# Reduced Cost Bond Layers for Multi-Layer Thermal/Environmental Barrier Coatings


AUBURN UNIVERSITY

SAMUEL GINN
COLLEGE OF ENGINEERING

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# Participants

- Auburn University
  - Jeff Fergus
  - Students
    - Graduate: Honglong (Henry) Wang, Wenzhou Deng, Xingxing Zhang
    - Undergraduate: Emily Tarwater, Kai Roebbecke
  - Visiting scholars
    - Ahmet Bakal, Sudip Dasgupta
- Plasma Processes LLC
  - Kyle Murphree
  - Tim McKechnie

# Introduction

- Thermal barrier coatings (TBCs) to increase operating temperature of gas turbine engines
- Ca-Mg-Al-Si oxides (CMAS) injected into engine degrade TBCs
- Pyrochlore oxides offer potential for improved resistance to CMAS corrosion and reduced thermal conductivity

# Original 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



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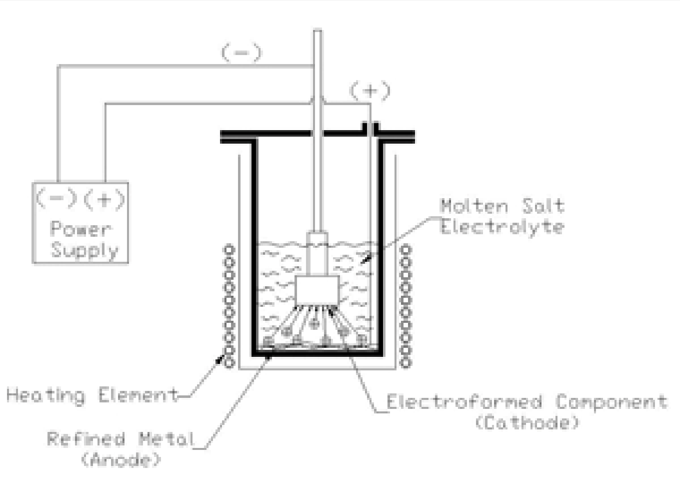
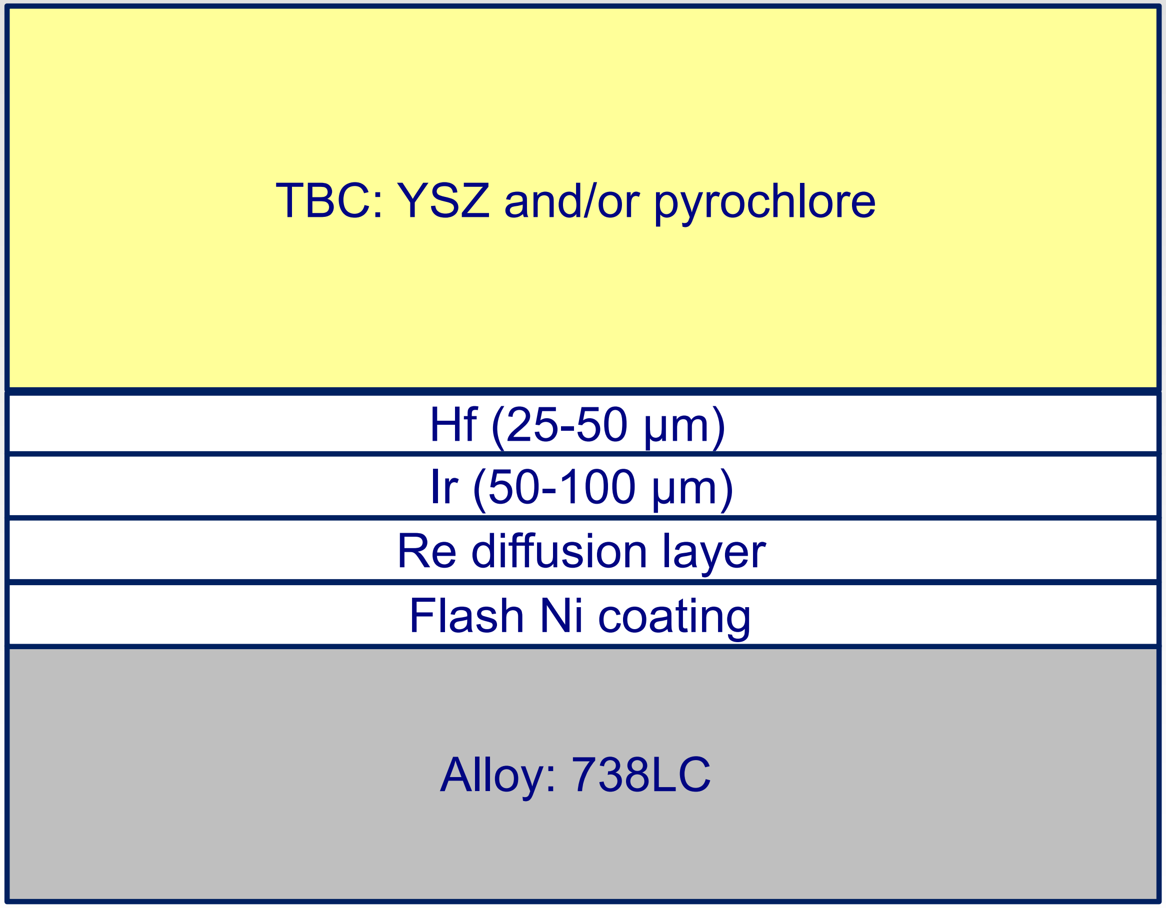
# Bond coat system

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




http://www.plasmapros.com/

# Thermal barrier coating system

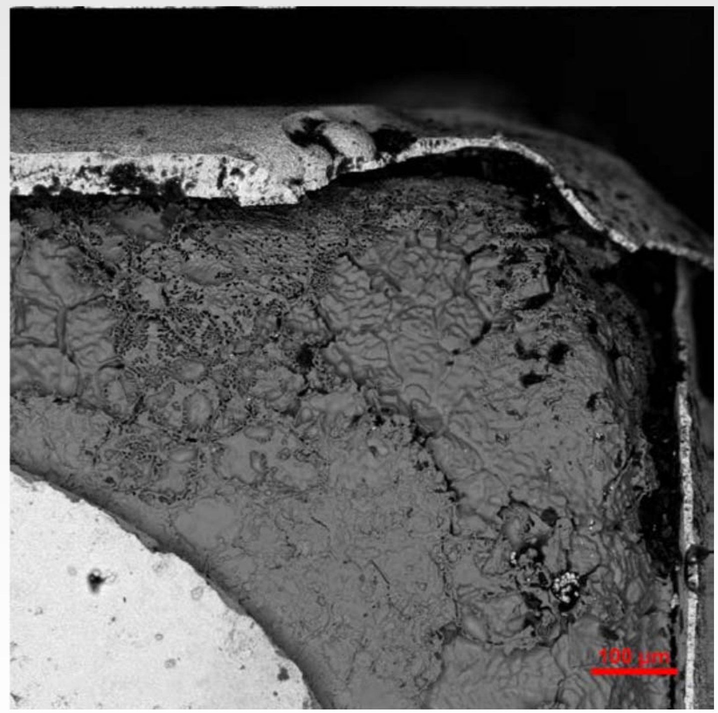



Plasma spray for YSZ / pyrochlore

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

# Iridium coatings on rectangular samples

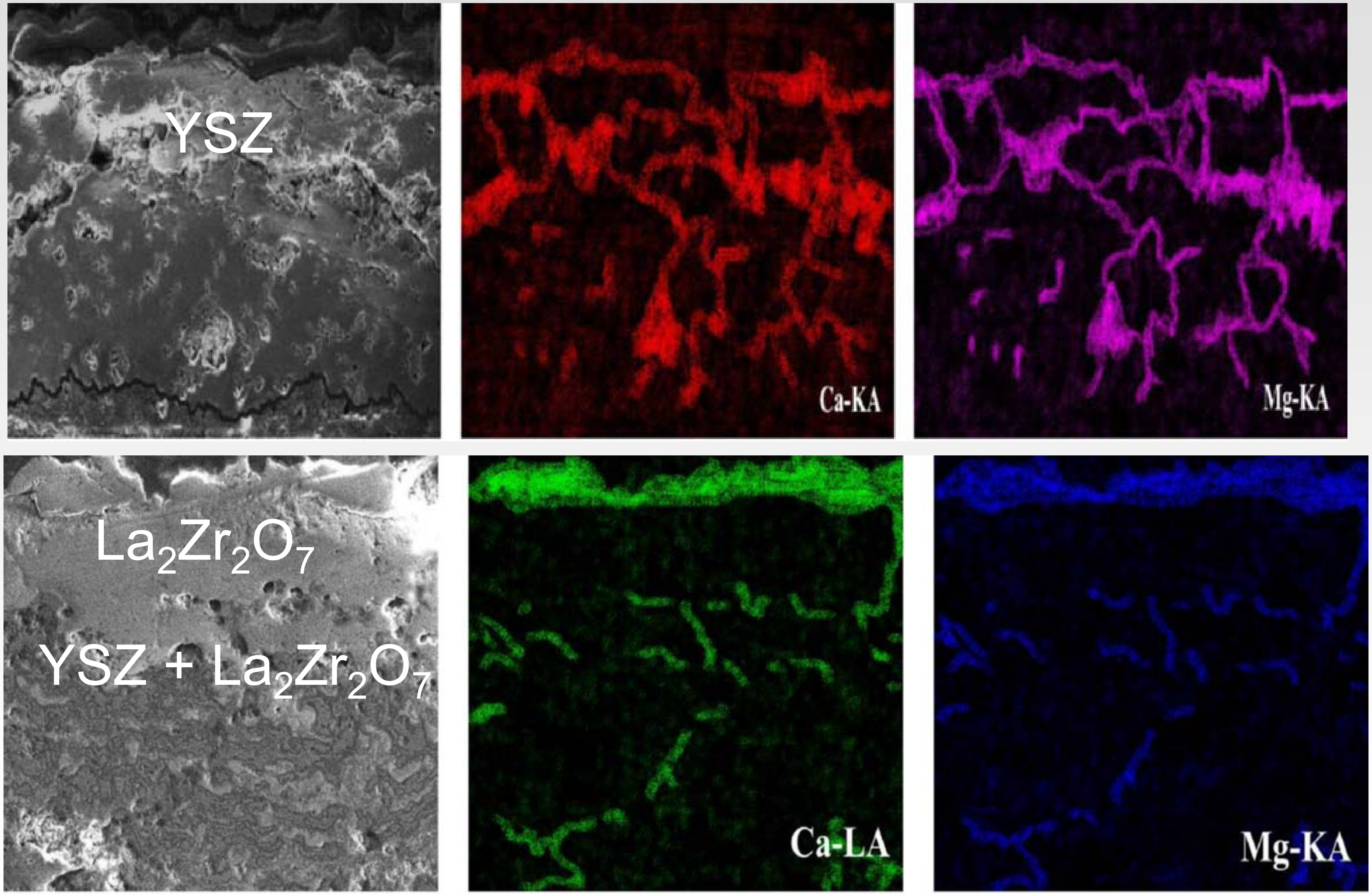
Rectangular coatings for
mechanical testing



# Revised approach

- Plasma-sprayed materials to corroborate results from sintered ceramics
  - YSZ (400 µm)
  - YSZ (225 µm) + AU $Gd_2Zr_2O_7$ synthesized (75 µm)
  - YSZ (100 µm) + yttrium oxide (175 µm)
  - YSZ (100 µm) + Sulzer Zr-Y oxide (175 µm)

# Reaction with CMAS




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



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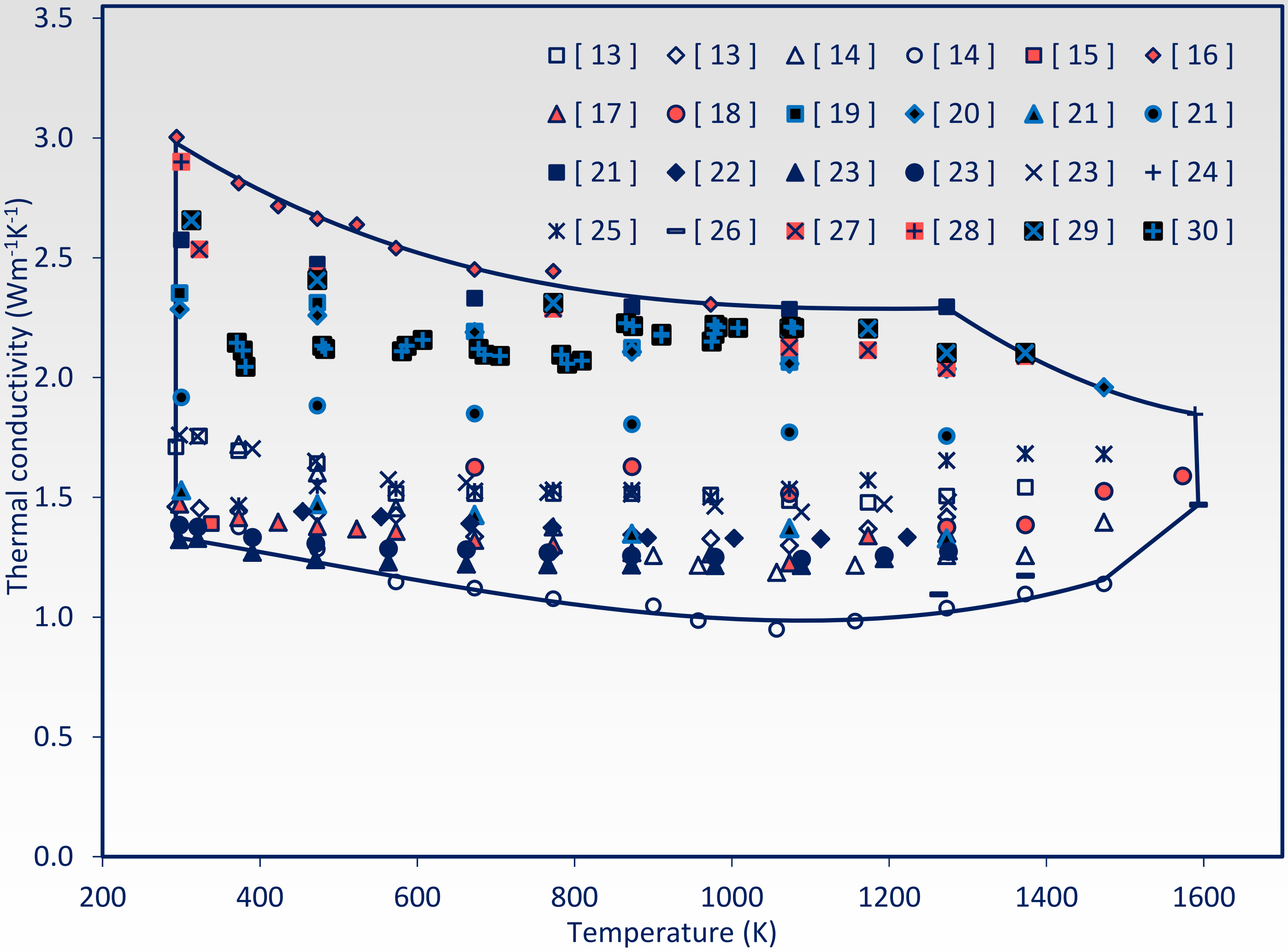
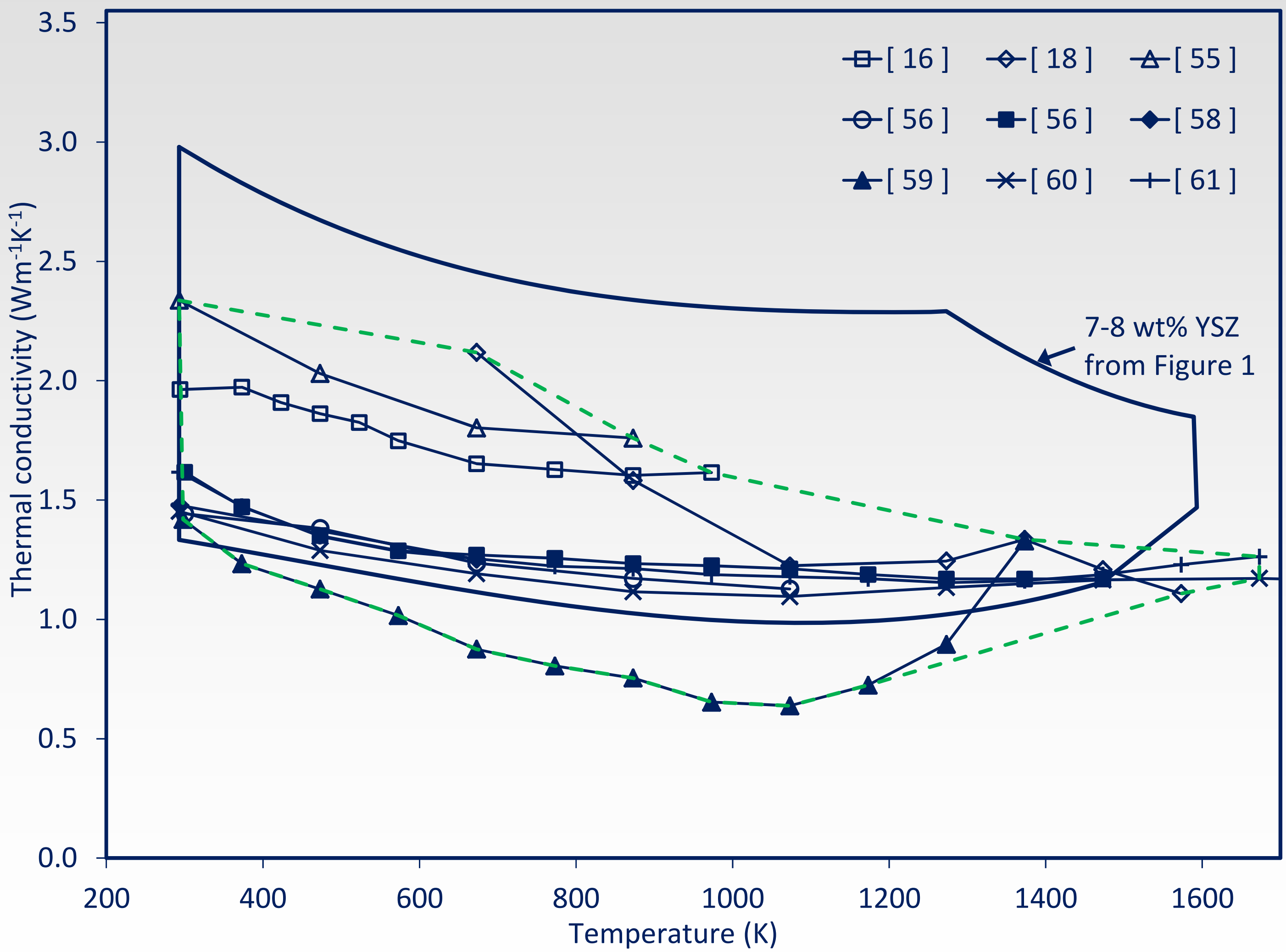
# Thermal conductivity of zirconia with 7-8% yttria




Range of thermal conductivities due to variations in morphology and microstructure

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

# 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).

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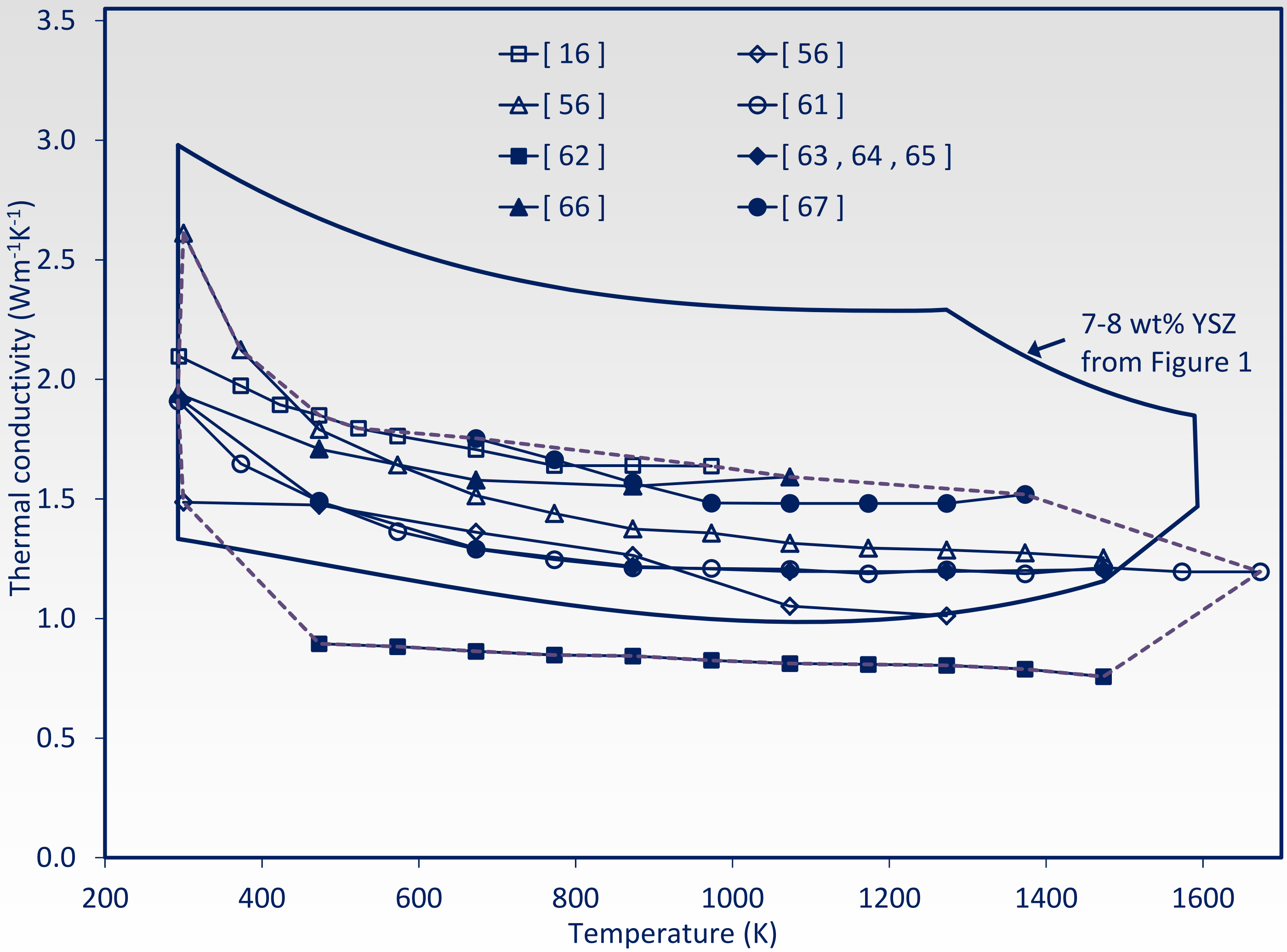
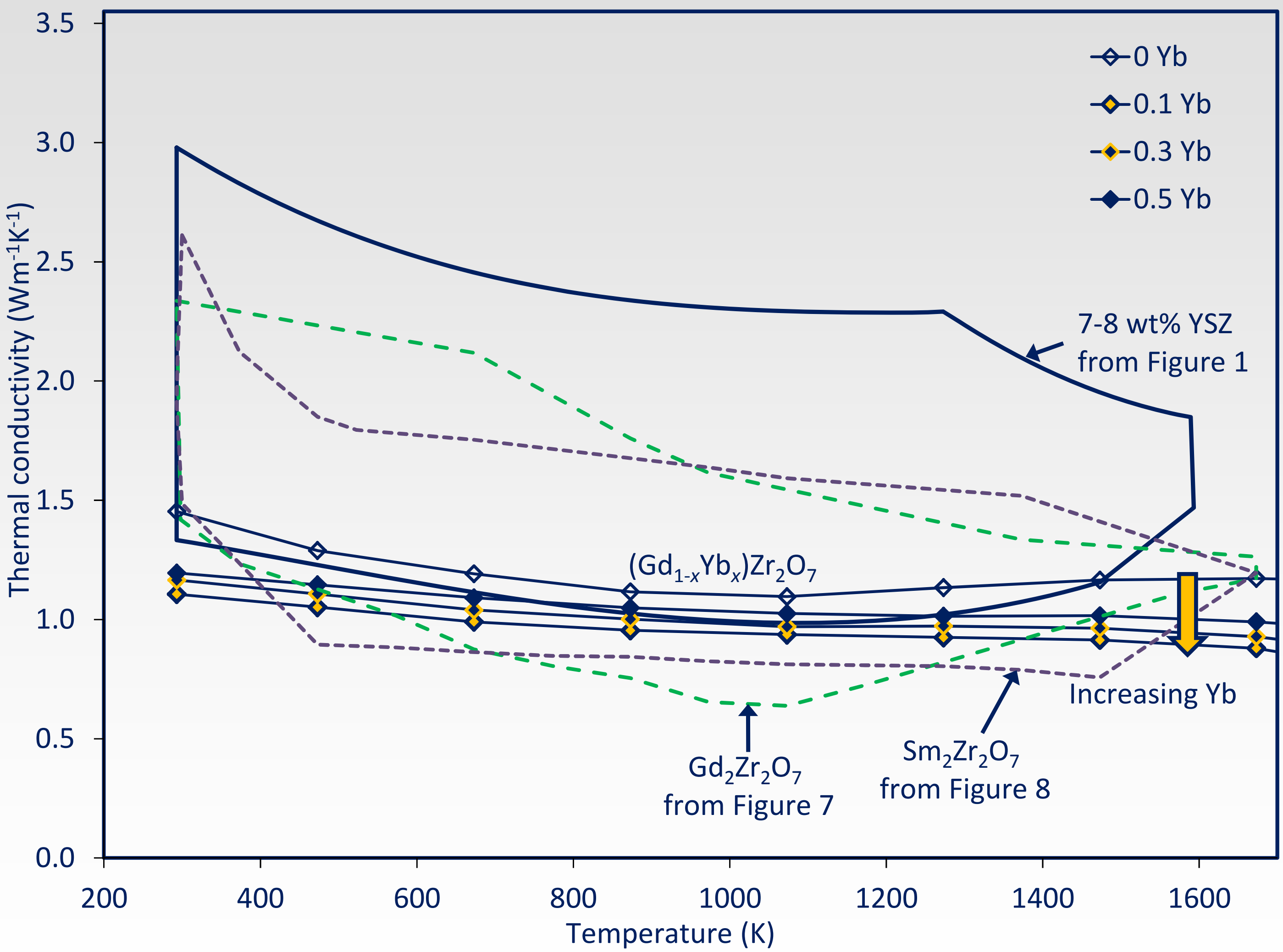
# Thermal conductivity of $Sm_2Zr_2O_7$




κ of $Sm_2Zr_2O_7$ in lower range of YSZ

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

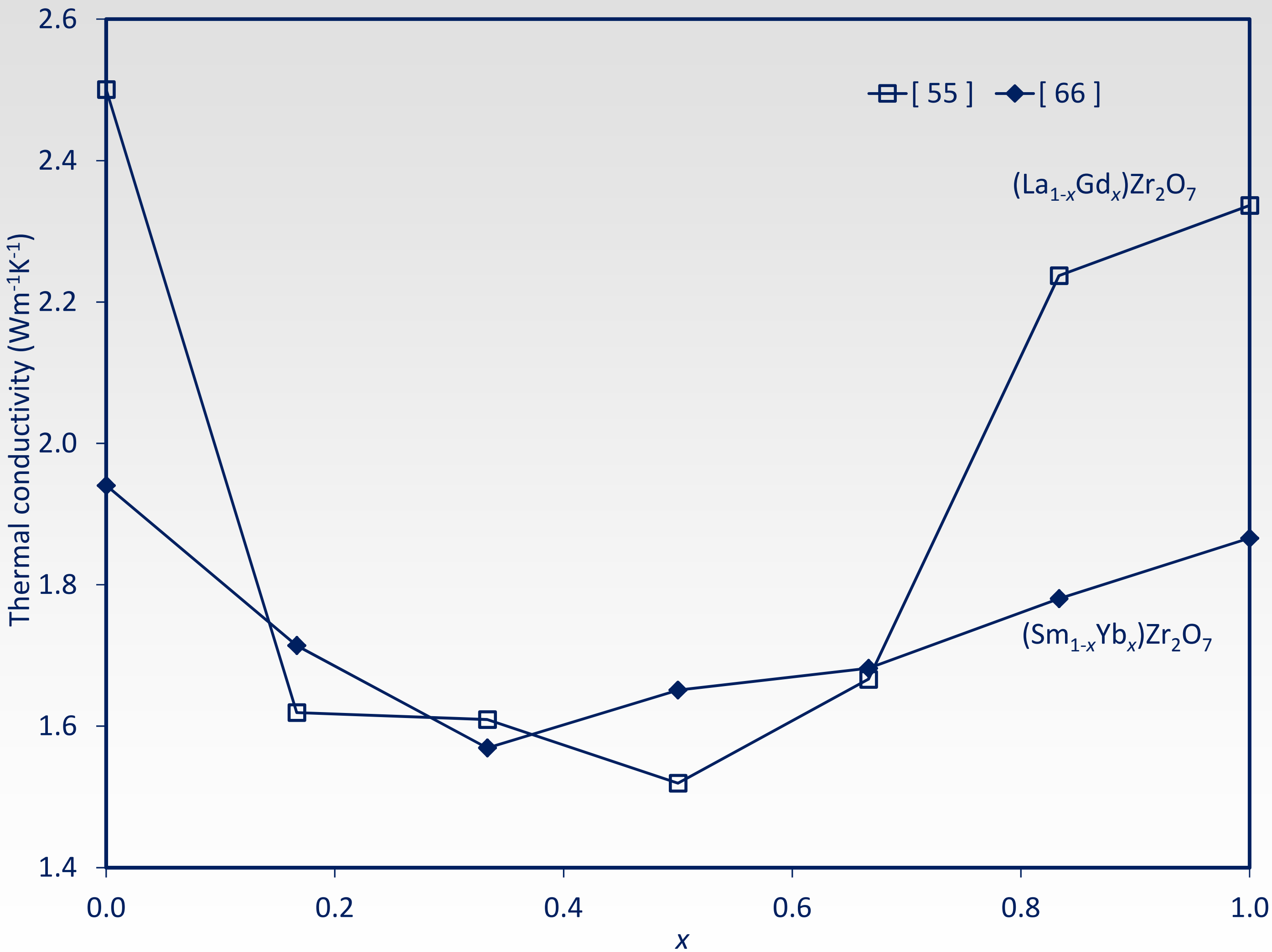
# Ytterbium-doping




Doping can reduce κ

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

# Thermal conductivity of mixed pyrochlores




Pyrochlore solid solutions have lower κ

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

# Experimental

- Synthesis of pyrochlore
  - Co-precipitation
- CMAS exposure
  - Melt / solidify Ca-Mg-Al-Si oxide mixtures
  - Crush glass, apply to pyrochlore pellet
  - Expose to 1200-1500°C
- Characterization
  - XRD, SEM, optical microscopy

| CMAS Composition | | |
|---|---|---|
| Oxide | Percentage | |
| | 1 | 2 |
| CaO | 33 | 29 |
| MgO | 9 | 8 |
| $AlO_{1.5}$ | 13 | 23 |
| $SiO_2$ | 45 | 40 |



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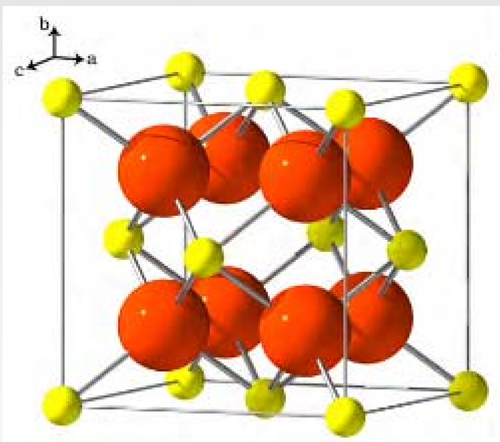
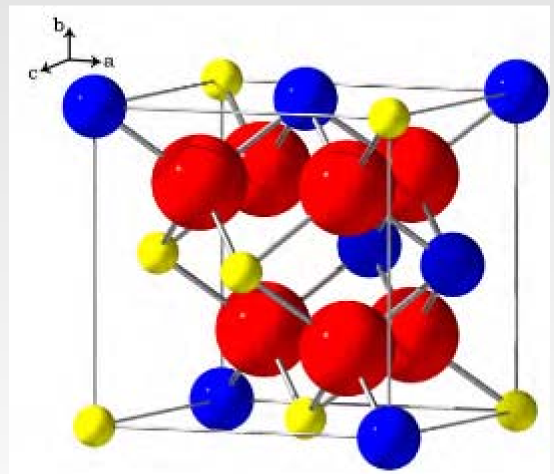
# Crystal Structure

Cubic Fluorite




Pyrochlore




Ordering of Ln / Zr

A.R. Cleave (2006)



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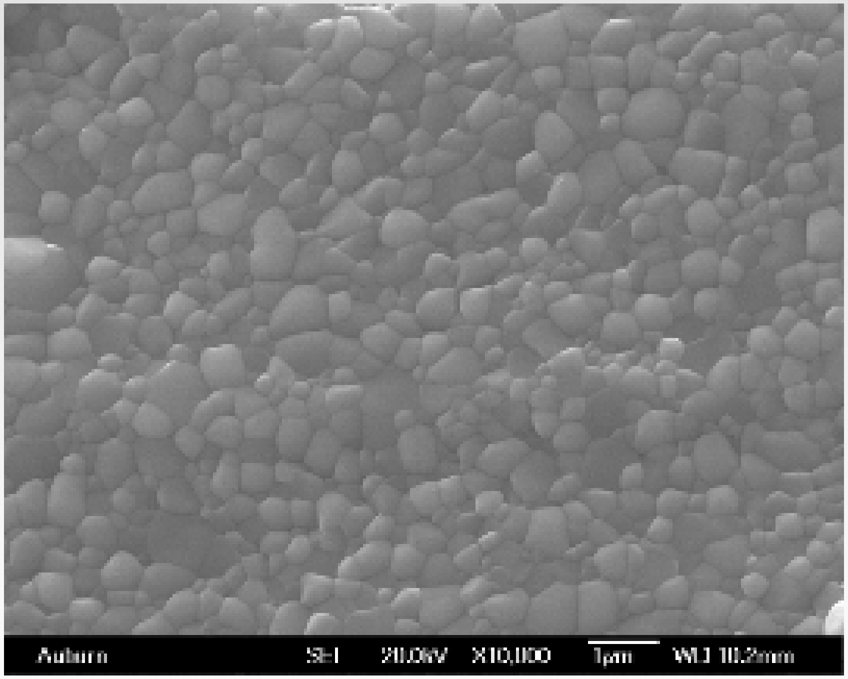
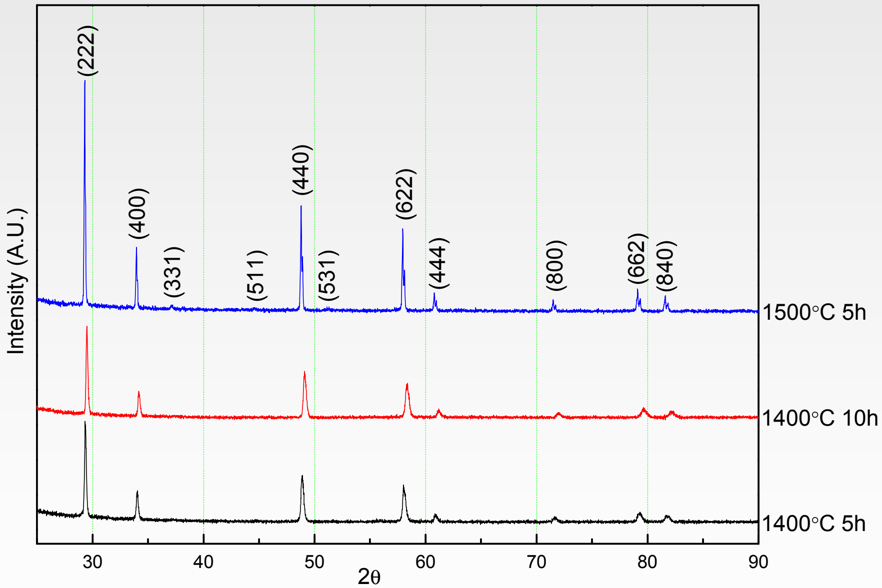
# As-Synthesized $Gd_2Zr_2O_7$




(331), (511), (531) indicate pyrochlore phase



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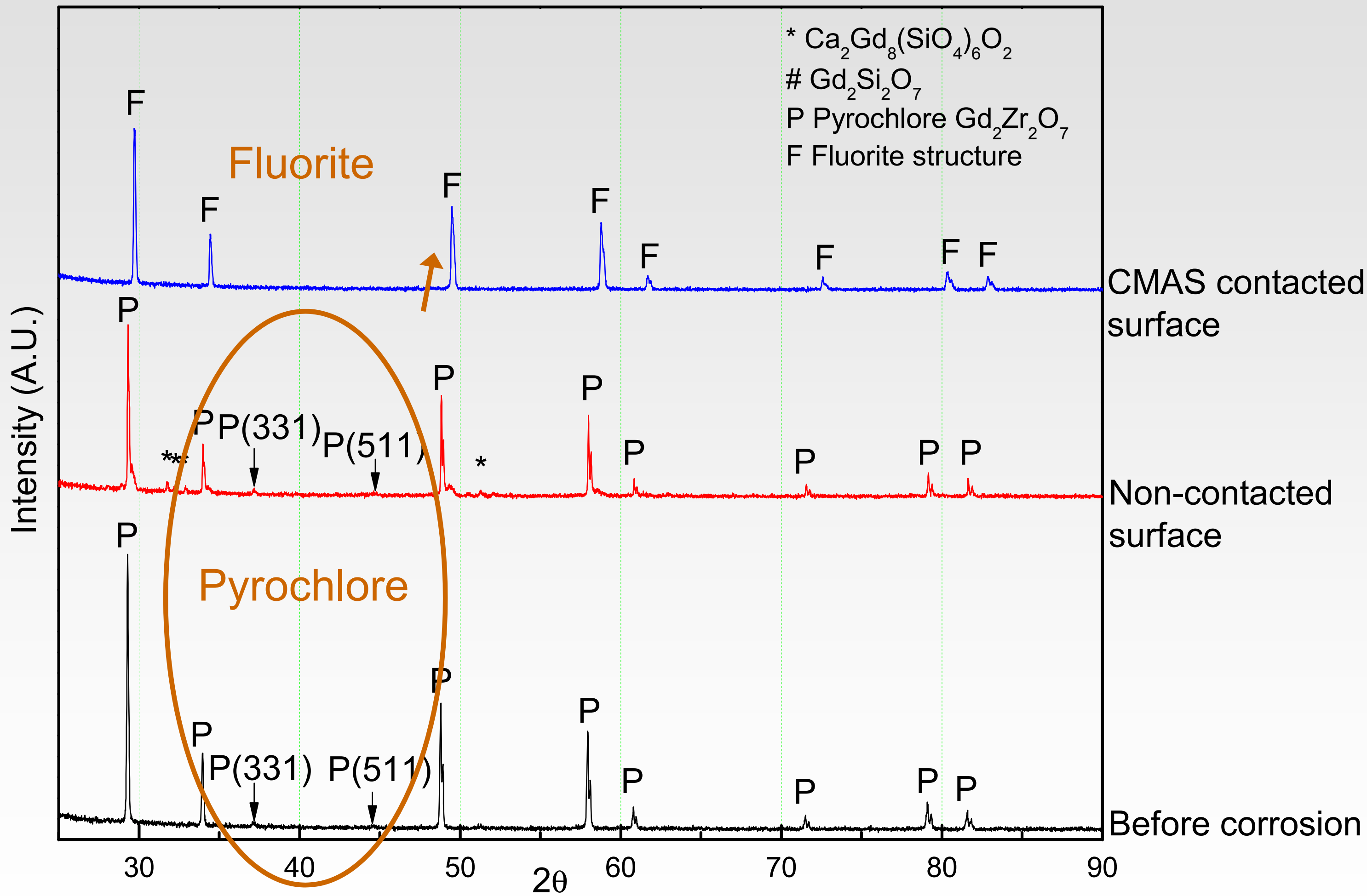
# $Gd_2Zr_2O_7$ after CMAS at 1400°C for 5 hours



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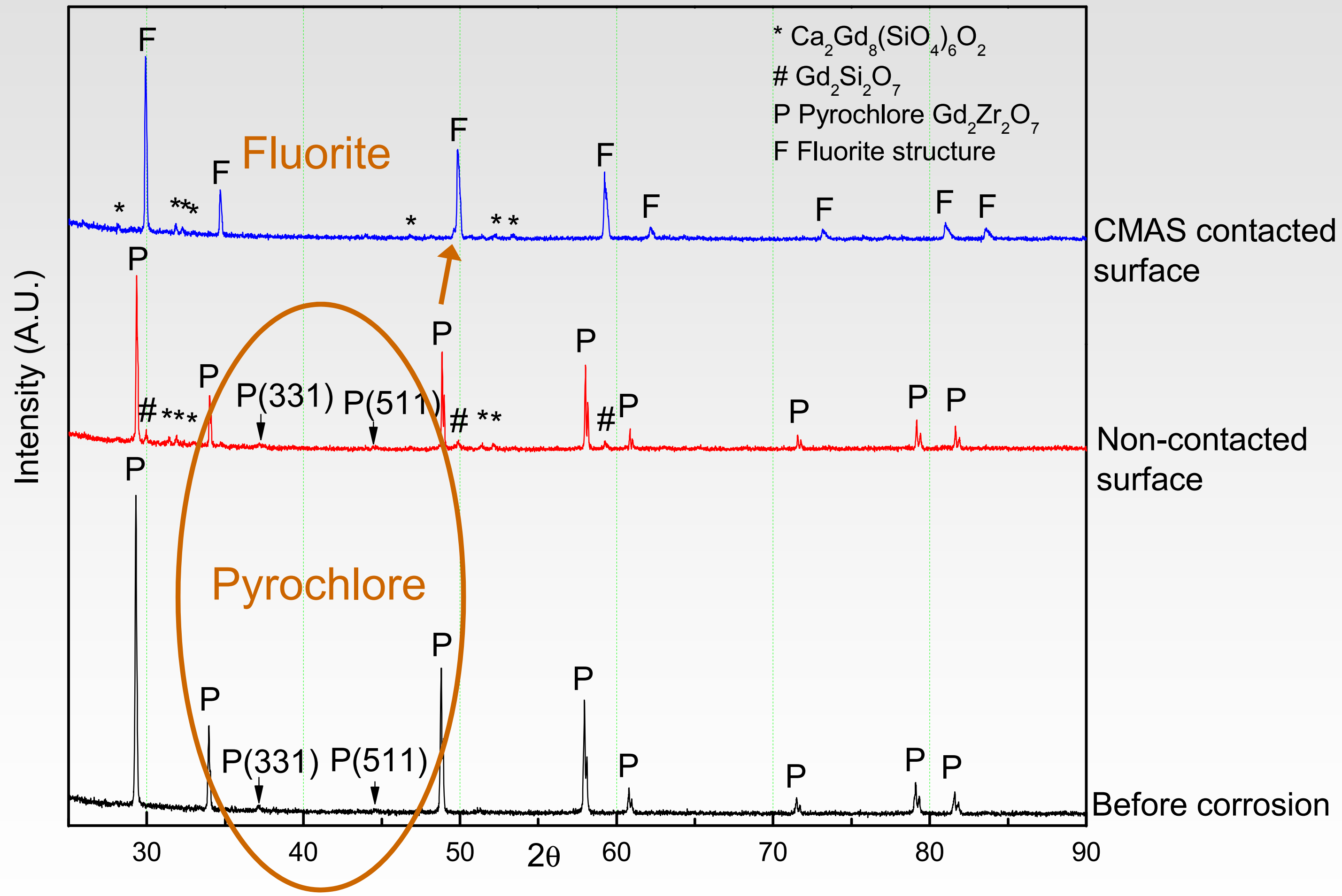
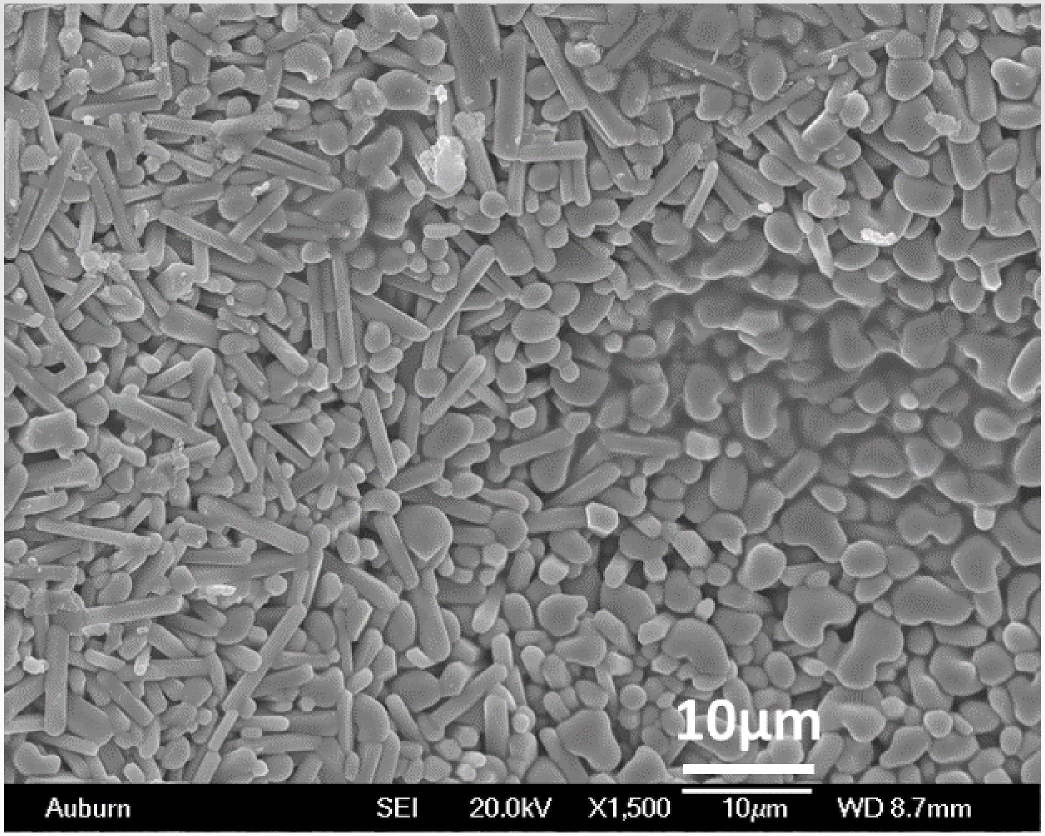
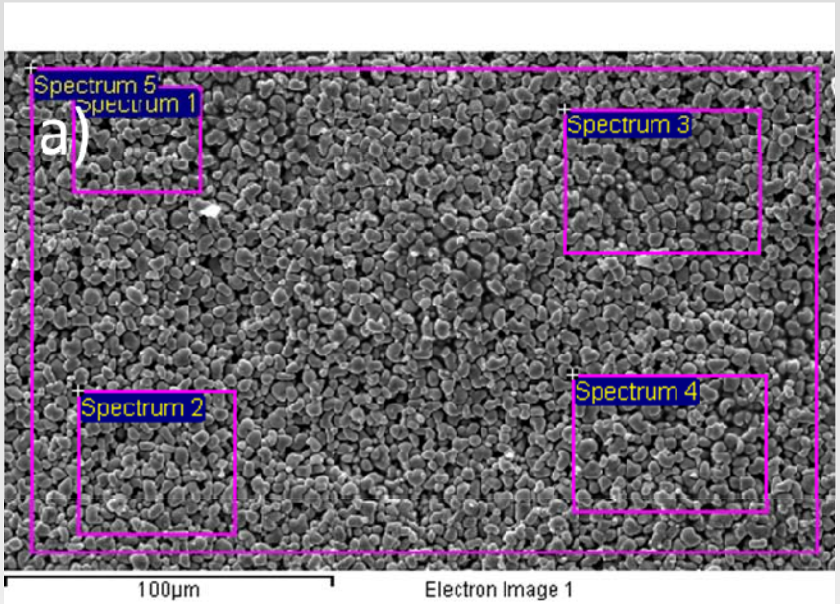
# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 5 hours



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

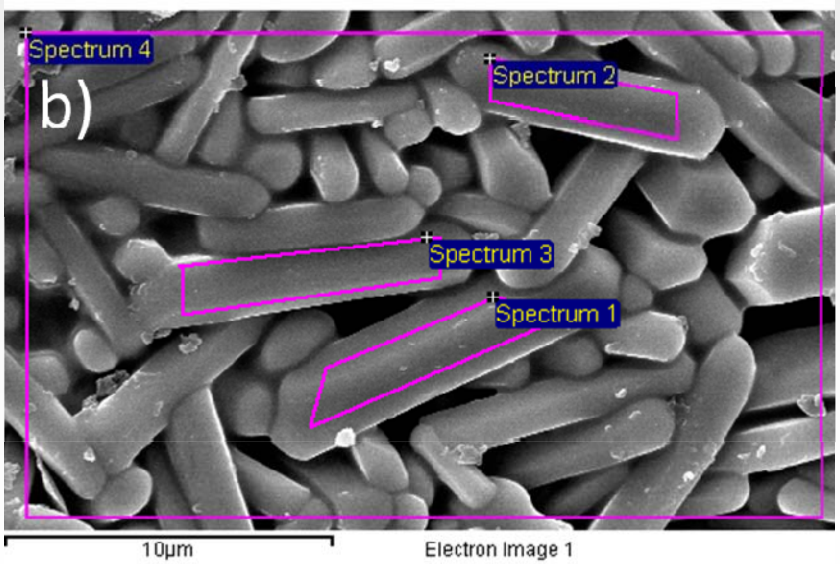





Atomic Percentage for a)

| | 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 |

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

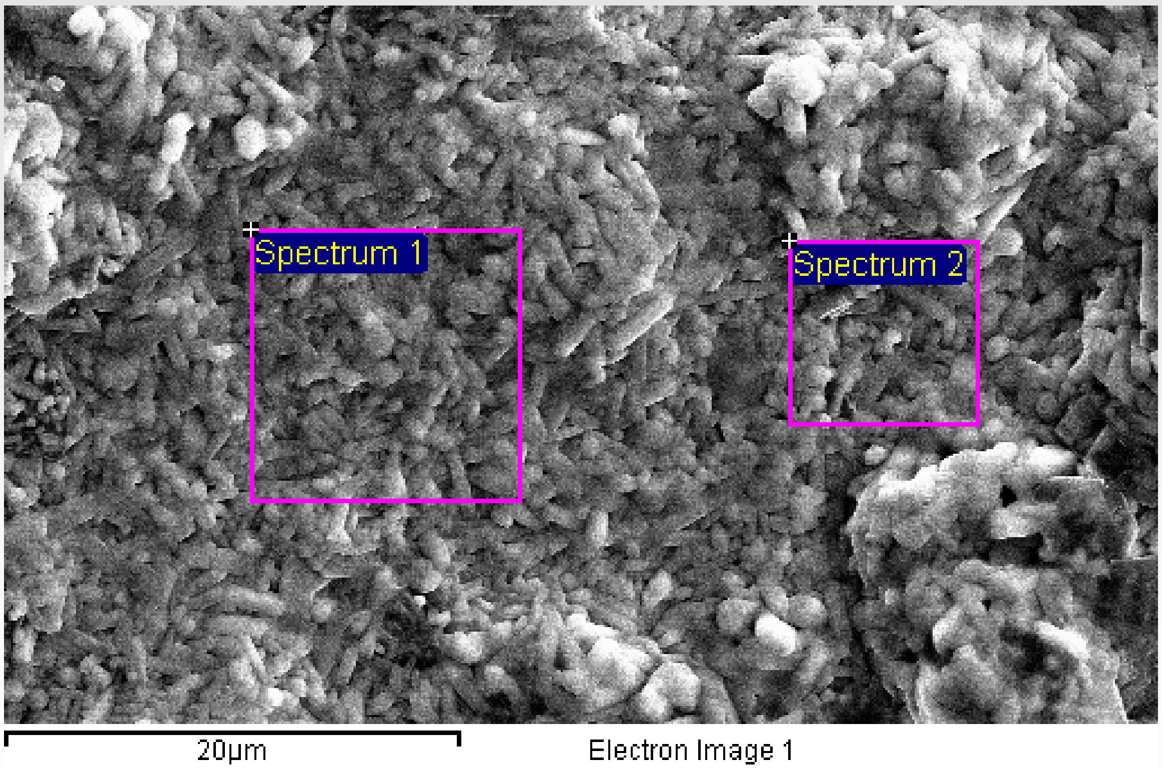



Atomic Percentage for b)

$Ca_2Gd_8(SiO_4)_6O_2$

| | 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 |

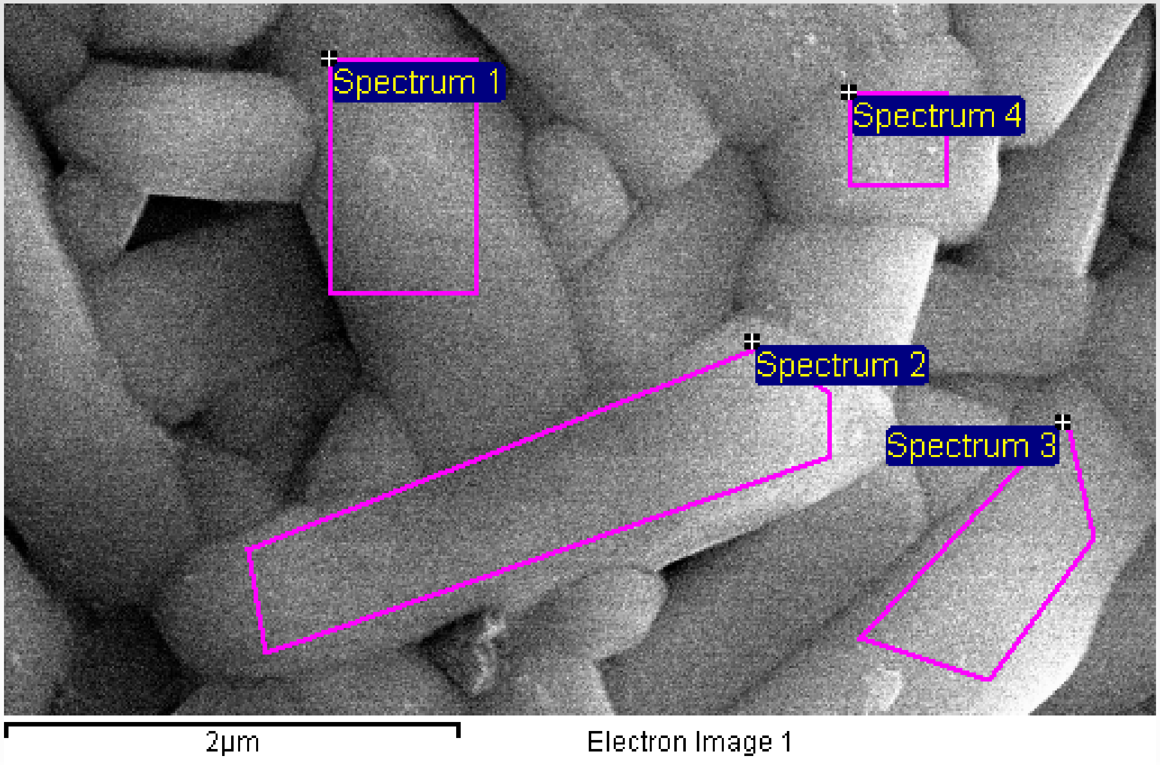
# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours




| 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

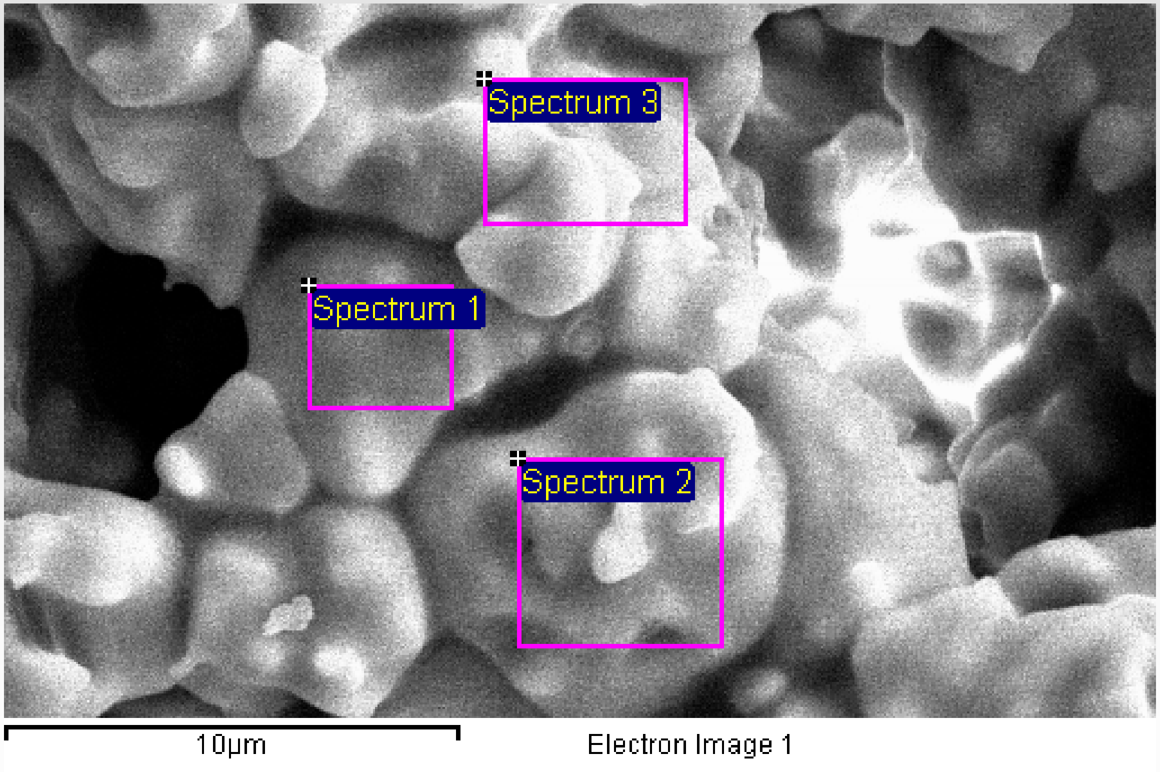
# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours




| 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

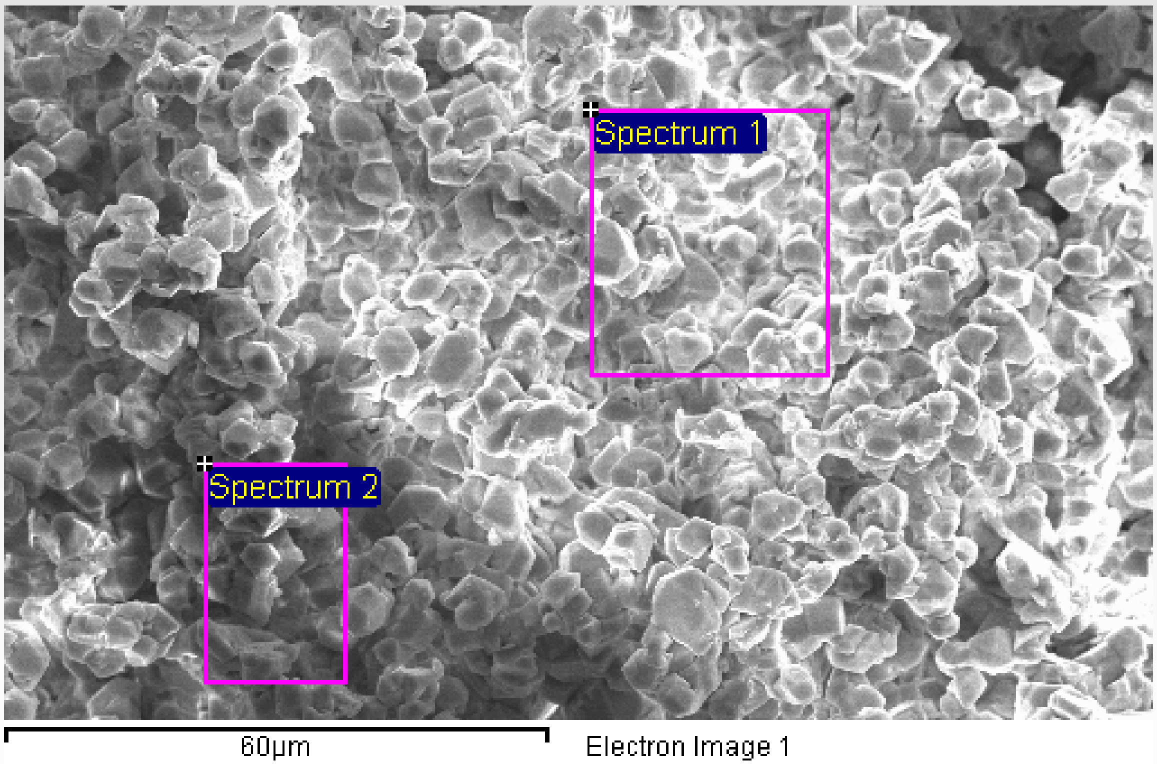
# $Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours




| 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

# $Gd_2Zr_2O_7$ 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



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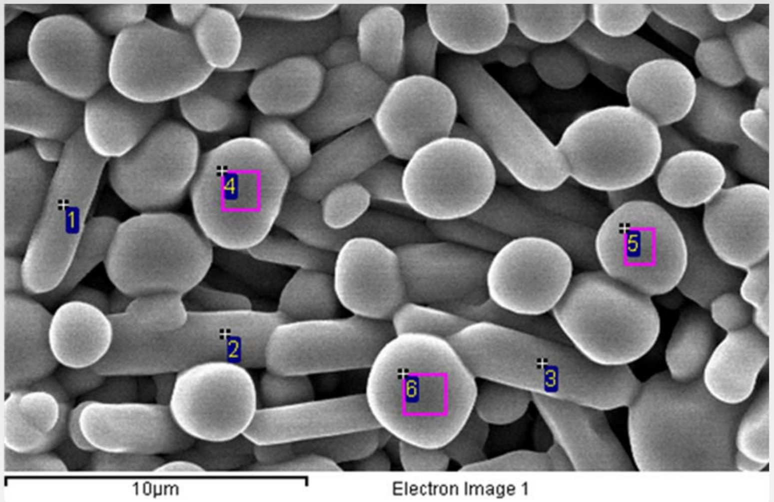
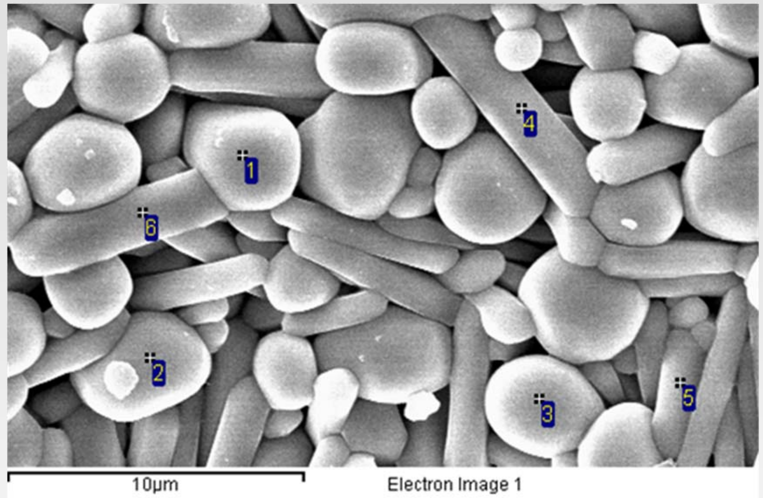
# $Gd_2Zr_2O_7$ after CMAS at 1200°C




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 |



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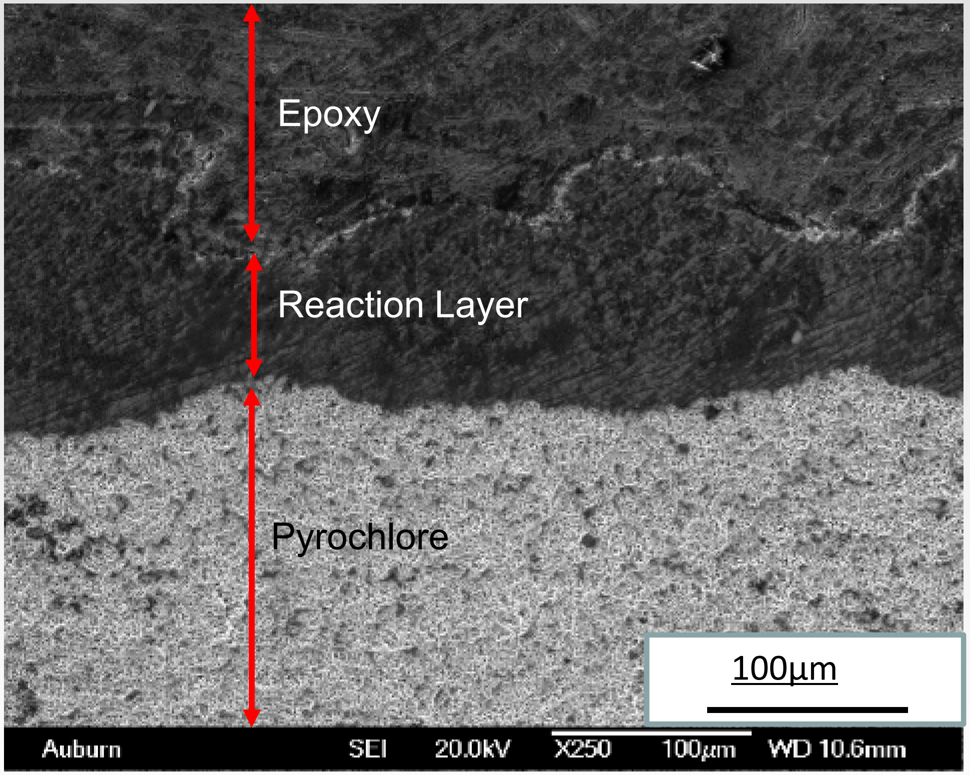
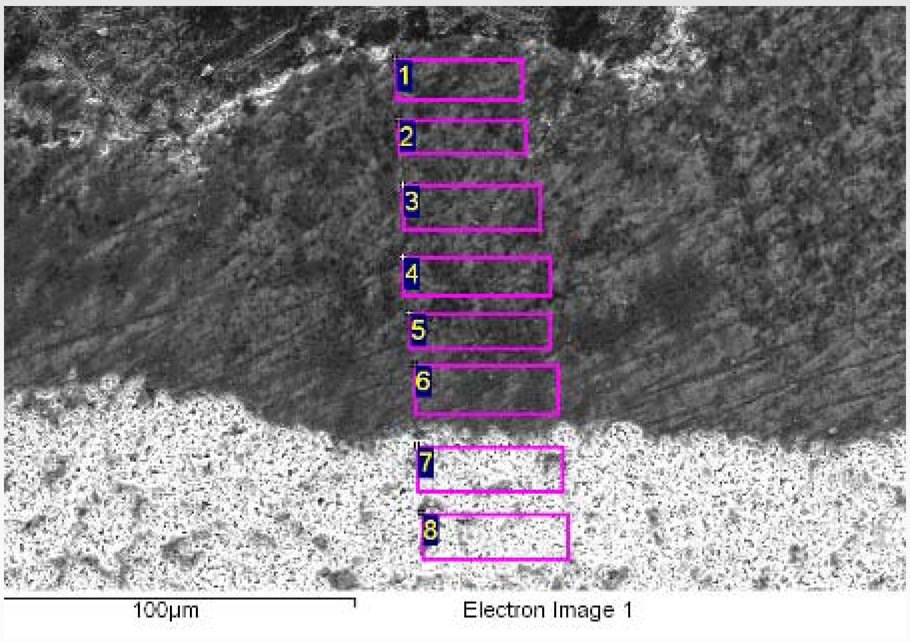
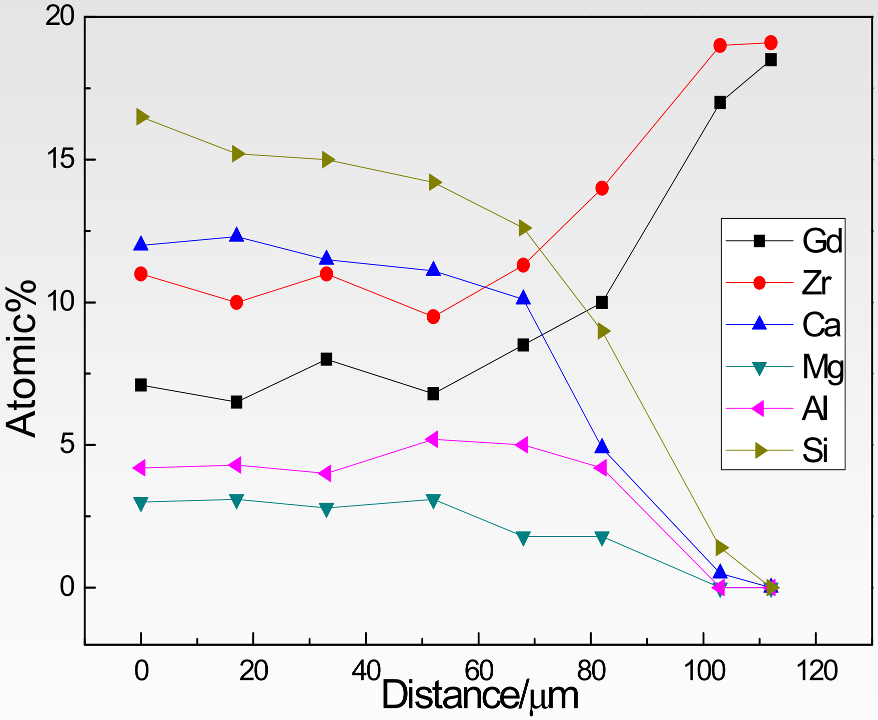
# $Gd_2Zr_2O_7$ after CMAS at 1200°C / 60 h




Distinct reaction layer boundary

# $Gd_2Zr_2O_7$ after CMAS at 1200°C / 60 h



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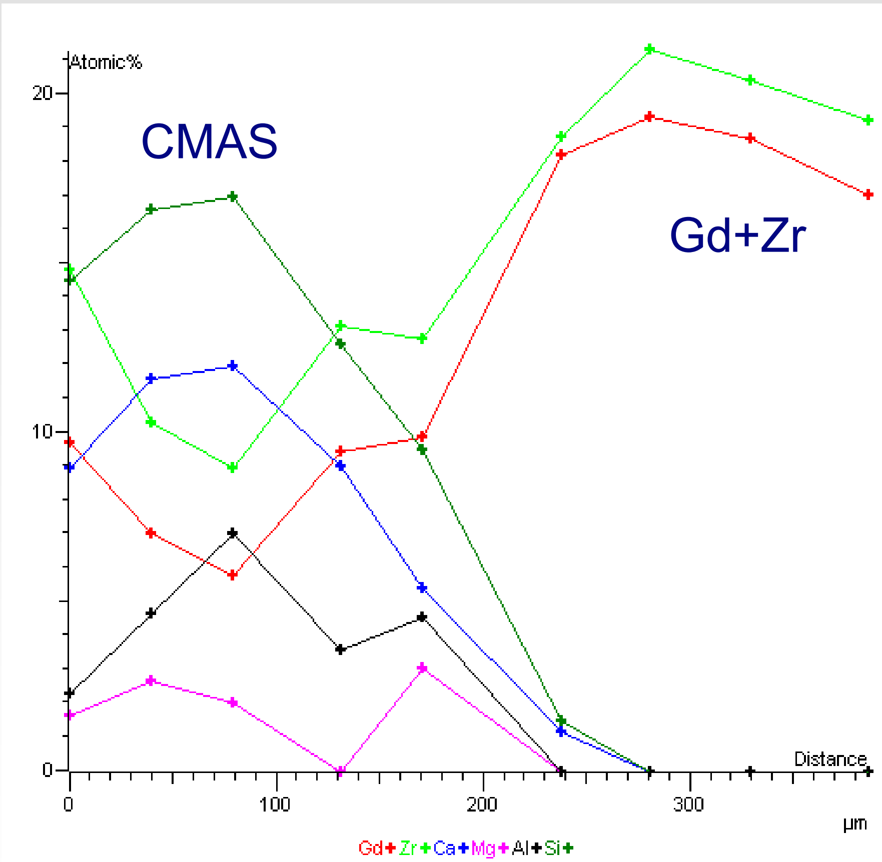
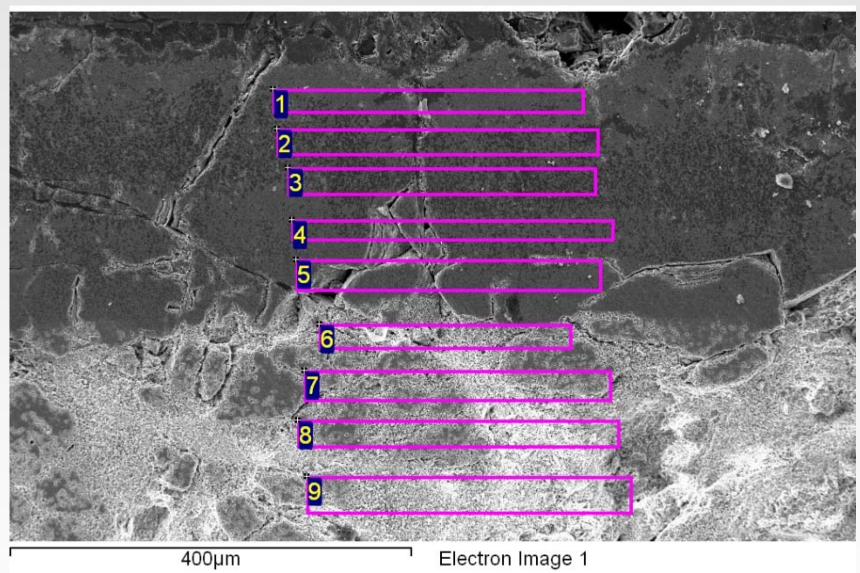
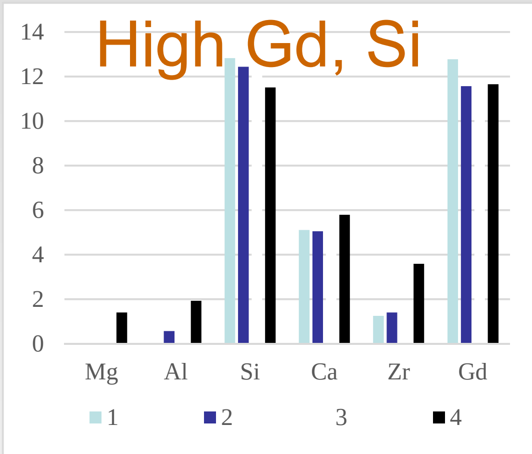
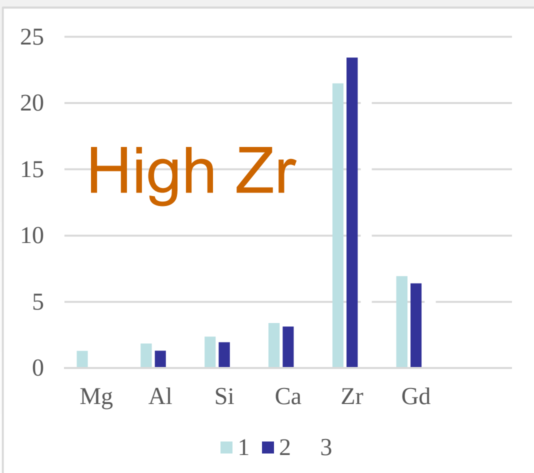
# $Gd_2Zr_2O_7$ after CMAS at 1200°C – 60 hours



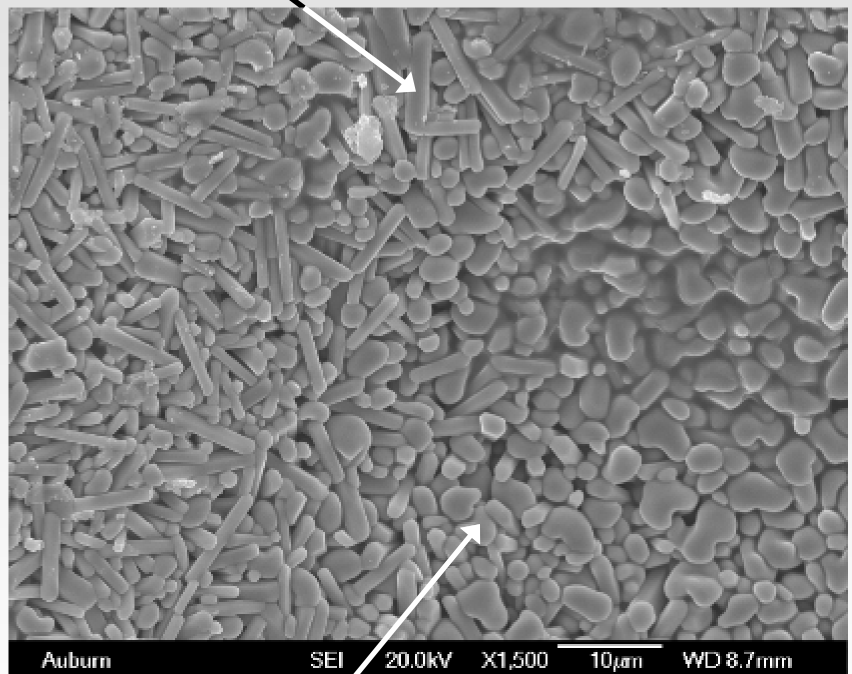



# $Gd_2Zr_2O_7$ after CMAS at 1300°C / 5 h



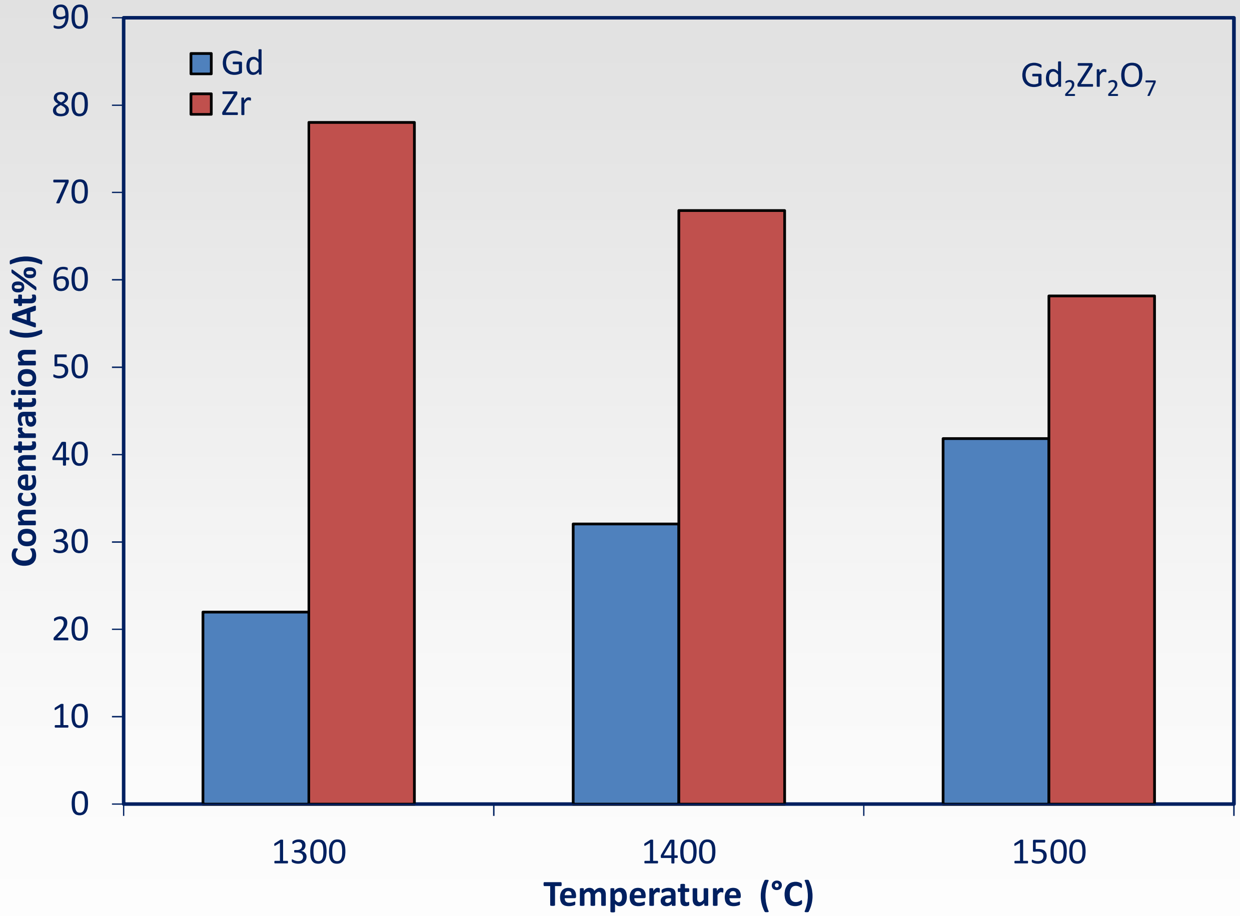




Gd silicate




Cubic fluorite

# $Gd_2Zr_2O_7$ – Composition of Cubic Fluorite Phase




Gd / Zr increases with increasing temperature



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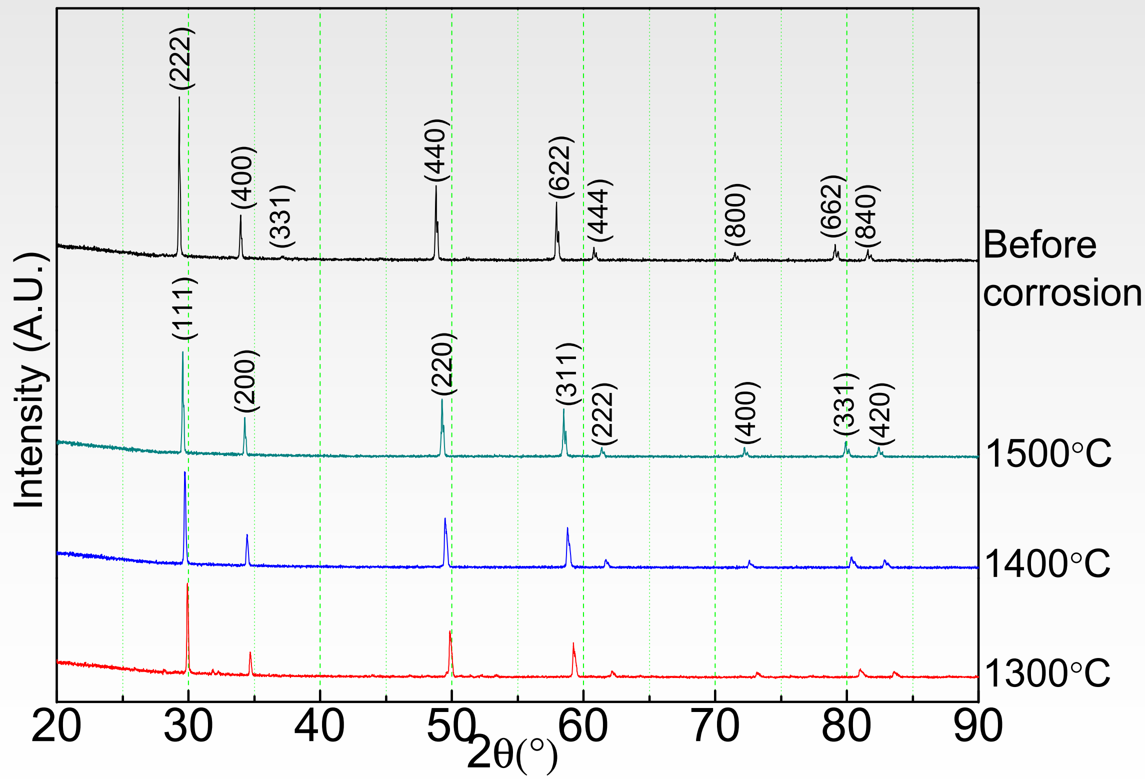
# XRD of $Gd_2Zr_2O_7$

| Exposure | Phase | Lattice Parameter (Å) |
|---|---|---|
| None | Pyrochlore | 5.272 |
| 1300°C | | 5.227 |
| 1400°C | Cubic fluorite | 5.201 |
| 1500°C | | 5.167 |




Cubic fluorite forms after corrosion



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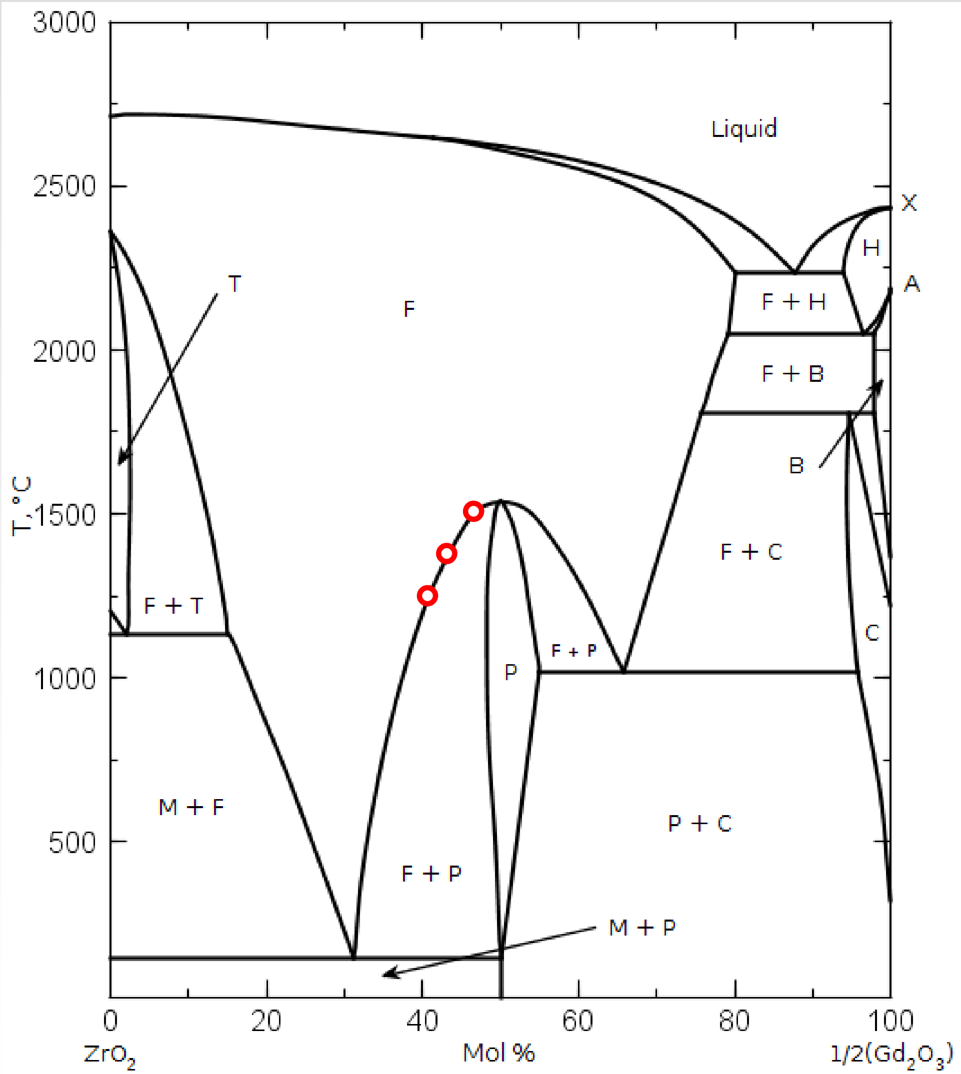
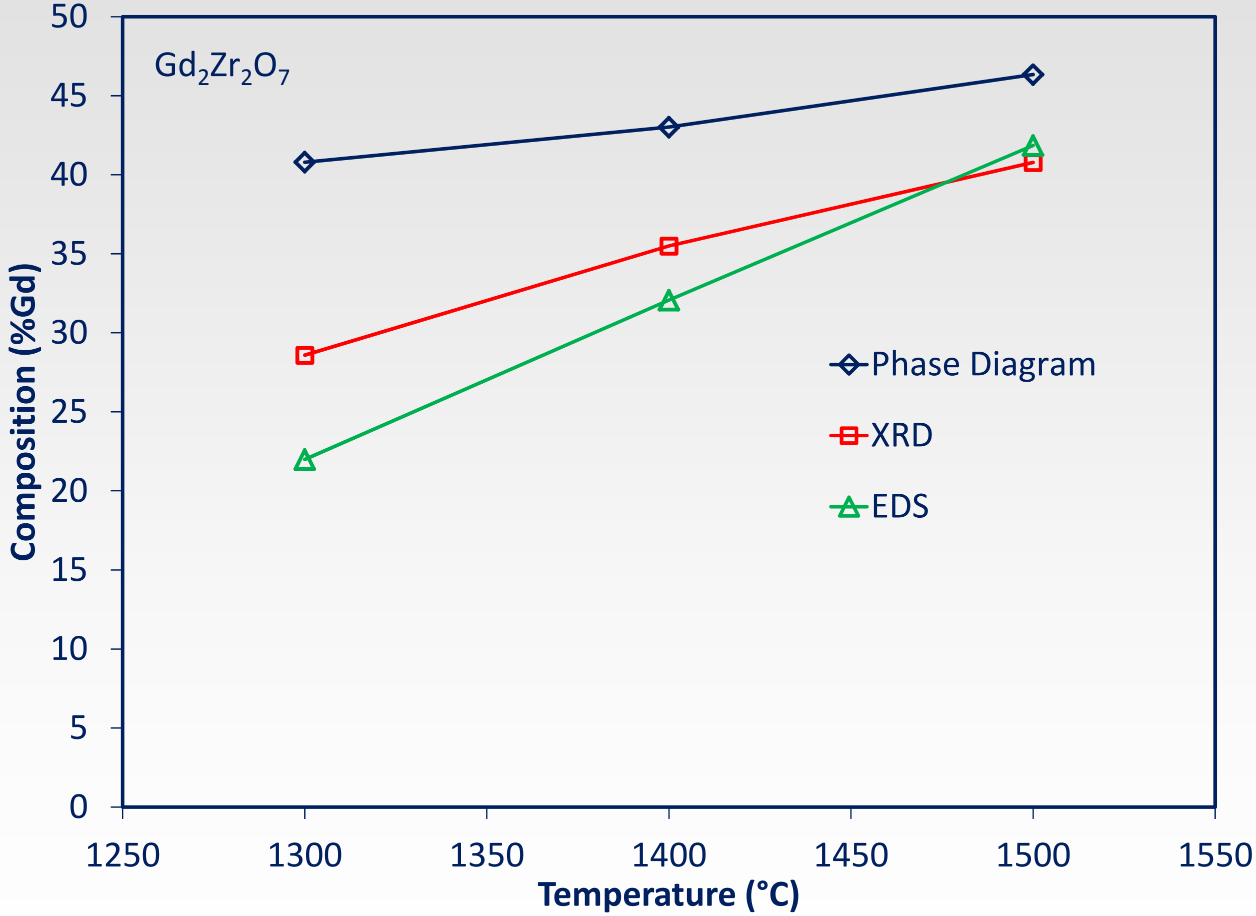
# $ZrO_2$-$Gd_2O_3$ Phase Diagram




Gd / Zr in cubic fluorite increases with increasing temperature

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

# $Gd_2Zr_2O_7$ – Composition of Cubic Fluorite Phase




Phase diagram, XRD, EDS consistent trend



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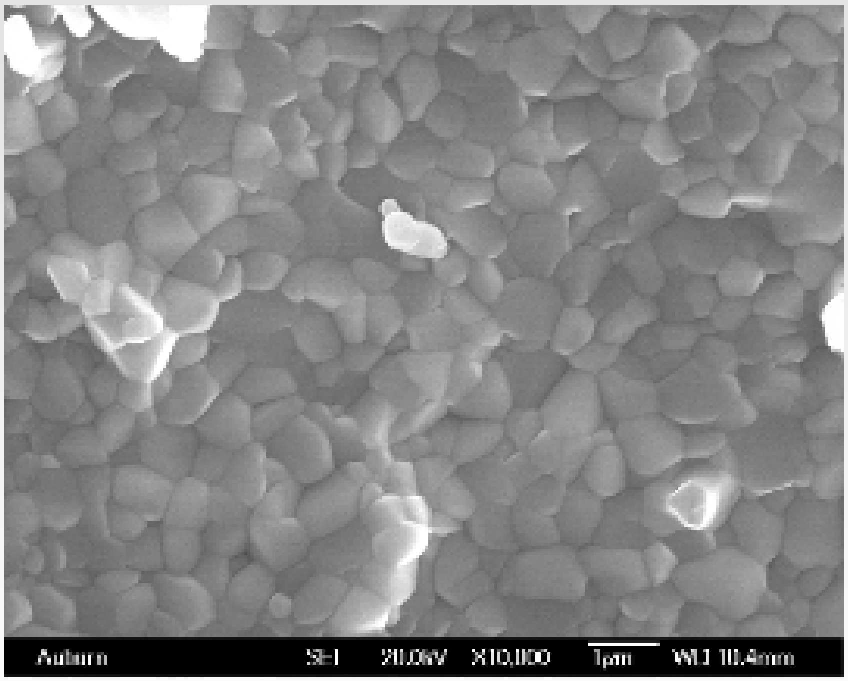
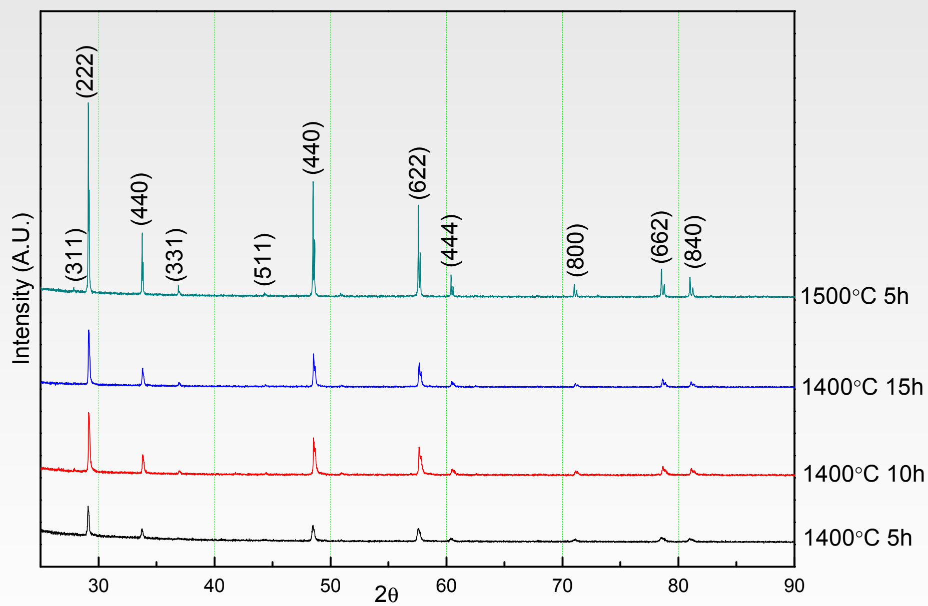
# As-Synthesized $Sm_2Zr_2O_7$




(311), (331), (511) indicate pyrochlore phase



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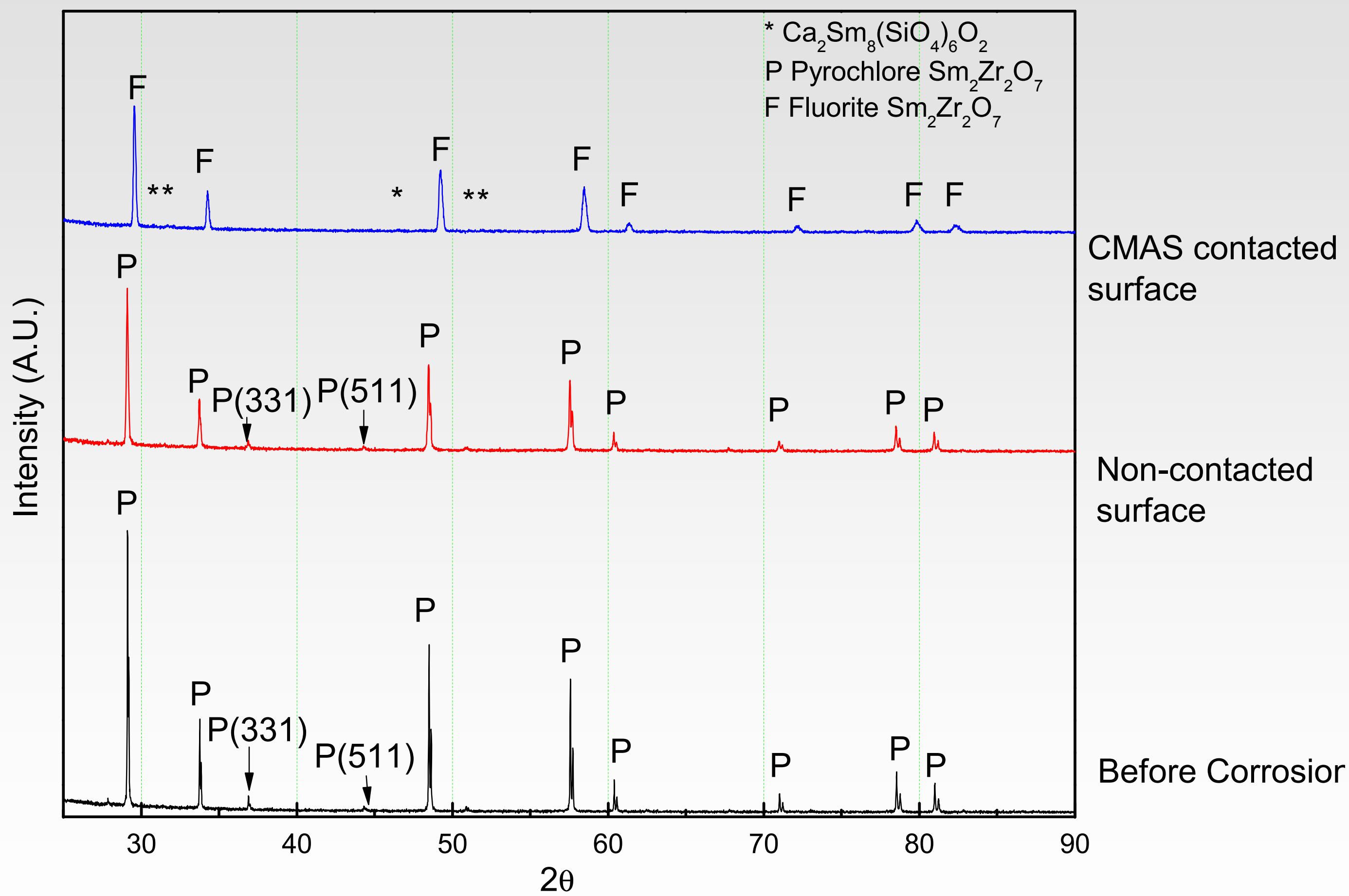
# $Sm_2Zr_2O_7$ after CMAS at 1400°C for 5 hours

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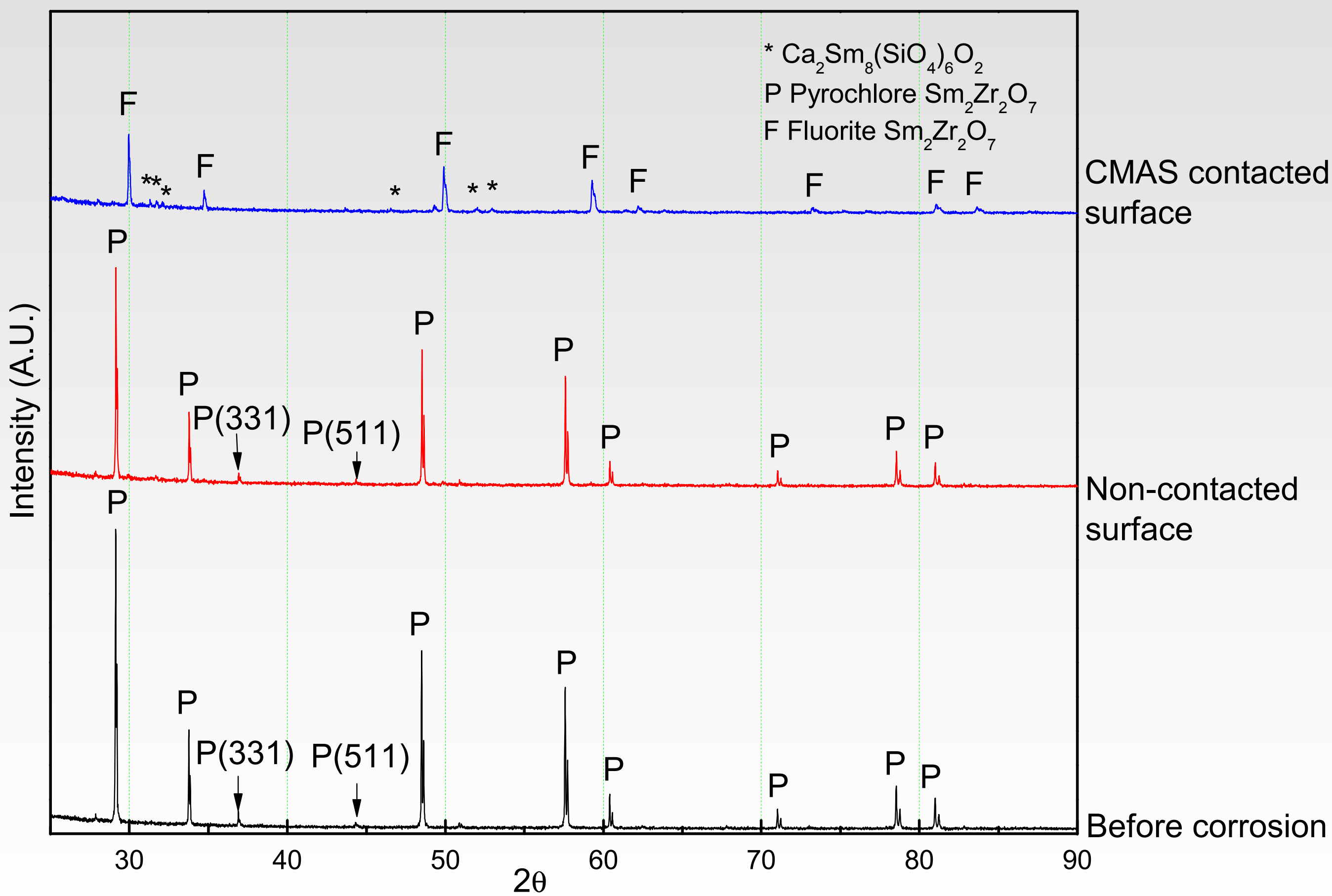
# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 5 hours



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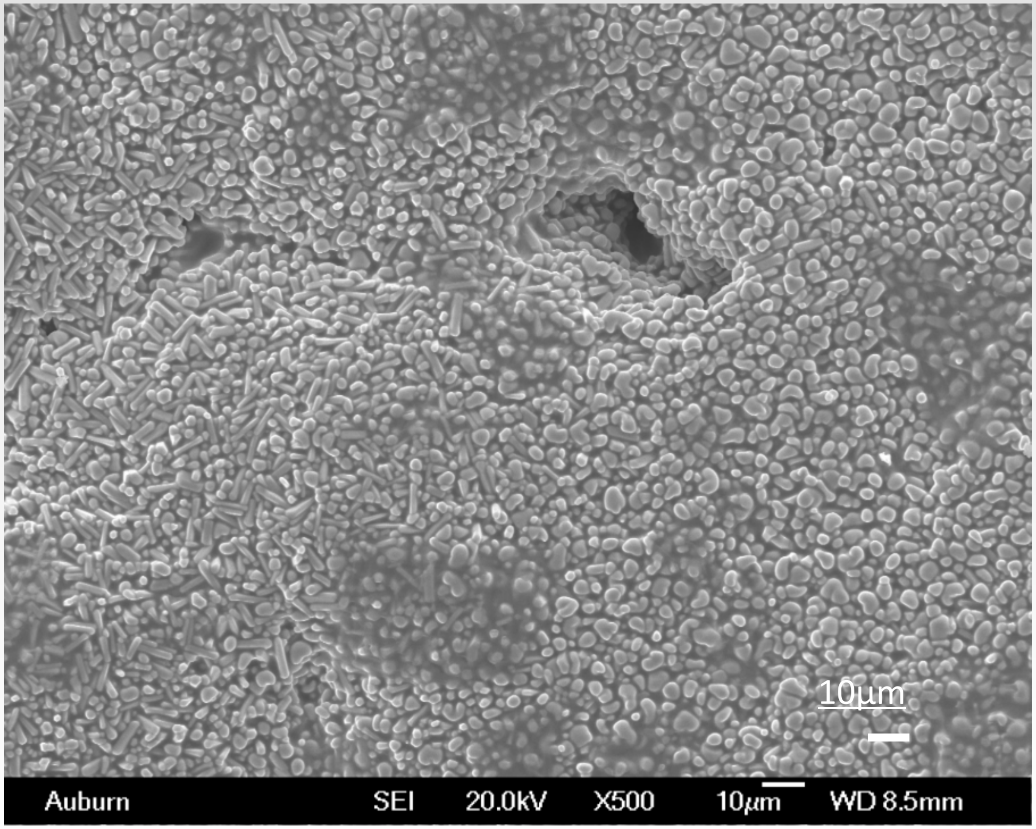
# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 5 hours



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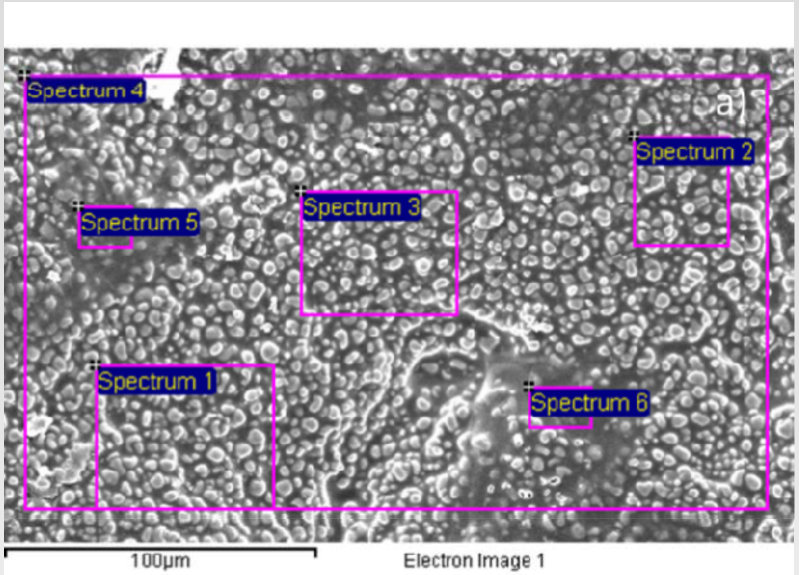
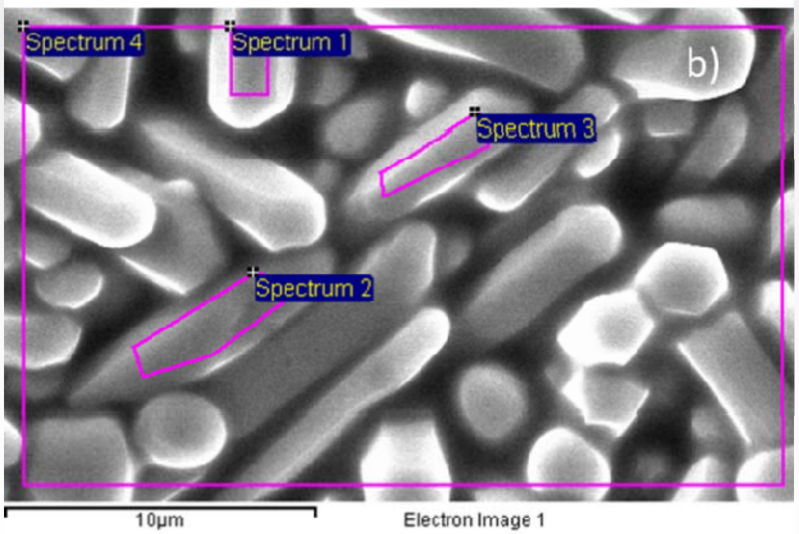



Atomic Percentage for a)

| | 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 |

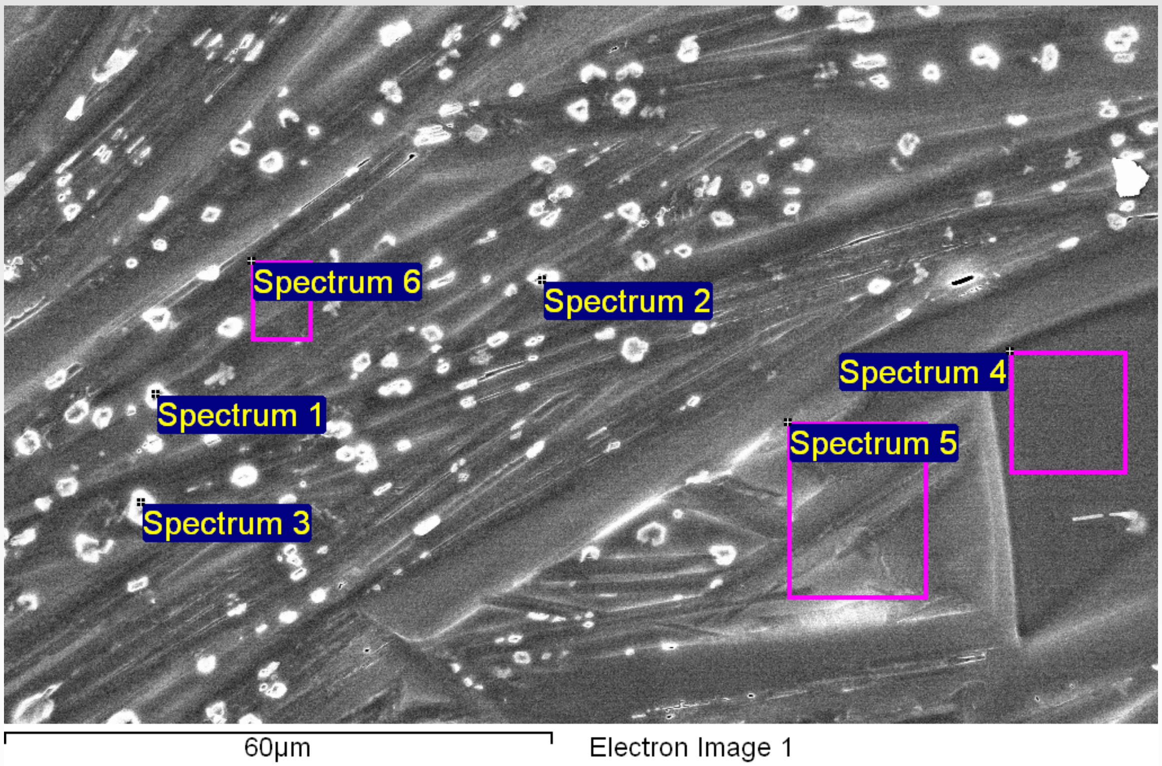
# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 5 hours




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 |

# $Sm_2Zr_2O_7$ 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



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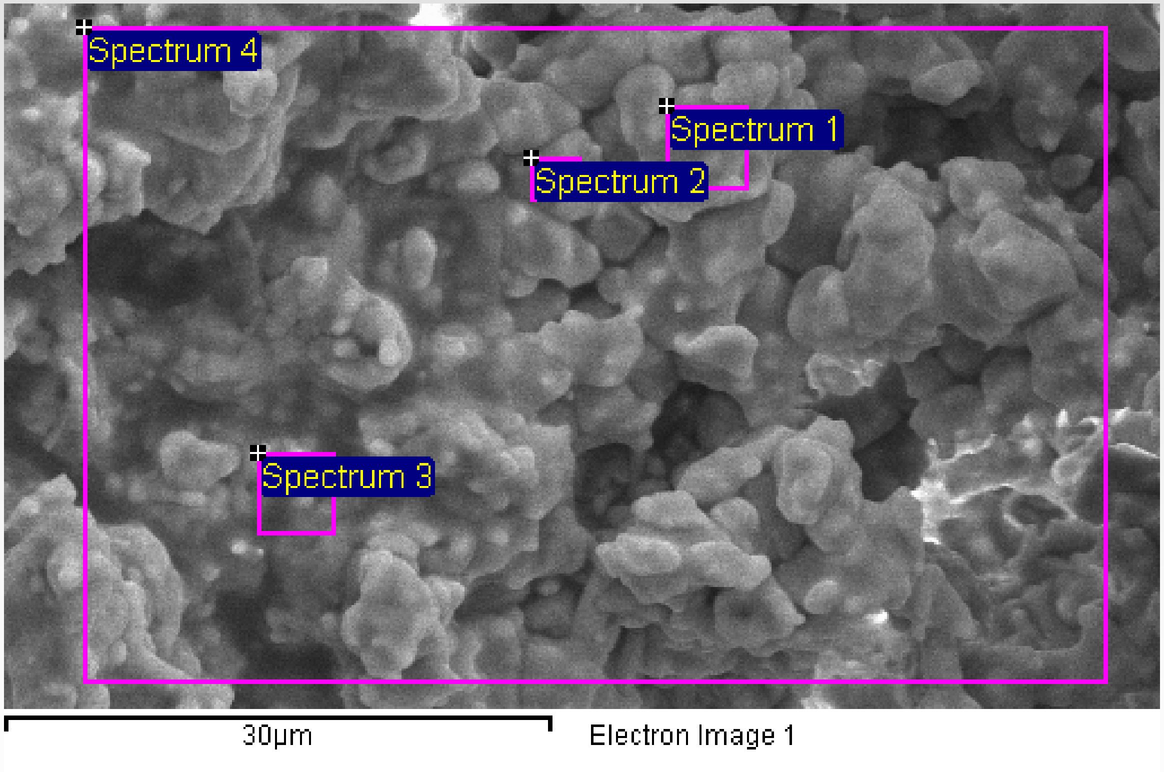
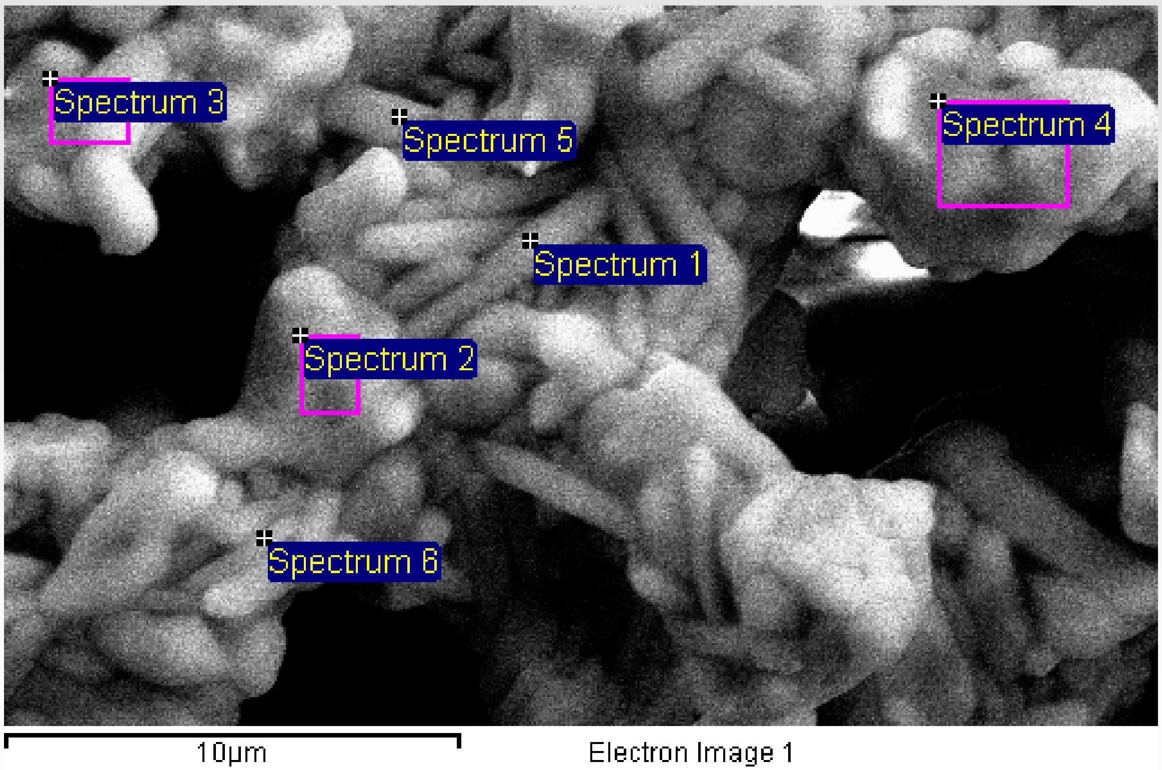
# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours




| 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



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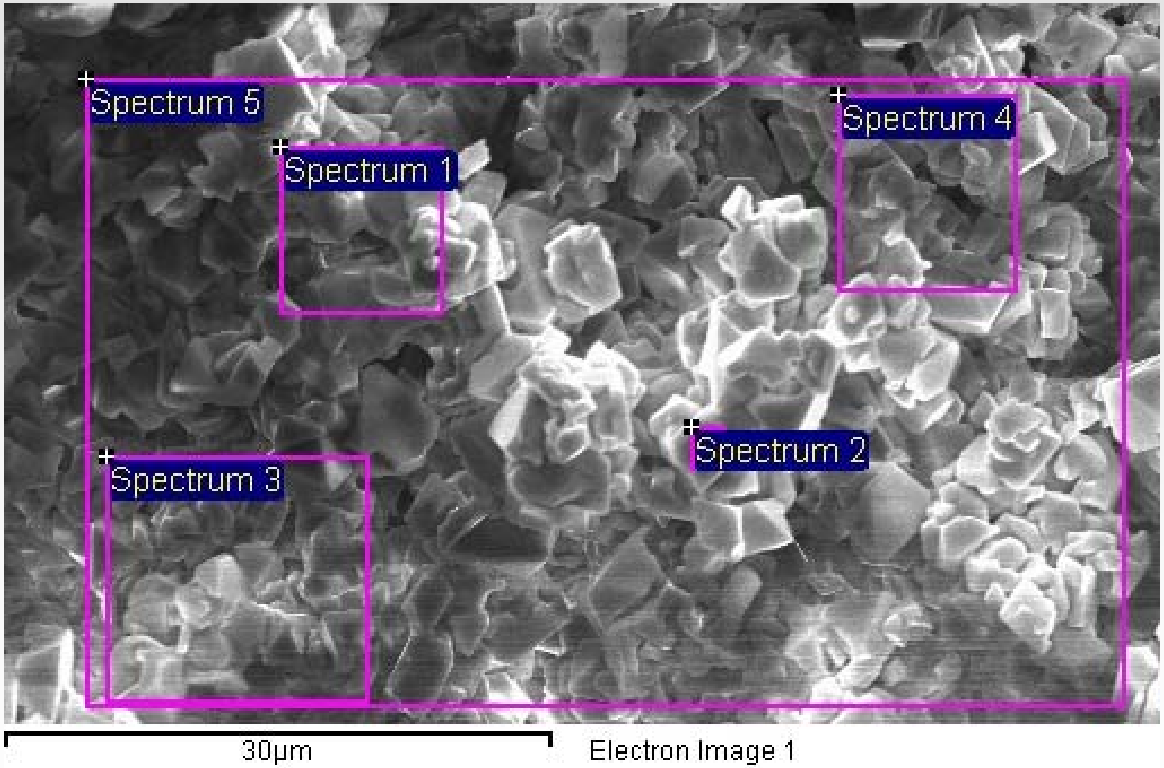
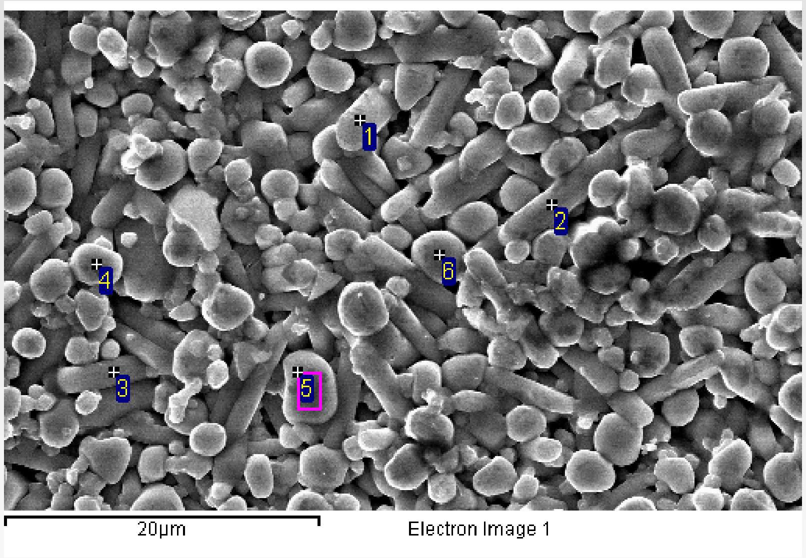
# $Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours




| 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 |

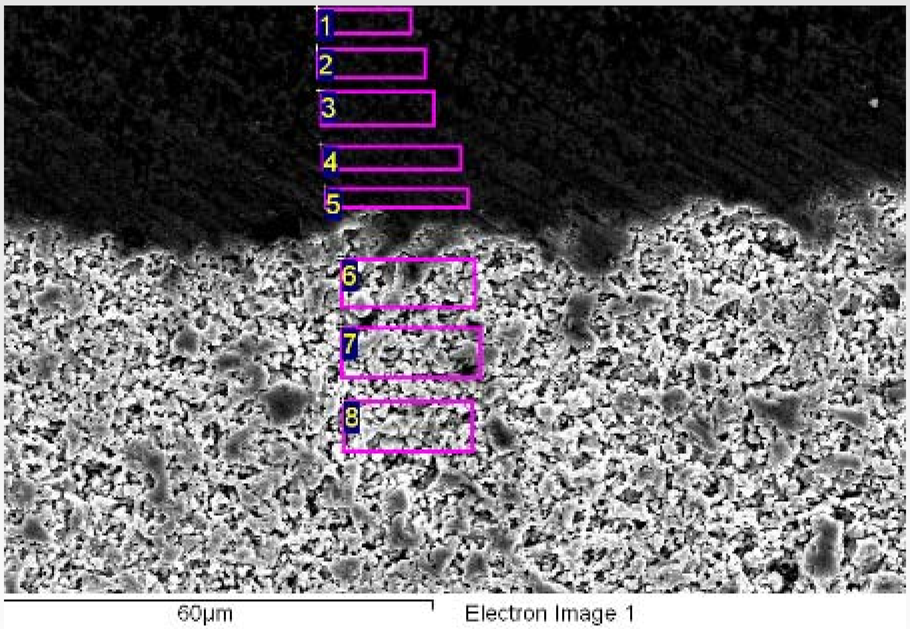
Pyrochlore

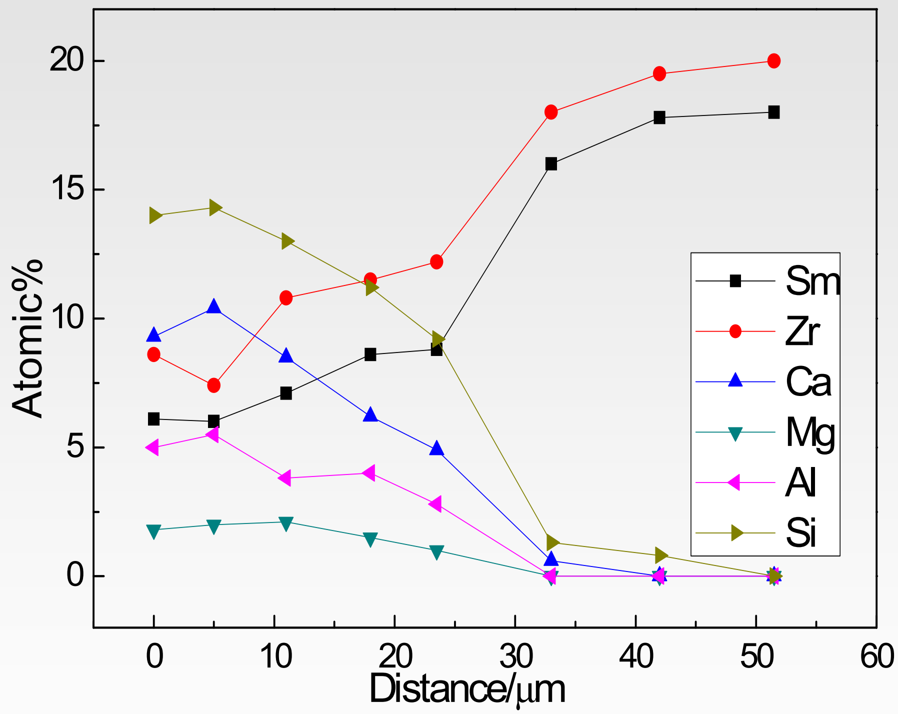
# $Sm_2Zr_2O_7$ after CMAS at 1200°C – 60 hours




| 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 h



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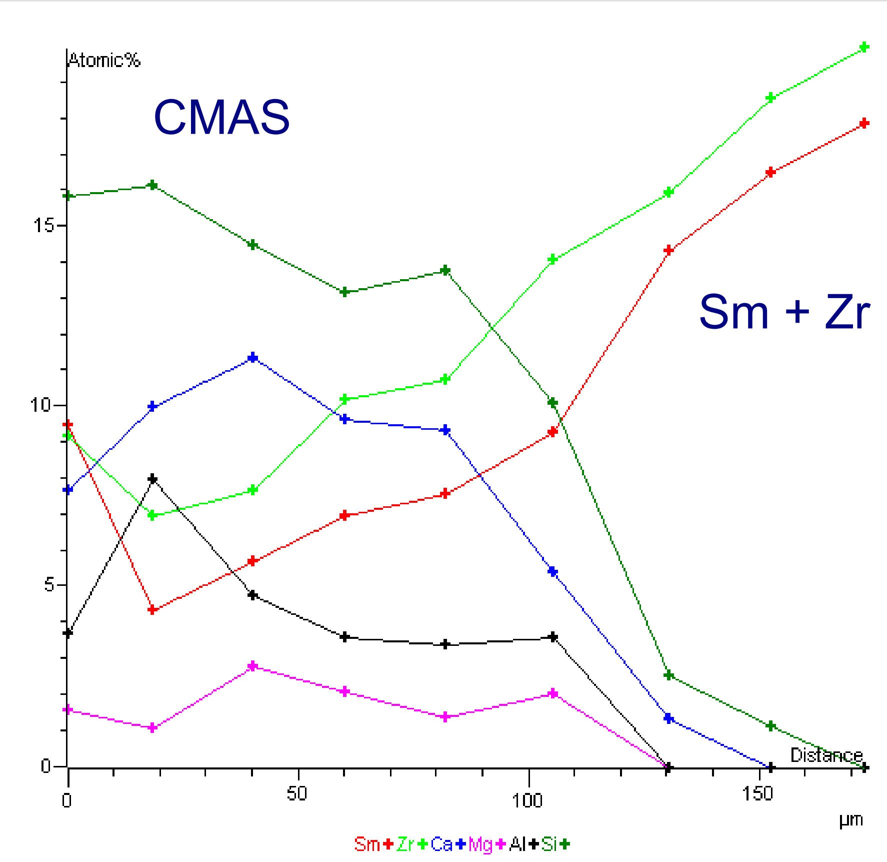
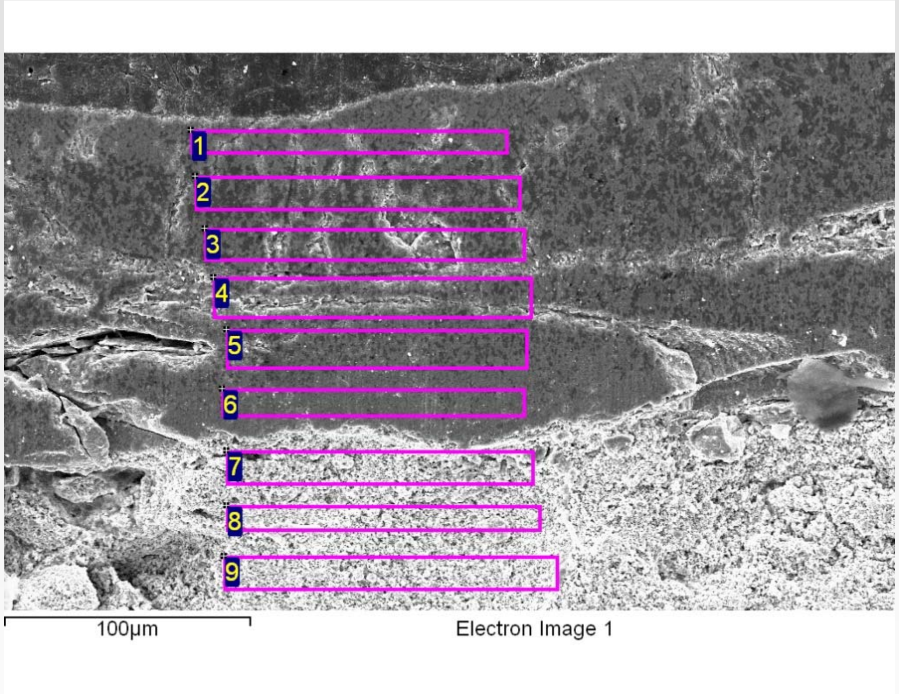
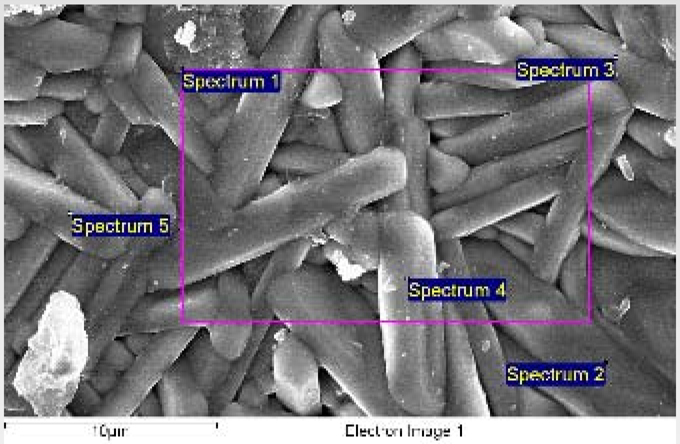
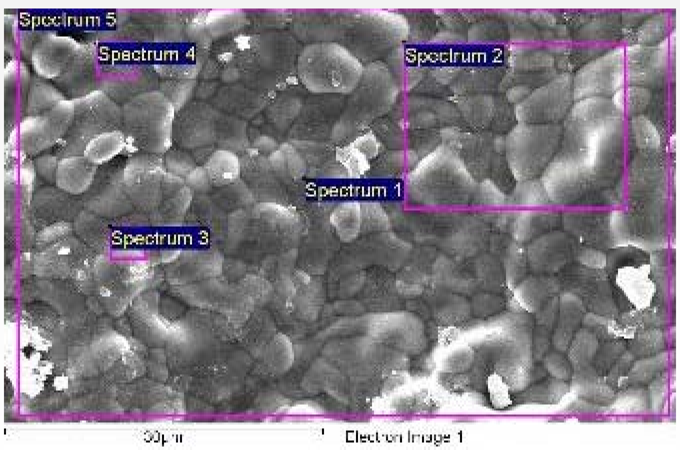
# $Sm_2Zr_2O_7$ after CMAS at 1200°C – 60 hours



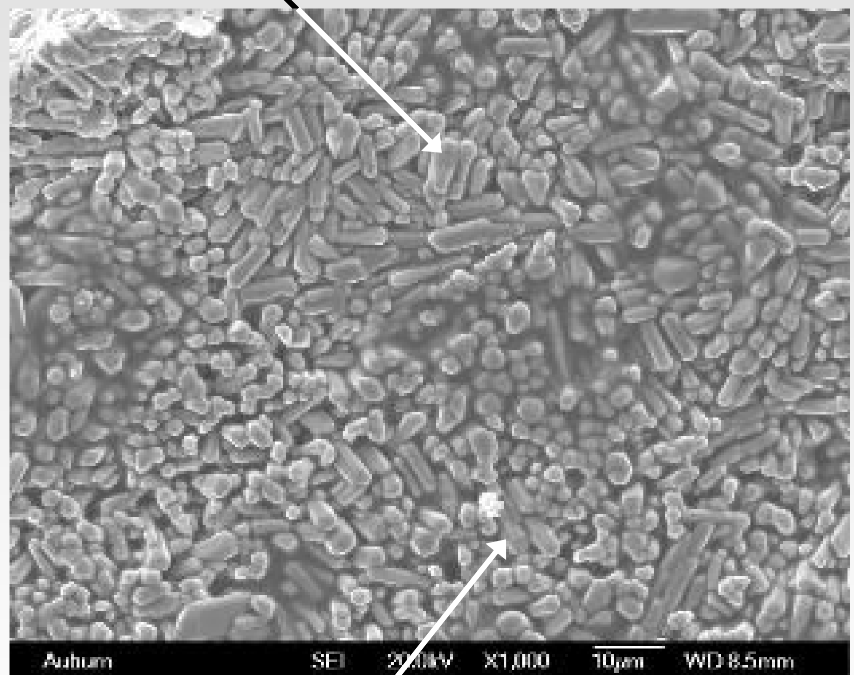



# $Sm_2Zr_2O_7$ after CMAS at 1300°C / 5 h



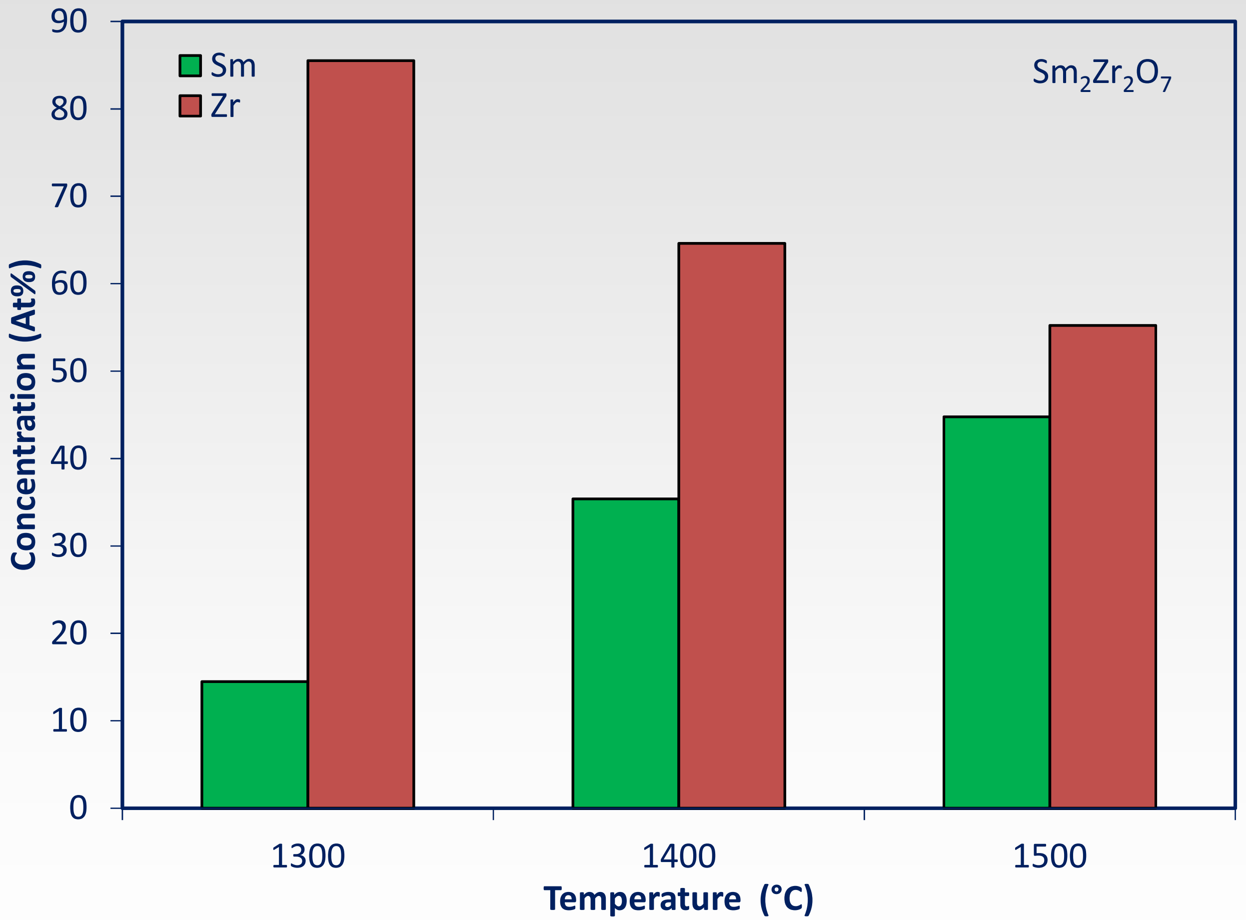




Gd silicate




Cubic fluorite

# $Sm_2Zr_2O_7$ – Composition of Cubic Fluorite Phase




Sm / Zr increases with increasing temperature



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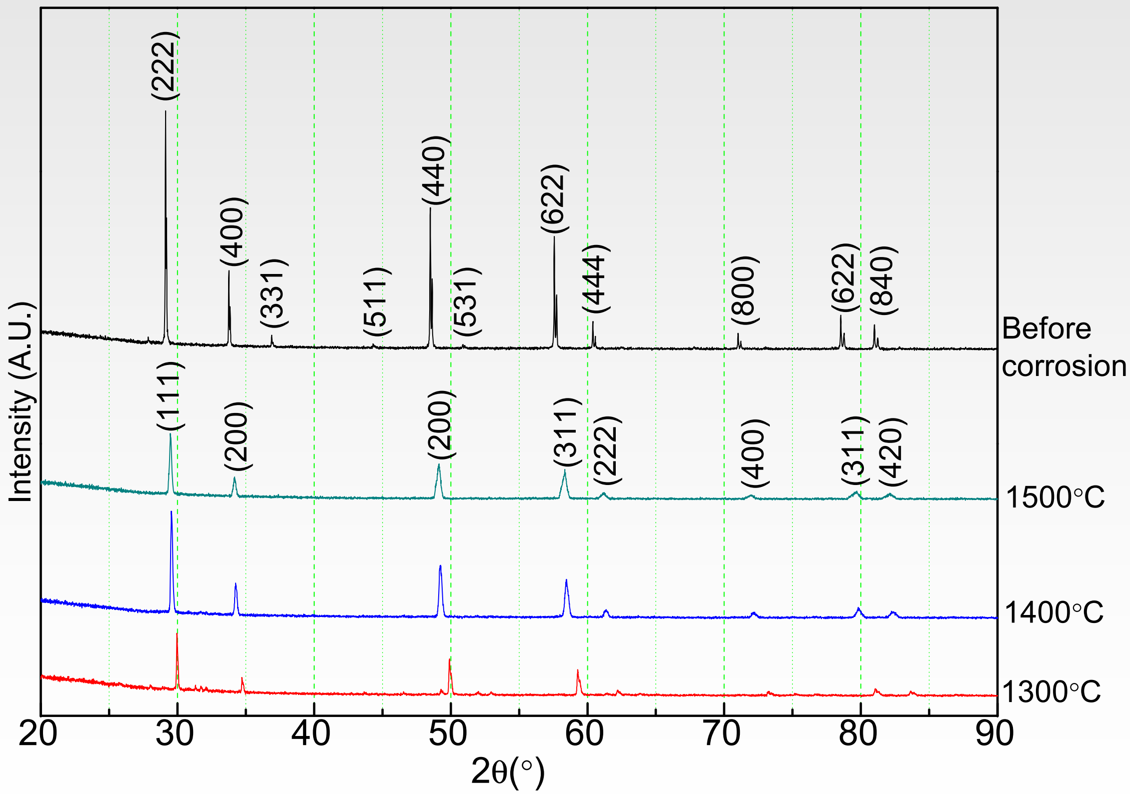
# XRD of $Sm_2Zr_2O_7$

| Exposure | Phase | Lattice Parameter (Å) |
|---|---|---|
| None | Pyrochlore | 5.304 |
| 1300°C | | 5.242 |
| 1400°C | Cubic fluorite | 5.230 |
| 1500°C | | 5.159 |




Cubic fluorite forms after corrosion



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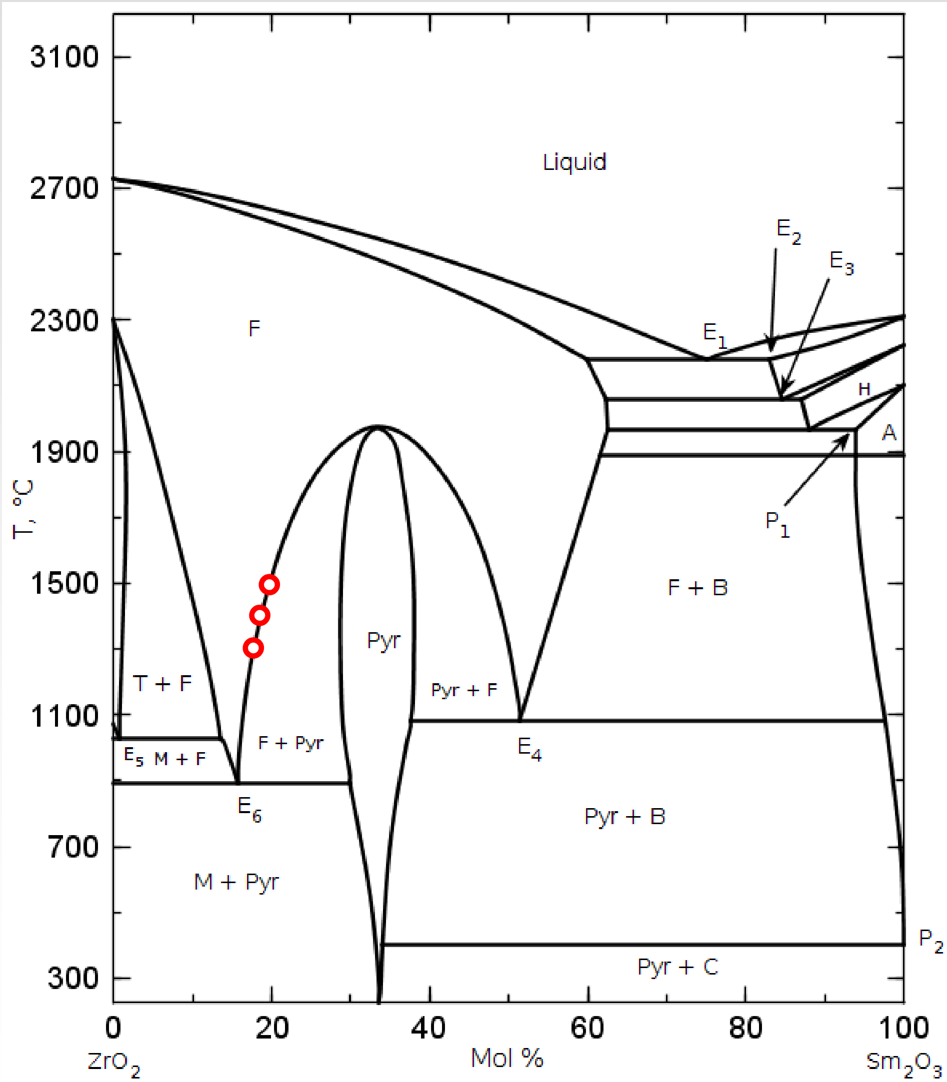
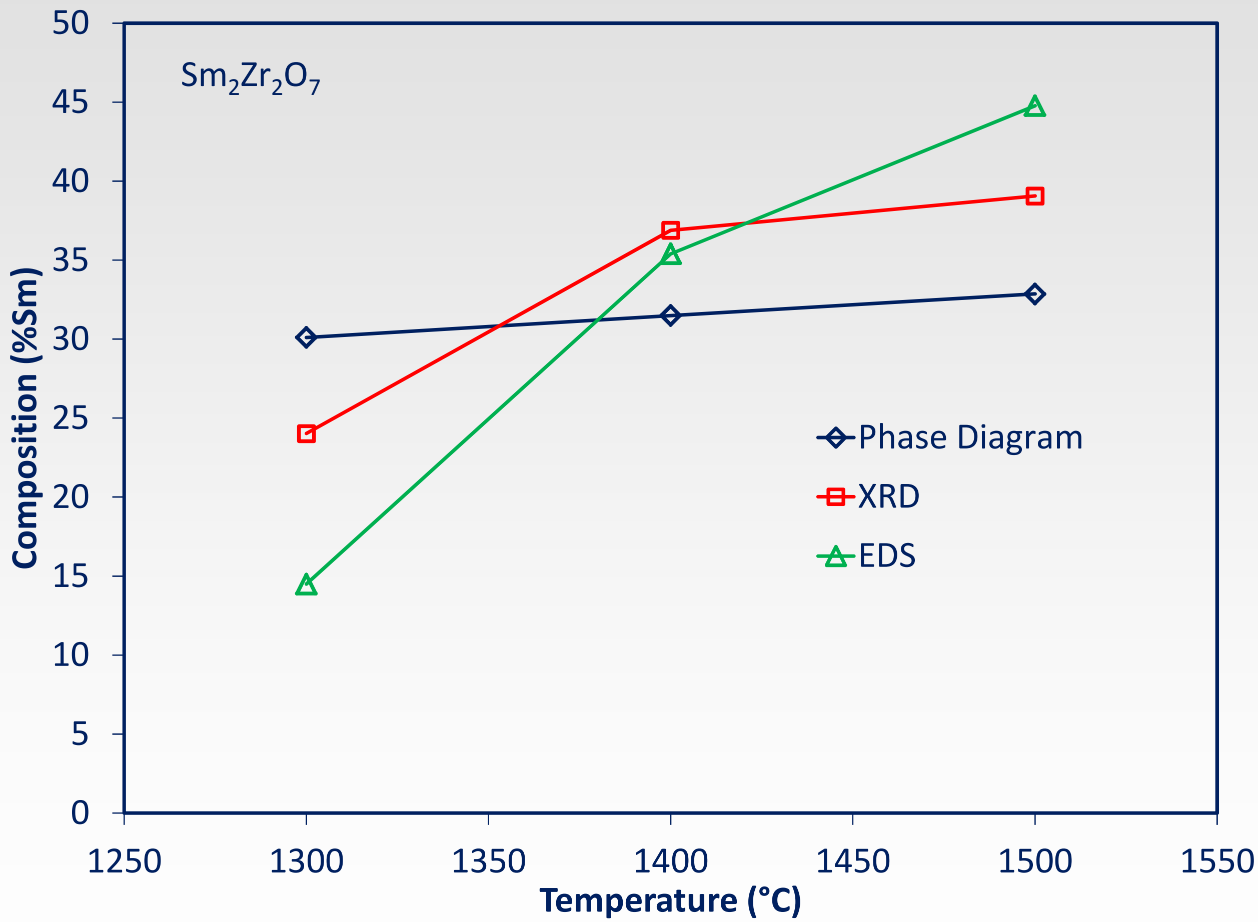
# $ZrO_2$-$Sm_2O_3$ Phase Diagram




Sm / Zr in cubic fluorite increases with increasing temperature

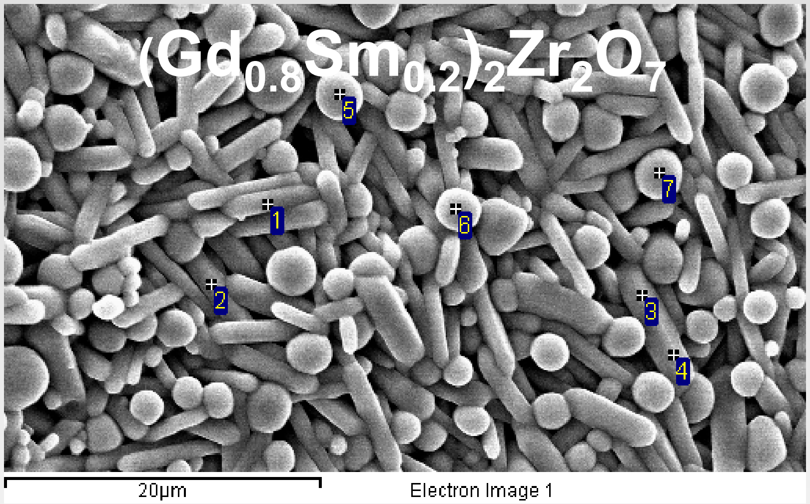
T = tetragonal
F = cubic fluorite
M – monoclinic
Pyr = pyrochlore
C, B, H = $Sm_2O_3$ phases

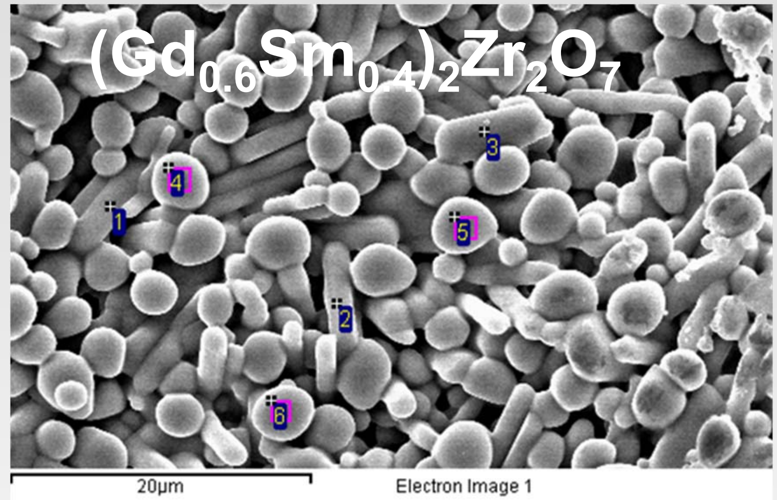
# $Sm_2Zr_2O_7$ – Composition of Cubic Fluorite Phase




Phase diagram, XRD, EDS consistent trend

# $(Gd,Sm)_2Zr_2O_7$ after CMAS at 1200°C / 60 h



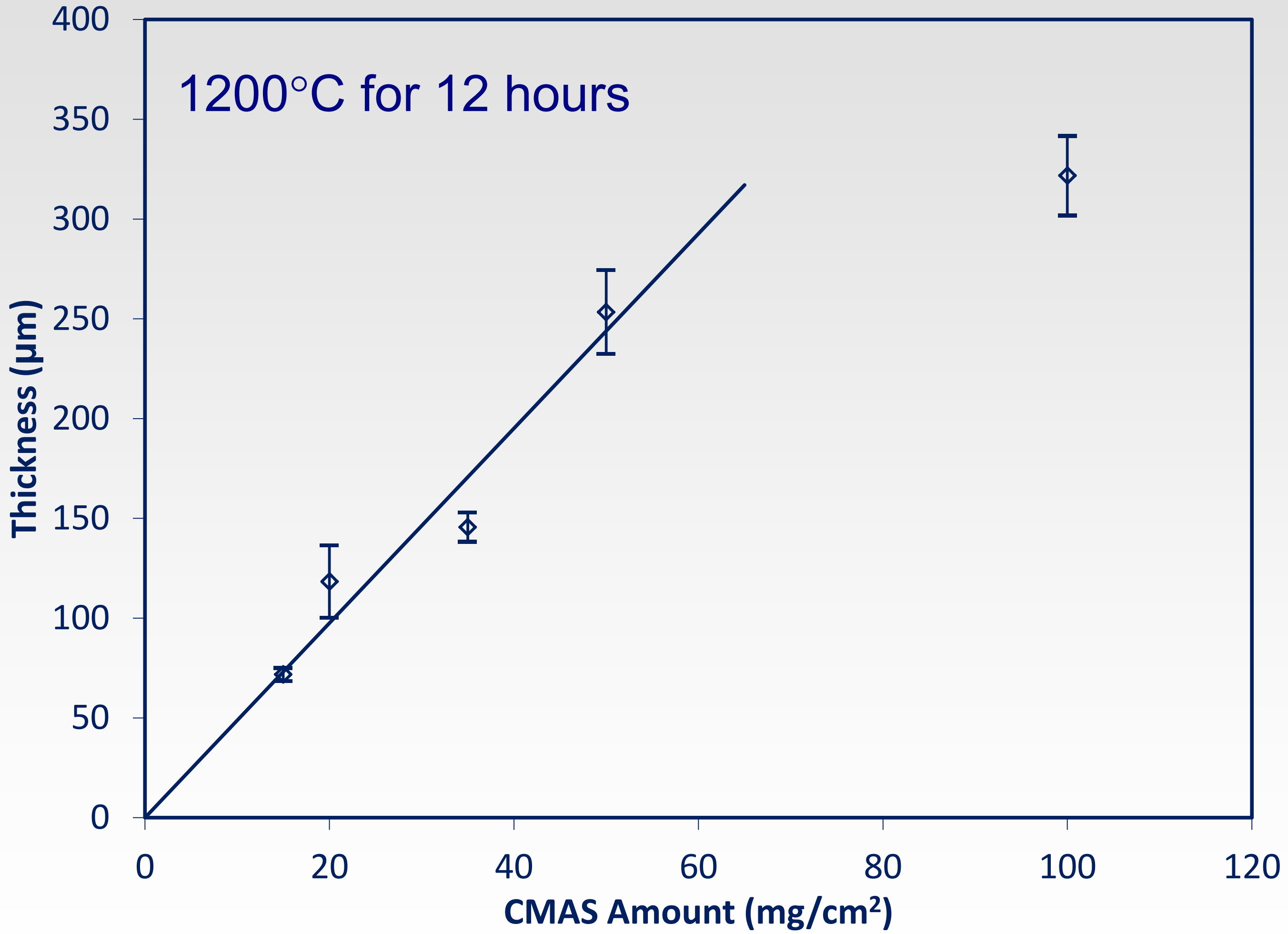

| Concentration | | | | | | | |
|---|---|---|---|---|---|---|---|
| # | Mg | Al | Si | Ca | Zr | Sm | Gd |
| 1 | 0 | 0 | 14 | 5 | 5 | 10 | 0 |
| 2 | 0 | 0 | 19 | 7 | 6 | 17 | 0 |
| 3 | 0 | 0 | 17 | 6 | 8 | 14 | 0 |
| 4 | 0 | 0 | 17 | 6 | 8 | 14 | 1 |
| 5 | 0 | 0 | 1 | 3 | 41 | 5 | 0 |
| 6 | 0 | 0 | 3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

(Sm,Gd) silicate

Cubic fluorite

| 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 |

# Effect of CMAS Amount




Reaction limited by supply for small amounts of CMAS



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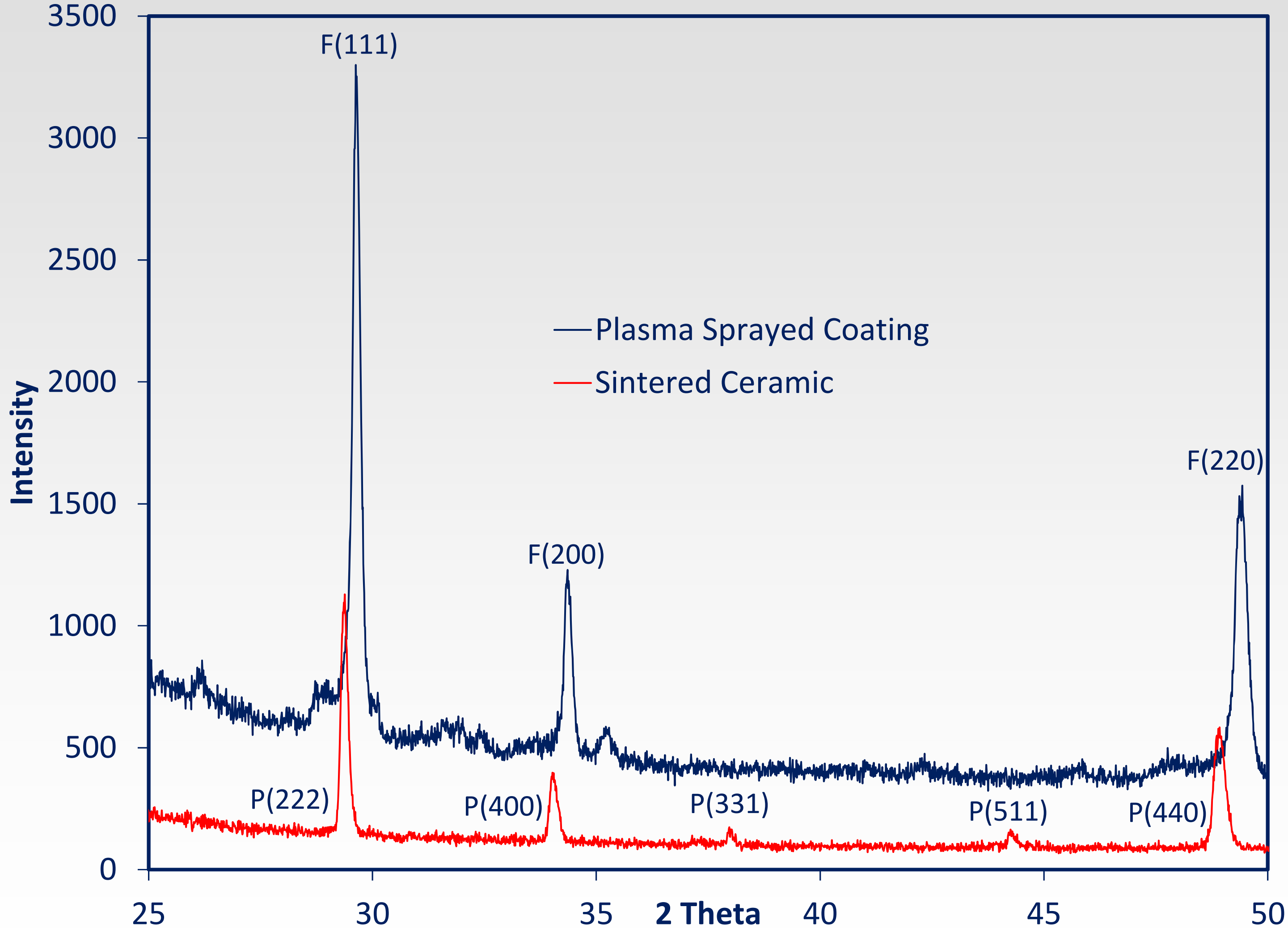
# Plasma Sprayed $Gd_2Zr_2O_7$




Pyrochlore structure not maintained during plasma spraying



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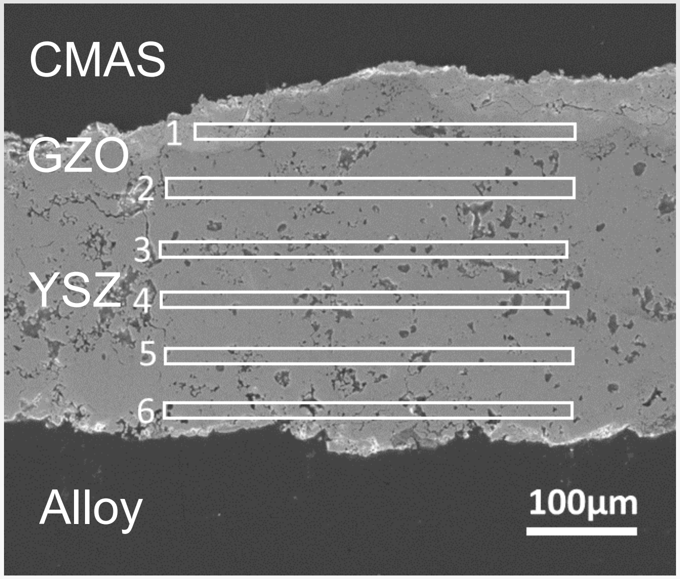
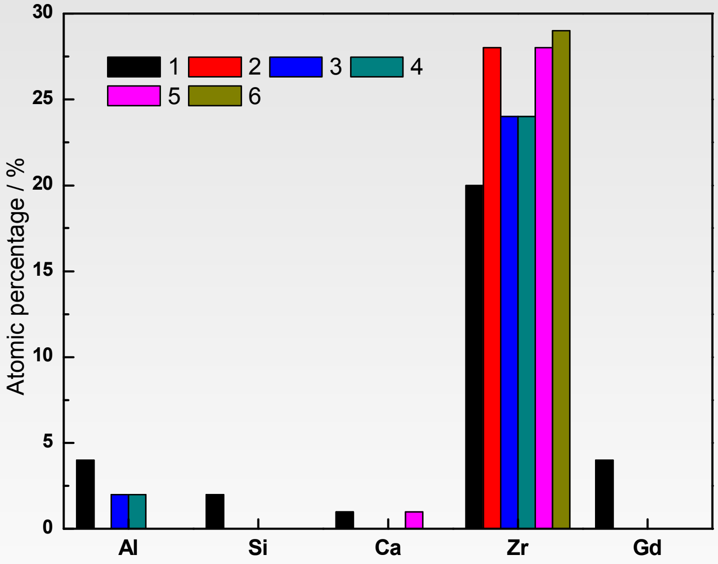
# Plasma Sprayed $Gd_2Zr_2O_7$ after CMAS at 1200°C / 20 h



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# Conclusions

- Reaction of pyrochlore with CMAS
  - Pyrochlore dissolves and reprecipitates as lanthanide silicate and cubic fluorite phase
  - Lanthanide concentration in cubic fluorite phase increases with increasing temperature as predicted by phase diagram
  - Reaction occurs below melting temperature of glass

# Acknowledgment

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