Refractory Metal Bond Coats and Pyrochlore Environmental Barrier Coating Materials

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Jeffrey W. Fergus

2014 University Turbine Systems
Research Workshop
West Lafayette, IN
22 October 2014

Participants

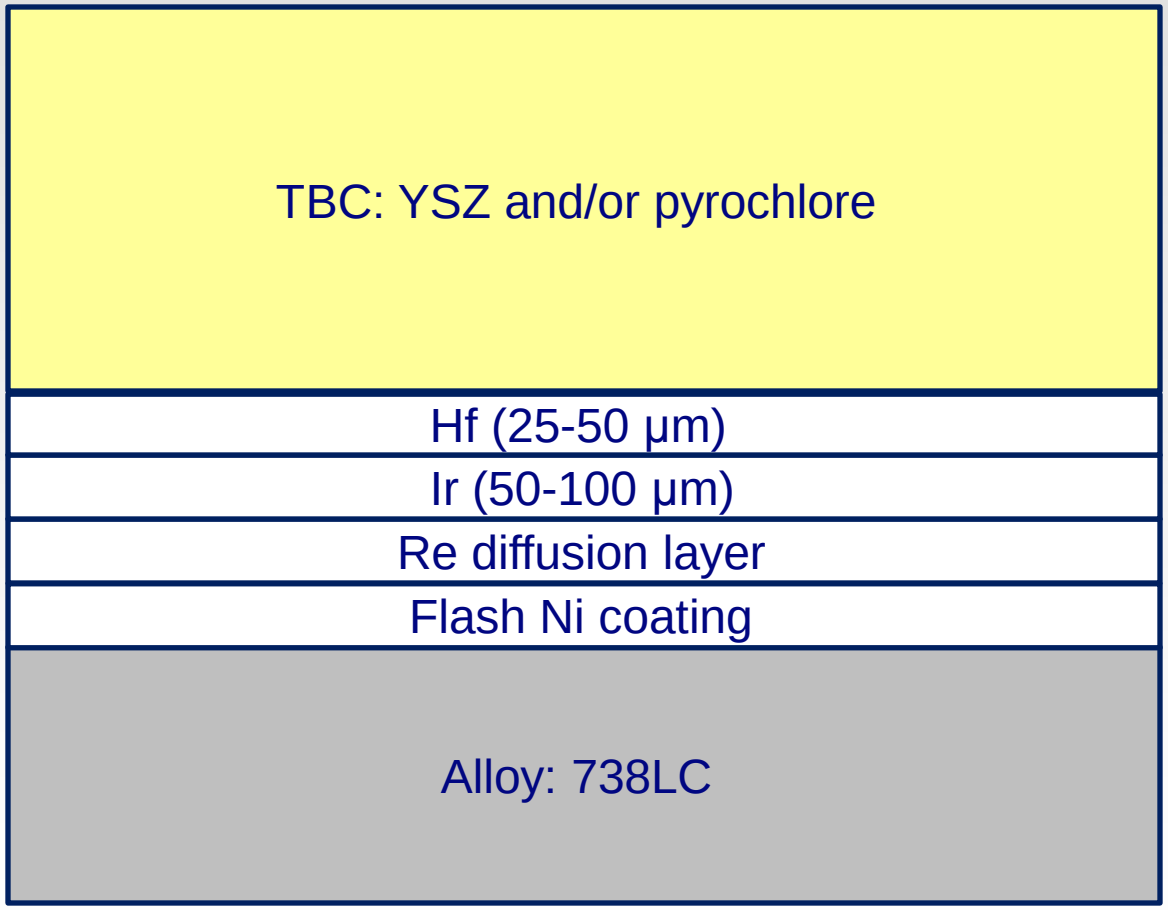
- Auburn University
  - Jeff Fergus
  - Honglong (Henry) Wang – Ph.D. Student
  - Xingxing Wang – Ph.D. Student
  - Emily Tarwater – Undergraduate Student
  - Sudip Dasgupta – Visiting Scholar (Summer 2014)
- Plasma Processes LLC
  - Kyle Murphree
  - Tim McKechnie

University Coal Research (UCR) project

- Collaboration with Plasma Processes LLC
- Alternative bond coat layers
- YSZ / pyrochlore zirconate coatings
- “God made the bulk; the surface was invented by the devil”
  - Wolfgang Pauli

http://www.plasmapros.com/

Thermal barrier coating system



Plasma spray for YSZ / pyrochlore

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

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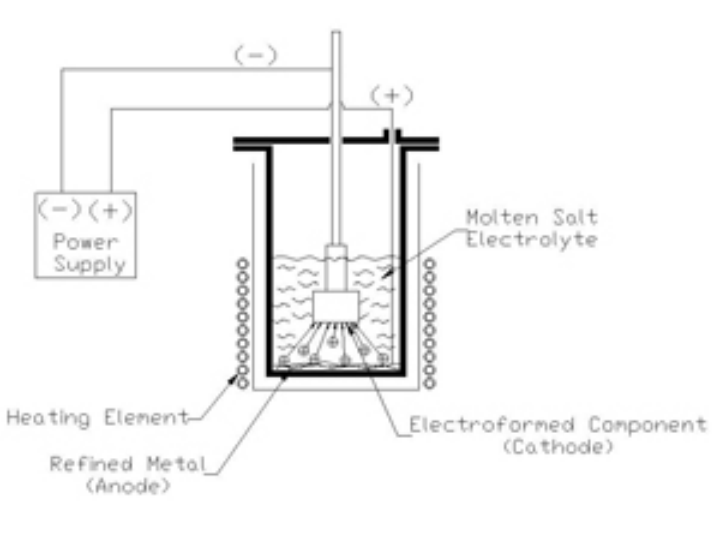
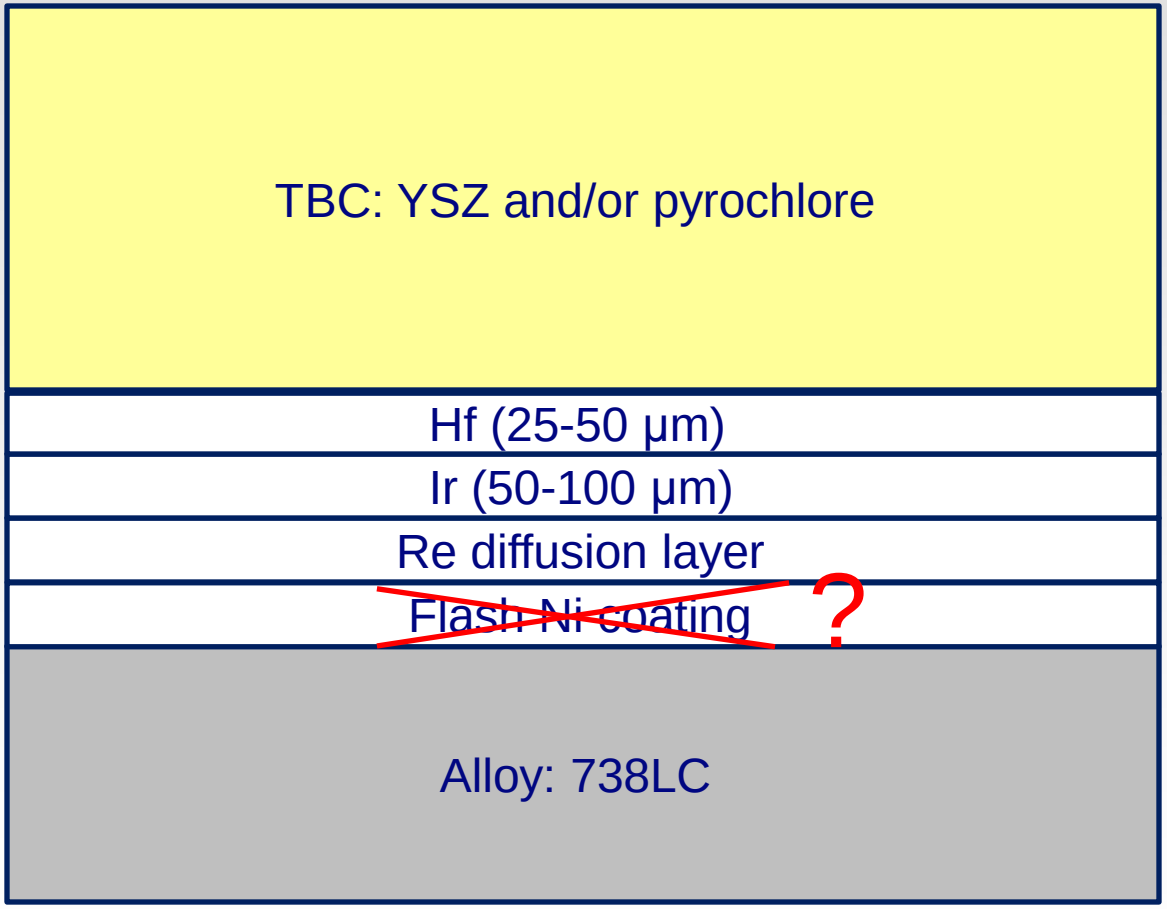
Approach

- 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 / doped
  - Accelerate with high temperature exposures



Need for nickel layer



Evaluate possible elimination of Ni coating

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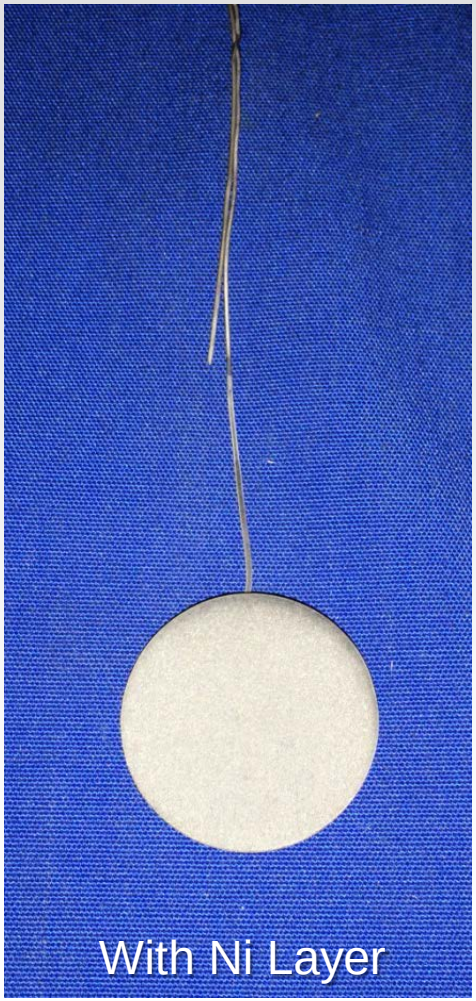
Rhenium coating with/without nickel



Nickel coating needed

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Pyrochlore coating materials

- Thermal Conductivity
- Reaction with CMAS

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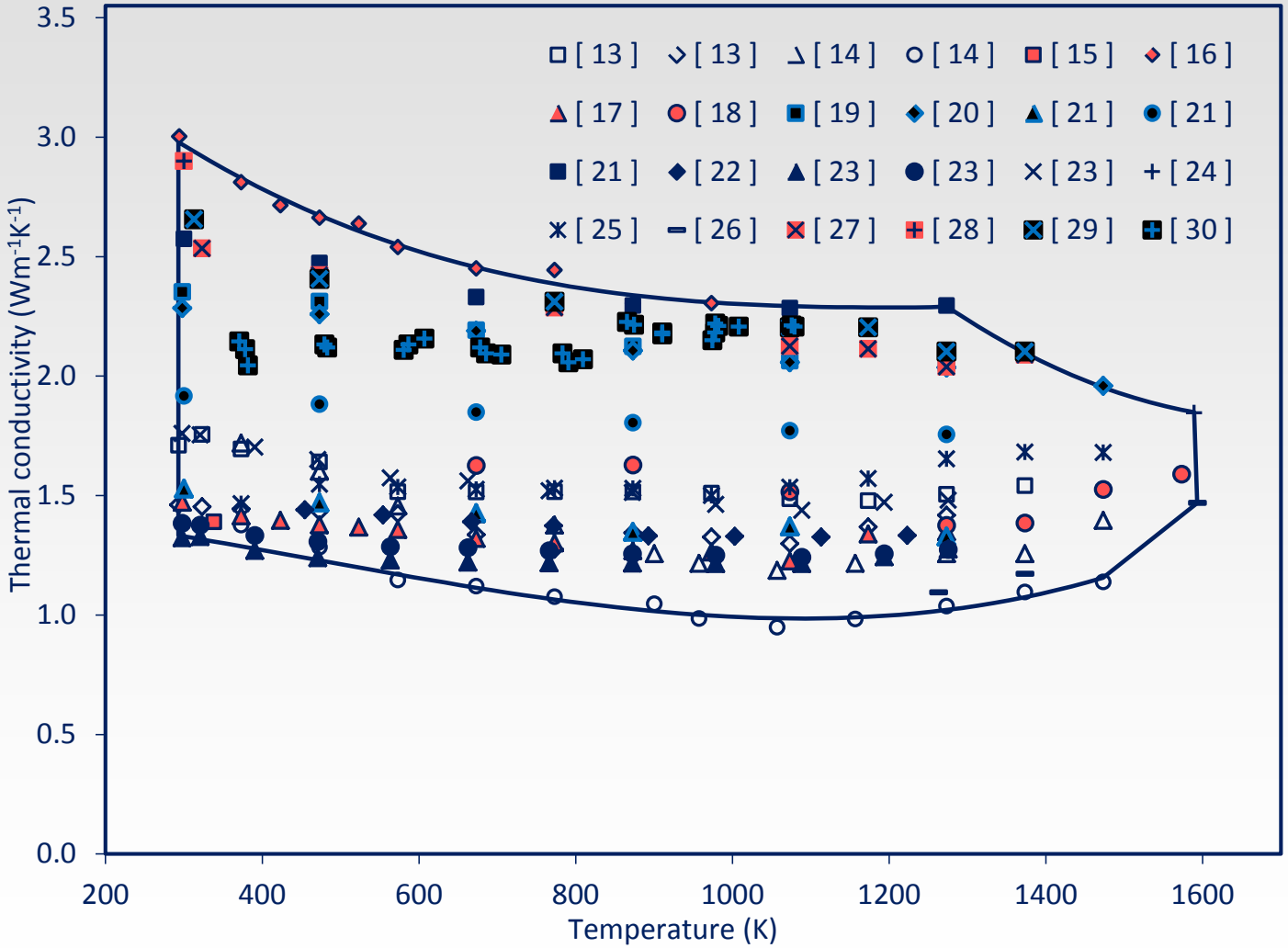
Thermal conductivity of zirconia with 7-8% yttria



Range of thermal conductivities due to variations in morphology and microstructure

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

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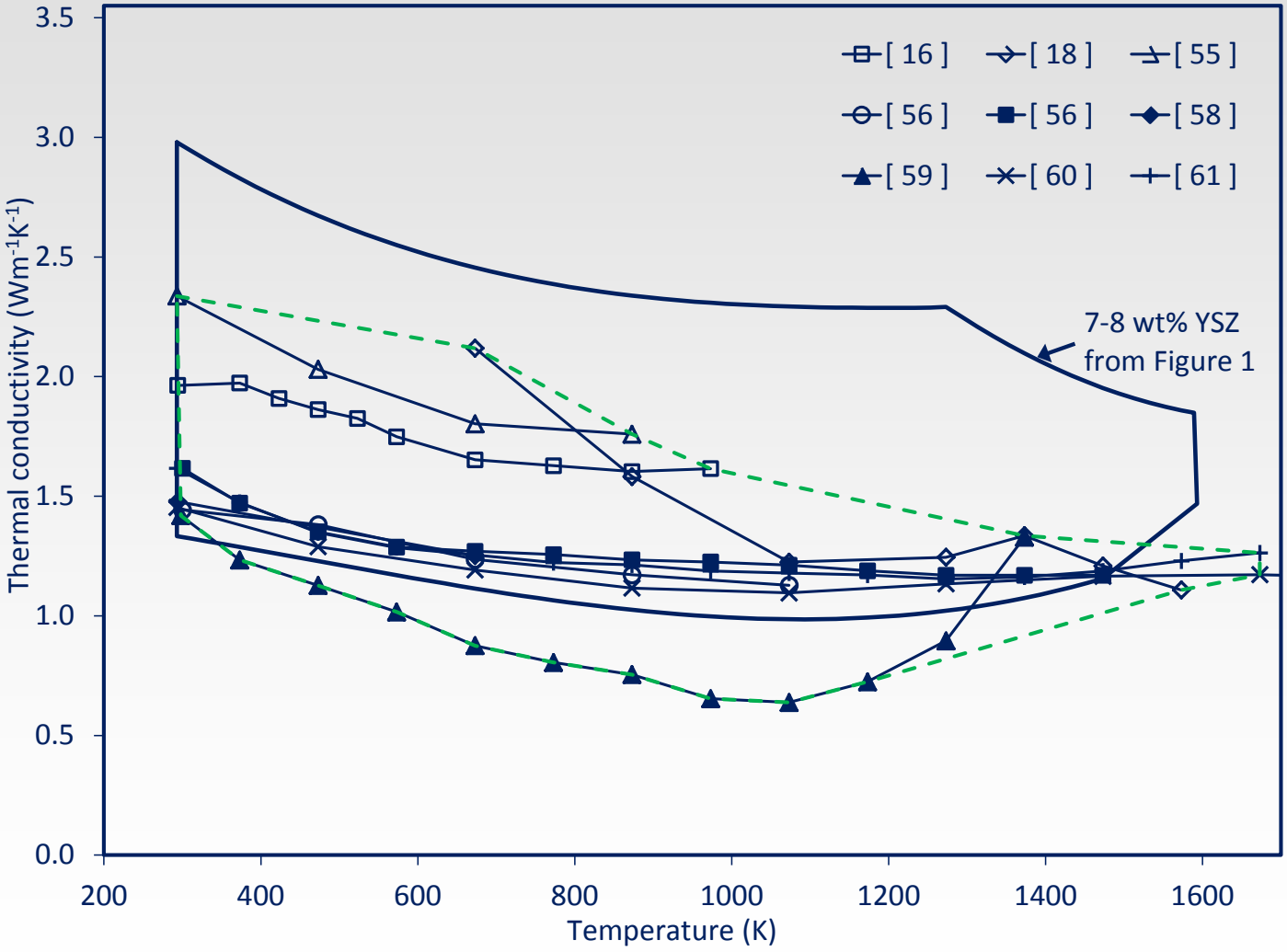
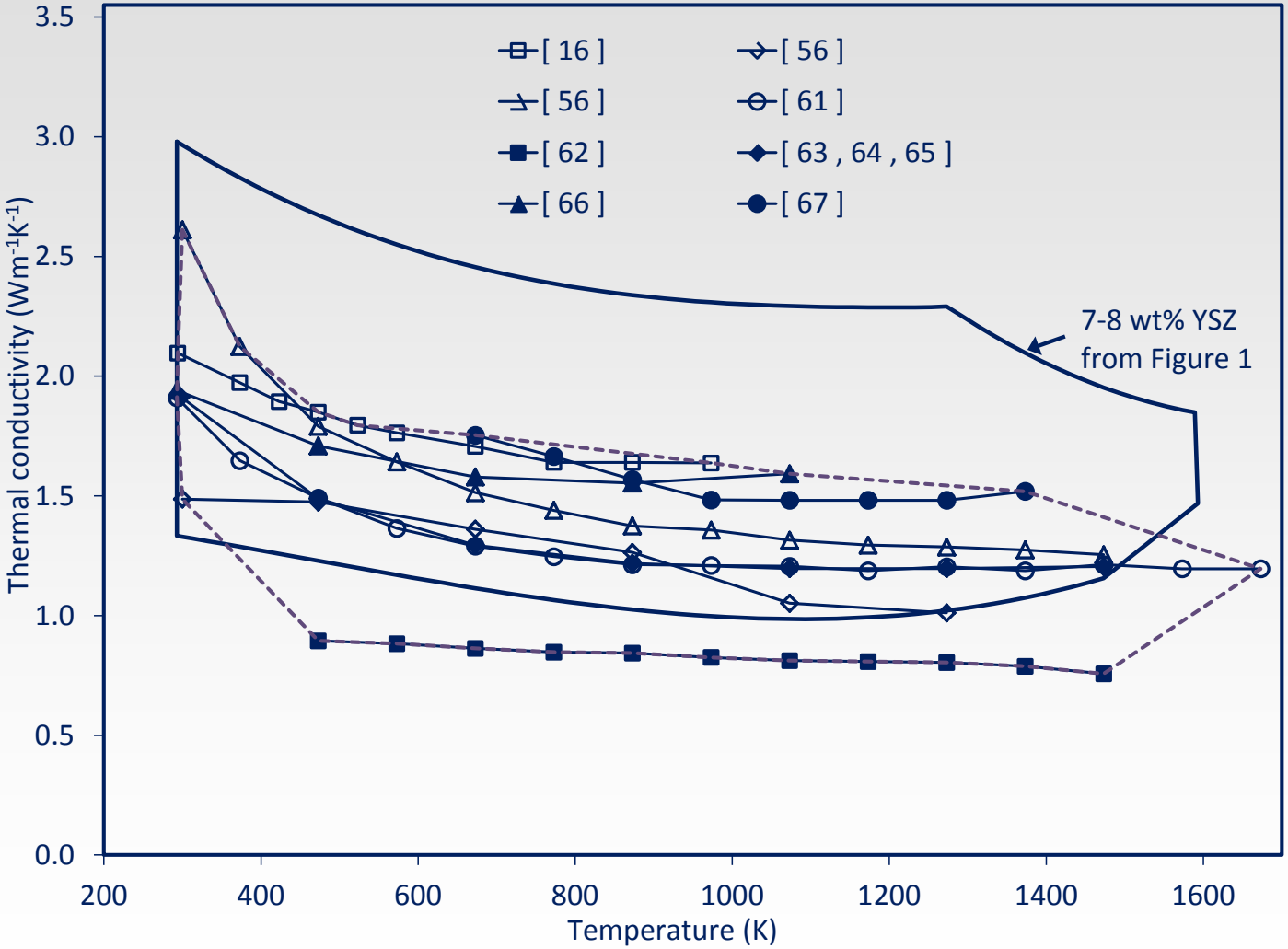
Thermal conductivity of $Gd_2Zr_2O_7$



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).

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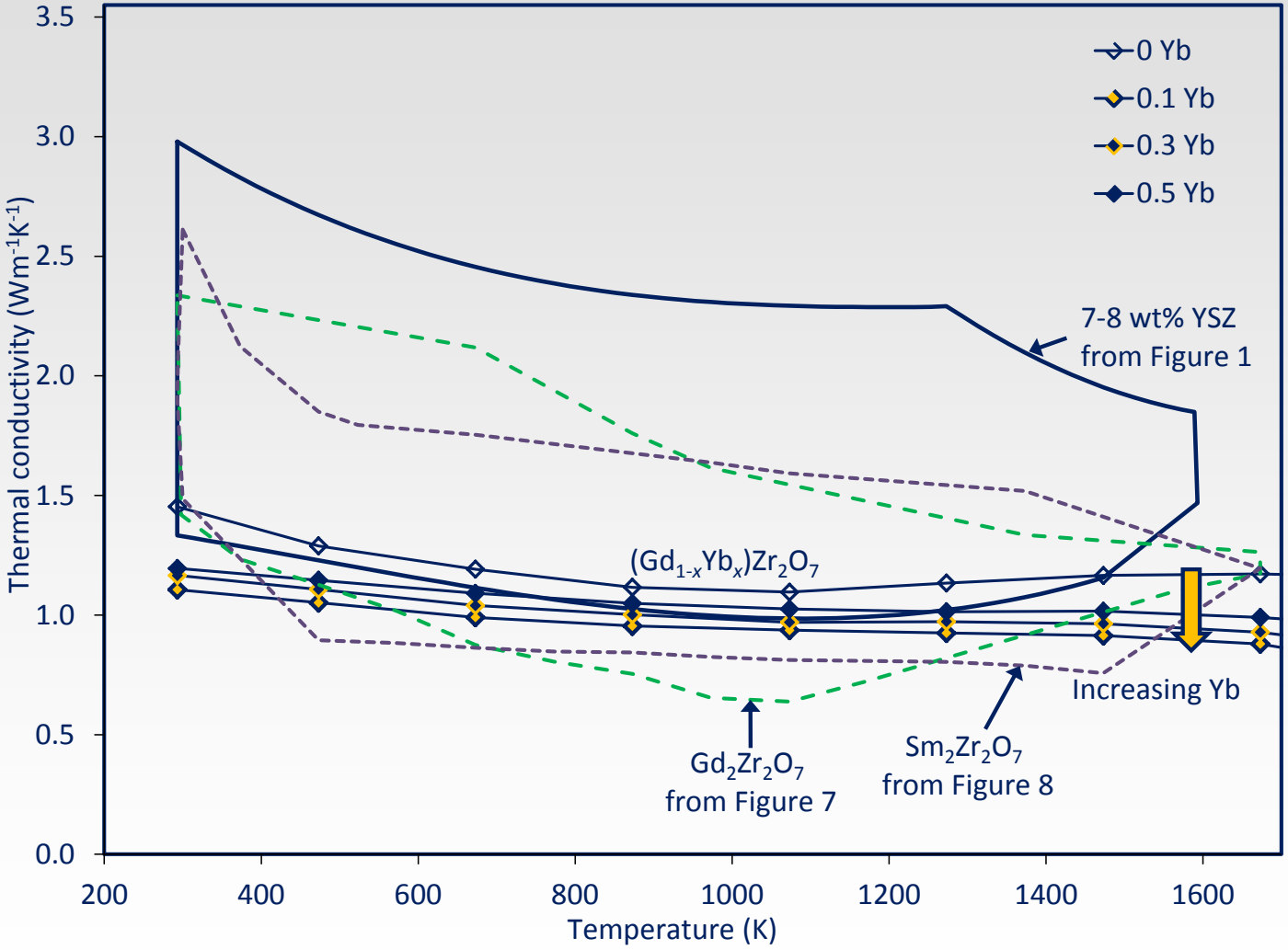
Ytterbium-doping



Doping can reduce κ

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

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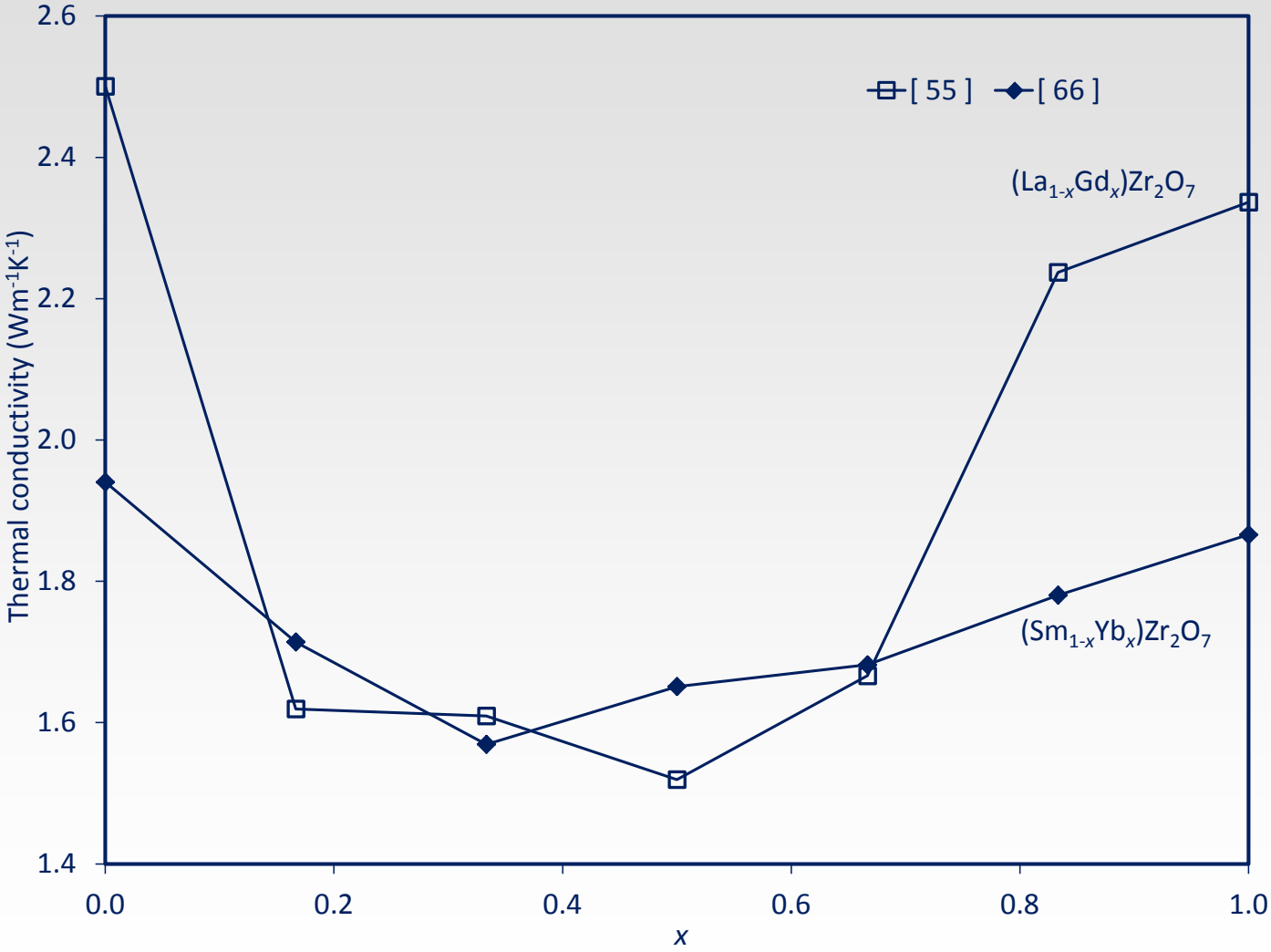
Thermal conductivity of mixed pyrochlores



Pyrochlore solid solutions have lower κ

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

Pyrochlore coating materials

- Synthesis of pyrochlore
  - Solid oxide sintering
  - Co-precipitation
- CMAS exposure
  - Melt / solidify Ca-Mg-Al-Si oxide mixtures
  - Crush glass, apply to pyrochlore pellet
  - Expose to 1300-1400°C
- Characterization
  - XRD, SEM

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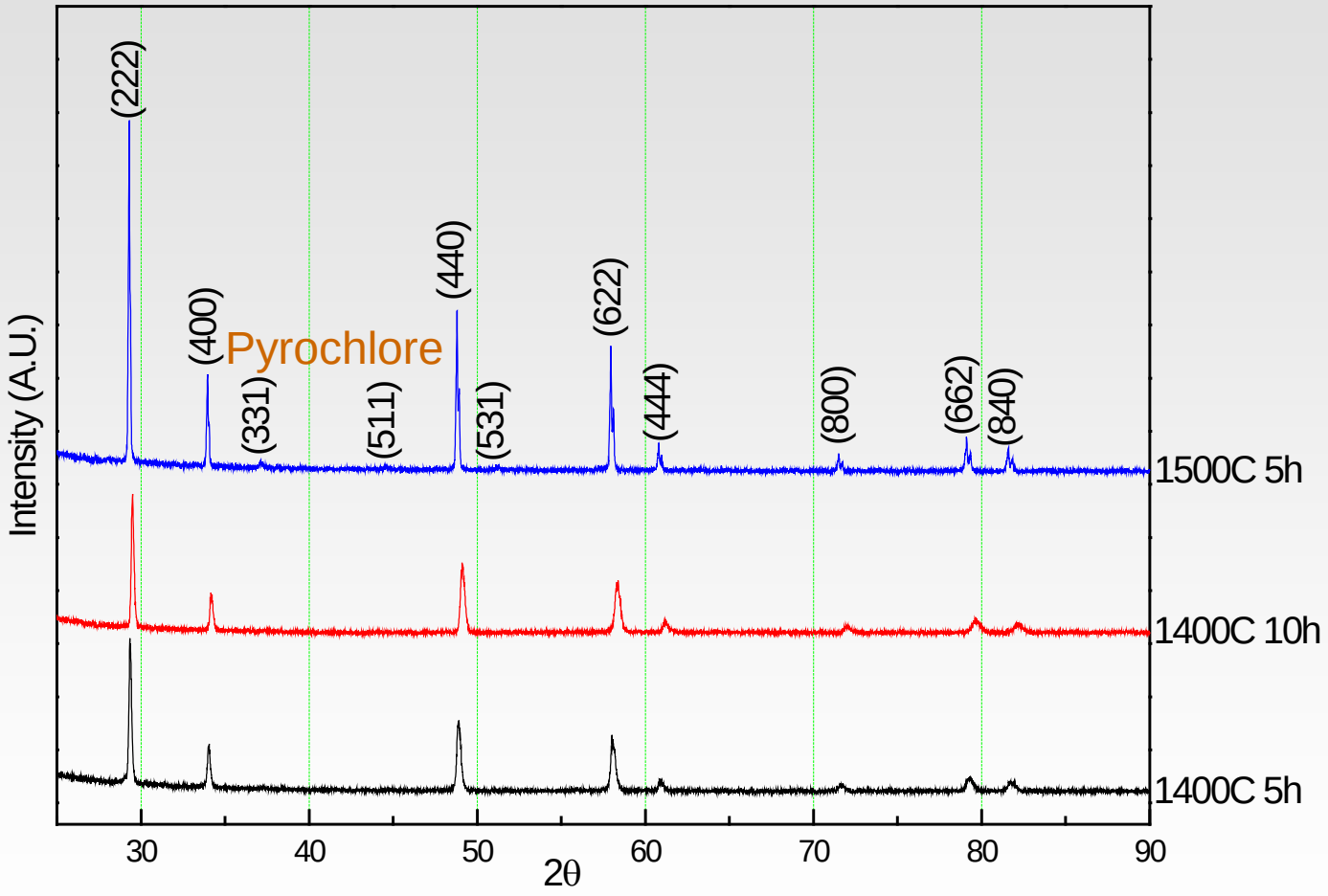
Phase content of $Gd_2Zr_2O_7$ – Co-precipitation



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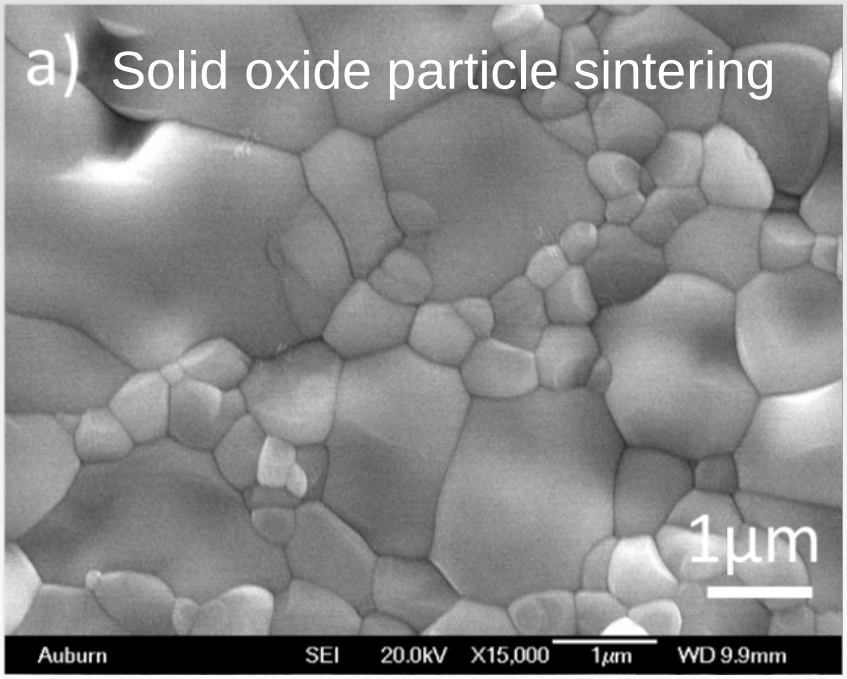
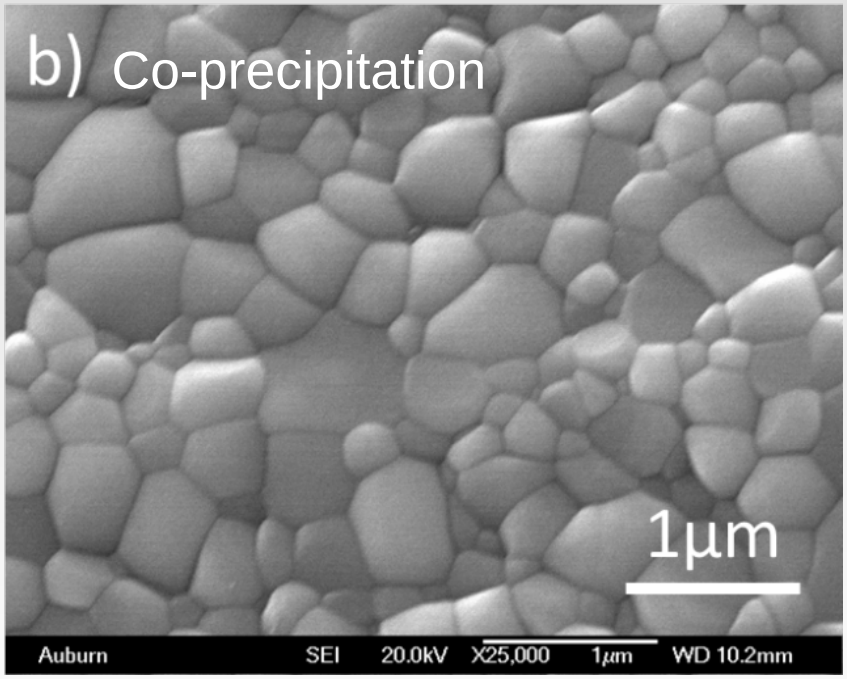
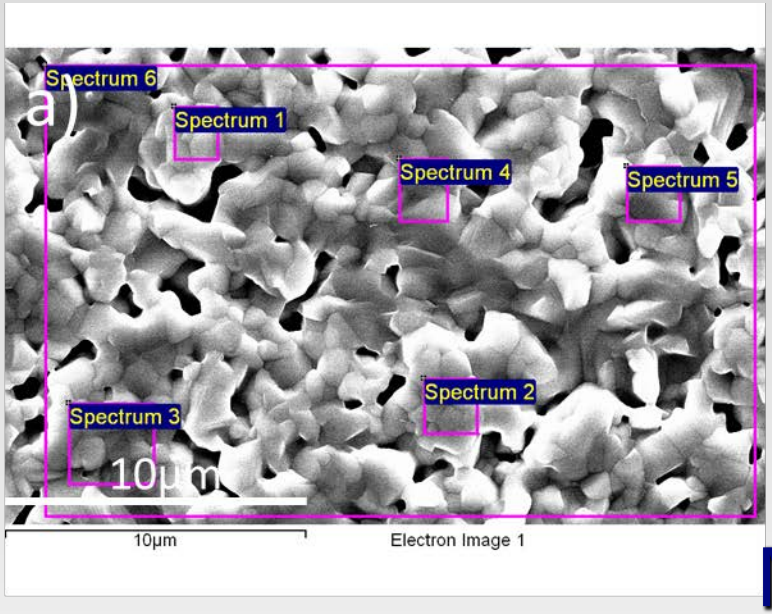
Microstructure of $Gd_2Zr_2O_7$



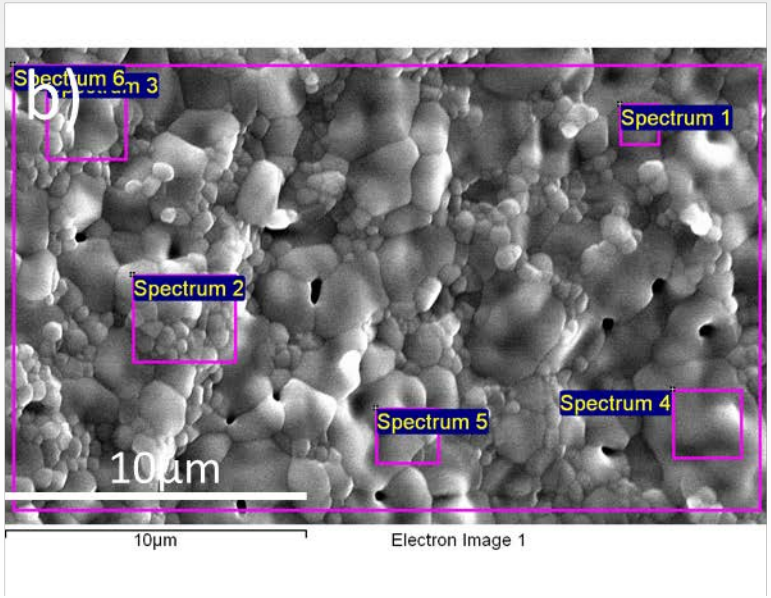




Atomic Percentage for a)

	O	Zr	Gd	Au
Spectrum 1	48		39	14
Spectrum 2	55		34	11
Spectrum 3	54		34	12
Spectrum 4	48	9	32	11
Spectrum 5	52		36	12
Spectrum 6	50	7	33	10

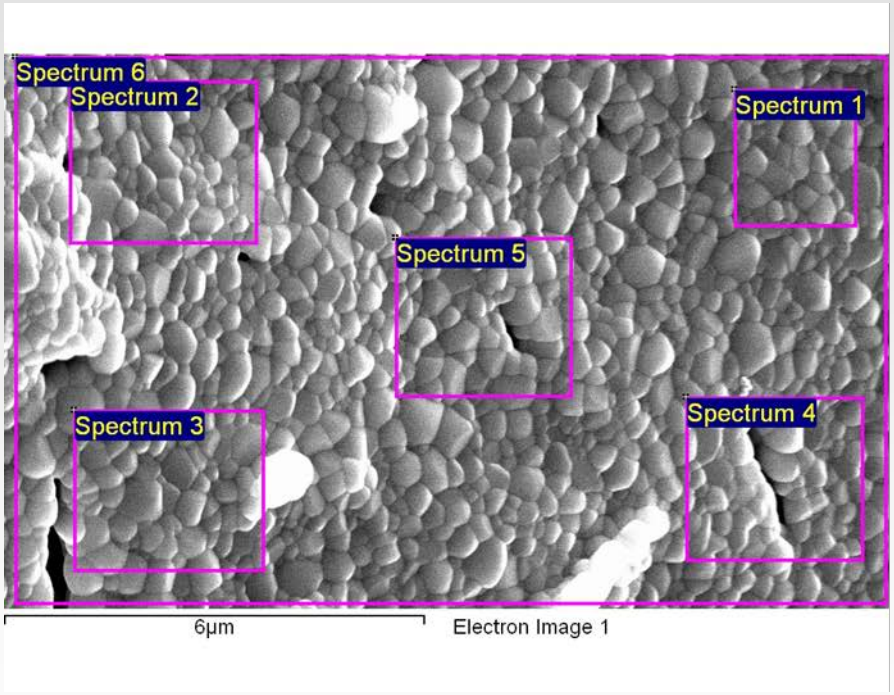
Microstructure – Solid oxide particle sintering



Atomic Percentage for b)

	O	Zr	Gd	Au
Spectrum 1	60	30	5	5
Spectrum 2	58	34	3	5
Spectrum 3	61	31	3	5
Spectrum 4	51	37	6	6
Spectrum 5	57	32	5	6
Spectrum 6	58	32	4	5

Microstructure – Co-precipitation



Atomic Percentage

	O	Zr	Gd	Au
Spectrum 1	58	20	17	5
Spectrum 2	57	20	17	5
Spectrum 3	59	20	16	6
Spectrum 4	59	20	16	5
Spectrum 5	59	19	16	6

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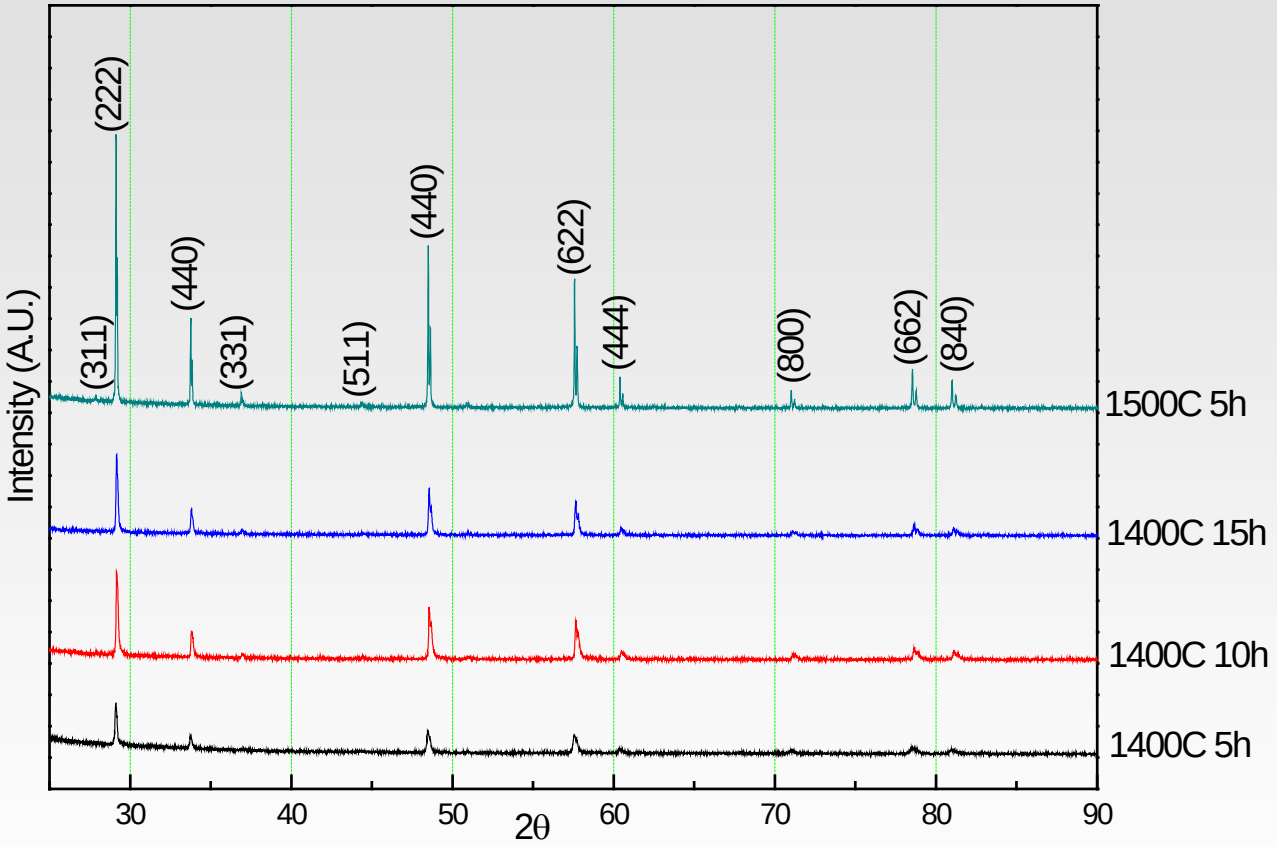
Phase content of $Sm_2Zr_2O_7$ – Co-precipitation



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Microstructure of $Sm_2Zr_2O_7$

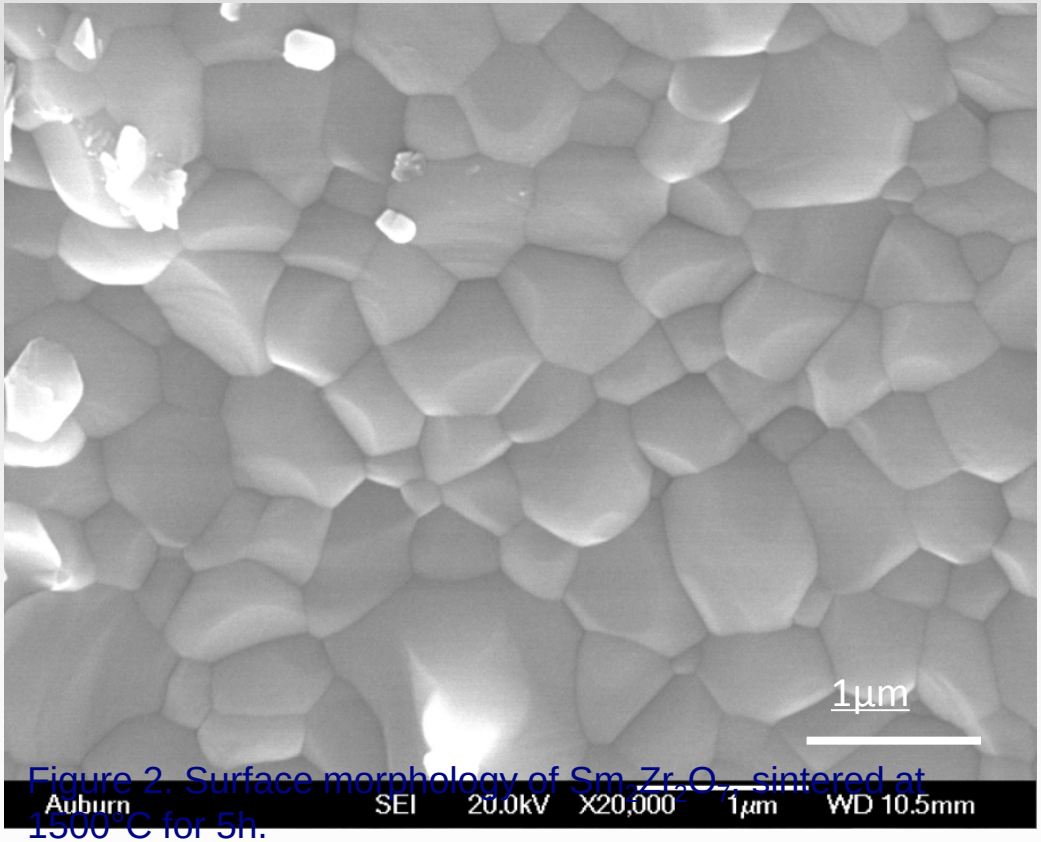
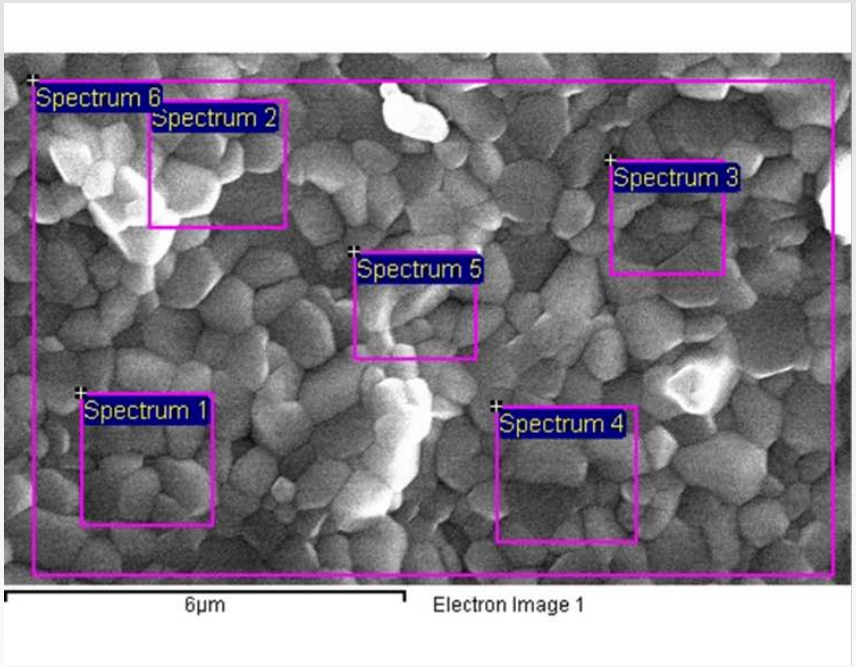


Figure 2. Surface morphology of $Sm_2Zr_2O_7$ sintered at 1500°C for 5h.

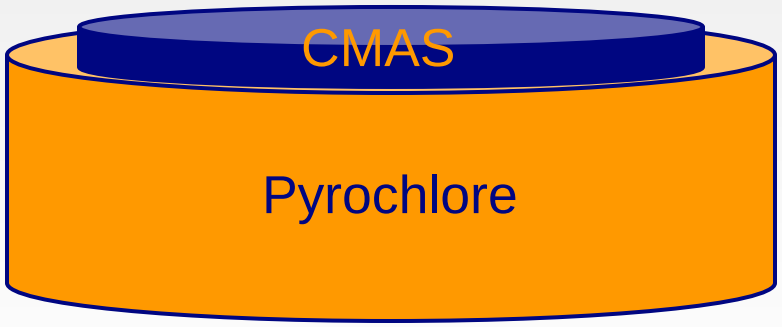
Microstructure of $Sm_2Zr_2O_7$



	O	Zr	Sm	Au
Spectrum 1	53	23	17	7
Spectrum 2	60	20	14	6
Spectrum 3	54	22	17	7
Spectrum 4	53	24	17	7
Spectrum 5	57	21	16	6
Spectrum 6	55	22	17	7

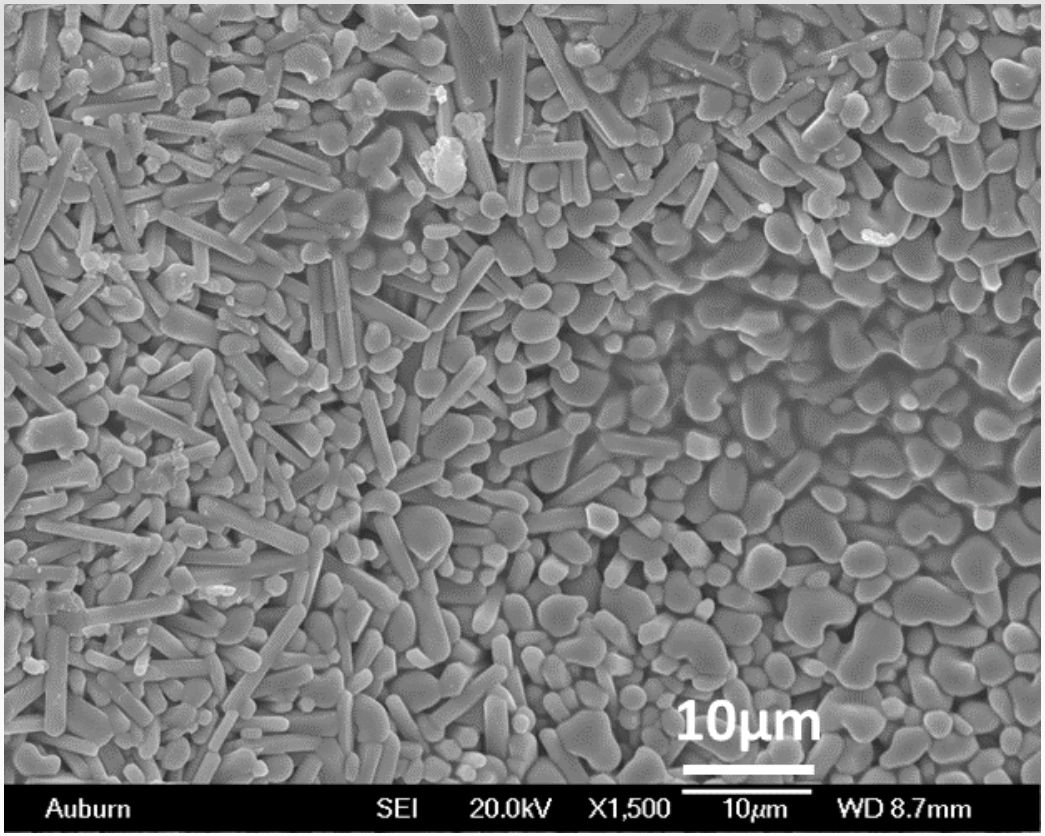
CMAS exposure

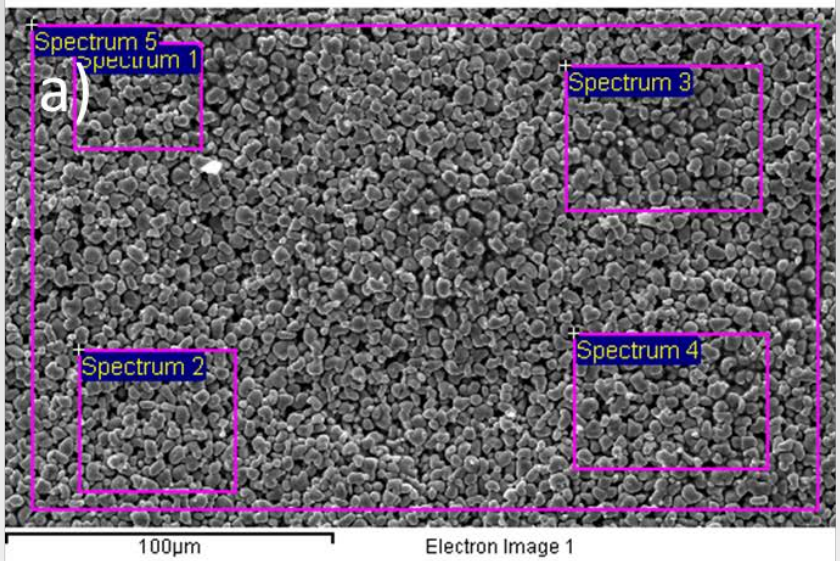
- Melt / solidify Ca-Mg-Al-Si oxide mixtures
- Crushed CMAS applied to pyrochlore pellet
- 1300-1400°C

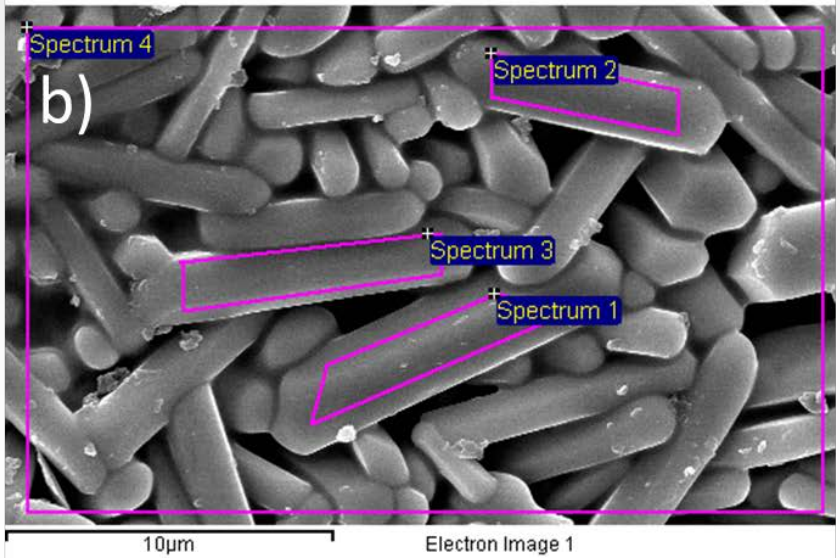


CMAS Composition	
Oxide	**Percentage**
CaO	33
MgO	9
$AlO_{1.5}$	13
SiO_2	45

$Gd_2Zr_2O_7$ 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

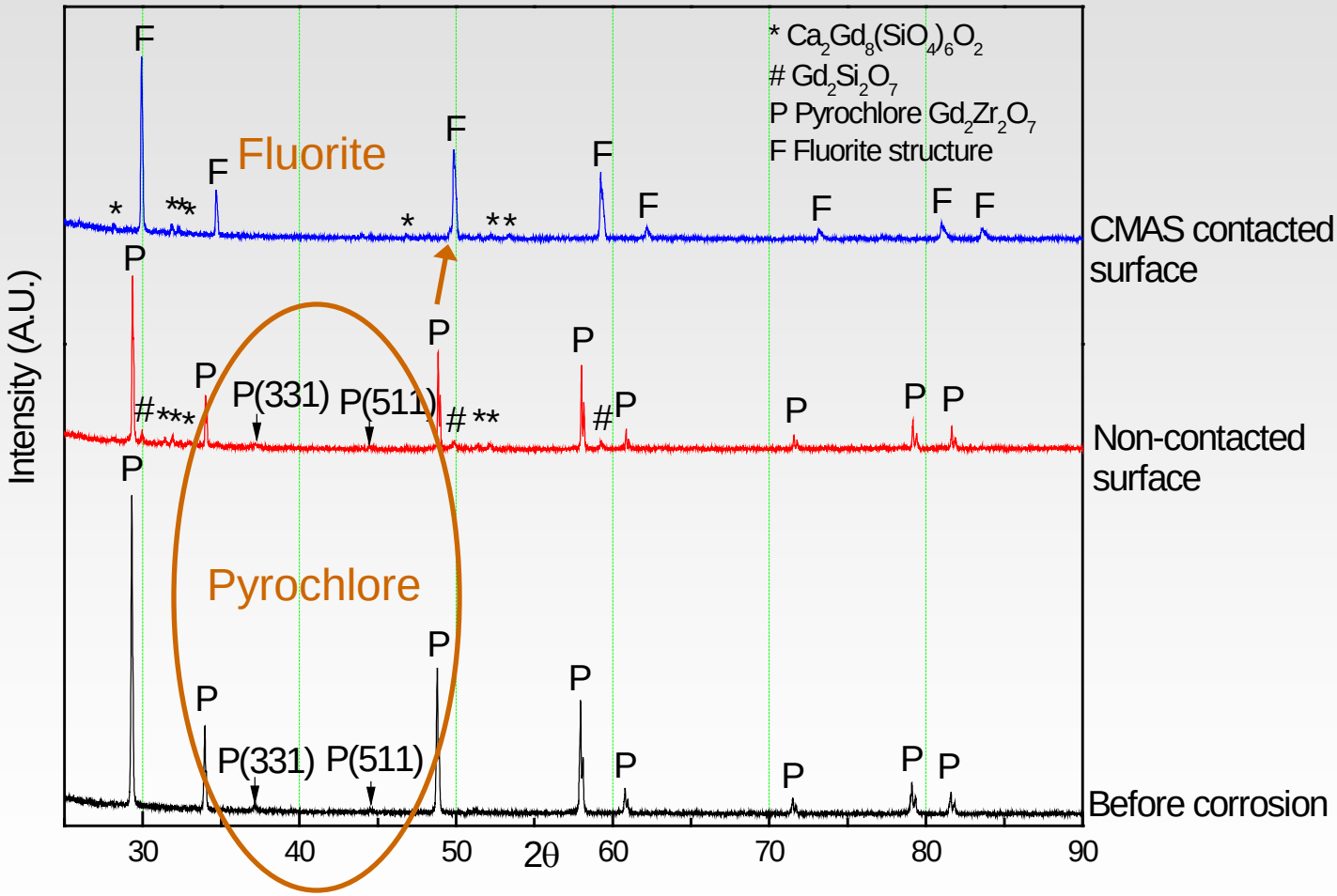
$Gd_2Zr_2O_7$ after CMAS at 1300°C for 5 hours

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 5 hours



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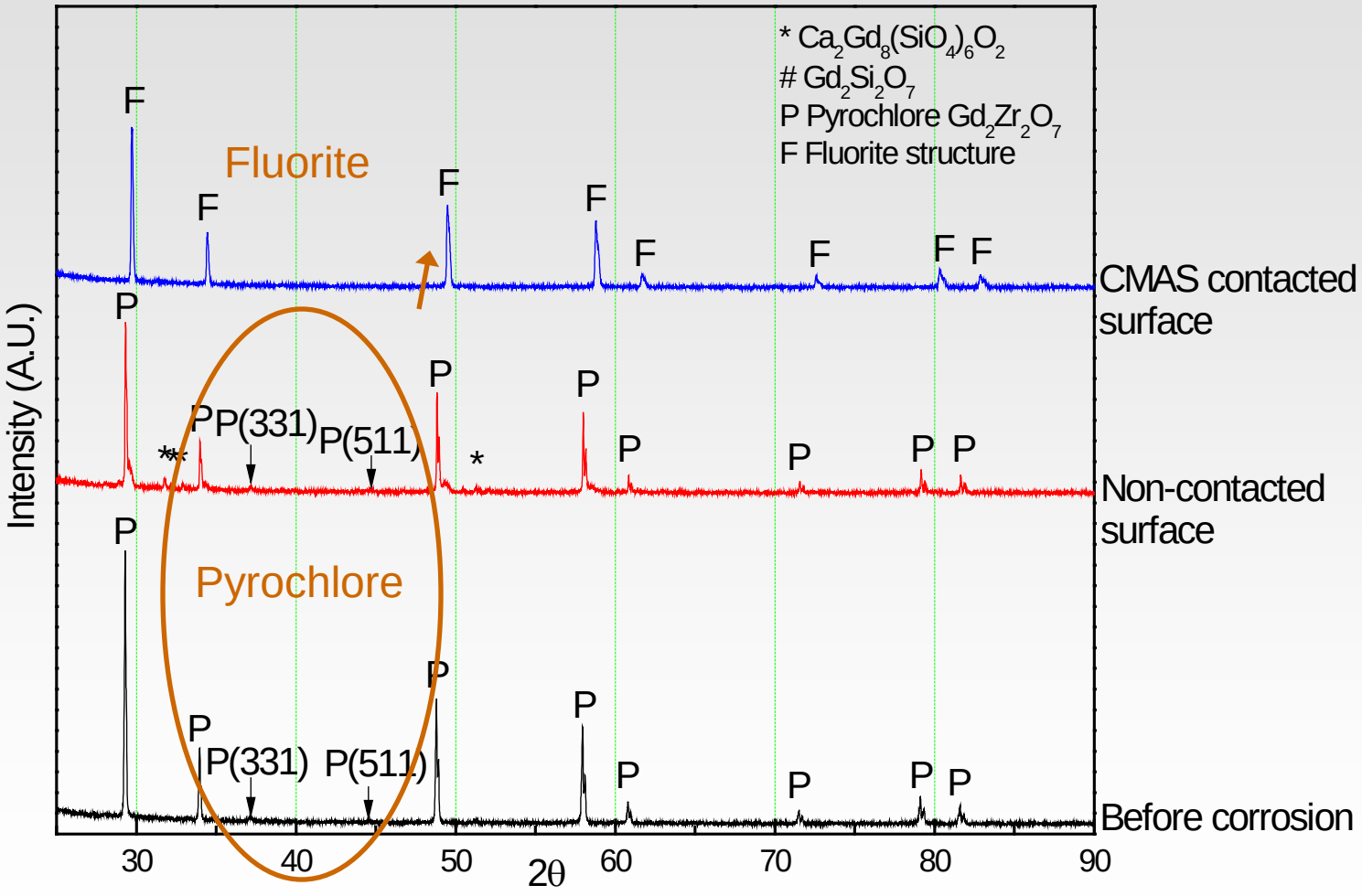
$Gd_2Zr_2O_7$ after CMAS at 1400°C for 5 hours



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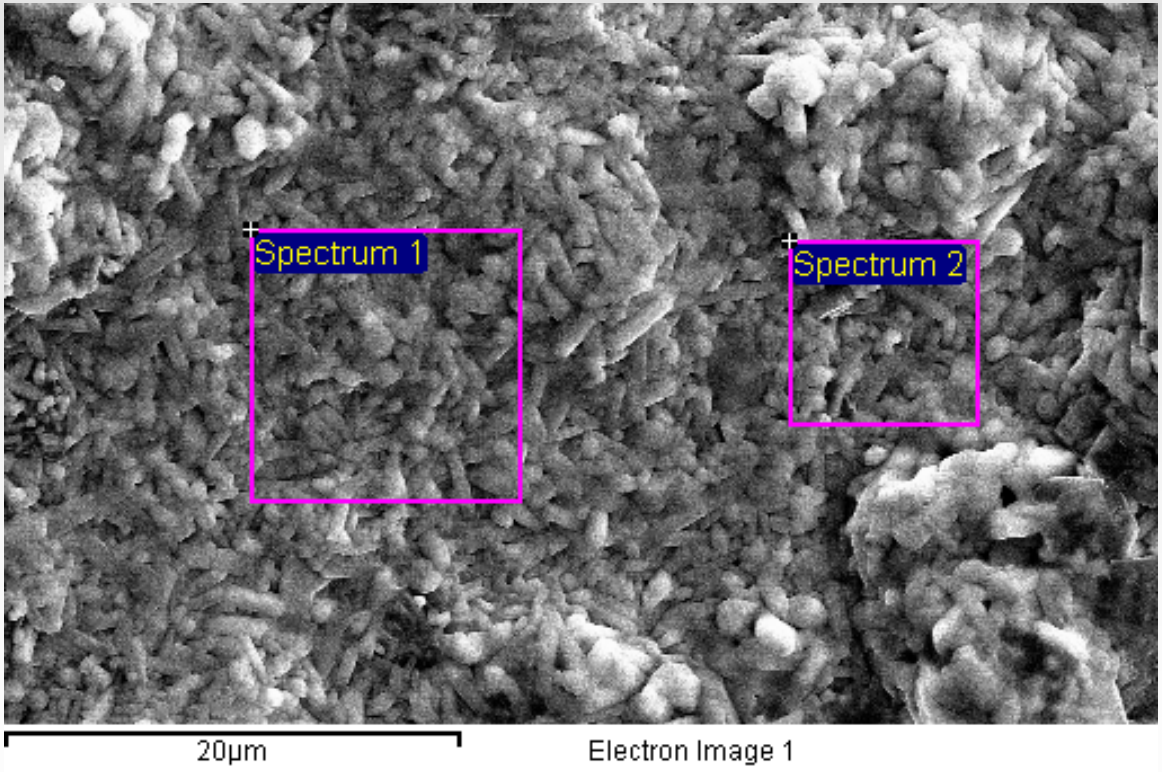
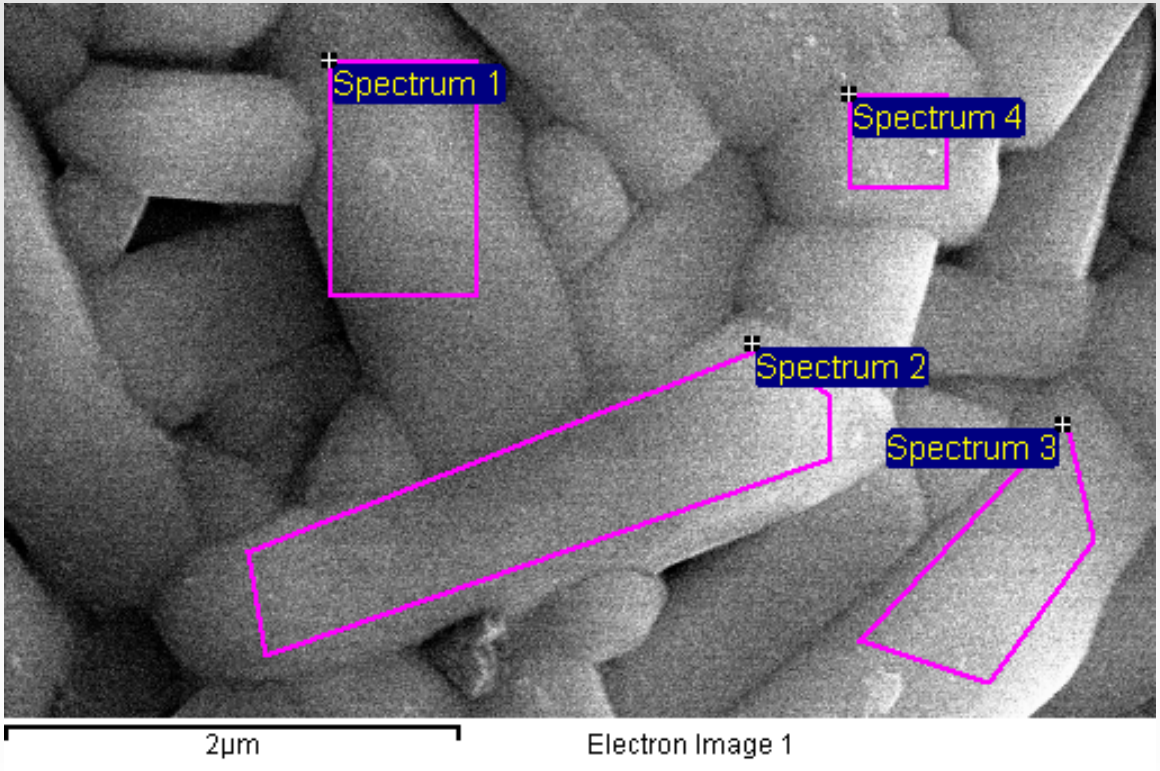
$Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



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

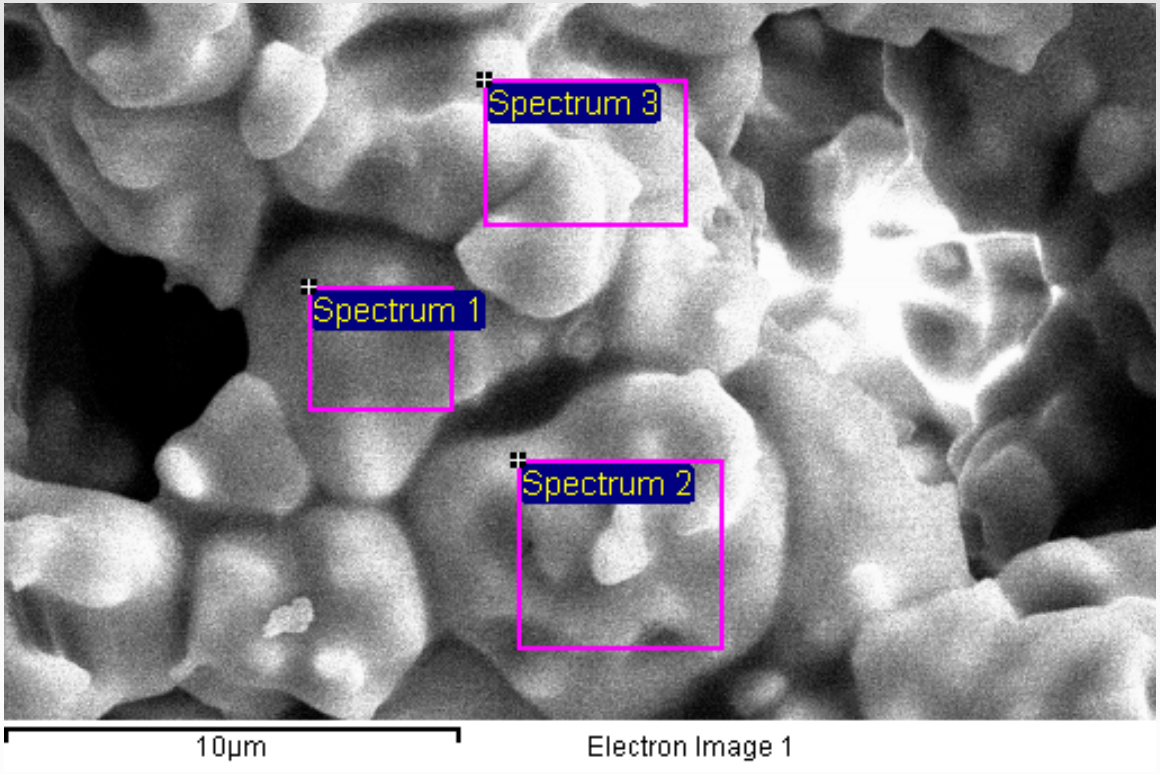
$Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



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

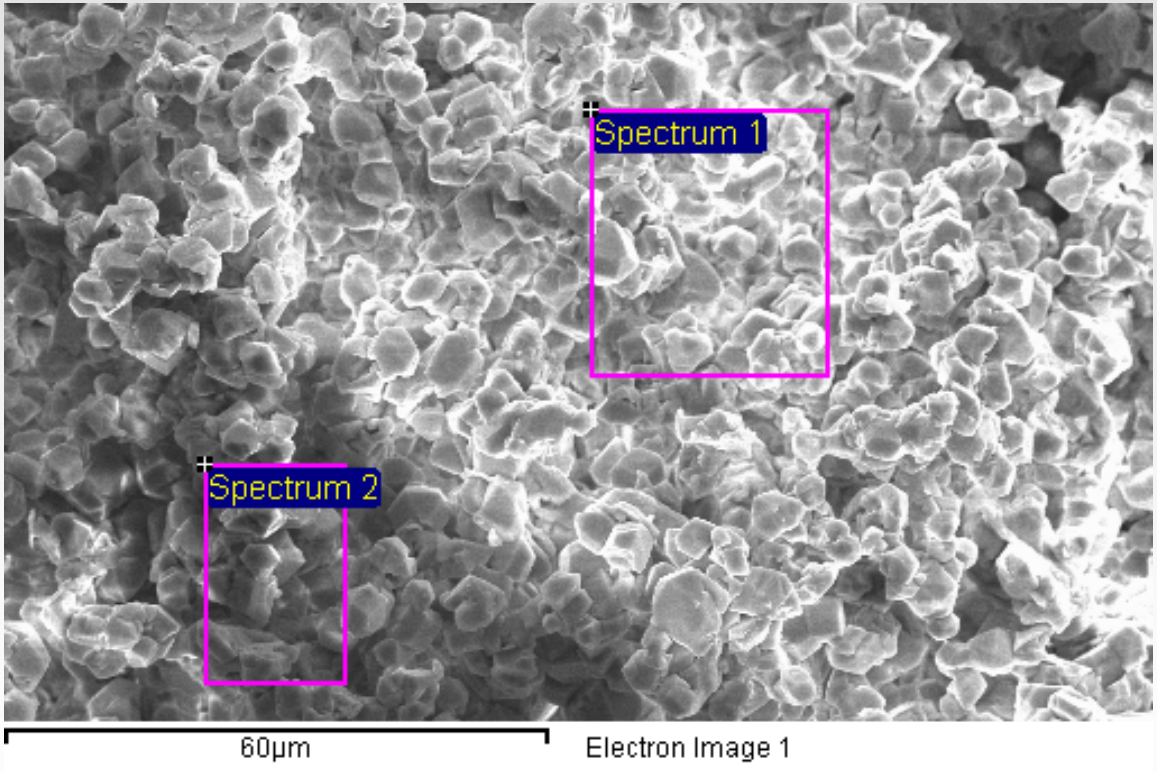
$Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



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

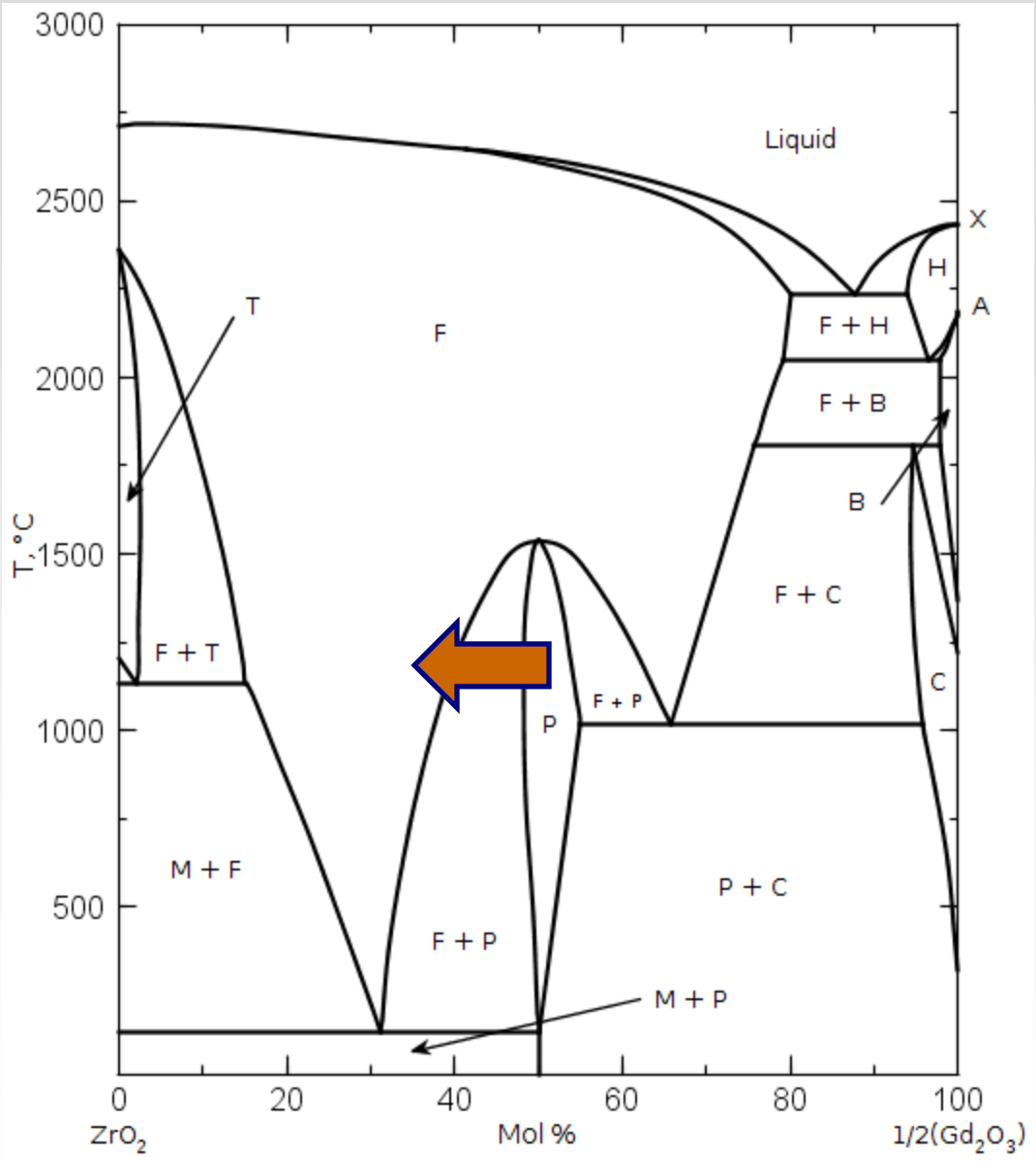
$Gd_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



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

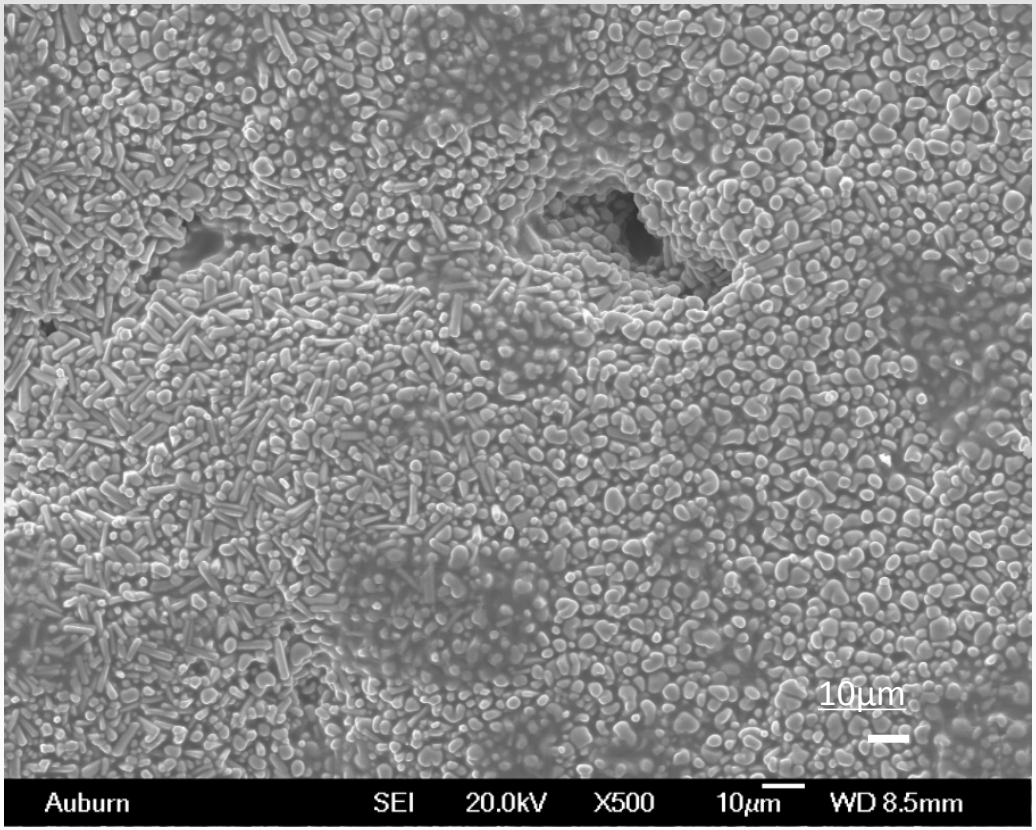
Pyrochlore

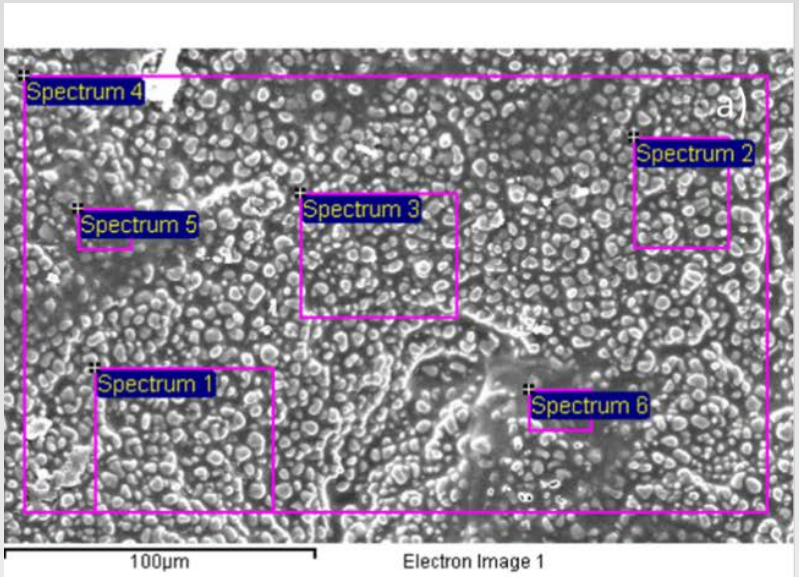
ZrO_2-Gd_2O_3 phase diagram

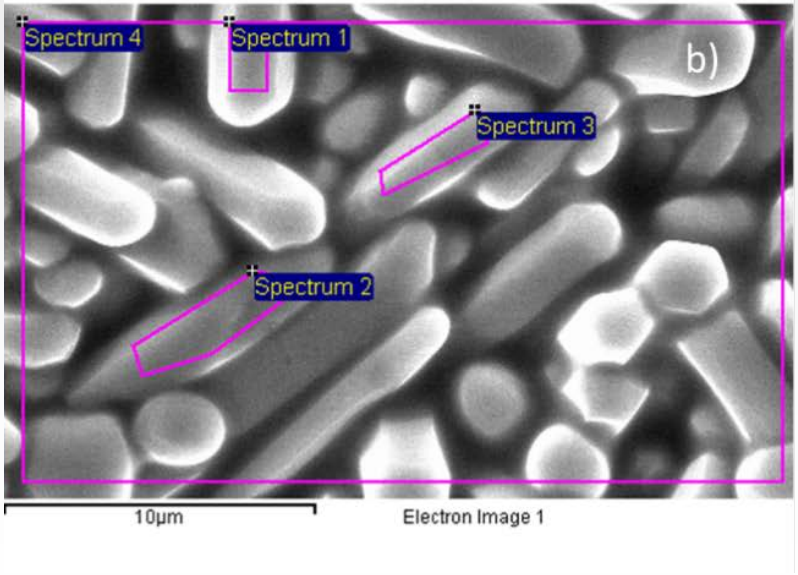


T = tetragonal
F = cubic fluorite
M – monoclinic
P = pyrochlore
C, B, H = Gd_2O_3 phases

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







Atomic Percentage for a)

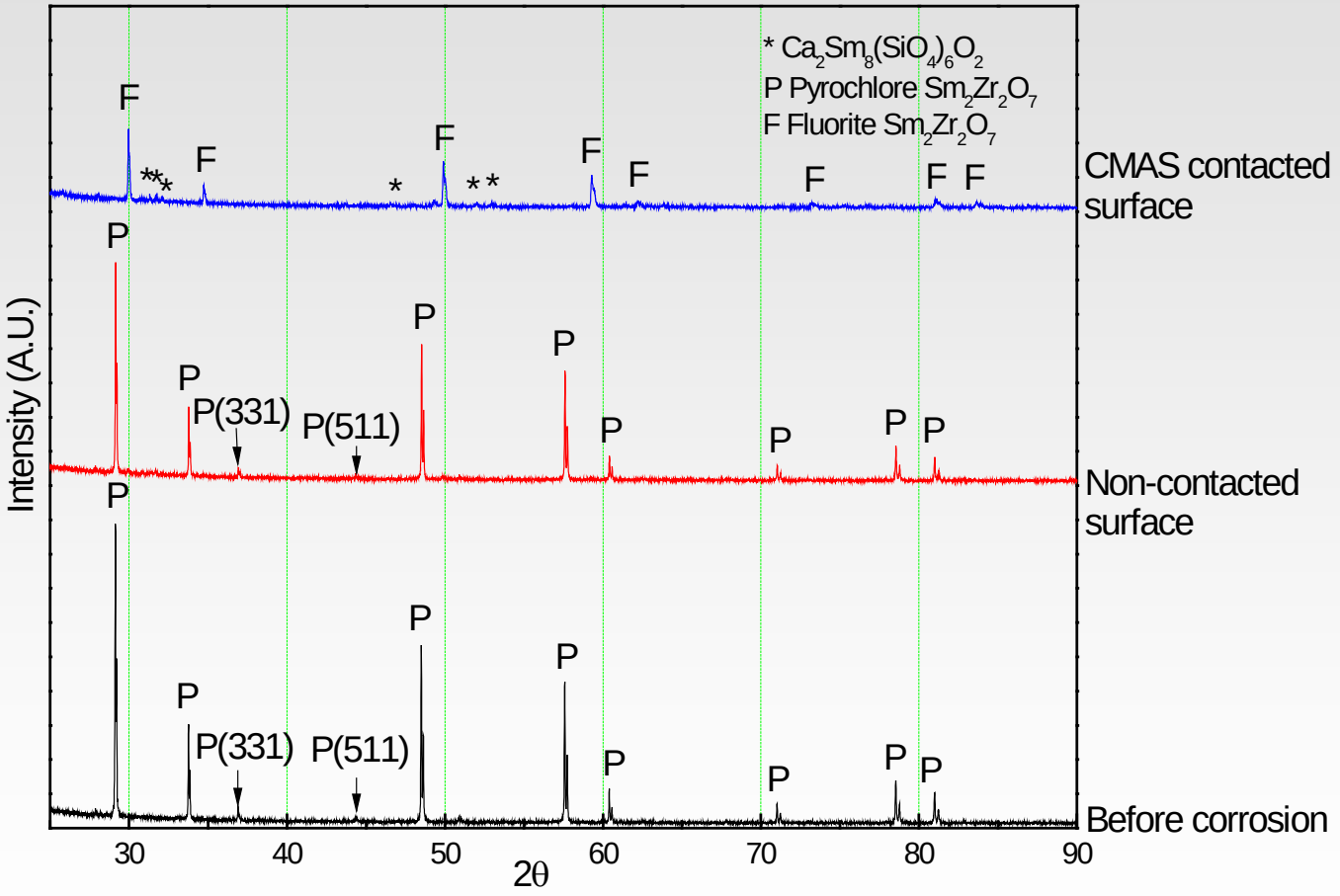
	O	Mg	Al	Si	Ca	Zr	Sm
Spectrum 1	62	2	5	8	5	13	3
Spectrum 2	62	2	5	8	6	12	3
Spectrum 3	63	3	5	8	5	11	3
Spectrum 4	61	3	5	8	7	11	2
Spectrum 5	58	4	6	10	11	7	2
Spectrum 6	44	3	7	13	19	7	2

$Sm_2Zr_2O_7$ 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 5 hours



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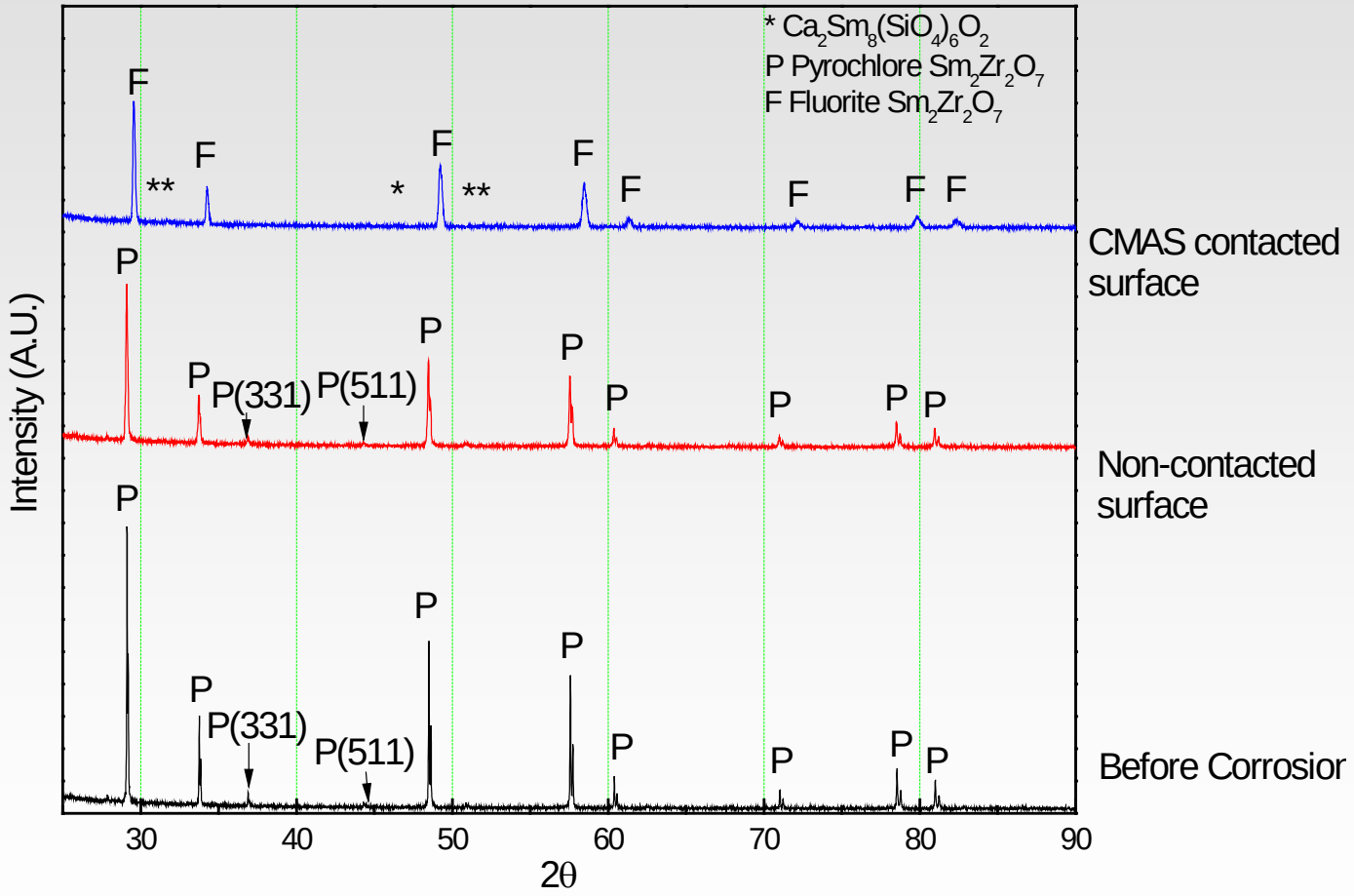
$Sm_2Zr_2O_7$ after CMAS at 1400°C for 5 hours



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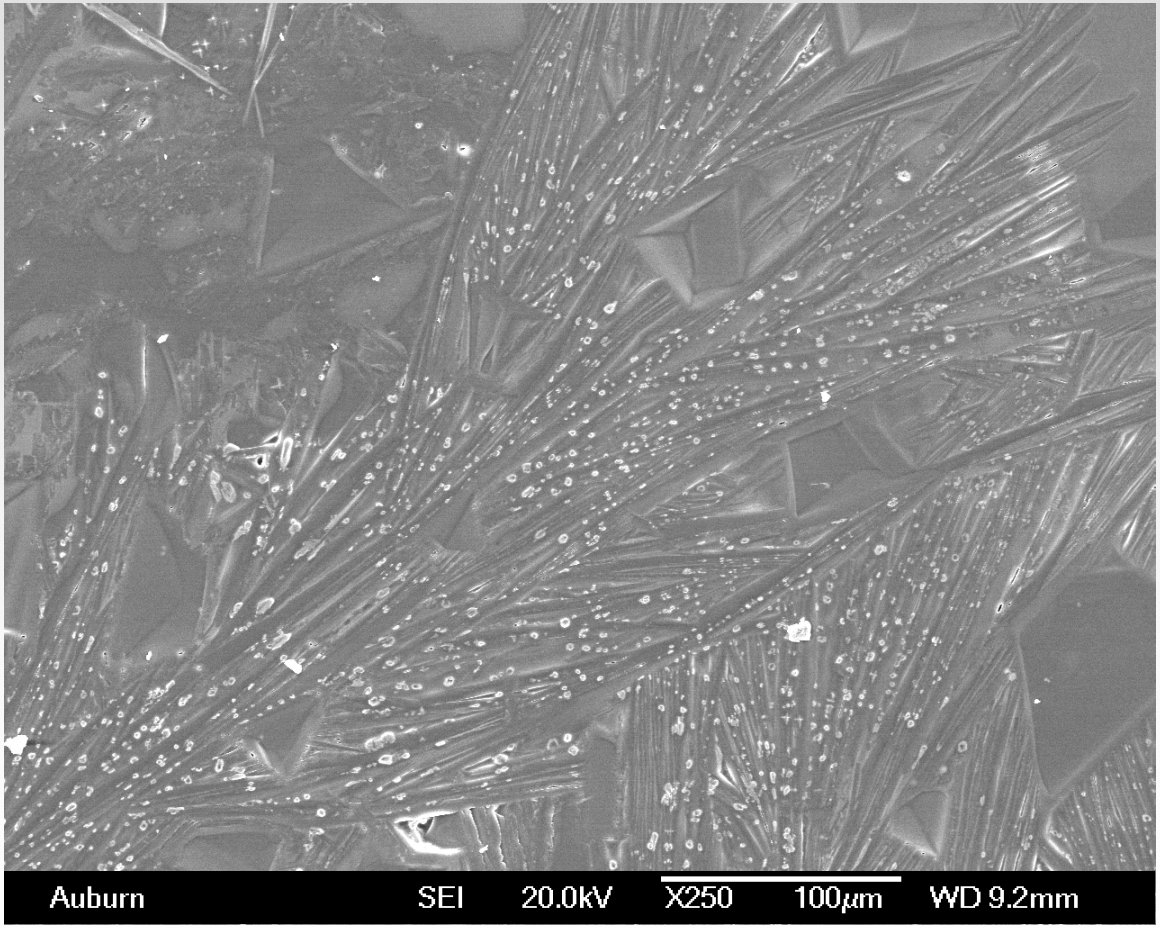
$Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



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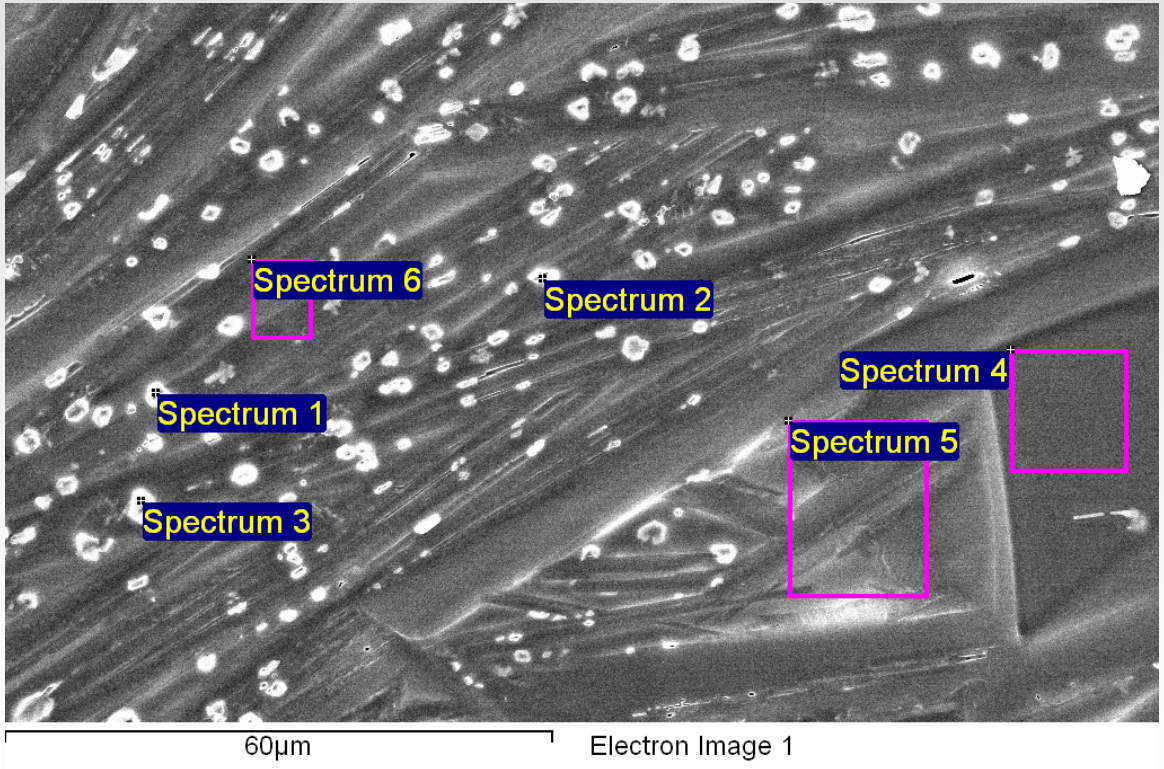
$Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



Concentration								
#	O	Mg	Al	Si	Ca	Zr	Gd	Au
1	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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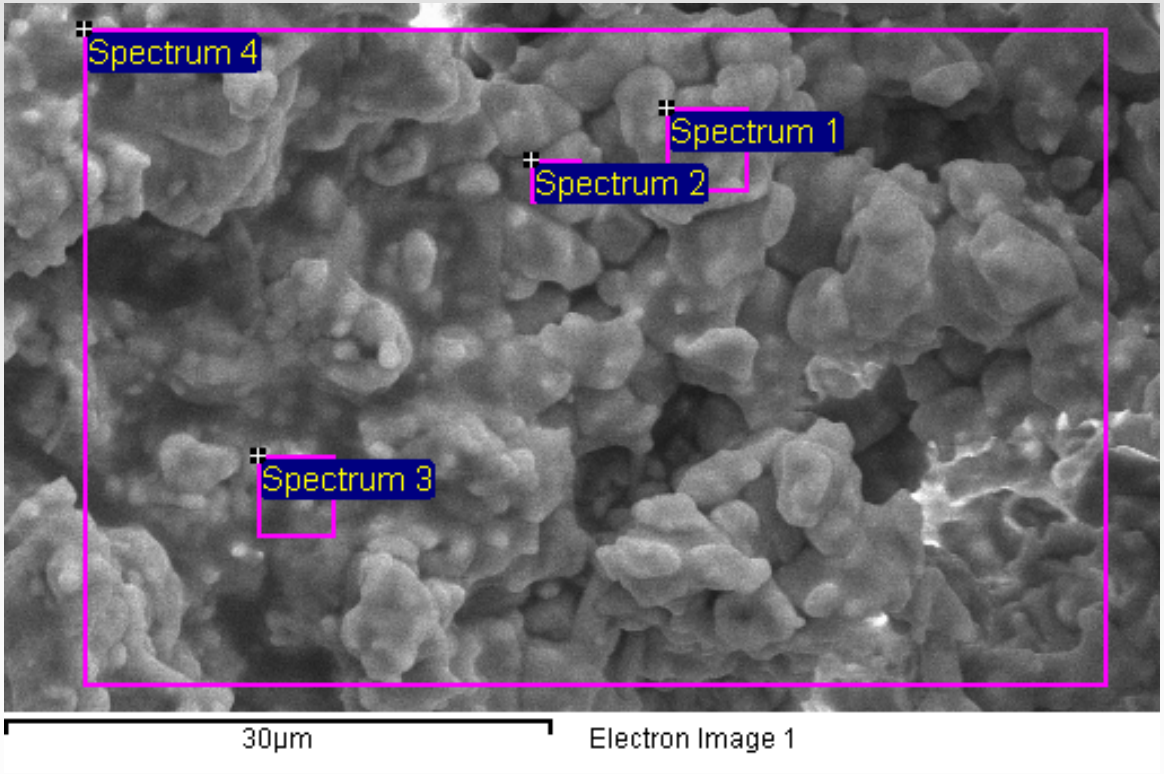
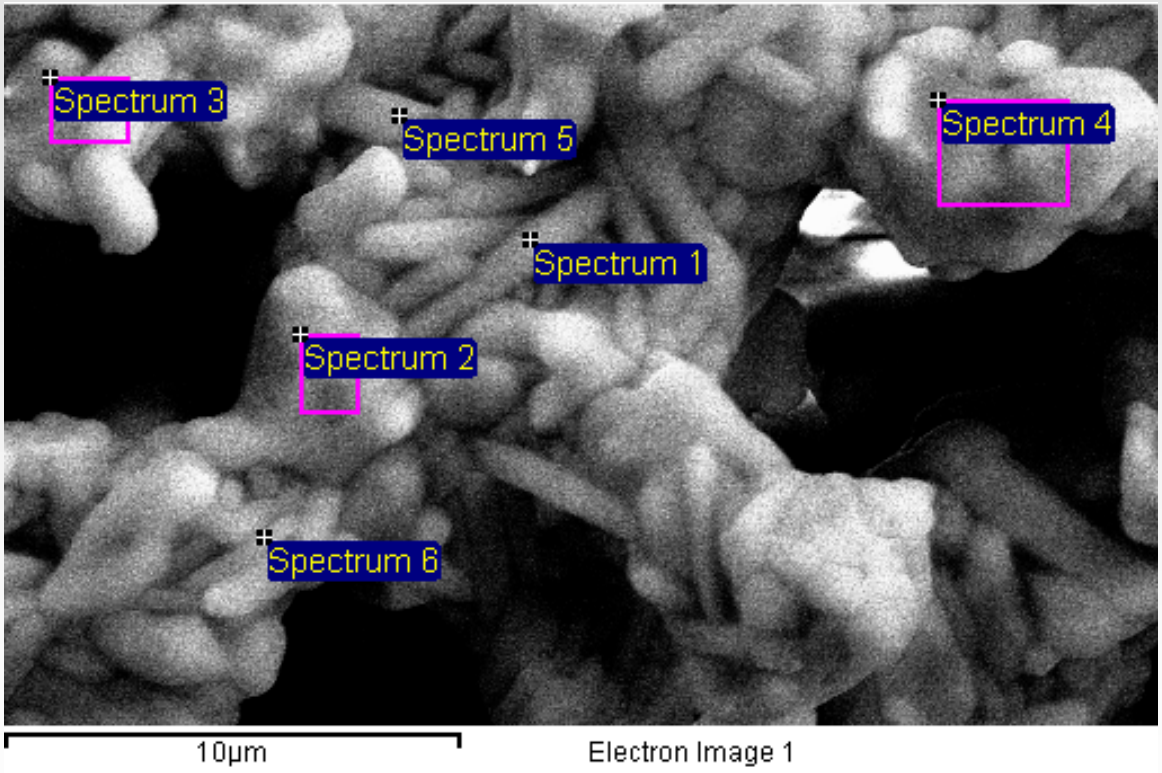
$Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



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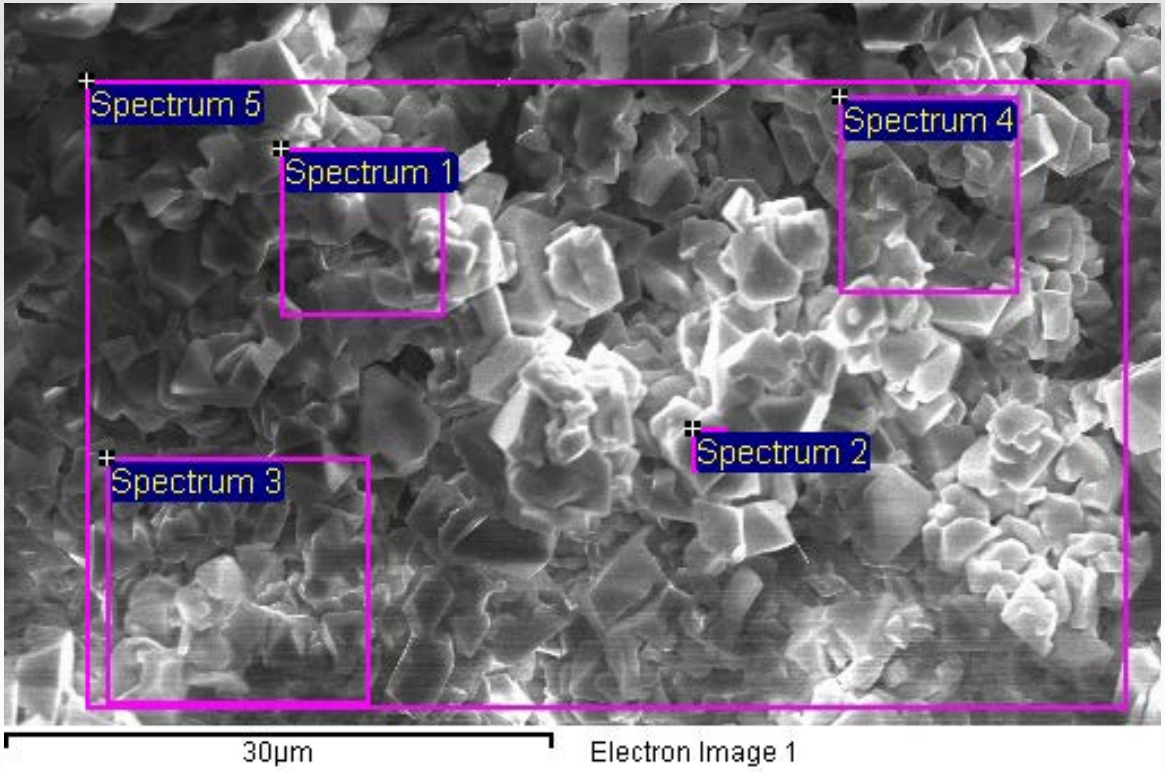
$Sm_2Zr_2O_7$ after CMAS at 1300°C for 15 minutes + 1200°C for 30 hours



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

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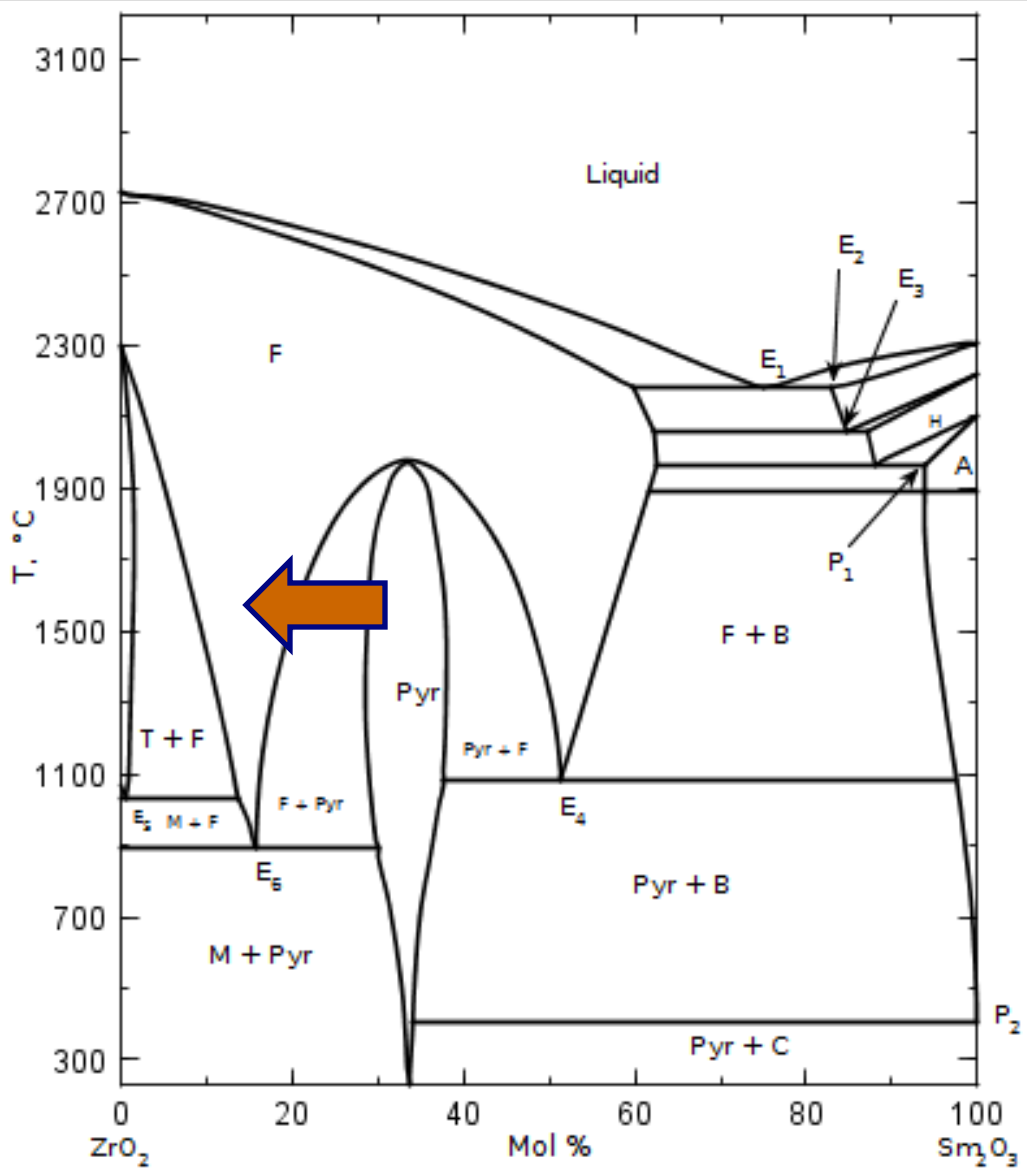
ZrO_2-Sm_2O_3 phase diagram



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

Conclusions

- Bond coat
  - Nickel flash coating needed to obtain quality rhenium coating
- Reaction of pyrochlore with CMAS
  - $Gd_2Zr_2O_7$ and $Sm_2Zr_2O_7$ evaluated
  - Pyrochlore dissolves in CMAS
  - Reprecipitates as lanthanide silicate and cubic fluorite phase

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