HR-TEM study of the silicon segregation at grain boundaries in Yb:YAG ceramics for laser applications

T. EPICIER, A. MALCHÈRE, ***MATEIS, INSA-Lyon - CNRS,*** **Villeurbanne FRANCE**

L. ESPOSITO, J. HOSTASA, A. PIANCASTELLI, ***Research Council of Italy, ISTEC*****, Faenza ITALY**

M. GUZIK, ***Faculty of Chemistry,*** **University of Wrocław POLAND**

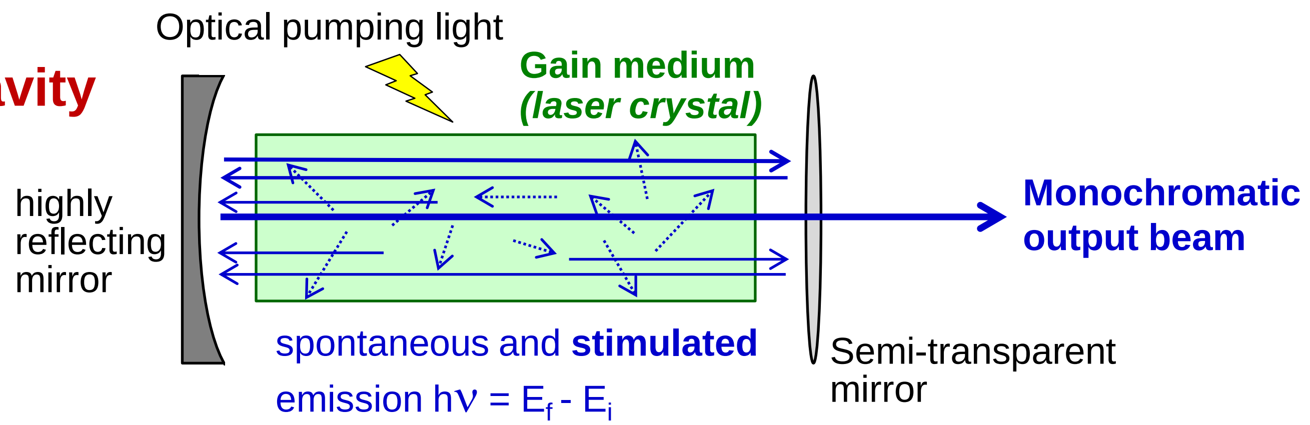
G. BOULON, ***ILM, Université Lyon 1-CNRS*****, Villeurbanne FRANCE**

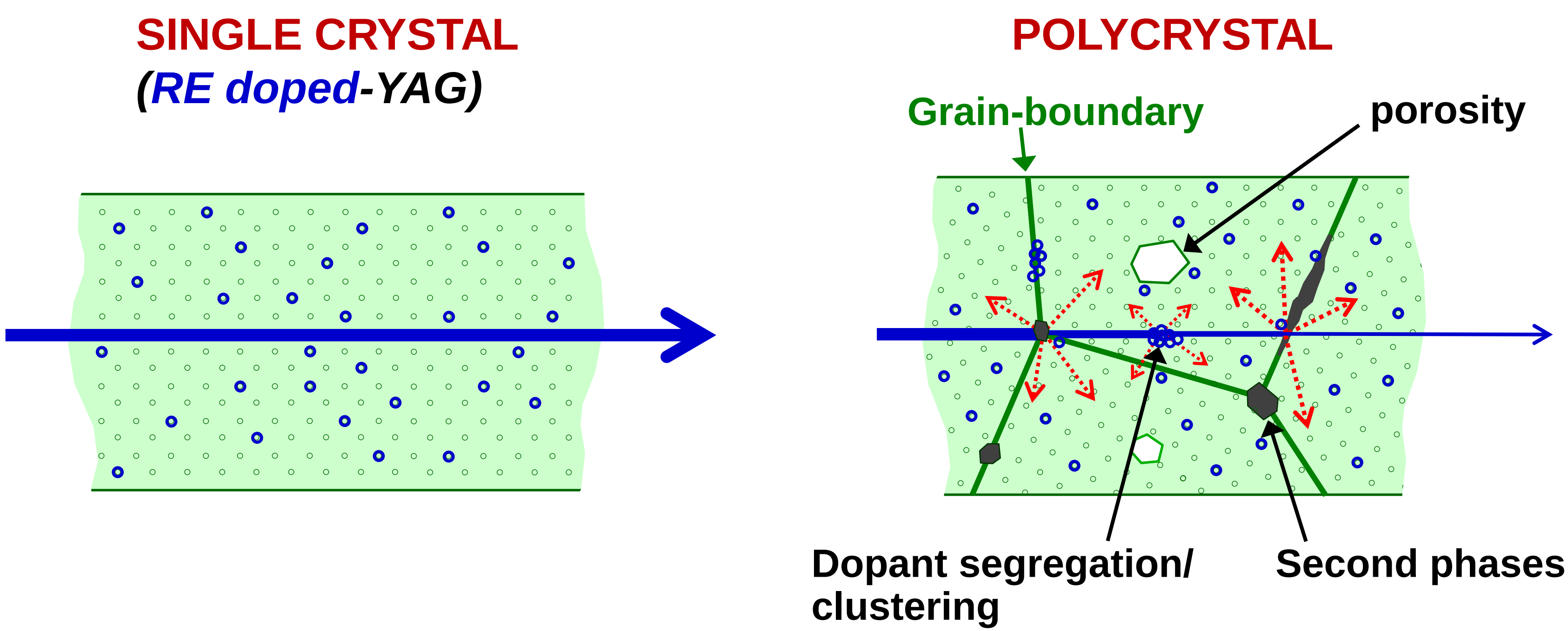
OUTLINE

- INTRODUCTION: POLYCRYSTALLINE CERAMICS for LASER APPLICATIONS
- HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY and NANO-ANALYTICAL RESULTS
- DISCUSSION and CONCLUSIONS

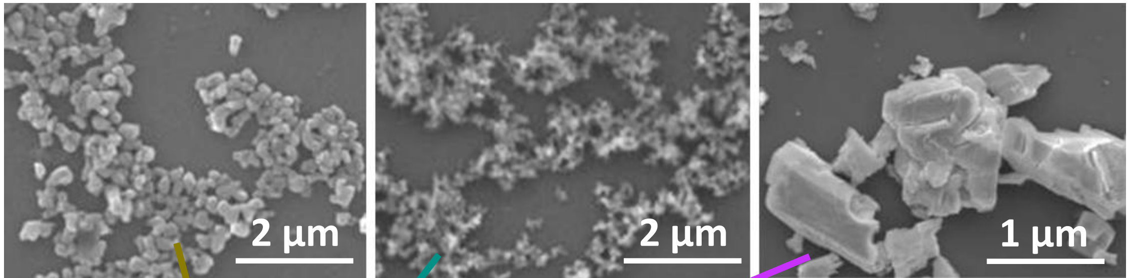
1. INTRODUCTION: POLYCRYSTALLINE CERAMICS for LASER APPLICATIONS

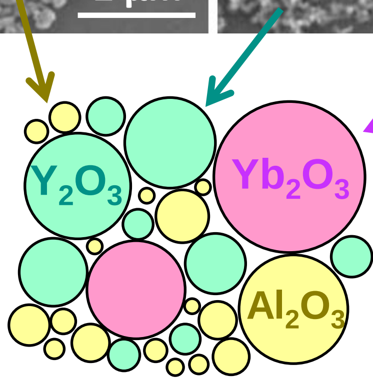
LASER resonating cavity





• Relation OPTICAL PROPERTIES / SEGREGATION EFFECTS

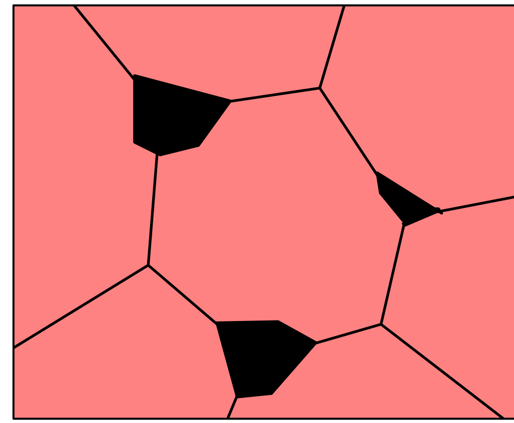




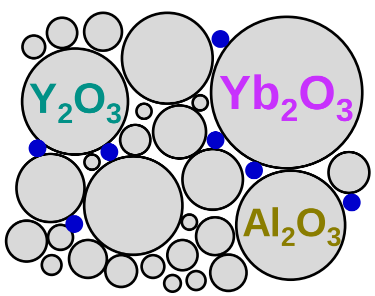
4N Commercial oxides
(Taimei, Nanocerox, Alfa Aesar Reacton)

Sintering

1735°C, 16 h,
high vacuum (10^{-6} mbar)

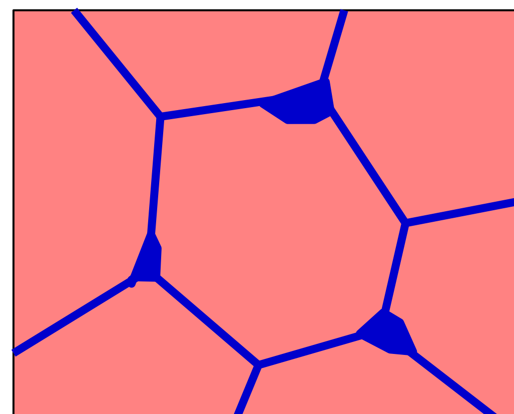


• Internal porosity



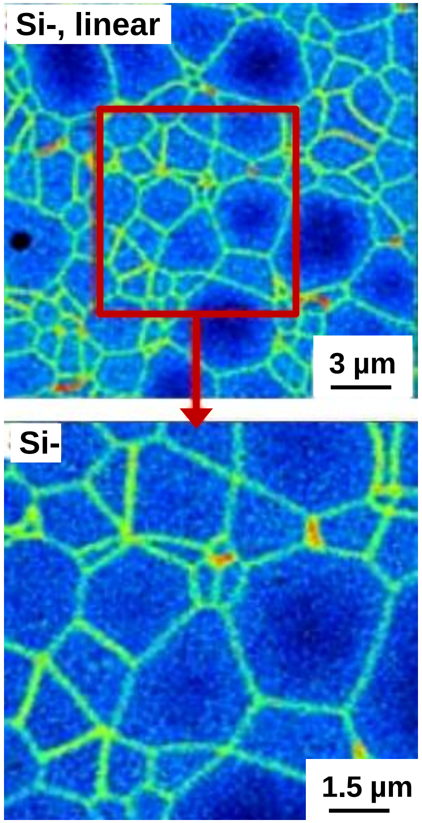
Sintering aid: SiO_2
1.4 at. %

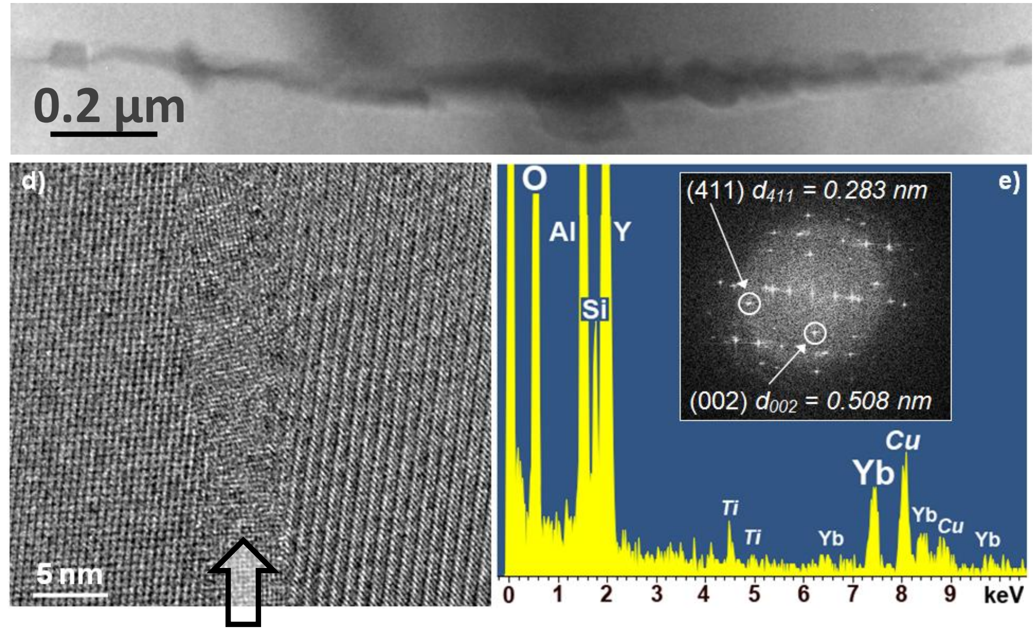
eutectic SiO_2 - Y_2O_3 - Al_2O_3 at 1371°C
[U. KOLITSCH et al., *J. Mater. Res.*, **14** (1999) 447–55]



• Si segregation at GB
• crystallisation of Y_2SiO_5 / $Y_2Si_2O_7$

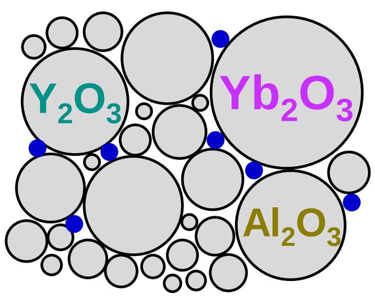
Si segregation *(nano-SIMS)* http://www.cameca.com/applications/materials/ns-trace-element-yag.aspx





Y_2SiO_5

[L. ESPOSITO, T. EPICIER et al., *J. Eur. Ceram. Soc.* **32** (2012) 227]

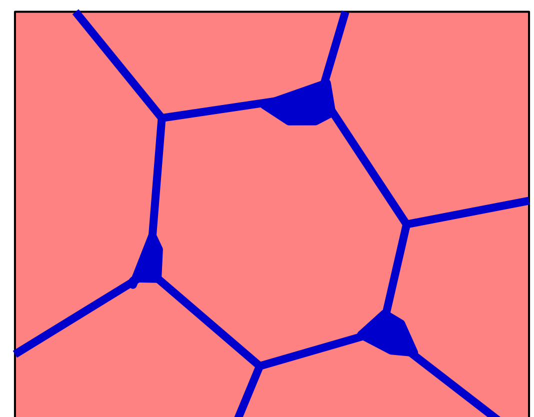


Sintering aid: SiO_2

1.4 at. %

eutectic SiO_2 - Y_2O_3 - Al_2O_3 at 1371°C

[U. KOLITSCH et al., *J. Mater. Res.*, **14** (1999) 447–55]

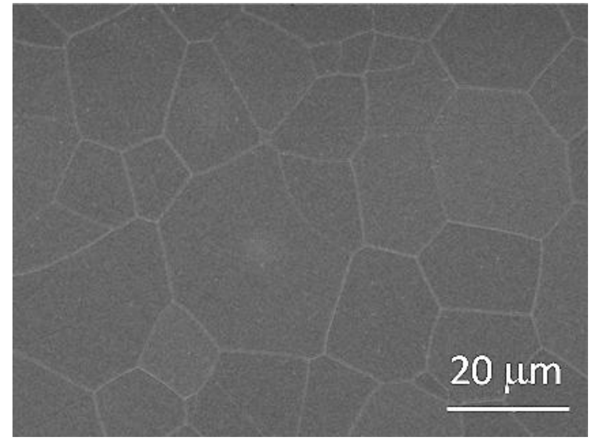


- **Si segregation at GB**
- **crystallisation of Y_2SiO_5 / $Y_2Si_2O_7$**

• GB Engineering through adequate ANNEALING?

→ Re-oxidizing Yb (Yb^{3+})

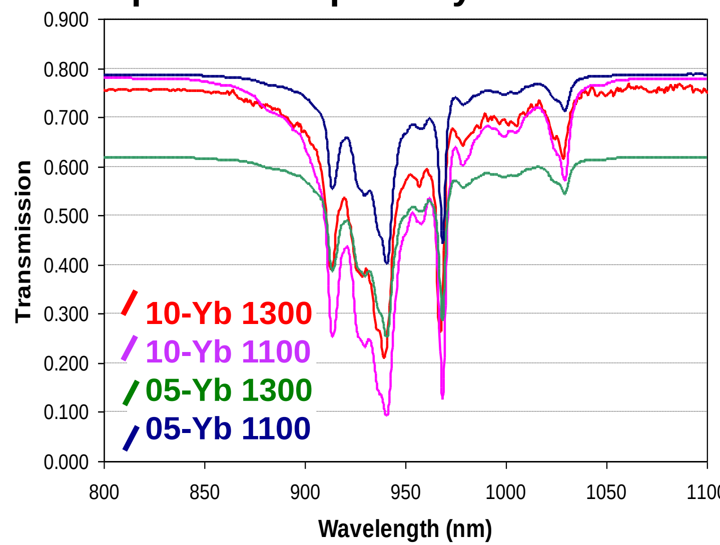
As sintered | Partially annealed | **Fully annealed**



• Comparison of TWO different ANNEALING scheme; a): OPTICAL PROPERTIES

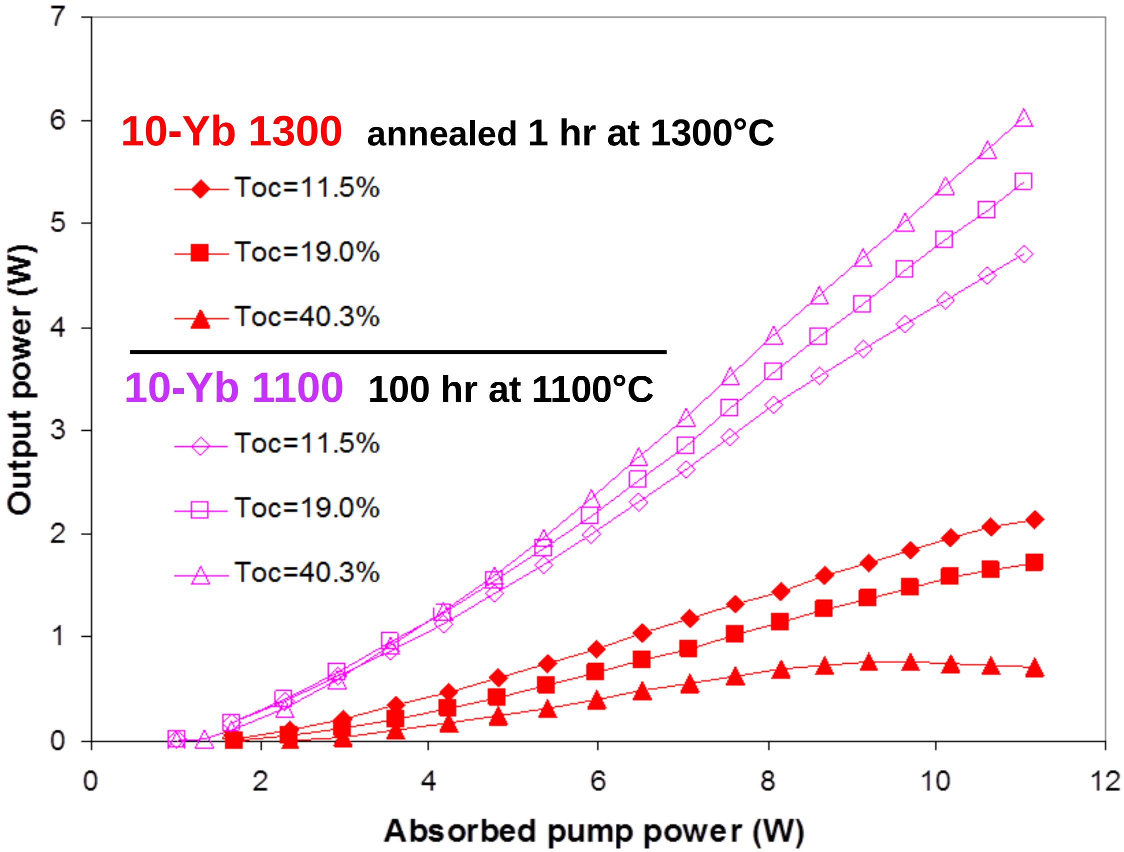
	Sample	annealing treatment	scattering coef. α_{sc} (cm^{-1})
10 at.% Yb/Y	10-Yb 1300	1 hr at 1300°C	0.88
	10-Yb 1100	100 hr at 1100°C	↘ 0.58
5 at.% Yb/Y	05-Yb 1300	1 hr at 1300°C	1.85
	05-Yb 1100	100 hr at 1100°C	↘ 0.55

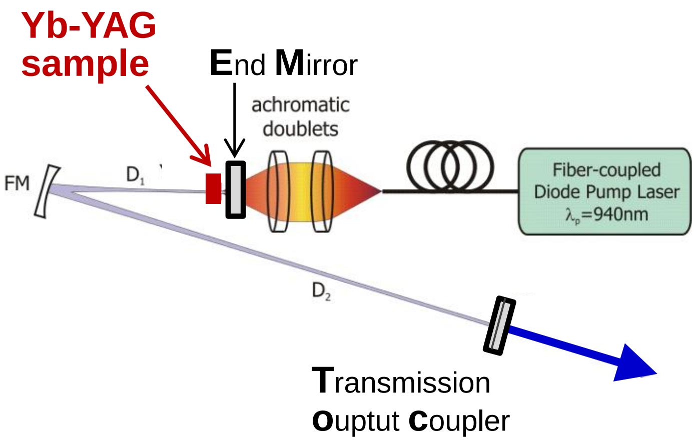
Optical transparency



⇨ **BETTER TRANSPARENCY after ANNEALING at 1100°C**

• **Comparison of TWO different ANNEALING scheme; b): LASER POWER**





⇨ **BETTER ENERGY CONVERSION after ANNEALING at 1100°C**

2. HRTEM and NANO-ANALYTICAL RESULTS

• EXPERIMENTAL BACKGROUND

JEOL **2010F** 200 kV

OXFORD INSTRUMENTS **SDD XMAX**-80 mm²

Conventional HREM imaging

Nano-probe (0.8 – 2.4 nm) **EDX analysis**

Thin foils (Ar Ion Beam thinning
+ O_2-N_2 plasma cleaning)

FEI **TITAN HB** 300 kV, **double C_s-corrected**

gatan **EELS** 866 spectrometer

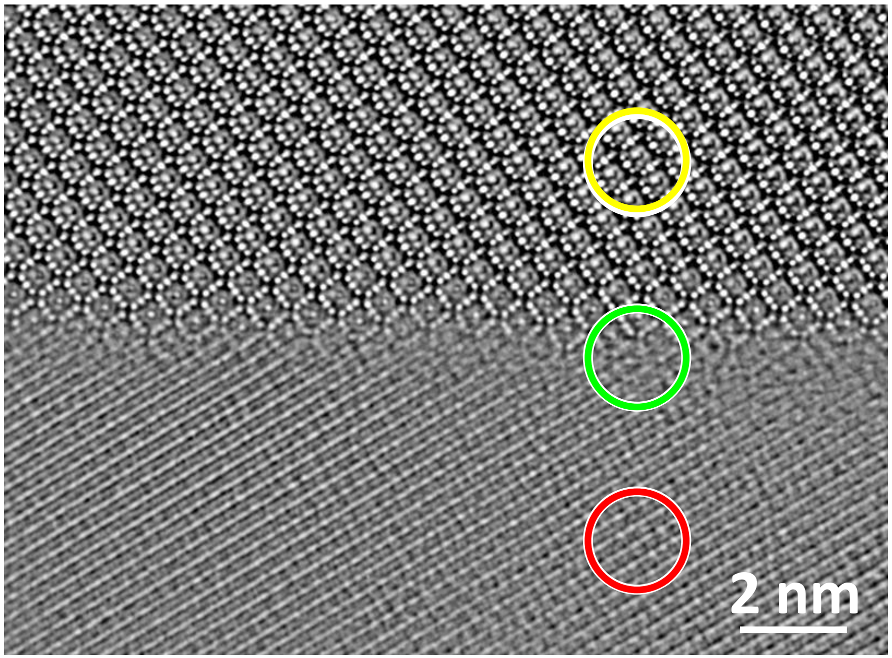
ccem Canadian Centre for Electron Microscopy

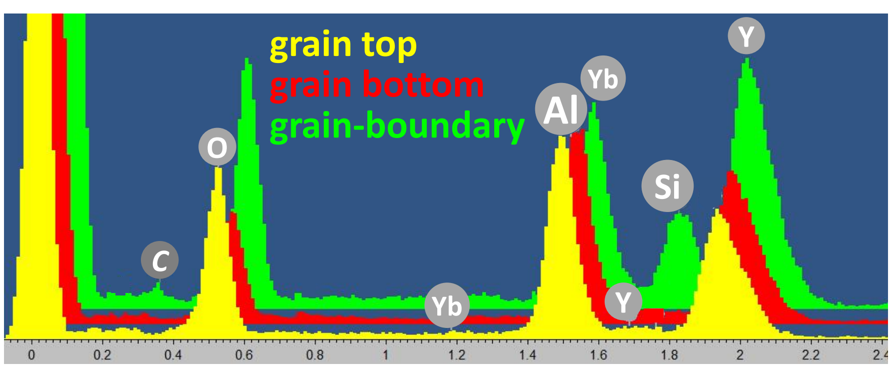
Atomic STEM-HAADF (EELS) **imaging**

2. HRTEM and NANO-ANALYTICAL RESULTS

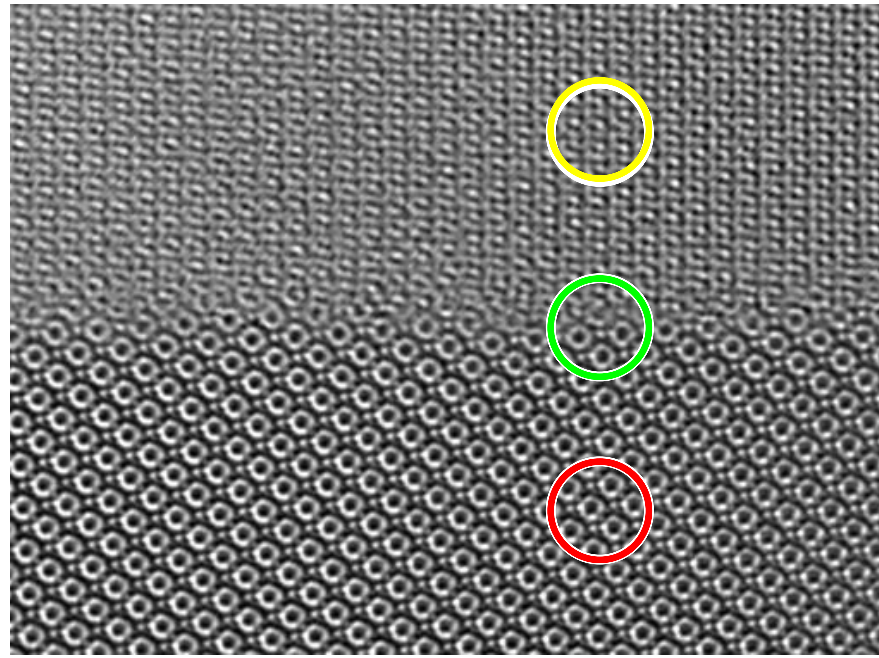
• SEGREGATION at Grain-Boundaries

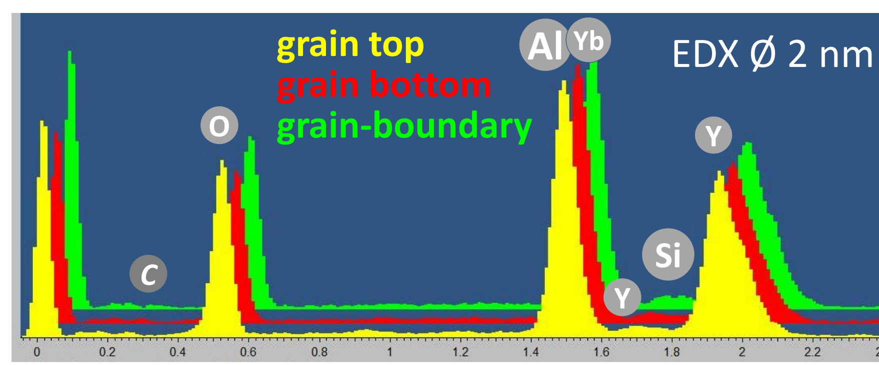
Annealing at 1300°C: ***blurred HREM contrast at GB…***





Annealing at 1100°C: ***much cleaner contrast at GB…***

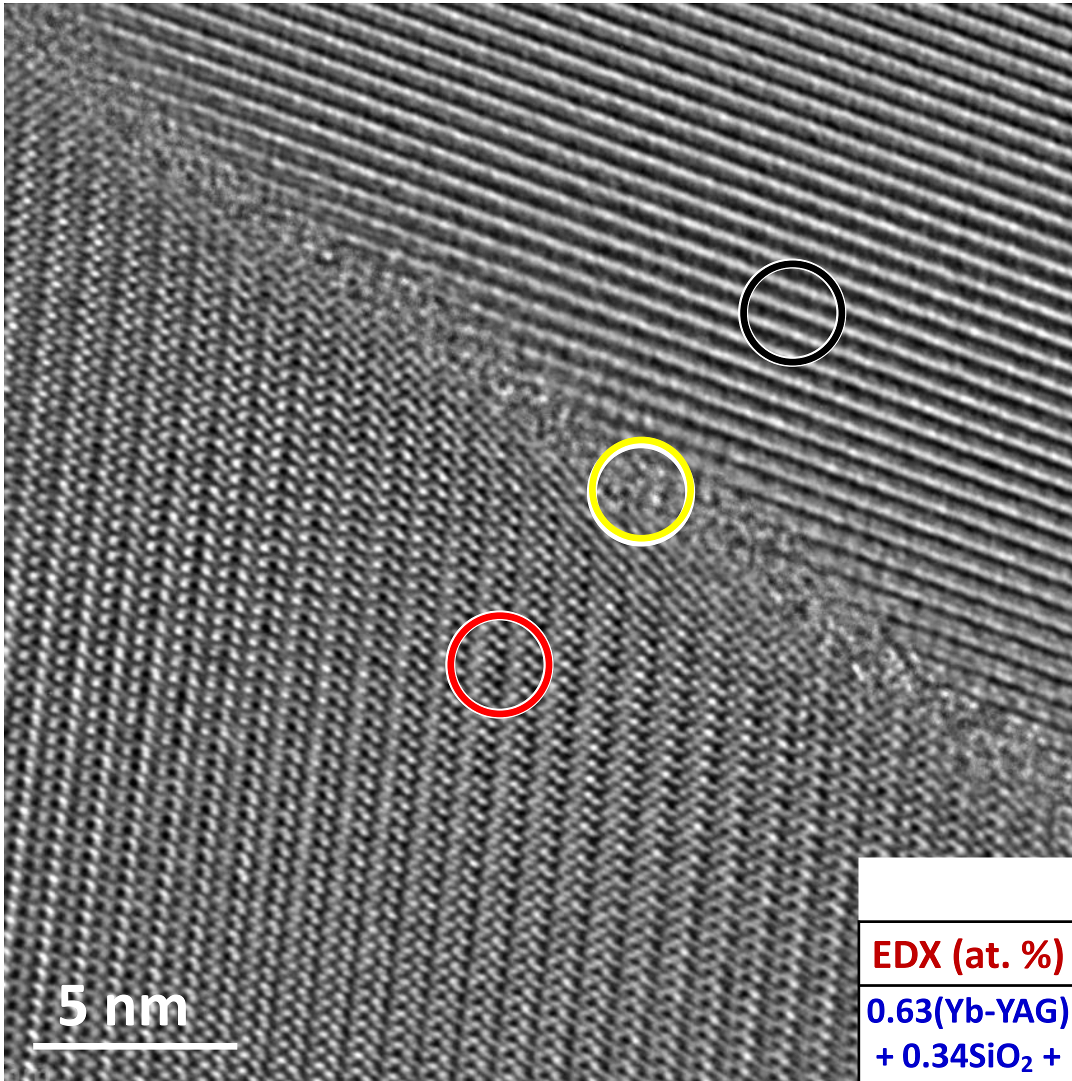


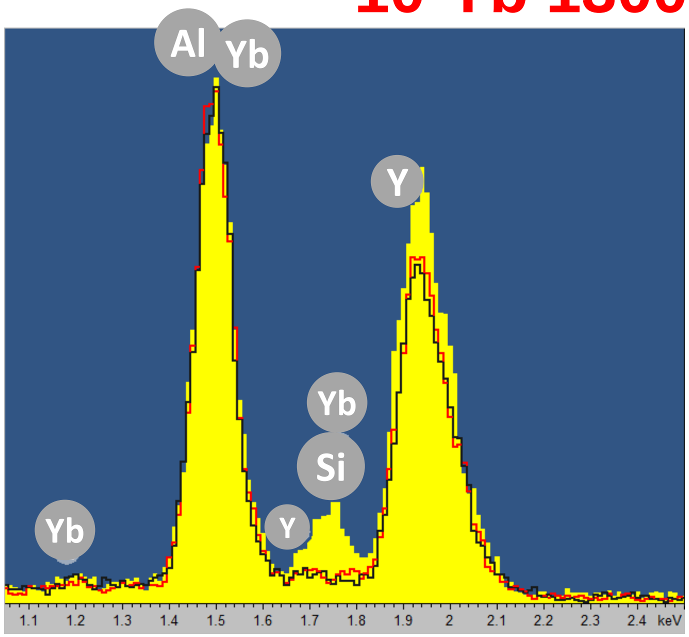


2. HRTEM and NANO-ANALYTICAL RESULTS

- **Note: quantitative EDX Measurement**

10-Yb 1300





LMS fitting:

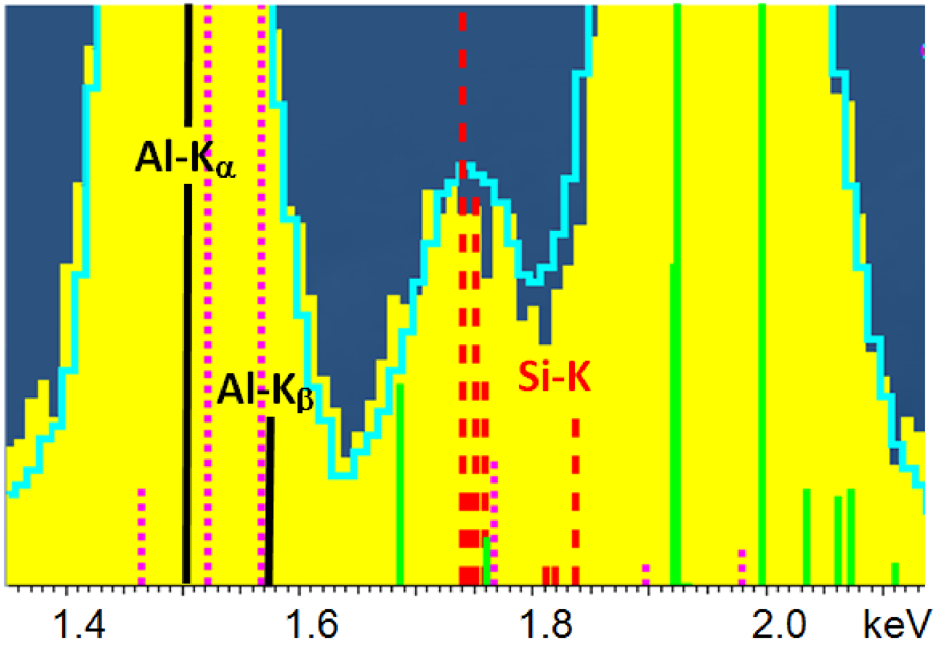
$\alpha(\text{Yb-}Y_3Al_5O_{12}) + \beta SiO_2 + \gamma Y_2O_3$

	Yb	O	Y	Al	Si
EDX (at. %)	1.29%	60.55%	12.72%	22.95%	2.49%
0.63(Yb-YAG) + 0.34SiO_2 + 0.03Y_2O_3	1.38%	60.50%	12.71%	22.92%	2.49%

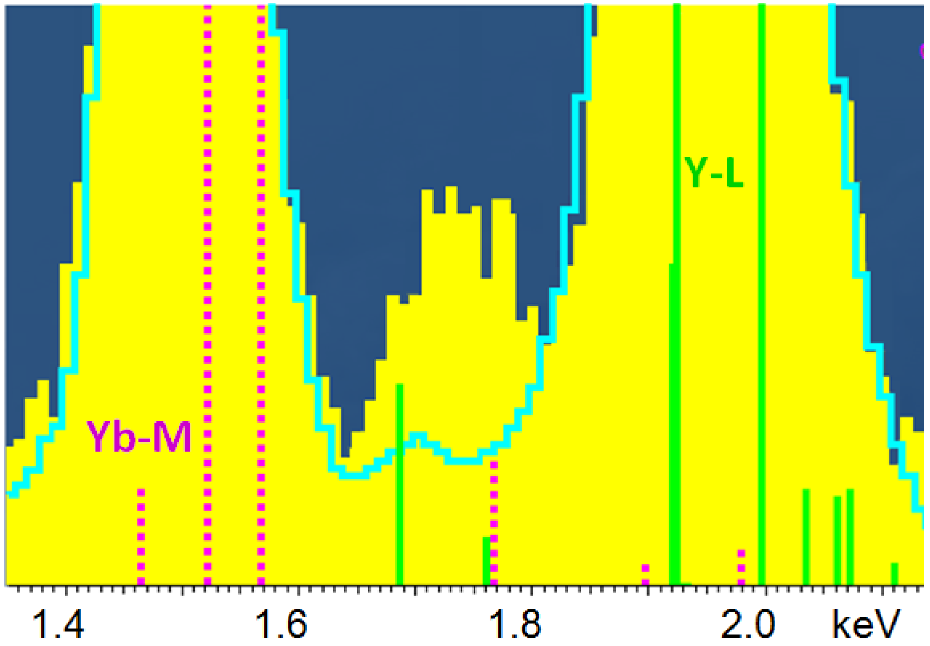
2. HRTEM and NANO-ANALYTICAL RESULTS

• Note: quantitative EDX Measurement

spectrum reconstruction *with* 2.4$_9$ at. % Si



spectrum reconstruction *without any* Si

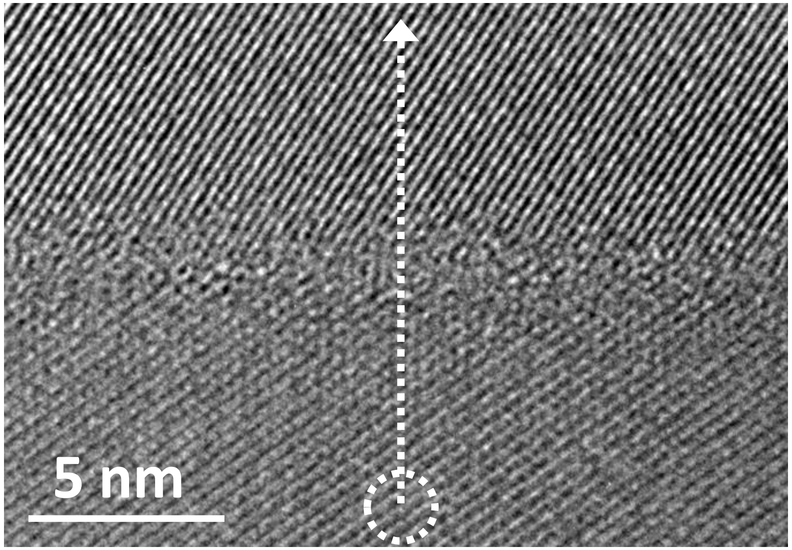


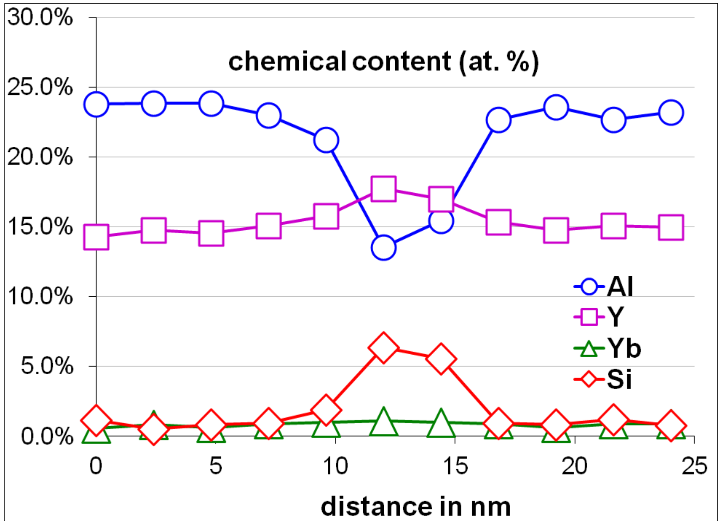
⇨ **ACCURACY ≈ 0.2 at. % for each element**

2. HRTEM and NANO-ANALYTICAL RESULTS

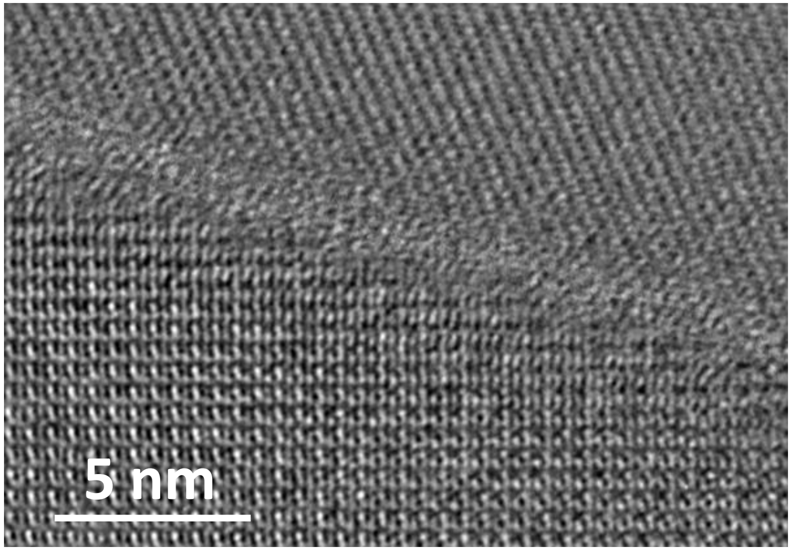
- **SEGREGATION at Grain-Boundaries**

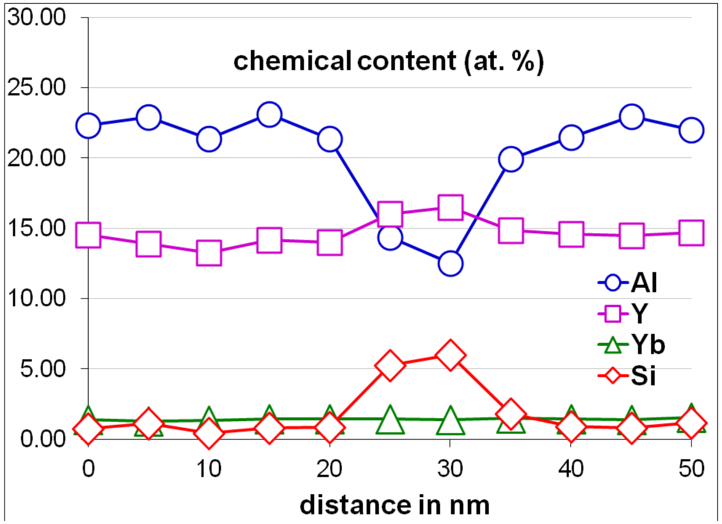
05-Yb 1300





10-Yb 1300

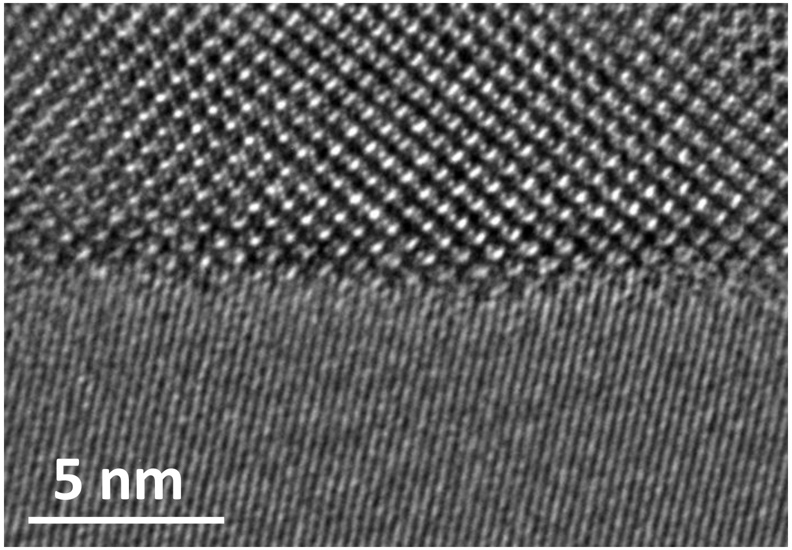


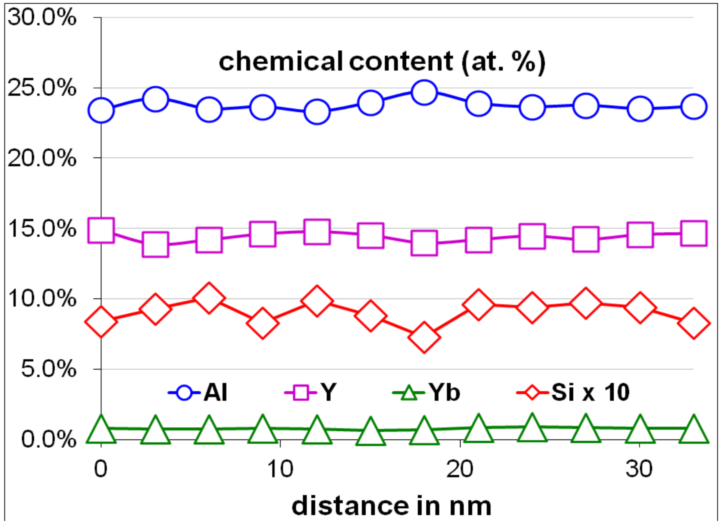


2. HRTEM and NANO-ANALYTICAL RESULTS

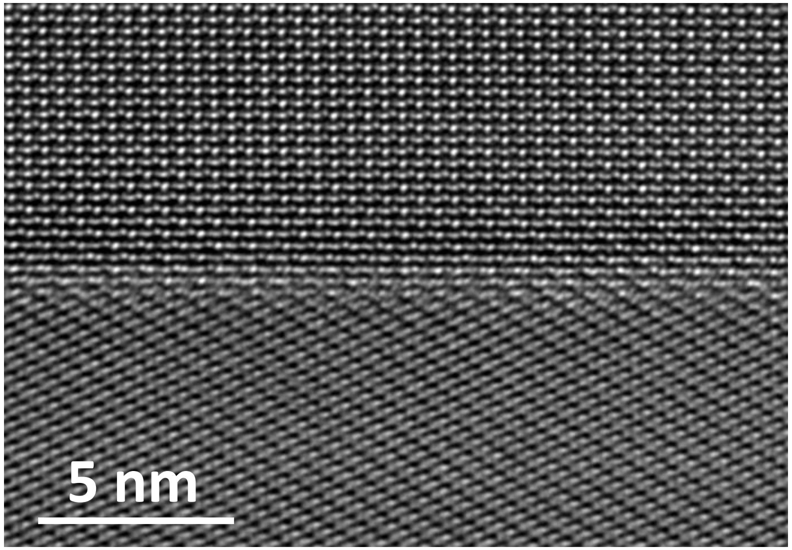
• SEGREGATION at Grain-Boundaries

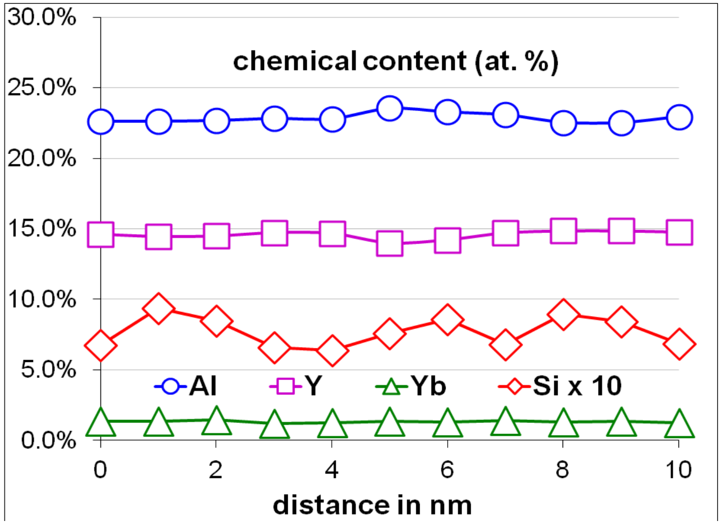
05-Yb 1100





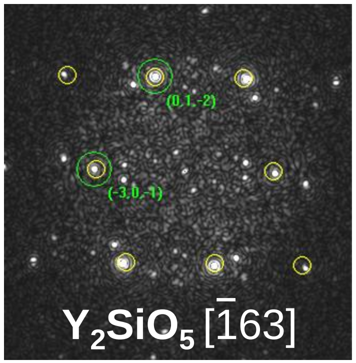
10-Yb 1100



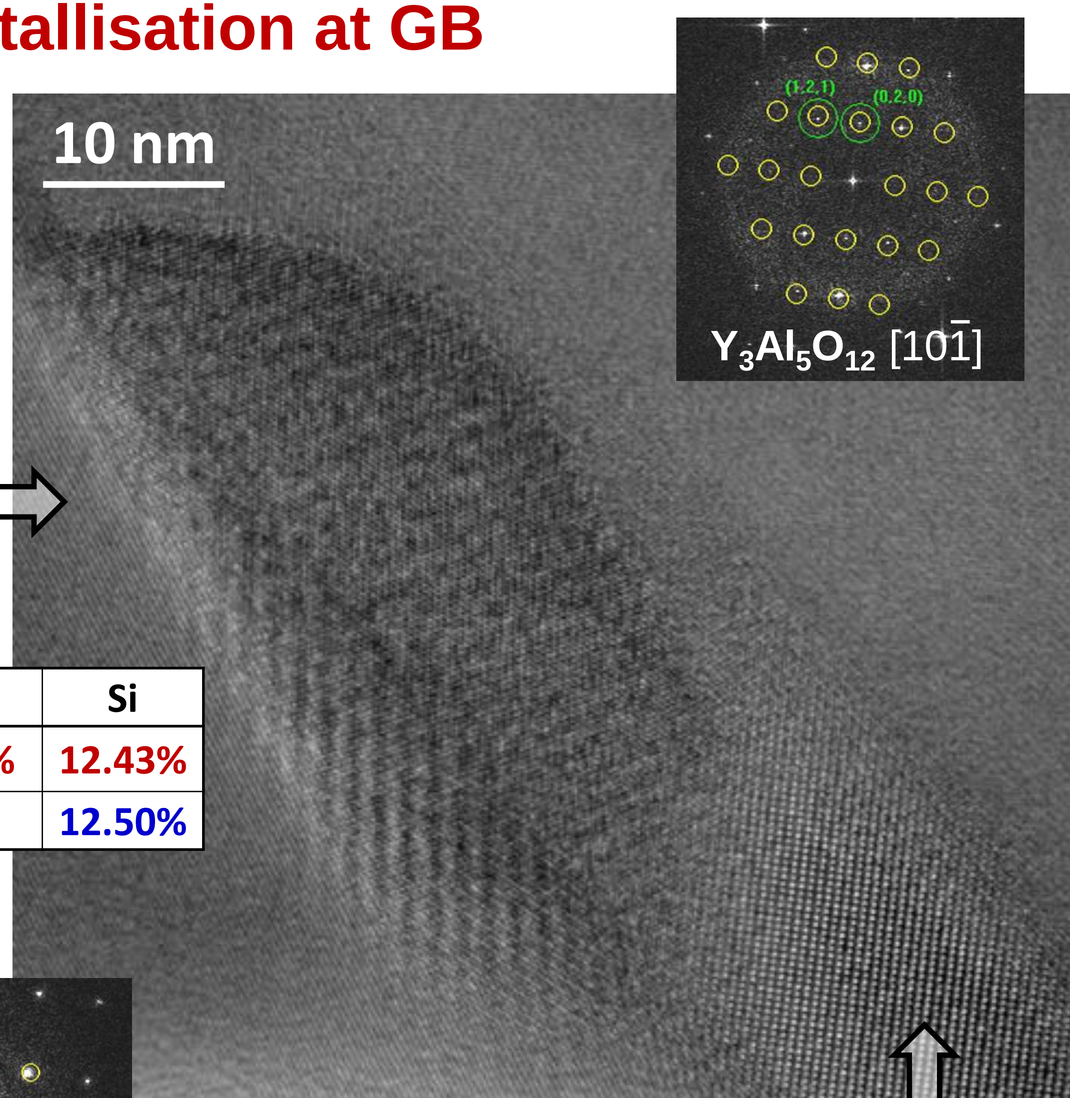


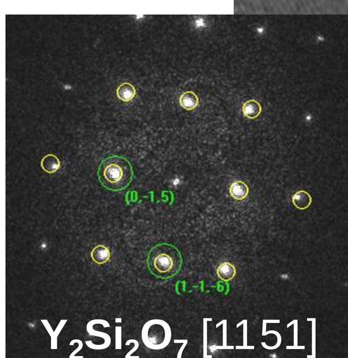
• SECOND PHASE Crystallisation at GB

10-Yb 1100



	Yb	O	Y	Al	Si
EDX	1.78%	62.21%	21.30%	2.27%	12.43%
Y_2SiO_5		62.50%	25.00%		12.50%





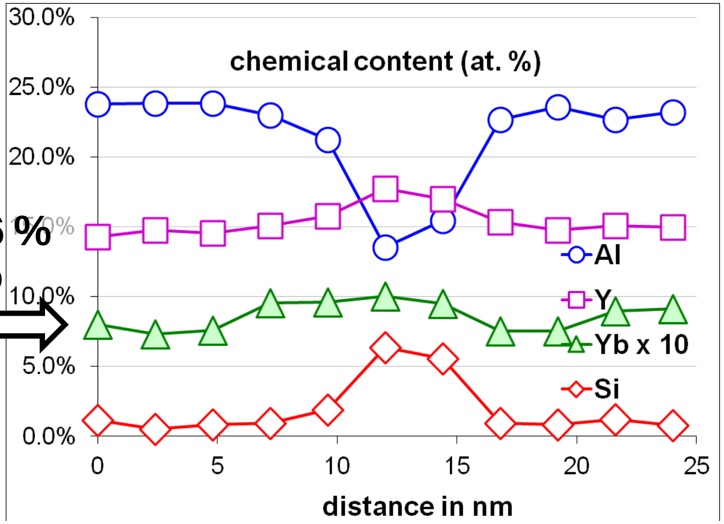
	Yb	O	Y	Al	Si
EDX	1.40%	63.35%	20.01%	1.74%	13.50%
$Y_2Si_2O_7$		63.64%	18.18%		18.18%

• **Ytterbium distribution?**

Substitution 5 % Yb: [Yb] = 0.75 at. %
Substitution 10 % Yb: [Yb] = 1.5 at. %
(without Si)

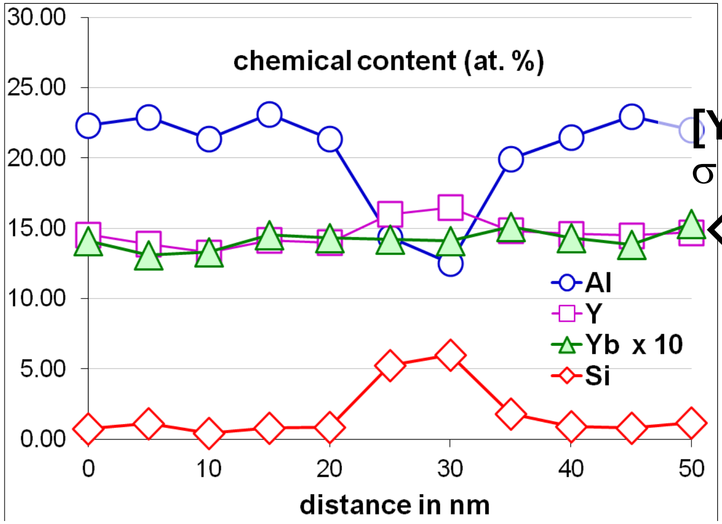
05-Yb 1300

[Yb] = 0.86 %
σ = 0.10 %



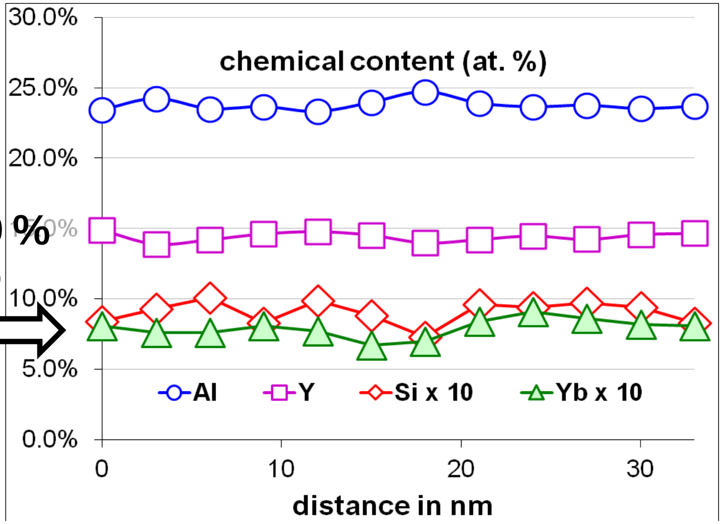
10-Yb 1300

[Yb] = 1.42 %
σ = 0.07 %



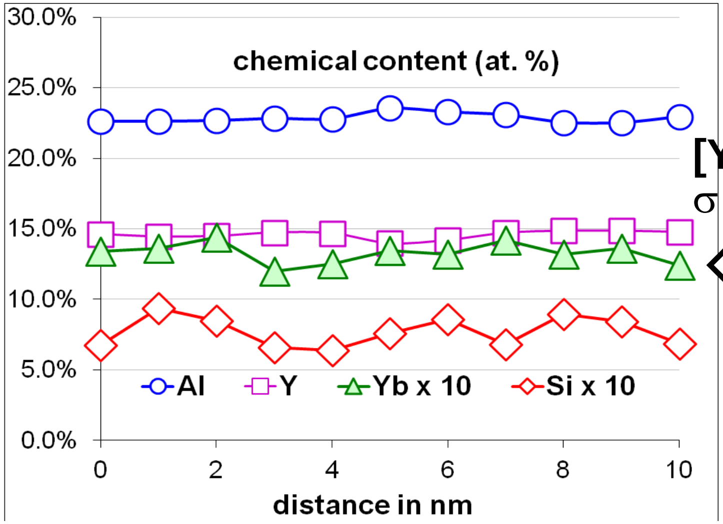
05-Yb 1100

[Yb] = 0.79 %
σ = 0.07 %



10-Yb 1100

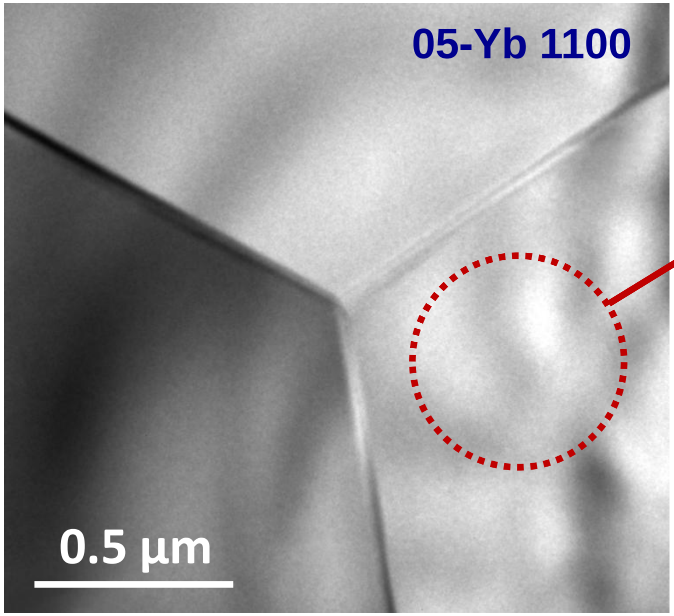
[Yb] = 1.33 %
σ = 0.07 %



3. DISCUSSION and CONCLUSIONS

• SUMMARY of ANALYSES

			Grain analysis		GB analysis	
Annealing	sample #	doping	average [Si] at. %	Nb. analysis	average [Si] at. %	Nb. analysis
1300°C, 1 h.	05-Yb 1300	Yb- 5%	0.90 ± 0.35	16	4.24 ± 0.63	6
	10-Yb 1300	Yb- 10%	0.94 ± 0.20	40	5.00 ± 1.30	20
1100°C, 100 h.	05-Yb 1100	Yb- 5%	0.91 ± 0.30	70	0.97 ± 0.38	14
	10-Yb 1100	Yb- 10%	0.89 ± 0.23	35	0.96 ± 0.18	16



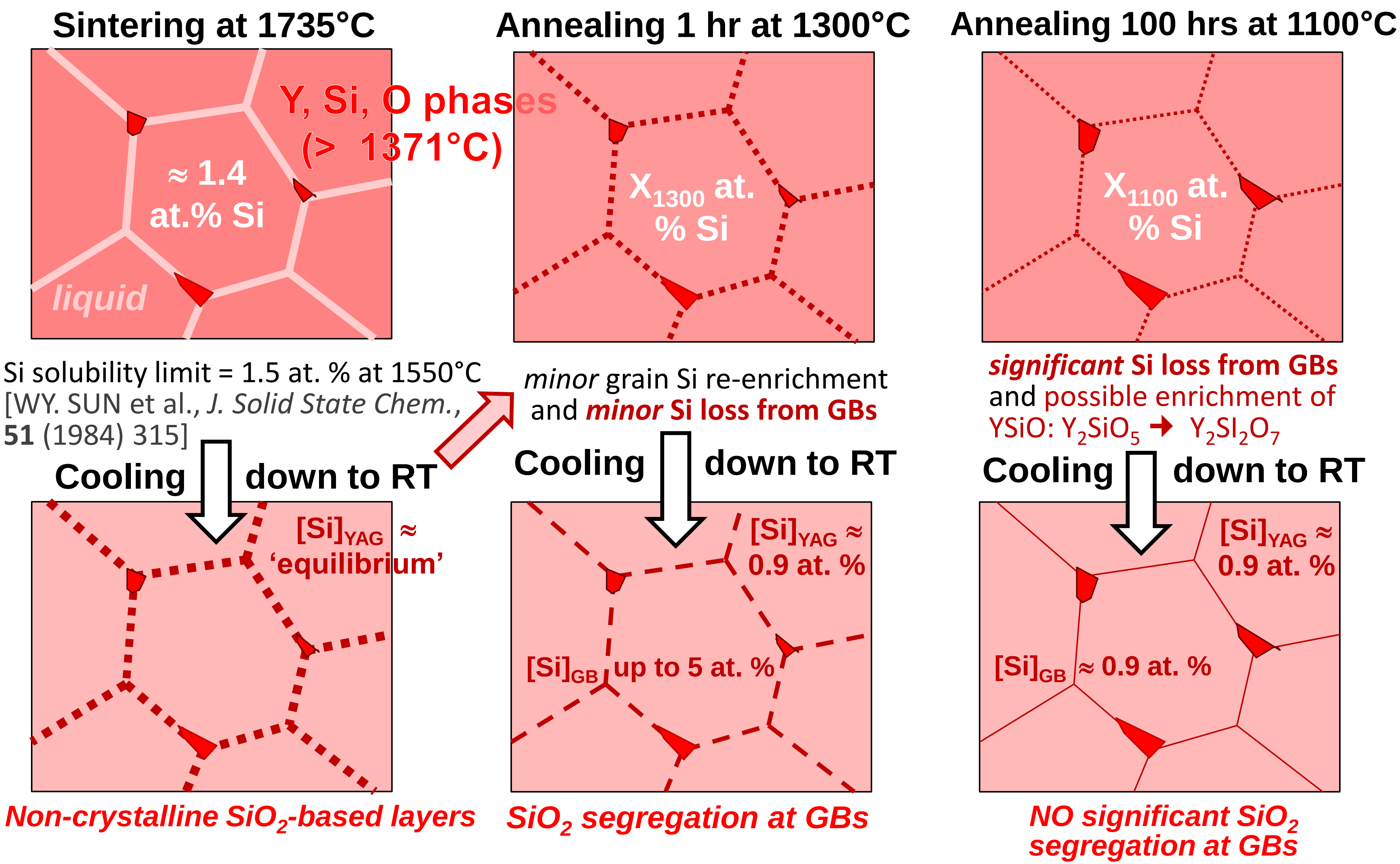
	Yb	O	Y	Al	Si
EDX	0.85%	60.12%	14.39%	23.86%	0.78%
0.84(Yb-YAG) + 0.11SiO2 + 0.05Y2O3	0.72%	60.12%	14.39%	24.16%	0.60%

⇨ **NO Yb segregation**

[T. EPICIER et al., J. *Mater. Chem.* **22** (2012) 18221]

3. DISCUSSION and CONCLUSIONS

• POSSIBLE PROCESSES involved during annealing



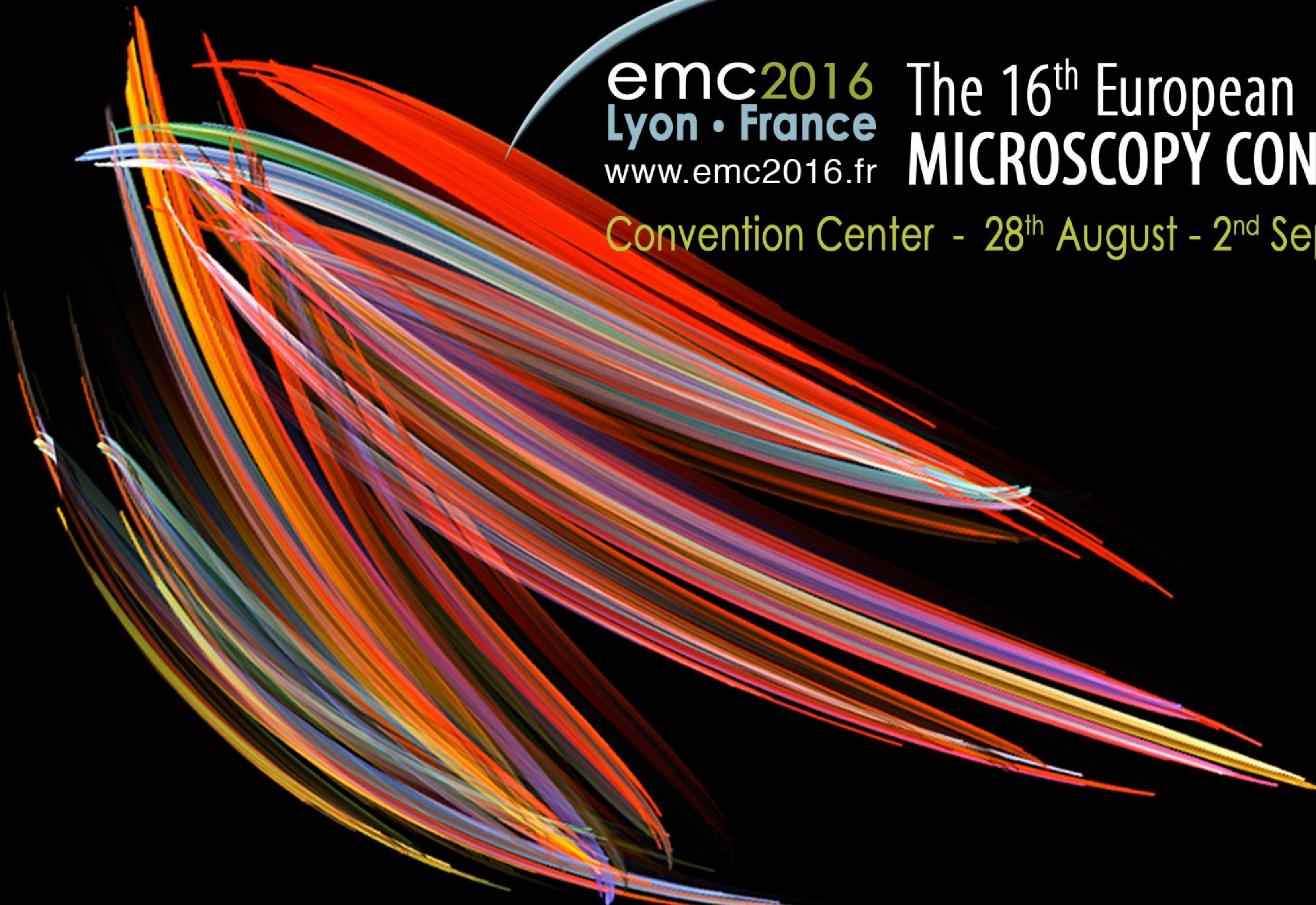
Acknowledgements

- Centre Lyonnais de Microscopie www.clym.fr
- bilateral FRANCE-ITALIA project
- the French TEM & Atom Probe network, FR CNRS 3507

emc2016
Lyon • France
www.emc2016.fr

The 16th European MICROSCOPY CONGRESS

Convention Center - 28th August - 2nd September



Organised by Sfμ and Under the auspices of EMS