Grain Boundary Engineering for Improved Mechanical Properties in SiAlON Ceramics

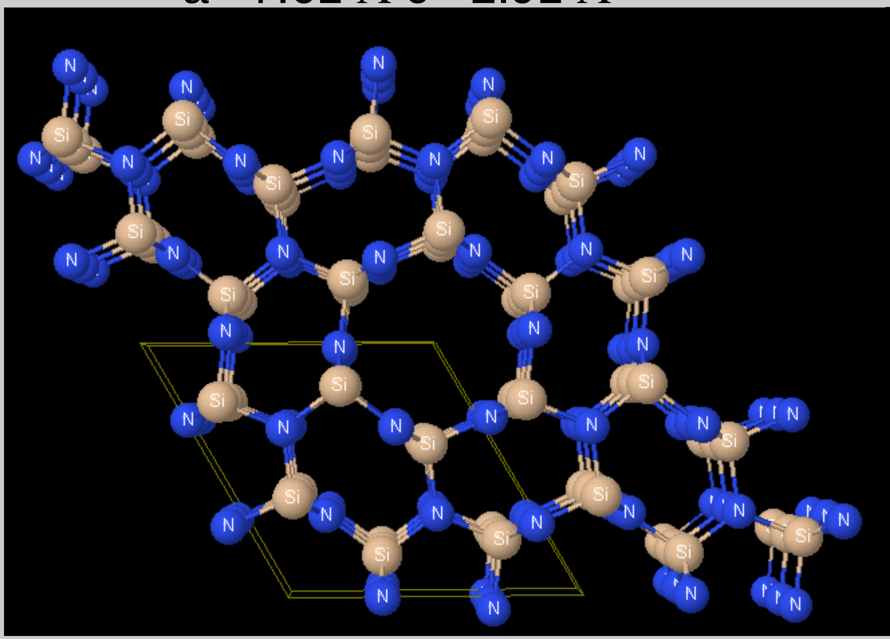
Hasan Mandal

Sabancı University, Istanbul, TURKEY

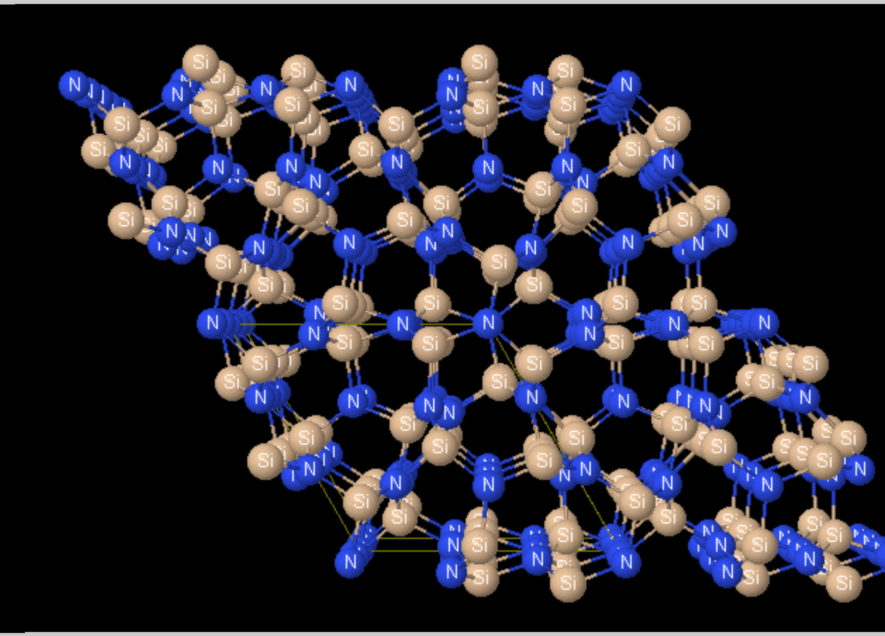
MDA Advanced Ceramics Ltd, Eskisehir, TURKEY

Si_3N_4 and SiAlONs

β-Si3N4
a= 7.61 Å c= 2.91 Å



α-Si3N4
a= 7.76 Å c=5.62 Å



Si^{+4} ⬌ Al^{+3}

N^{-3} ⬌ O^{-2}

$Si_{6-z}Al_zO_zN_{8-z}$

Si^{+4} ⬌ Al^{+3}

N^{-3} ⬌ O^{-2}

$Me_{m/val}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$

SiAlONs

α-Si_3N_4 +AlN/Al_2O_3 + Sintering additives

(Y_2O_3, rare earths)

α-SiAlON

α-β SiAlON*

β-SiAlON

+

Grain Boundary phase

*Reversible $\alpha \rightarrow \beta$ SiAlON Transformation in Heat-Treated Sialon Ceramics
Mandal et al, 1993, Journal of European Ceramic Society

SiAlONs

α-SiAlON — ***Hard***

α-β SiAlON — ***Hard & Tough***

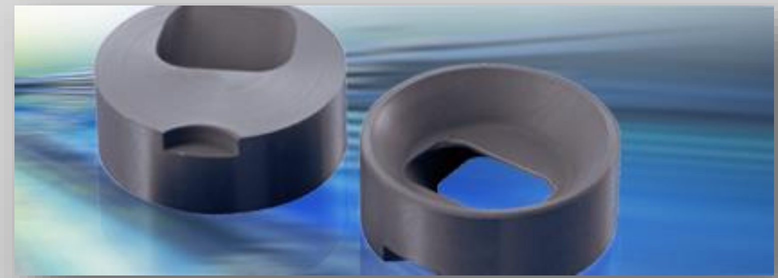
β-SiAlON — ***Tough***

Application Areas of Si_3N_4 and SiAlONs

Cutting Inserts
image courtesy of CeramTec Germany

Turbochargers
image Courtesy of NGK/NTK Spark Plug Co

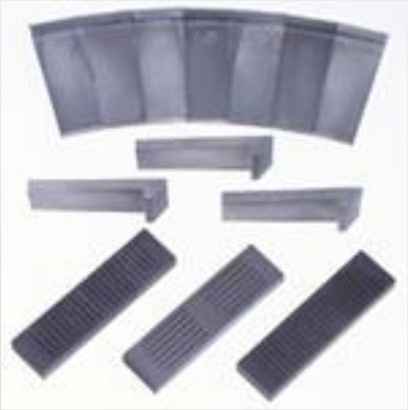
Bearing Applications



Swirl Chamber
image courtesy of Kyocera company

Potential Application Areas of Si_3N_4 and SiAlONs

Wind Turbine Parts

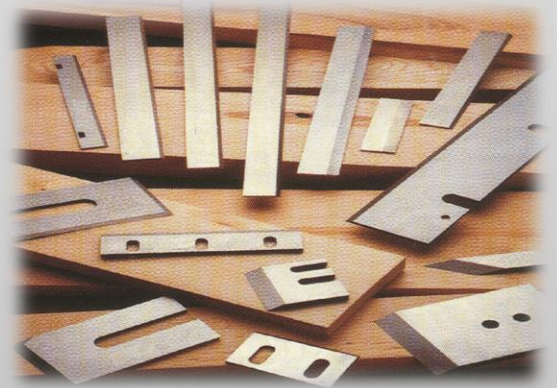


mineral processing tiles

Diesel particulate filters

Sand Blast Nozzle Liners

paper processing
dewatering tiles



Cutting blades for wood machining

DESIRE

- Wider mechanical, chemical and refractory applications

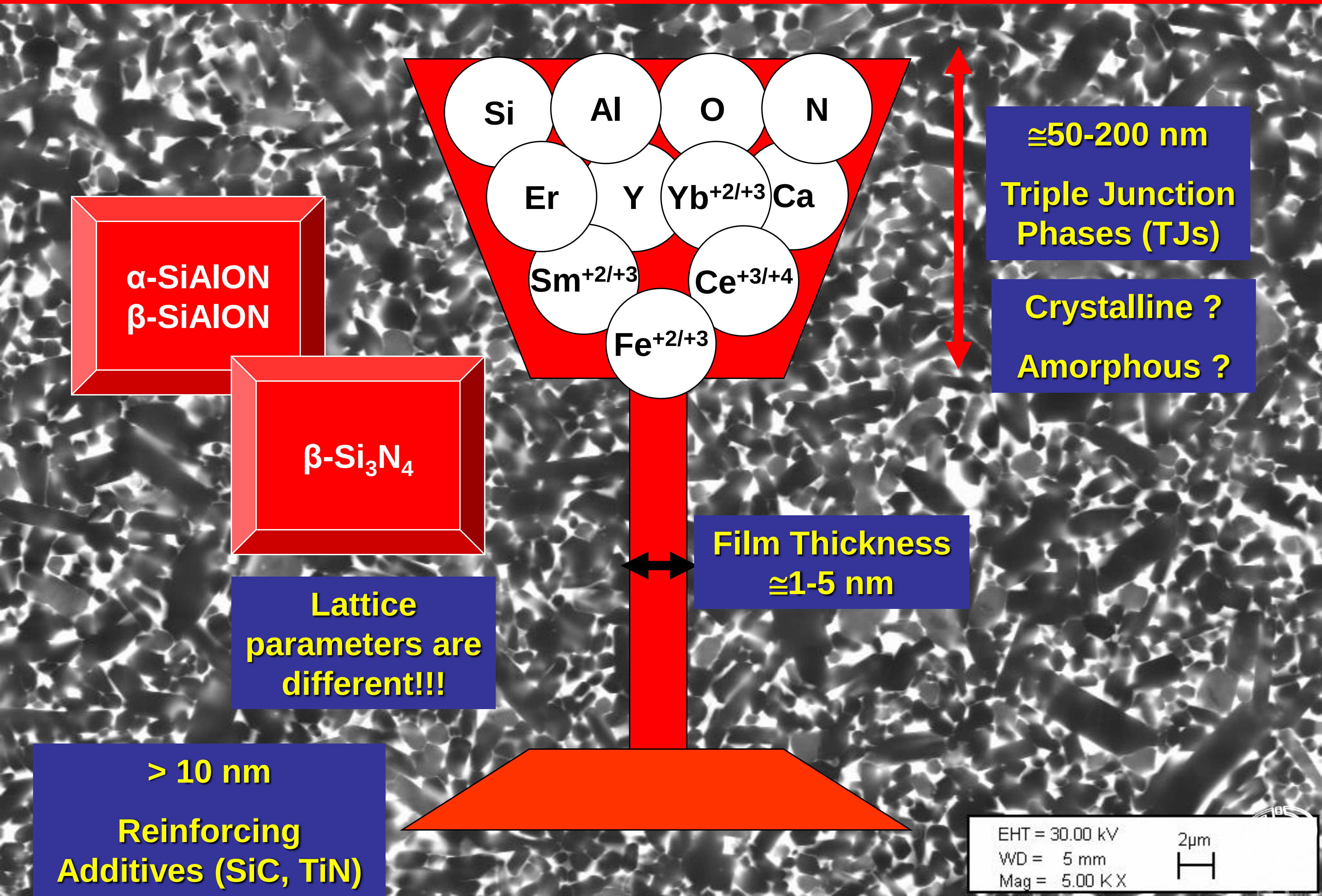
CHALLENGES

- Properties in severe conditions
- Cost of powders and processing

DEVELOPMENT STRATEGIES

- Phase relationships and grain boundary chemistry

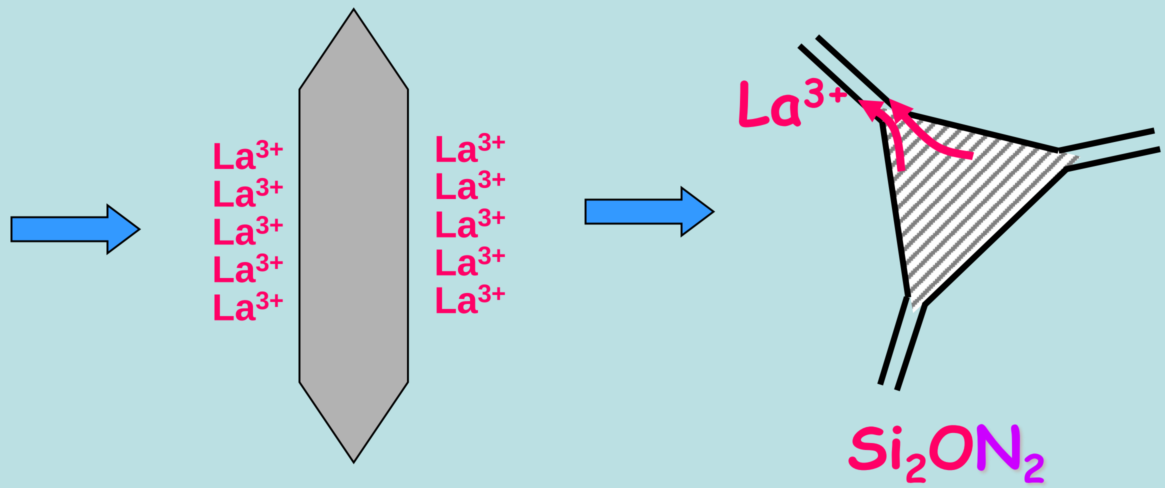
SiAlON Cocktail



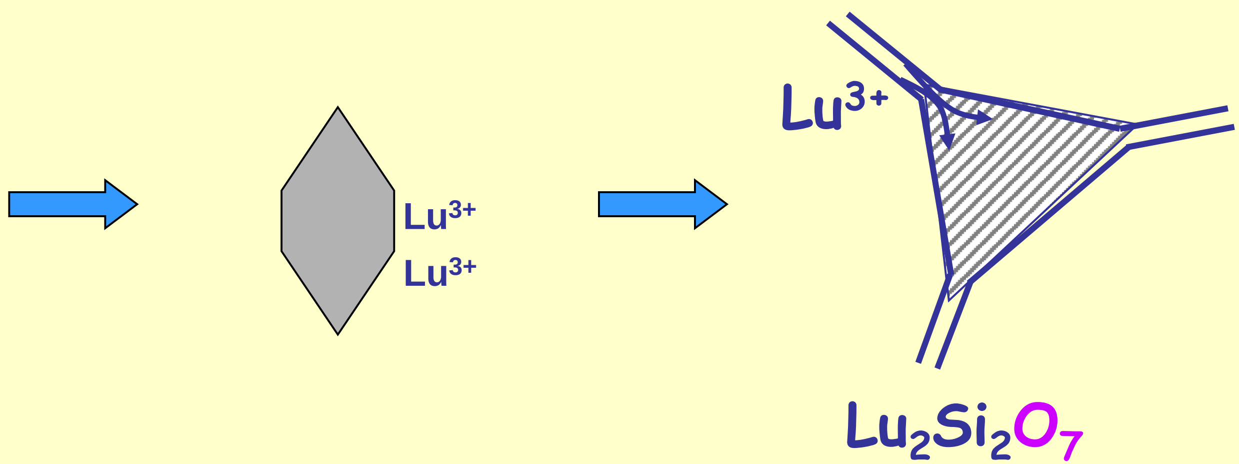
EFFECT OF INTERGRANULAR PHASE CHEMISTRY

Crystalline Grain Boundary Phases

High Absorption
High Anisotropy
Low Interfacial Strength



Low Absorption
Low Anisotropy
High Interfacial Strength



Hoffmann, M.J. and Satet R., “Impact of Intergranular Film Properties on Microstructure and Mechanical Behavior of Silicon nitride”, Key Eng. Mater. Vols. 264-268, (2004), 775-780.

Shibata, N., Pennycook S., Gosnell, T.R., Painter, G.S., Shelton W.A. and Becher P.F.”Observation of rare earth segregation in silicon nitride ceramics at subnanometre dimensions”, Nature, Vol 428, (2004), 730-733

SINTERING ADDITIVES FOR α/β SiAlON CERAMICS DEVELOPED by MDA

- CaO

  (To avoid $\alpha \rightarrow \beta$ SiAlON transformation)

- Y_2O_3 and/or Re_2O_3 (where $Z_{Re} \geq 62$)

  (To increase the stability and hardness of α-SiAlON)

- Re_2O_3 (where $Z_{Re} < 62$)

  (To develope elongated β-SiAlON grains and increase fracture toughness)

US Patent No: US 7,064,095 B2
EP Patent No: 1 414 580 B1
2002

PROCESSING

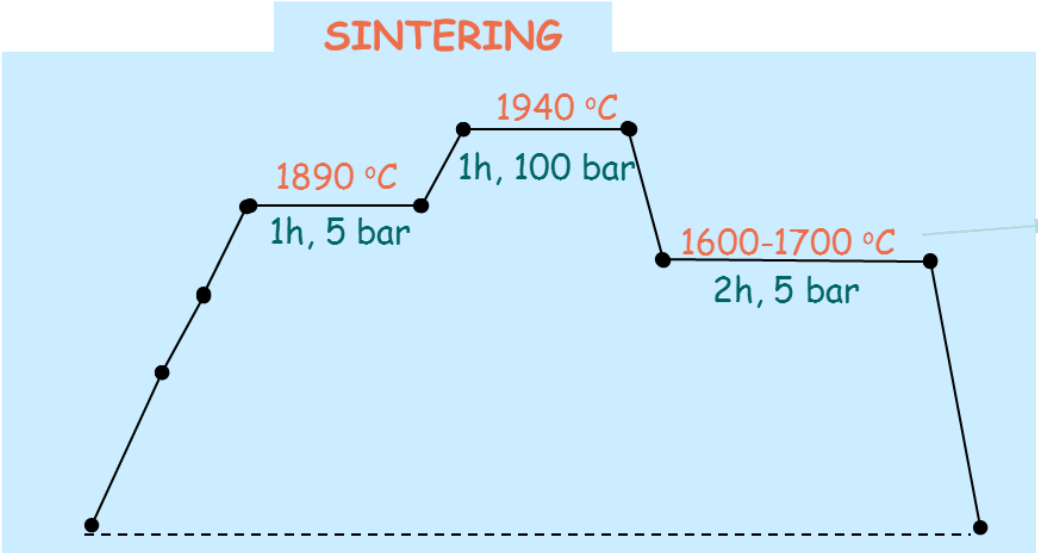
- Powder:
  - α-Si3N4 (SN E-10, UBE/Japan)
- Composition:

Y
Er:Sm:Ca
Yb

Total additive content: 6.5 vol%

Designed phase composition: 25% α-SiAlON - 75% β-SiAlON

(x:0.42, m=1.25, n=1.3) **(z = 0.2)**



Heat treatment above eutectic (AET) to enable crystallisation of sintering additives

CRYSTALLISATION-AFFECTING FACTORS

(i) EFFECT OF DOPANTS

	CATION SYSTEMS					
	Yb	1Yb:1Ce	Ce	Yb:Sm:Ca	Y:Sm:Ca	Y:Ce:Ca
Sintering	S_s/Y_s	-	-	-	M_W	M_S

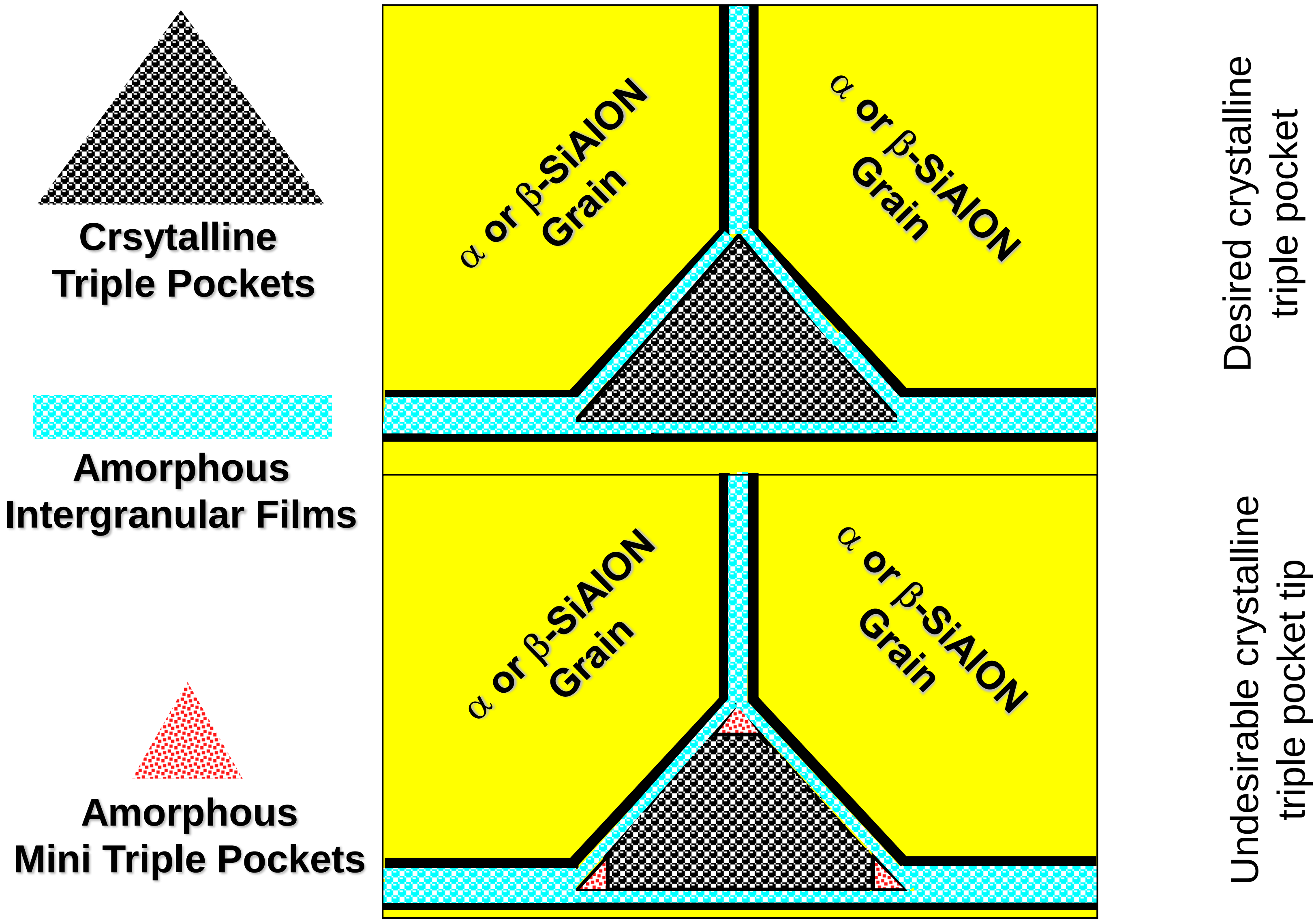
(ii) EFFECT OF HEAT TREATMENT

	CATION SYSTEMS				
	Yb	Yb:Sm	Yb:Sm:Ca	Y:Sm:Ca	Y:Ce:Ca
Sintering	S_s/Y_s	-	-	M_W	M_S
HT-1500	S_s/Y_s	S_s/Y_s	S_w/Y_w , M_w		
HT-1600	S_s/Y_s		M_w	M_s	M_{vs}

Y: Ln_4SiAlO_8N ; S: $Ln_2Si_2O_7$; M: $Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$

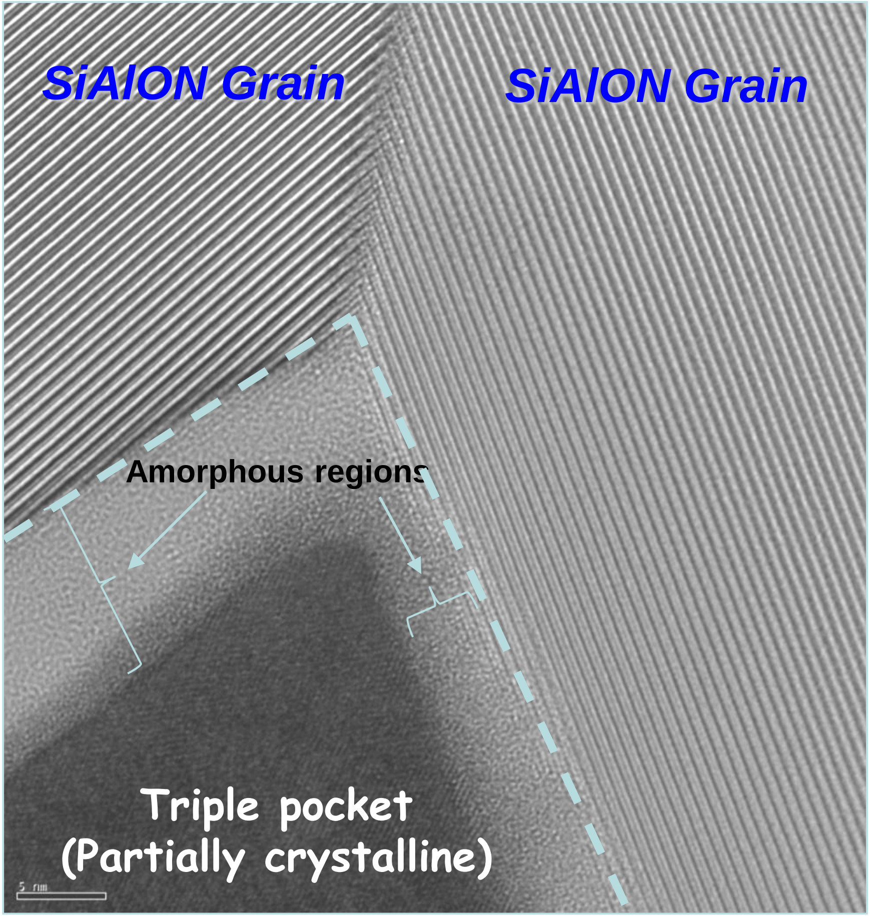
EP12185237, OZ12031EP-Q2/BR, 20 September 2012

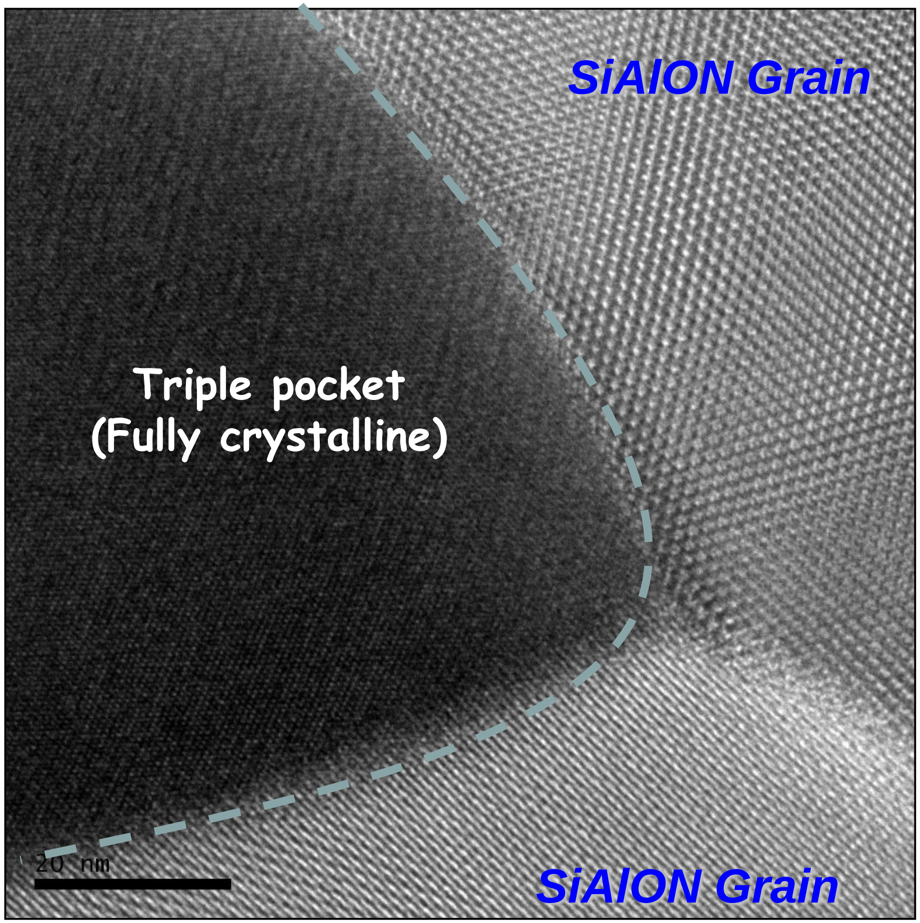
Good or Bad Crystallinity!



EP12185237, OZ12031EP-Q2/BR, 20 September 2012

Good or Bad Crystallinity!

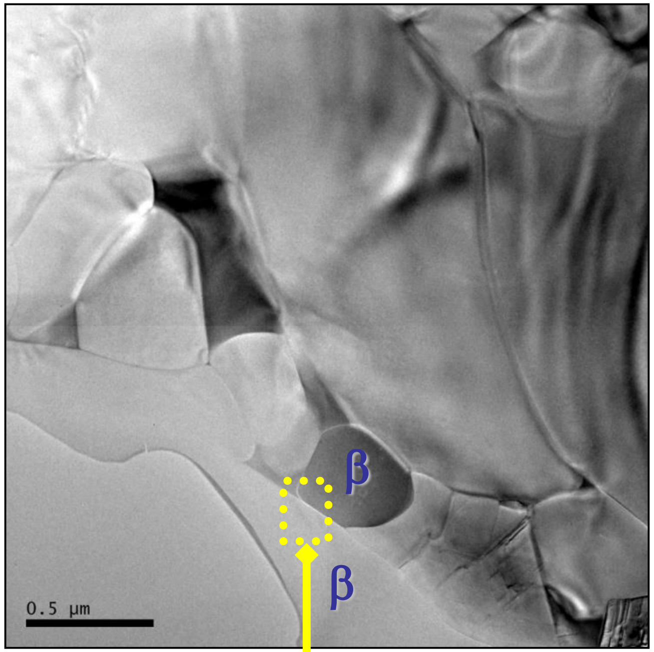


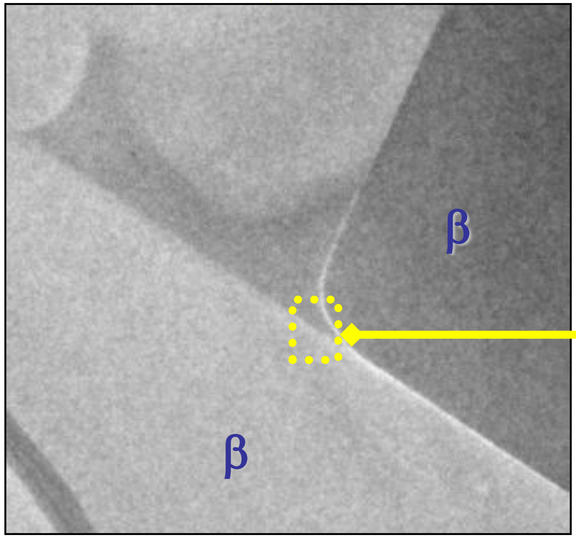


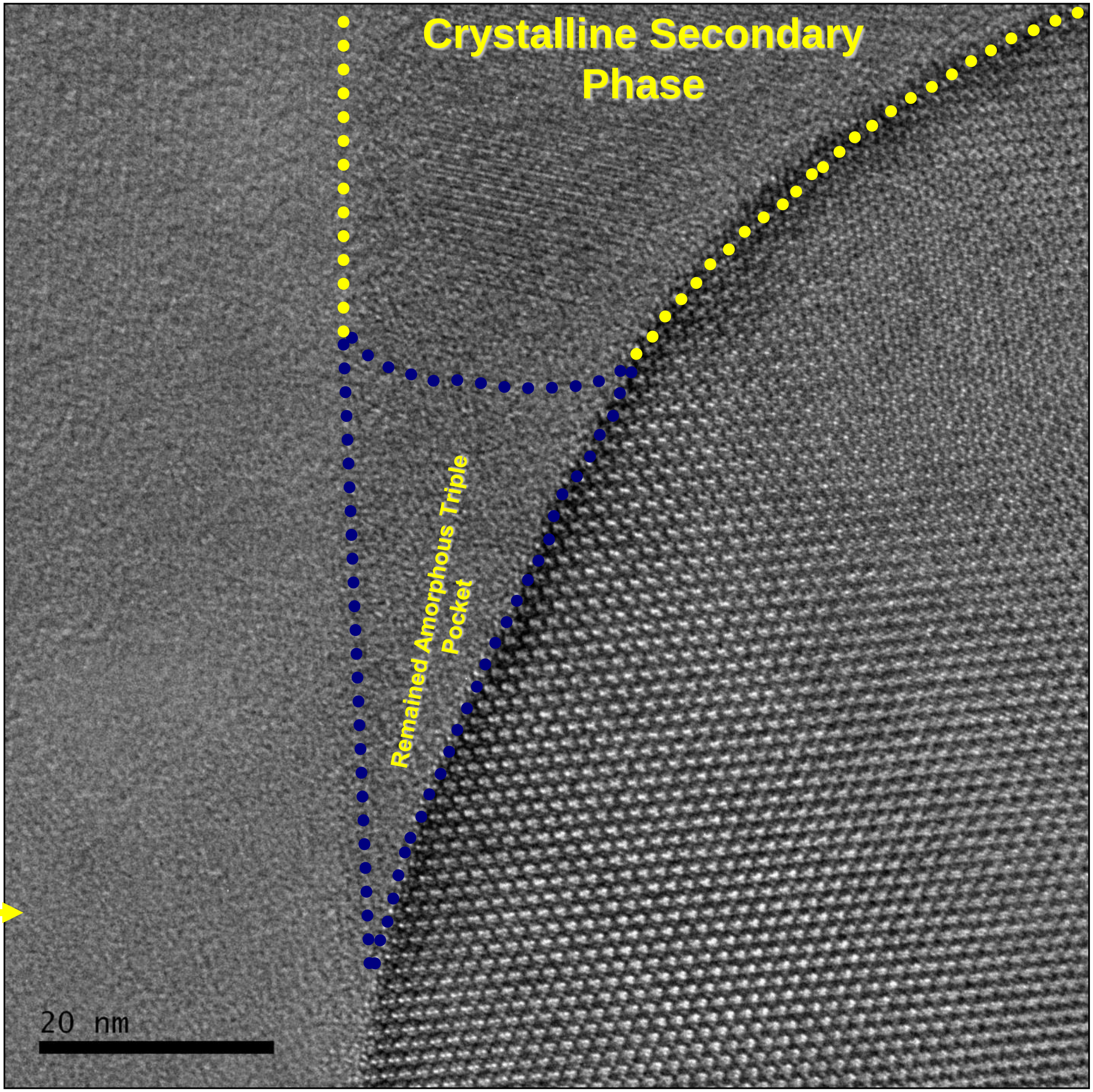
Insufficient Crystallisation

Good Crystallisation

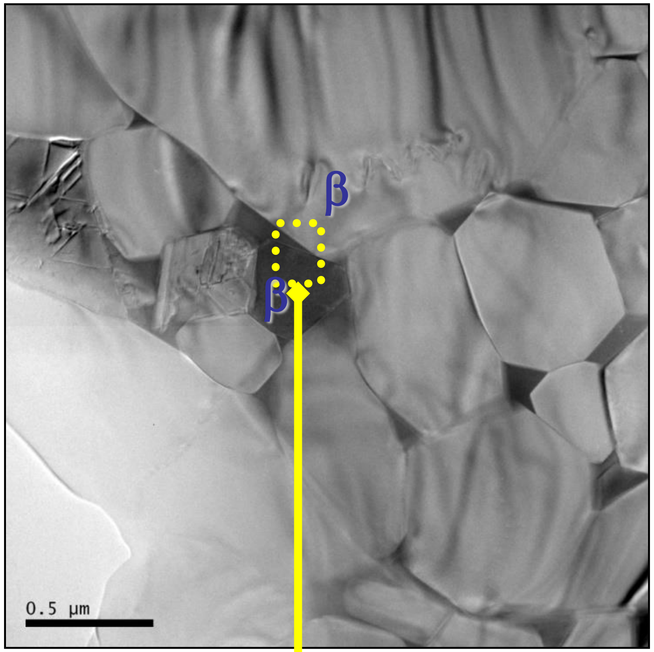
Y-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)

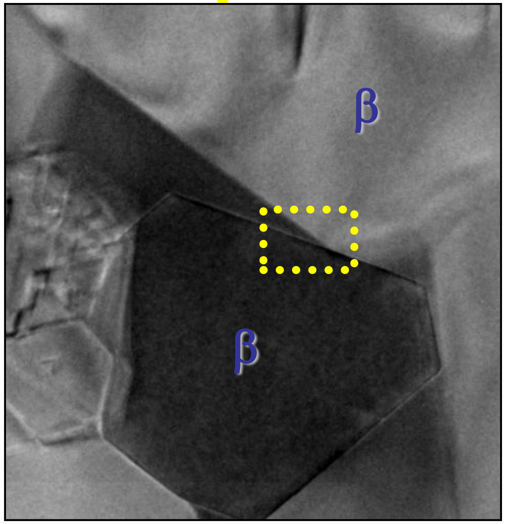


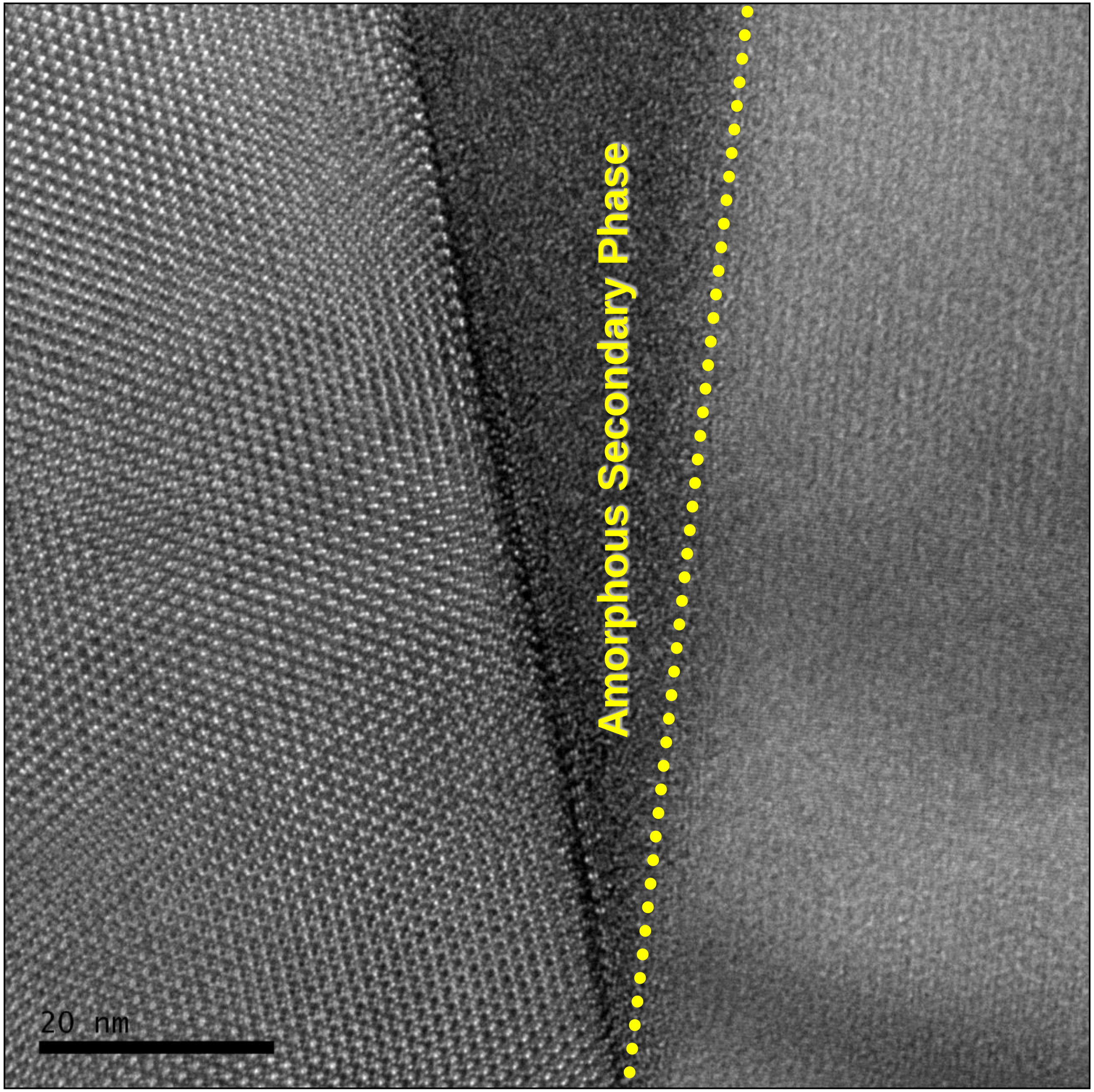




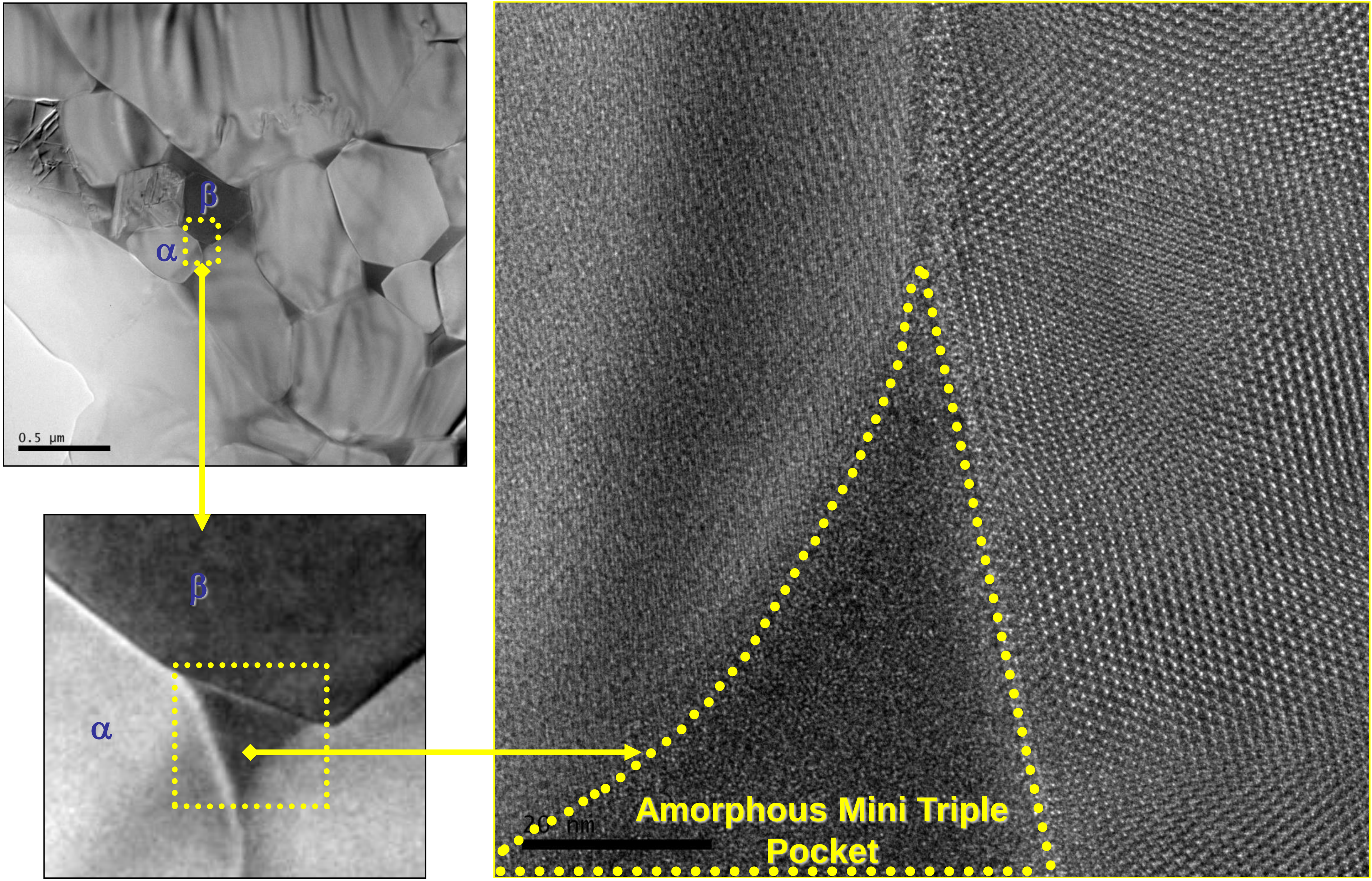
Y-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



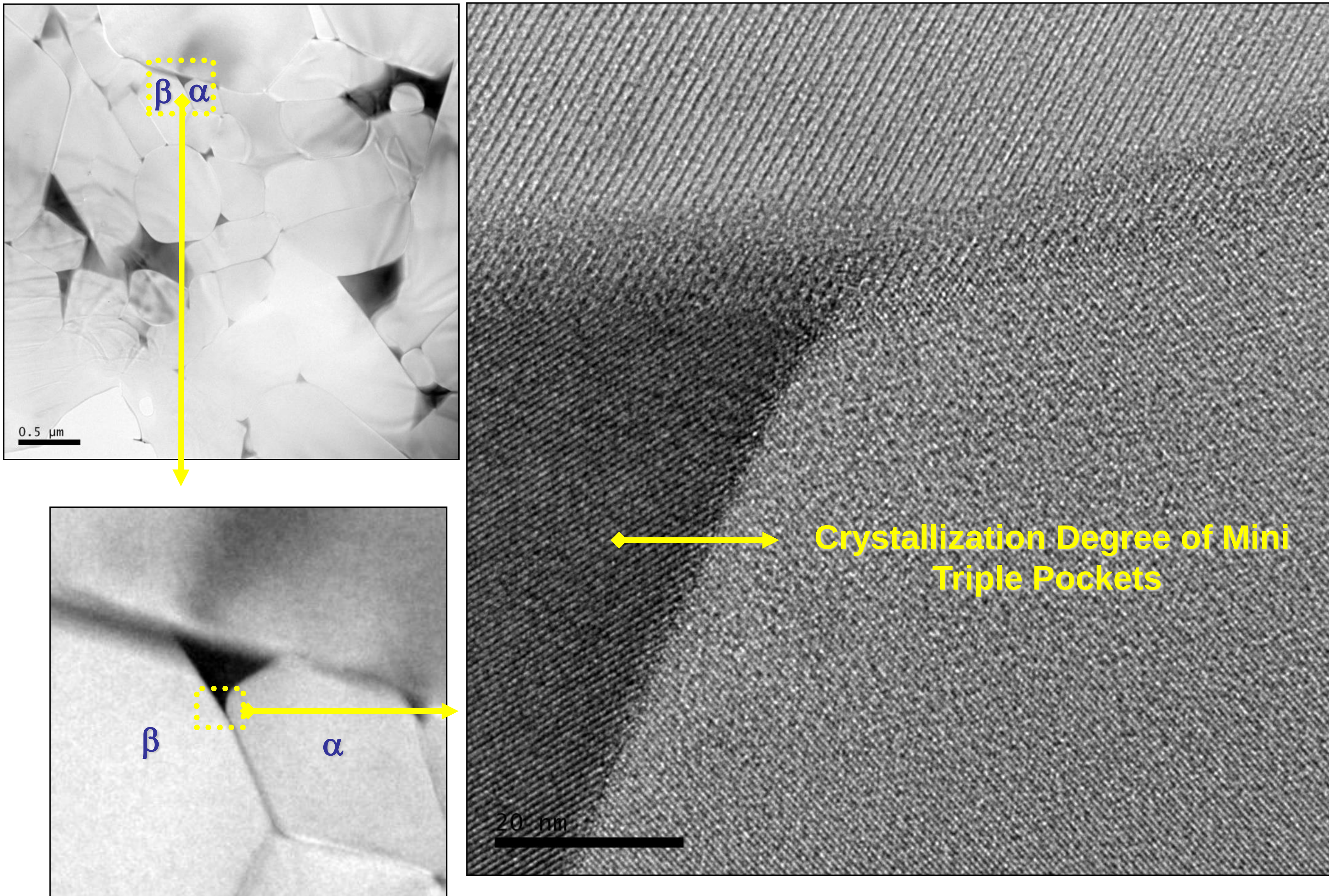




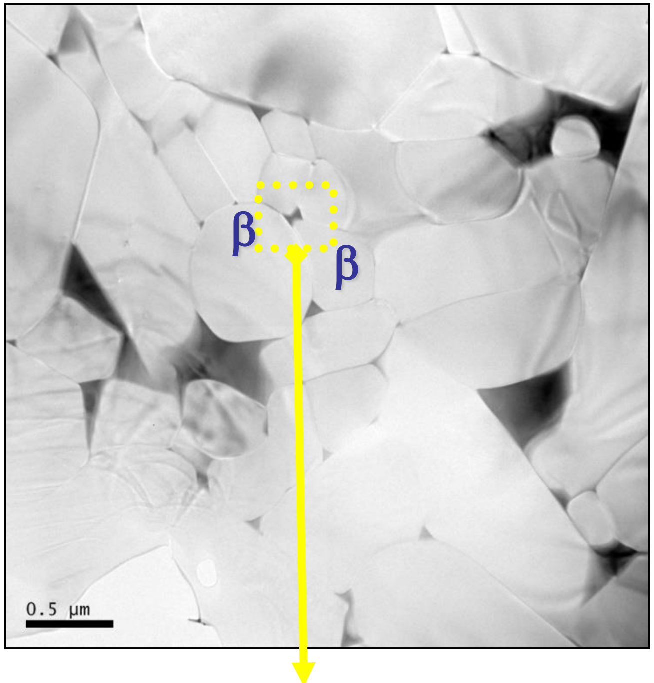
Y-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)

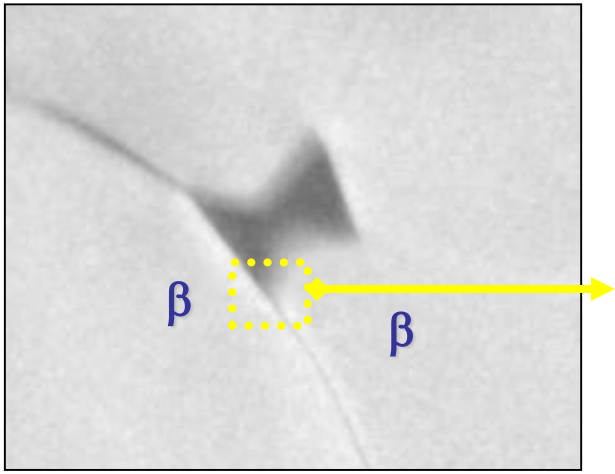


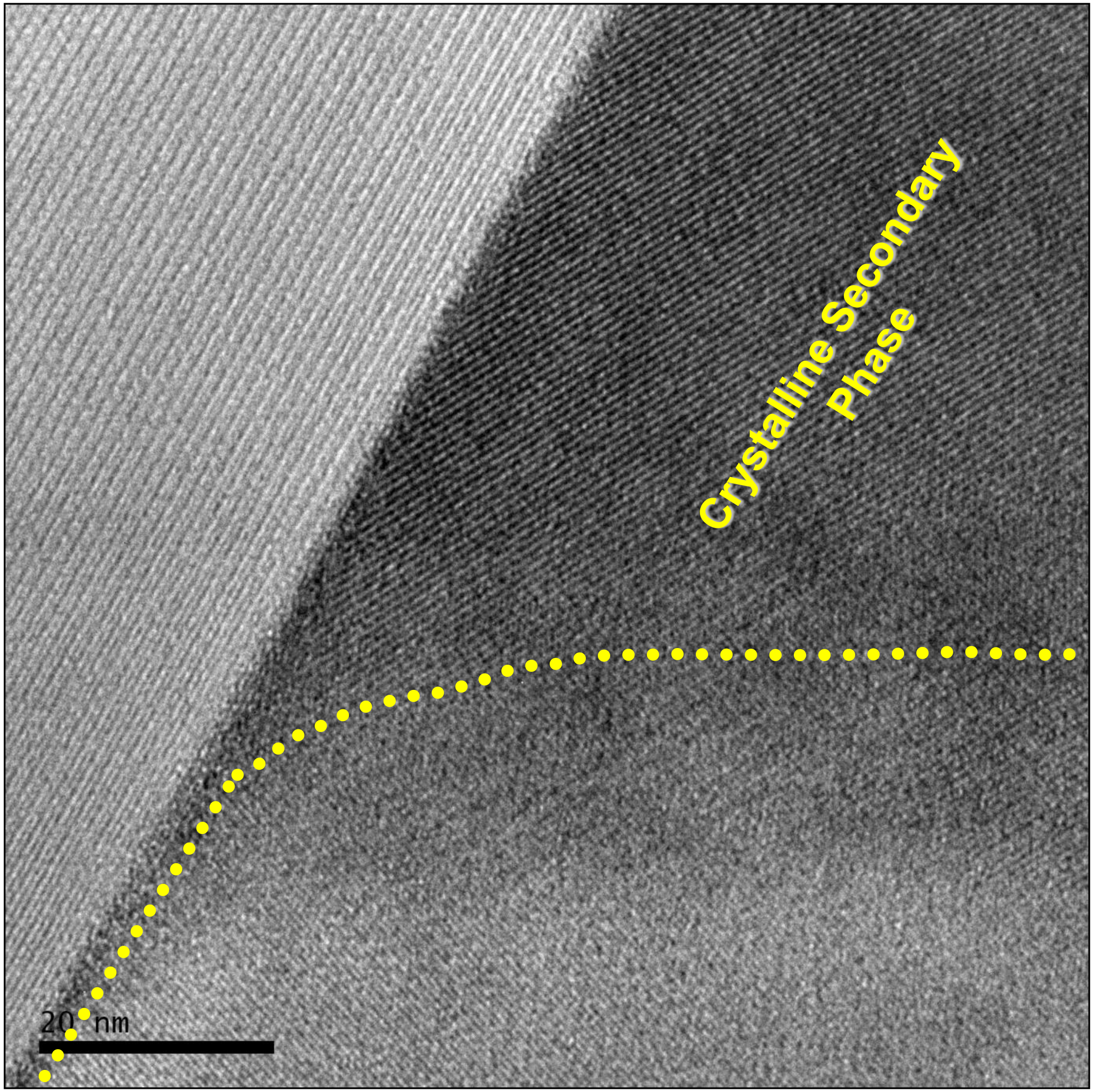
Er-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



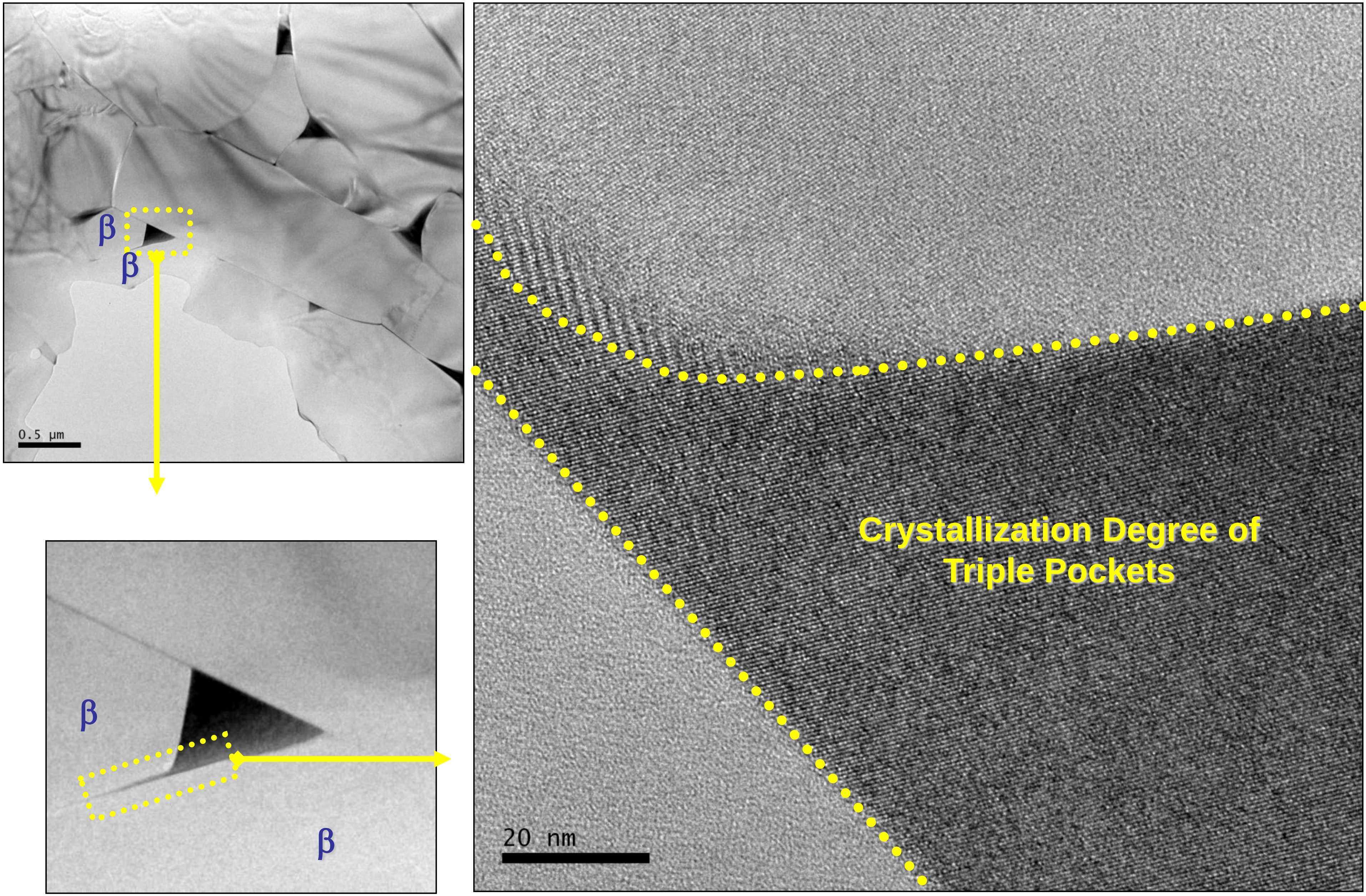
Er-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



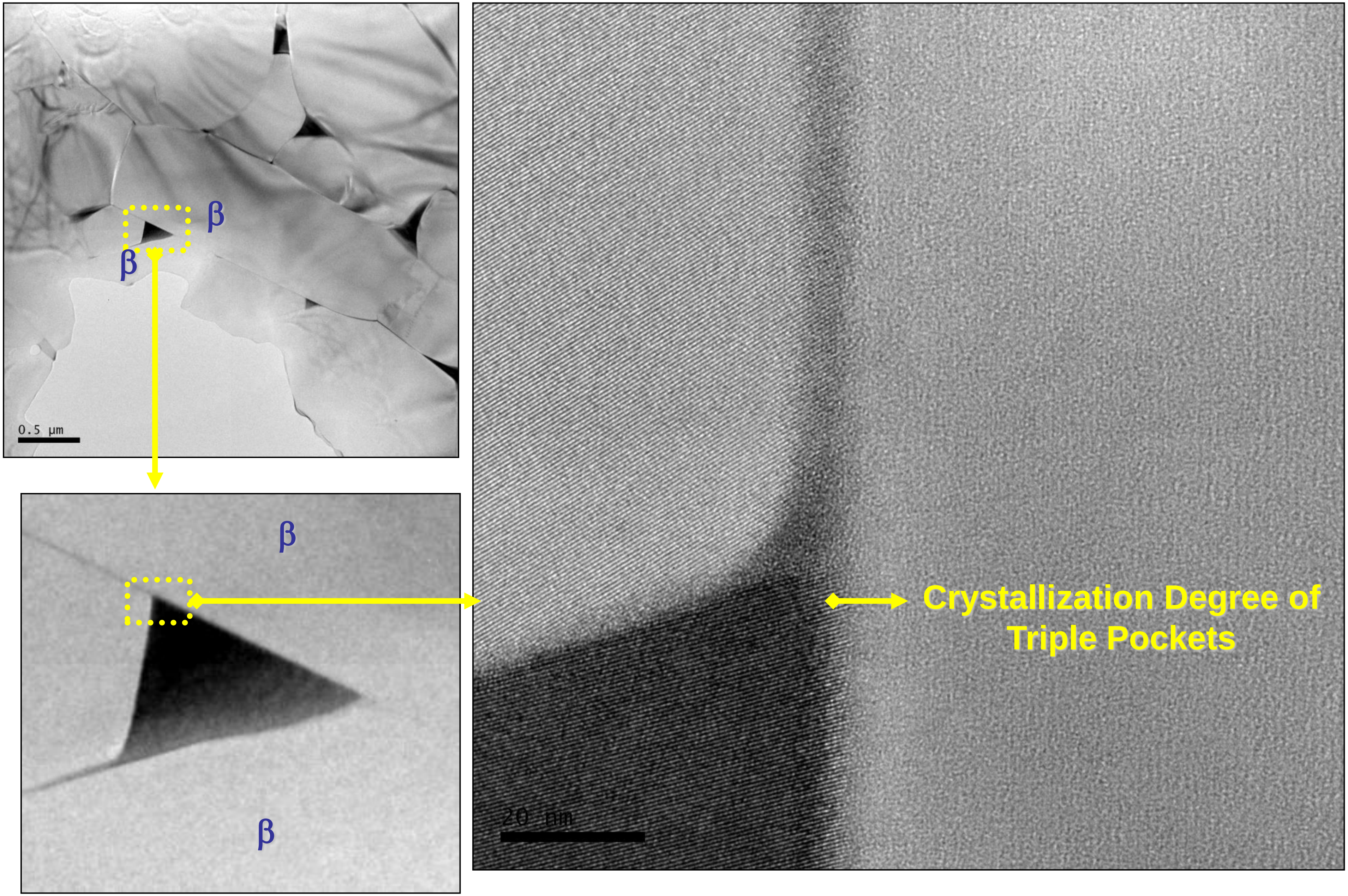




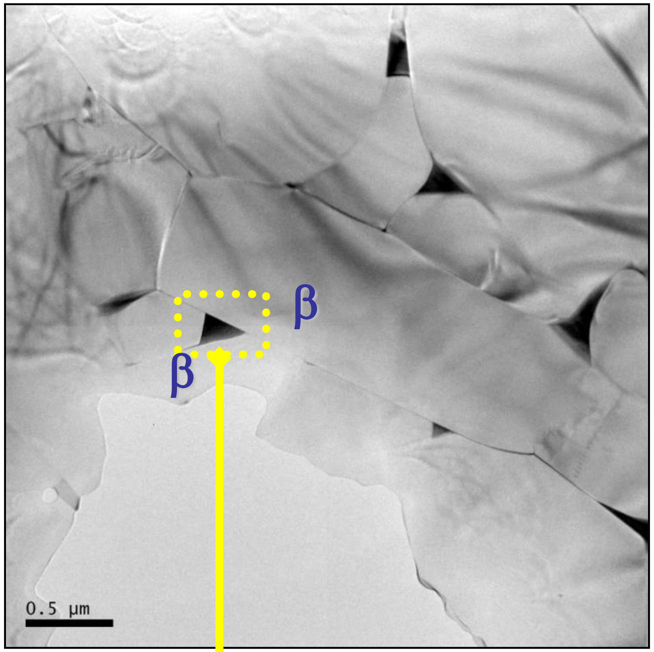
Er-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)

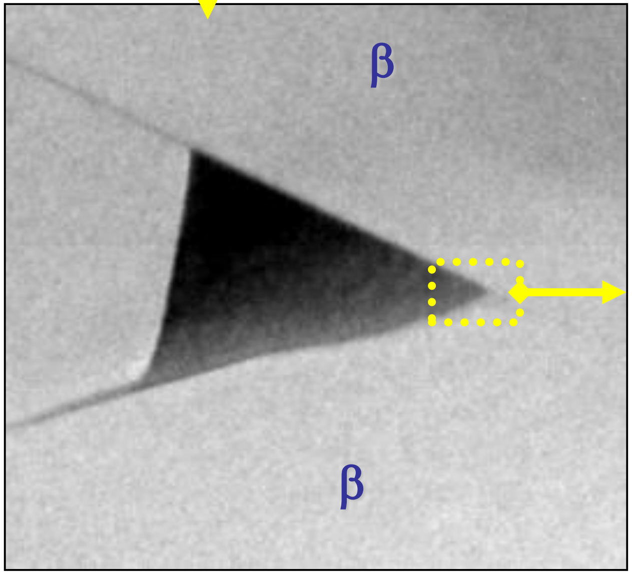


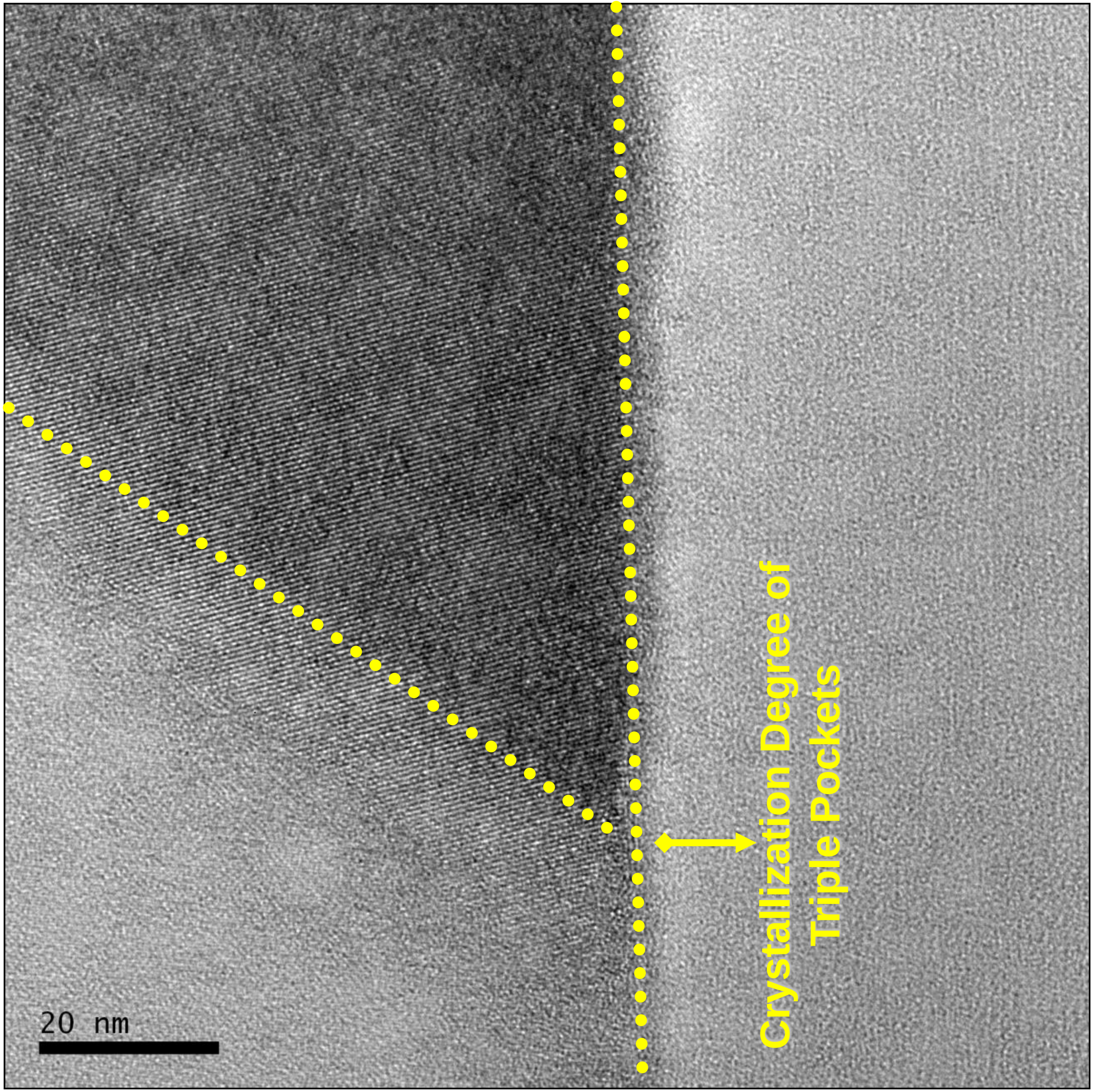
Er-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



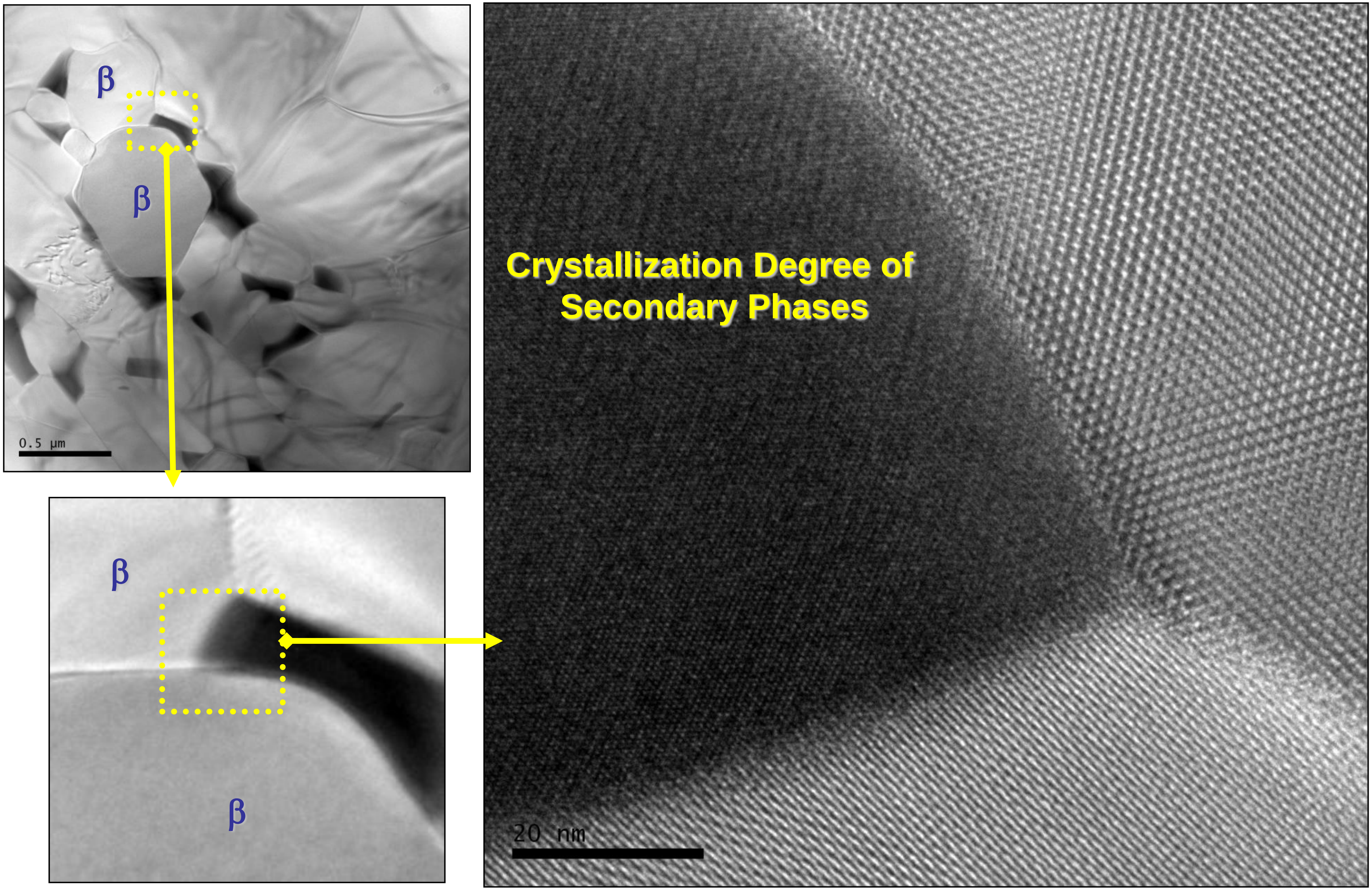
Er-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



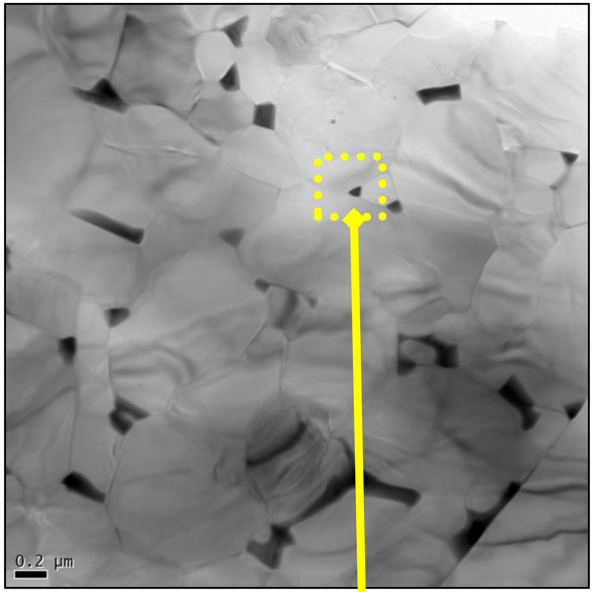


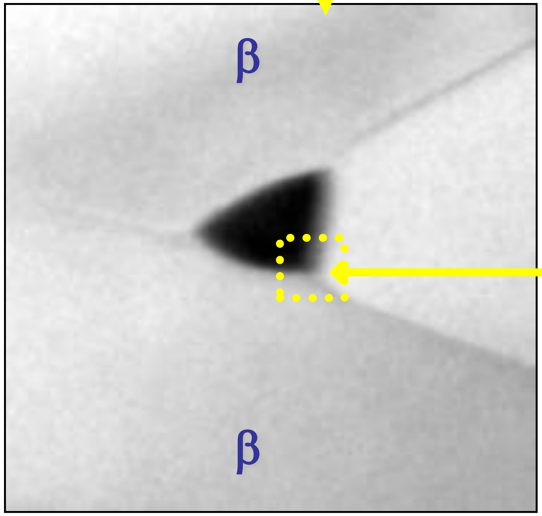


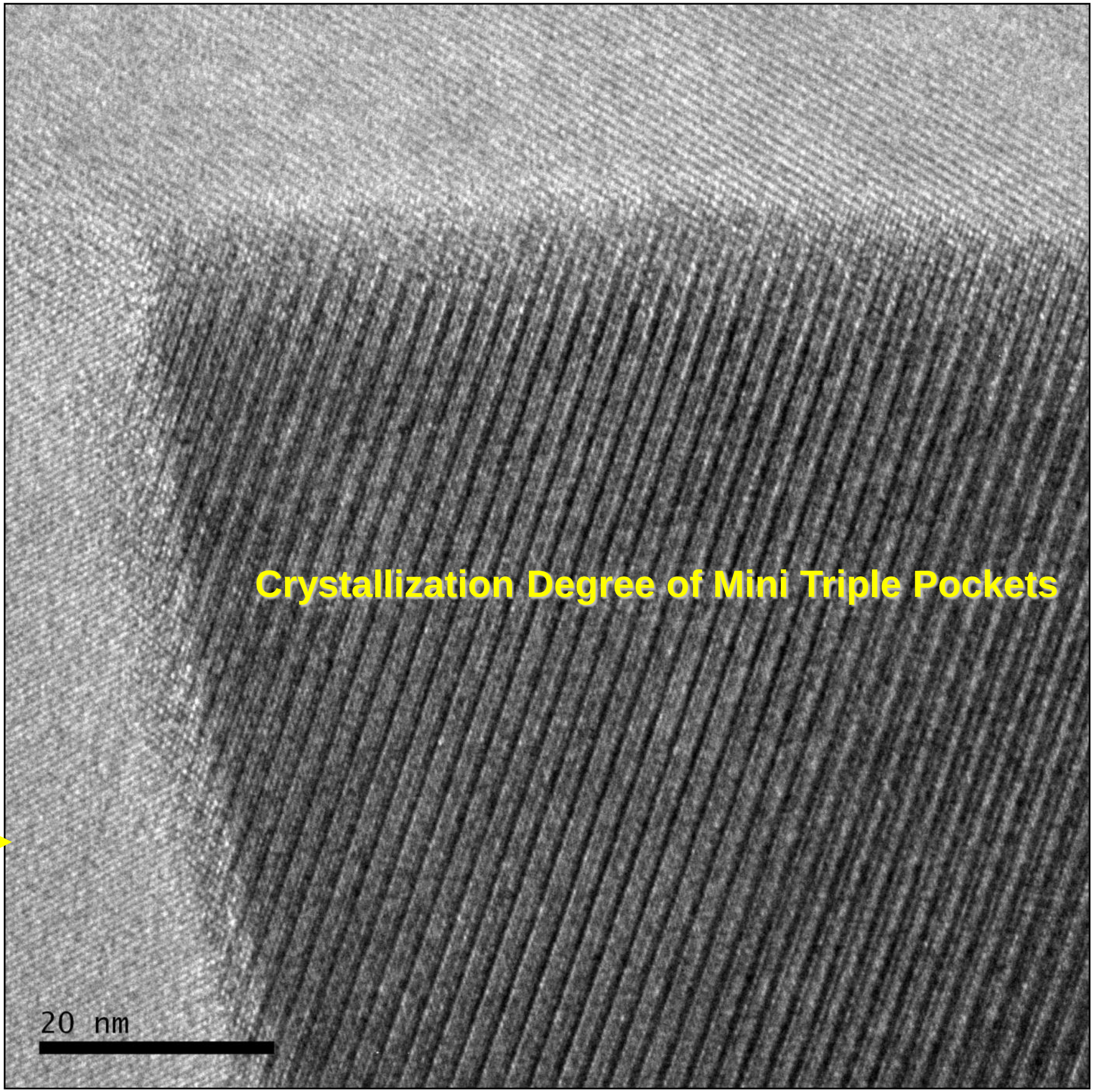
Yb-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



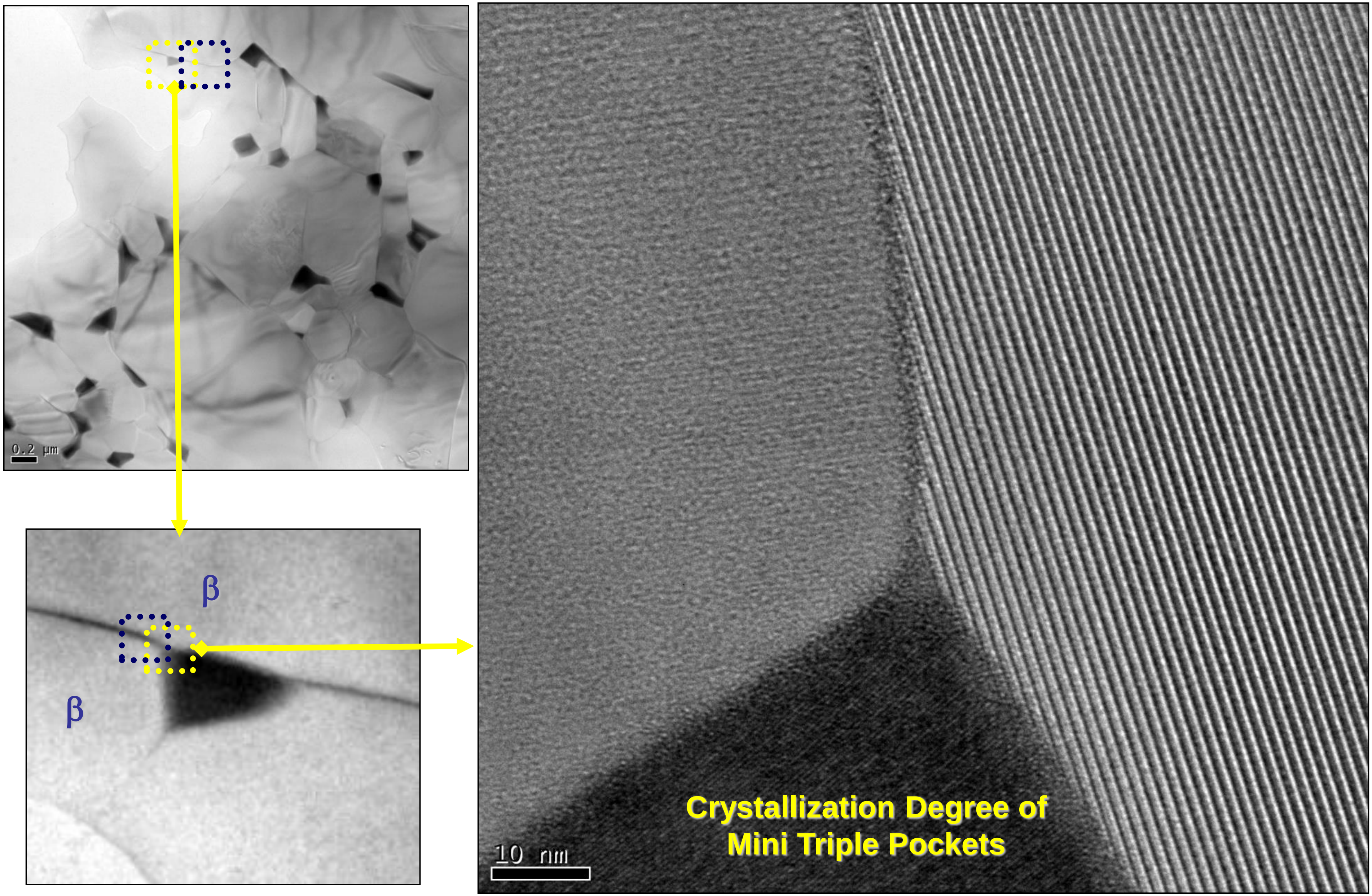
Yb-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



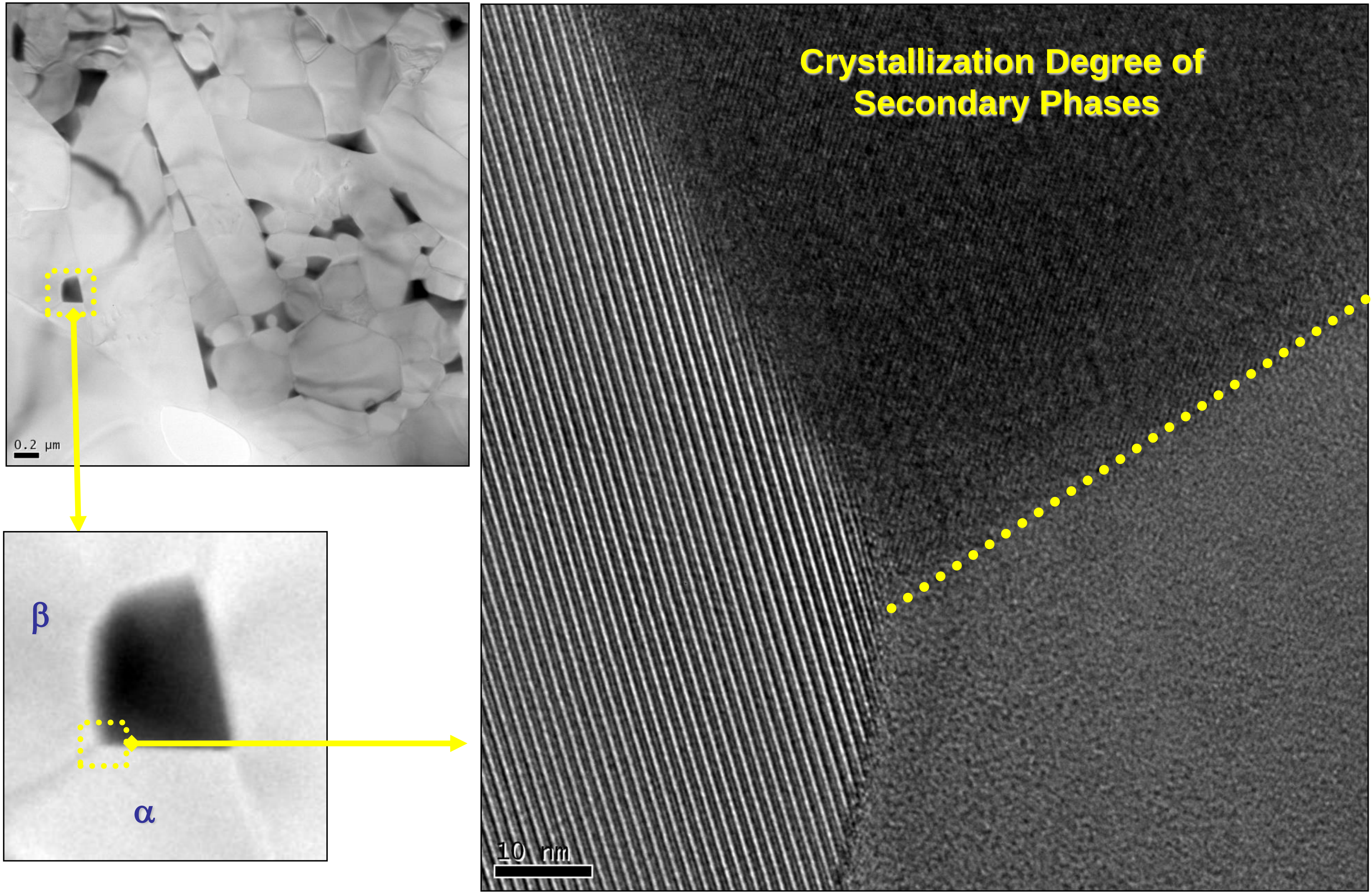




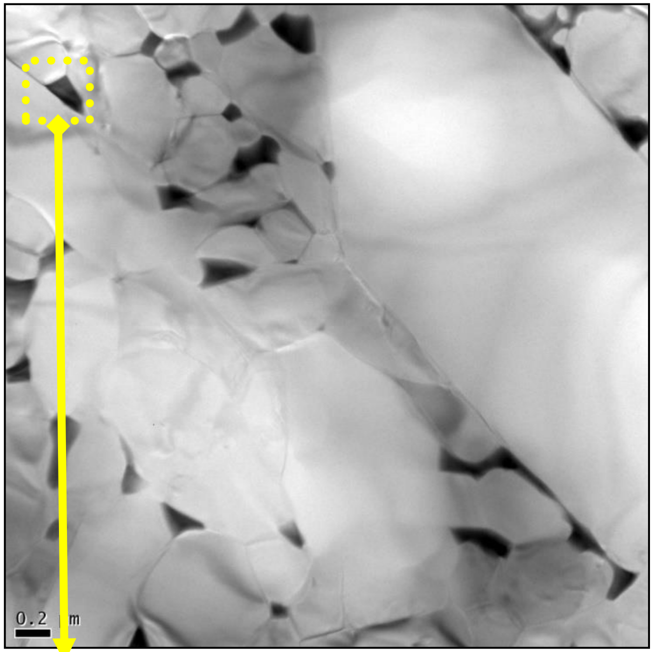
Yb-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)

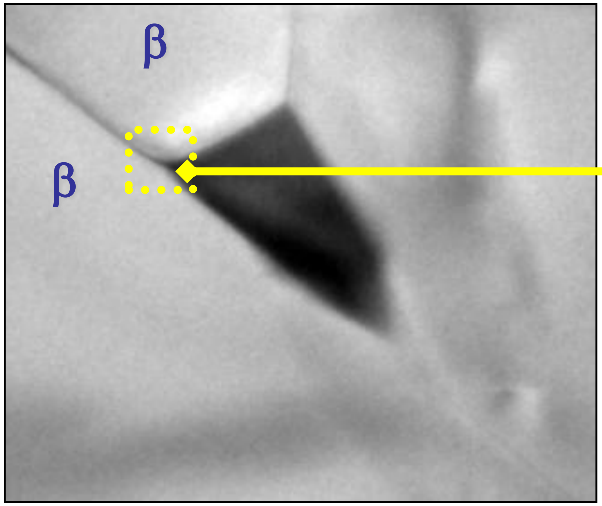


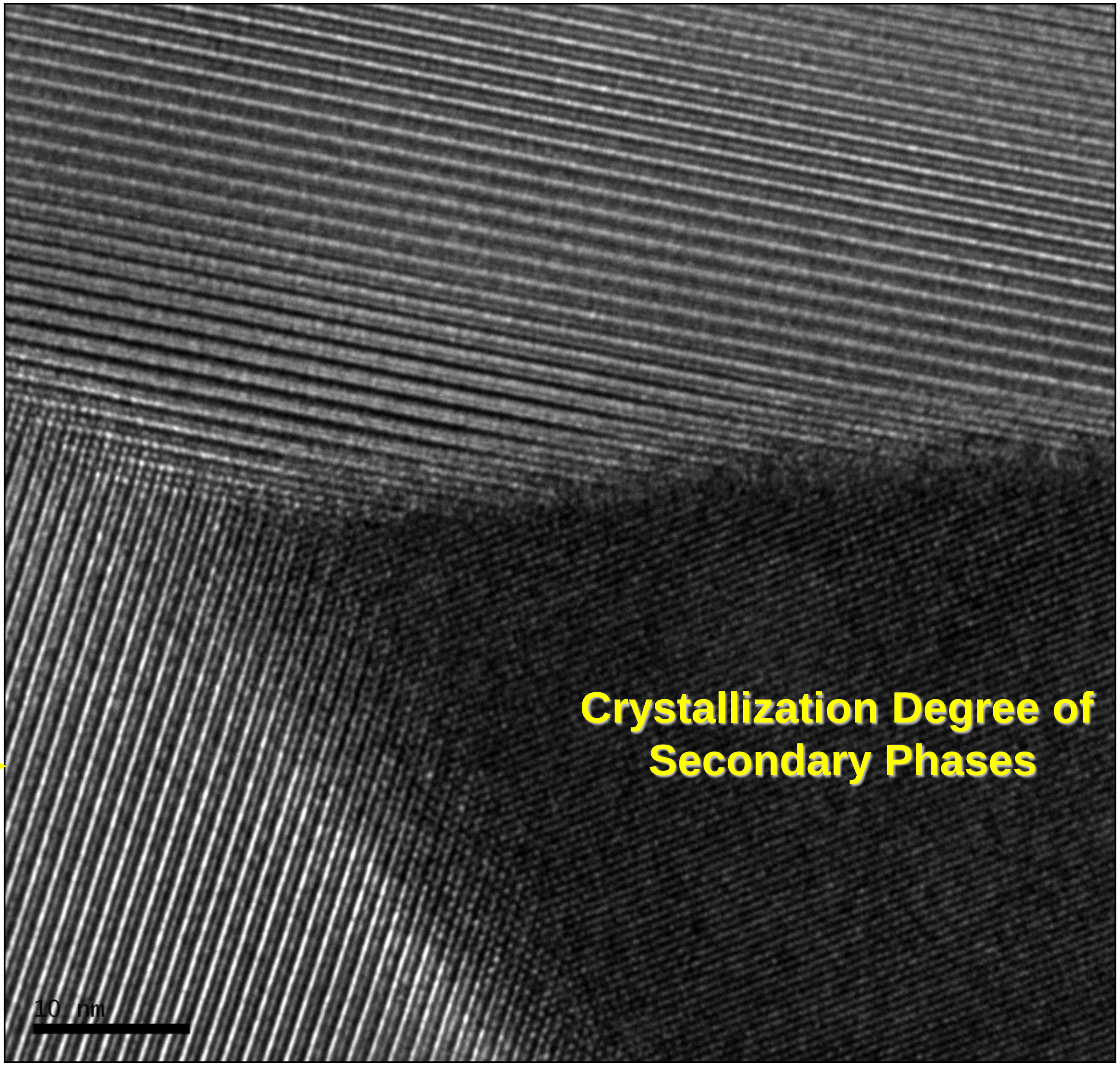
Yb-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)



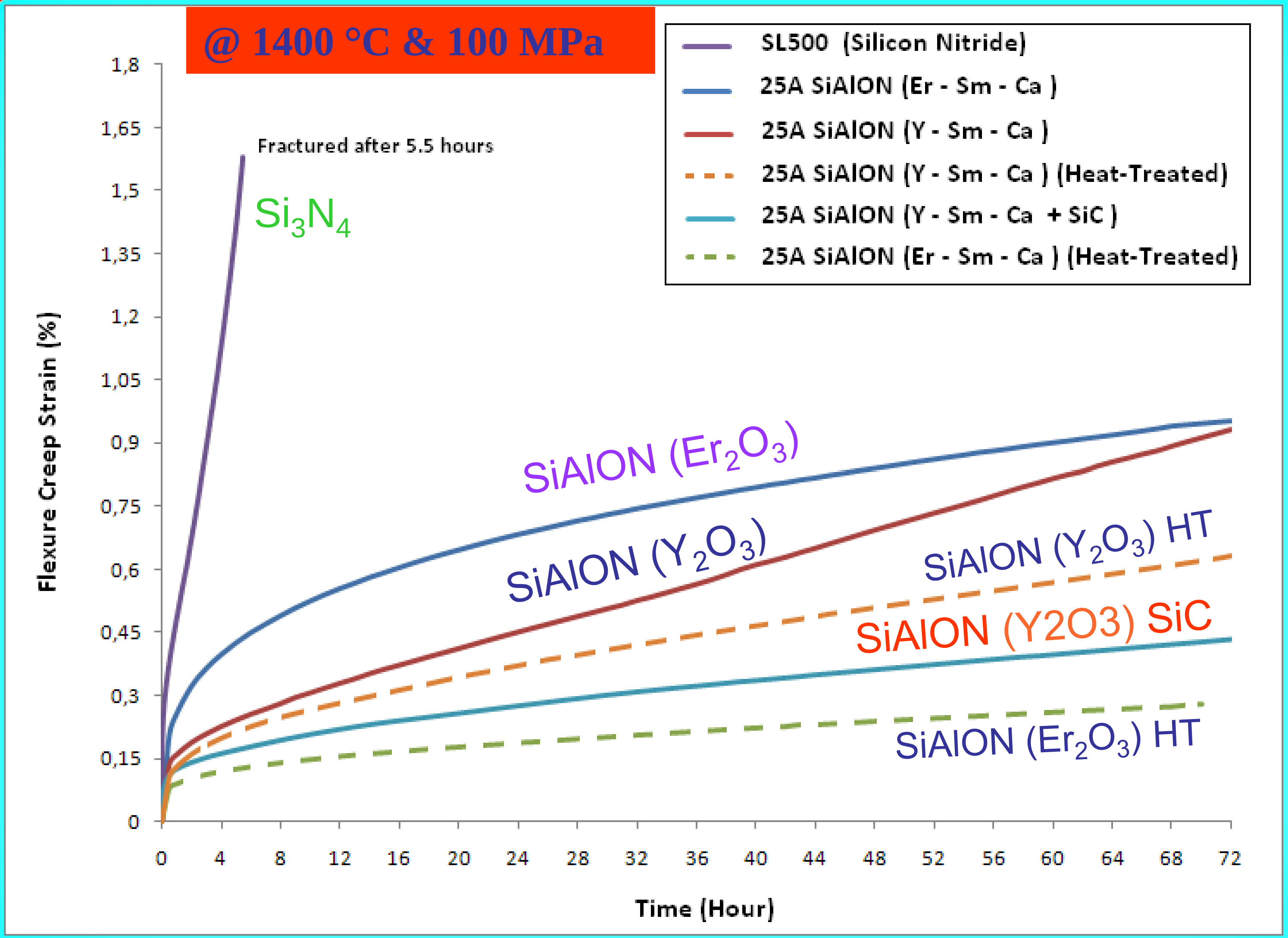
Yb-Sm-Ca Added α/β-SiAlON System (1990 °C sintered and AET)

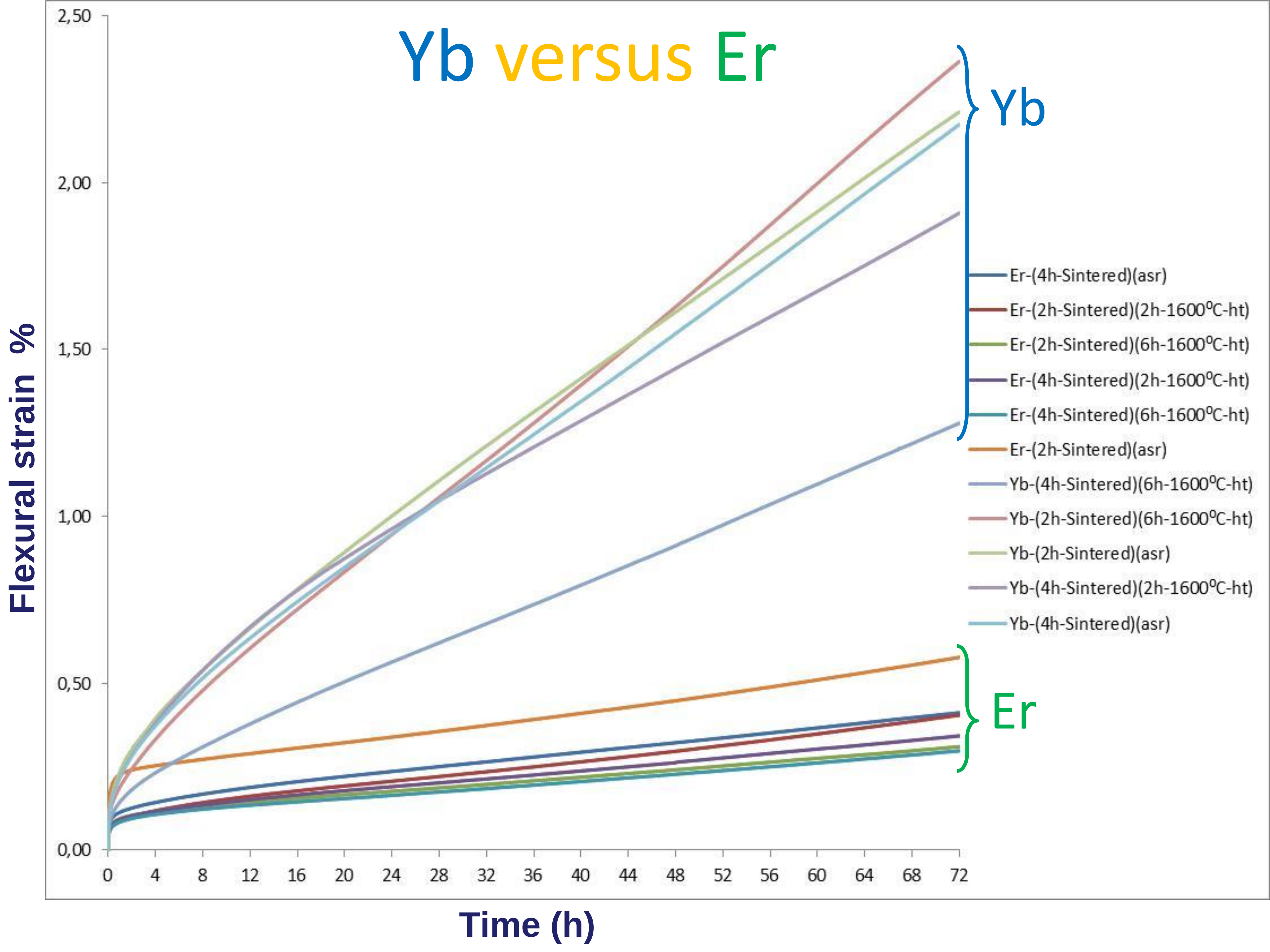






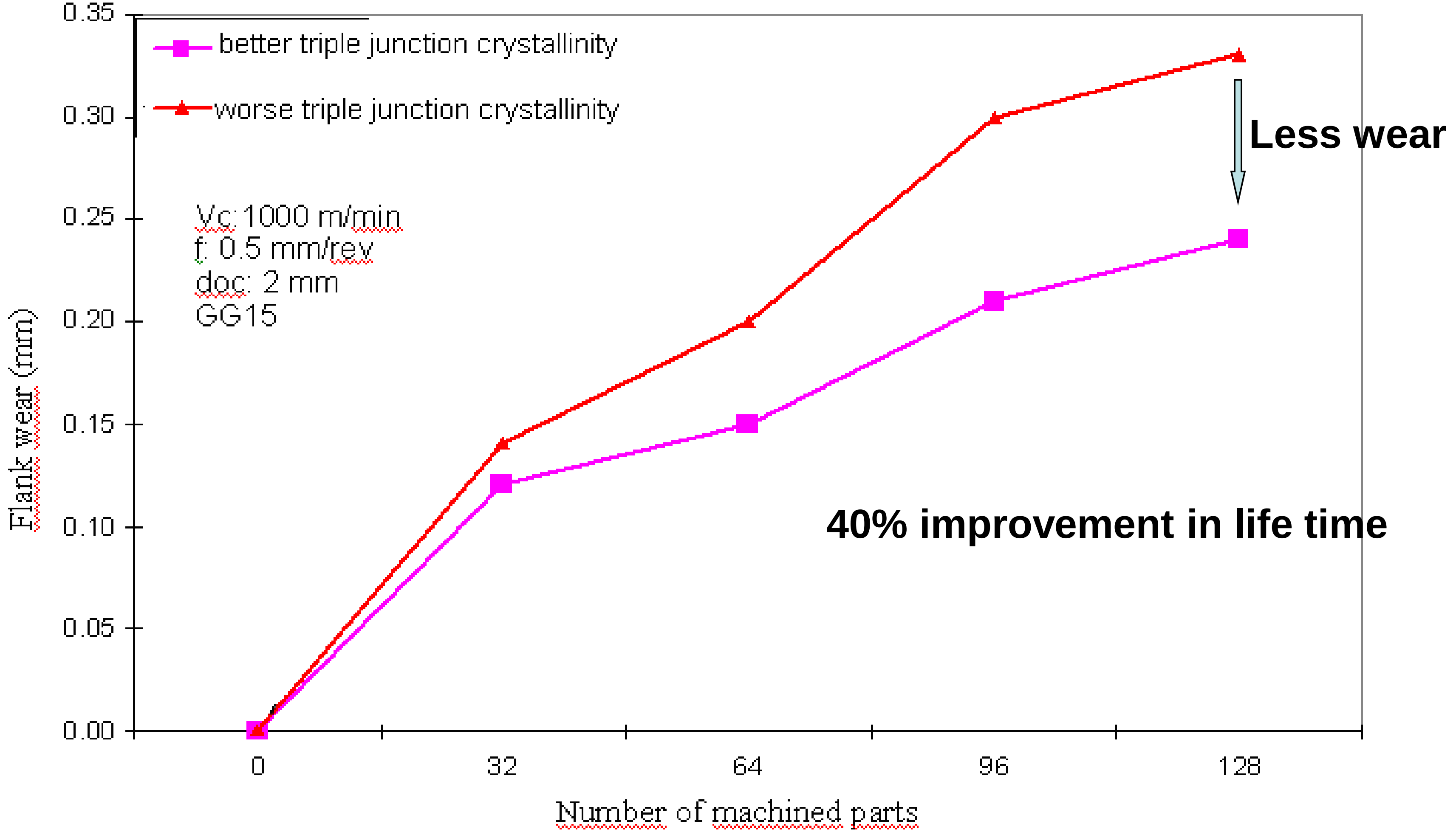
Comparison of Creep Behavior of Si_3N_4 and α/β-SiAlONs





Yb versus Er
Yb
Er
Flexural strain %
Time (h)
2,50
2,00
1,50
1,00
0,50
0,00
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
Er-(4h-Sintered)(asr)
Er-(2h-Sintered)(2h-1600°C-ht)
Er-(2h-Sintered)(6h-1600°C-ht)
Er-(4h-Sintered)(2h-1600°C-ht)
Er-(4h-Sintered)(6h-1600°C-ht)
Er-(2h-Sintered)(asr)
Yb-(4h-Sintered)(6h-1600°C-ht)
Yb-(2h-Sintered)(6h-1600°C-ht)
Yb-(2h-Sintered)(asr)
Yb-(4h-Sintered)(2h-1600°C-ht)
Yb-(4h-Sintered)(asr)

Effect of Crystallinity on the Performance



DESIRE

- Wider mechanical, chemical and refractory applications

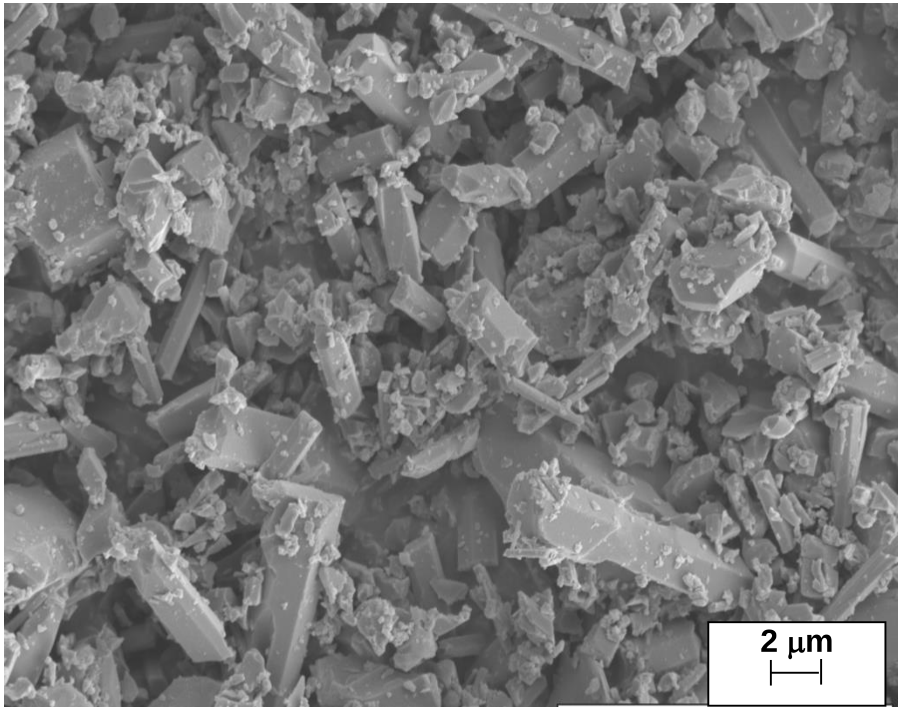
CHALLENGES

- Properties in severe conditions
- Cost of powders and processing

DEVELOPMENT STRATEGIES

- Phase relationships and grain boundary chemistry

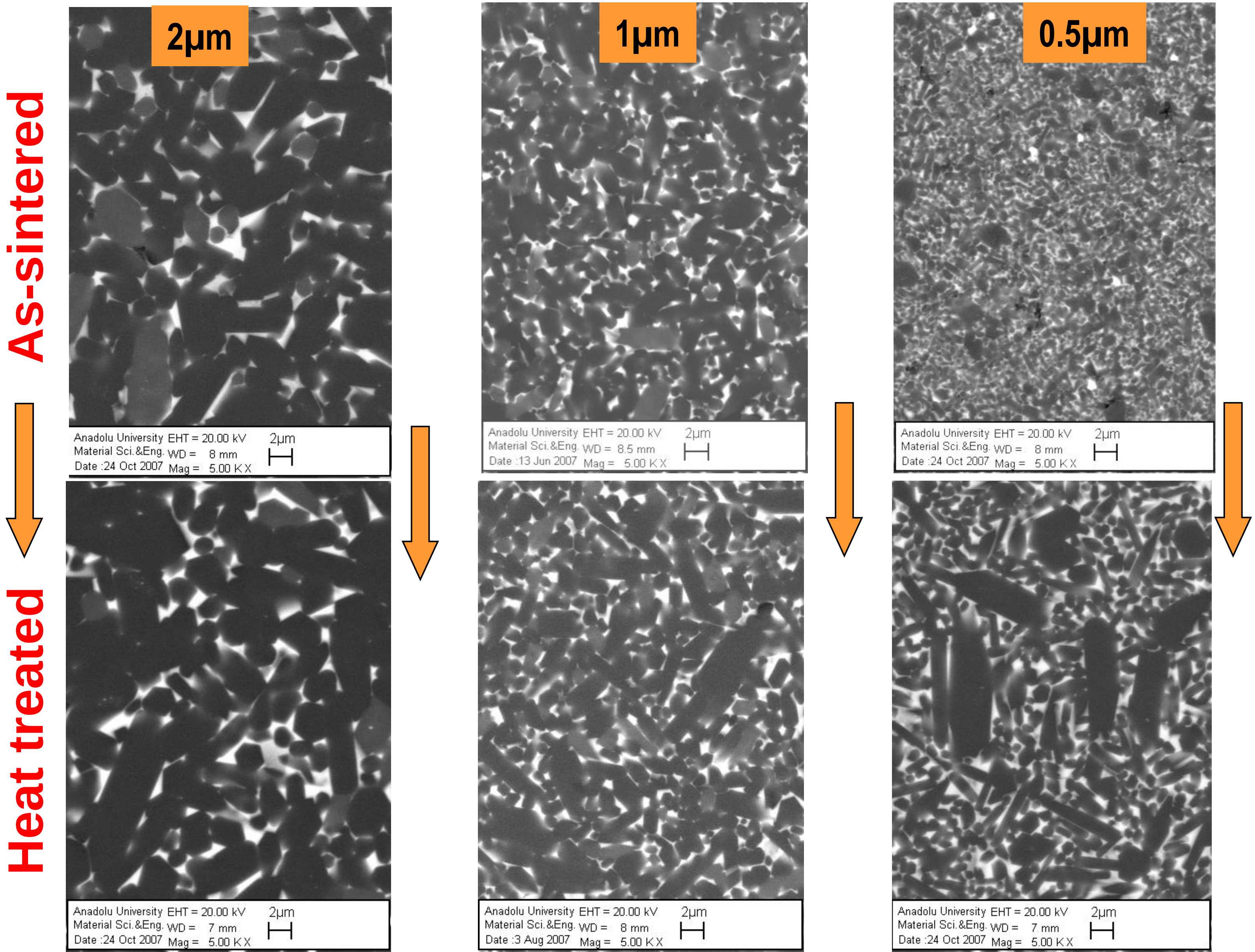
α-β SiAlON from β-Si_3N_4 powder containing impurities



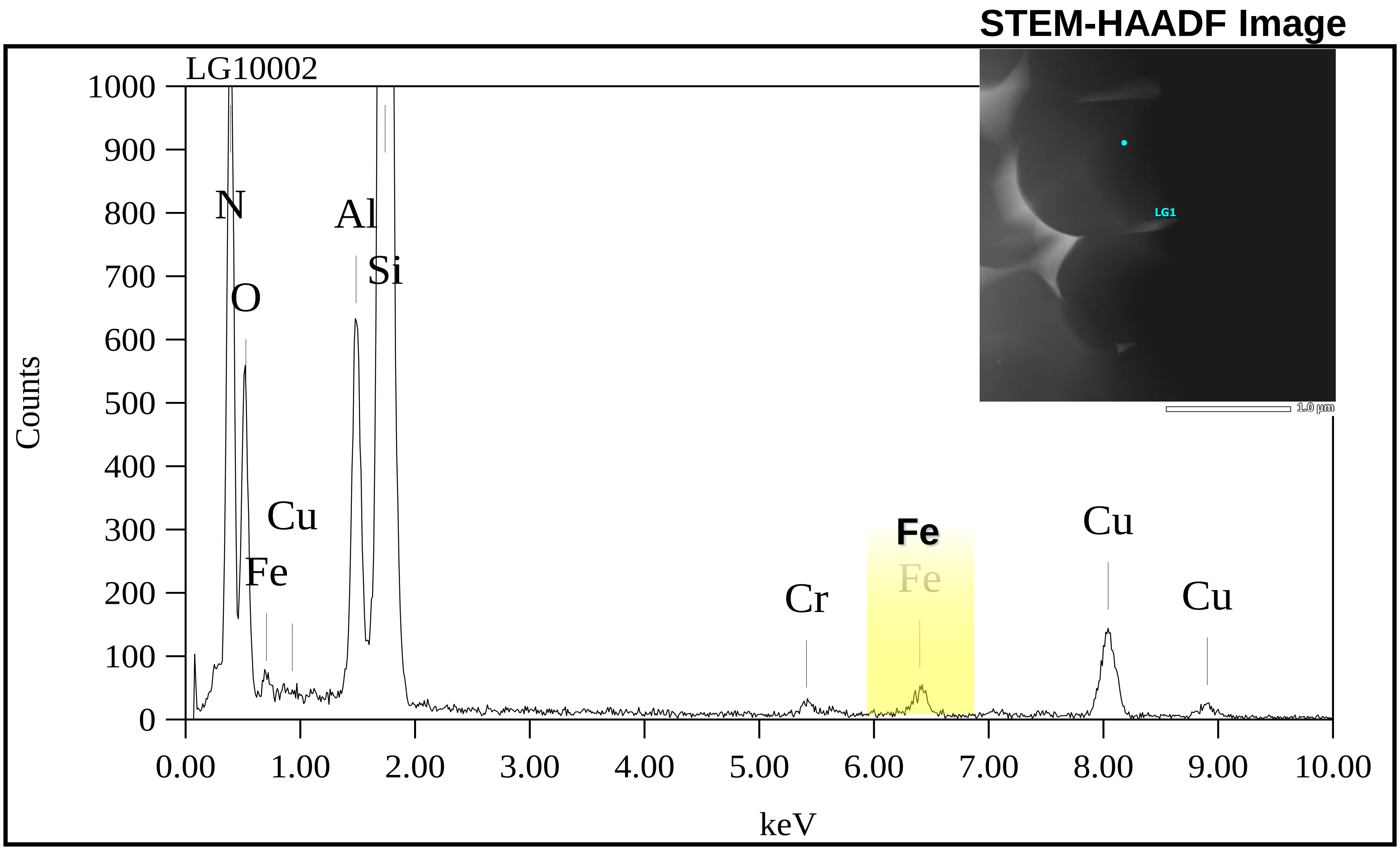
D_{50} = 5 µm

	Al2O3	MgO	CaO	Fe2O3	TiO2
β-Si_3N_4	1,4	≤0,05	0,40	0,60	0,07

Microstructures of SiAlON from different particles size β –Si_3N_4 powders



Impurity/dopant incorporation into β-SiAlON



Si6-z(Al,Fe)zOzN8-z

Improved grain boundary crystallization
Transient liquid phase sintering
Impurity incorporation

↓ to enable

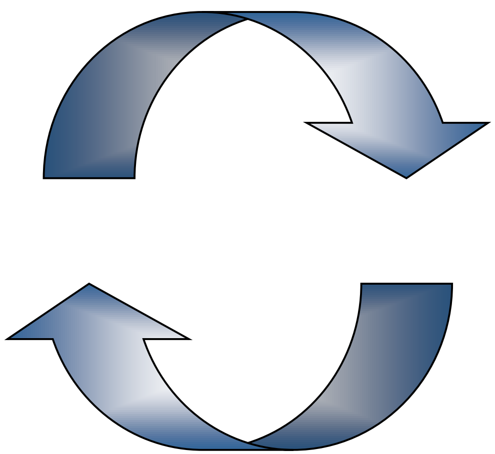
Cost reduction

- Use of coarse and/or impure and/or β-Si_3N_4 powders
- Increased amount of (crystallizable) liquid phase
- Lower temperature and/or pressureless sintering

Conclusion

Opportunities are present to increase the applications of SiAlON based ceramics by **chemistry** and **process improvement**.

MARKET SIZE



- **BETTER PROPERTIES**
- **COST**