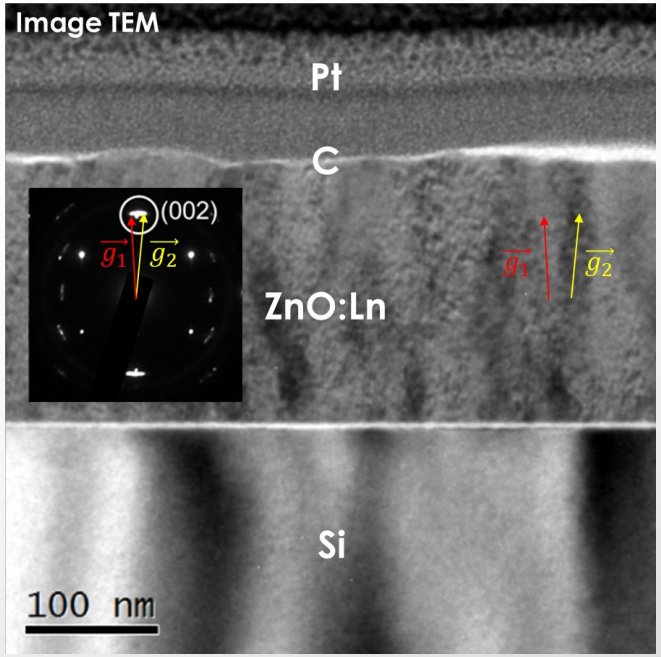
Structural Evolution in Annealed (Eu,Tb) Doped ZnO/Si Nanoscale Junction



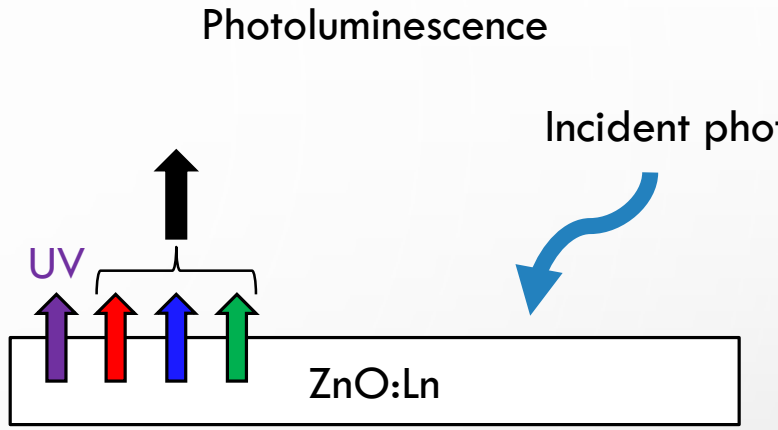
DENIS PELLOQUIN

CRISMAT, UMR CNRS 6508, ENSICAEN, Normandie Université,
6 Boulevard du Maréchal Juin, 14050 Caen Cedex 04, France

Studium Conference. New Inorganic Functional Oxides: Synthesis, Characterisation and Simulations. 4-6 oct 2023 Orléans

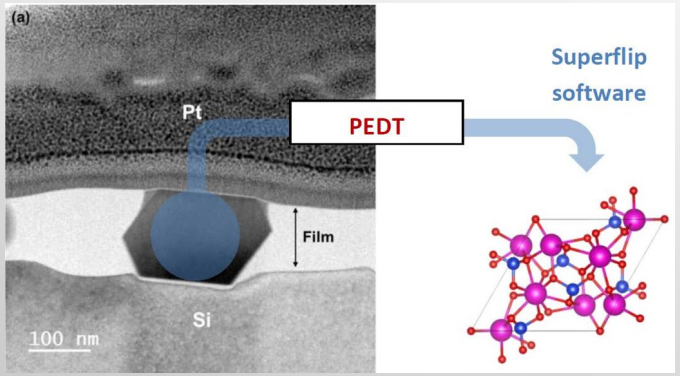
MOTIVATIONS

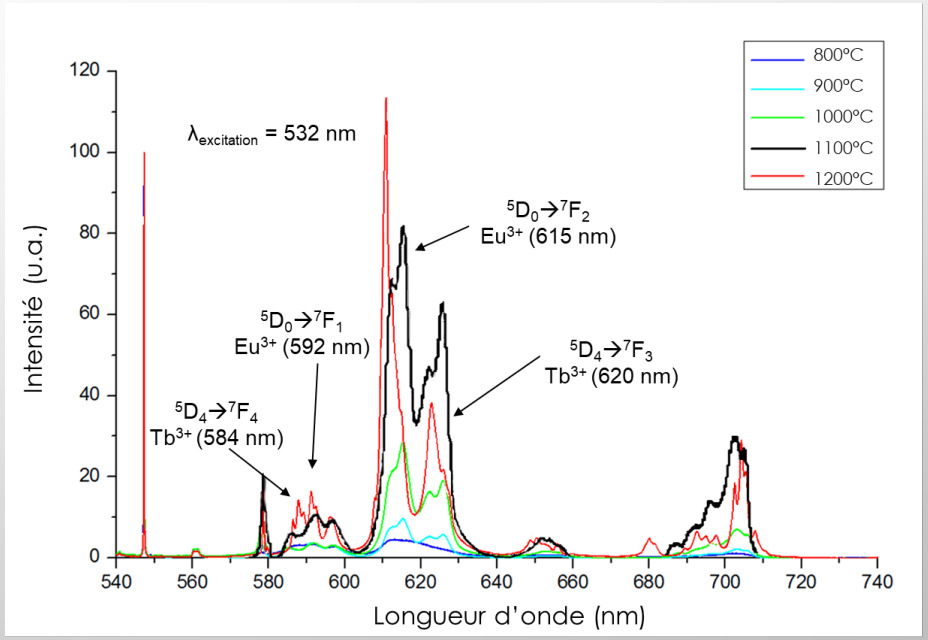
- **Ln doped ZnO /Si junction induces photoluminescence properties in visible spectra.**
- **Ln codoping and thermal annealings are efficient to improve the photoluminescence properties (selection of emitted color - best lighty intensity)**



Structural studies of annealed Ln doped ZnO /Si junction Case of Eu/Tb codoping

Nanometric objet



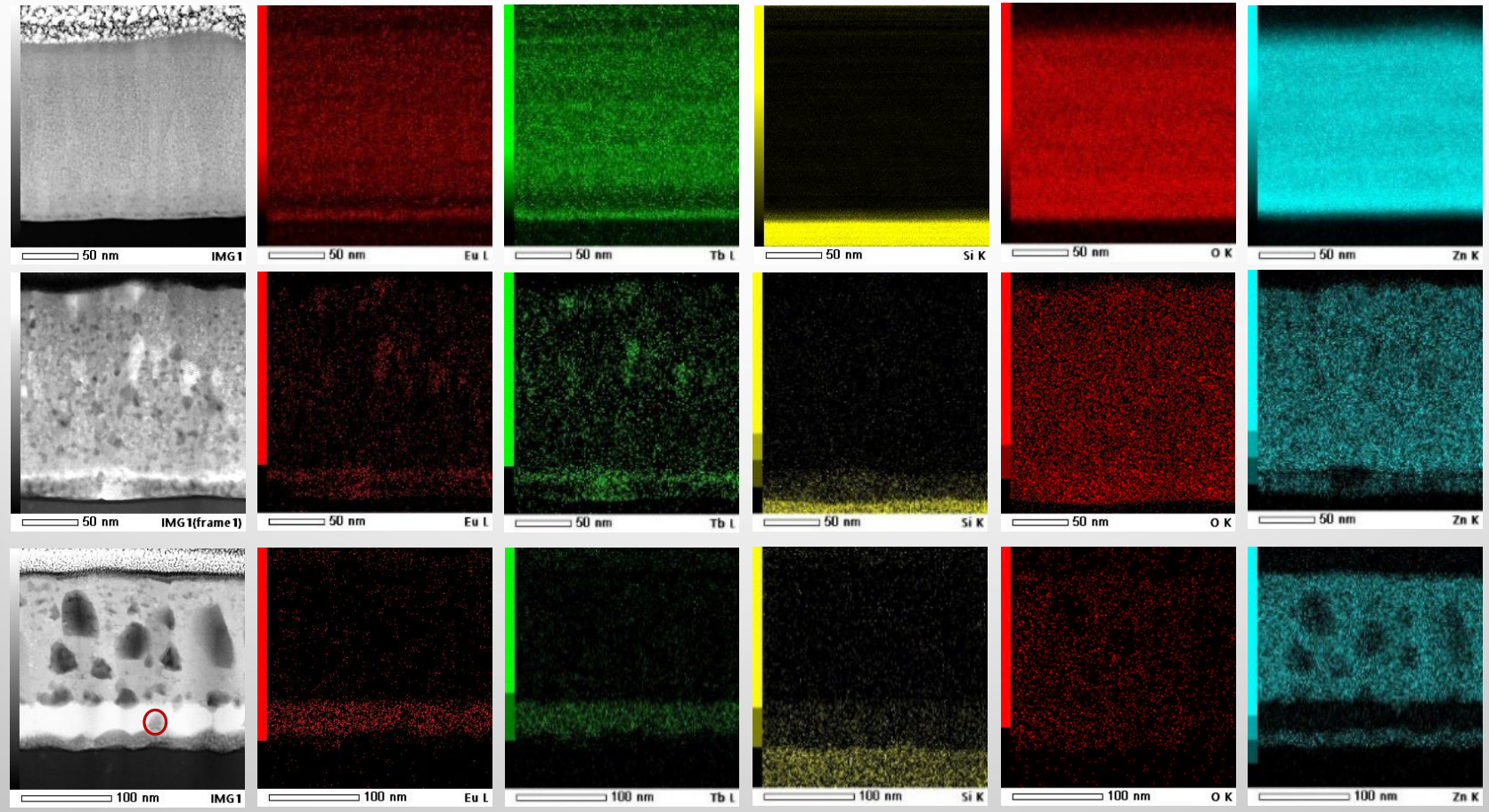


To avoid the quenching effect that limits the 4f-4f radiation (leading to the emission in the visible spectra), a low Ln doping is applied.

EUROPIUM/TERBIUM CODOPING

Nominal codoping Eu 1.2 % and Tb 1.6 %

EDS mapping the versus annealing temperature



STEM-HAADF

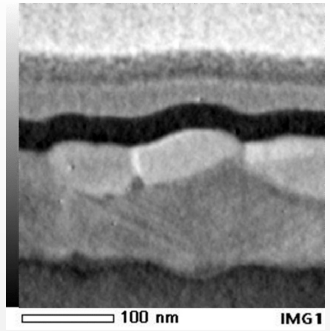
From 800°C :

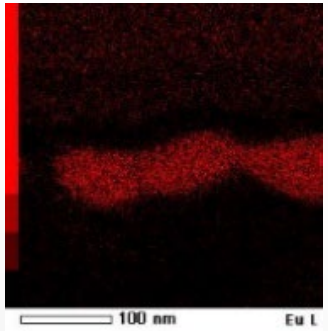
- Si species begin to migrate inside ZnO matrix
- Ln species move towards the Si interface
- Zn species crystallise with Si to form Zn_2SiO_4 willemite structure

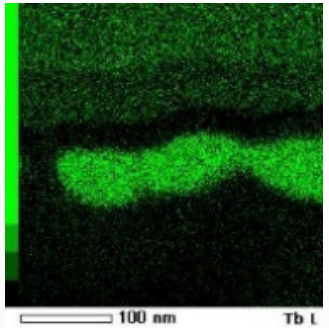
C.Guillaume, C.Leroux et al.
Applied Surface Science, *Volume 556*, **2021**

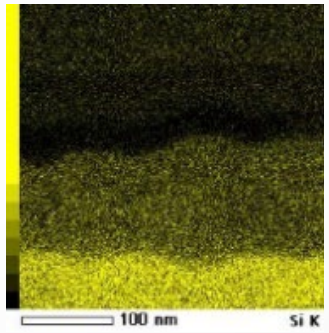
EUROPIUM/TERBIUM CODOPING

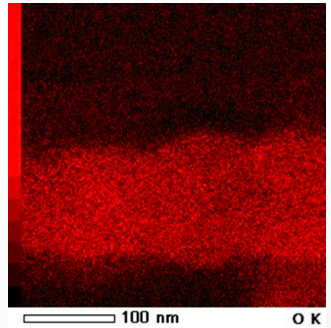
1000°C

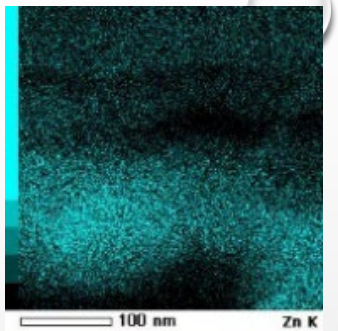




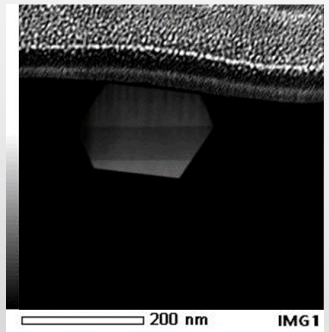


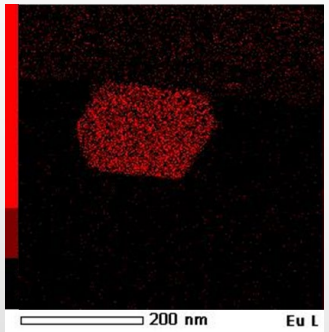


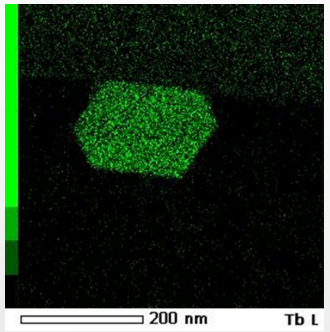


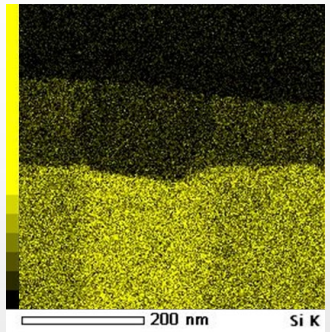


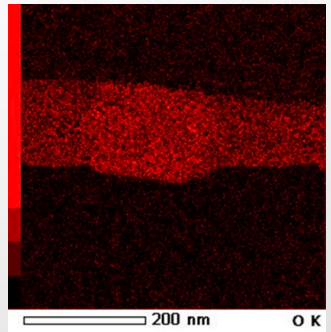
1100°C

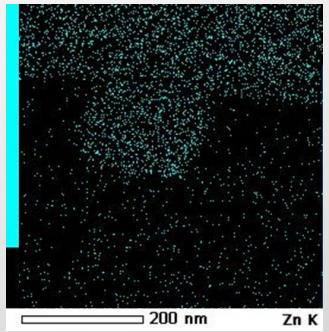




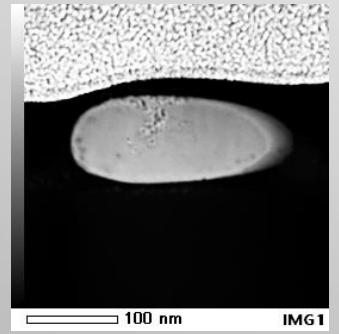


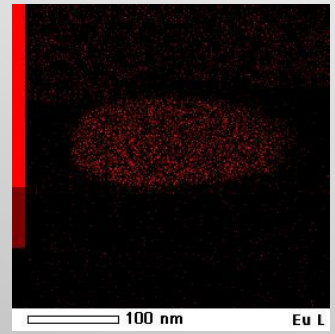


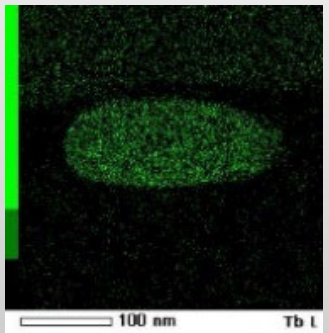


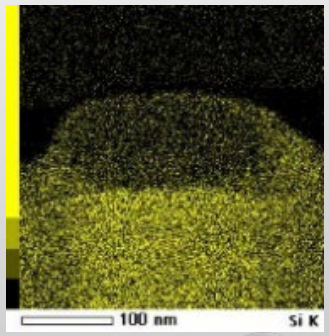


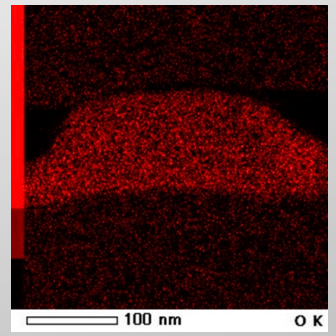
1200°C

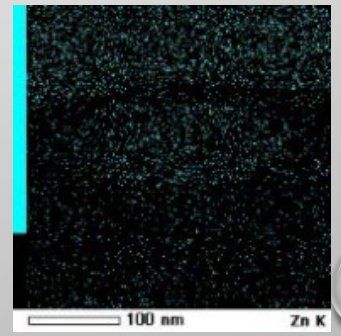










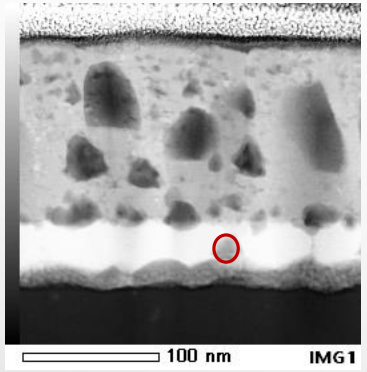


C.Guillaume, C.Leroux et al.
Applied Surface Science, *Volume 556*, **2021**

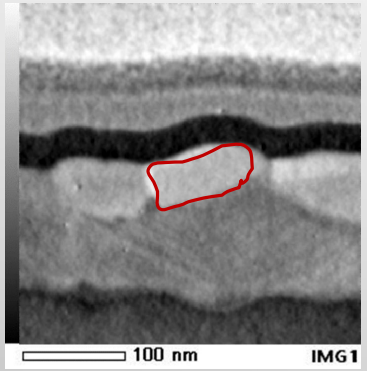
EUROPIUM/TERBIUM CODOPING

De 900 à 1100°C :

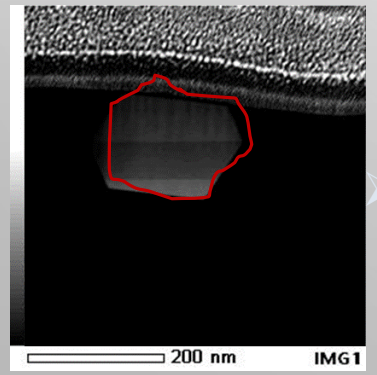
900°C



1000°C

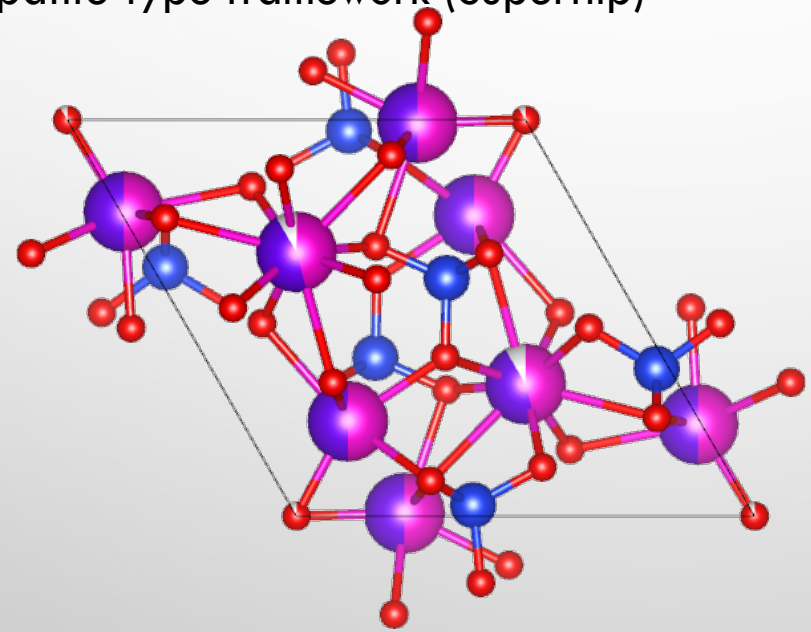


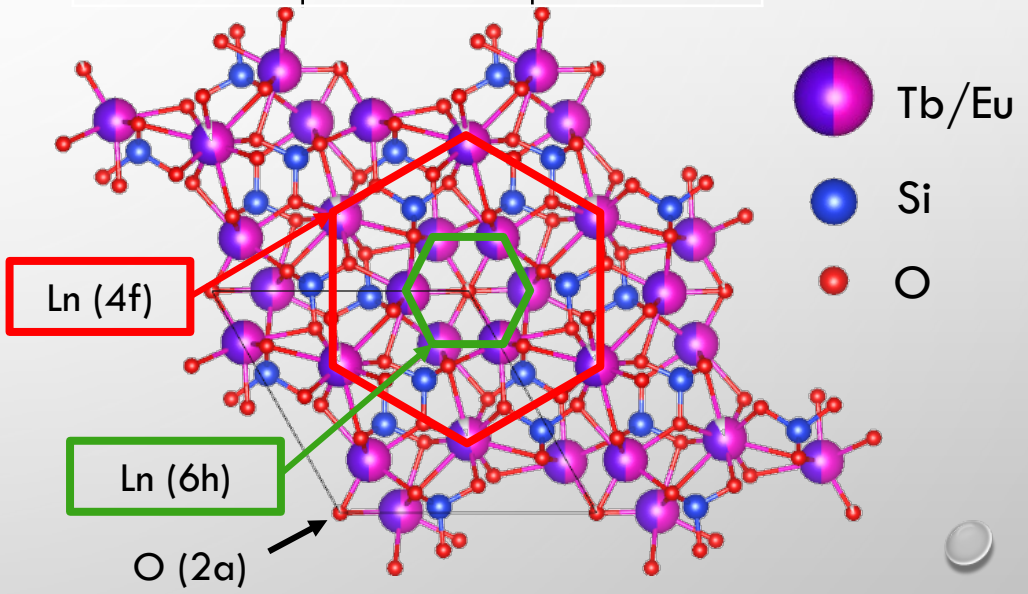
1100°C



- Common EDS results with a Ln/Si ratio close to1.5
- PED tomography data set :
  - Space group: $P6_3/m$
  - apatite-type framework (Superflip)

a (Å)	b (Å)	c (Å)
9.276(3)	9.276(3)	6.758(1)
α (°)	β (°)	γ (°)
90	90	120





- Dynamicals refinements :
  - Occupation site 4f ≈ 80 % ➔ $(Eu,Tb)_{9,33}(SiO_4)_6O_x$

C.Leroux et al.
Inorg. Chem. 2021, 60, 7, 4508−4516

Codoping Europium/Terbium

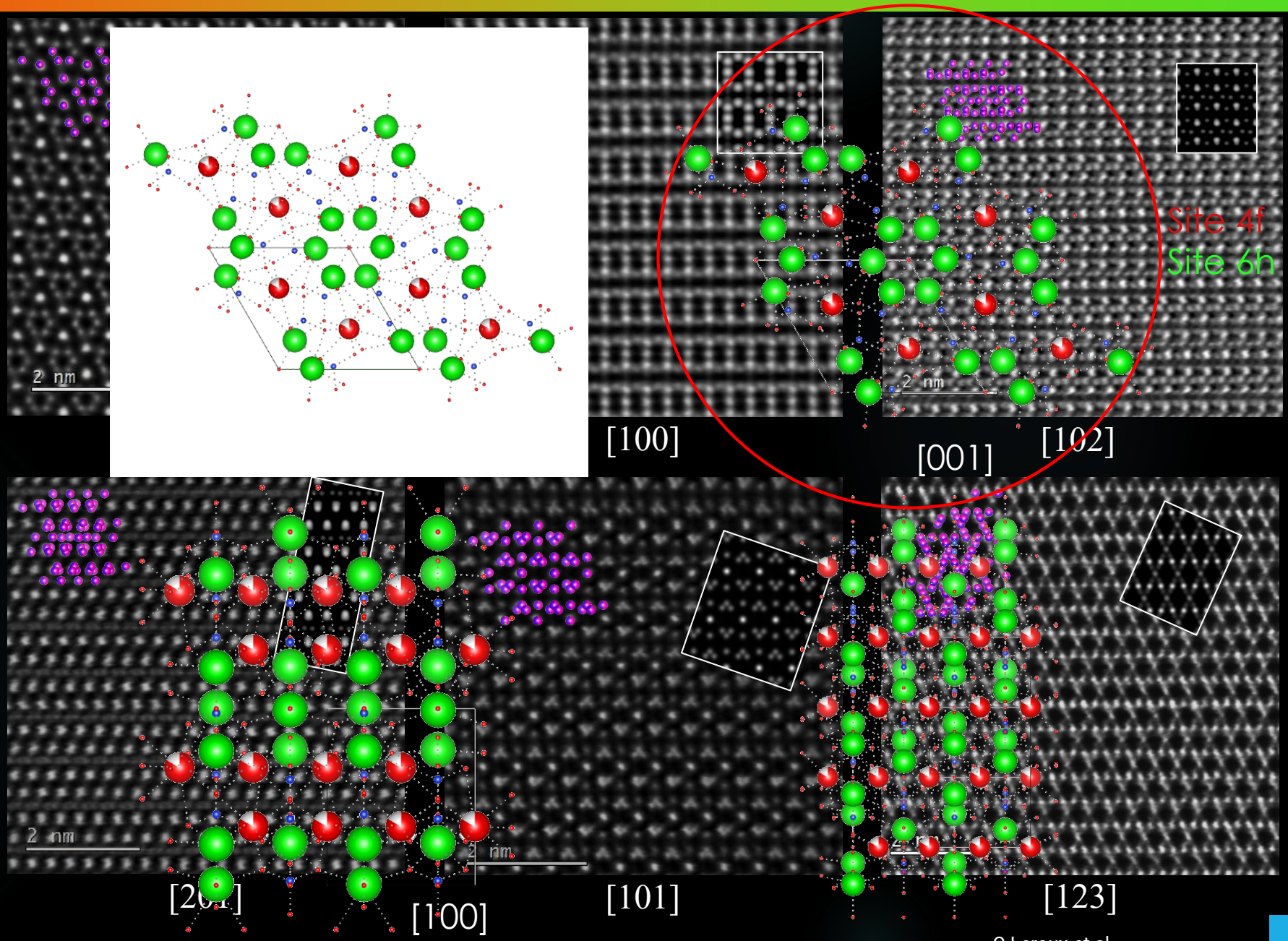
From 900 to 1000°C :

- Calculated images fit well the experimental ones

➔ Ordered or ramdom Tb/Eu distribution ?
➔ State valence of Eu species ?

EDX et EELS spectroscopy at atomic scale on specific zone axes :

[001] or [100] or [210]



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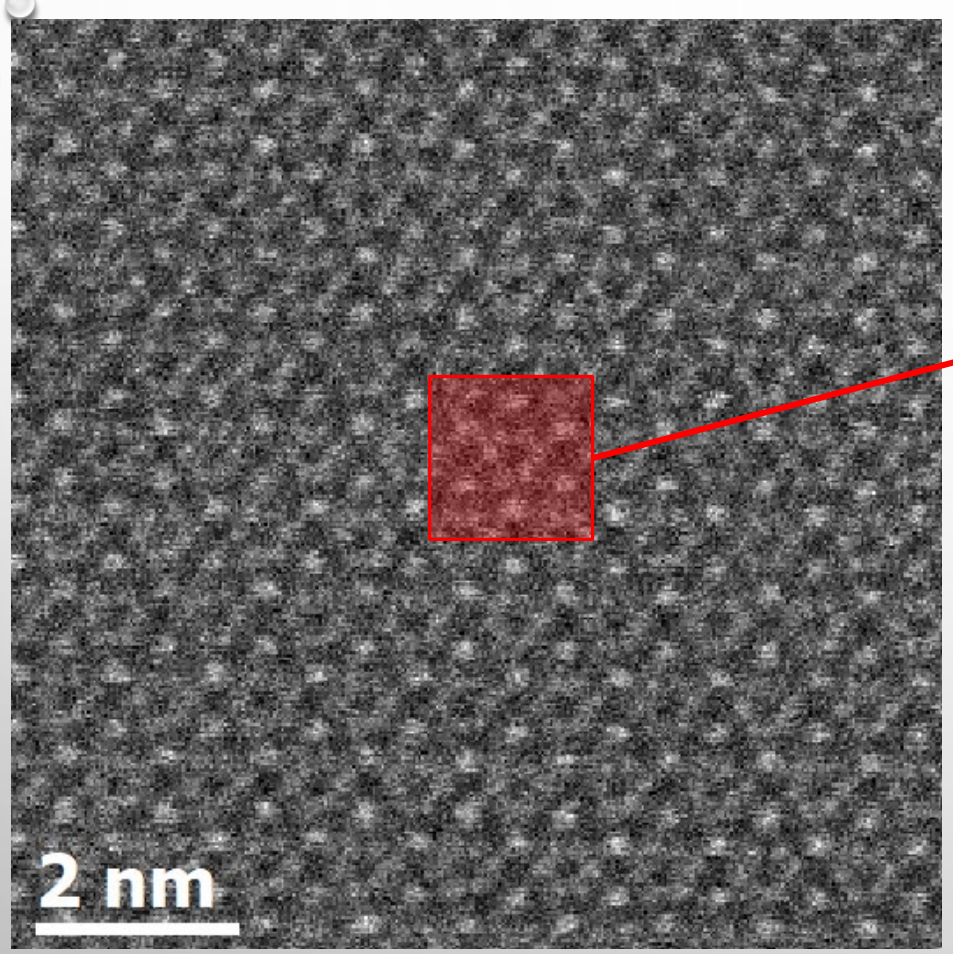
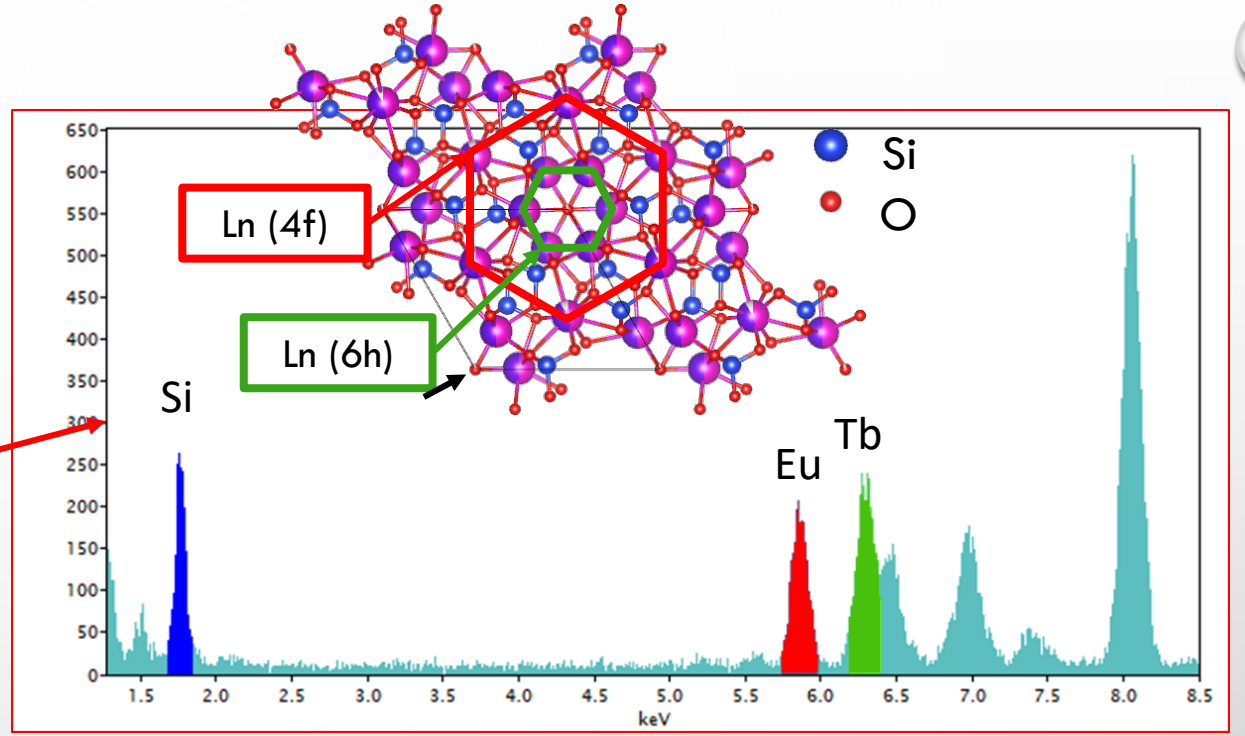
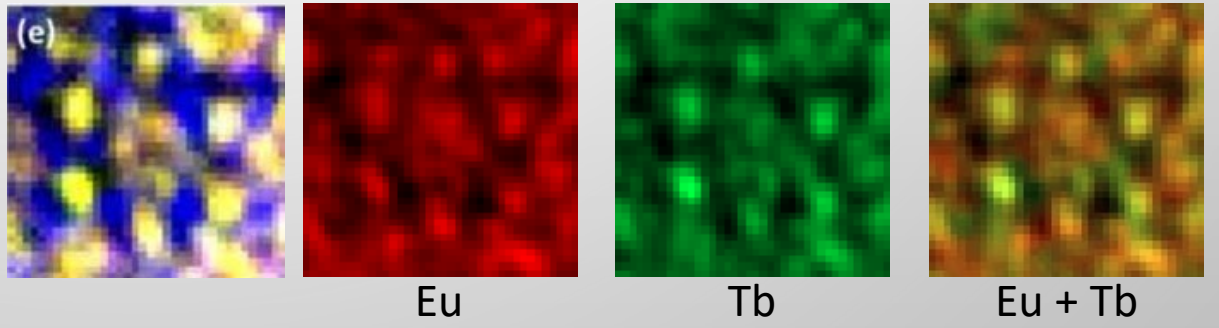
EUROPIUM/TERBIUM CODOPING







STEM-EDX : preferential occupation *6h* site by Eu and *4f site* by Tb

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Inorg. Chem. 2021, 60, 7, 4508−4516

EUROPIUM/TERBIUM CODOPING

At 1200°C :

- EDS results : Ln/Si and Tb/Eu ratios lead to 1 and 1.2 respectively
- New structure : triclinic $P\bar{1}$

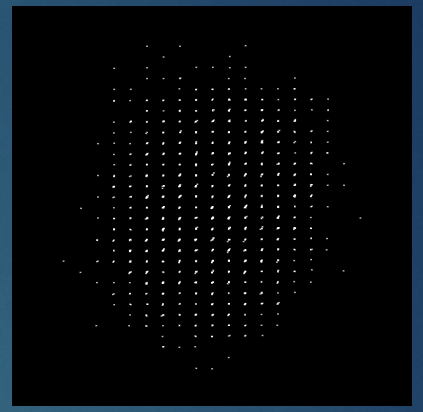
a (Å)	b (Å)	c (Å)
5.33(1)	8.33(1)	2,75(1)
α (°)	β (°)	γ (°)
90.09(3)	91.95(4)	93,07(3)

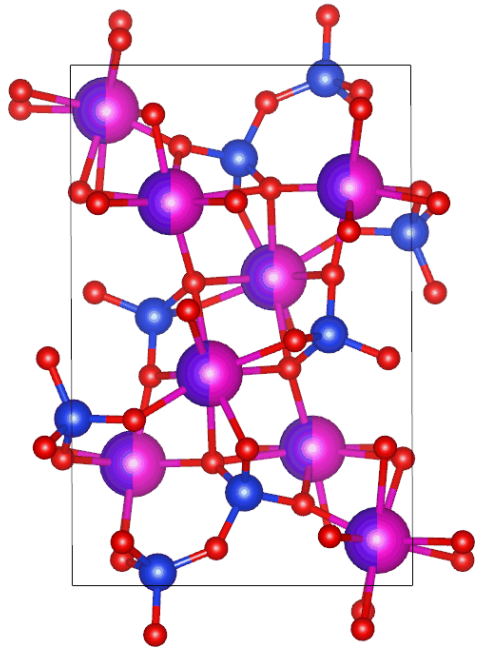
Tb/Eu
Si
O

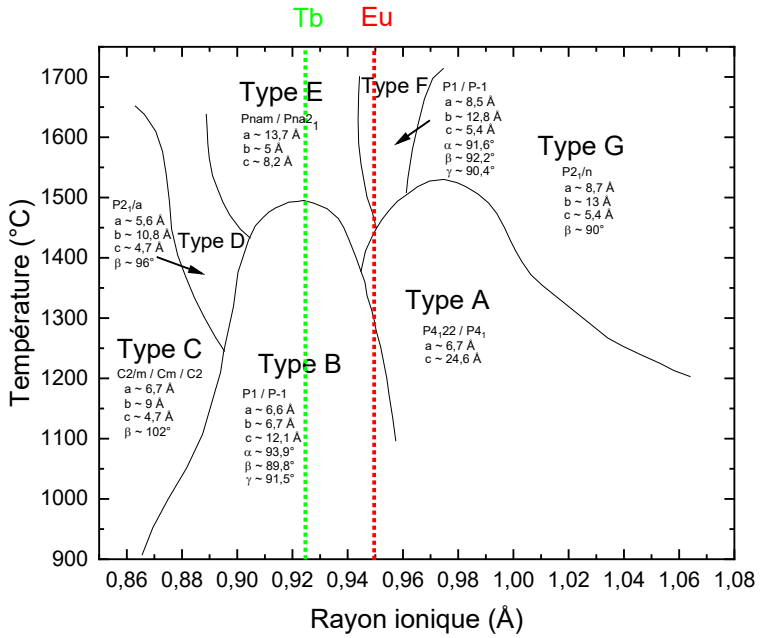
- 4 independant sites for the lanthanides
- Chemical formula: $(Eu,Tb)_2Si_2O_7$
- type F disilicate from Felsche's nomenclatur
- No deficient atomic sites

Diffraction

Réseau réciproque 3D







C.Leroux et al.
ACS Appl. Nano Mater. 2022, 5, 12, 18545-18552

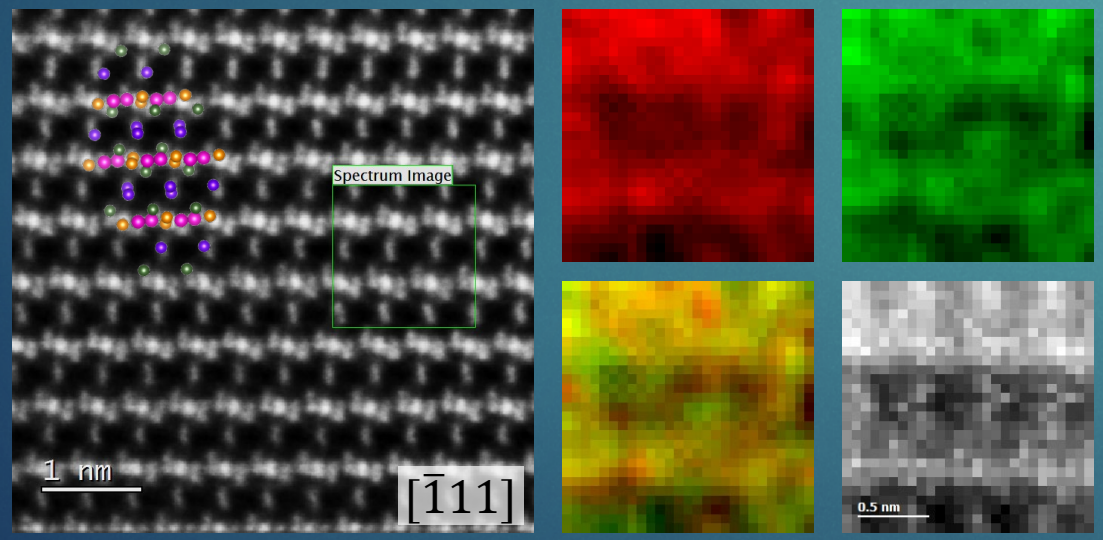
EUROPIUM/TERBIUM CODOPING

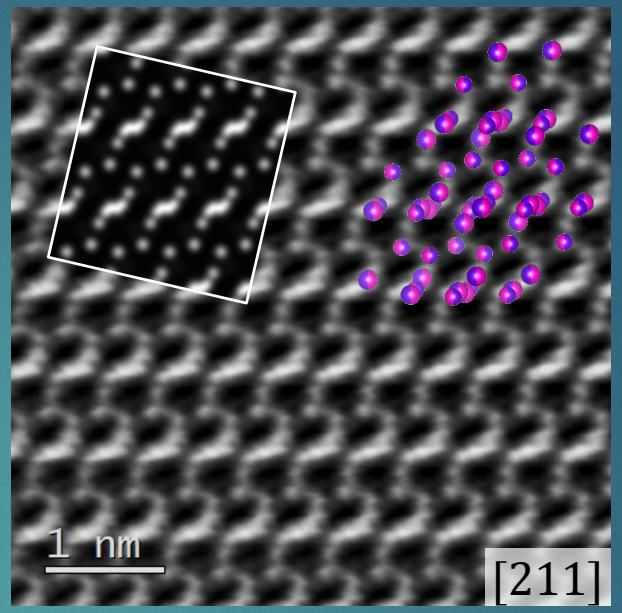
At 1200°C :

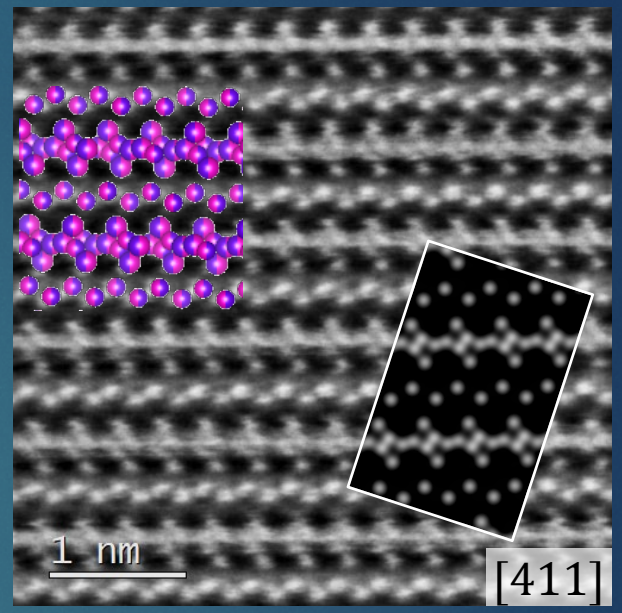
- Calculated images fit well the experimental ones

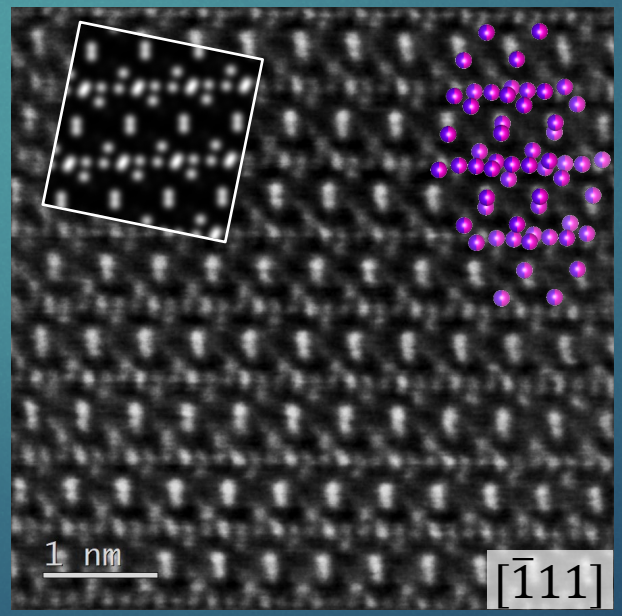
➔ **No prefential Eu or Tb occupation sites ? Difficult to find zone axes leading to the projection of single Ln rows**

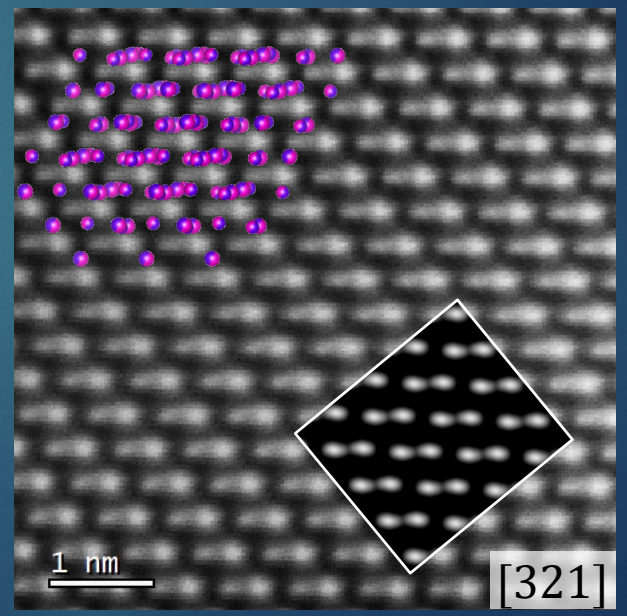
STEM-EDX











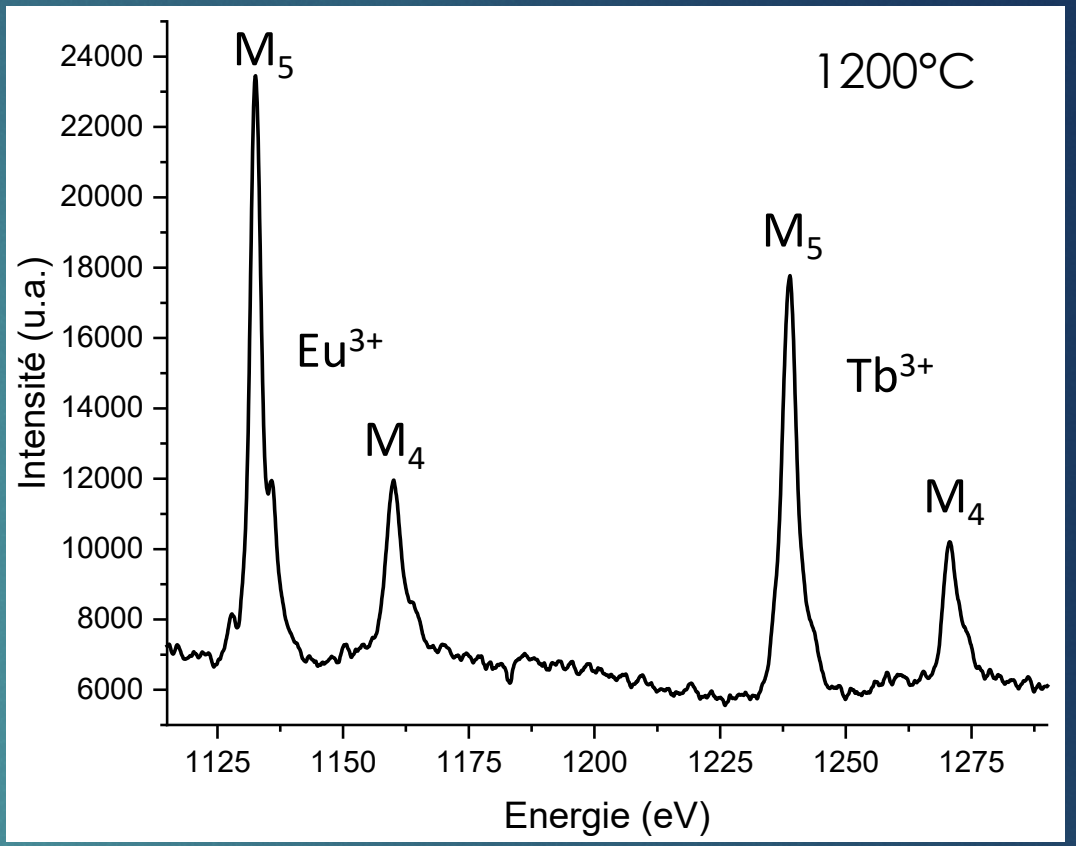
Europium/Terbium Codoping

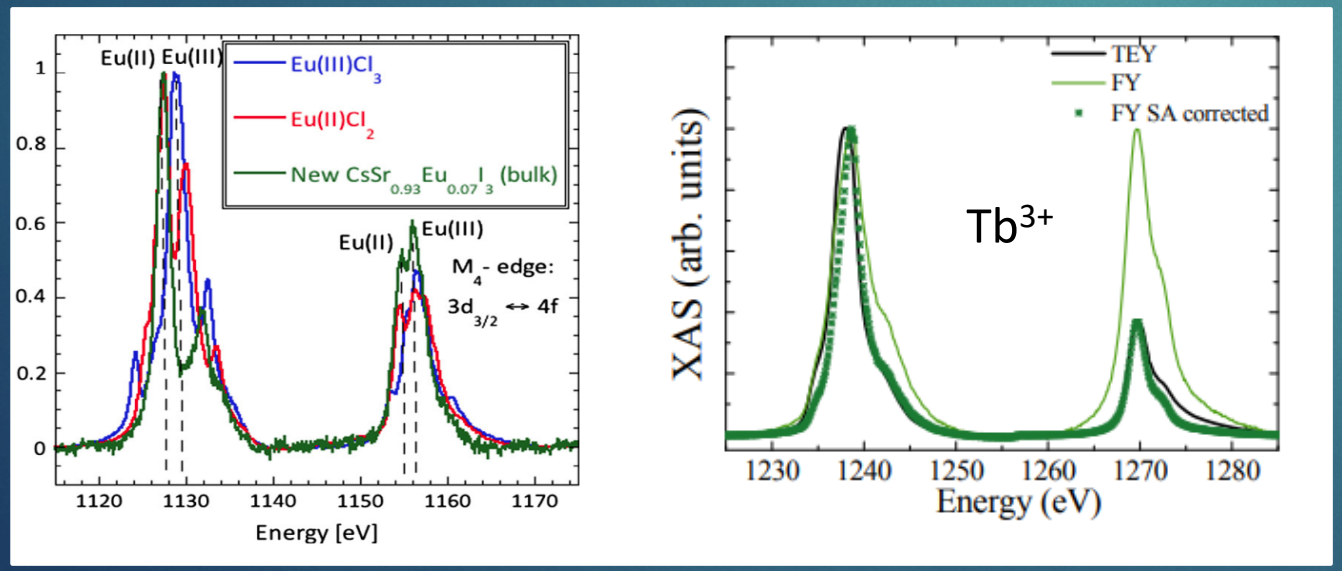
EELS analyses

- Whatever the annealing temperature and the probed structures similar M (Ln) edges are observed on the spectra :

➔ **M_5 Eu edge can be deconvoluted in 3 components with a main component at 1130 eV : Eu 3+**

➔ **Characteristic shoulders on M_4 and M_5 Tb edges : Tb 3+**



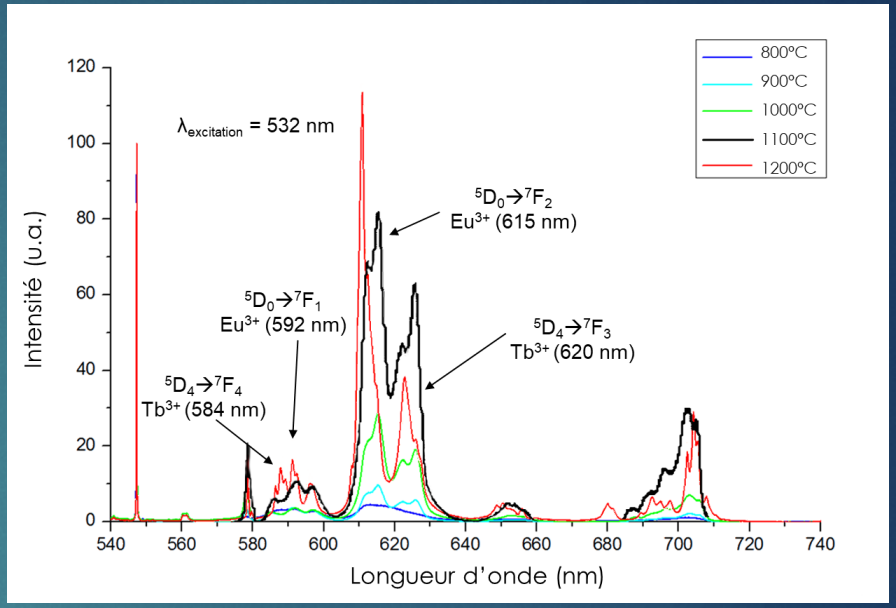


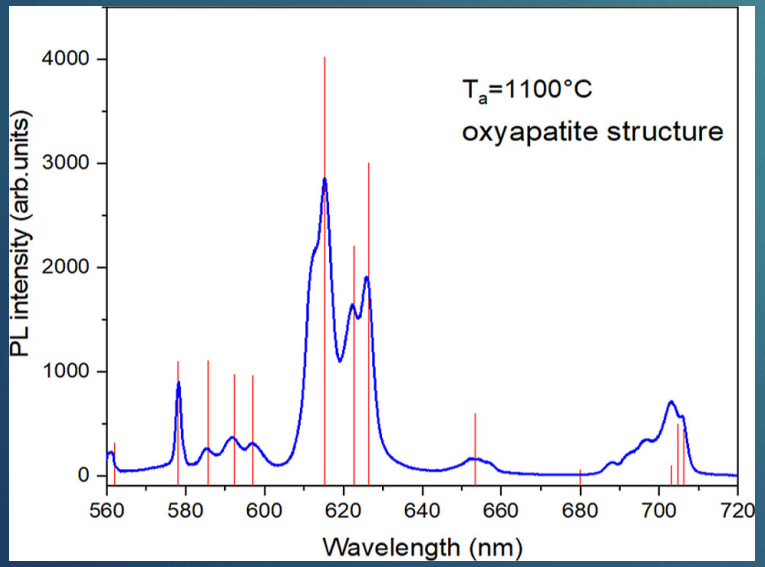
M. Zhuravleva et al. / Optical Materials 36 (2014) 670–674 V. Cuartero et al. / Phys. Rev. B **91**, 165111

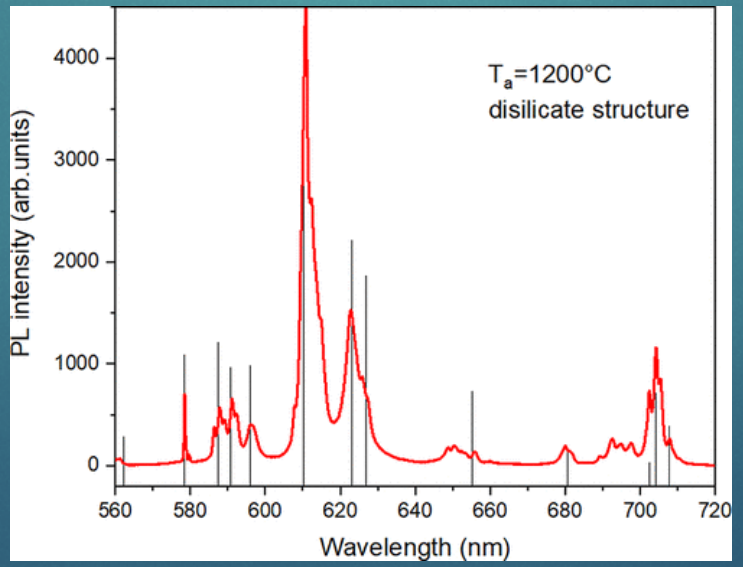
Europium/Terbium Codoping

PL simulations from structural models :
(collaboration with the *Institute of Semiconductor Physics of the NAS – Kiev / Ukraine*)

- Fit well the experimental PL spectra
- Taking into account the intensity and the width of peaks, the best PL properties are observed in disilicate $(Eu,Tb)_2Si_2O_7$ structure







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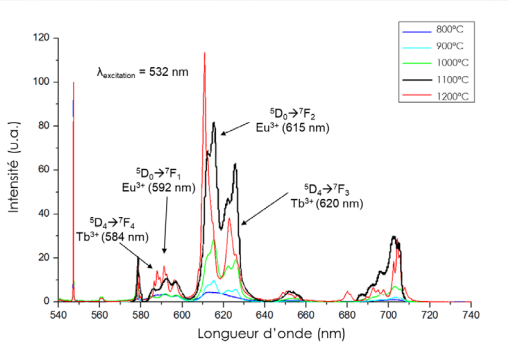
Concluding remarks

Annealing temperature	Structure	<6h-6h>	<6h-4f>	<4f-4f>	<Si-O>
900°C	Oxyapatite $(Eu,Tb)_{9,33}(SiO_4)_6O_x$	3.99 Å	4.05 Å	3.40 Å	1.62 Å
1000°C		3.96 Å	4.02 Å	3.38 Å	1.61 Å
1100°C		4.04 Å	4.08 Å	3,48 Å	1.63 Å
		RE-RE ranging from 3.4 to 4.04 Å			
1200°C	F- Disilicate $(Eu,Tb)_2Si_2O_7$	<RE-RE>			1.60 Å
		4.02 Å (ranging from 3.68 to 4.47 Å)			1.60 Å



The non-stoichiometric oxyapatite structure is an intermediate phase before the final disilicate formation : the gradually increasing of the average size of nanometric inclusions (from 170nm at 1100°C up to 225nm at 1200°C) bases this interpretation

The distances between RE elements in disilicate compound are more favorable to the observed energy transfer from Tb^{3+} to Eu^{3+}

ACKNOWLEDGEMENTS

Thanks to

- Dr Chris Leroux and Philippe Boullay (CRISMAT-Caen)
- Pr Xavier Portier and Dr Clement Guillaume (CIMAP/CRISMAT-Caen)
- Dr Z. Zhuchenko and A. Zolotovsky (Institute of Semiconductor Physics-Kiev)