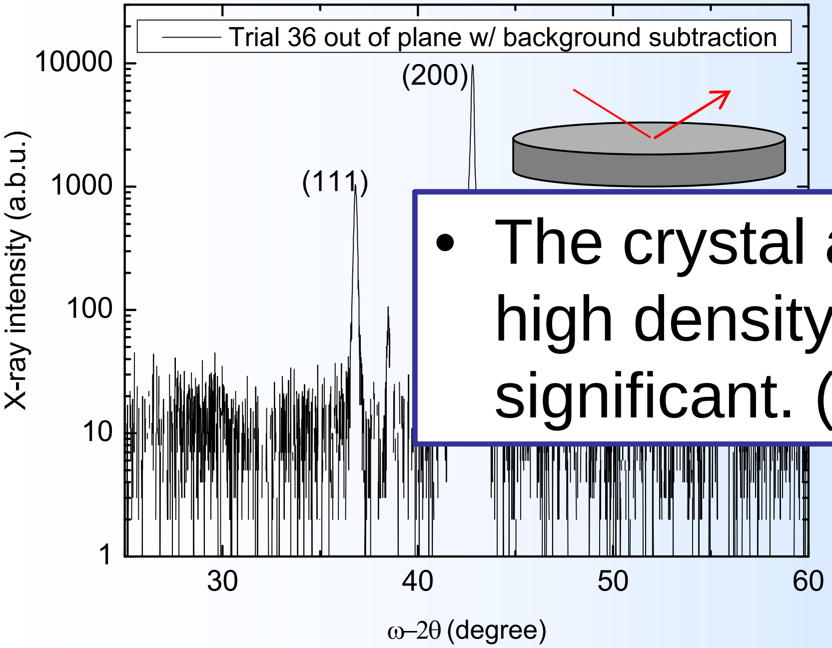


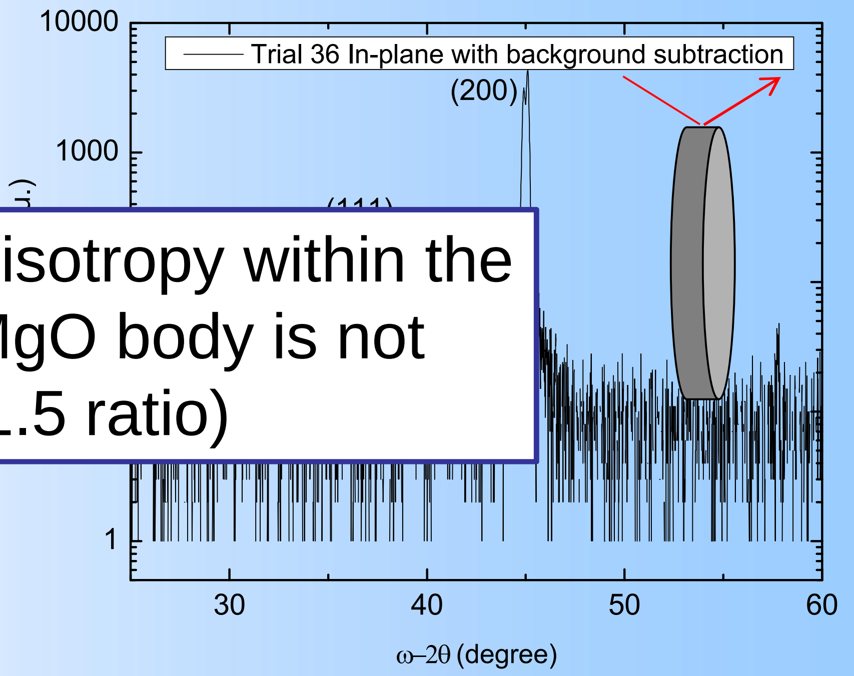


| Intensity | I (111) | I (200) | α (111) | ratio |
|---|---|---|---|---|
| Out of plane | 1400 | 11237 | 0.11 | 1.41 |
| In plane | 474 | 5610 | 0.078 | |

# High density MgO manufacture

- Anisotropy analysis of high density MgO



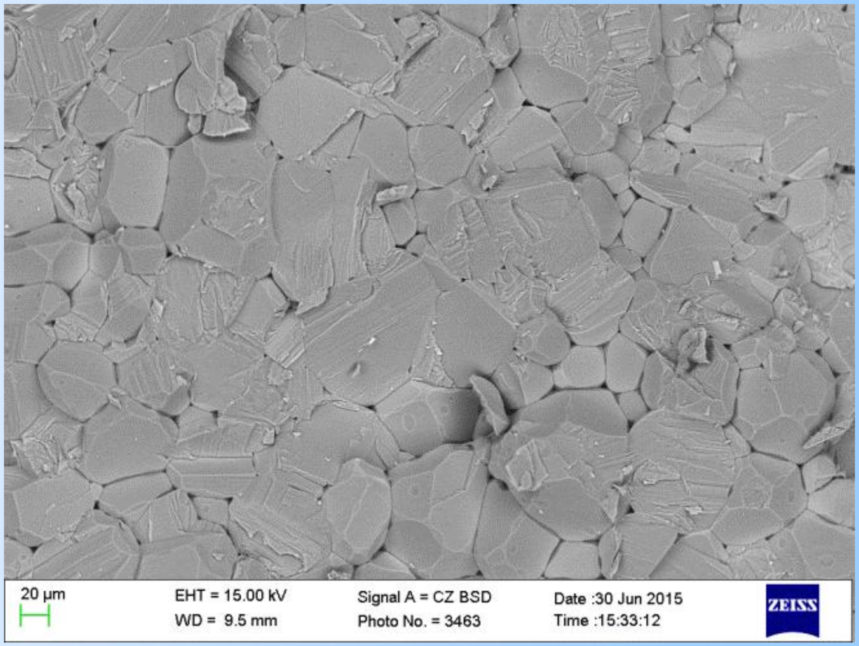


- The crystal anisotropy within the high density MgO body is not significant. (<1.5 ratio)

| Intensity | I (111) | I (200) | α (111) | ratio |
|---|---|---|---|---|
| Out of plane | 1400 | 11237 | 0.11 | 1.41 |
| In plane | 474 | 5610 | 0.078 | |

# High density MgO manufacture

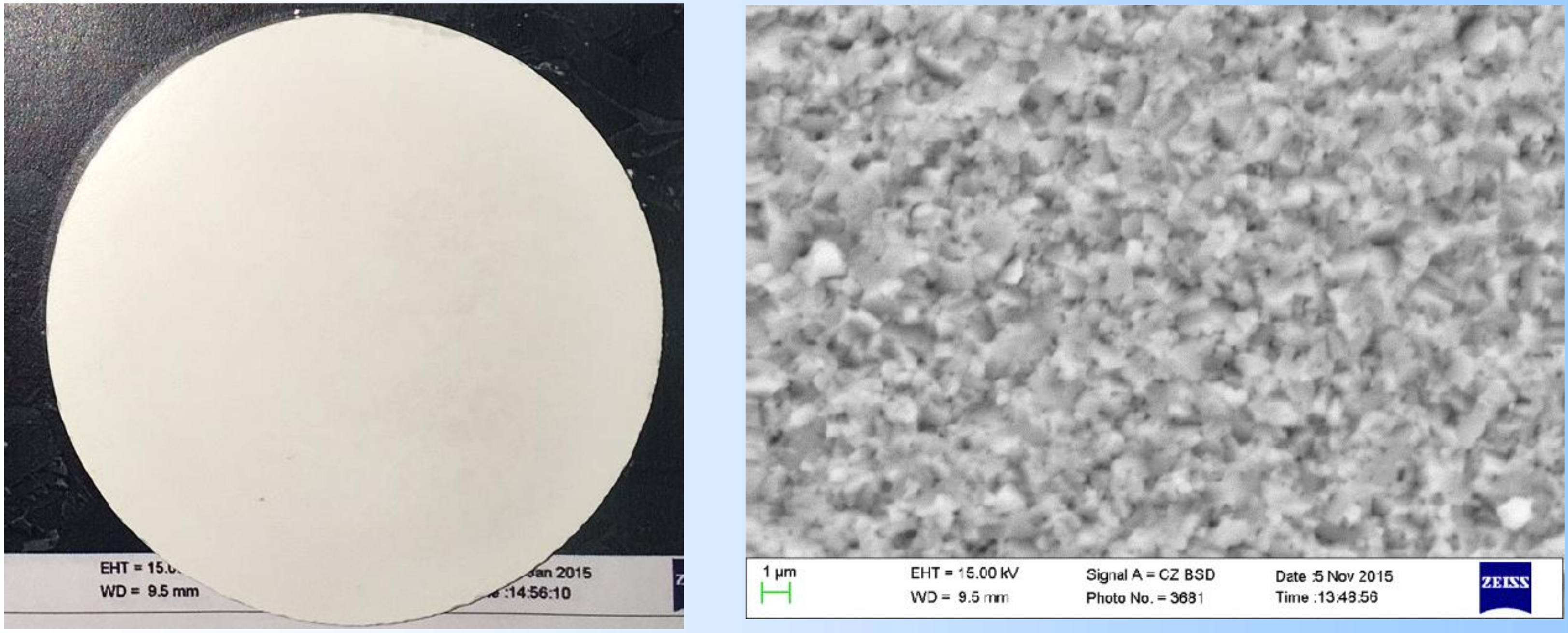
- High density MgO with large grains:



  - Translucent
  - ~ 50um grains
  - 99.99% purity
  - Up to 8” *diameter (3” OD in display)*

# High density MgO manufacture

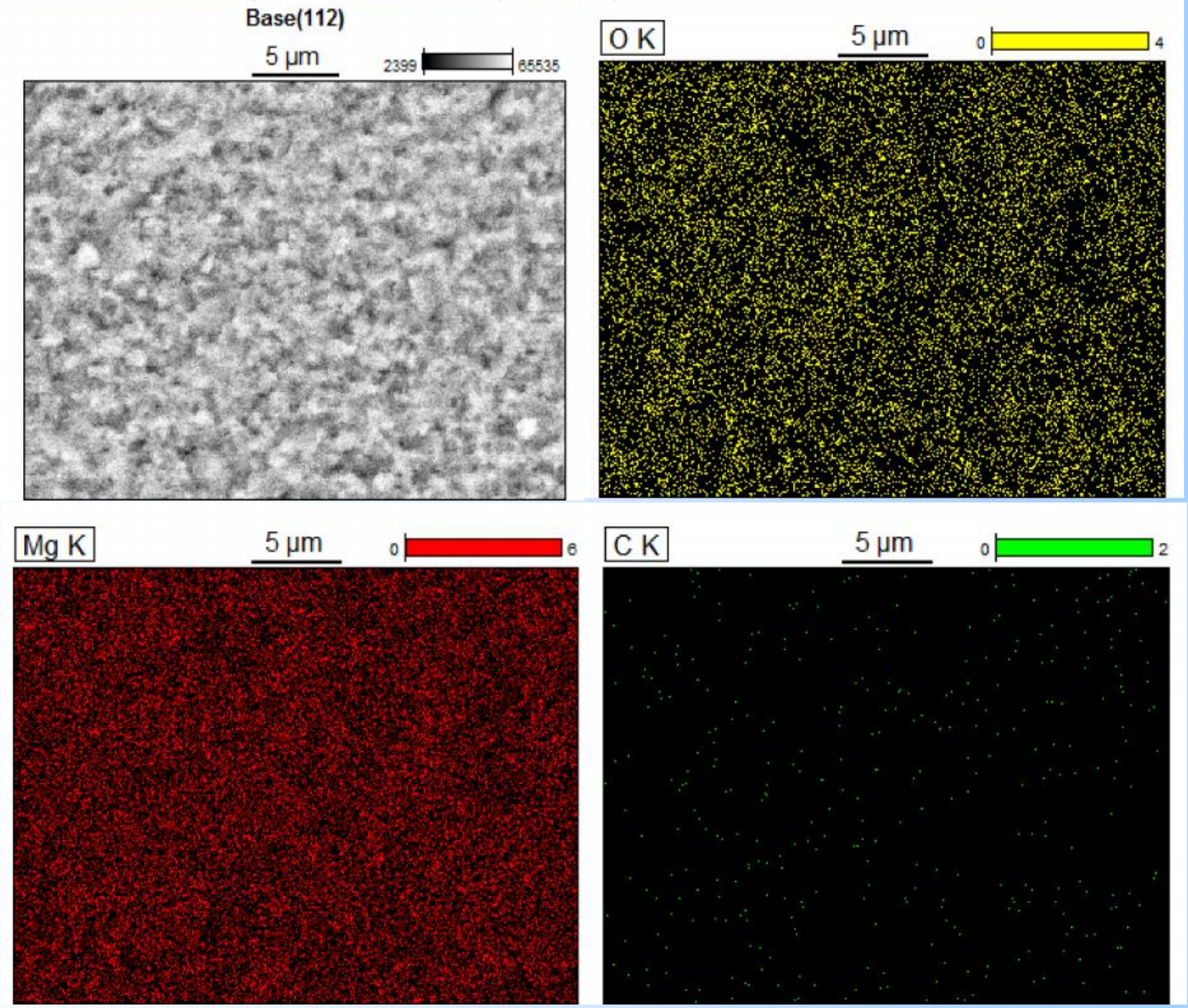
- High density MgO with small grains:



  - Lower sintering temperature
  - White, opaque
  - < 5um grains
  - 99.99% purity (3” OD in display)

# High density MgO manufacture

- EDS analysis of high density MgO:



# Summary

- *Using selected commercial nano-powders, SCI successfully manufactured MgO ceramics with density close to 100% of TD (porosity less than 0.5%) and min. 99.95% purity.*
- *By controlling sintering conditions, the grain size of the MgO ceramics can be tuned for different applications without sintering aids.*
- *Discs with diameters up to 8" (~200 mm) have been successfully manufactured without special investment.*

*Thank you!*