# Reaction of Lanthanide Zirconate Pyrochlore Environmental Barrier Coating Materials in CMAS

AUBURN UNIVERSITY

SAMUEL GINN COLLEGE OF ENGINEERING

Jeffrey W. Fergus

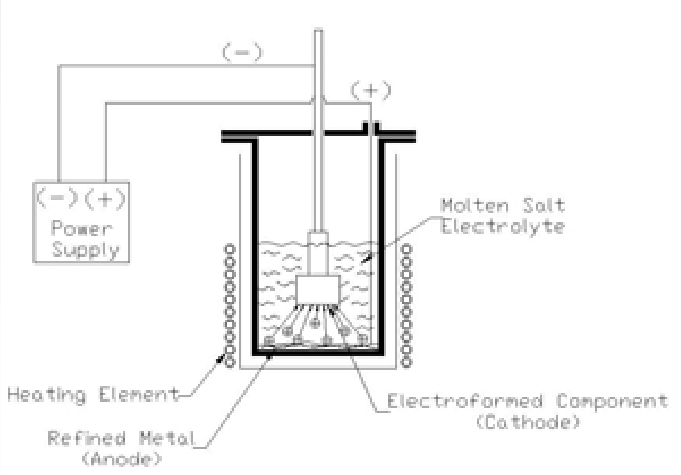
2015 Crosscutting Research Review
Pittsburgh, PA
28 April 2015

# Participants

- Auburn University
  - Jeff Fergus
  - Honglong (Henry) Wang – Ph.D. Student
  - Xingxing Zhang – Ph.D. Student
  - Emily Tarwater – Undergraduate Student
  - Sudip Dasgupta – Visiting Scholar (Summer 2014)
- Plasma Processes LLC
  - Kyle Murphree
  - Tim McKechnie

# Bond coat system

- Collaboration with Plasma Processes LLC
- Alternative bond coat layers
- YSZ / zirconate coatings

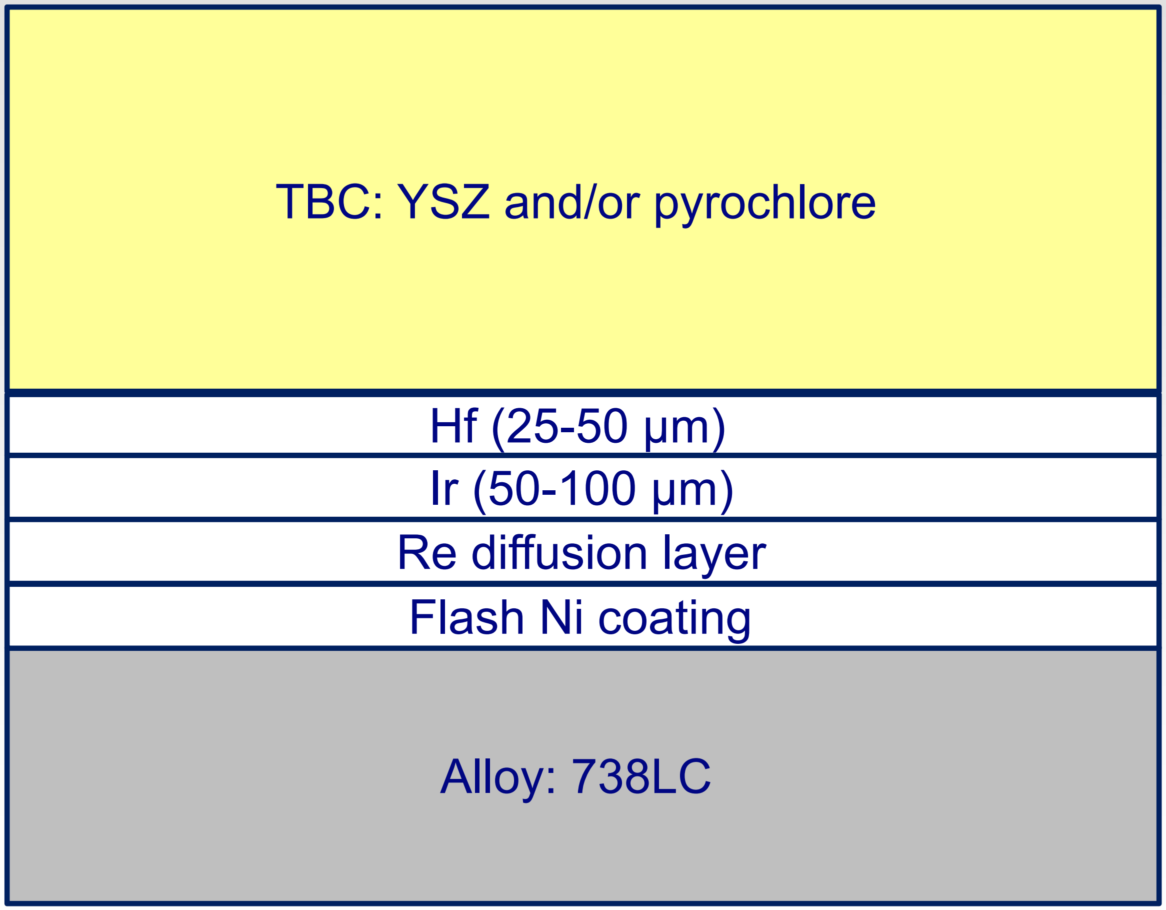



http://www.plasmapros.com/



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Thermal barrier coating system




Plasma spray for YSZ / pyrochlore

Molten salt electrochemical deposition (El-Form®) for Re/Hf/Ir

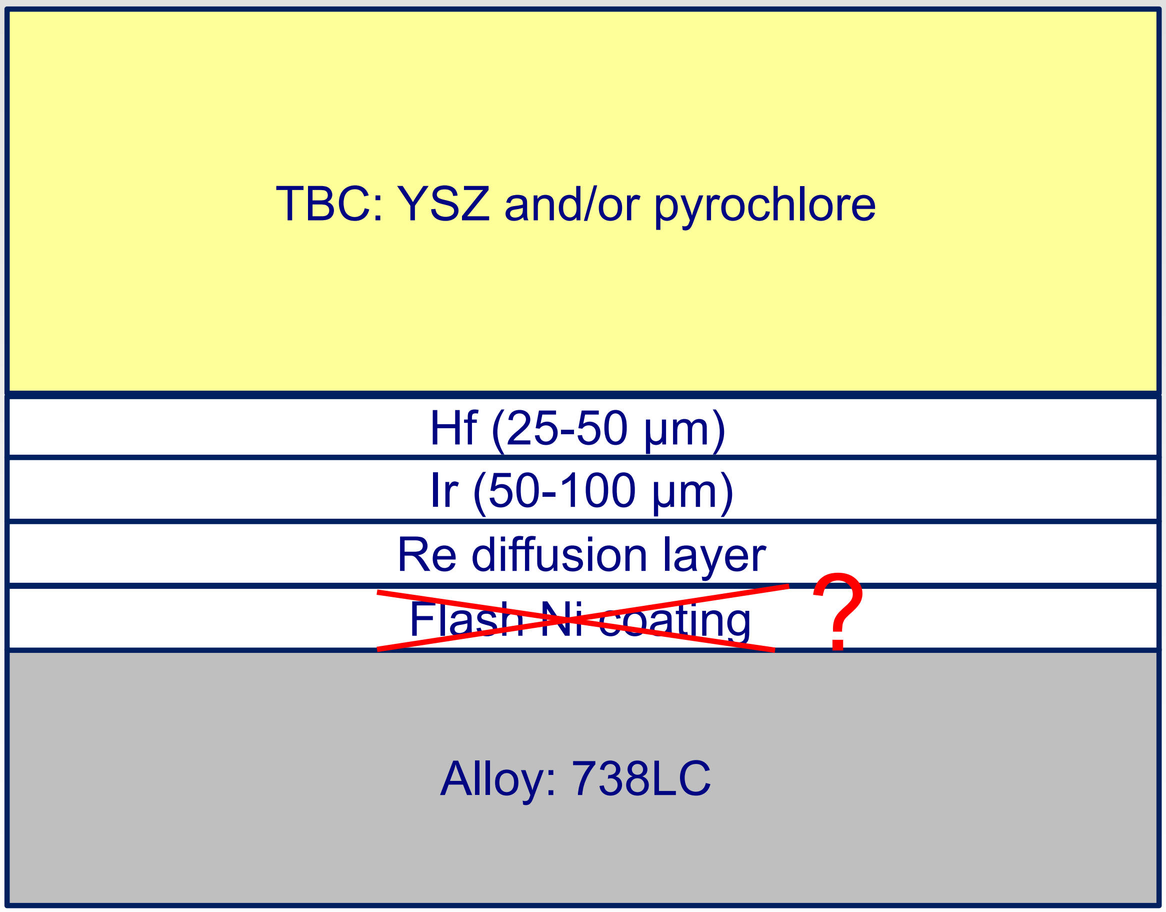


AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Approach

- Coating development
  - Evaluate need for Ni coating
  - Optimize Hf/Ir for YSZ
  - Feasibility Hf/Ir for pyrochlore
  - YSZ + pyrochlore
- Coating materials
  - Stability of pyrochlore in CMAS
    - $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$, mixed
  - Accelerate with high temperature exposures

# Need for nickel layer

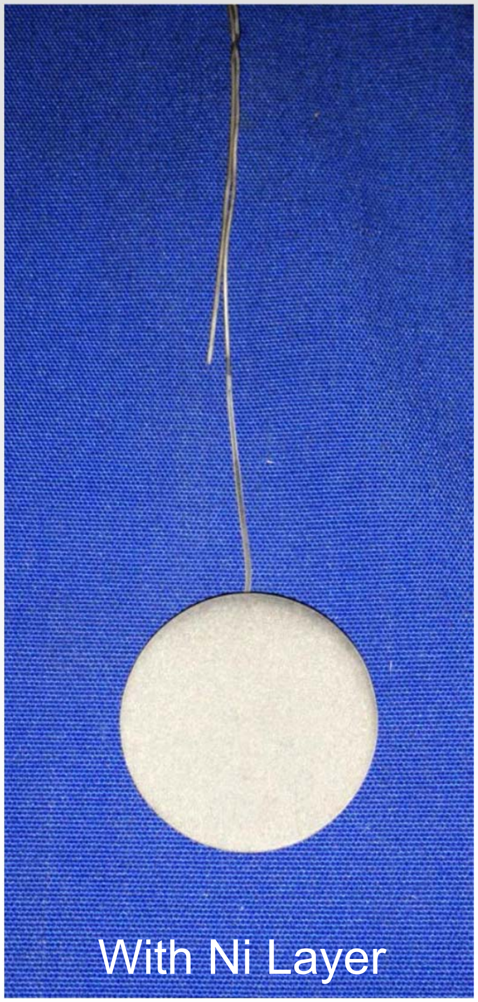


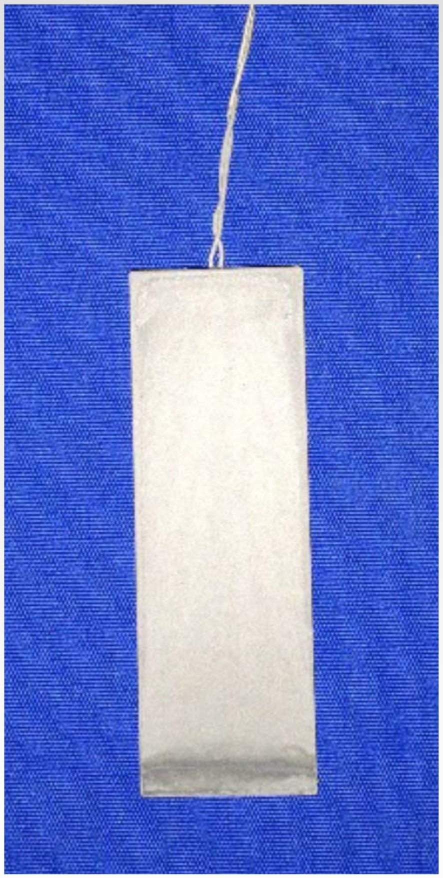

Evaluate possible elimination of Ni coating



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Rhenium coating with/without nickel

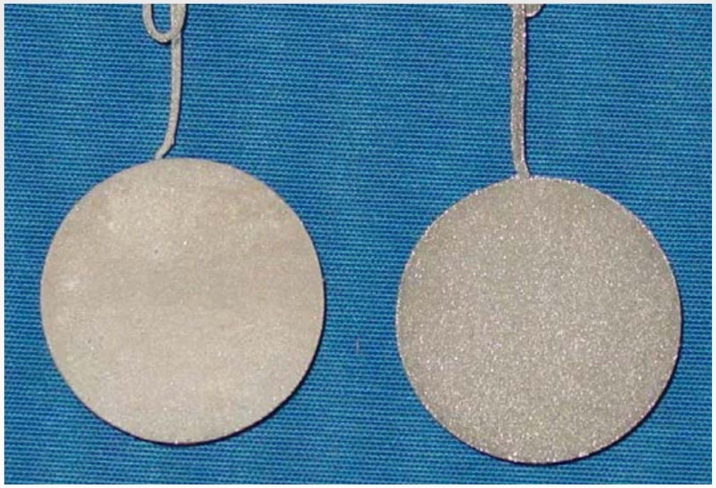



Nickel coating needed

# Iridium coatings on round samples

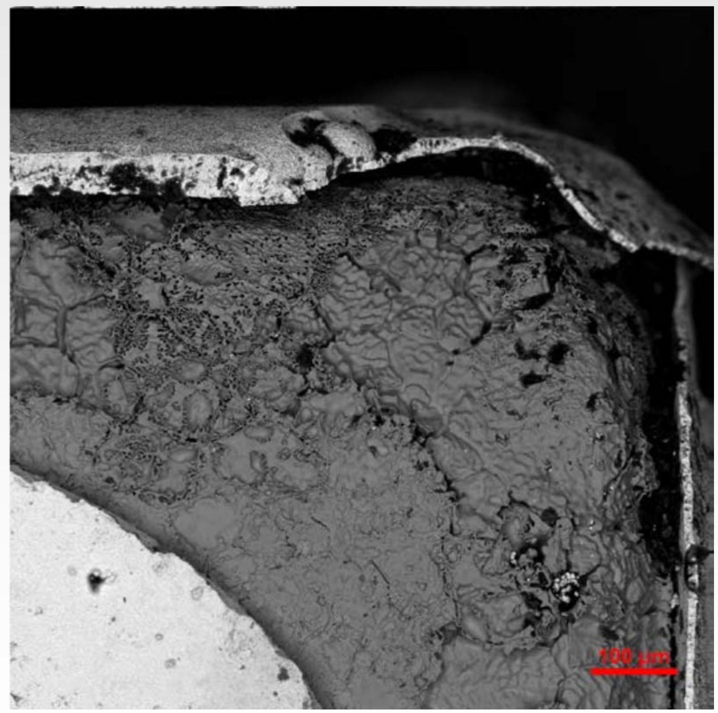
2 out of 20 iridium coatings good quality



Electrochemical deposition reveals non-visible defects in Re coating

# Iridium coatings on rectangular samples

Rectangular coatings for mechanical testing



# Revised approach

- Electrochemical deposition process sensitive to defects in substrate coating
- Focus coating efforts on environmental barrier coatings
- Plasma-sprayed materials to corroborate results from sintered ceramics

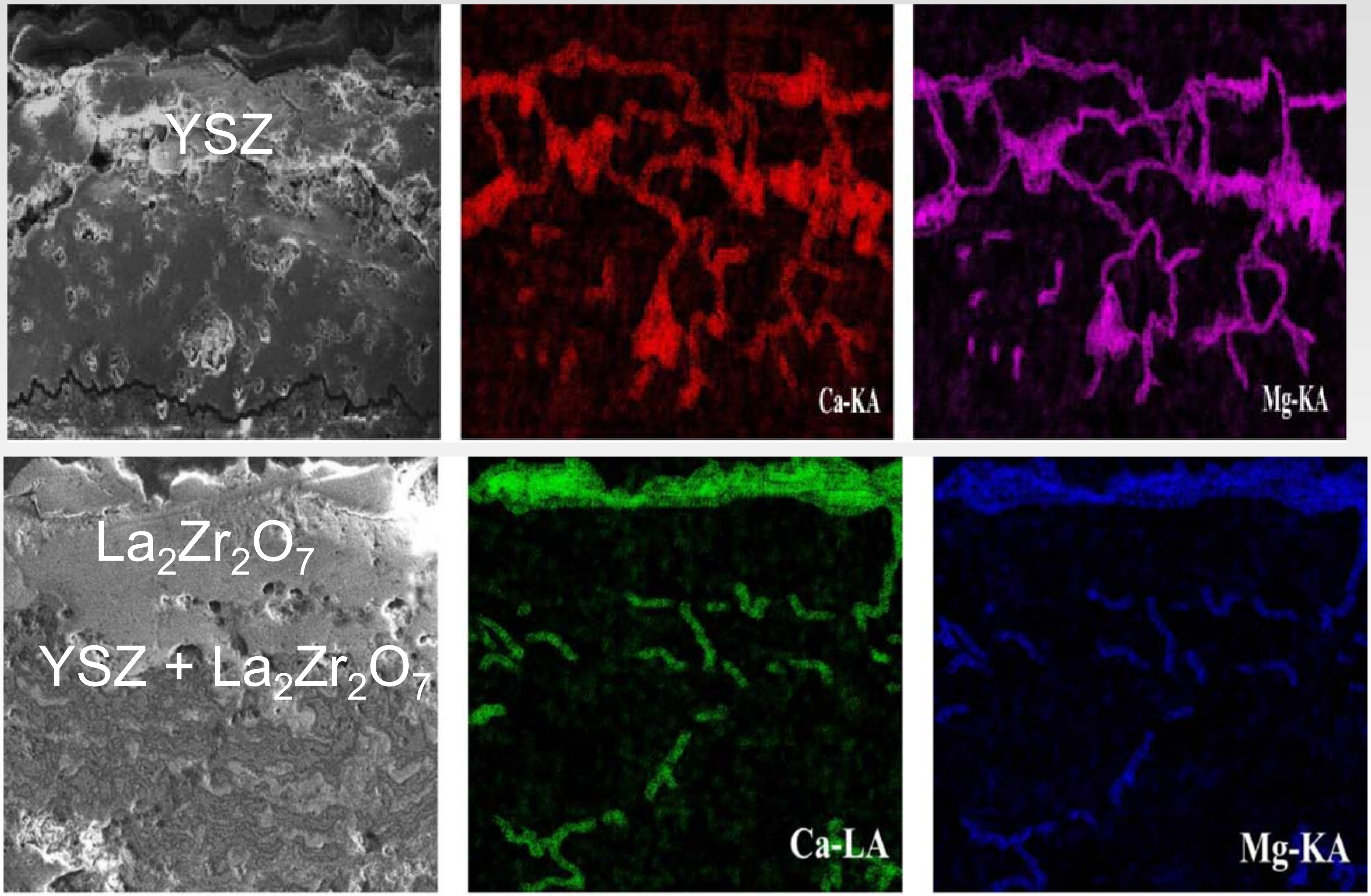


AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Pyrochlore coating materials

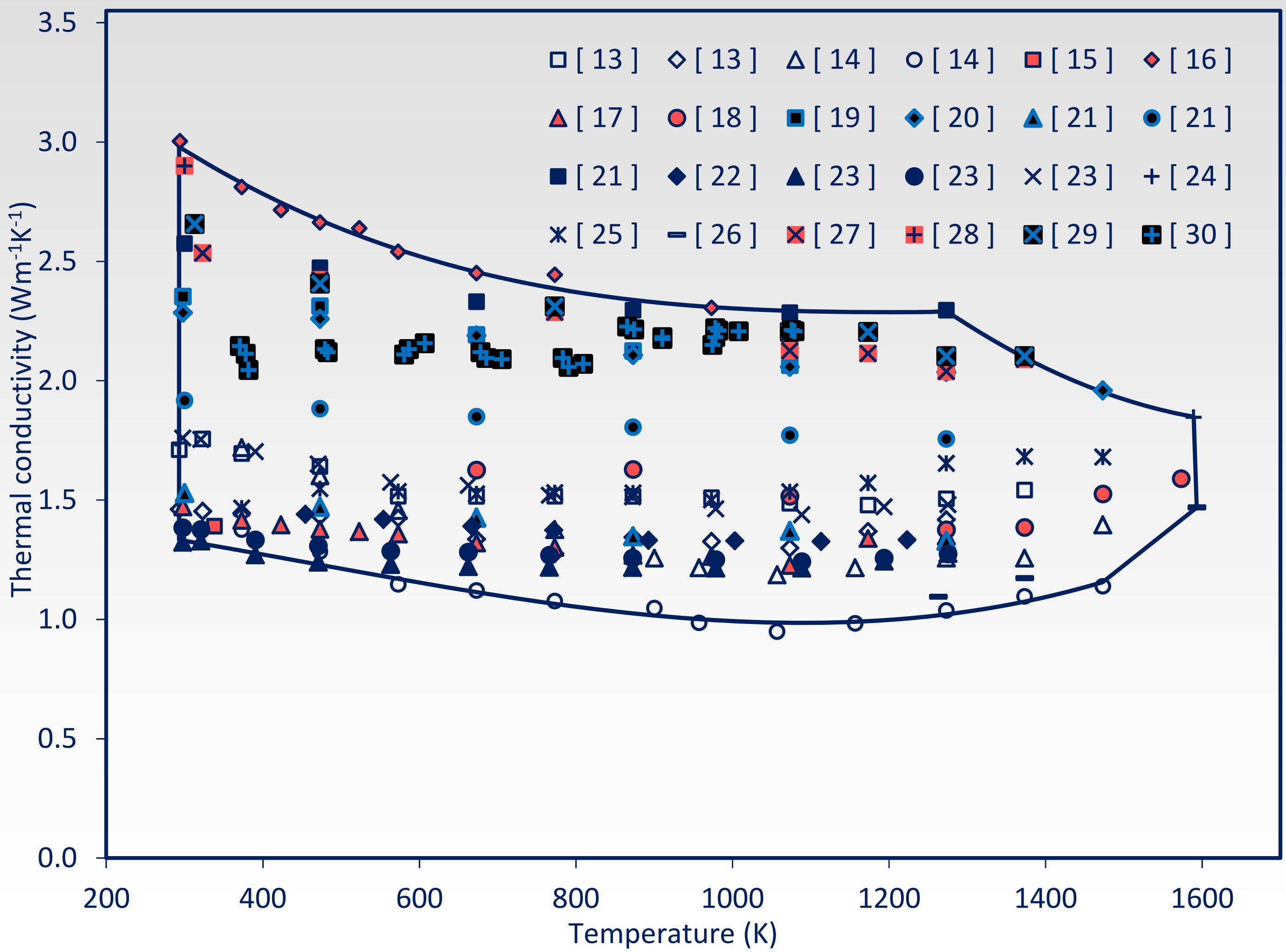
- Reaction with CMAS
- Thermal conductivity

# Reaction with CMAS




C.S. Ramachandran *et al.*, *Ceram. Int.* **39**, 1413 (2013)

# Thermal conductivity of zirconia with 7-8% yttria



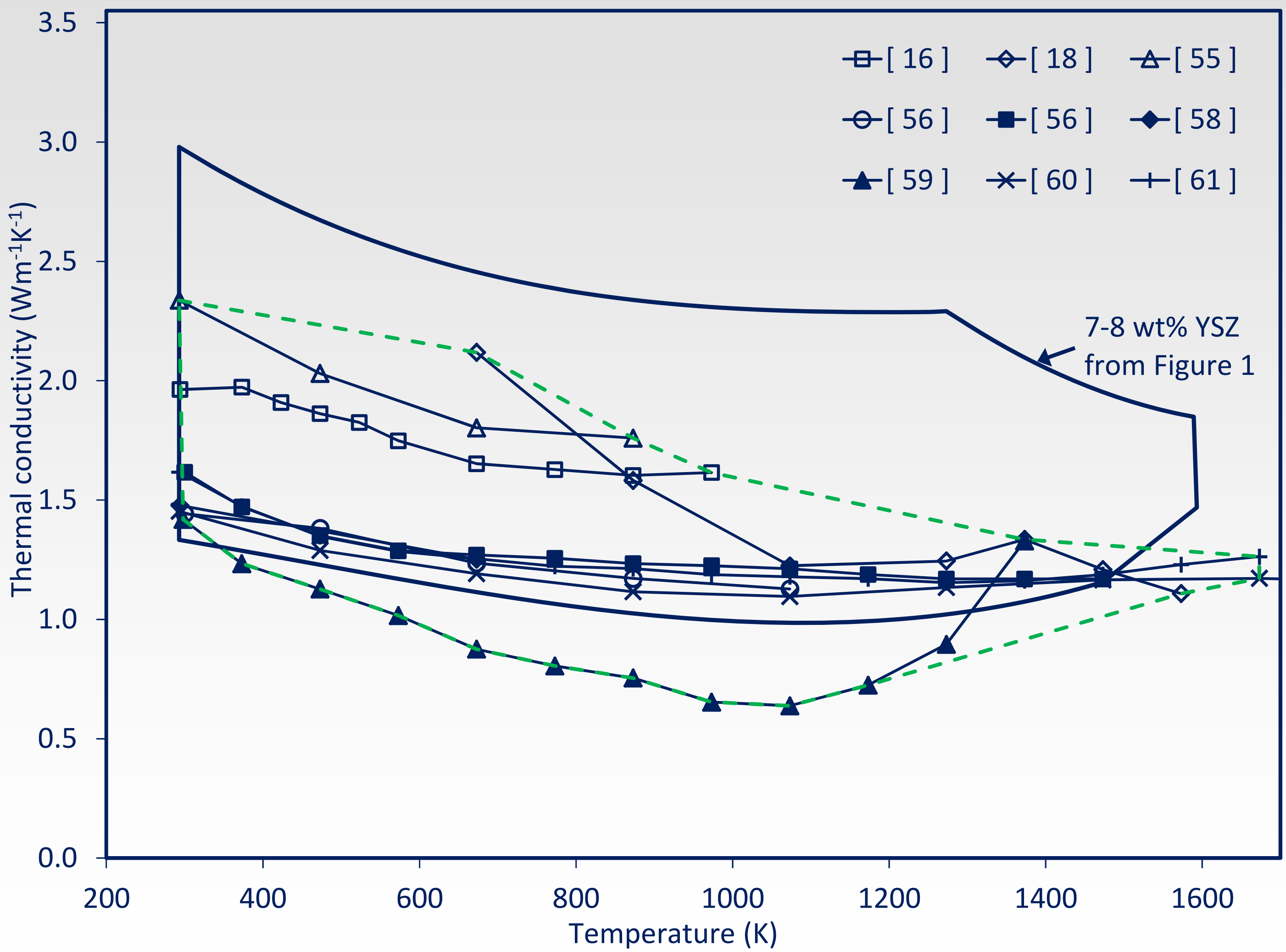

Range of thermal conductivities due to variations in morphology and microstructure

J. Fergus. *Met. Mater. Trans E* **1**, 118 (2014).



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

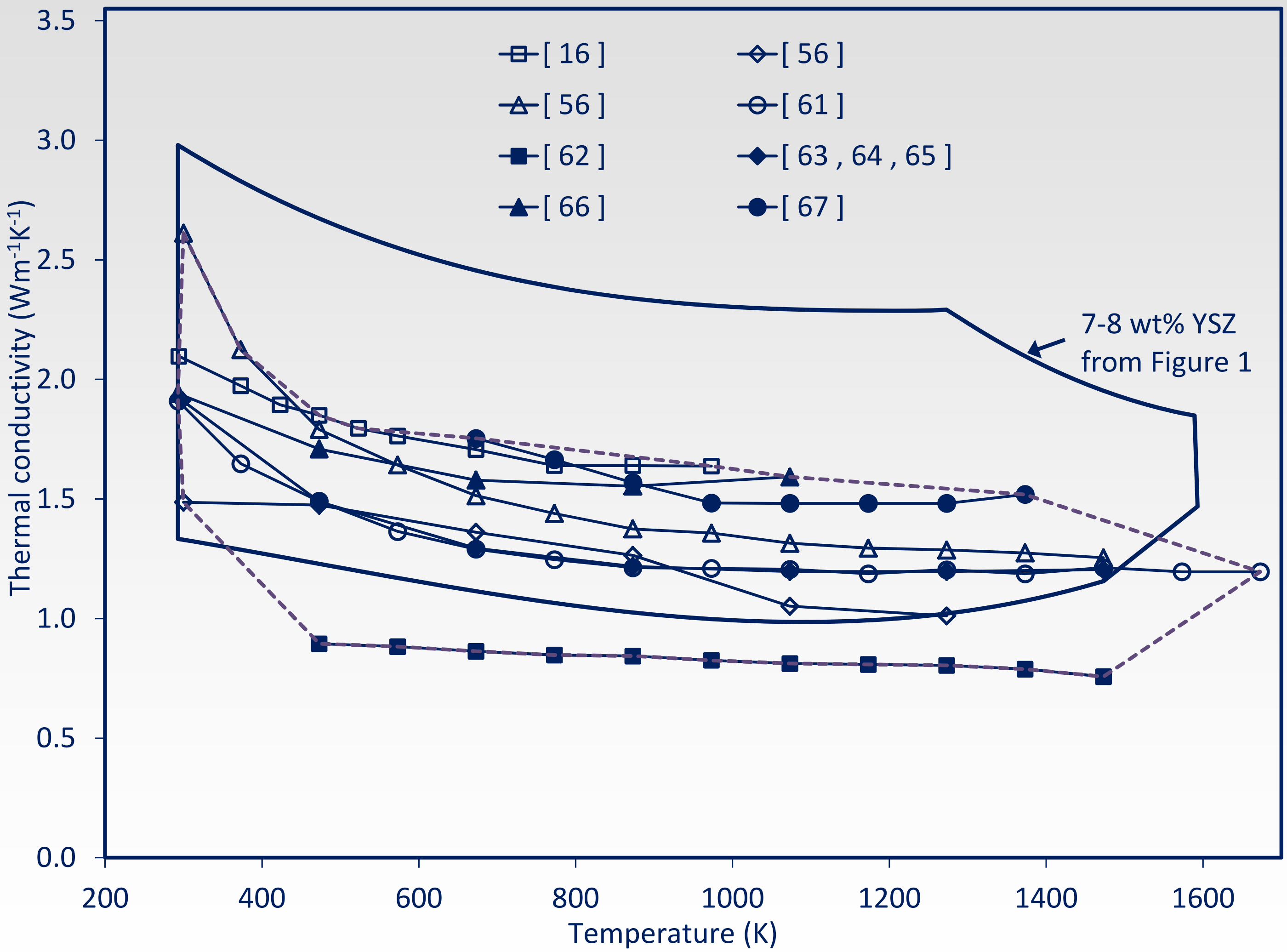
# Thermal conductivity of $Gd_2Zr_2O_7$




κ of $Gd_2Zr_2O_7$ in lower range of YSZ

J. Fergus. *Met. Mater. Trans E* **1**, 118 (2014).

# Thermal conductivity of $Sm_2Zr_2O_7$

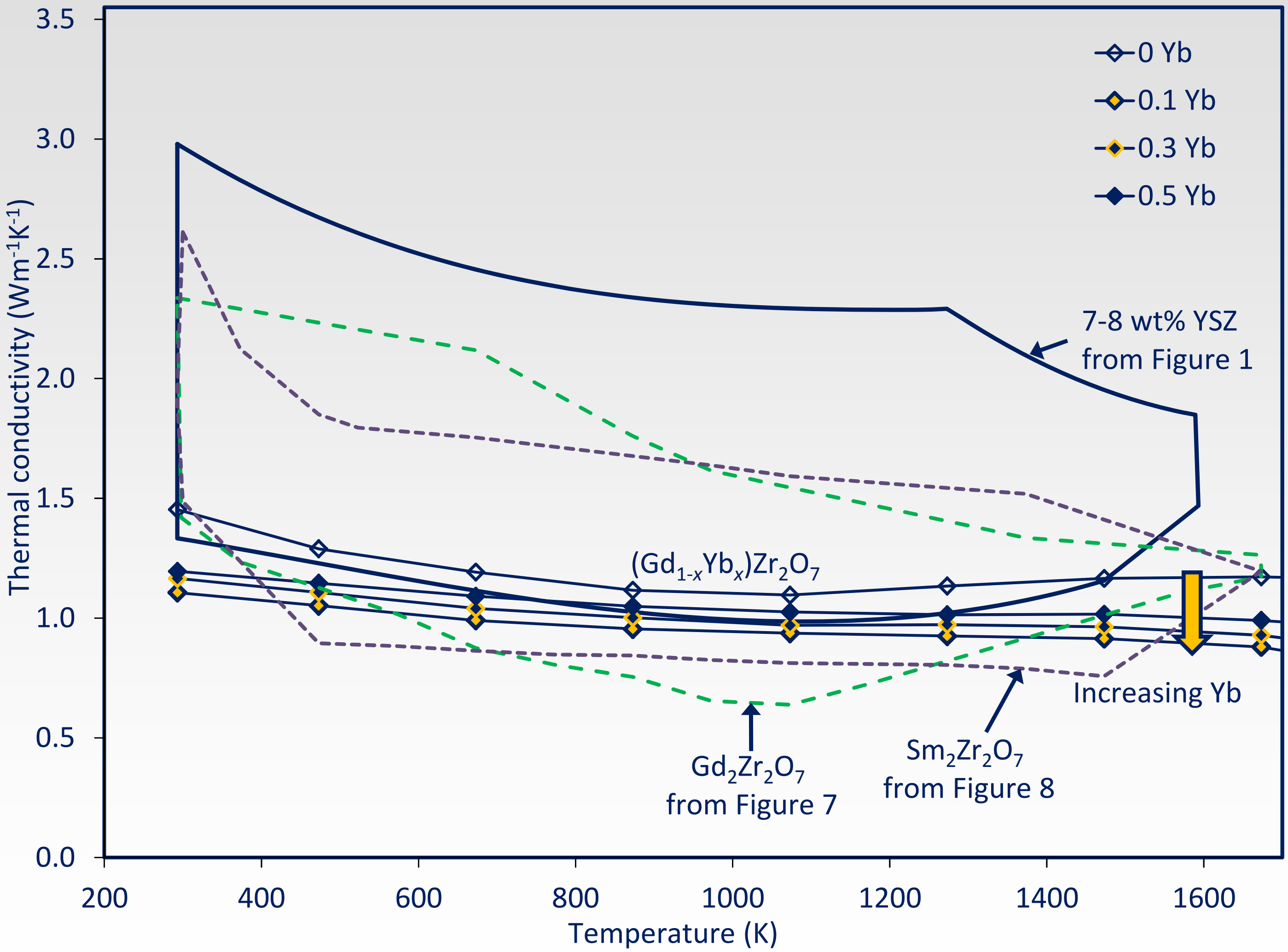



κ of $Sm_2Zr_2O_7$ in lower range of YSZ

J. Fergus. *Met. Mater. Trans E* **1**, 118 (2014).

AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Ytterbium-doping



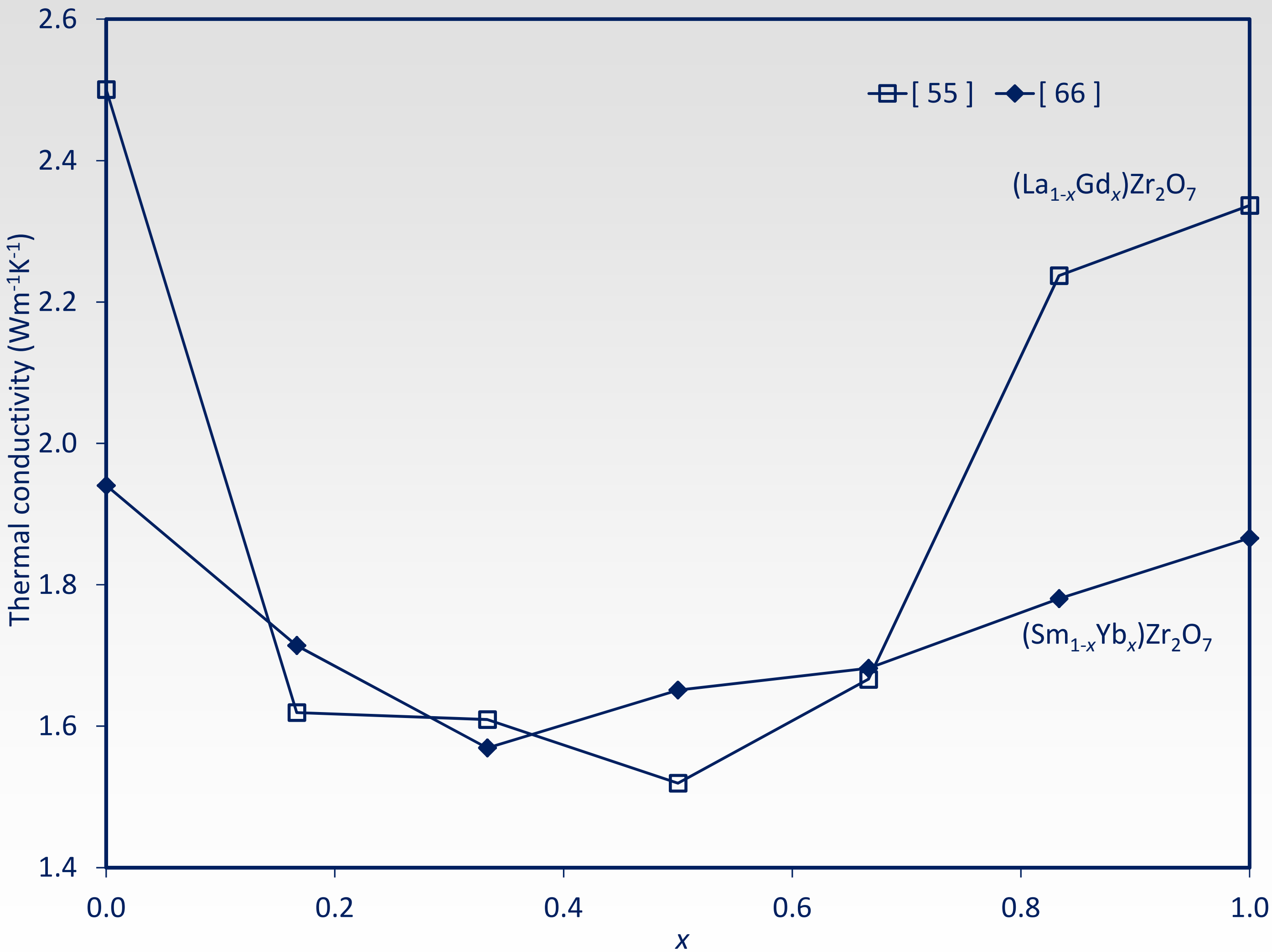

Doping can reduce κ

J. Fergus. *Met. Mater. Trans E* **1**, 118 (2014).



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Thermal conductivity of mixed pyrochlores




Pyrochlore solid solutions have lower κ

J. Fergus. *Met. Mater. Trans E* **1**, 118 (2014).



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Pyrochlore coating materials

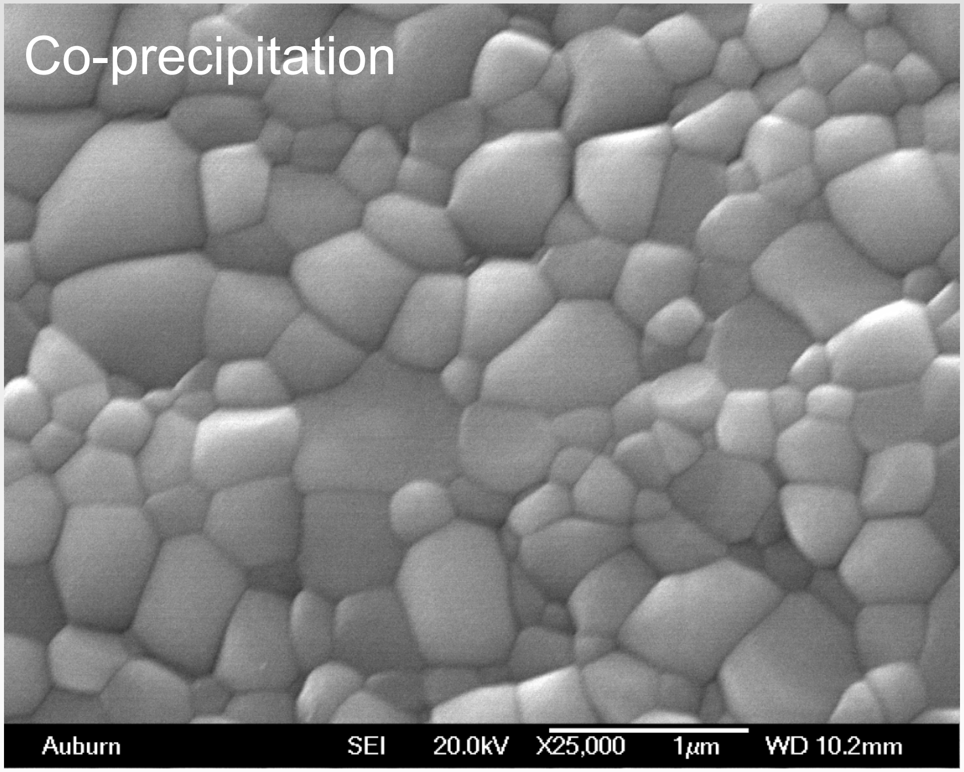
- Synthesis of pyrochlore
  - Co-precipitation
- CMAS exposure
  - Melt / solidify Ca-Mg-Al-Si oxide mixtures
  - Crush glass, apply to pyrochlore pellet
  - Expose to 1200-1400°C
- Characterization
  - XRD, SEM, optical microscopy

| CMAS Composition | |
|---|---|
| **Oxide** | **Percentage** |
| CaO | 33 |
| MgO | 9 |
| $AlO_{1.5}$ | 13 |
| $SiO_2$ | 45 |



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

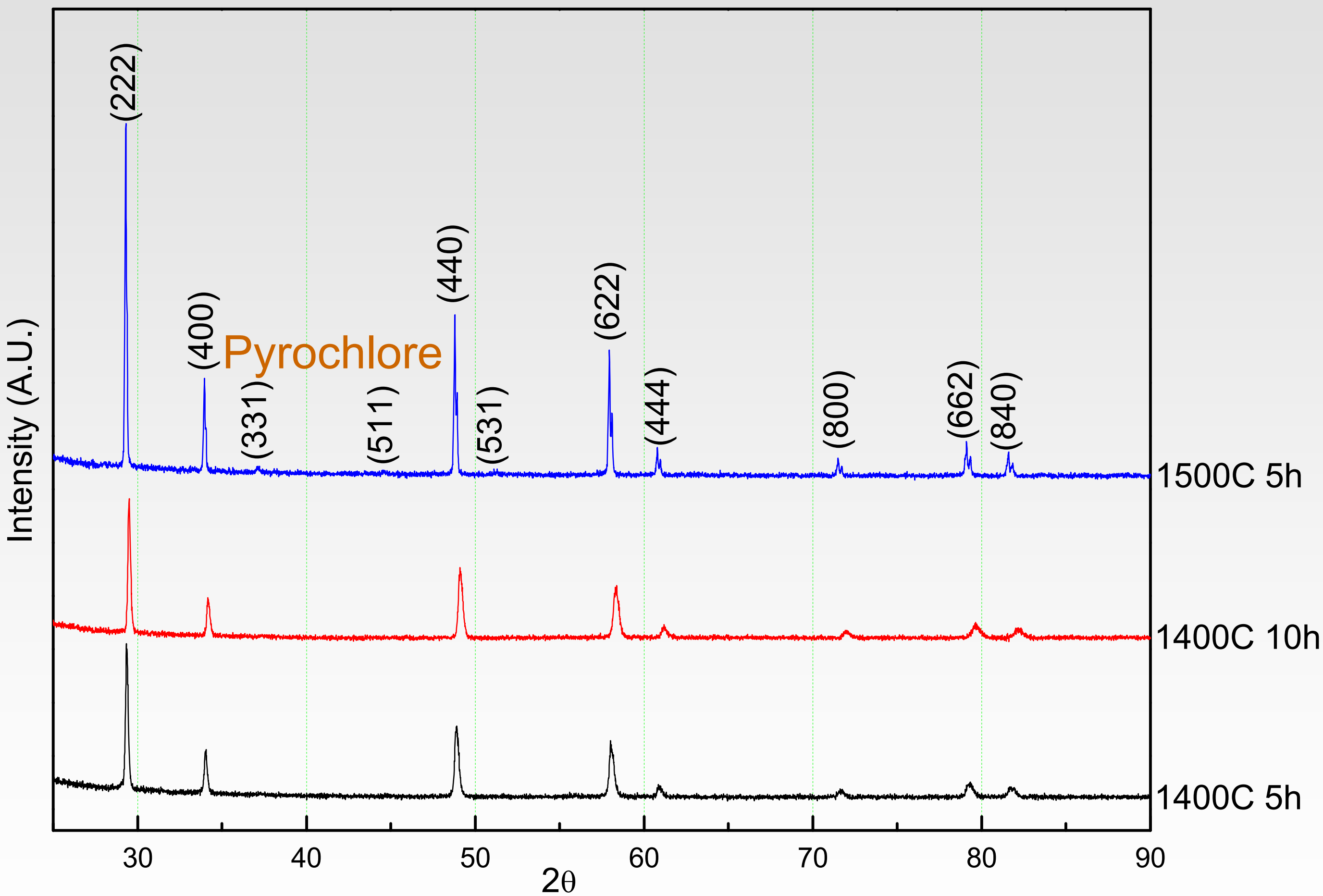
# Microstructure of $Gd_2Zr_2O_7$



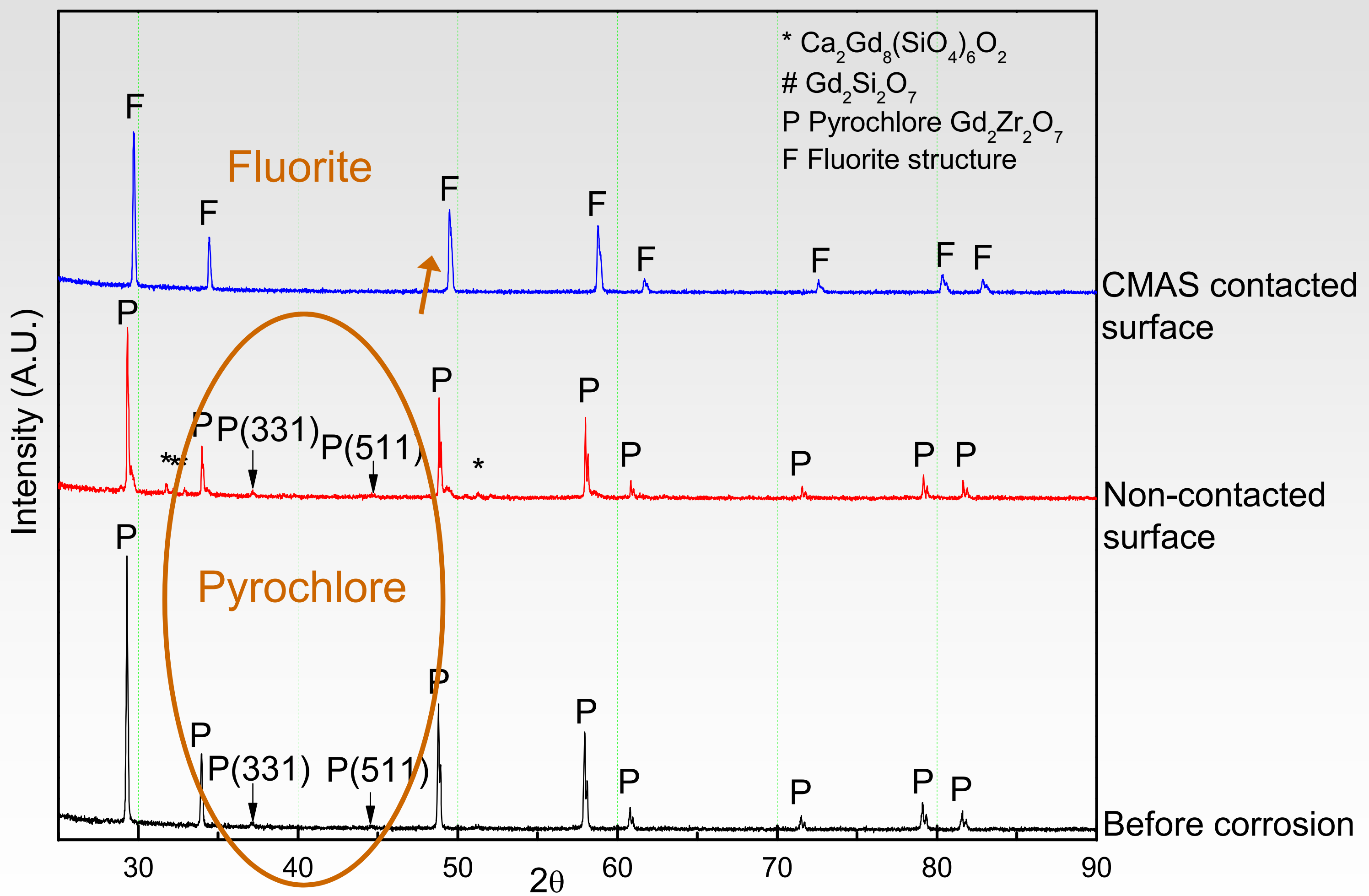



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Phase content of $Gd_2Zr_2O_7$



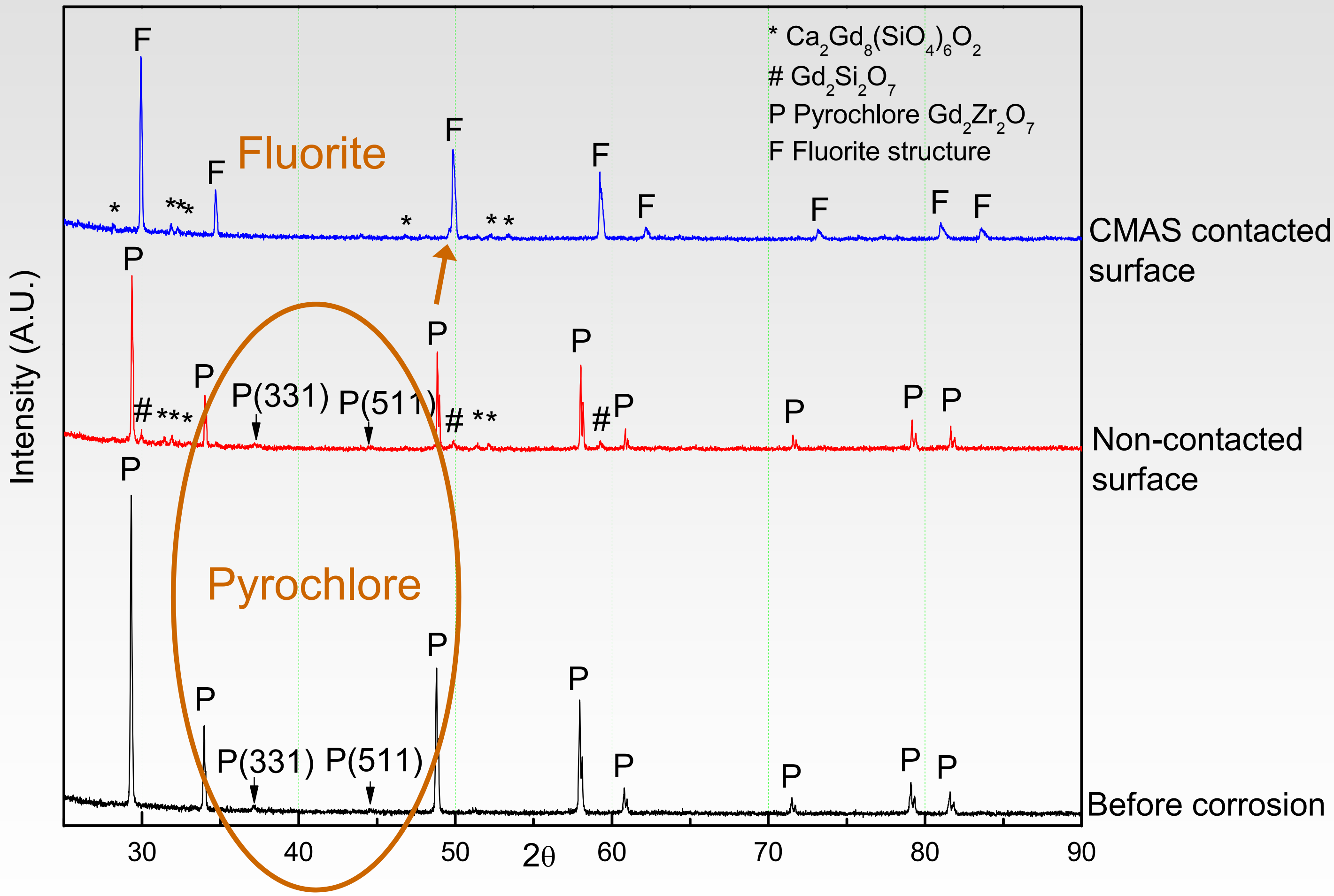
# $Gd_2Zr_2O_7$ after CMAS at 1400°C for 5 hours






AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

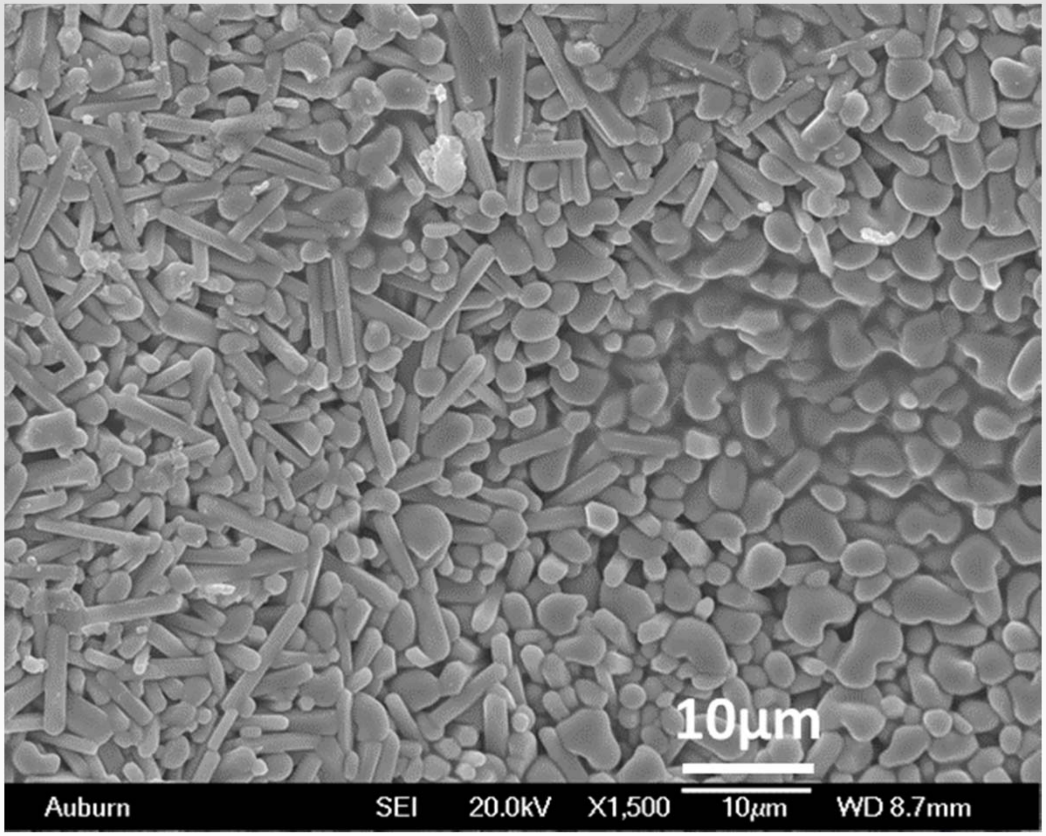
# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 5 hours






AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

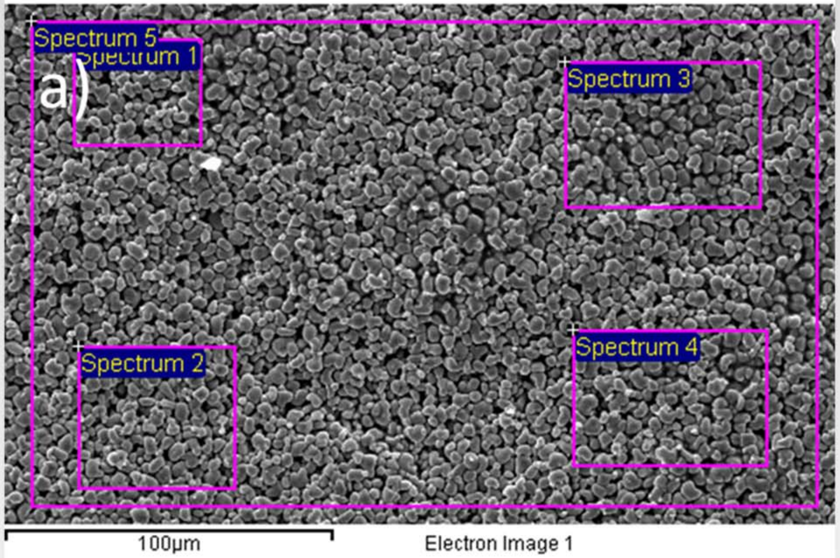
# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 5 hours





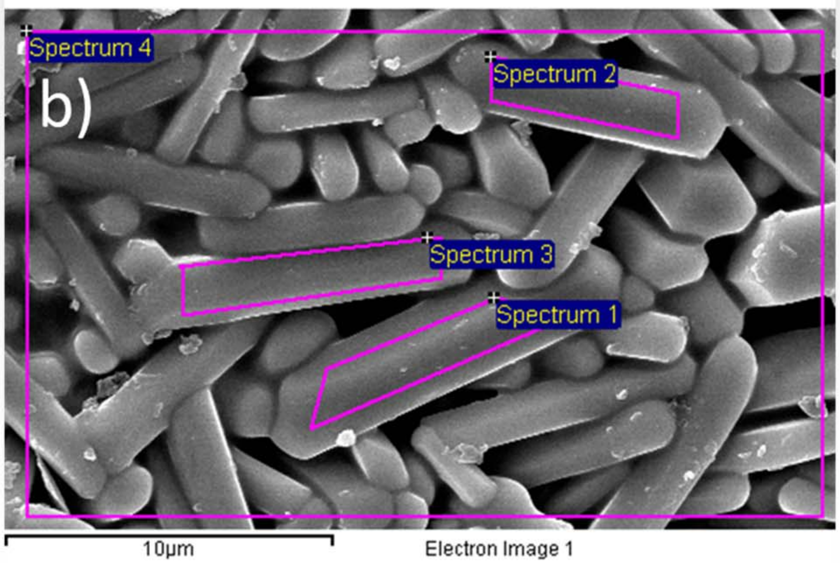

AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 5 hours




Atomic Percentage for a)

| | O | Mg | Al | Si | Ca | Zr | Gd | Au |
|---|---|---|---|---|---|---|---|---|
| Spectrum 1 | 62 | | 1 | 2 | 3 | 22 | 6 | 4 |
| Spectrum 2 | 59 | | 1 | 2 | 2 | 24 | 7 | 4 |
| Spectrum 3 | 61 | | 2 | 3 | 4 | 21 | 6 | 4 |
| Spectrum 4 | 60 | | 1 | 3 | 4 | 22 | 6 | 4 |
| Spectrum 5 | 62 | | 1 | 3 | 3 | 21 | 6 | 4 |




Atomic Percentage for b)

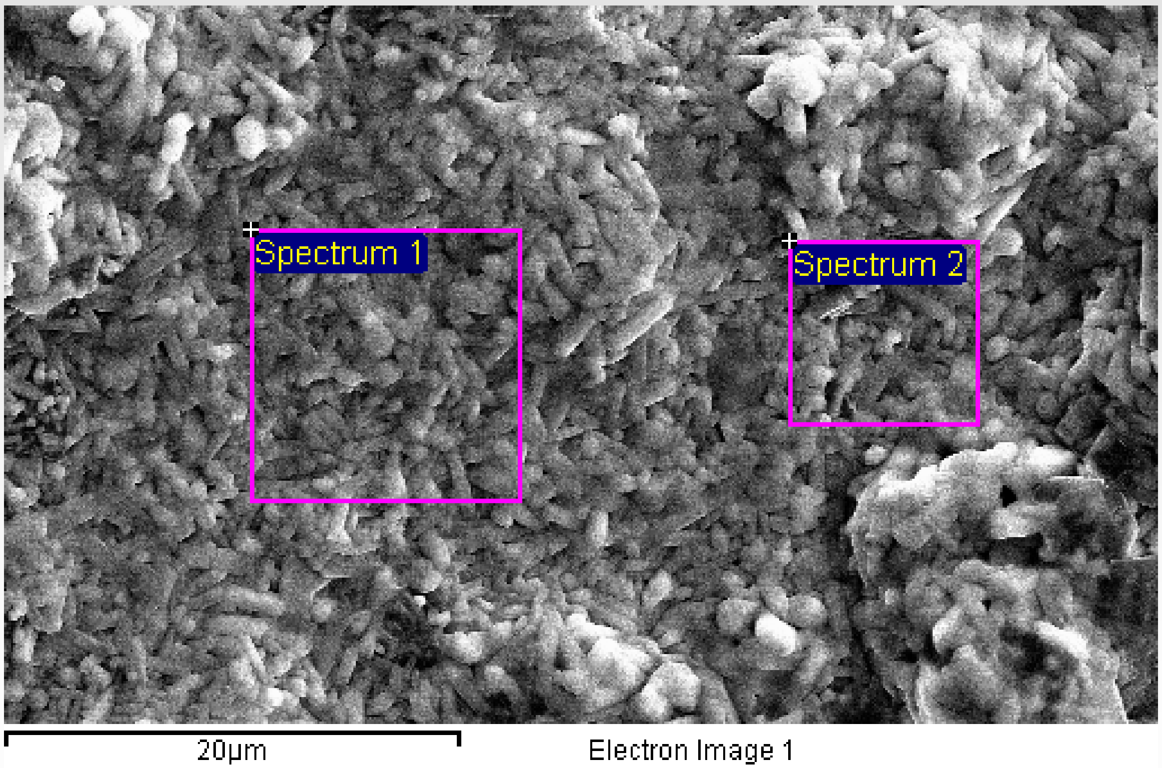
$Ca_2Gd_8(SiO_4)_6O_2$

| | O | Mg | Al | Si | Ca | Zr | Gd | Au |
|---|---|---|---|---|---|---|---|---|
| Spectrum 1 | 64 | | | 13 | 5 | 1 | 13 | 4 |
| Spectrum 2 | 65 | | 1 | 12 | 5 | 1 | 12 | 4 |
| Spectrum 3 | 66 | | 1 | 13 | 5 | 1 | 11 | 3 |
| Spectrum 4 | 60 | 1 | 2 | 12 | 6 | 4 | 12 | 4 |



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



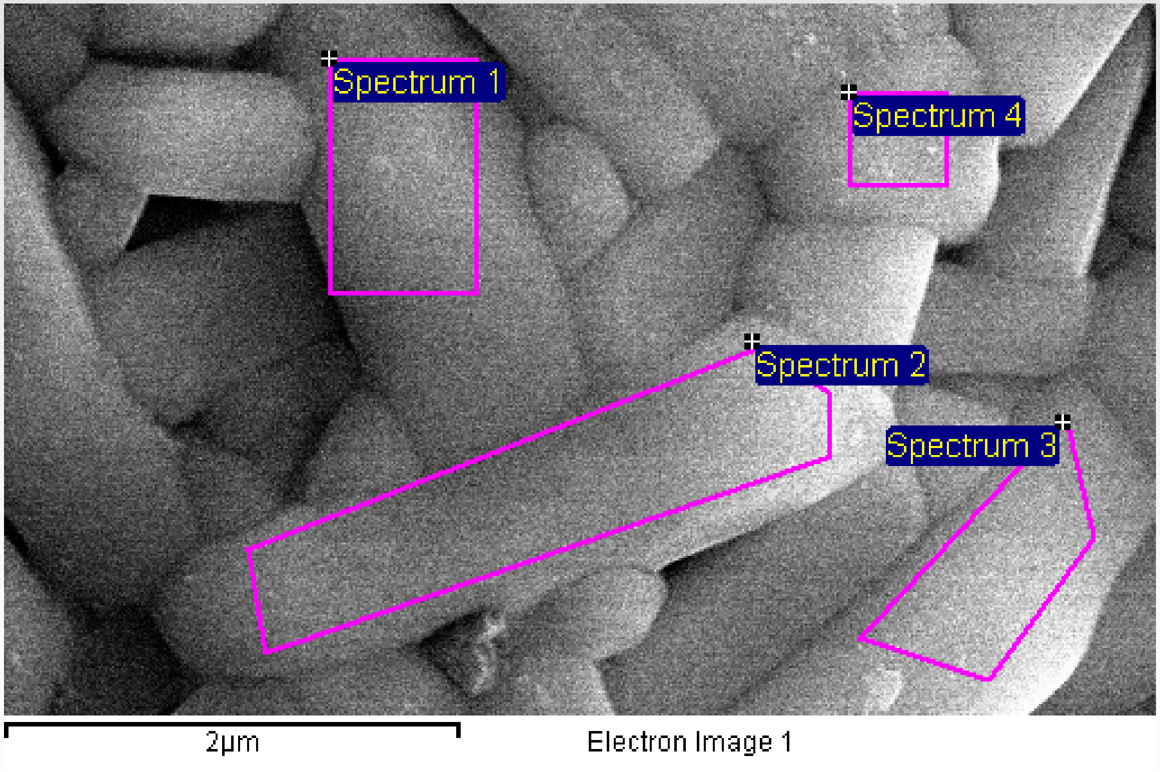

| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 62 | - | - | 14 | 5 | - | 15 | 4 |
| 2 | 60 | 2 | 4 | 12 | 5 | - | 13 | 4 |

Gd silicate



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



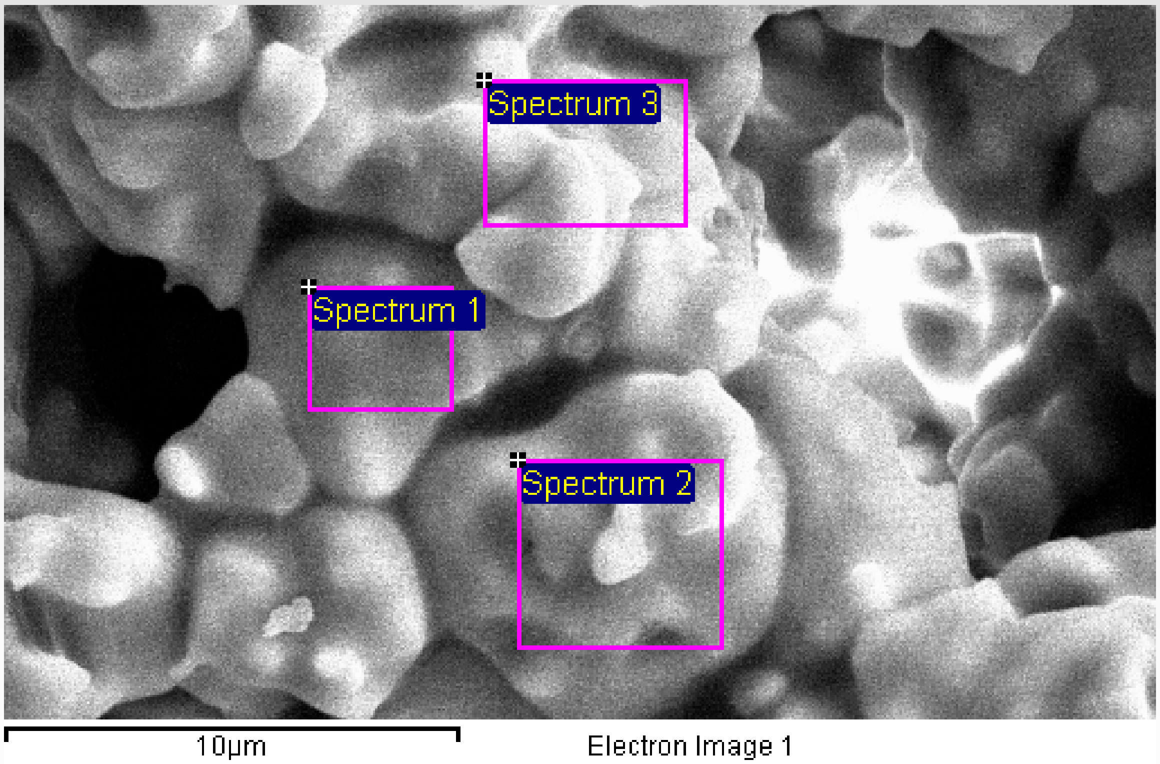

| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 56 | - | - | 14 | 6 | 1 | 17 | 5 |
| 2 | 63 | - | 3 | 12 | 5 | 1 | 13 | 4 |
| 3 | 67 | - | 1 | 12 | 4 | 1 | 12 | 3 |
| 4 | 64 | - | 1 | 1 | 5 | - | 13 | 4 |

Gd silicate



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



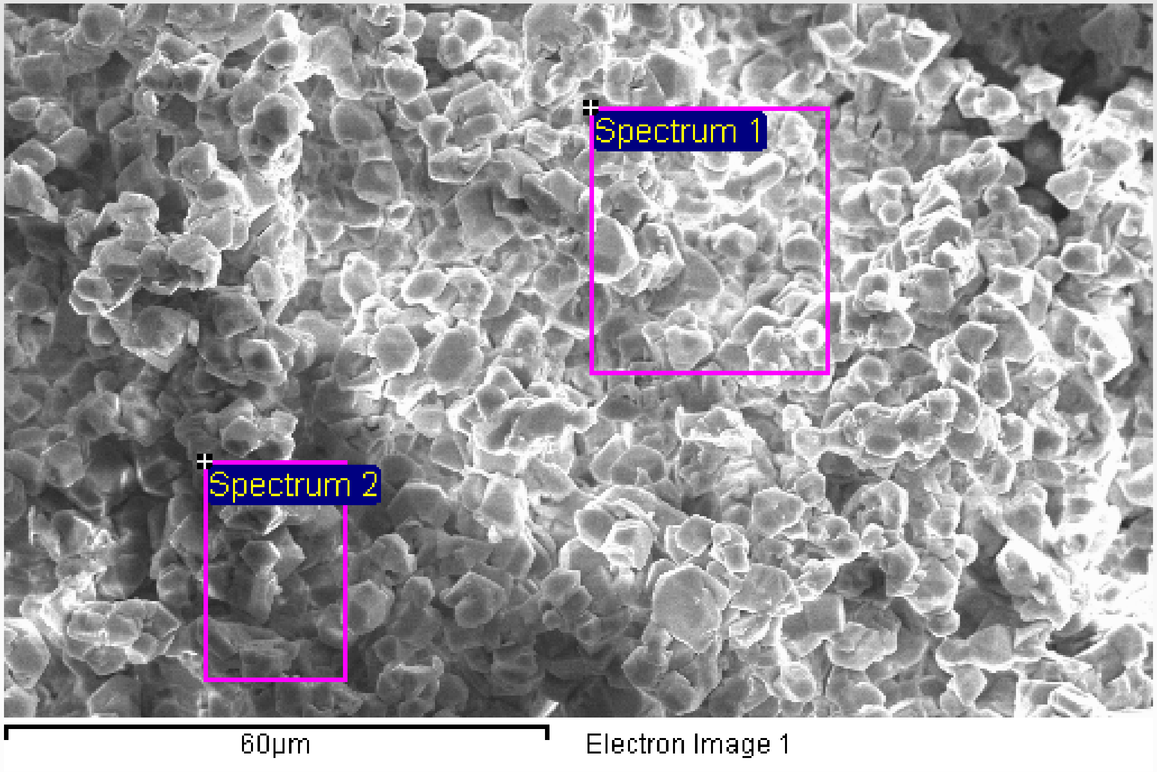

| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 60 | 1 | 1 | 1 | 2 | 27 | 5 | 4 |
| 2 | 67 | - | 1 | 1 | 2 | 23 | 4 | 3 |
| 3 | 61 | - | 1 | 2 | 2 | 25 | 6 | 4 |

Cubic fluorite



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

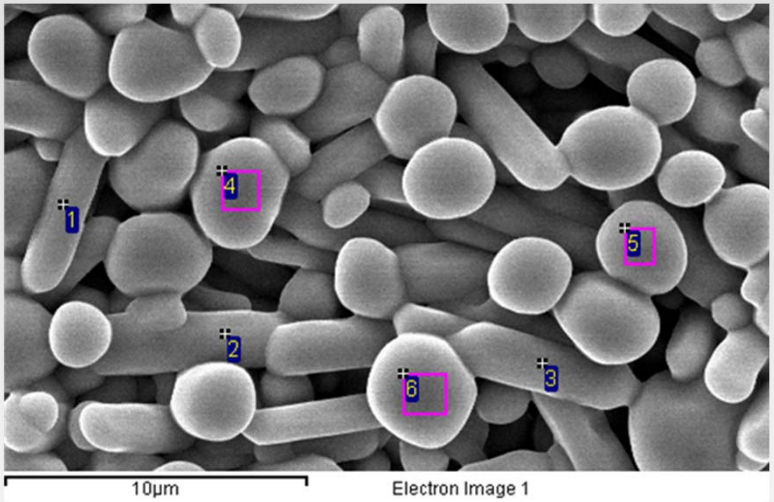
# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours

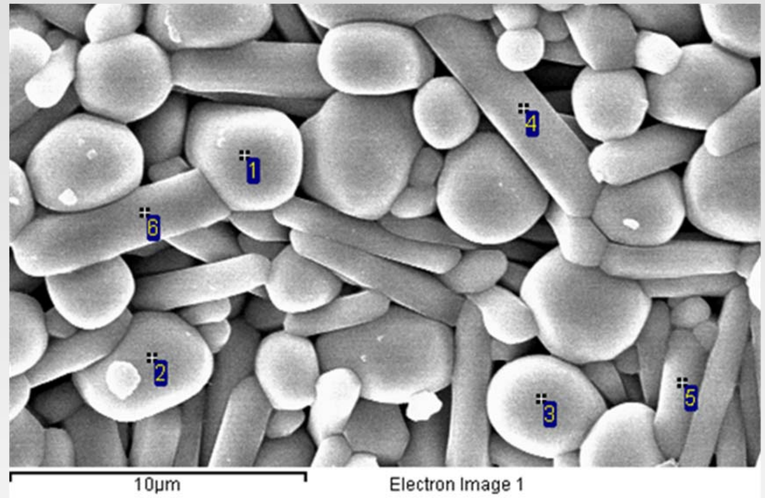



| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 59 | - | - | - | - | 17 | 18 | 5 |
| 2 | 65 | - | - | - | - | 18 | 17 | - |

Pyrochlore

# $Gd_2Zr_2O_7$ after CMAS at 1200°C



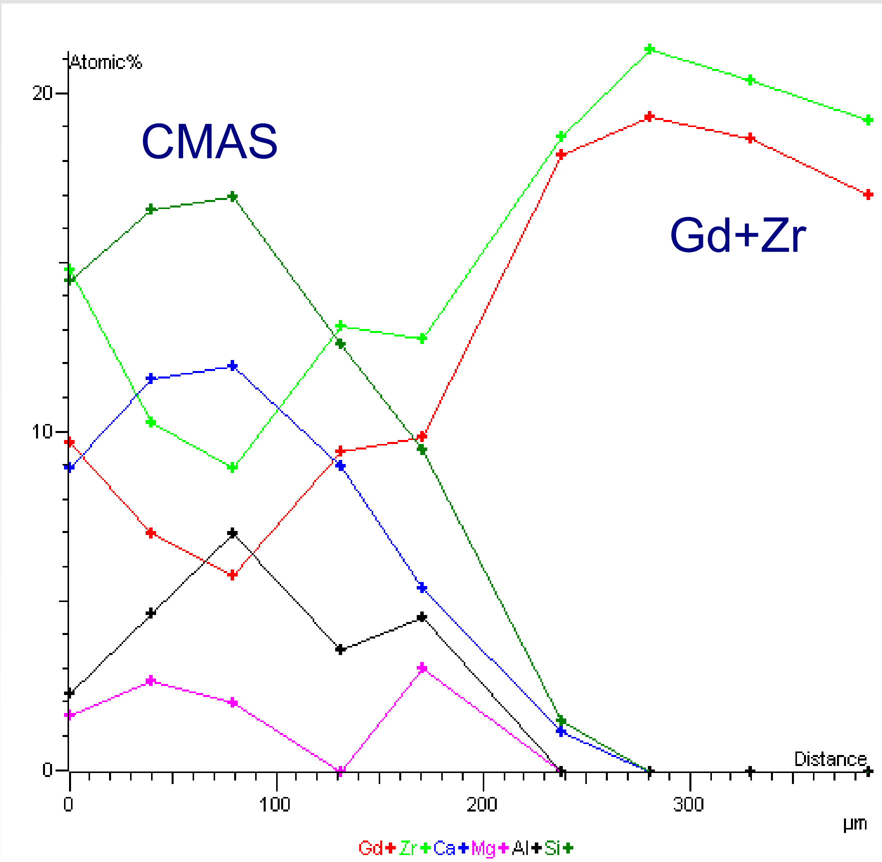

40 hours

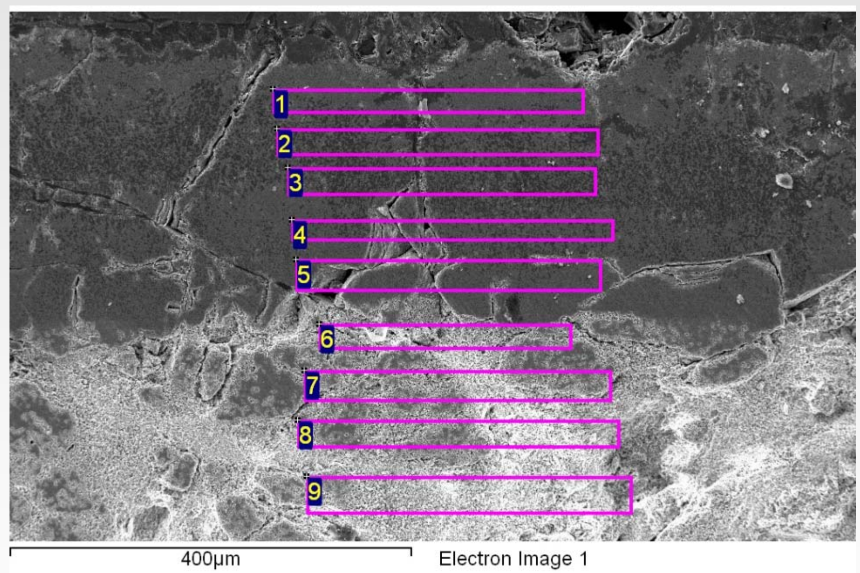
| Concentration | | | | | | |
|---|---|---|---|---|---|---|
| # | Mg | Al | Si | Ca | Zr | Gd |
| 1 | 0 | 0 | 15 | 7 | 9 | 14 |
| 2 | 0 | 0 | 15 | 6 | 11 | 20 |
| 3 | 0 | 0 | 14 | 6 | 7 | 12 |
| 4 | 0 | 0 | 2 | 2 | 33 | 5 |
| 5 | 0 | 0 | 2 | 3 | 34 | 7 |
| 6 | 0 | 0 | 2 | 2 | 29 | 5 |

60 hours

| Concentration | | | | | | |
|---|---|---|---|---|---|---|
| # | Mg | Al | Si | Ca | Zr | Gd |
| 1 | 0 | 0 | 2 | 3 | 32 | 4 |
| 2 | 0 | 0 | 2 | 3 | 38 | 6 |
| 3 | 0 | 0 | 2 | 3 | 35 | 6 |
| 4 | 0 | 0 | 15 | 6 | 6 | 13 |
| 5 | 0 | 0 | 13 | 11 | 10 | 28 |
| 6 | 0 | 0 | 5 | 4 | 18 | 7 |

# $Gd_2Zr_2O_7$ after CMAS at 1200°C – 60 hours

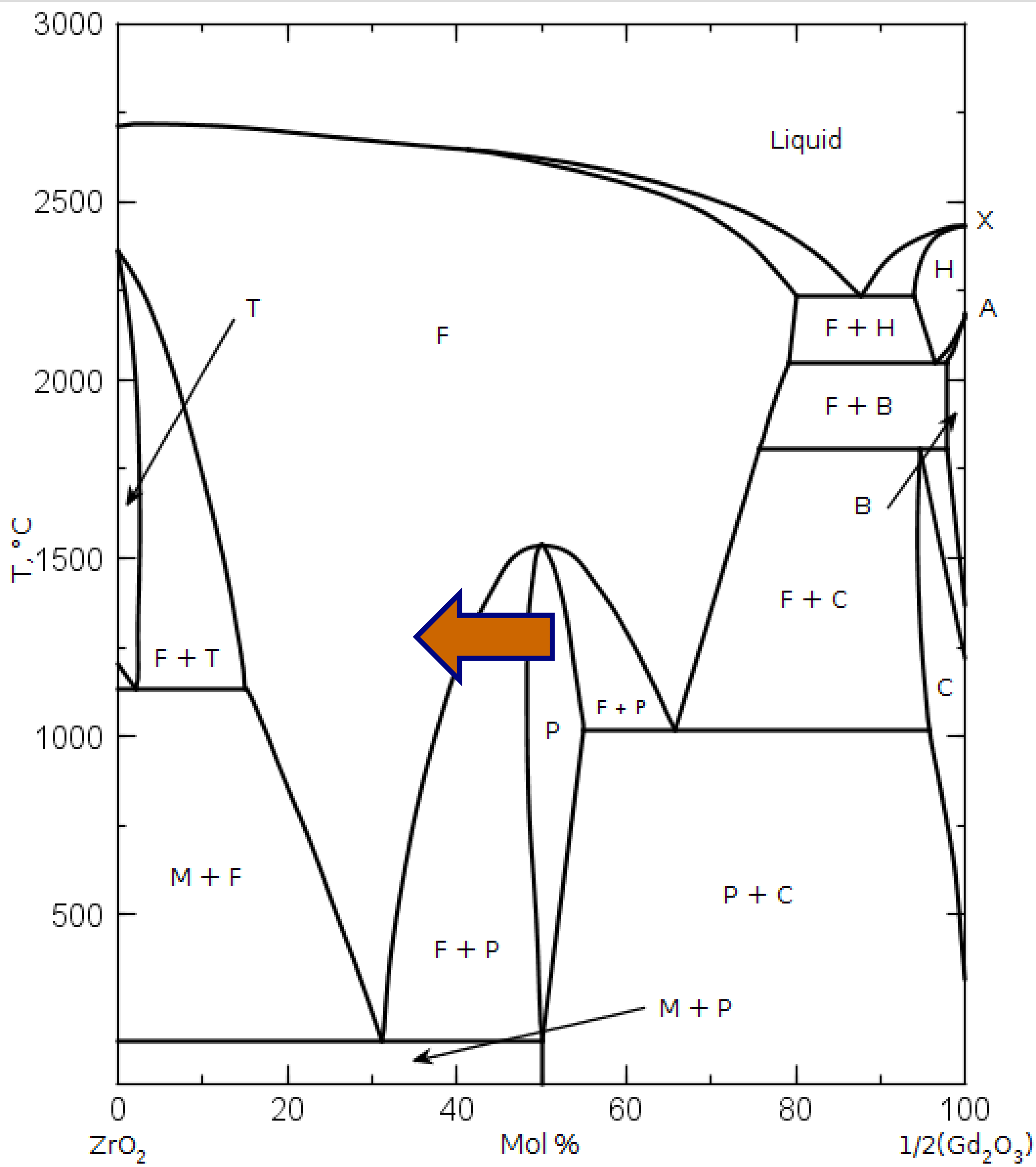





AUBURN
UNIVERSITY
SAMUEL GINN
COLLEGE OF ENGINEERING

# $ZrO_2$-$Gd_2O_3$ phase diagram




T = tetragonal
F = cubic fluorite
M – monoclinic
P = pyrochlore
C, B, H = $Gd_2O_3$ phases



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Microstructure of $Sm_2Zr_2O_7$

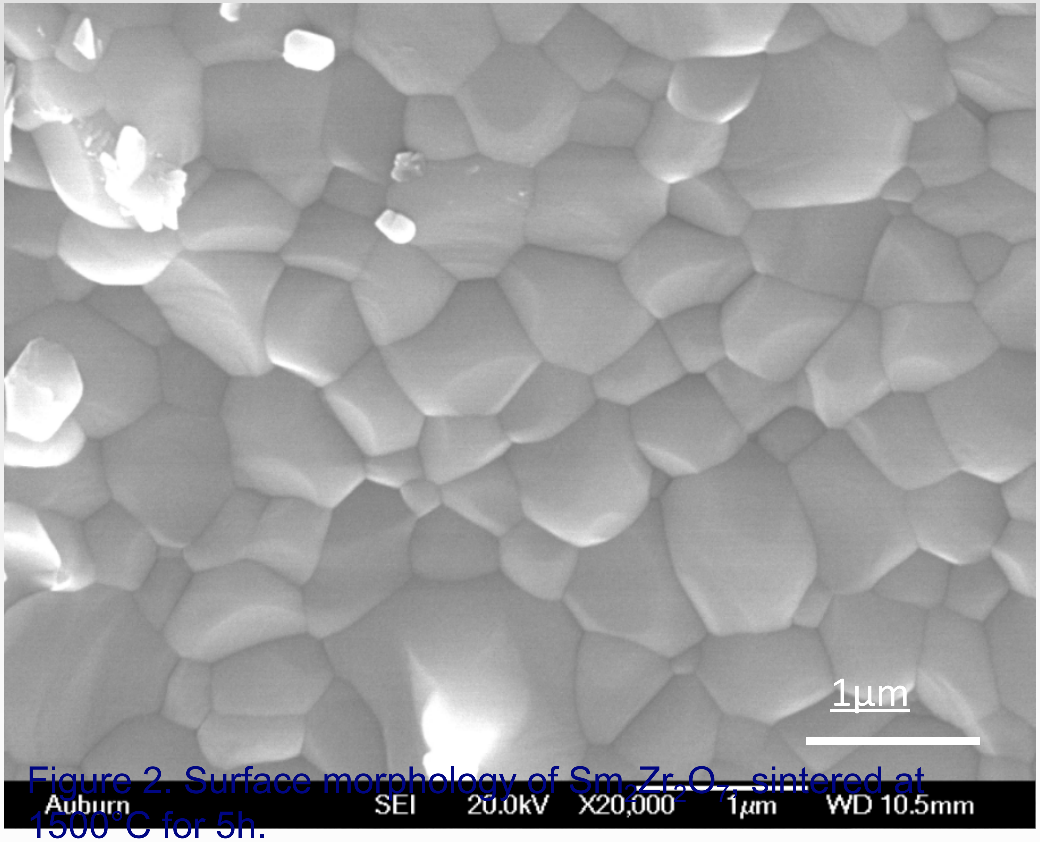
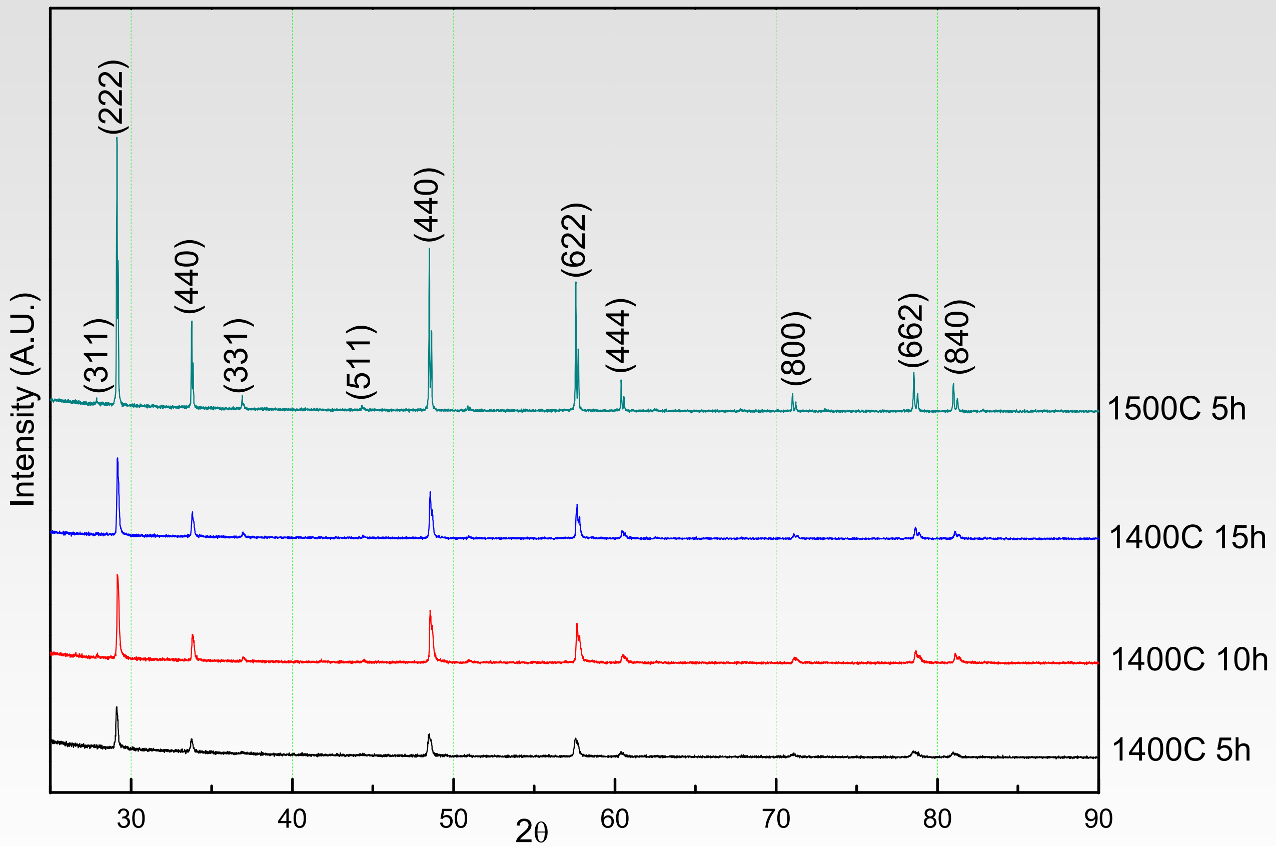



Figure 2. Surface morphology of $Sm_2Zr_2O_7$ sintered at 1500°C for 5h.



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# Phase content of $Sm_2Zr_2O_7$



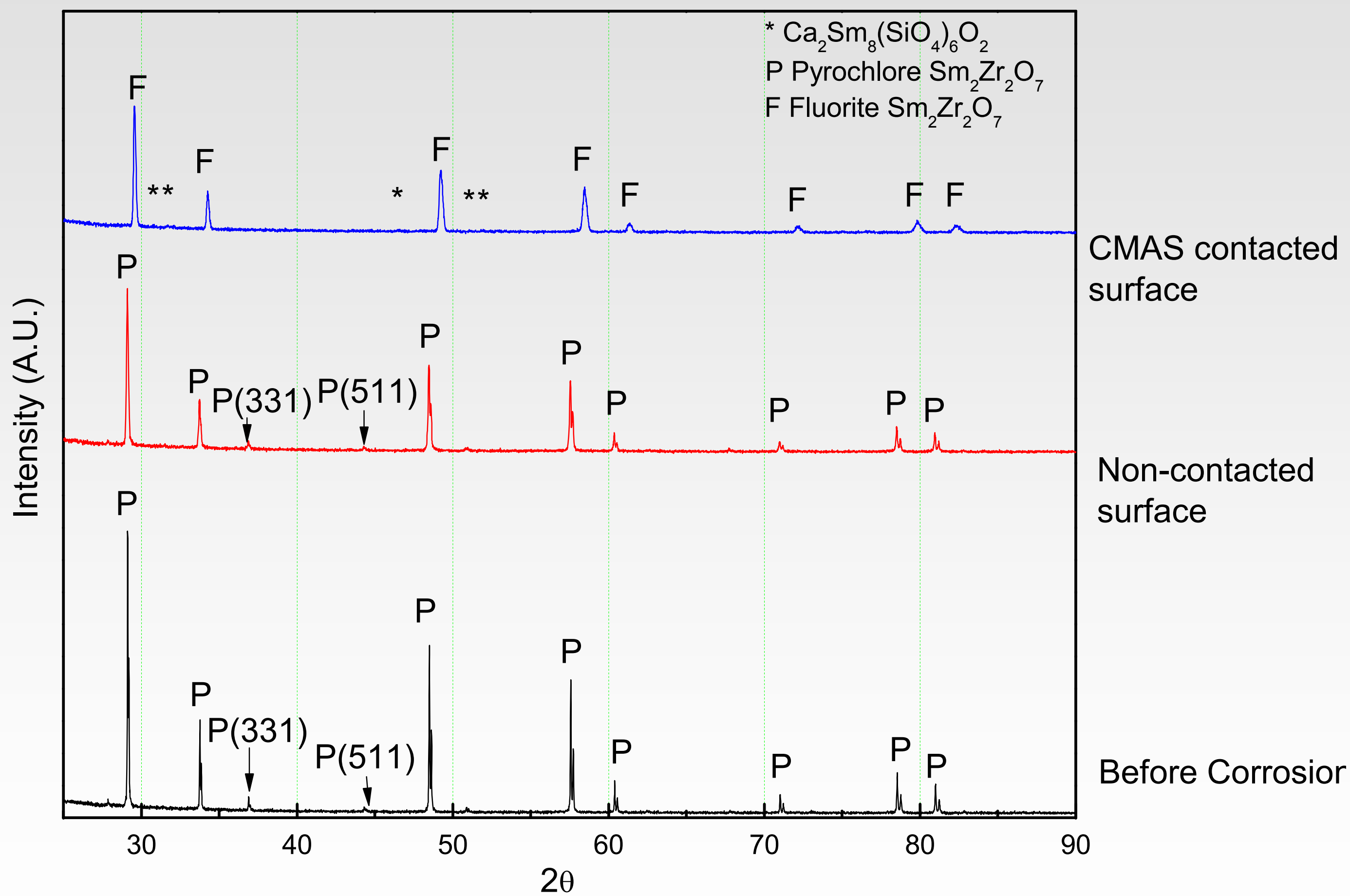





AUBURN UNIVERSITY

SAMUEL GINN COLLEGE OF ENGINEERING

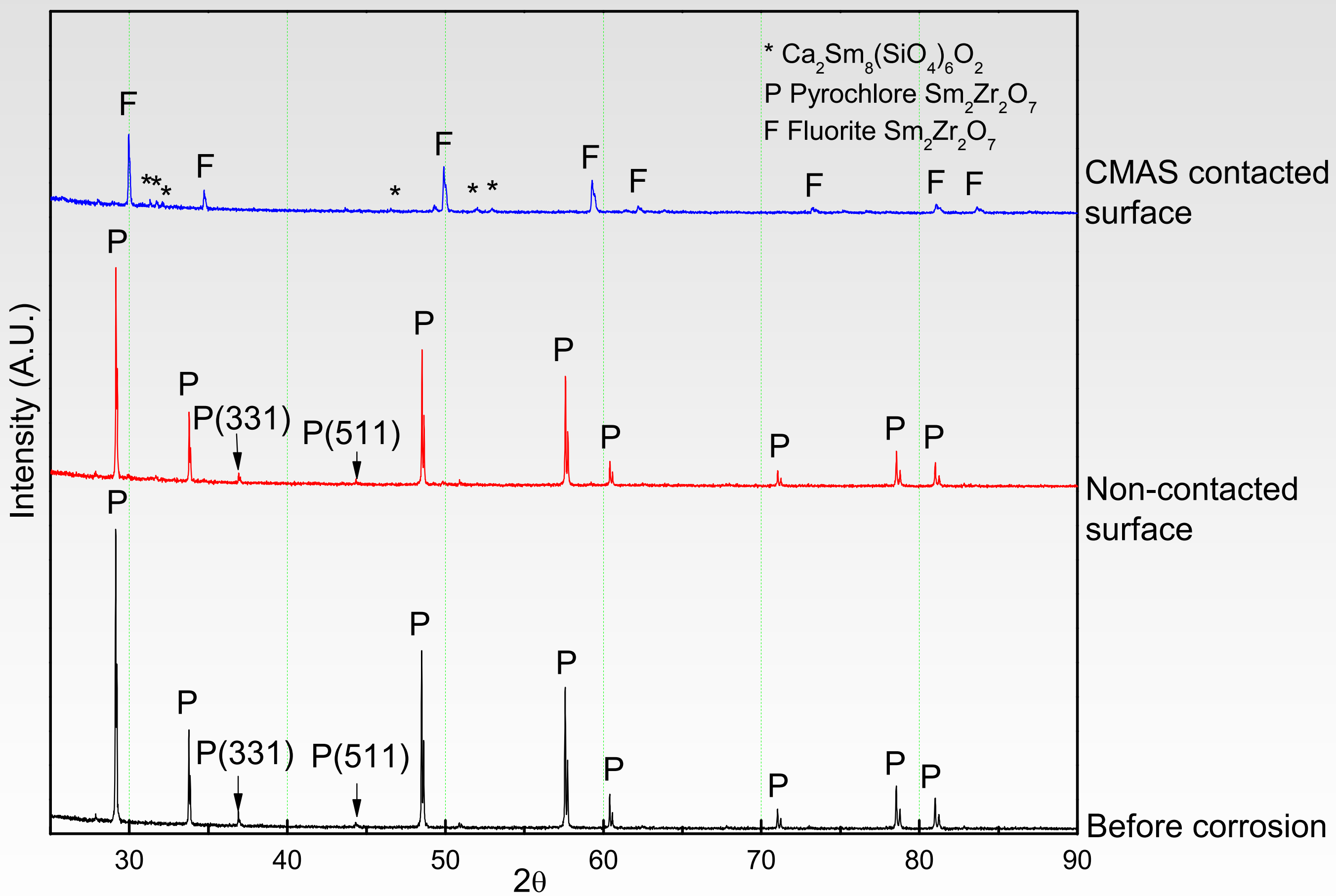
# $Sm_2Zr_2O_7$ after CMAS at 1400°C for 5 hours






AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 5 hours



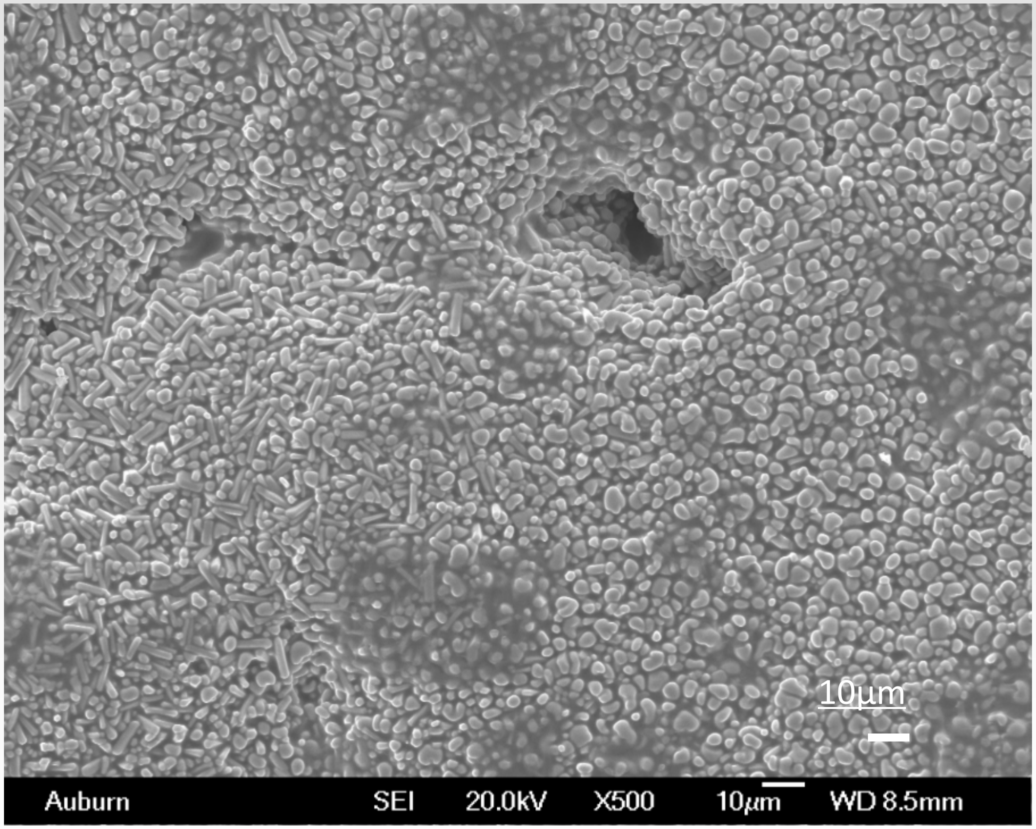




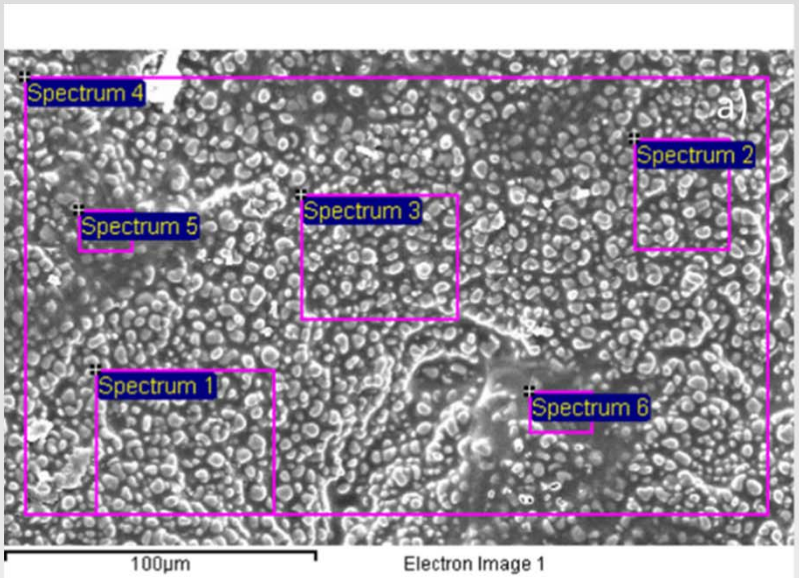

AUBURN UNIVERSITY

SAMUEL GINN COLLEGE OF ENGINEERING

# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 5 hours

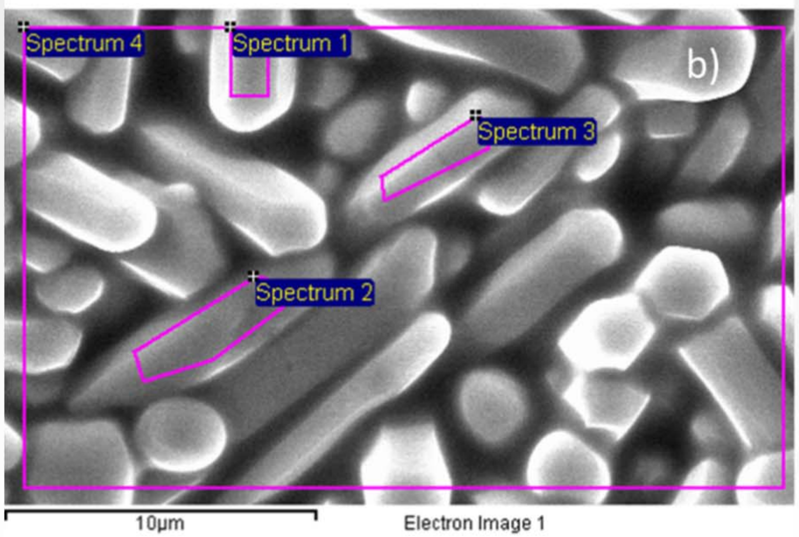


# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 5 hours




Atomic Percentage for a)

| | O | Mg | Al | Si | Ca | Zr | Sm |
|---|---|---|---|---|---|---|---|
| Spectrum 1 | 62 | 2 | 5 | 8 | 5 | 13 | 3 |
| Spectrum 2 | 62 | 2 | 5 | 8 | 6 | 12 | 3 |
| Spectrum 3 | 63 | 3 | 5 | 8 | 5 | 11 | 3 |
| Spectrum 4 | 61 | 3 | 5 | 8 | 7 | 11 | 2 |
| Spectrum 5 | 58 | 4 | 6 | 10 | 11 | 7 | 2 |
| Spectrum 6 | 44 | 3 | 7 | 13 | 19 | 7 | 2 |




Atomic Percentage for b)

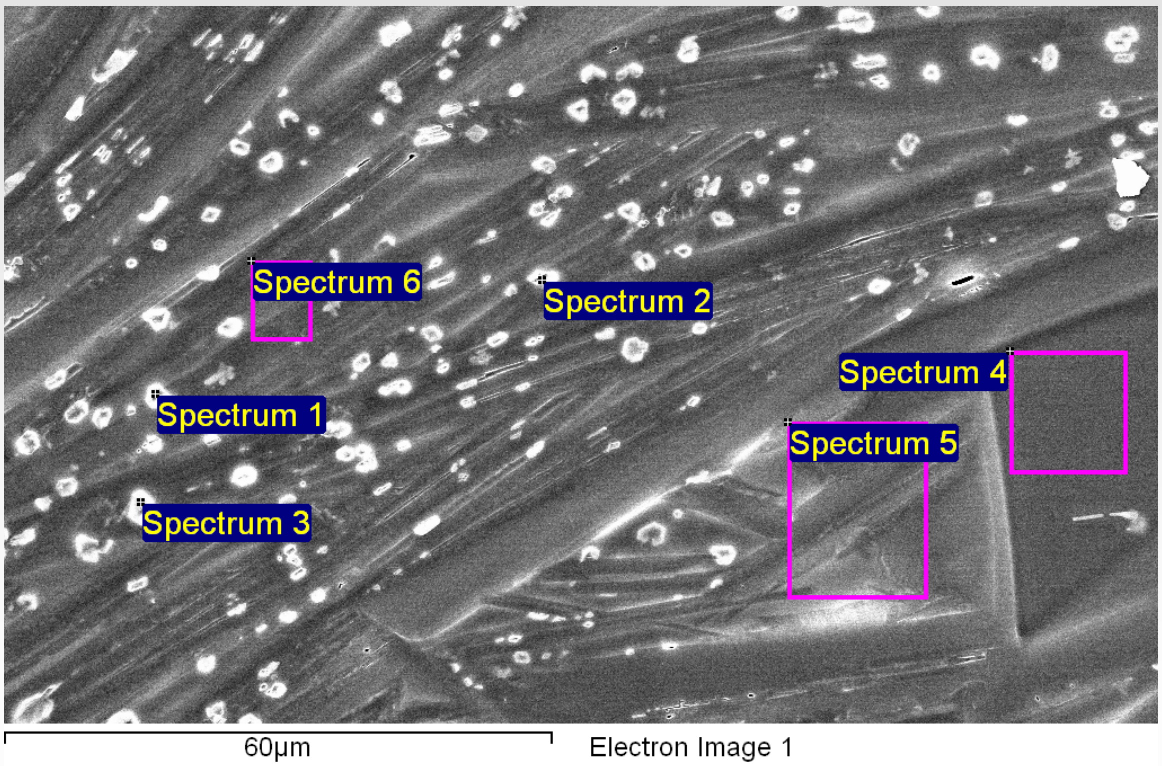
| | O | Mg | Al | Si | Ca | Zr | Sm |
|---|---|---|---|---|---|---|---|
| Spectrum 1 | 58 | | 1 | 15 | 6 | 1 | 15 |
| Spectrum 2 | 66 | | 1 | 13 | 5 | 1 | 11 |
| Spectrum 3 | 62 | | | 14 | 5 | 1 | 14 |
| Spectrum 4 | 60 | 2 | 3 | 12 | 6 | 4 | 10 |



AUBURN UNIVERSITY

SAMUEL GINN COLLEGE OF ENGINEERING

# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



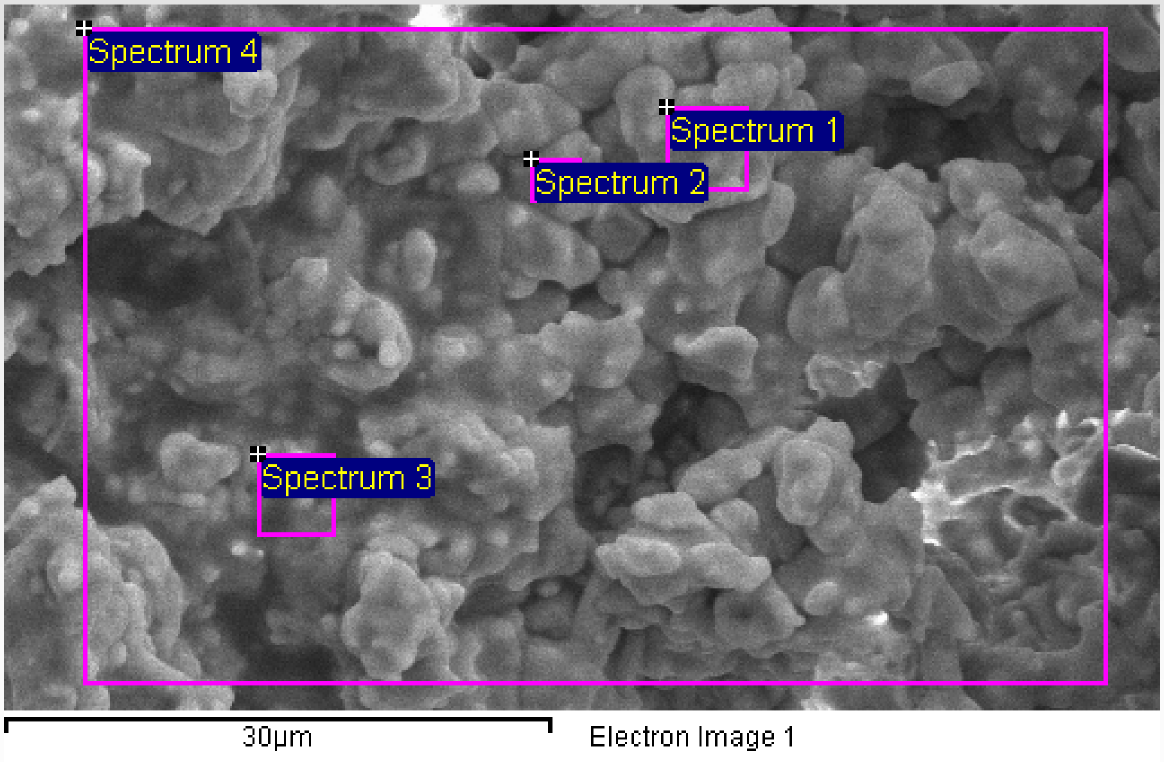

| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 47 | 1 | 8 | 20 | 11 | 2 | 8 | 3 |
| 2 | 60 | 3 | 10 | 18 | 7 | 1 | 1 | 2 |
| 3 | 58 | 1 | 5 | 16 | 9 | 1 | 7 | 3 |
| 4 | 53 | 6 | 5 | 17 | 18 | - | - | 2 |
| 5 | 54 | 4 | 7 | 17 | 13 | - | 1 | 2 |
| 6 | 55 | 3 | 10 | 19 | 10 | 1 | 1 | 2 |

1,3: Bright spots
Sm silicate



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

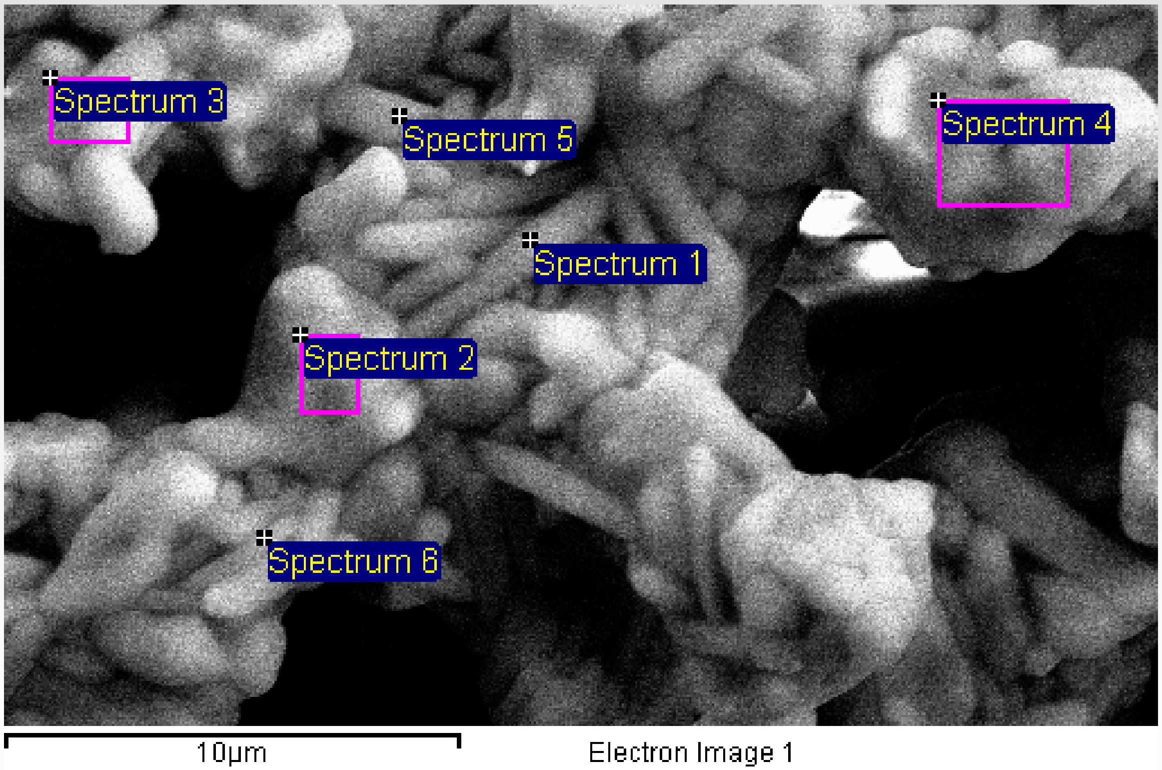
# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours




| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 62 | - | 1 | 1 | 2 | 27 | 4 | 3 |
| 2 | 66 | - | - | 1 | 2 | 25 | 3 | 3 |
| 3 | 58 | 2 | 5 | 7 | 10 | 13 | 3 | 3 |
| 4 | 65 | 1 | 2 | 3 | 5 | 18 | 4 | 2 |

Cubic fluorite

# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



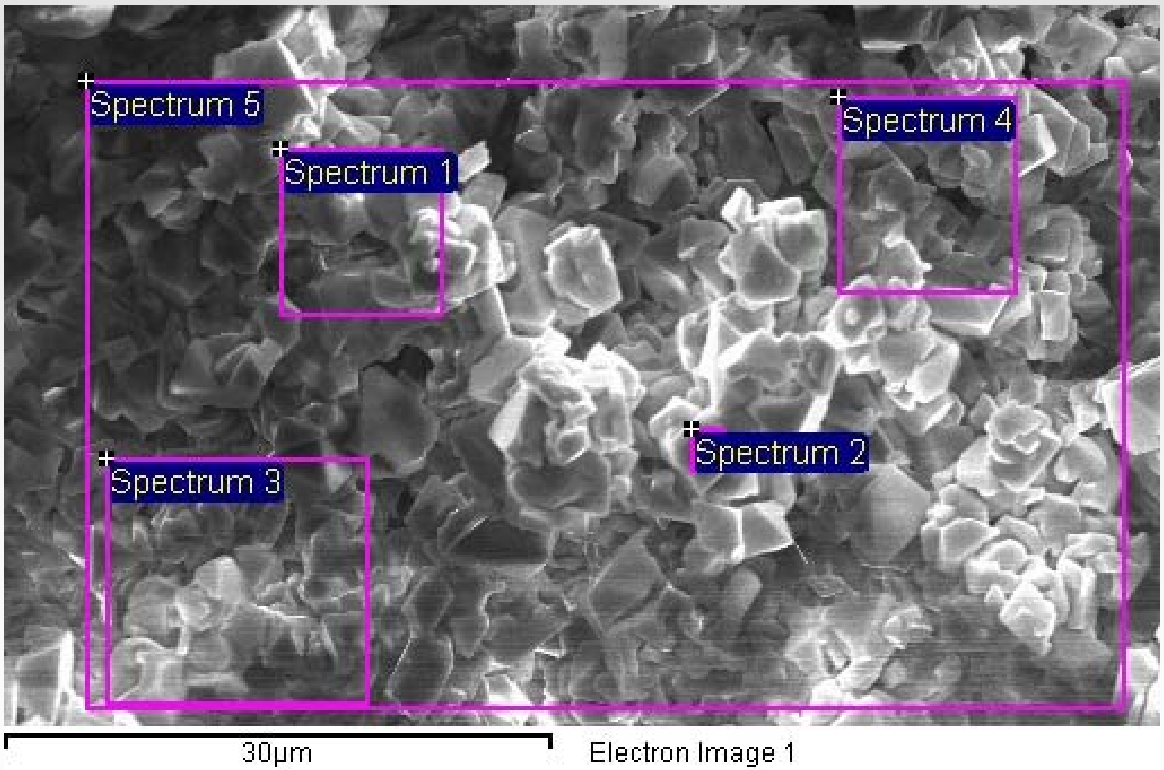

| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 47 | - | - | 10 | 6 | 6 | 23 | 9 |
| 2 | 44 | - | - | 2 | 4 | 38 | 7 | 5 |
| 3 | 51 | - | - | 7 | 7 | 15 | 15 | 5 |
| 4 | 54 | - | - | 2 | 3 | 31 | 6 | 4 |
| 5 | 40 | - | - | 8 | 7 | 12 | 26 | 9 |
| 6 | 53 | - | 1 | 4 | 4 | 26 | 7 | 5 |

1,3,5: Sm silicate
2,4,6: Cubic fluorite



AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



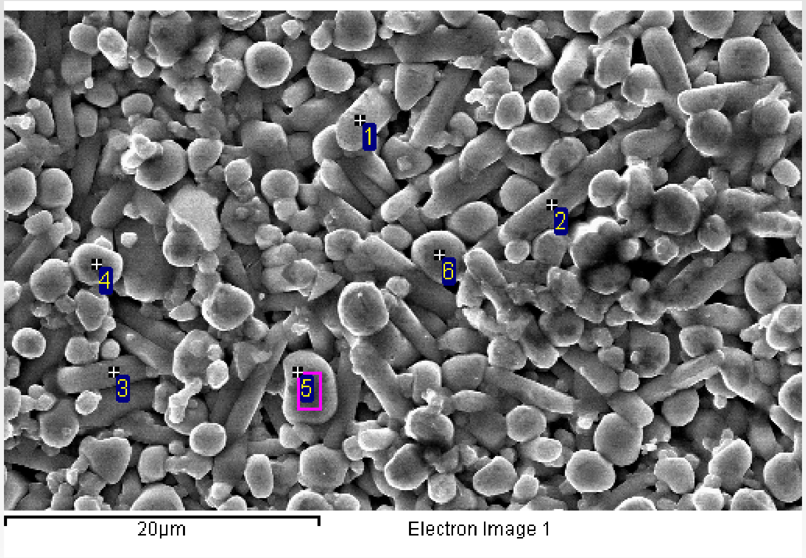

| Concentration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| # | O | Mg | Al | Si | Ca | Zr | Gd | Au |
| 1 | 67 | - | 1 | - | - | 18 | 12 | 2 |
| 2 | 72 | - | - | 1 | - | 17 | 7 | 3 |
| 3 | 68 | - | - | - | - | 19 | 13 | - |
| 4 | 65 | - | - | - | - | 18 | 15 | 3 |
| 5 | 66 | - | - | 1 | - | 18 | 12 | 3 |

Pyrochlore



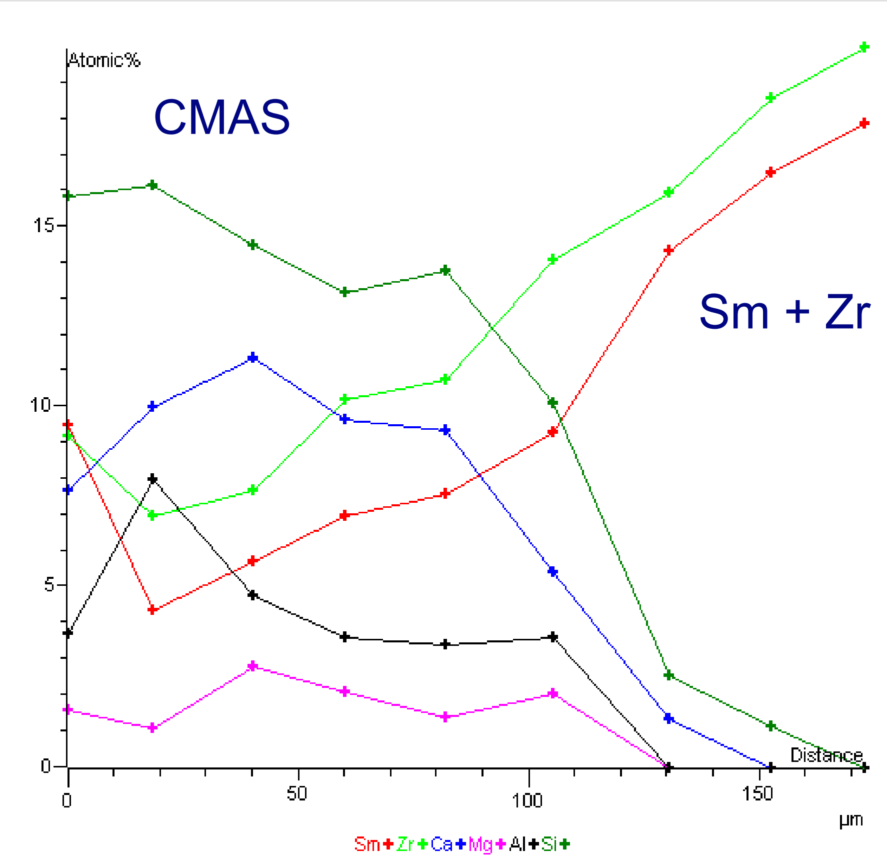
AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

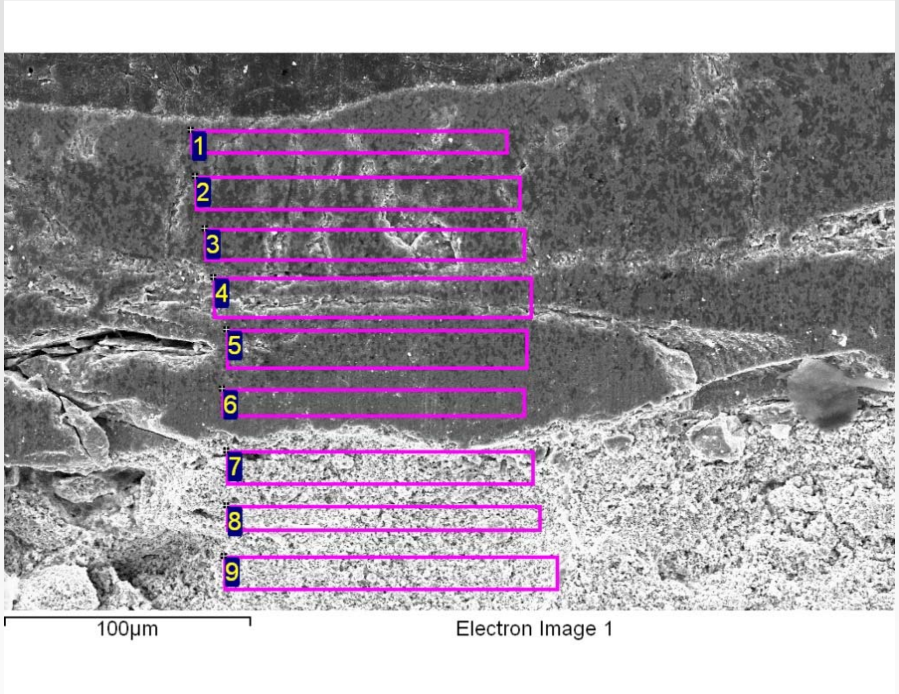
# $Sm_2Zr_2O_7$ after CMAS at 1200°C – 60 hours




| Concentration | | | | | | |
|---|---|---|---|---|---|---|
| # | Mg | Al | Si | Ca | Zr | Gd |
| 1 | 0 | 0 | 15 | 6 | 7 | 13 |
| 2 | 0 | 0 | 16 | 6 | 5 | 14 |
| 3 | 0 | 0 | 15 | 6 | 6 | 12 |
| 4 | 0 | 0 | 0 | 3 | 33 | 3 |
| 5 | 0 | 0 | 1 | 2 | 33 | 3 |
| 6 | 0 | 0 | 1 | 3 | 37 | 4 |

# $Sm_2Zr_2O_7$ after CMAS at 1200°C – 60 hours

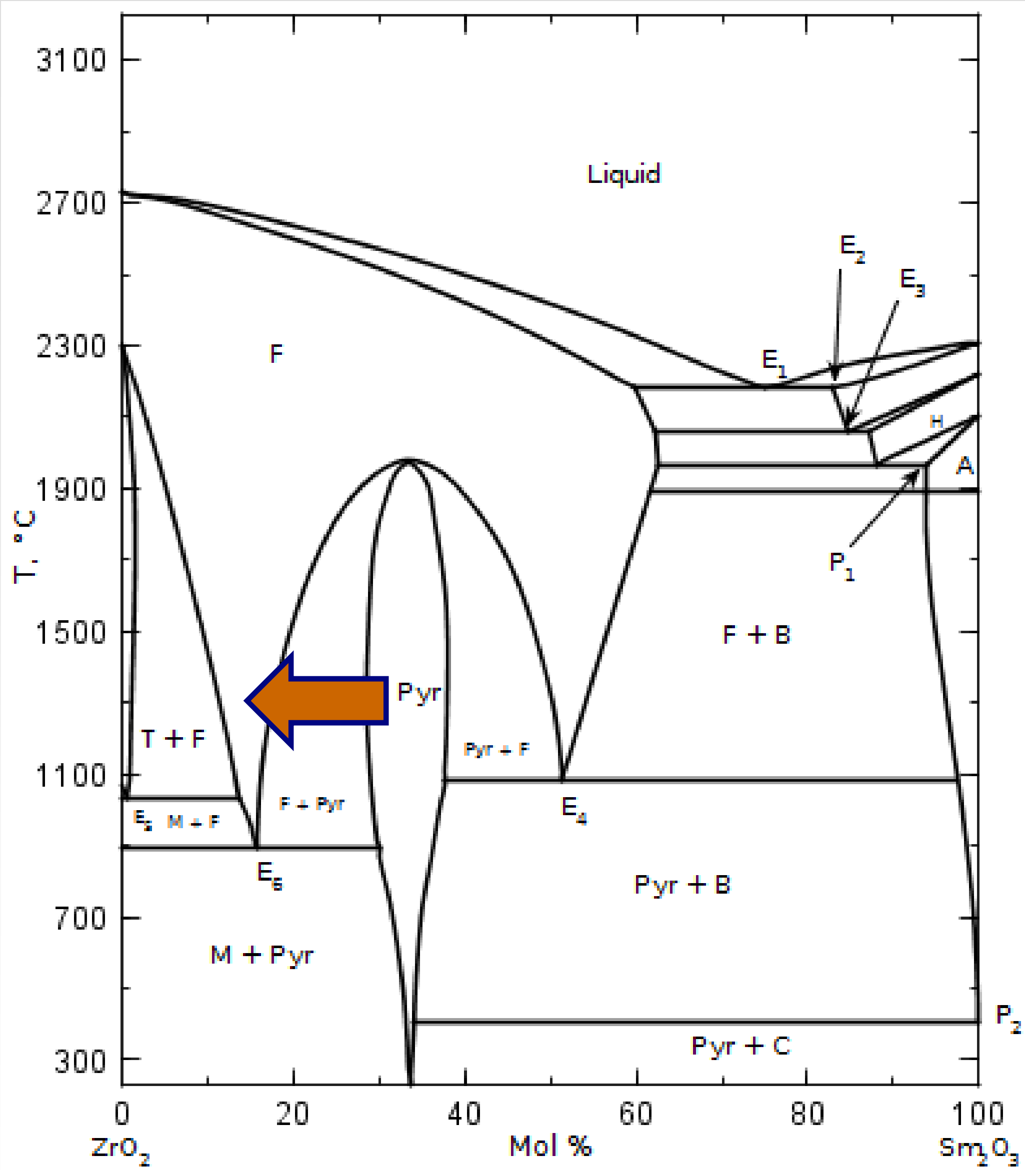





AUBURN UNIVERSITY
SAMUEL GINN COLLEGE OF ENGINEERING

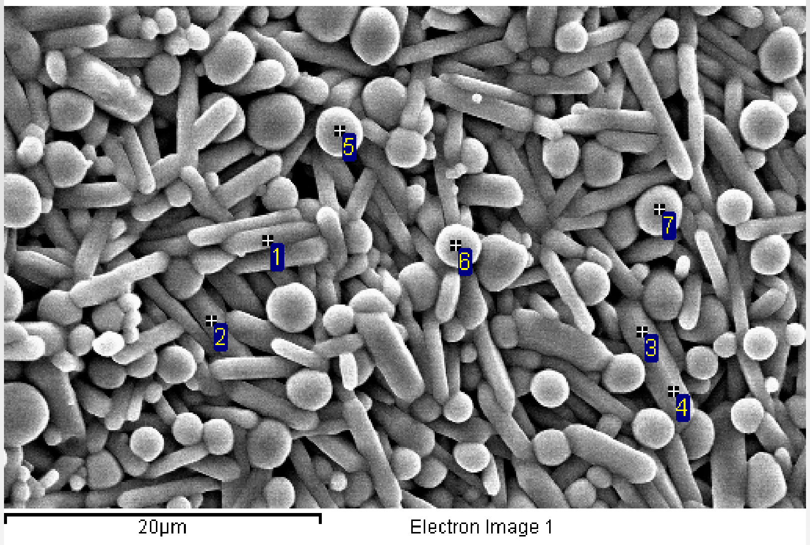
# $ZrO_2$-$Sm_2O_3$ phase diagram




T = tetragonal
F = cubic fluorite
M – monoclinic
Pyr = pyrochlore
C, B, H = $Sm_2O_3$ phases

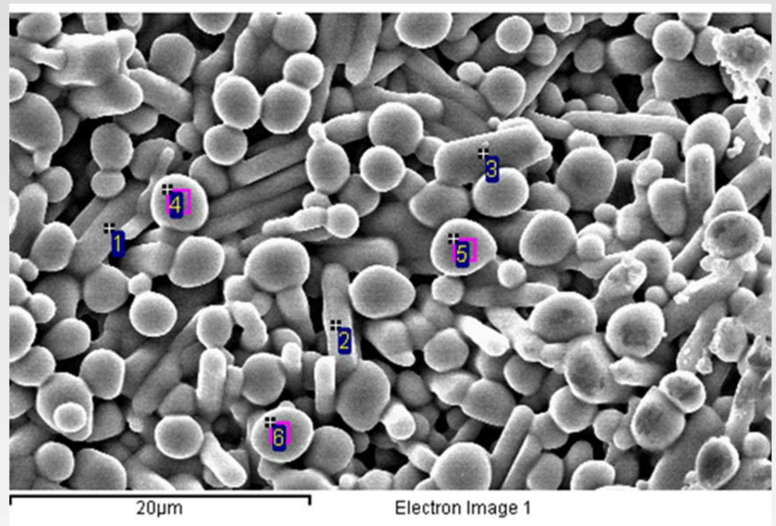
# $(Gd,Sm)_2Zr_2O_7$ after CMAS at 1200°C for 60 hours

$(Gd_{0.8}Sm_{0.2})_2Zr_2O_7$




| Concentration | | | | | | | |
|---|---|---|---|---|---|---|---|
| # | Mg | Al | Si | Ca | Zr | Sm | Gd |
| 1 | 0 | 0 | 14 | 5 | 5 | 10 | 0 |
| 2 | 0 | 0 | 19 | 7 | 6 | 17 | 0 |
| 3 | 0 | 0 | 17 | 6 | 8 | 14 | 0 |
| 4 | 0 | 0 | 17 | 6 | 8 | 14 | 1 |
| 5 | 0 | 0 | 1 | 3 | 41 | 5 | 0 |
| 6 | 0 | 0 | 3 | 3 | 46 | 6 | 0 |
| 7 | 0 | 0 | 2 | 3 | 45 | 6 | 0 |

$(Gd_{0.6}Sm_{0.4})_2Zr_2O_7$




| Concentration | | | | | | | |
|---|---|---|---|---|---|---|---|
| # | Mg | Al | Si | Ca | Zr | Sm | Gd |
| 1 | 0 | 0 | 17 | 7 | 6 | 6 | 9 |
| 2 | 0 | 0 | 15 | 10 | 9 | 10 | 14 |
| 3 | 0 | 0 | 13 | 5 | 4 | 4 | 6 |
| 4 | 0 | 0 | 1 | 3 | 35 | 1 | 3 |
| 5 | 0 | 0 | 1 | 2 | 36 | 2 | 3 |
| 6 | 0 | 0 | 1 | 3 | 39 | 2 | 4 |

# Conclusions

- Coatings
  - Ni flash coating needed to obtain quality Re coating
  - Only 2 out of 20 Ir coatings on Re-coatings round samples were successful
  - No Ir coatings on rectangular samples were successful
- EBC materials
  - Reaction of $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$ and $(Gd,Sm)_2Zr_2O_7$ with CMAS evaluated
    - Pyrochlore dissolves in CMAS
    - Reprecipitates as lanthanide silicate and cubic fluorite phase