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

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COLLEGE OF ENGINEERING

Jeffrey W. Fergus

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Participants

- Auburn University
  - Jeff Fergus
  - Students
    - Graduate: Honglong (Henry) Wang, Wenzhou Deng, Xingxing Zhang
    - Undergraduate: Emily Tarwater, Kai Roebbecke, Ralf Fischer, Ashley Baerlocher, Tommy Britt
  - 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

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Outline

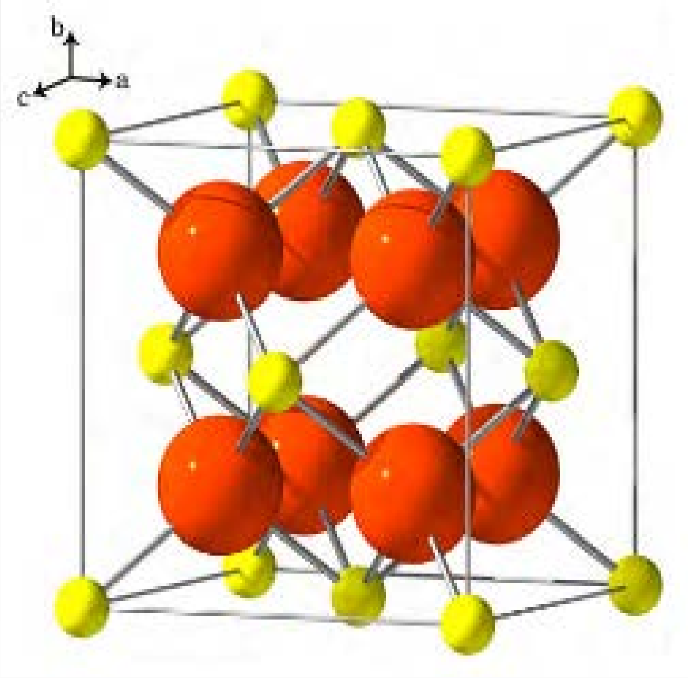
- Thermal conductivity
- Cubic fluorite vs. pyrochlore
- CMAS composition

Experimental

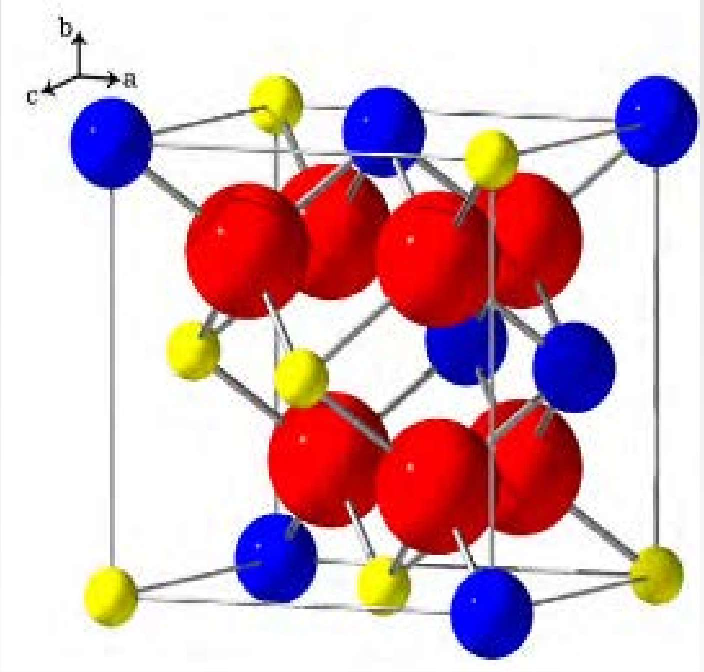
- Synthesis of pyrochlore
  - Co-precipitation
- CMAS exposure
  - Melt / solidify Ca-Mg-Al-Si oxide mixtures
  - Crush glass, apply to pyrochlore pellet
  - Expose to 1200-1300°C
- Characterization
  - XRD, SEM / EDS
- Thermal Conductivity

Crystal Structure

Cubic Fluorite



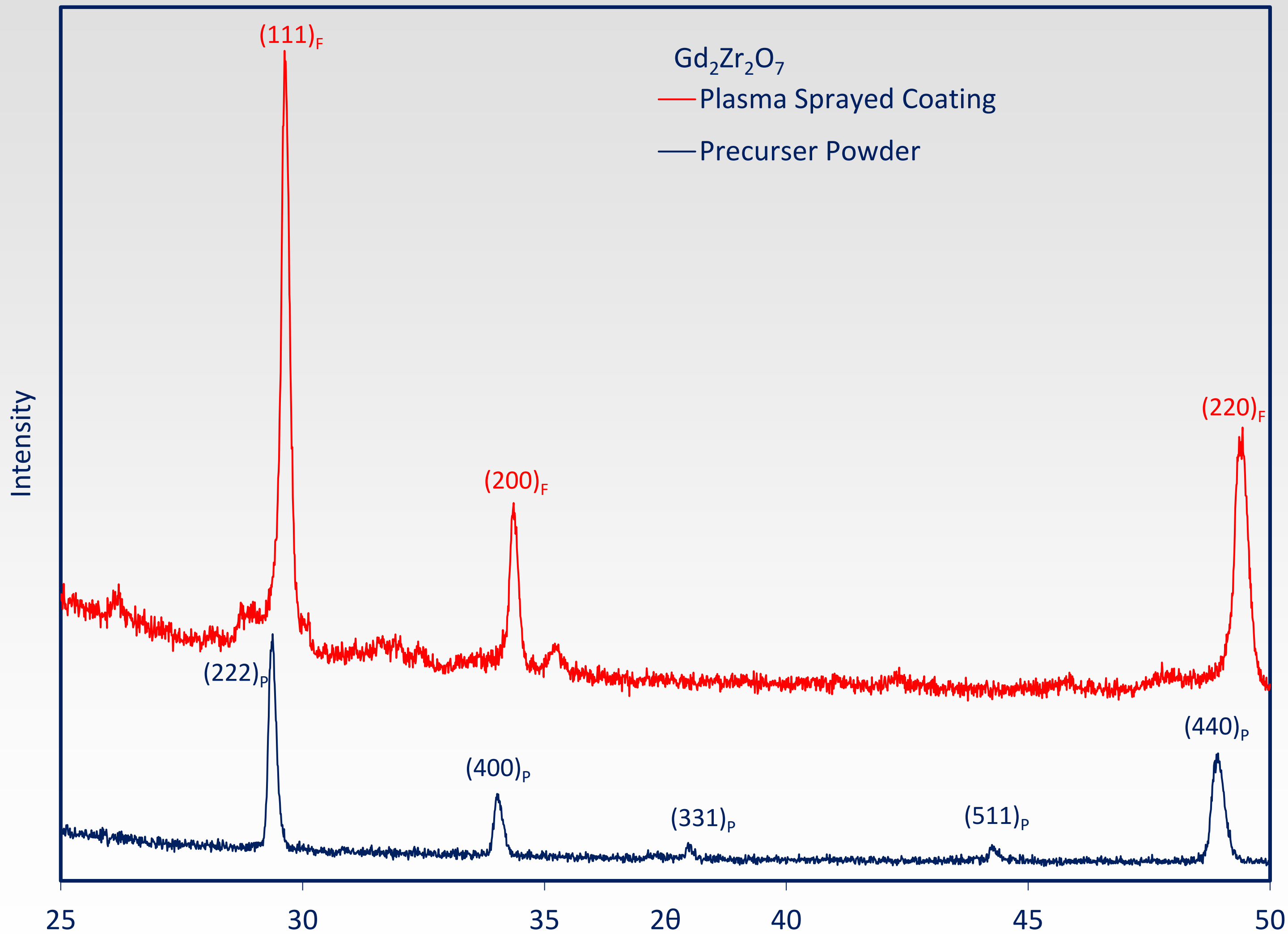
Pyrochlore



Ordering of Ln / Zr

A.R. Cleave (2006)

Plasma Sprayed $Gd_2Zr_2O_7$



Plasma-sprayed $Gd_2Zr_2O_7$ not pyrochlore

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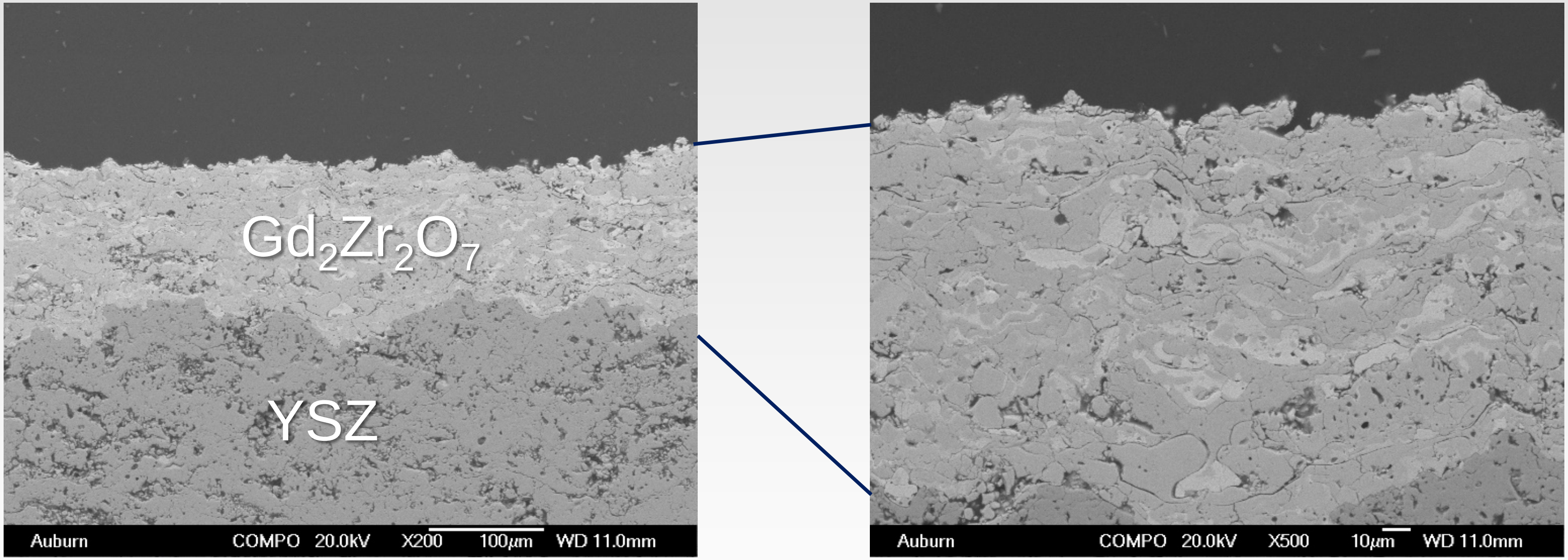
Plasma Sprayed YSZ / $Gd_2Zr_2O_7$



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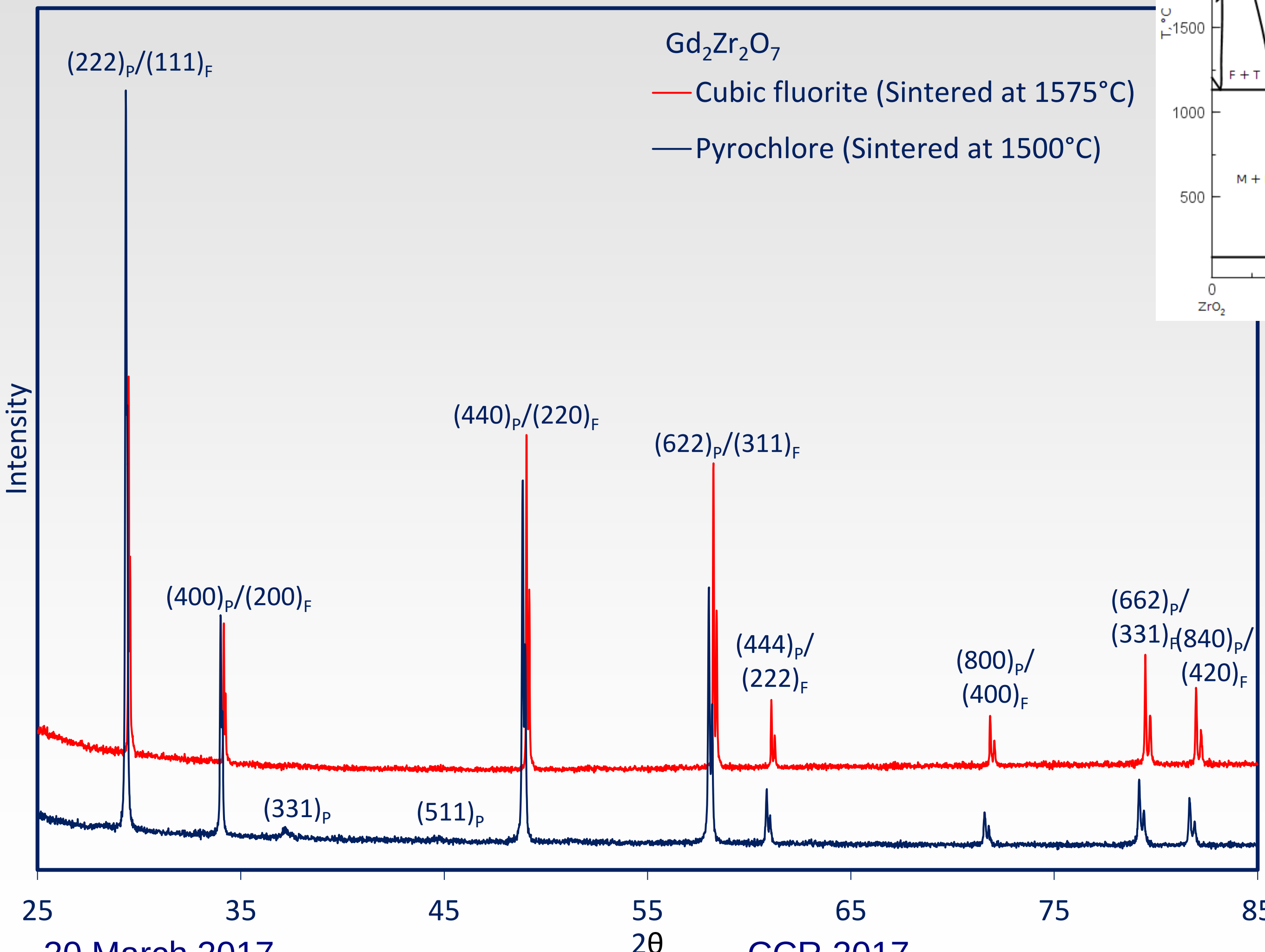
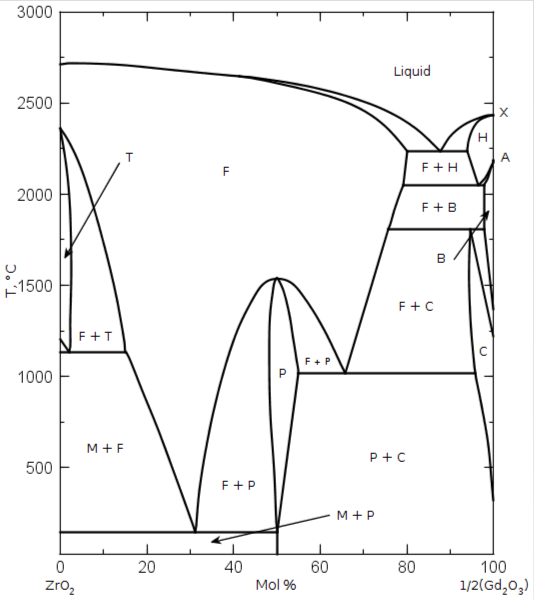
$Gd_2Zr_2O_7$: Cubic Fluorite and Pyrochlore





Synthesize cubic fluorite $Gd_2Zr_2O_7$ with higher sintering temperature

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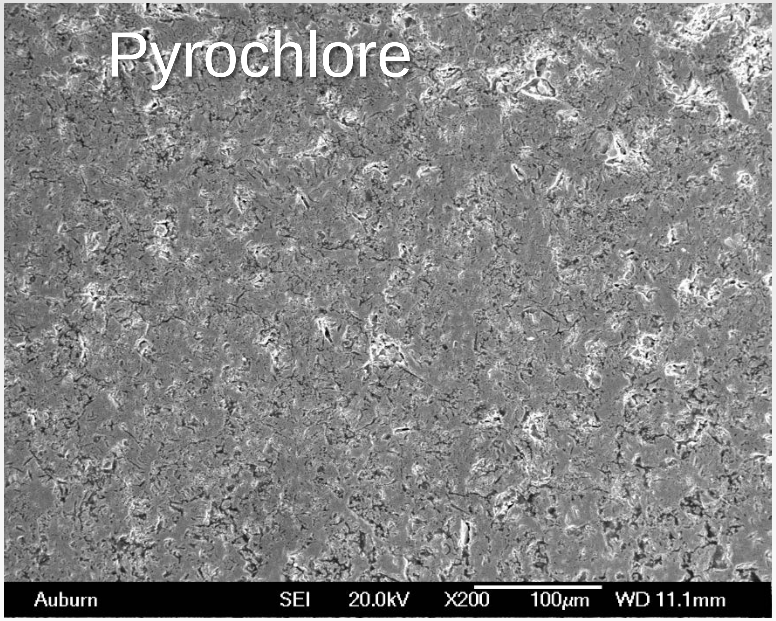
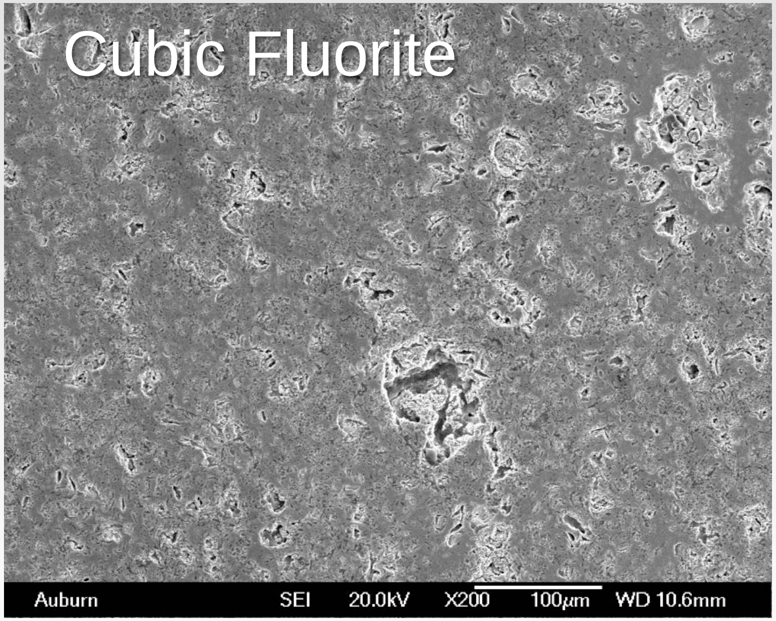
Sintered $Gd_2Zr_2O_7$





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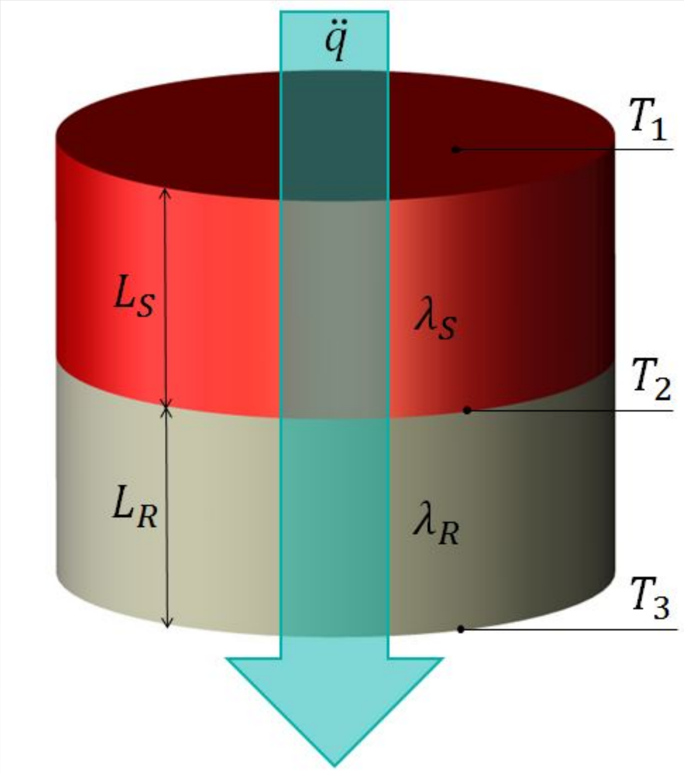
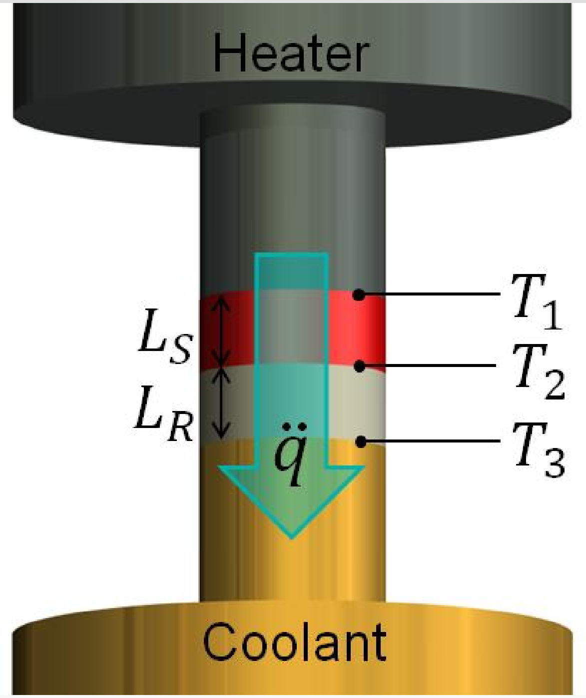
Thermal Conductivity Measurement





Constant heat flux through known / unknown samples
Measure temperature gradients

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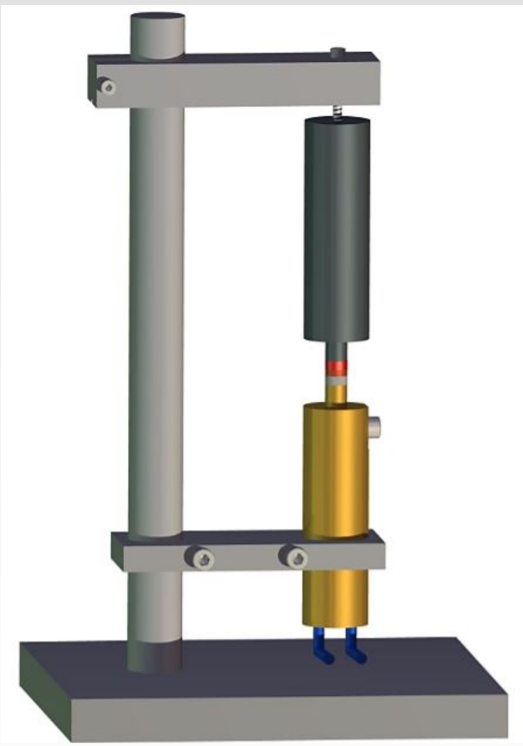
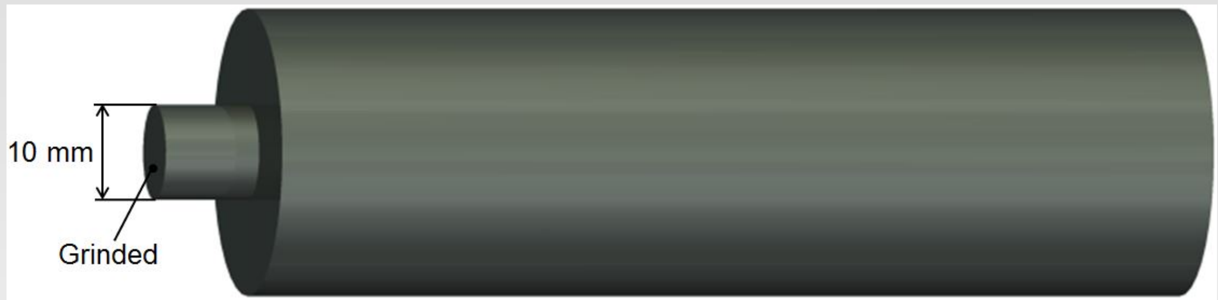
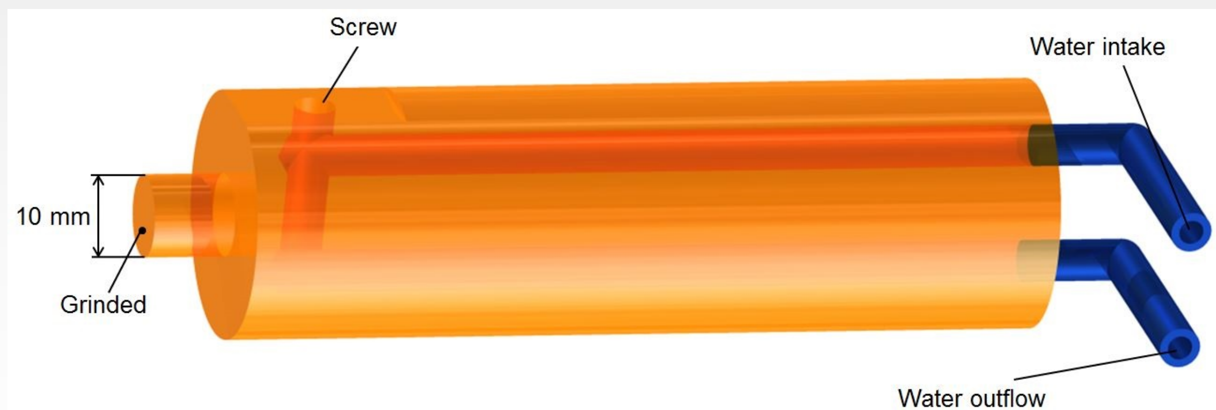
Thermal Conductivity Measurement

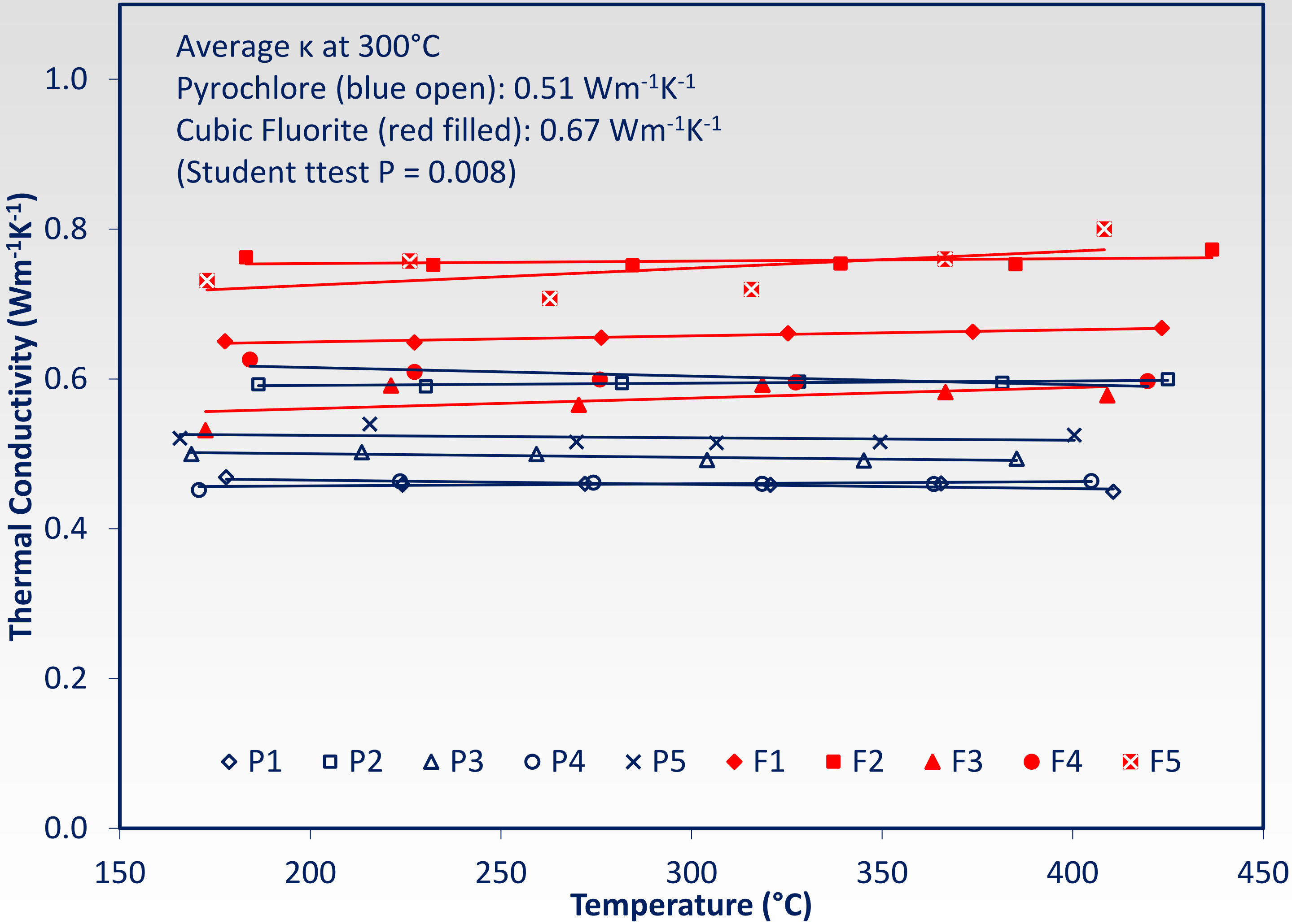




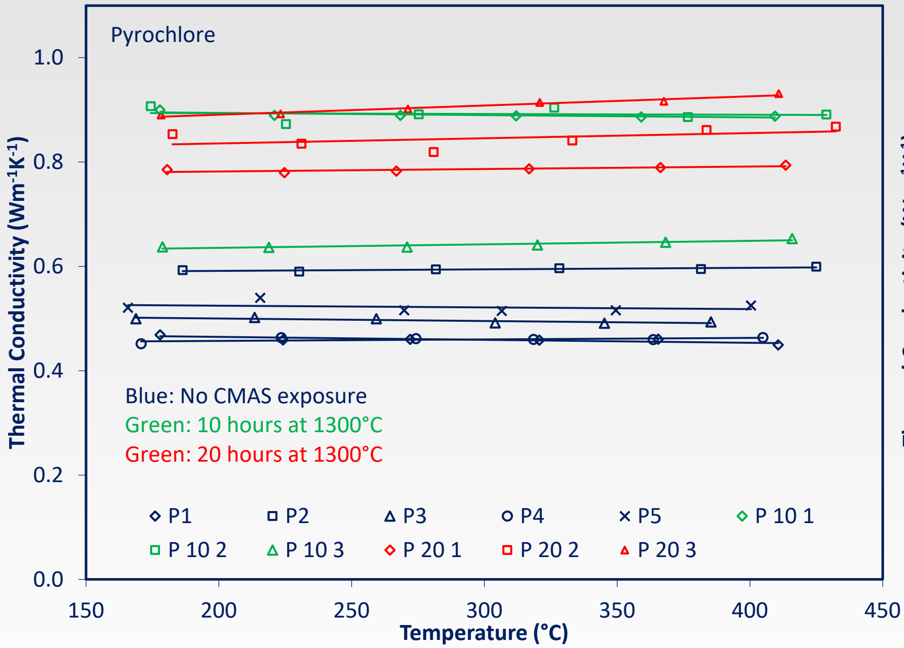
Steel heat source / sink

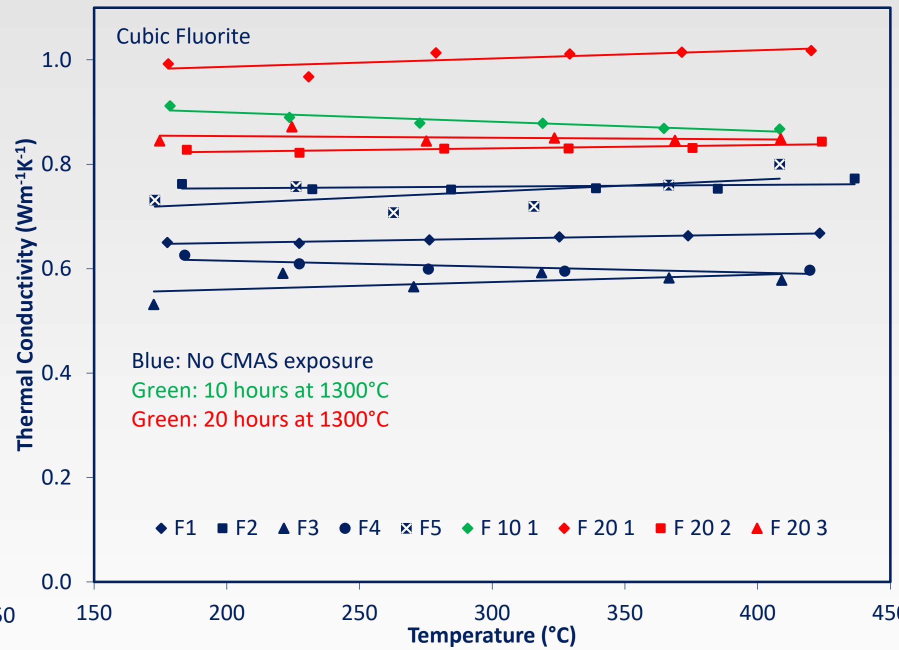


Thermal Conductivity of $Gd_2Zr_2O_7$

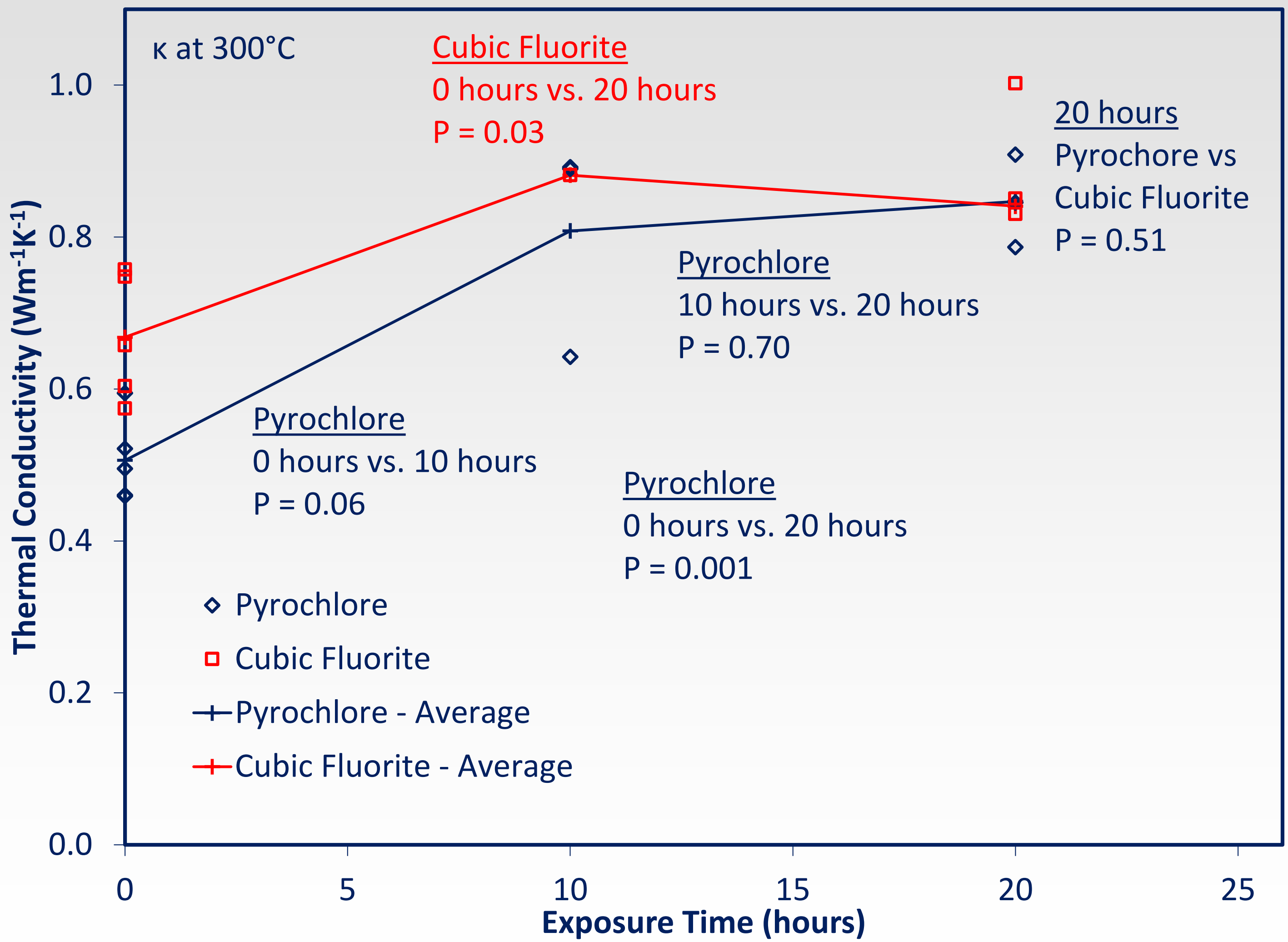


Thermal Conductivity of $Gd_2Zr_2O_7$ after CMAS Exposure at 1300°C





Thermal Conductivity of $Gd_2Zr_2O_7$ after CMAS Exposure at 1300°C



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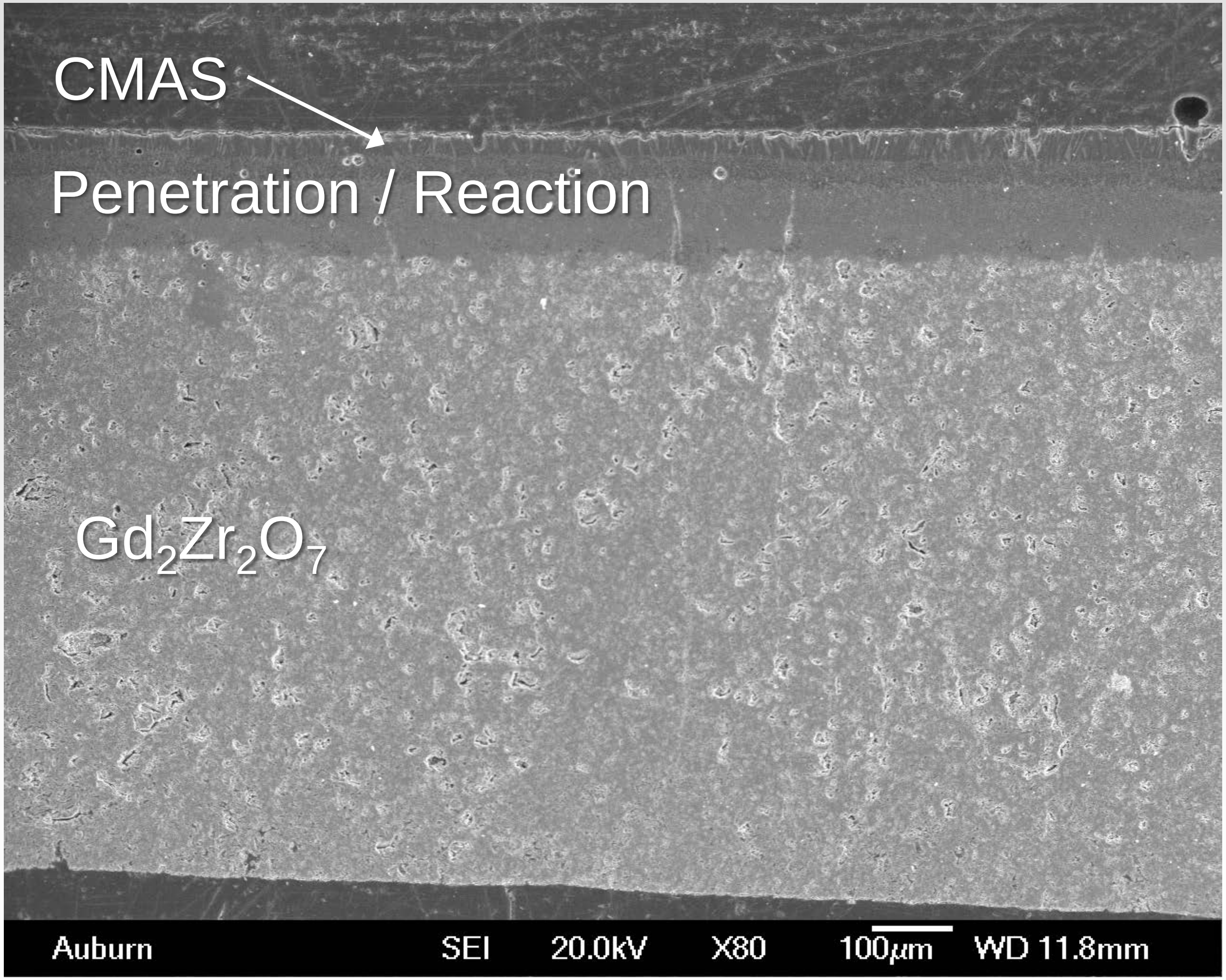
Cubic Fluorite $Gd_2Zr_2O_7$ after CMAS at 1300°C for 10 hours



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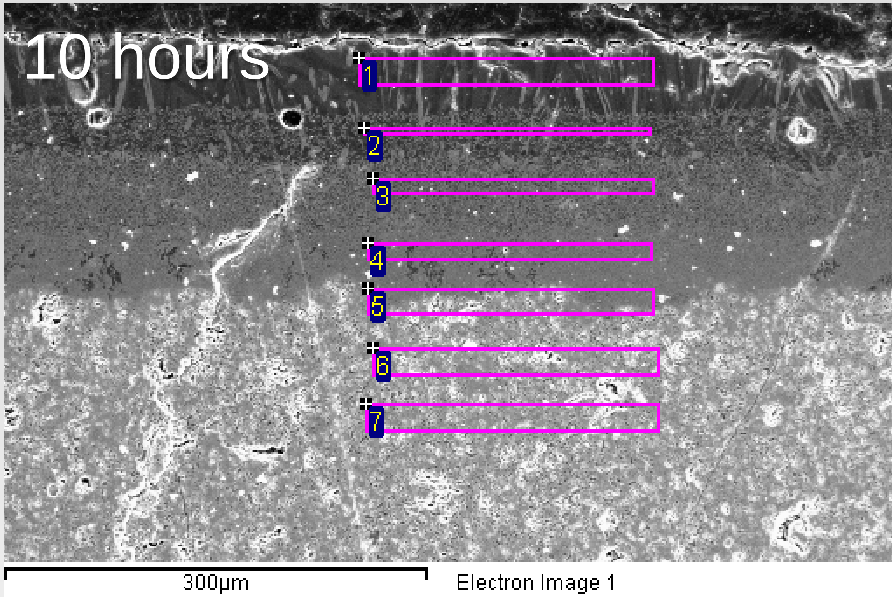
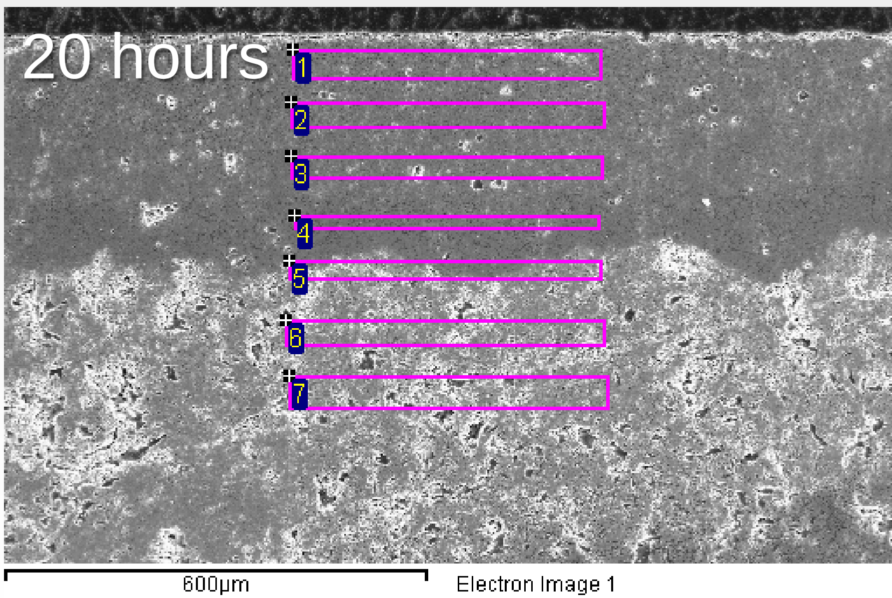
Cubic Fluorite $Gd_2Zr_2O_7$ after CMAS at 1300°C

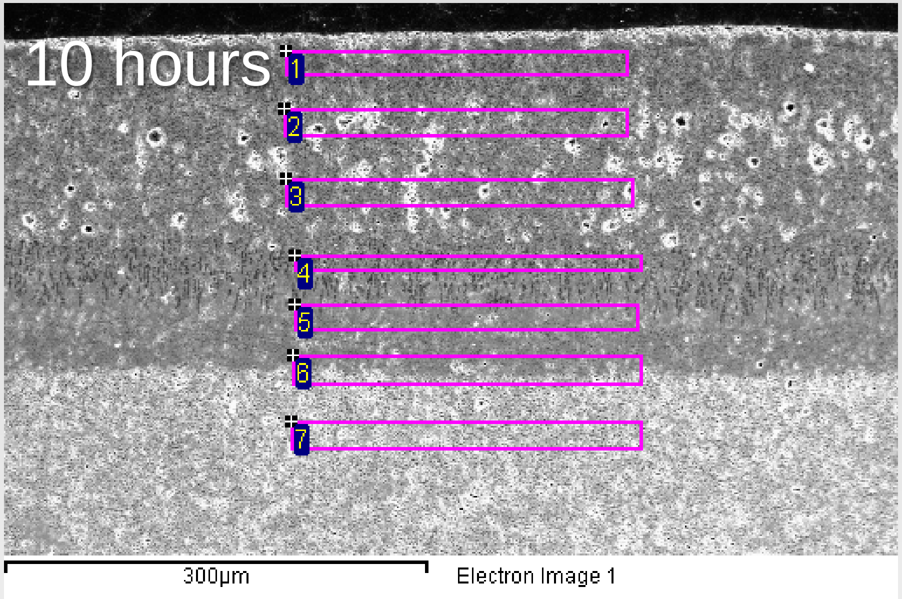


Mostly CMAS
+Mg / ↓ Gd

Al-Si-Ca-Gd-Zr-O

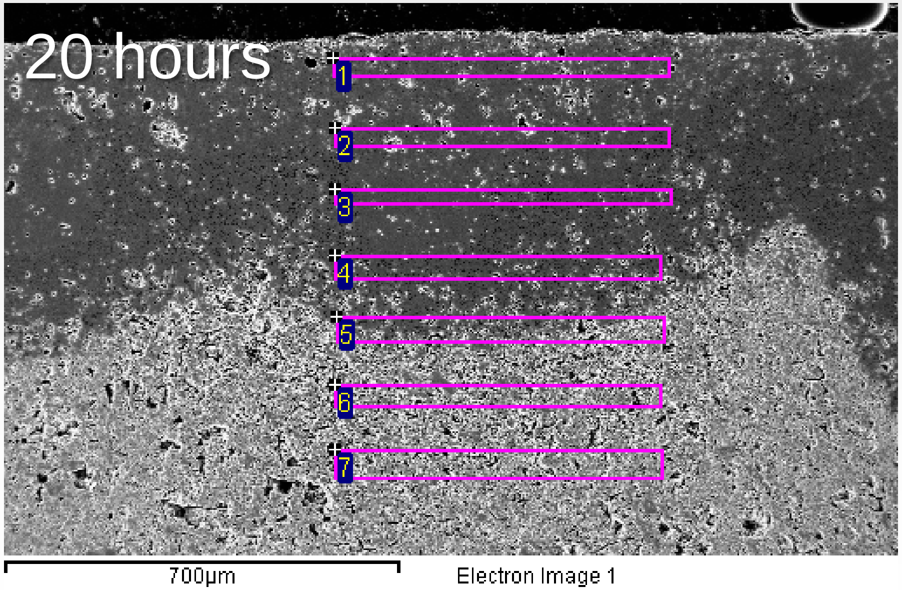


↑Al



↑Al

Pyrochlore $Gd_2Zr_2O_7$ after CMAS at 1300°C



↑Al, Mg

Increased variation in penetration depth after 20 hours

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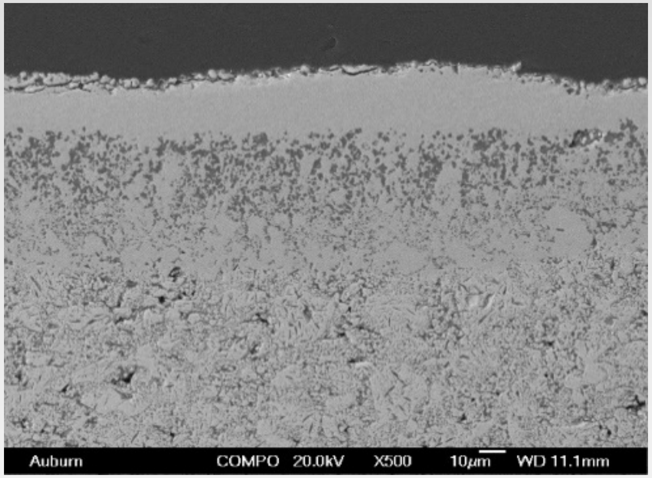
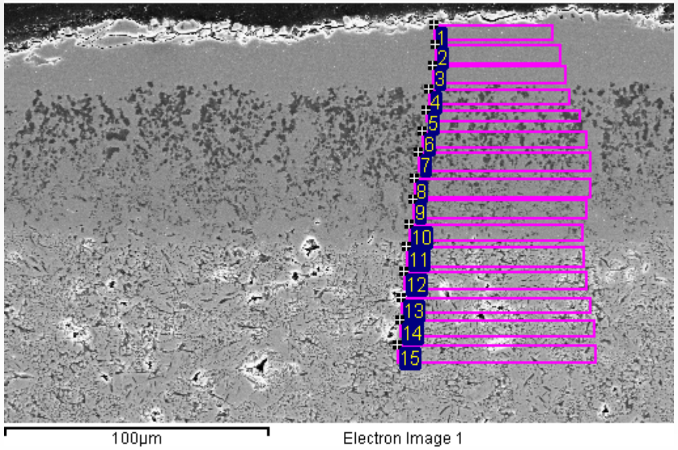
Pyrochlore $Gd_2Zr_2O_7$ after CMAS at 1200°C for 20 hours

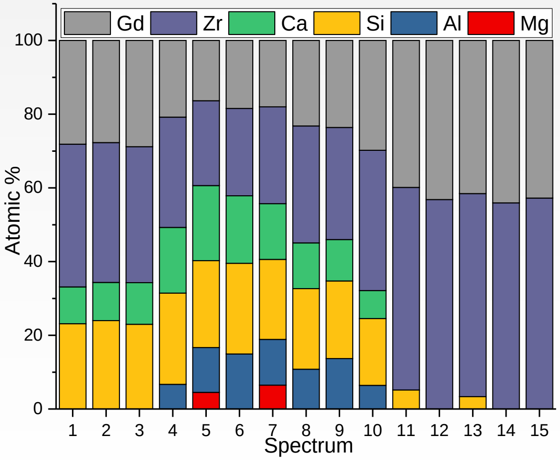
Reaction Layer

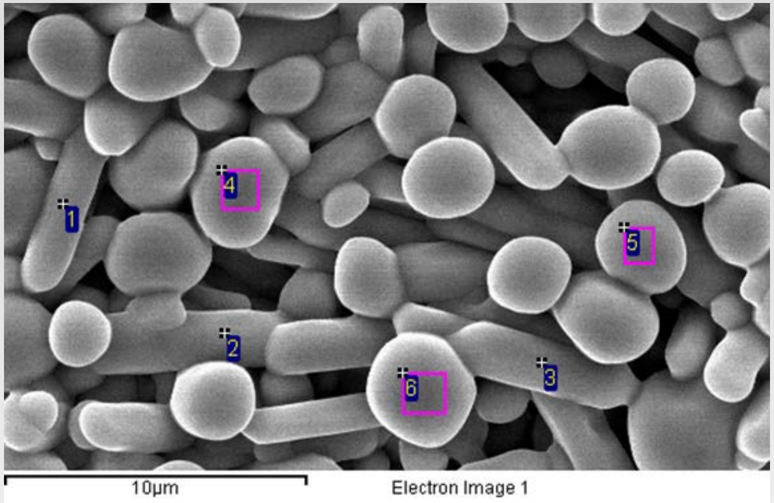
$Gd_2Zr_2O_7$



Dense layer forms after reaction with CMAS







Pyrochlore $Gd_2Zr_2O_7$ after CMAS at 1200°C for 40 hours

Gd-containing silicate

Zr-rich cubic fluorite

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

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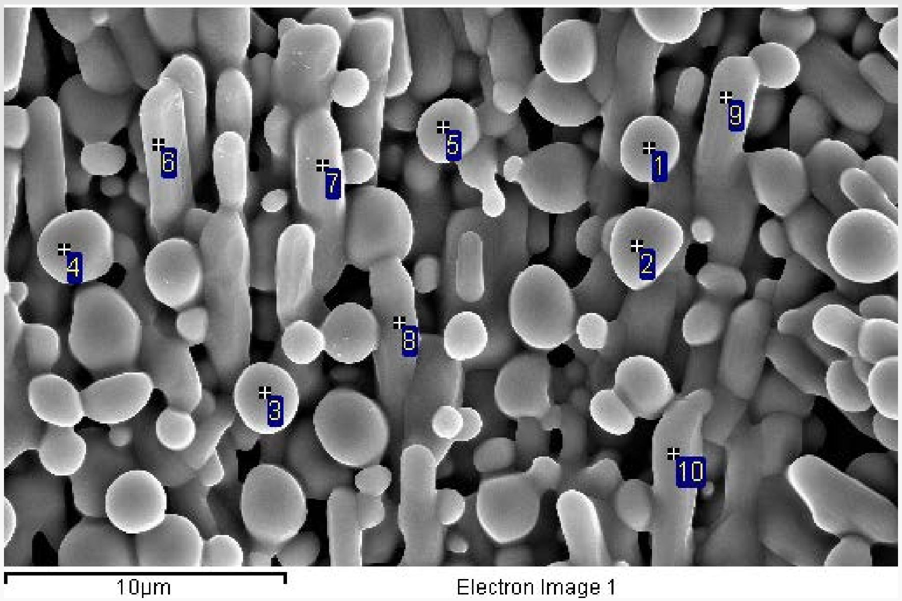
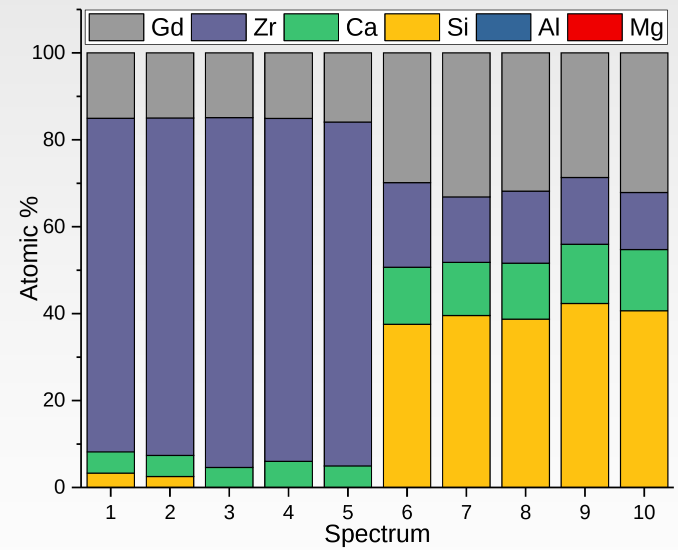
Cubic Fluorite $Gd_2Zr_2O_7$ after CMAS at 1200°C for 5 hours

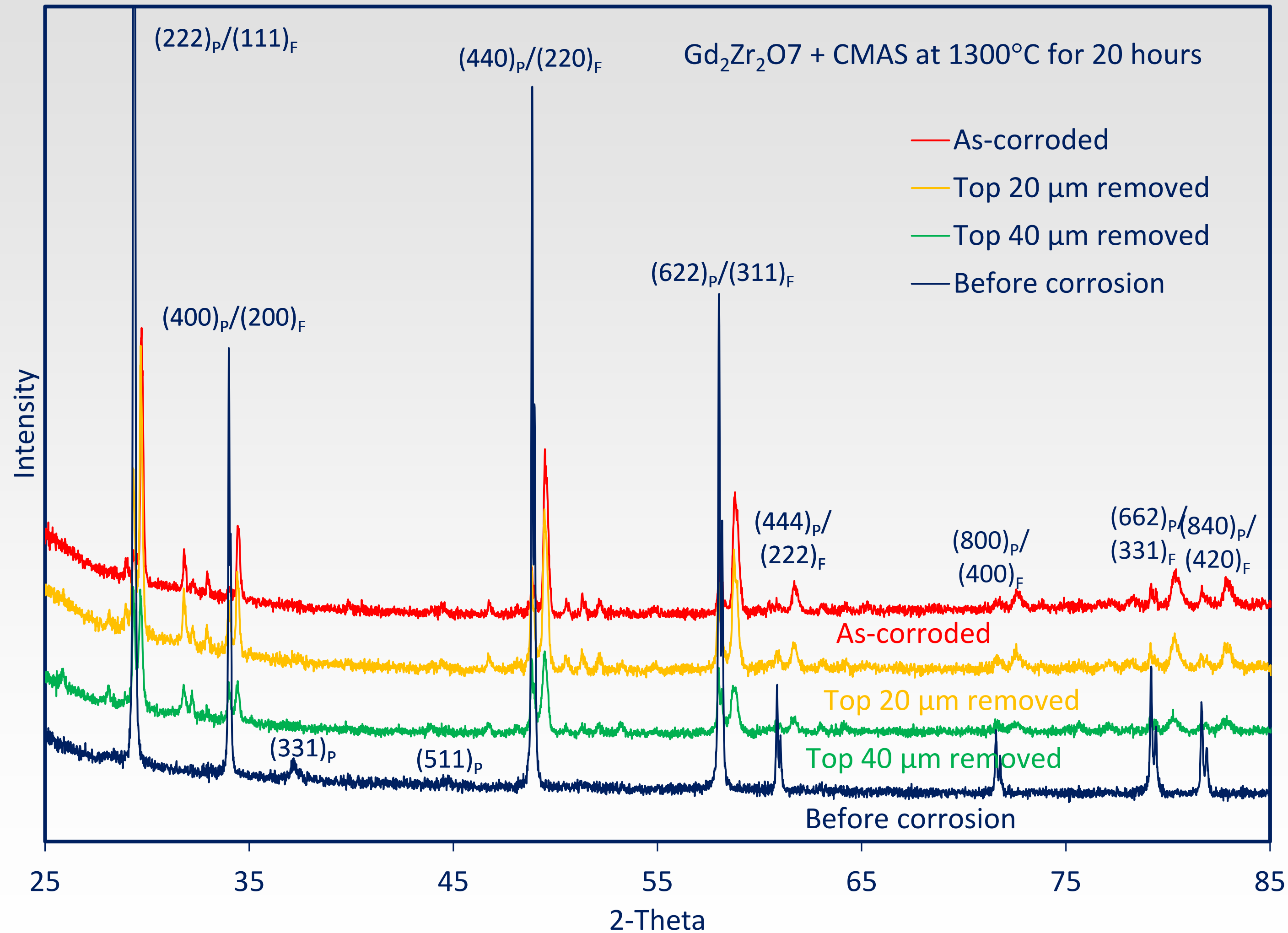


Zr-rich cubic fluorite

Gd-containing silicate

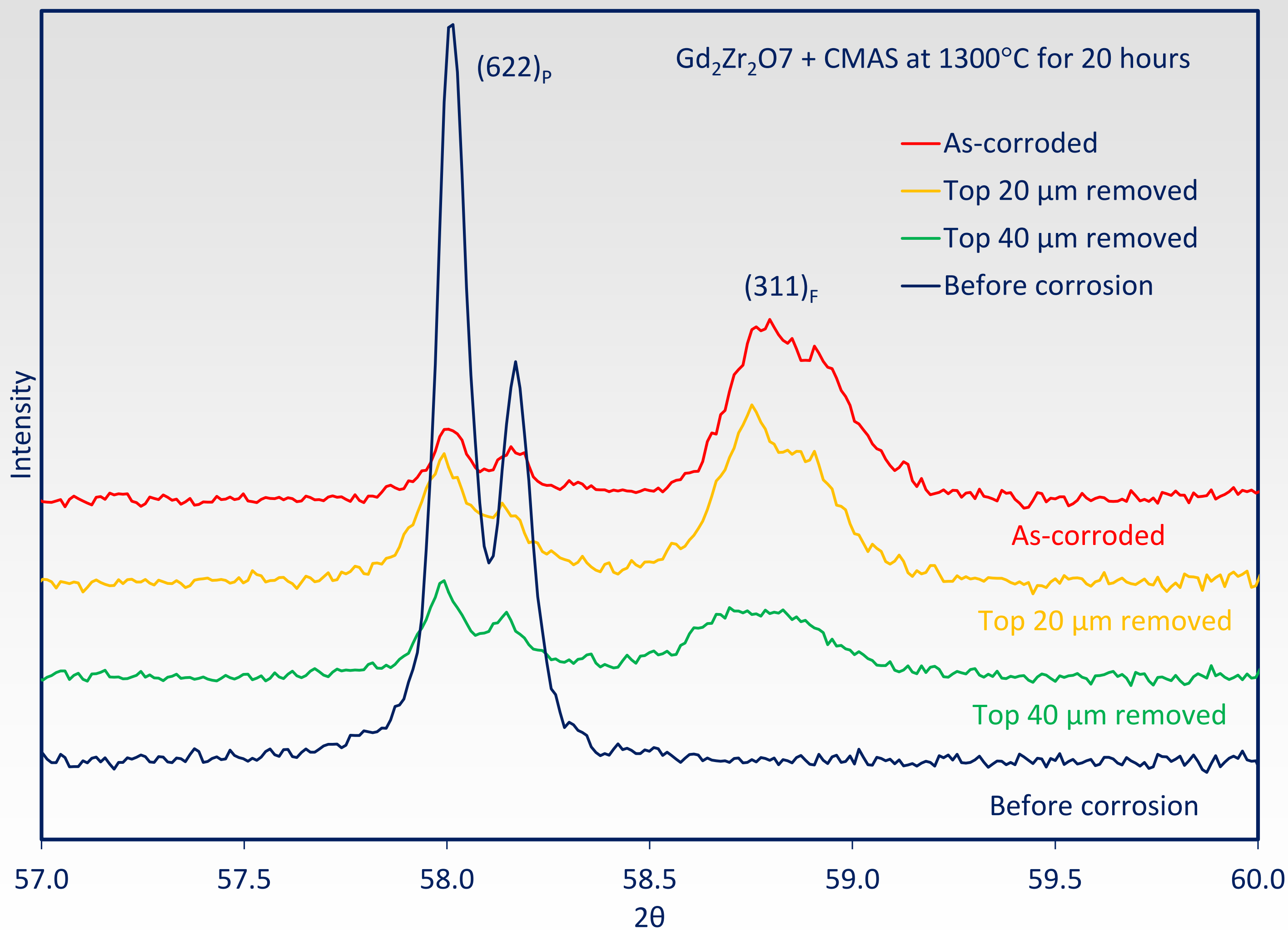


Pyrochlore $Gd_2Zr_2O_7$ after CMAS at 1300°C for 20 hours



Cubic fluorite structure after reaction

Pyrochlore $Gd_2Zr_2O_7$ after CMAS at 1300°C for 20 hours



Proportion of cubic fluorite higher near surface

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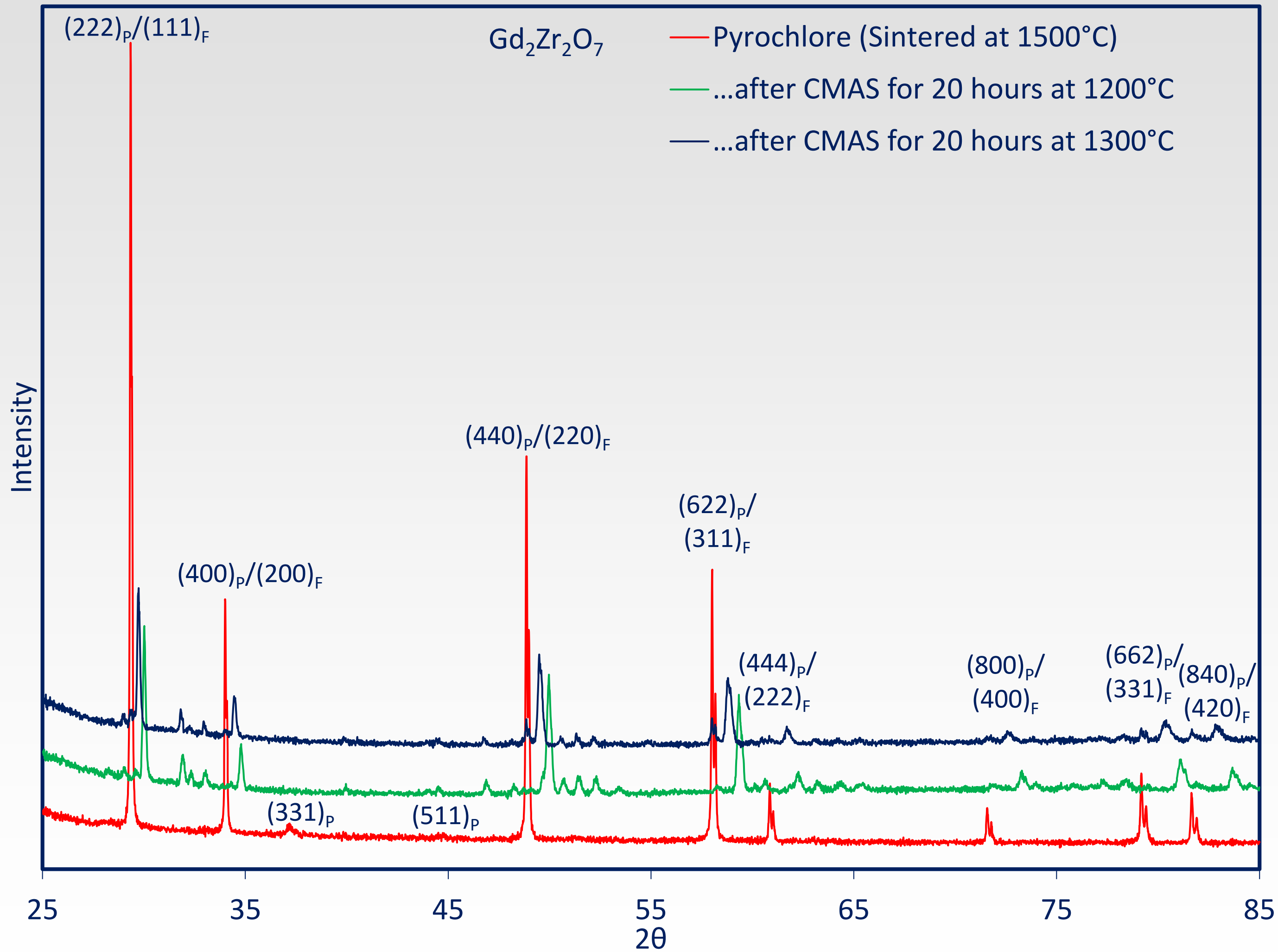
Pyrochlore $Gd_2Zr_2O_7$ after CMAS for 20 hours



Peak position of cubic fluorite (*i.e.* composition) function of temperature

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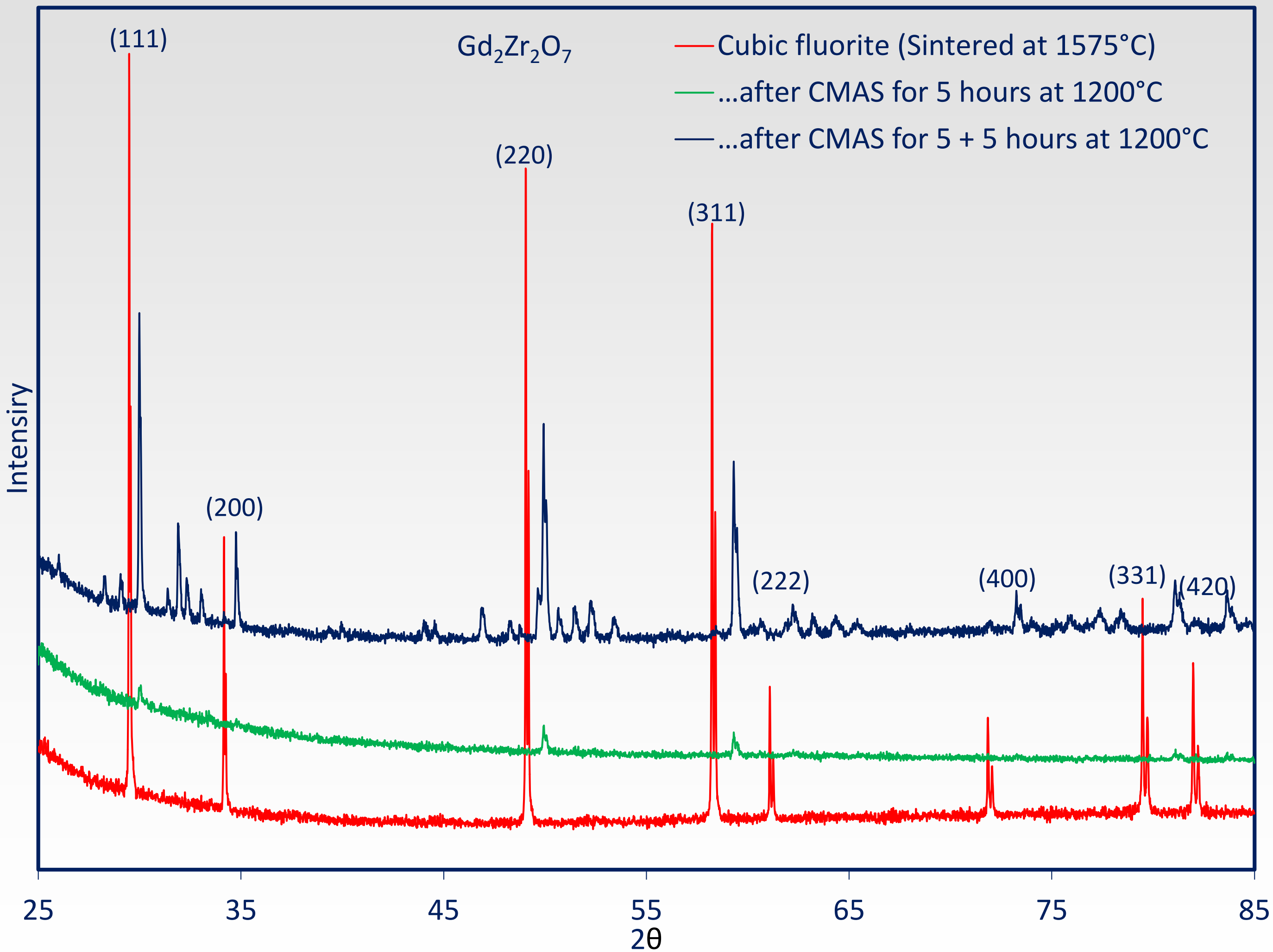
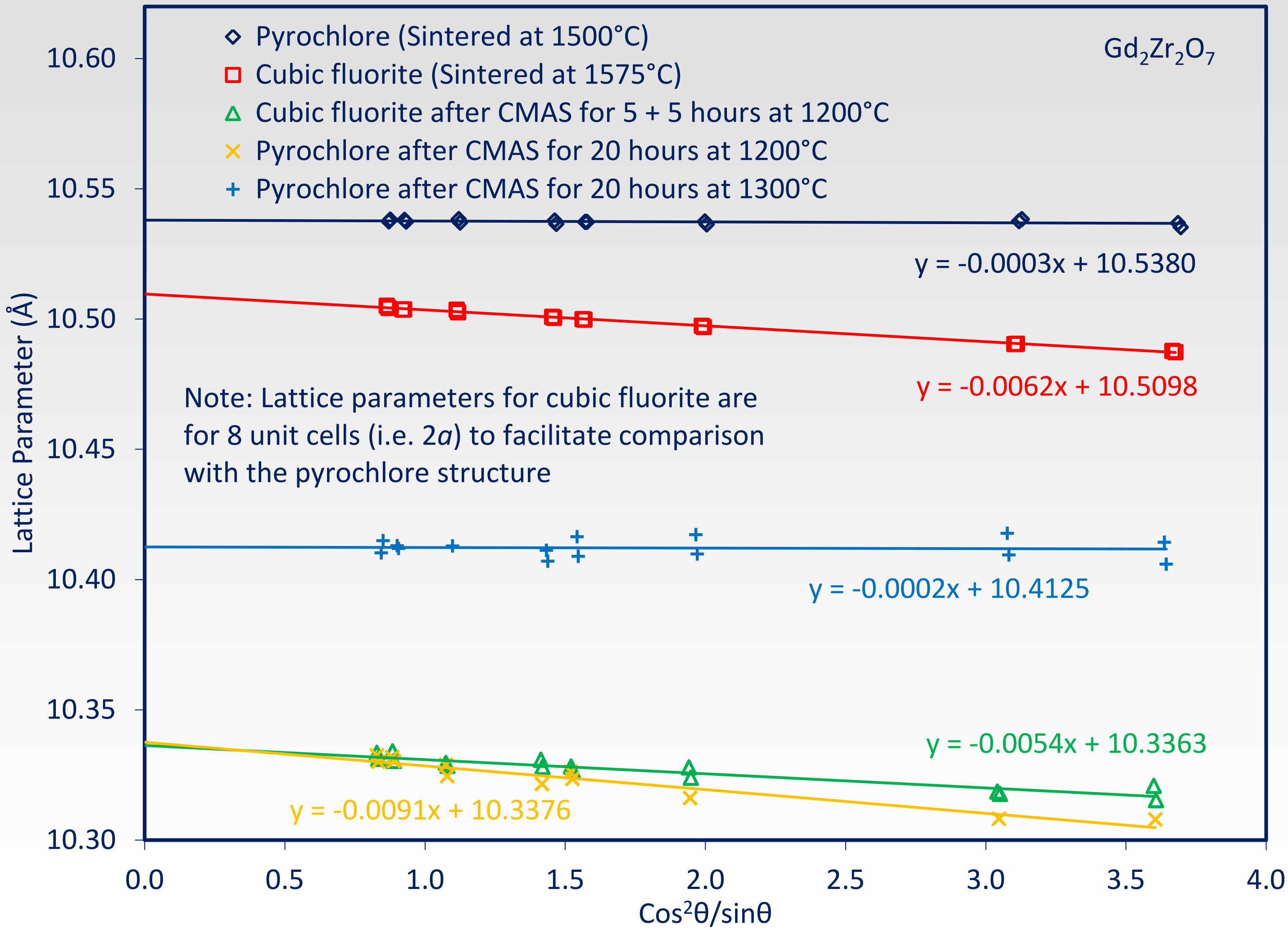
Cubic Fluorite $Gd_2Zr_2O_7$ after CMAS at 1200°C



Cubic fluorite peak shifts for cubic fluorite $Gd_2Zr_2O_7$

$Gd_2Zr_2O_7$ Lattice Parameter Correction



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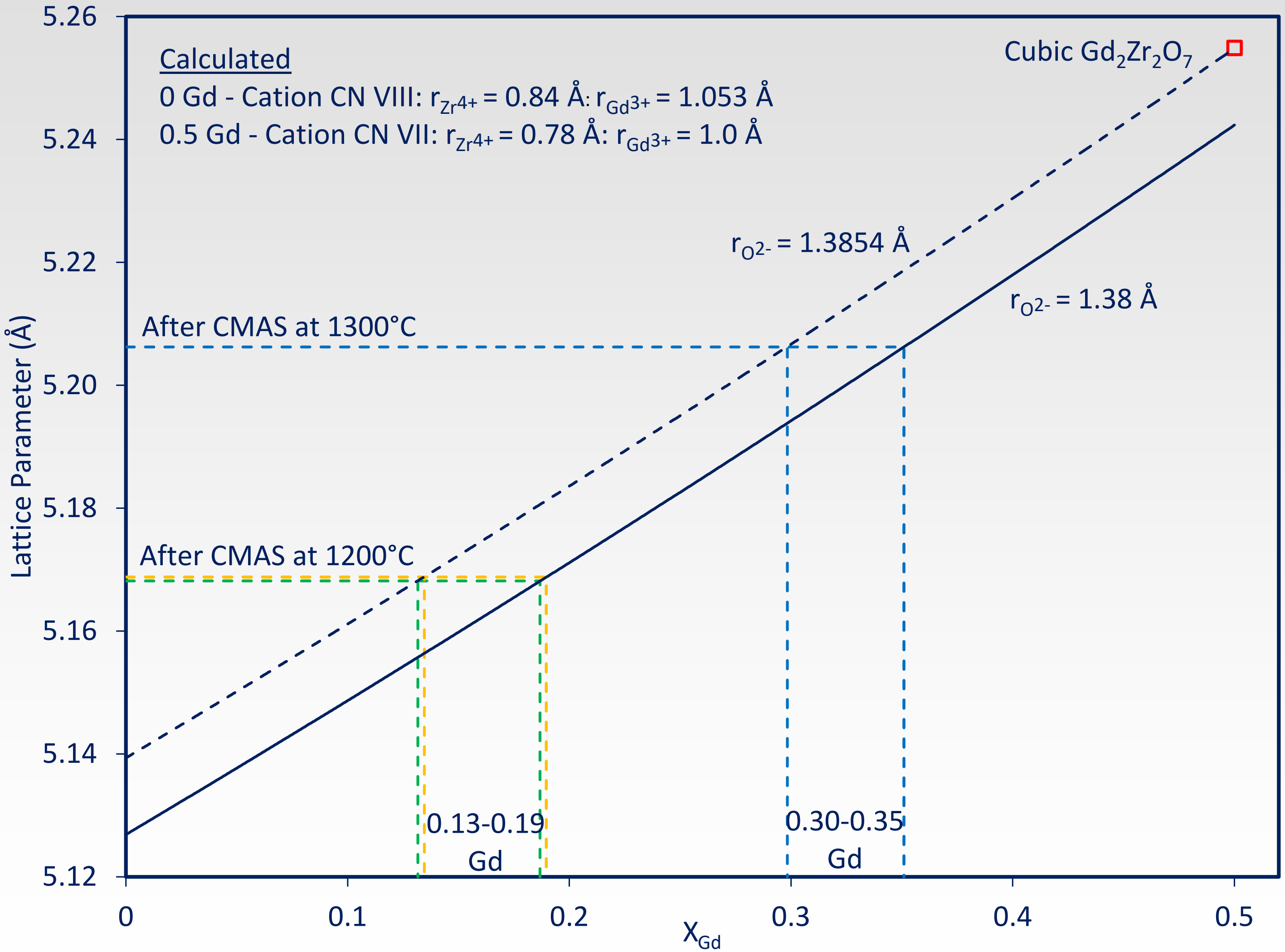
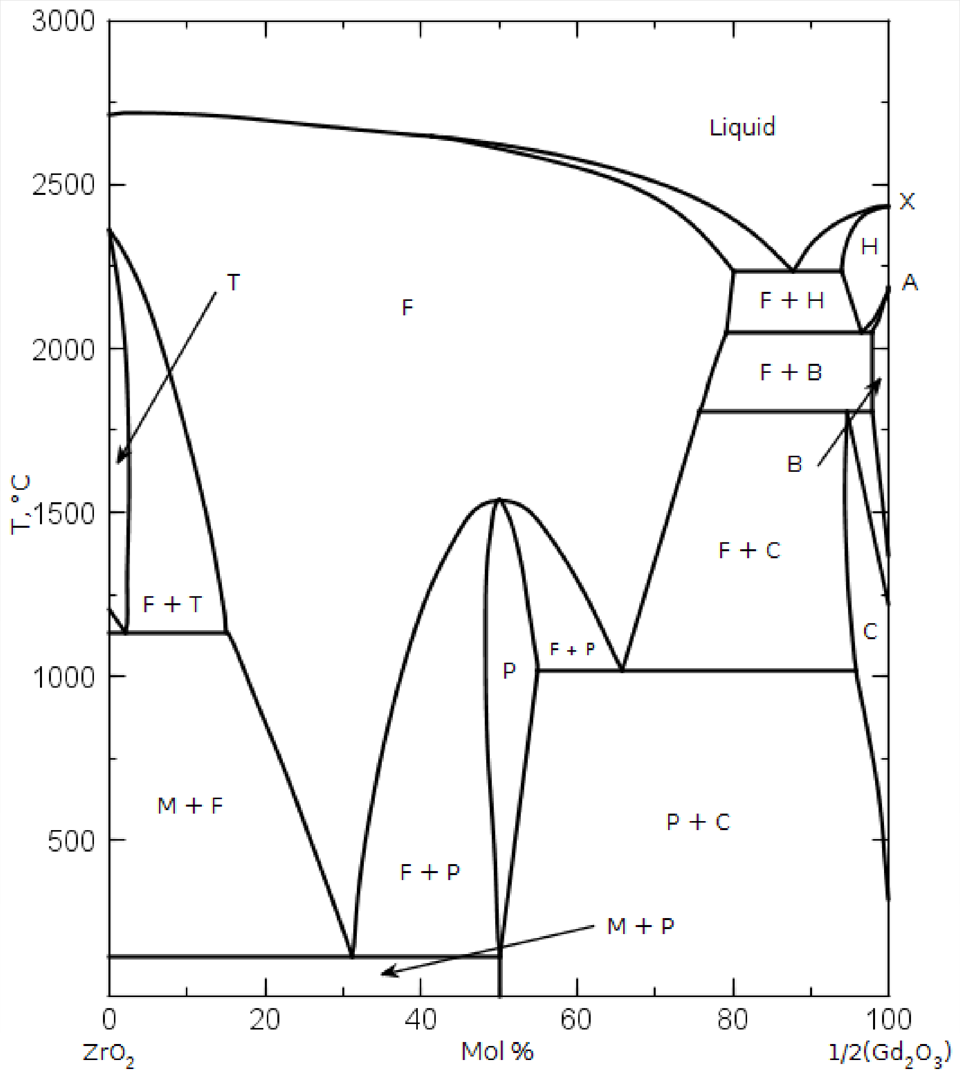
$Gd_2Zr_2O_7$ Lattice Parameter



Cubic fluorite peak position not affected by original crystal structure

ZrO_2-Gd_2O_3 Phase Diagram

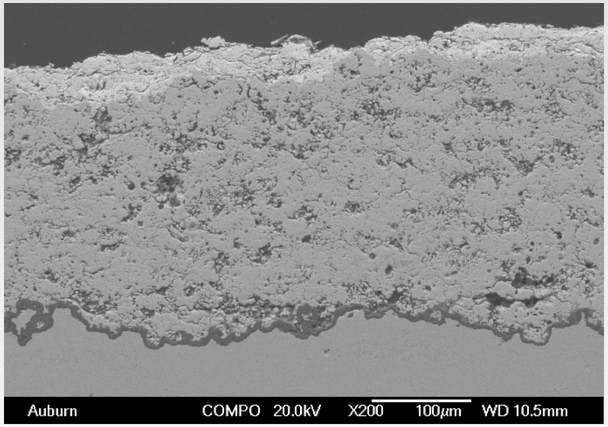


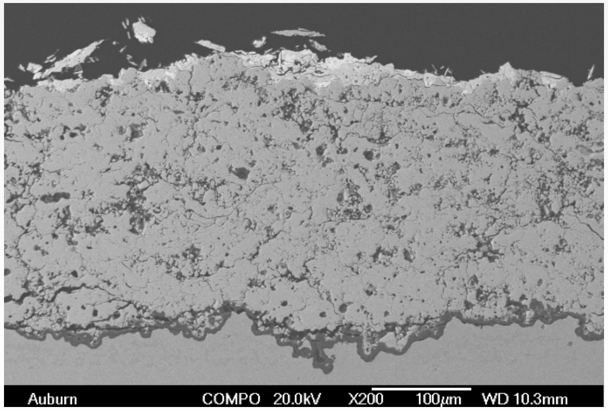
Gd / Zr in cubic fluorite increases with increasing temperature

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

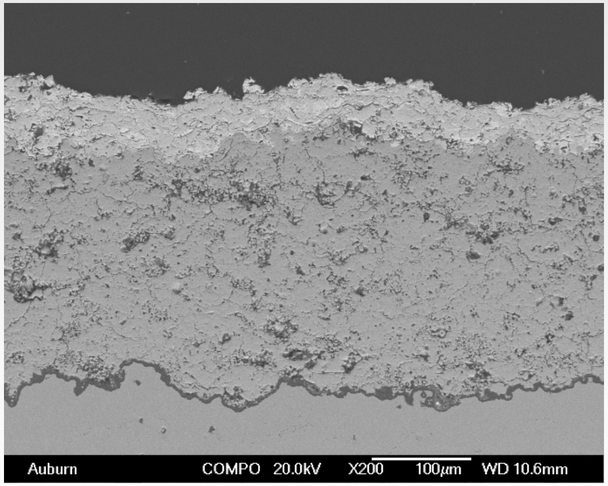
YSZ / $Gd_2Zr_2O_7$ coating exposure at 1200°C for 20 hours

CMAS

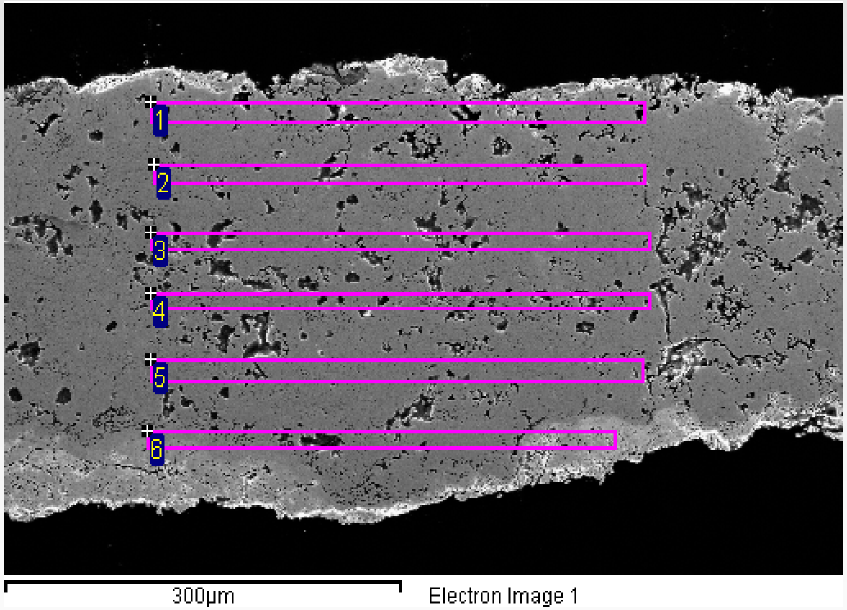




Air

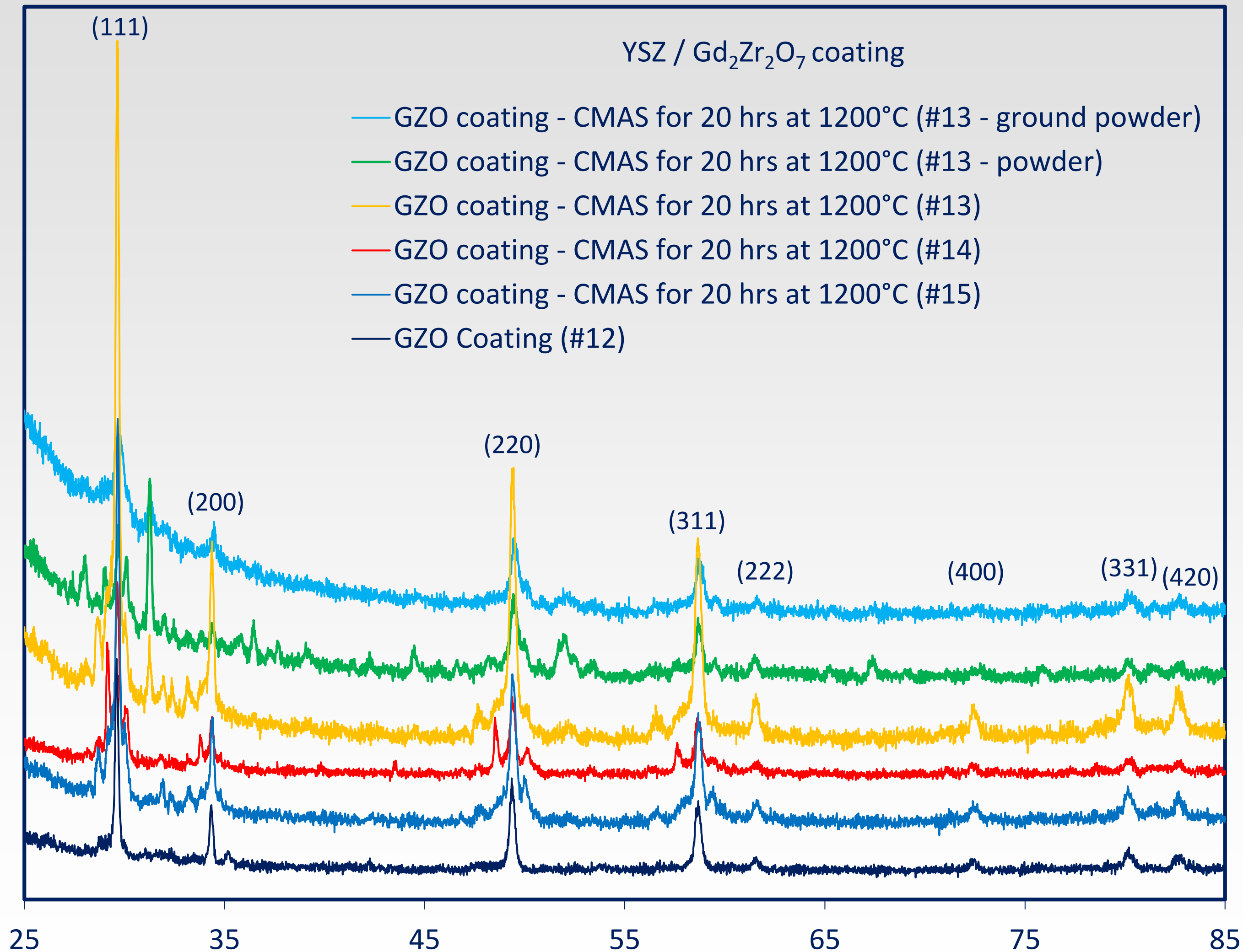


YSZ / $Gd_2Zr_2O_7$ coating CMAS at 1200°C for 20 hours



EDS analysis (atomic%)						
Area	O	Al	Si	Ca	Zr	Gd
1	71				29	
2	72			1	28	
3	73	2			24	
4	74	2			24	
5	72				28	
6	70	4	2	1	20	4

YSZ / $Gd_2Zr_2O_7$ coating x-ray diffraction



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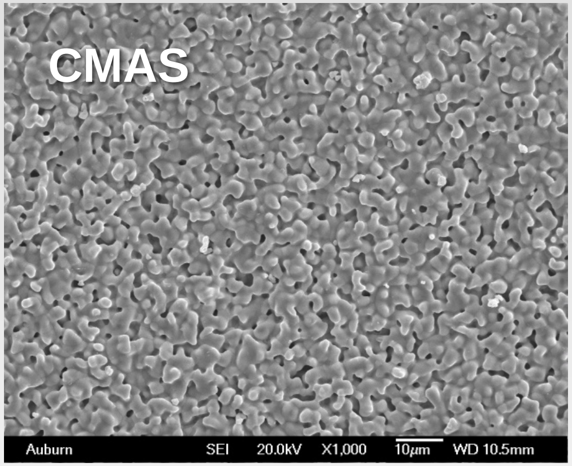
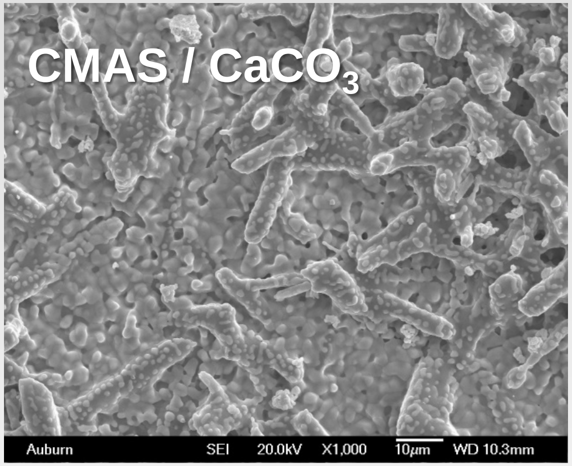
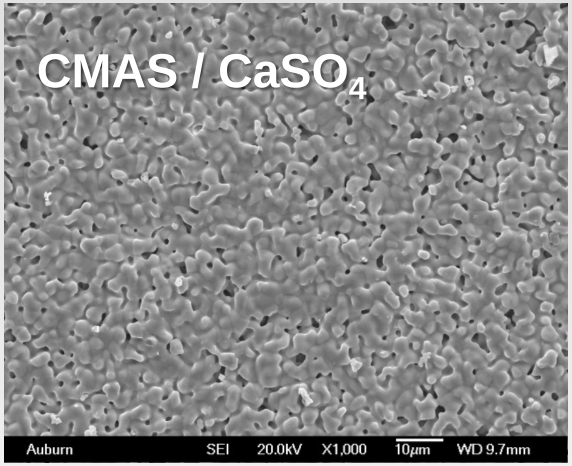
CMAS Compositions

CMAS Composition					
Source	Oxide	Percentage (mol%)			
		CMAS	CaO-lean CMAS	CMAS / $CaCO_3$	CMAS / $CaSO_4$
CMAS	CaO	33	20	17	17
	MgO	9	11	9	9
	$AlO_{1.5}$	13	16	13	13
	SiO_2	45	54	45	45
$CaCO_3$	CaO	—	—	17	—
$CaSO_4$	CaO	—	—	—	17
Total CaO		33	20	33	33

Surface after CMAS Exposure at 1300°C for 20 hours







Surface morphologies similar – larger crystals on sample with $CaCO_3$

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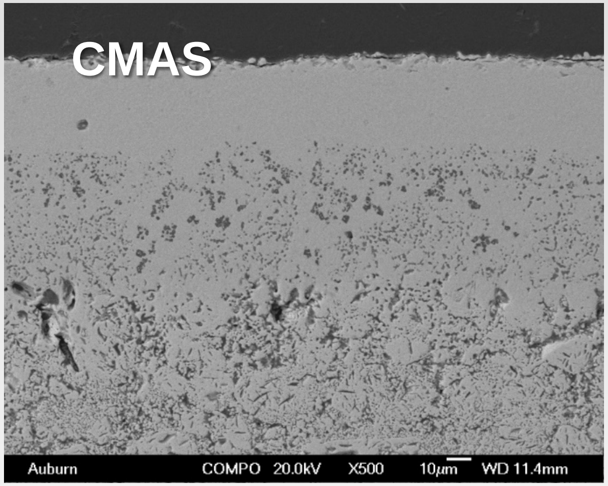
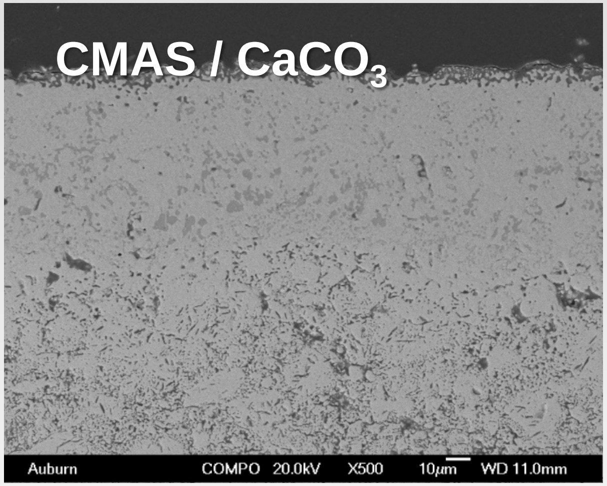
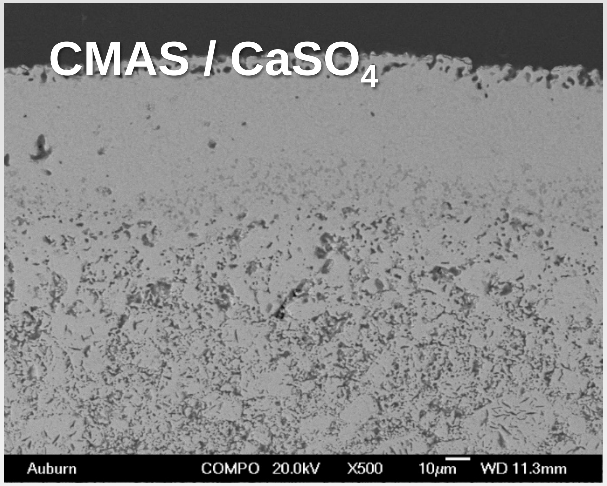
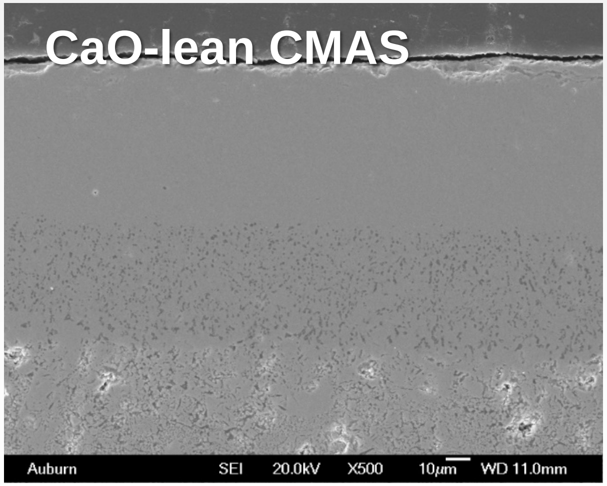
Cross-Section after CMAS Exposure at 1300°C for 20 hours









Dense reaction layer – thickest for CaO-deficient composition

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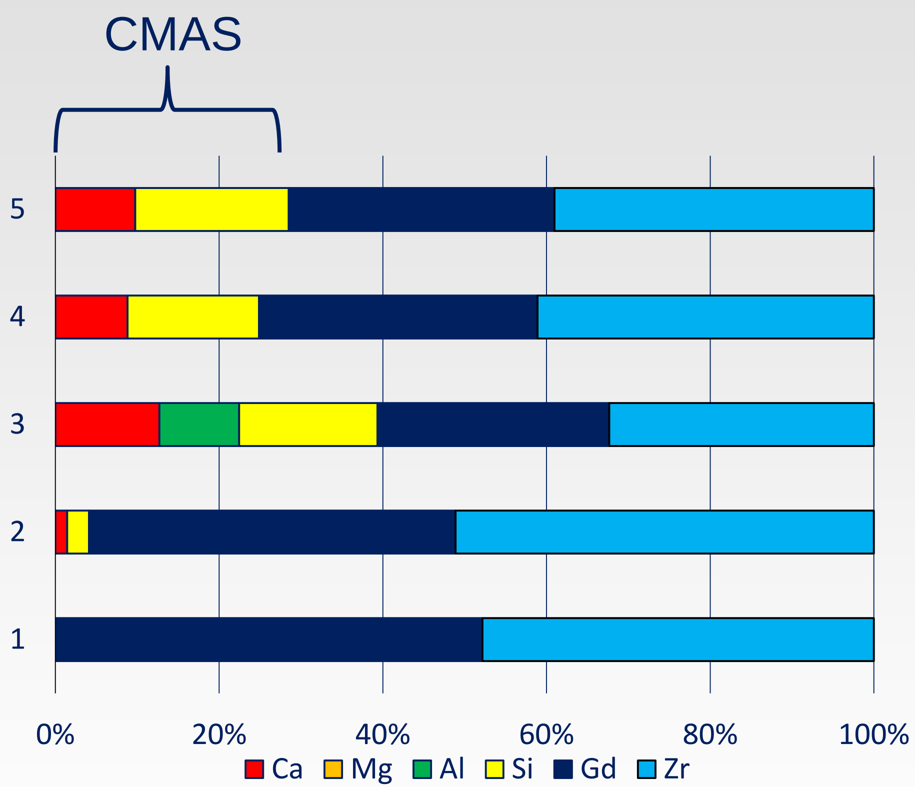
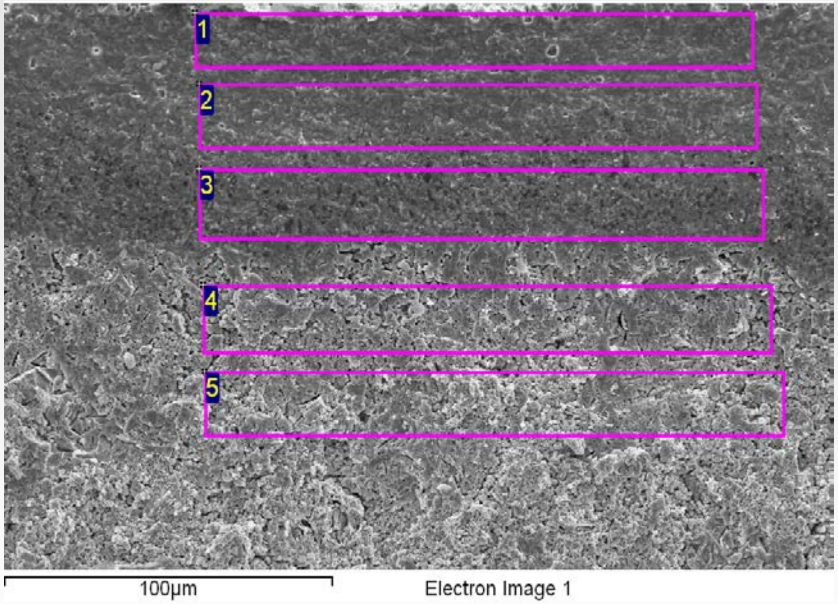
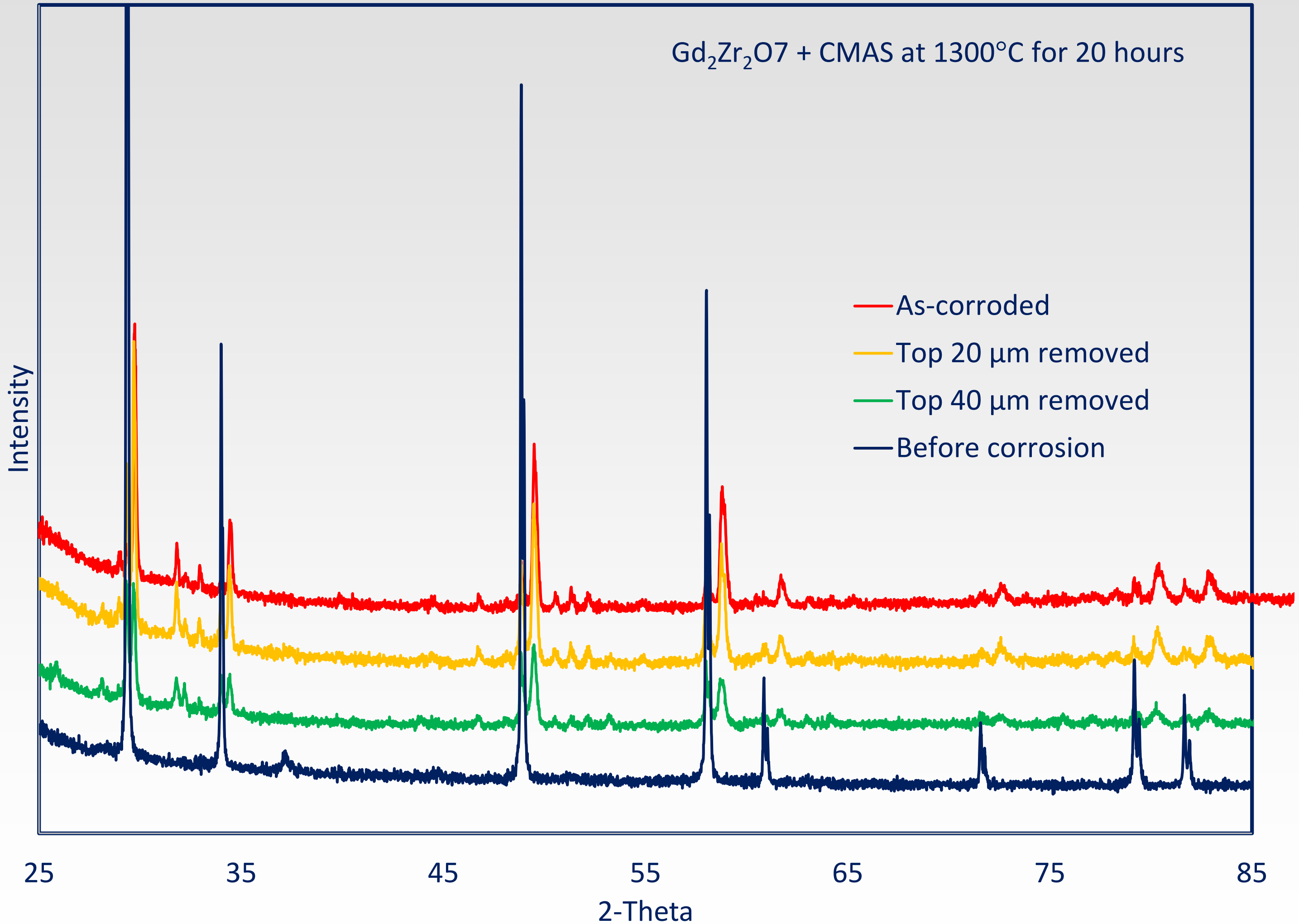
$Gd_2Zr_2O_7$ after CMAS at 1300°C for 20 hours – SEM / EDS





Elemental Distribution (mol%)

$Gd_2Zr_2O_7$ after CMAS at 1300°C for 20 hours – XRD



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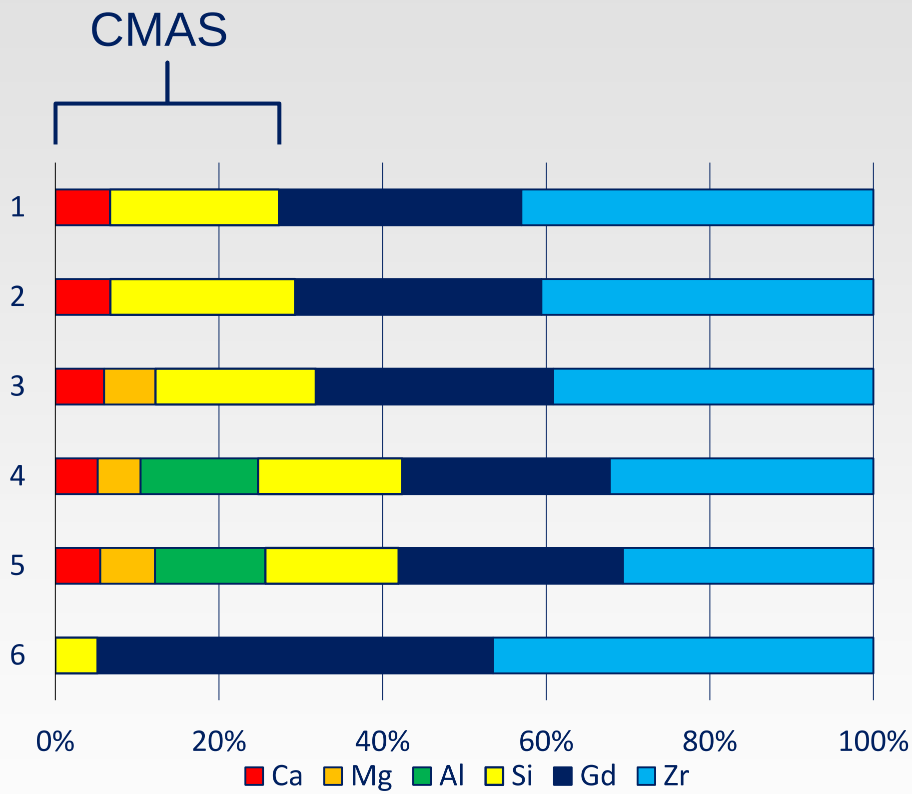
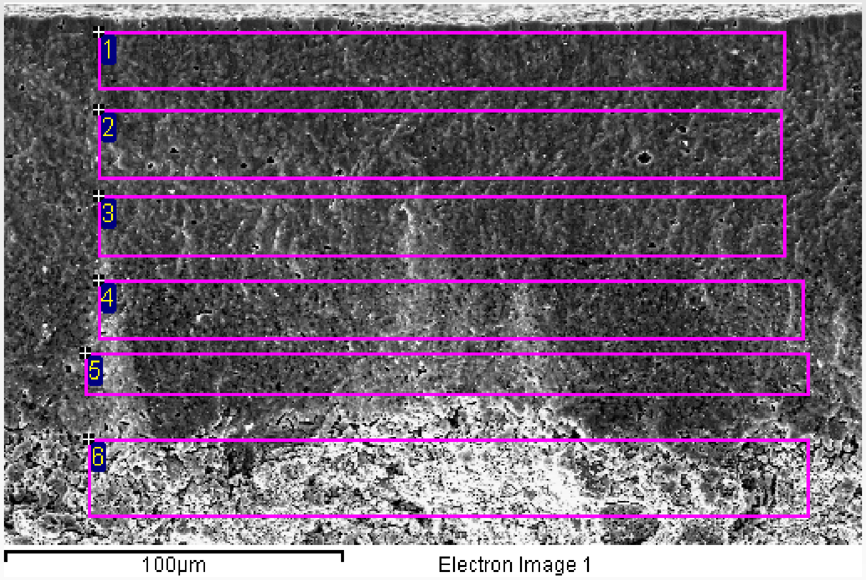
$Gd_2Zr_2O_7$ after CaO-lean CMAS at 1300°C for 20 hours – SEM / EDS



Elemental Distribution (mol%)



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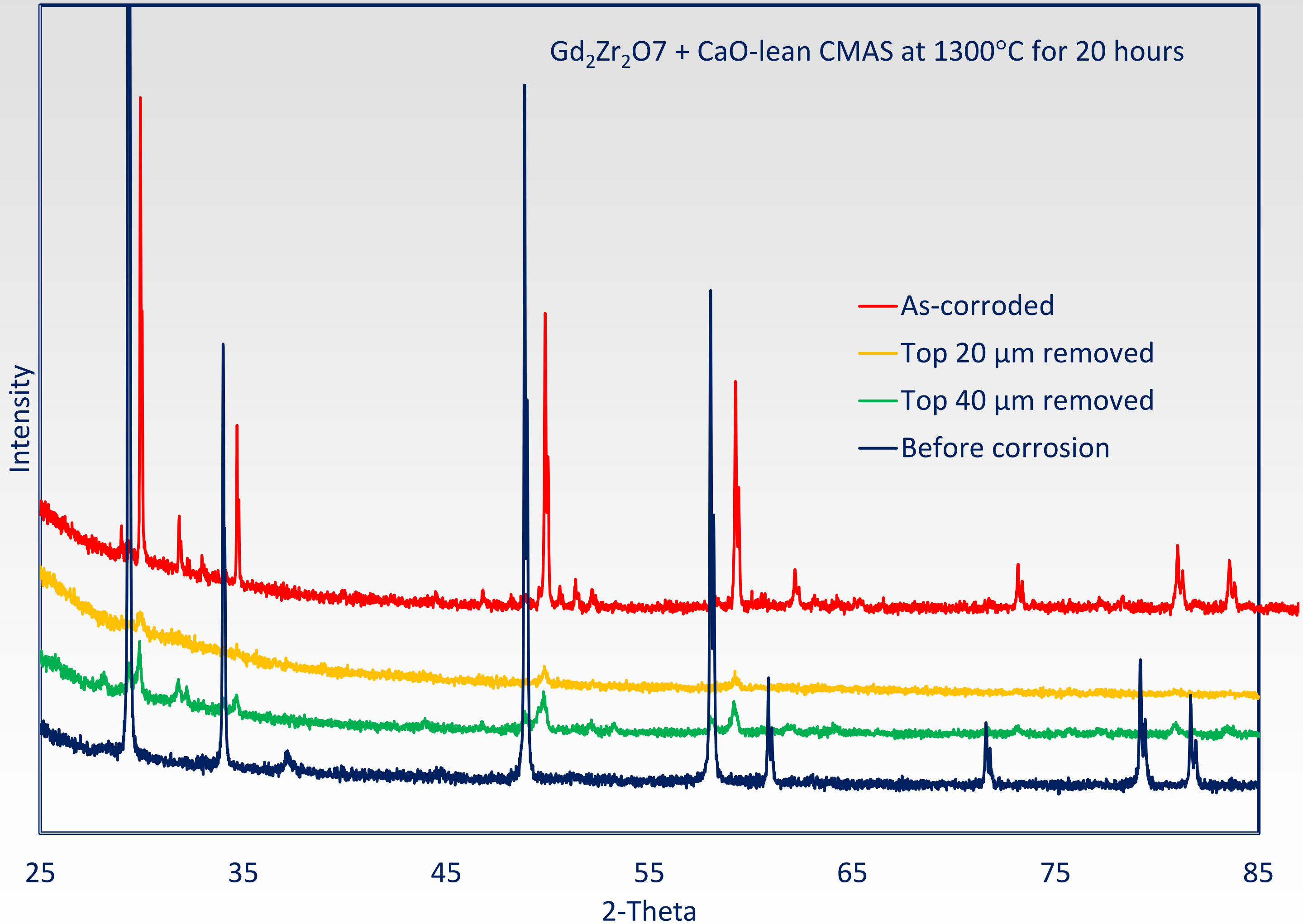
$Gd_2Zr_2O_7$ after CaO-lean CMAS at 1300°C for 20 hours – XRD



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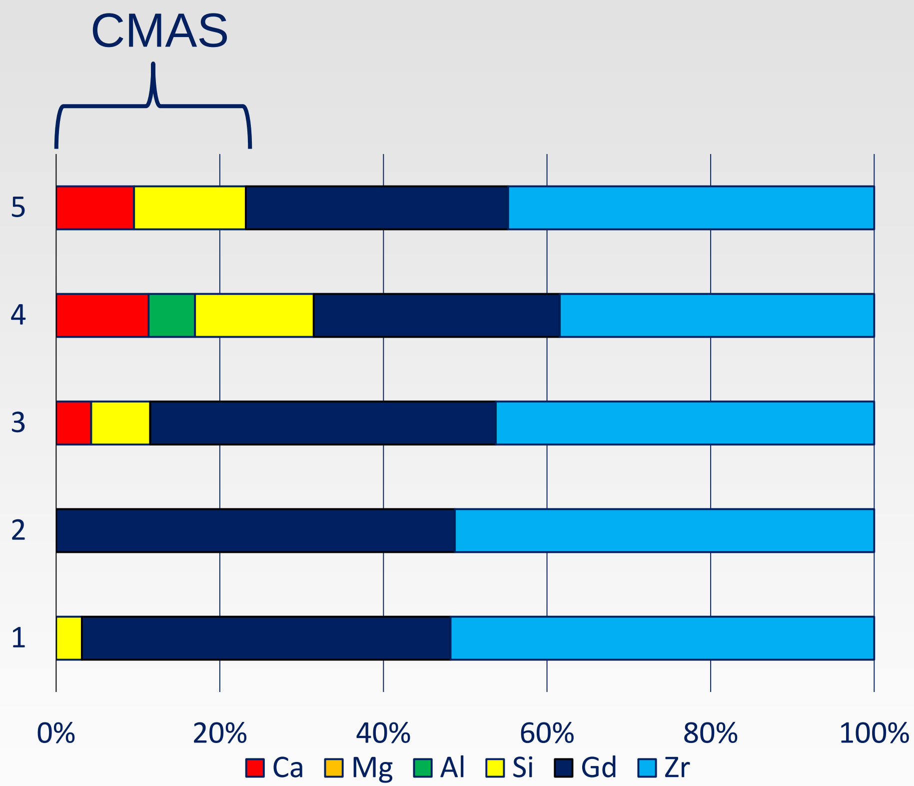
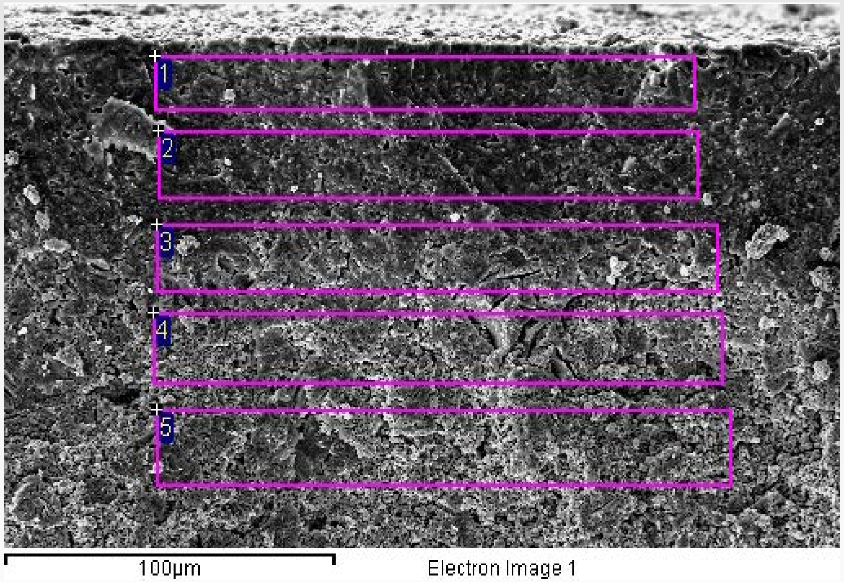
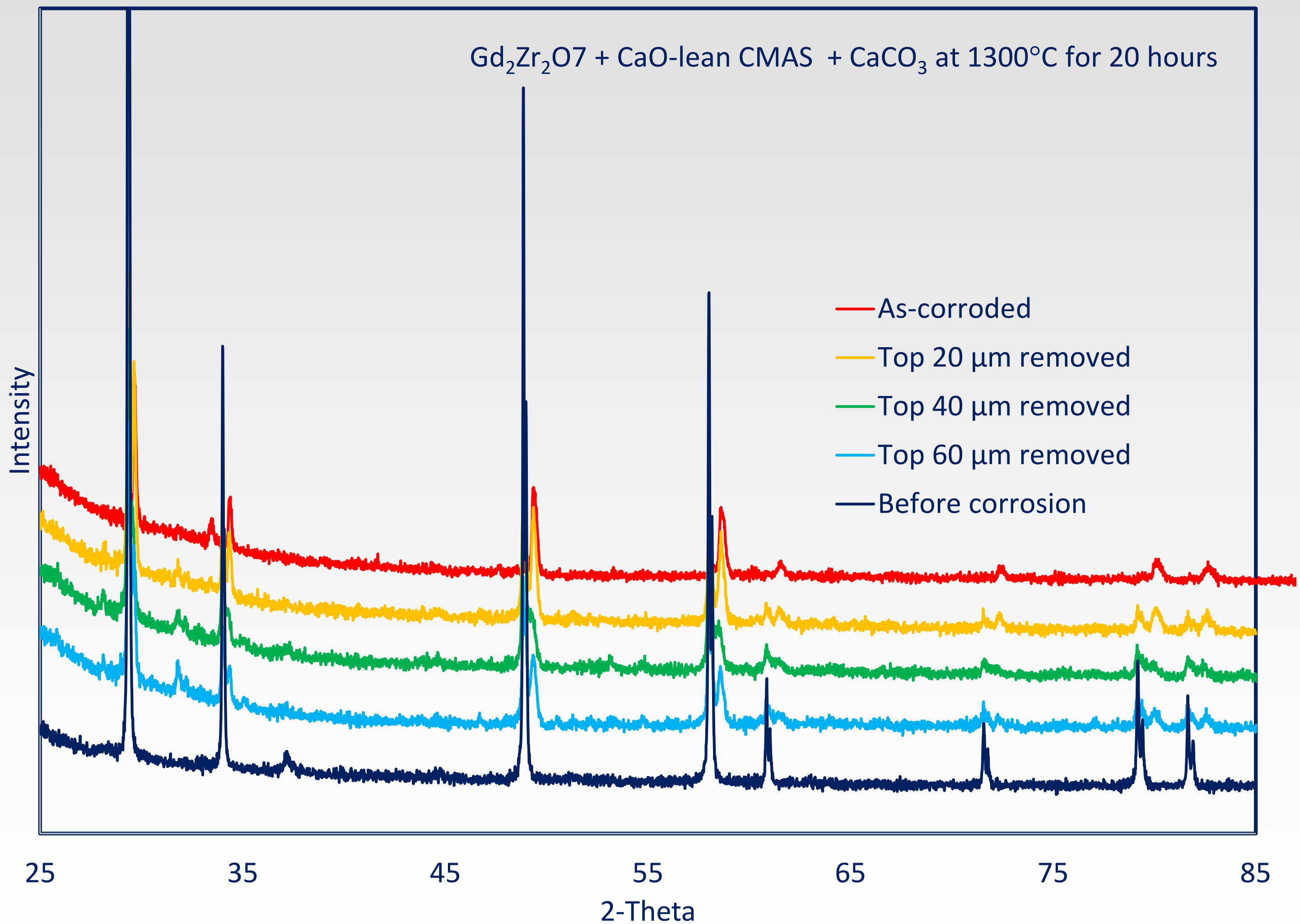
$Gd_2Zr_2O_7$ after CMAS / $CaCO_3$ at 1300°C for 20 hours – SEM / EDS





Elemental Distribution (mol%)

$Gd_2Zr_2O_7$ after CMAS / $CaCO_3$ at 1300°C for 20 hours – XRD



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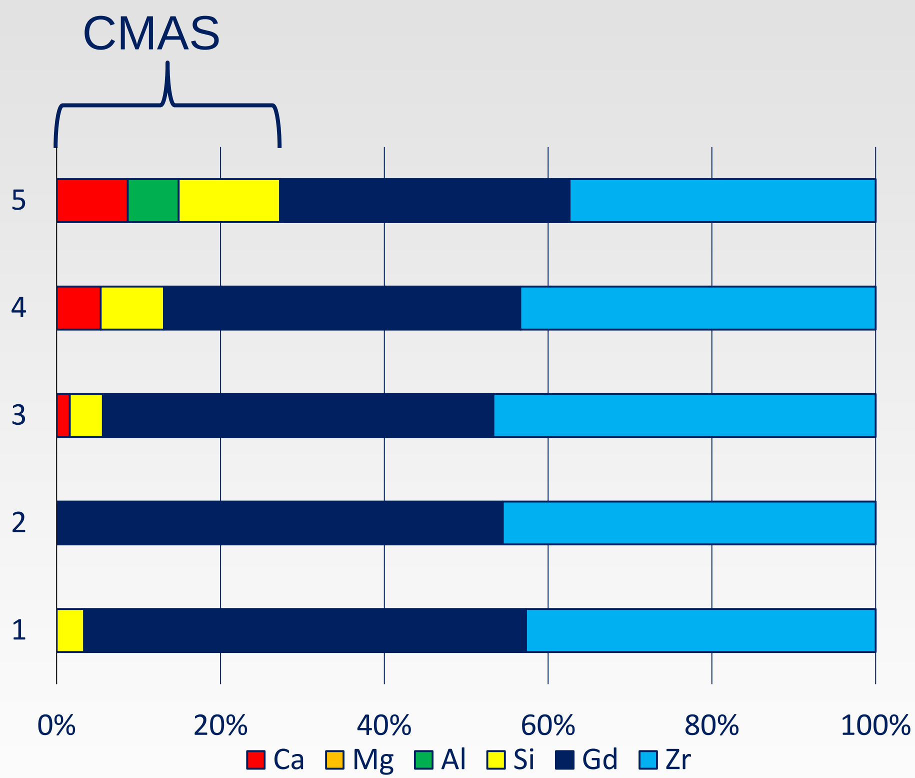
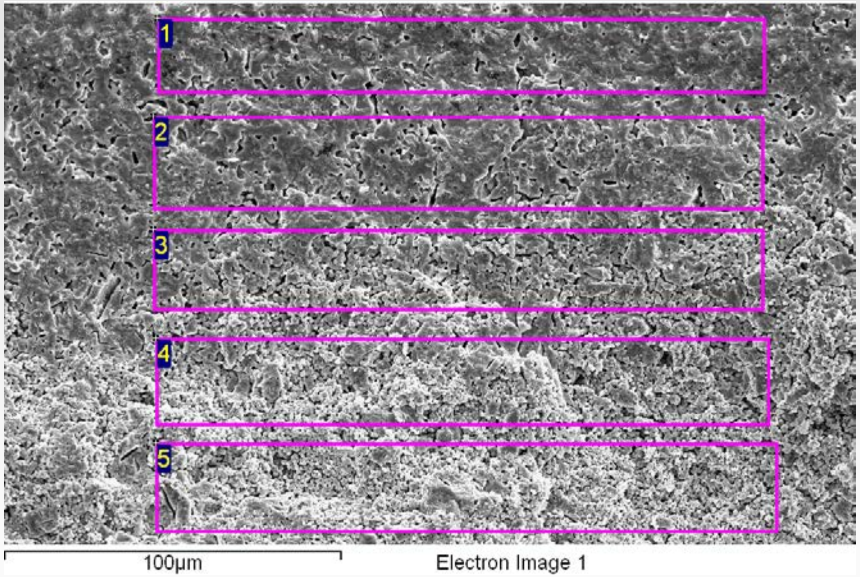
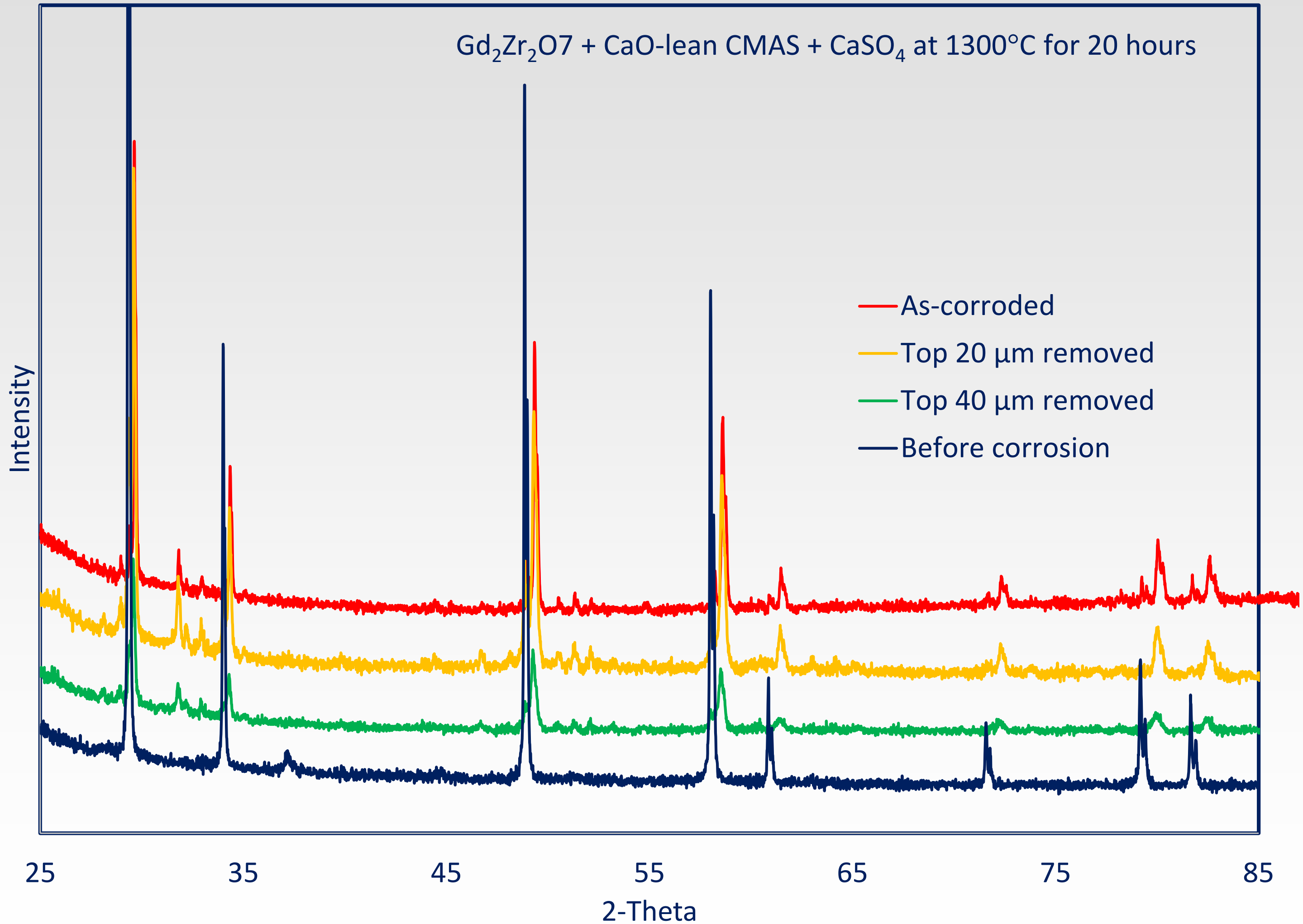
$Gd_2Zr_2O_7$ after CMAS / $CaSO_4$ at 1300°C for 20 hours – SEM / EDS





Elemental Distribution (mol%)

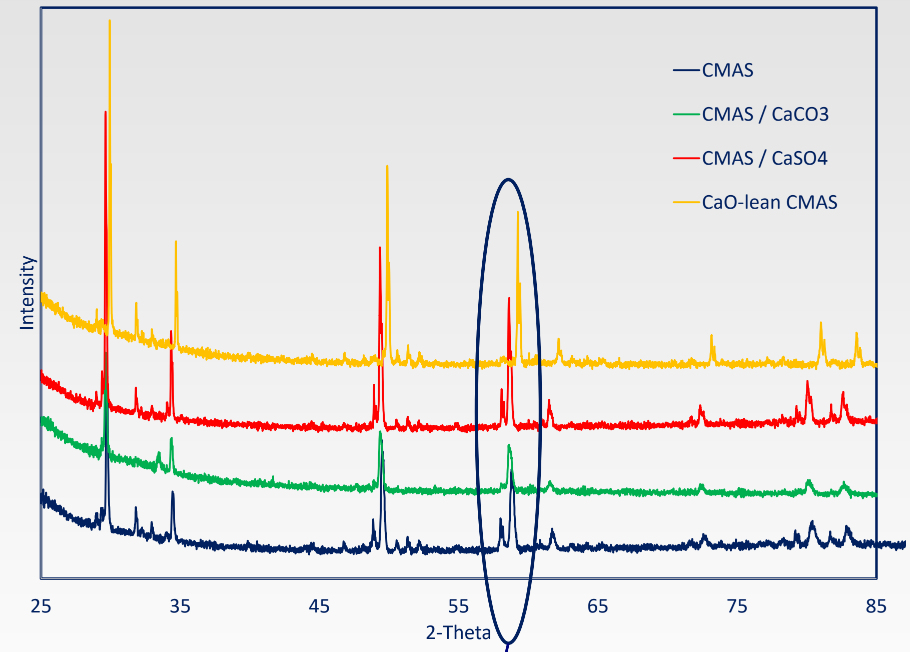
$Gd_2Zr_2O_7$ after CMAS / $CaSO_4$ at 1300°C for 20 hours – XRD

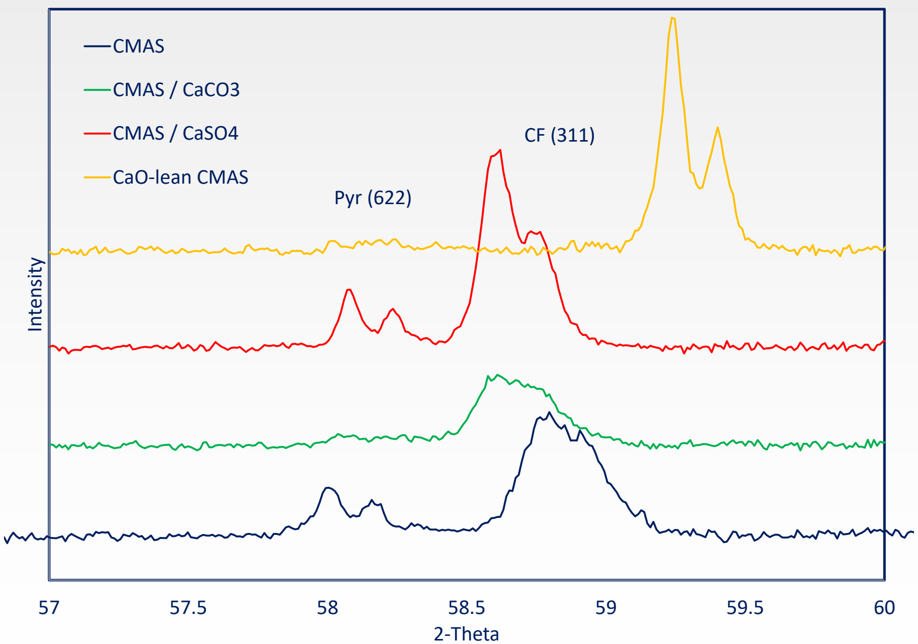


Effect of CMAS composition

CaO-lean reaction product

- Thickest reaction layer
  $(311)_{CF}$ / $(622)_{Pyr}$
- Lowest Gd – largest
  $(311)_{CF}$





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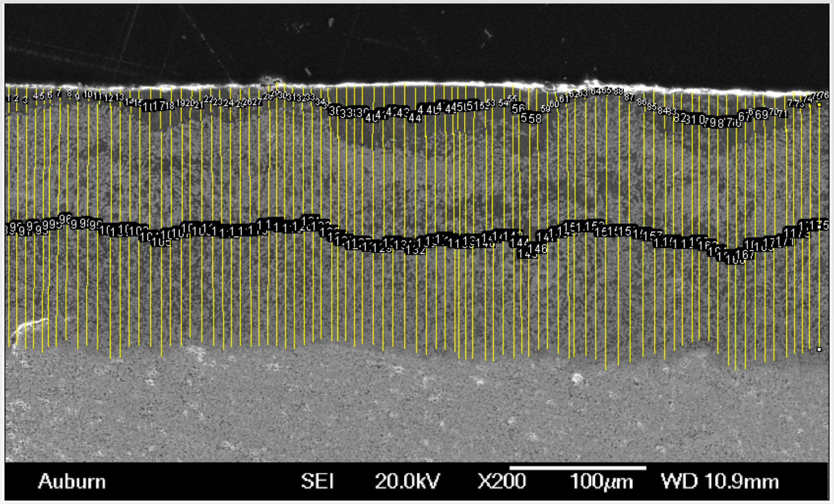
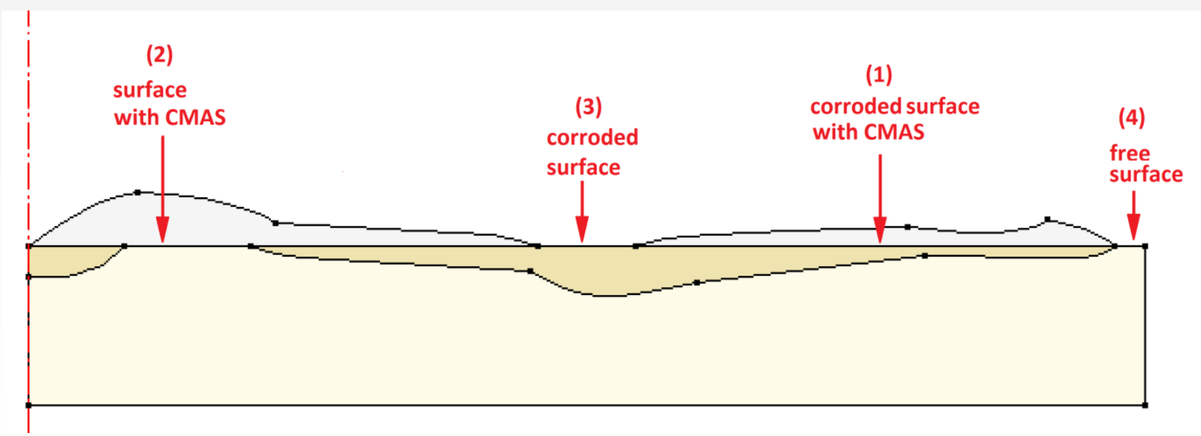
Stress / Temperature Modeling



Uneven CMAS loading can lead to different reaction geometries



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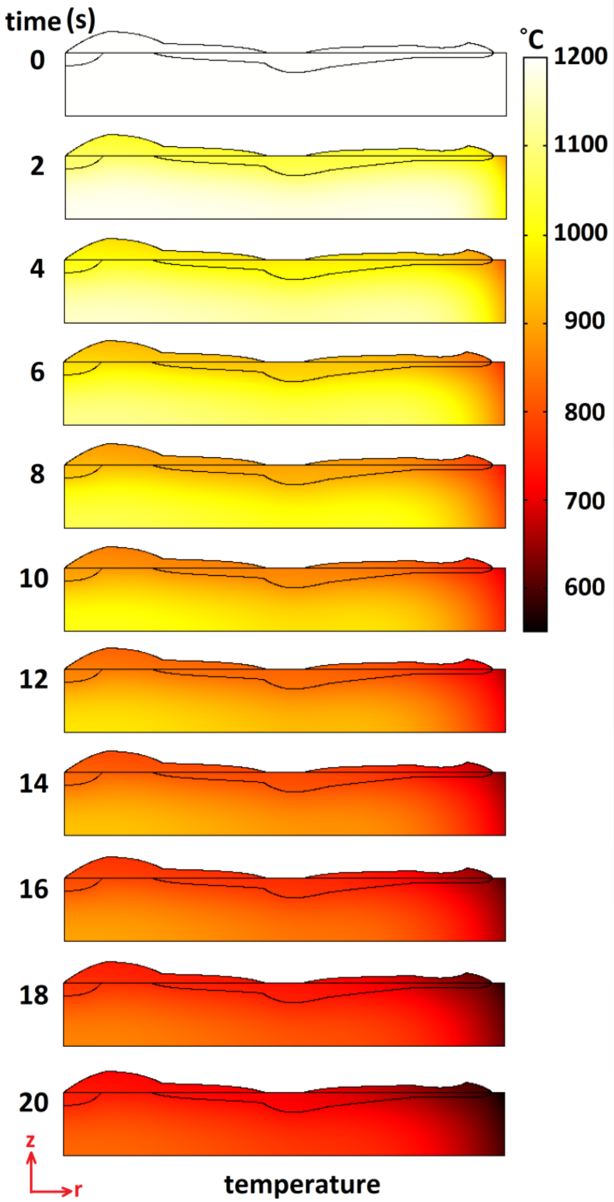
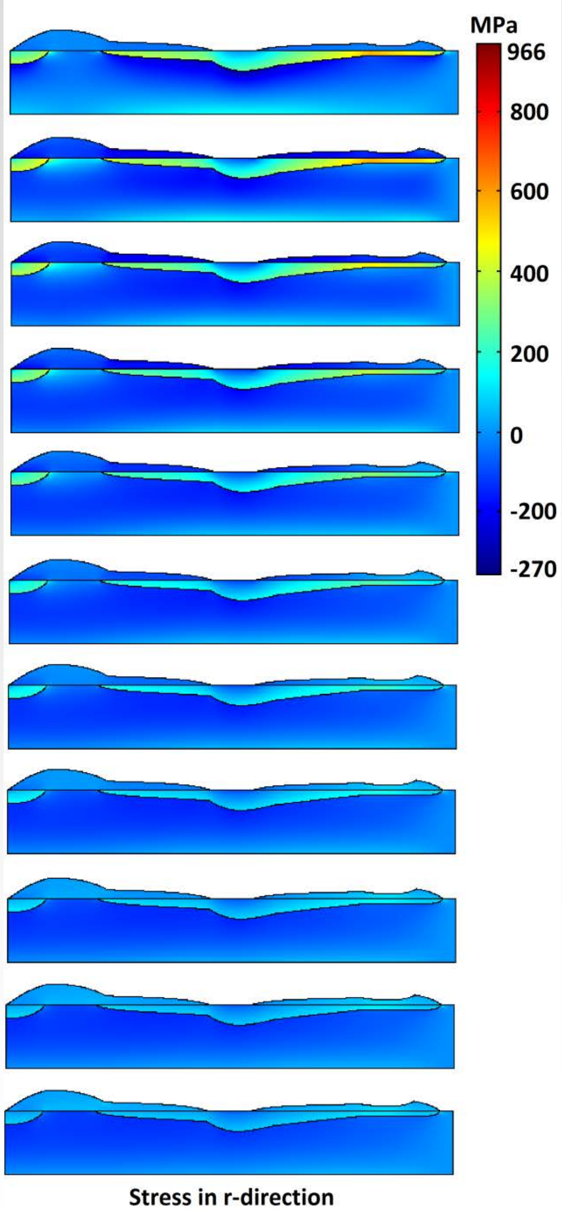
Stress and Temperature Distributions



temperature



Stress in r-direction

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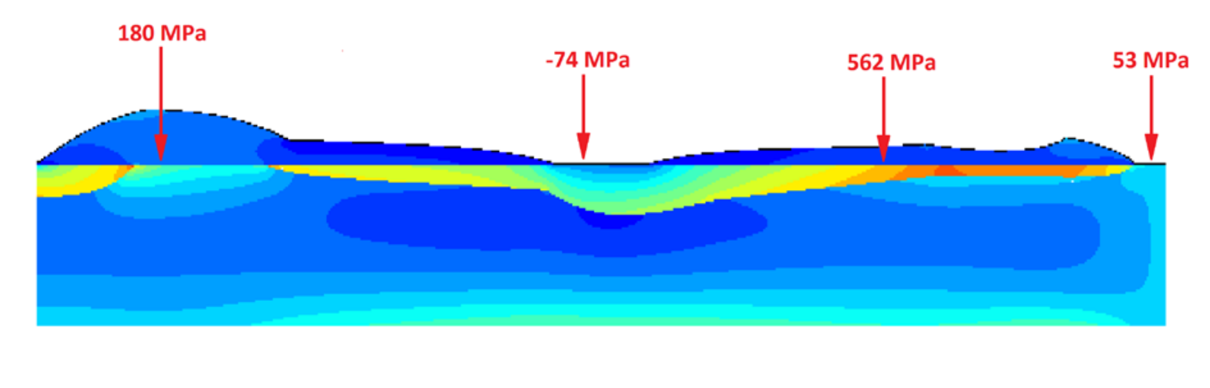
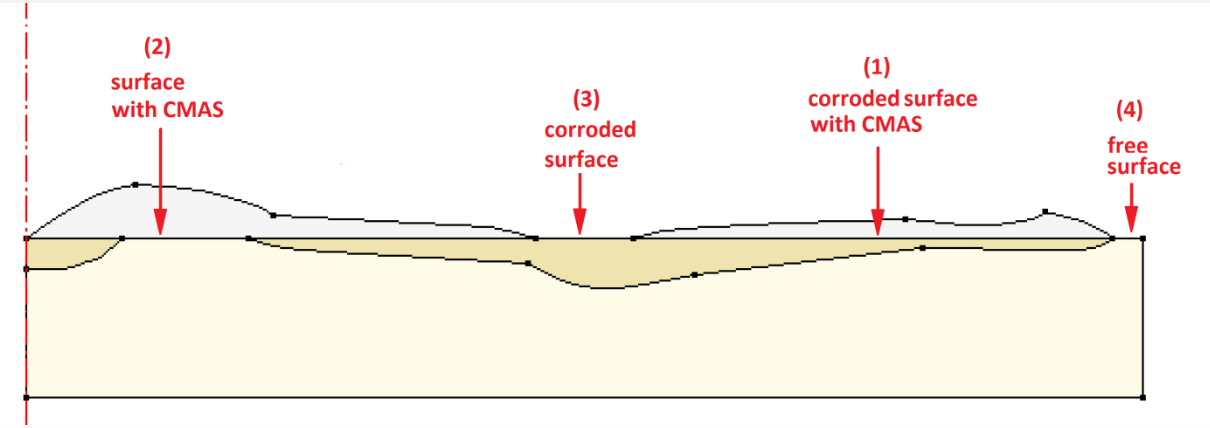
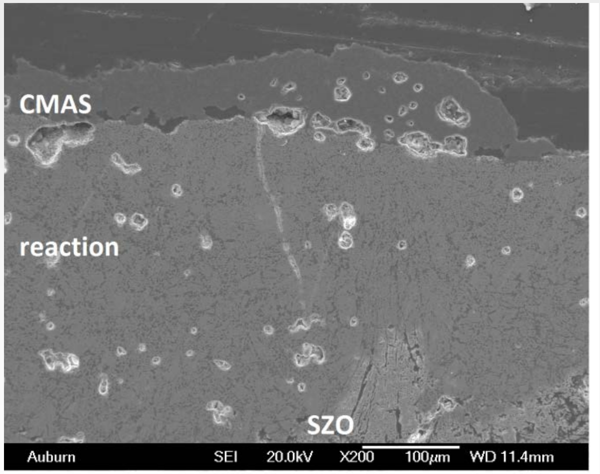
Stress Concentration



Highest stress at CMAS / reaction layer interface





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Conclusions

- Reaction product has higher thermal conductivity than lanthanide zirconate – higher conductivity material fills the pores
- Cubic fluorite and pyrochlore $Gd_2Zr_2O_7$ react similarly with CMAS
- More reaction with CaO-deficient CMAS

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