Cristallisation et terres rares dans des vitro-céramiques oxyfluorures: exemple du système PbF_2 – PbO GeO_2

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Context: materials for IR and visible photonic applications

goal: transparent system with RE-doped fluoride nanocrystals in an oxide glassy phase

rare-earth doped oxyfluoride glass-ceramics

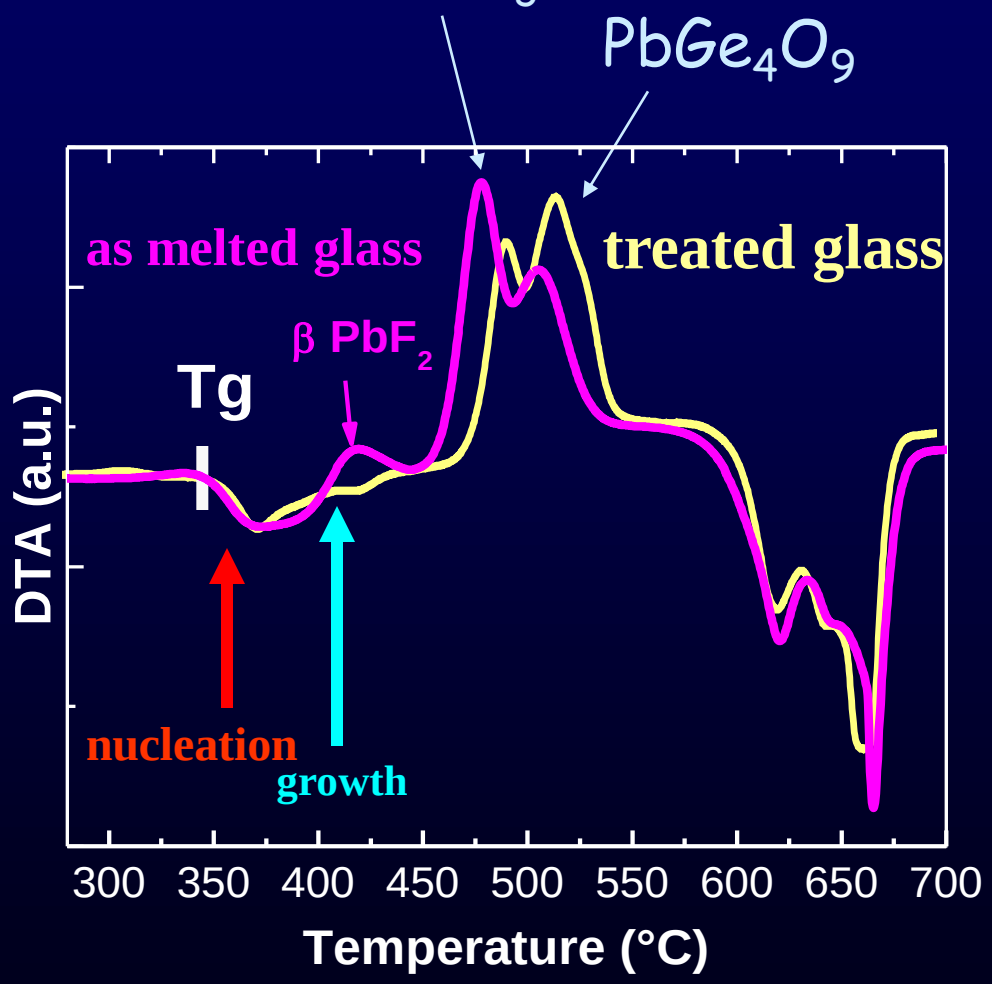
$50GeO_2$ $40PbO$ $10PbF_2$

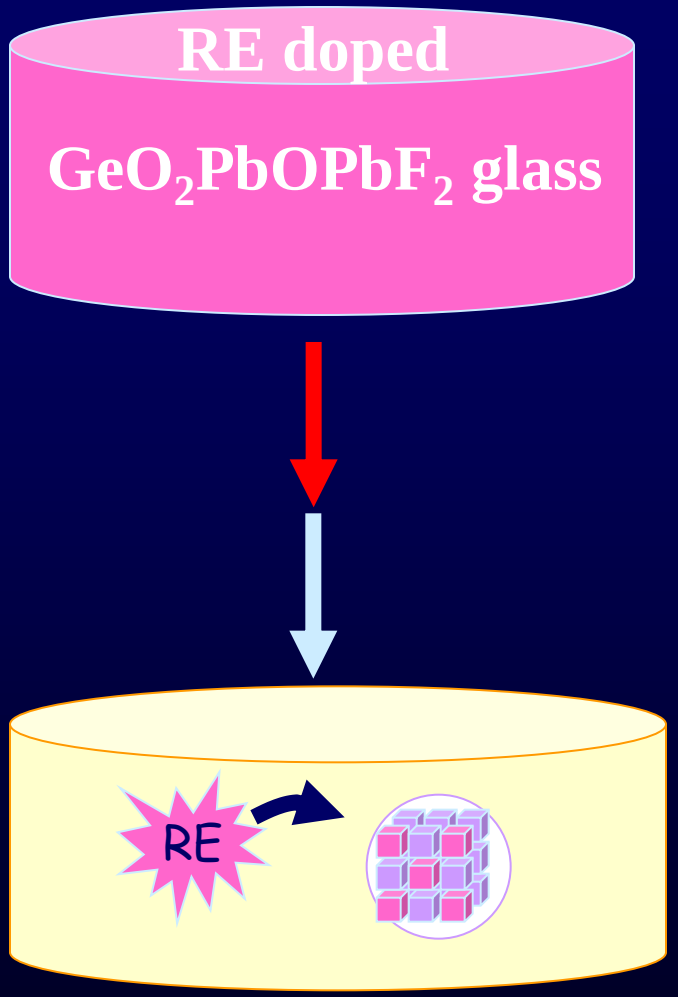
question today:

how does RE act or not on nucleation of PbF_2?

Synthesis principle

Melting 15 min at 1000°C in air





RE doped βPbF_2 crystals

GeO_2PbO undoped glass

Glasses doped with various Er^{3+} based compounds

:

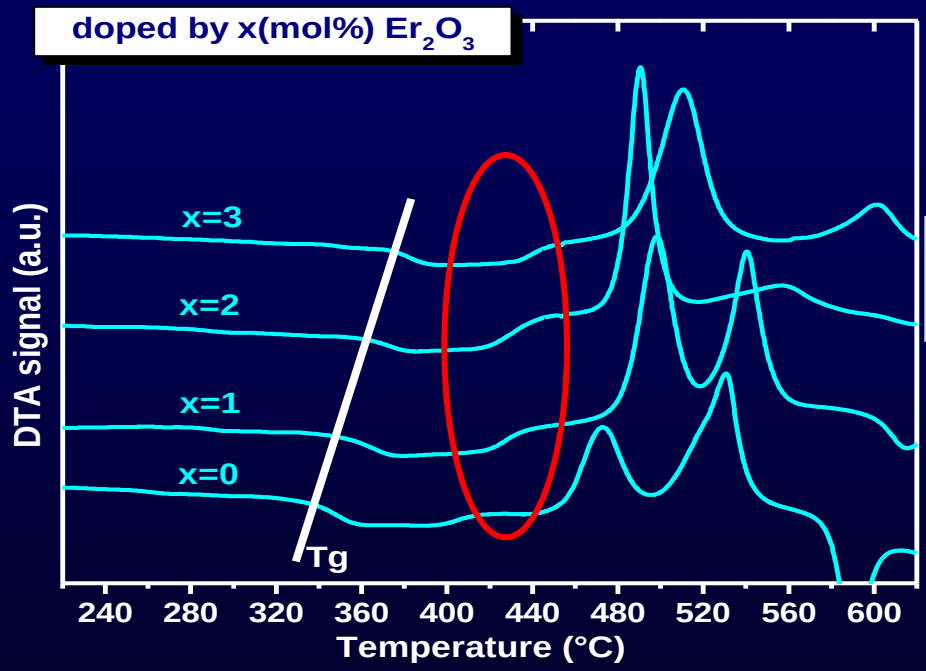
Er_2O_3

ErOF

ErF_3

$ErCl_3$

Effect of Er_2O_3 addition:

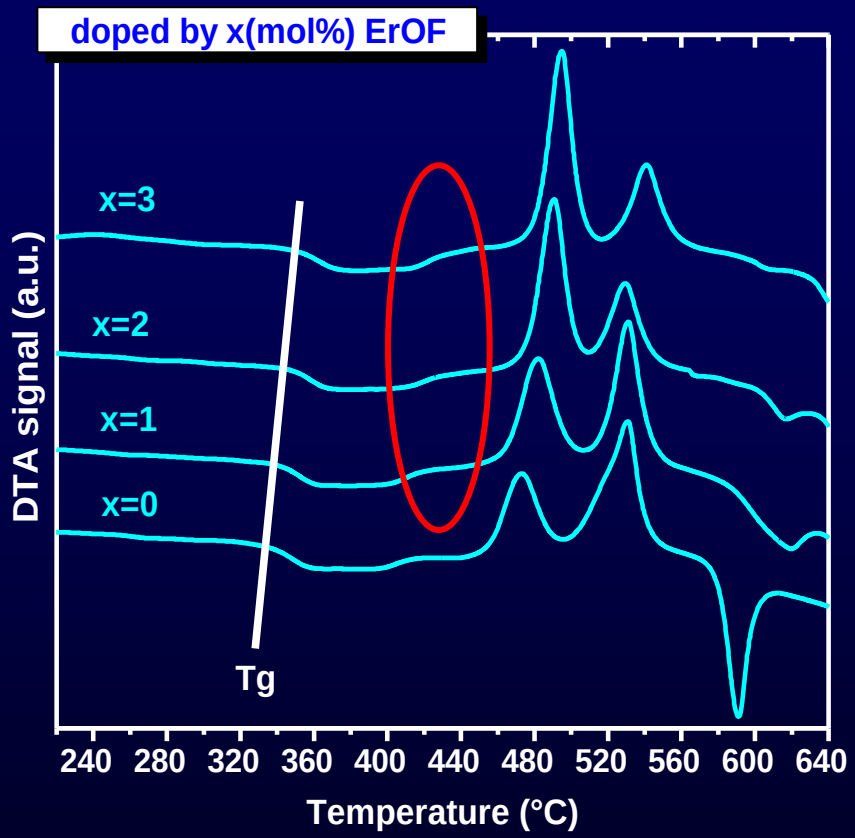


Heat treatment

up to Tg+50°C

Transparent fully amorphous or crystalline opaque material without precipitation of PbF_2

Effect of ErOF addition:

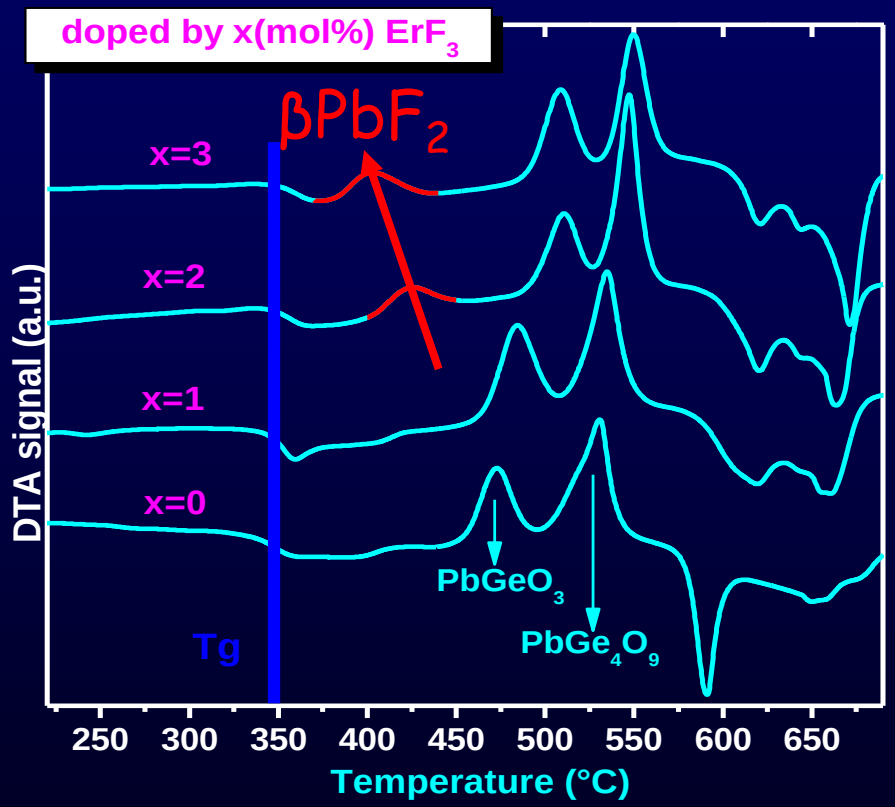


Heat treatment

up to Tg+50°C

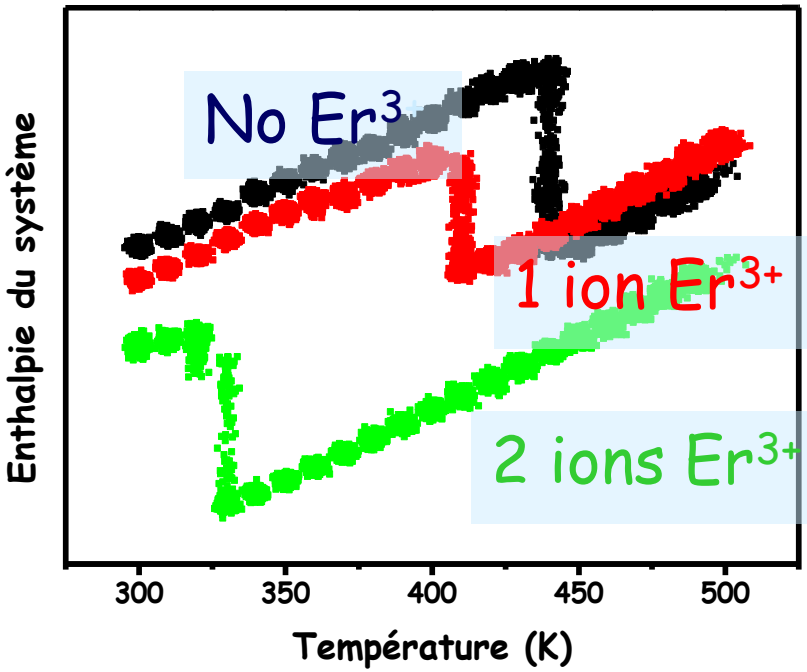
Transparent fully amorphous
or weakly crystalline opaque material
without precipitation of PbF_2

Effect of ErF_3 addition

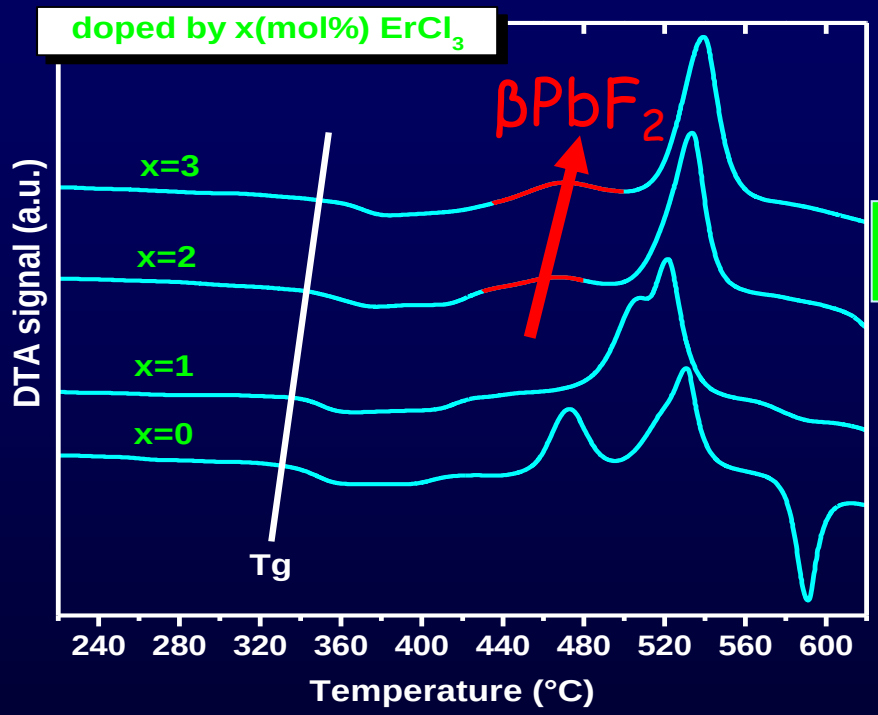


Heat

Molecular dynamics
(com. S Chaussedent)



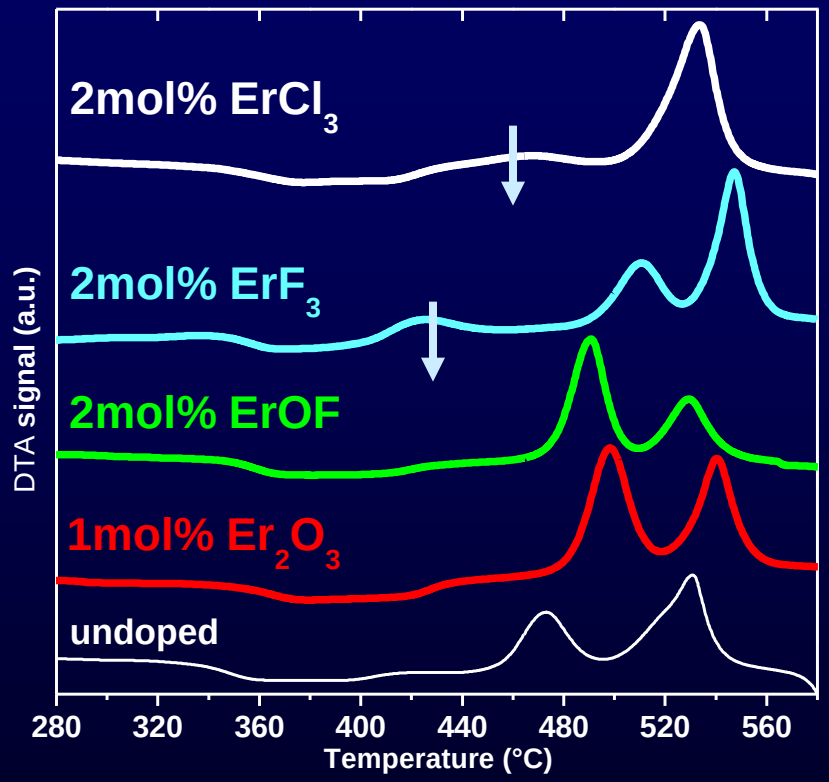
Effect of $ErCl_3$ addition:



Heat treatment

Translucent material
simultaneous phase separation
in the glass phase
weak nucleation of PbF_2

Summary of the effect of erbium precursor on DTA curves



weak nucleation of PbF_2

efficient nucleation of PbF_2

no nucleation of PbF_2

the as melted glass is affected by the compound used to introduce erbium

Optical properties of the parent glasses doped by the different erbium compounds

lifetime $\tau(^4I_{13/2})$ (ms)	ErF_3	$ErCl_3$	Er_2O_3	ErOF
measurement on powder	4.04	3.75	3.60	3.48
value in bulk sample	6.87	7.12	5.40	5.57
compared to powder	+70%	+90%	+50%	+60%

Lengthening of the lifetimes and radiative trapping
>> Direct effect of non radiative transitions
>> local vibration mode frequencies
>> various nature of the first neighboring anions

Inside the parent glass:

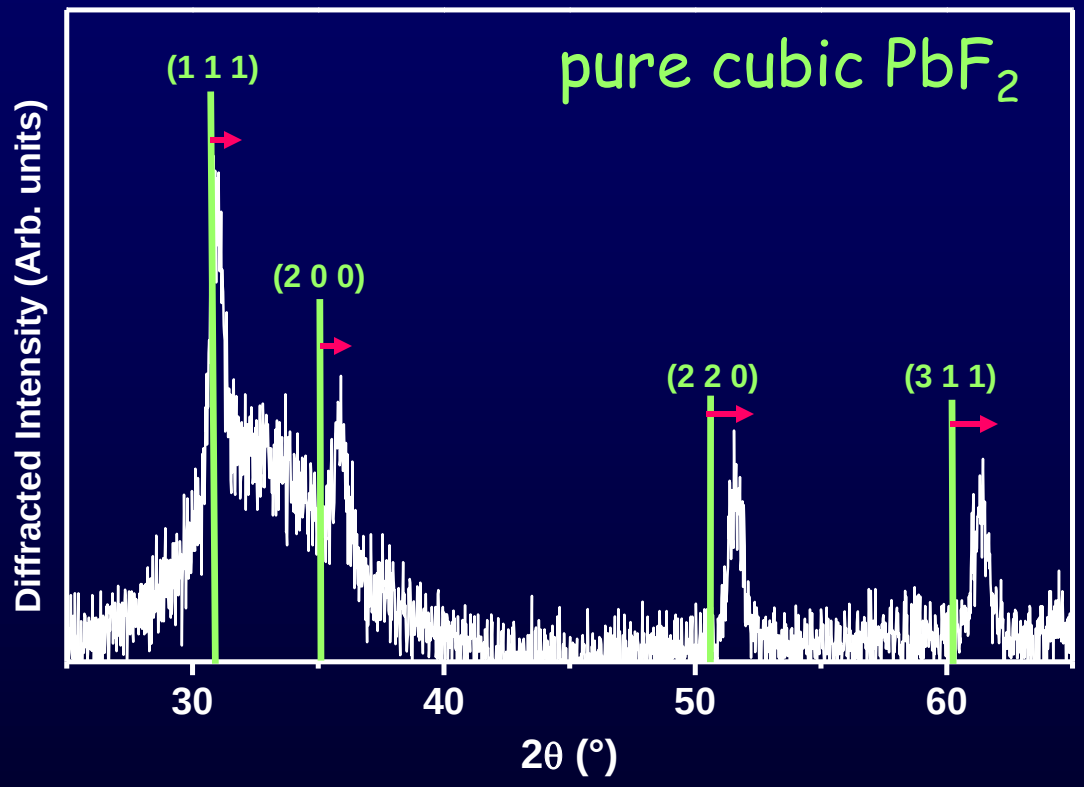
-after melting at 1000°C for 15 minutes: conservation of the initial anionic neighboring of the erbium ions present in the doping compound used

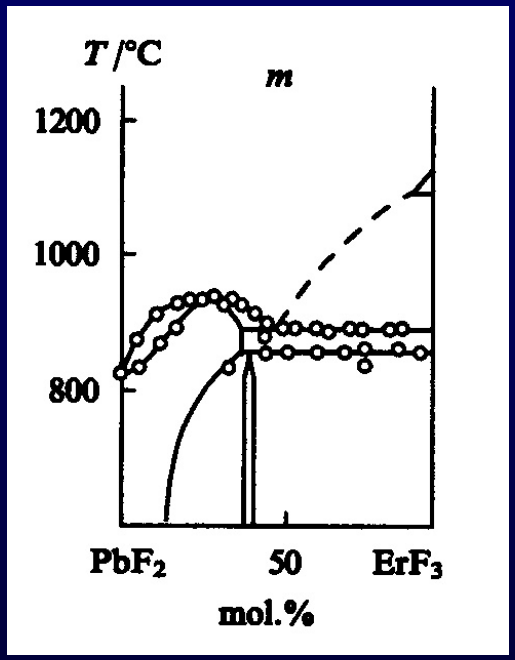
-importance of the precursor compound used to introduce the erbium ions on the nucleation efficiency

-efficient way to modify the optical properties of a glass

But why only ErF_3 is an efficient nucleating agent?

Structural and thermodynamical considerations





X-microanalysis and XRD

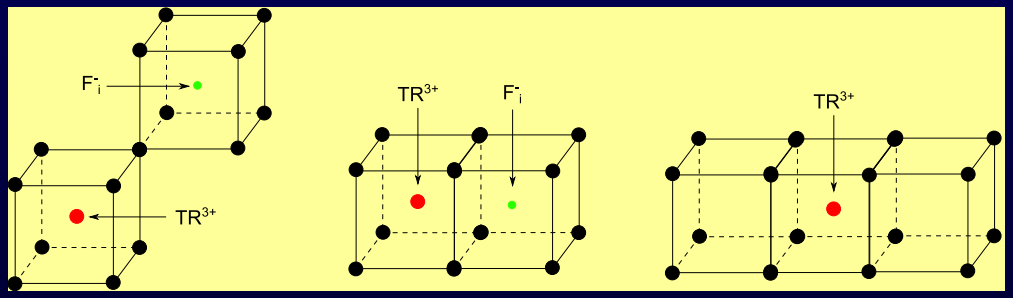
Cubic phase with reduced parameter: solid solution $Pb_{1-x}Er_xF_{2+x}$

Rare earth sites in fluorite type compounds (CaF_2, PbF_2, SrF_2, BaF_2)

A high solubility of rare earths in fluorite structure but many different possible sites due to **charge compensation by excess F^- anion**:

→Isolated ions (6Å between 2 Yb in cubic site) (e.g.: stable in CaF_2):

- Trigonal site (C_{3v})
- Tetragonal site (C_{4v})
- Cubic site (Oh)



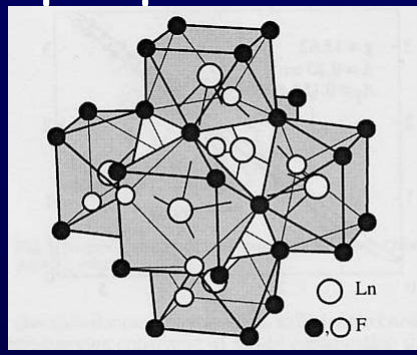
→Clusters

- Dimers (-0.212 eV / Yb^{3+} in CaF_2)
- Tetramers (-0.124 eV / Yb^{3+} in CaF_2)
- Hexameric cluster site (-0.319 eV / Yb^{3+} in CaF_2)

[stabilization energy values from Bendall, 1984]

Rare earth sites in fluorite type compounds (CaF_2, PbF_2, SrF_2, BaF_2)

At high concentration: hexameric cluster site largely dominant and mainly responsible for the optical properties:



- Ln_6F_{37} compatible with fluorite structure:
  - -short distances between Ln^{3+} ions (3 Å)
  - -favors energy transfers, cross relaxations, …
  - -low local symmetry enhancing transition probabilities

Anyway: solid solution or not,
the Ln^{3+} insertion requires simultaneous interstitial F^- ion

What happens with other REF_3?

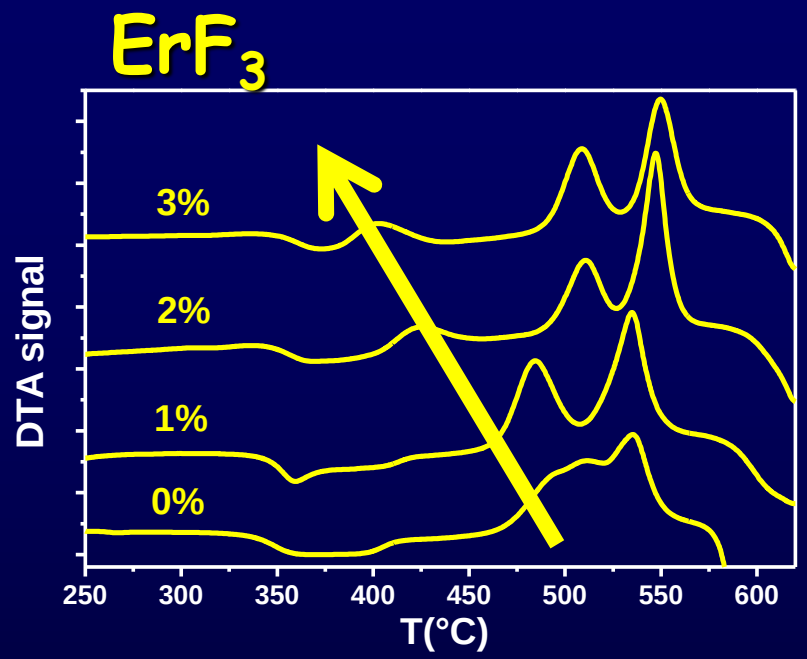
:

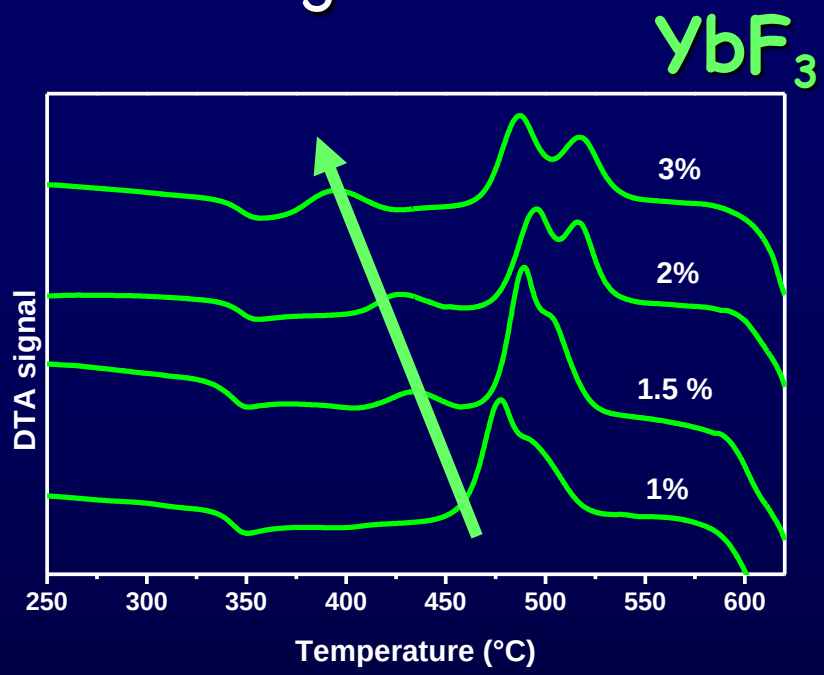
ErF_3

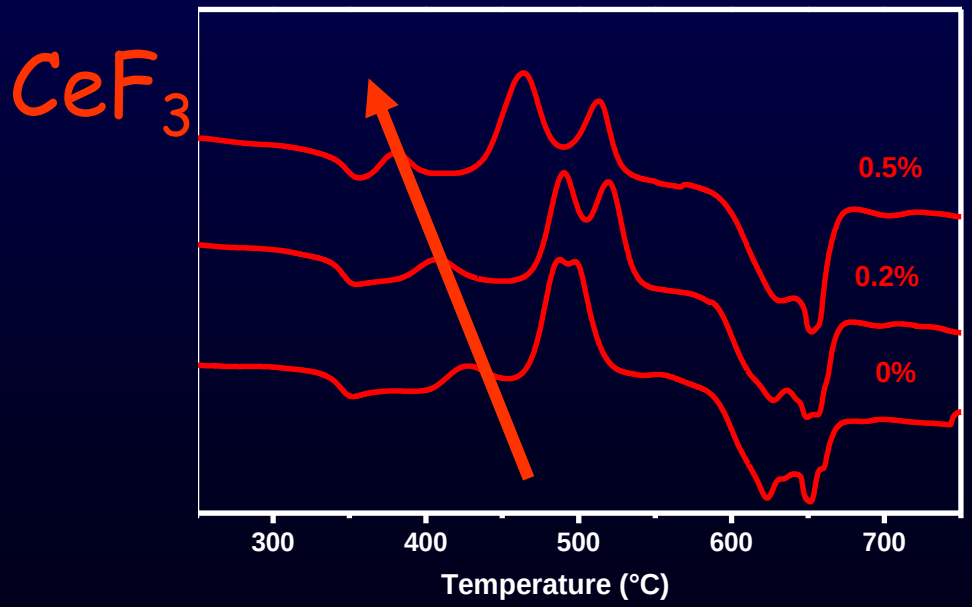
YbF_3

CeF_3

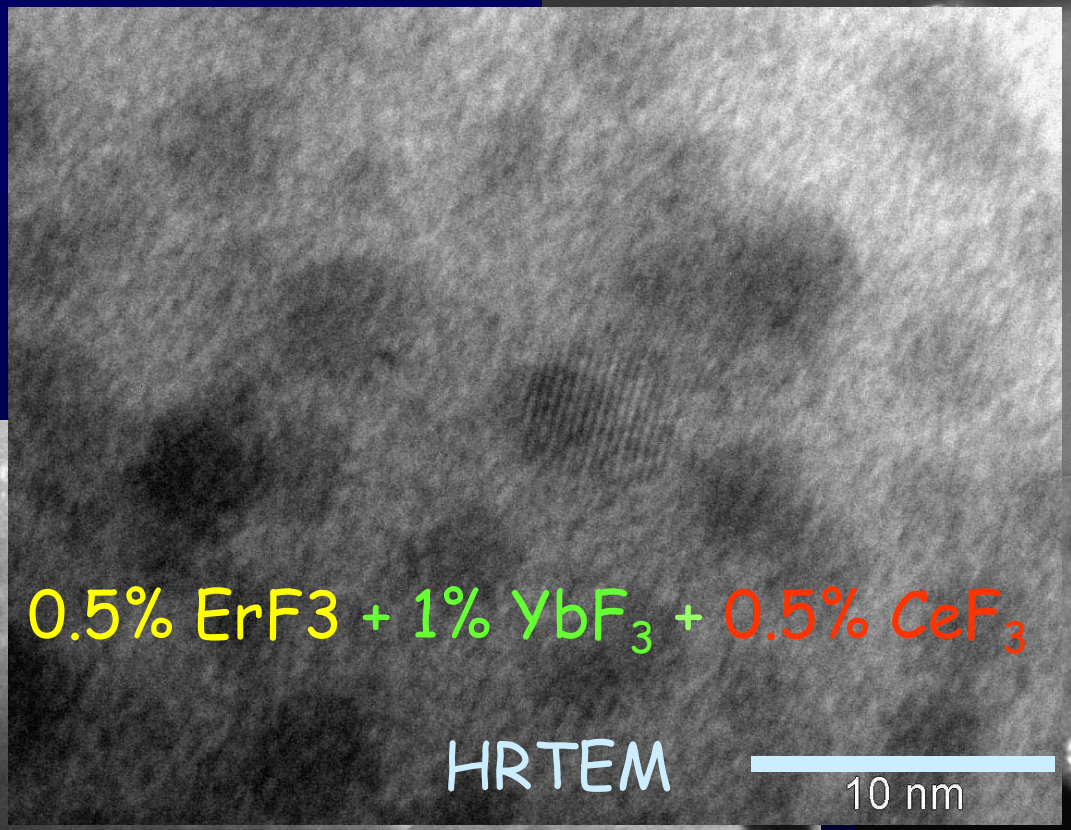
Use of various RE-F_3





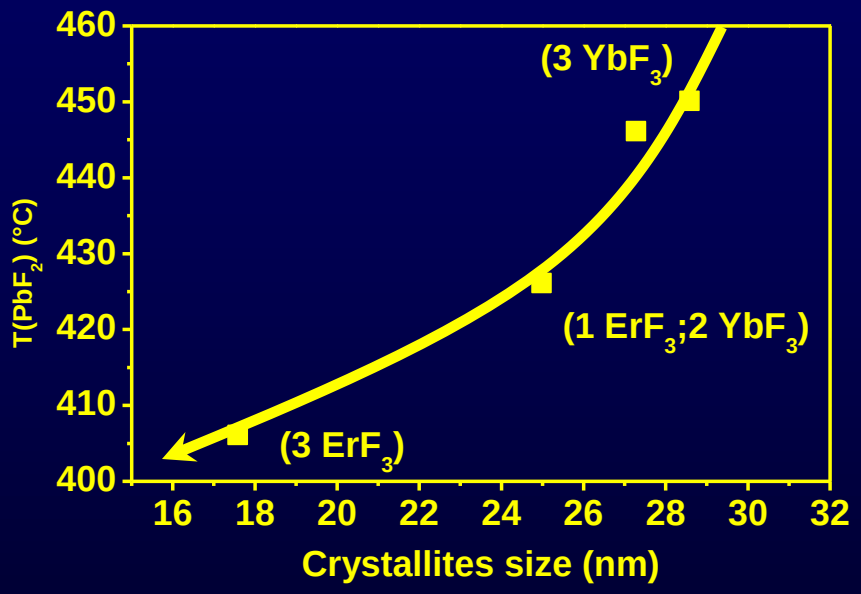


Morphology of glass-ceramics (after thermal treatment)

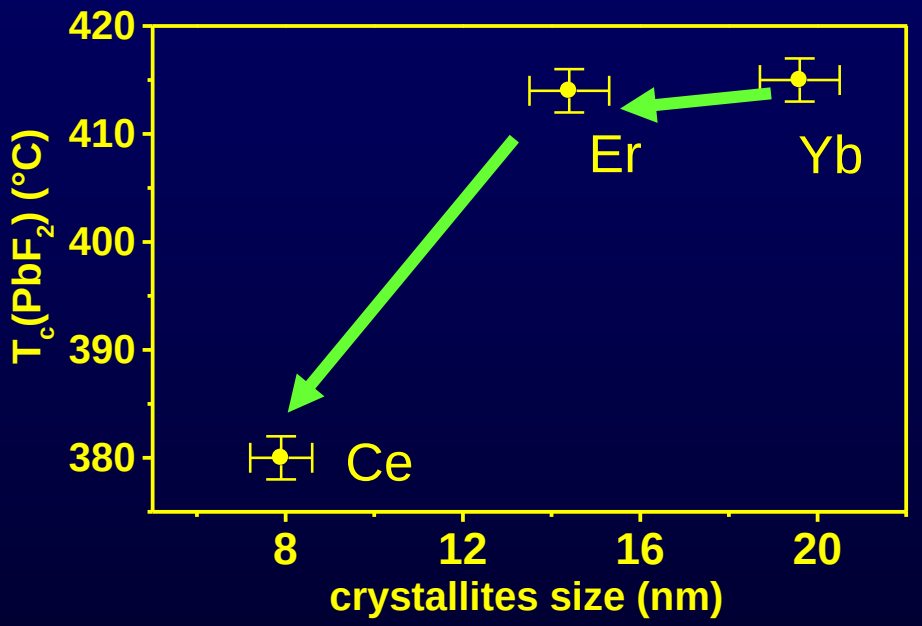


Relative nucleation efficiency within co-doped samples

Yb+Er=3%



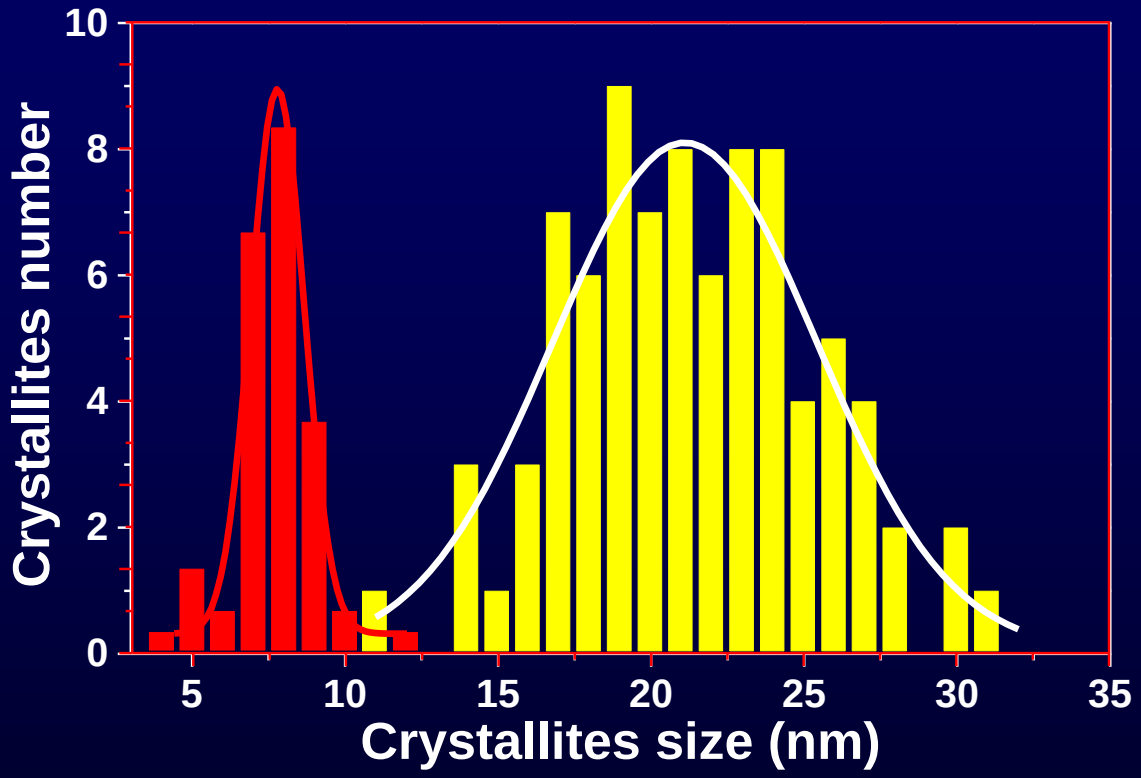
0.5 Er+ 1Yb +0.5 Ln



with a same crystallised volume

$YbF_3 < ErF_3 < CeF_3$

Size distribution of the PbF_2 crystallites

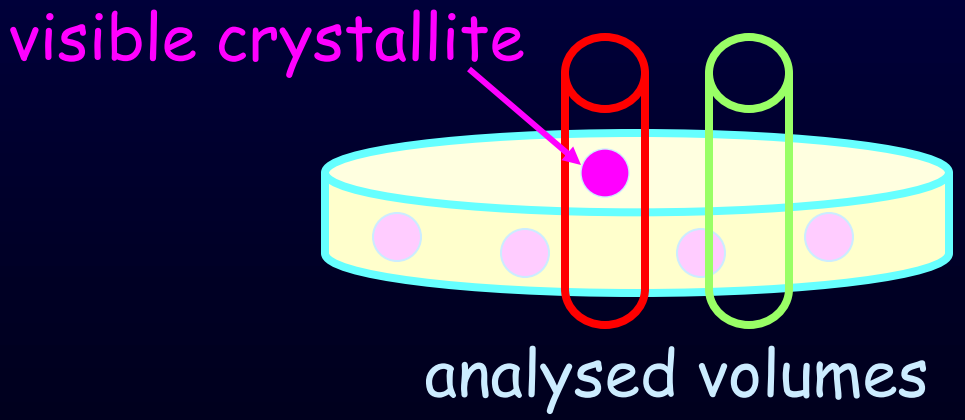


3% ErF_3
Size = 20 ± 5 nm

0.5% ErF_3 + 1% YbF_3 + 0.5% CeF_3
Size = 8 ± 1 nm

Segregation efficiency in PbF_2: X-microanalysis

Element	Crystalline domain (at.%)	Amorphous domain (at.%)	Ratio C/A
F/O	**41.7**	**14.4**	2.9
Ge/Pb	**31.3**	**108**	3.5
Er	**1.1**	**0.3**	3.5
Yb	**2.4**	**0.4**	6
Ce	**0.9**	**0.1**	9



Yb Er Ce inside crystallites

thin glass-ceramic sample

Cause of the various nucleating efficiency

Solid solution: $Pb_{1-x}Ln_xF_{2+x}$

	radius(Å) $8F^-$ coordinated	a(Å) for x=0.02
Pb^{2+}	1.45	5.940
Ce^{3+}	1.28	5.920
Er^{3+}	1.14	5.915
Yb^{3+}	1.12	5.905

$r_{(F^- \text{ coord4})}=1.17$

Solubility in βPbF_2: $CeF_3 > ErF_3 > YbF_3$

To the most soluble compound correspond the lowest energy necessary to crystallise the solid solution (smallest critical radius for nucleation)

→ Nucleation efficiency : $CeF_3 > ErF_3 > YbF_3$

Summary:

After melting at high temperature, the first anionic neighbors of the Er^{3+} ions are conserved (DTA, optical properties) in the glass

ErF_3 induces nucleation of PbF_2 when $ErCl_3$, ErOF and Er_2O_3 do not

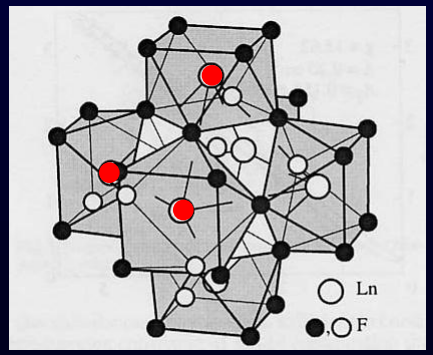
>>>>The way used to introduce the active ions is crucial

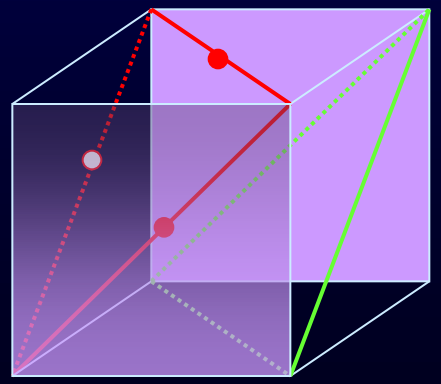
CeF_3, ErF_3, YbF_3 do not act as defects but contribute to crystallize a solid solution $Pb_{1-x}Ln_xF_{2+x}$ energetically favorable

>>>> the "nucleating character" reflects the solubility of the ions in the βPbF_2 phase and induces a reduction of the critical radius for nucleation

Looking for ytterbium ions (and clusters ?) inside crystallites thanks to HR-HAADF-STEM

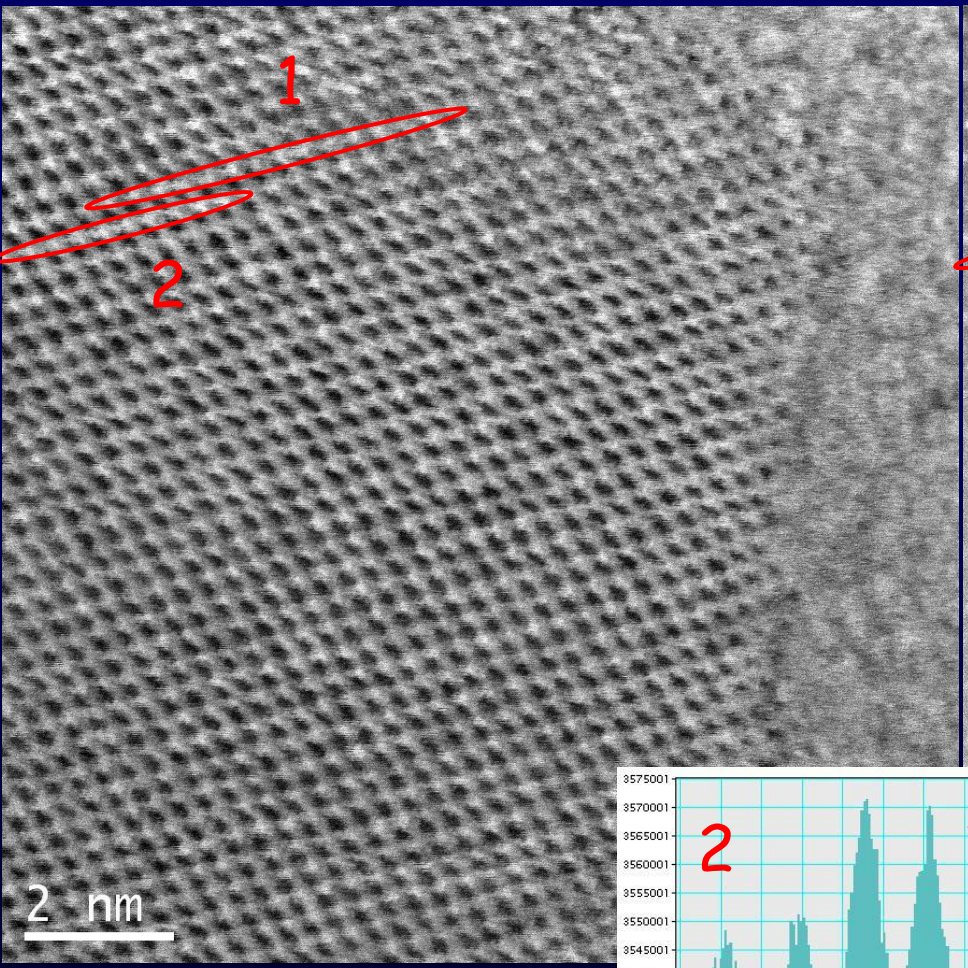
...some images in {111} plane of one grain of CaF_2

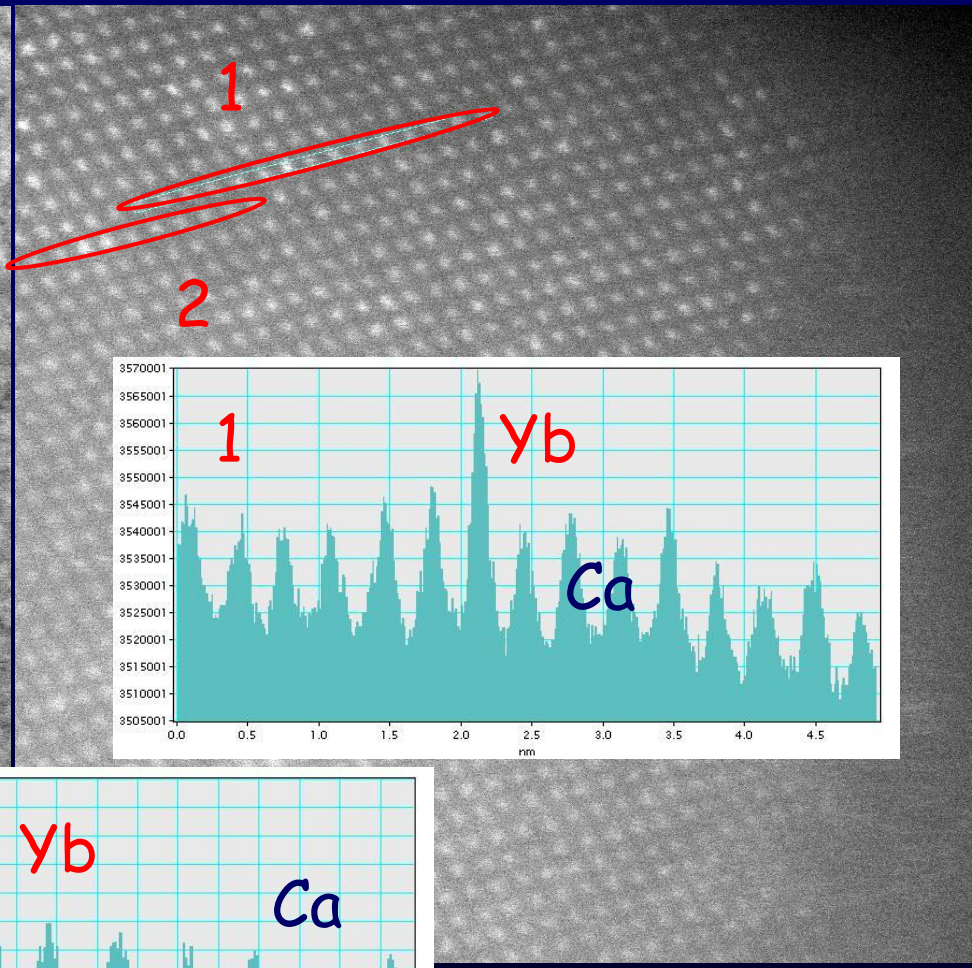


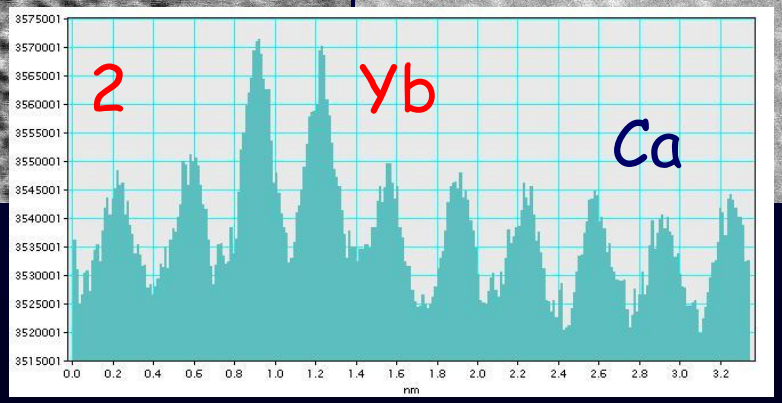


BF-STEM

Z contrast (HAADF)

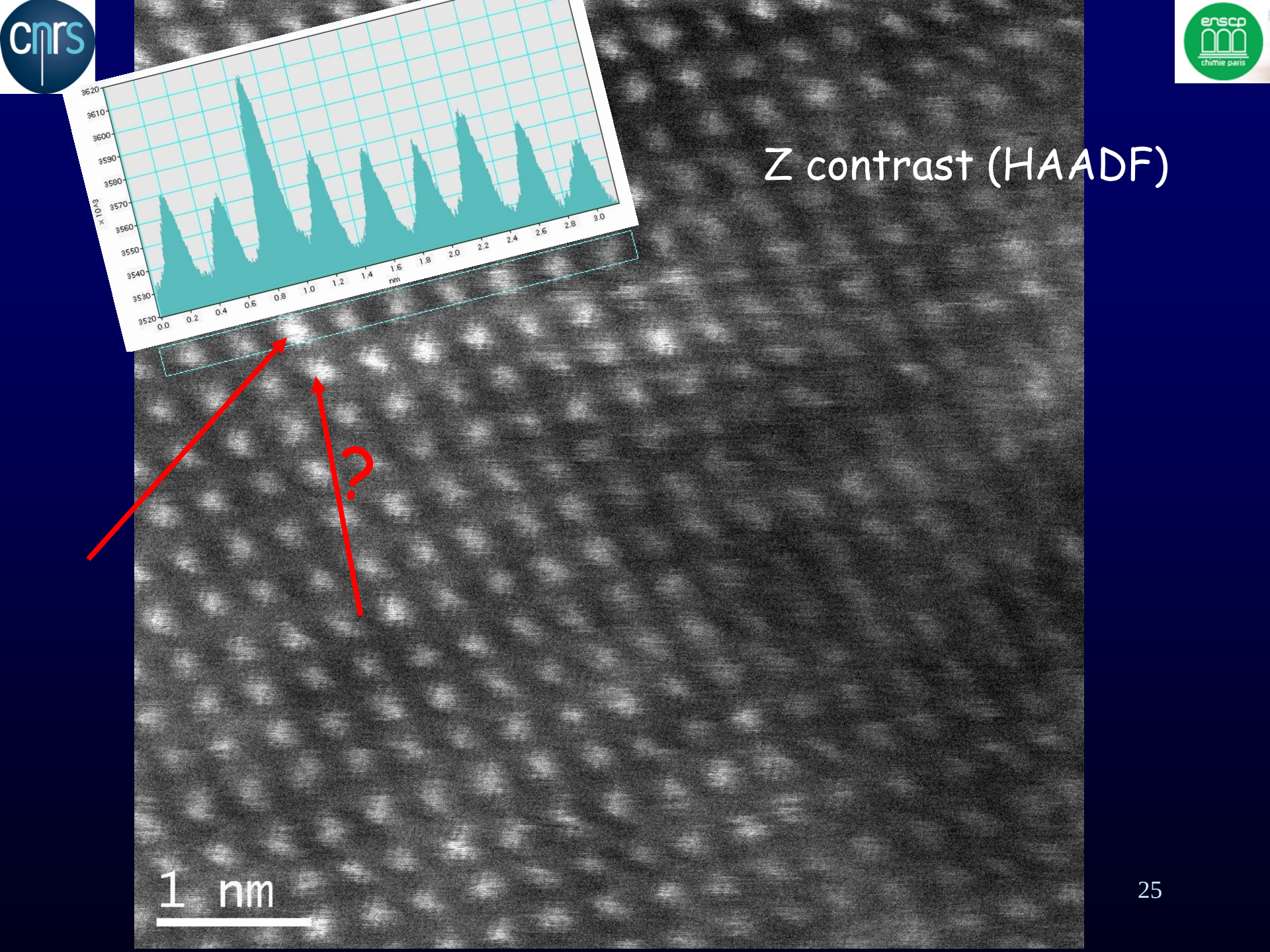




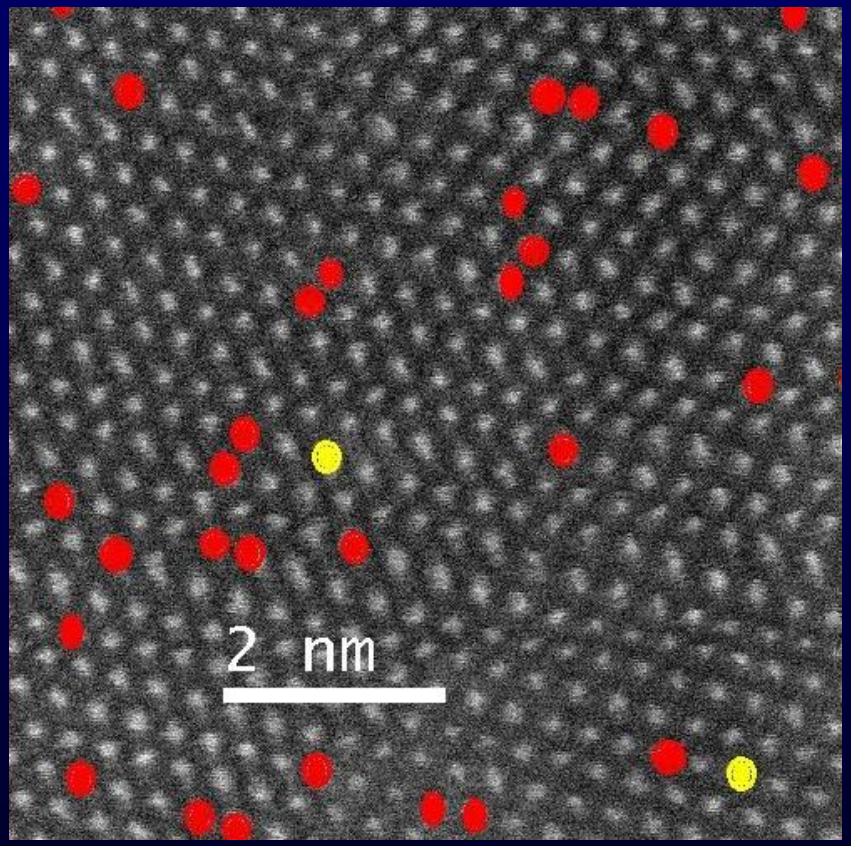


Resolution = 1 Angstrom

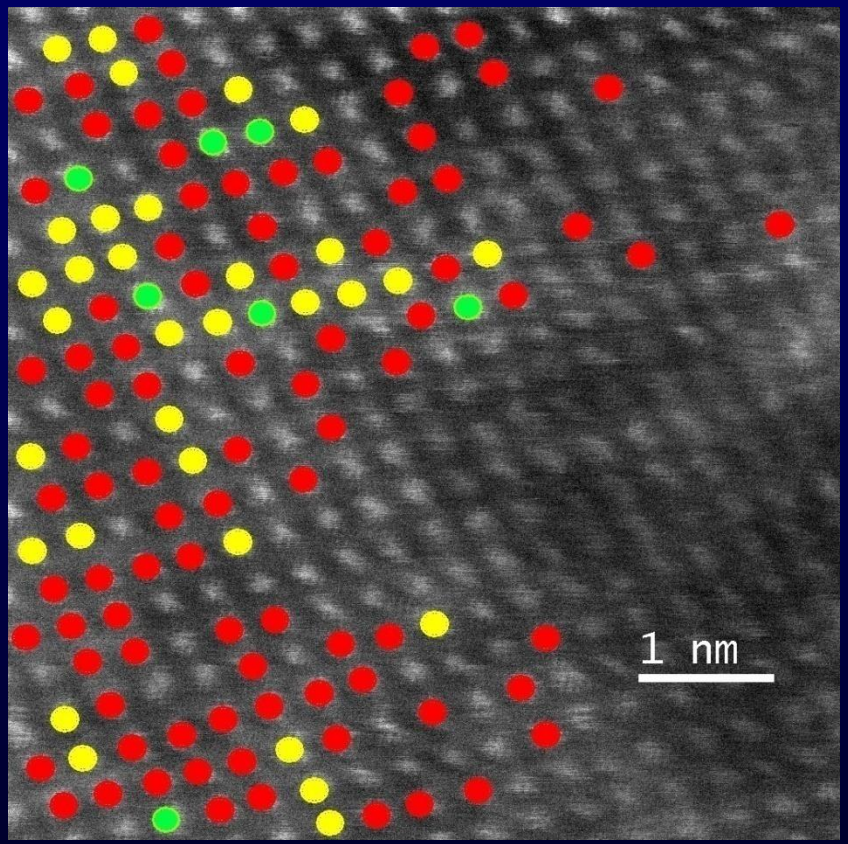
<110> zone axis


Z contrast (HAADF)
?
1 nm

Ytterbium clusters



CaF_2 : 0.5%Yb



CaF_2 : 5%Yb

1 2 3 Yb per atomic column

26

Thank you for your attention !