

# Structure and luminescence properties of highly nonstoichiometric gadolinium aluminium garnet (GAG)

**PhD Xue FANG**

xue.fang@cnrs-orleans.fr

**Supervisors: Mathieu Allix & Michael J. Pitcher**



**LE STUDIUM**  
Loire Valley  
**Institute for Advanced Studies**

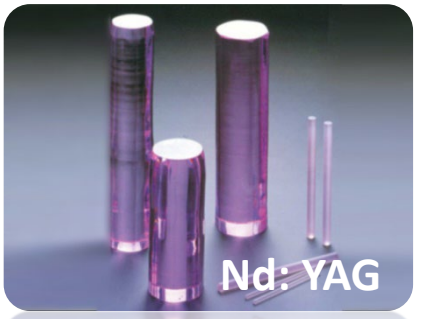
# Applications and structure of garnet

## Application

## Structure

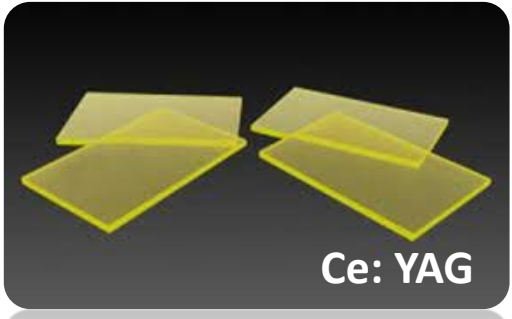


### Solid laser



Nd: YAG

### Scintillator

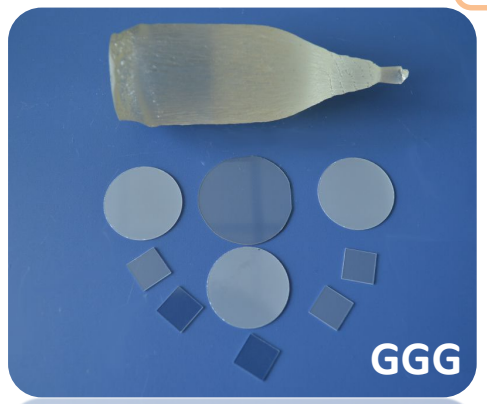


Ce: YAG

### Phosphor



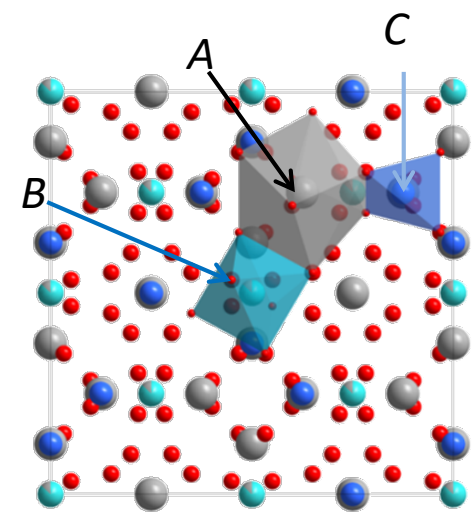
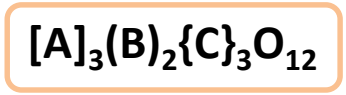
### Magneto-optical



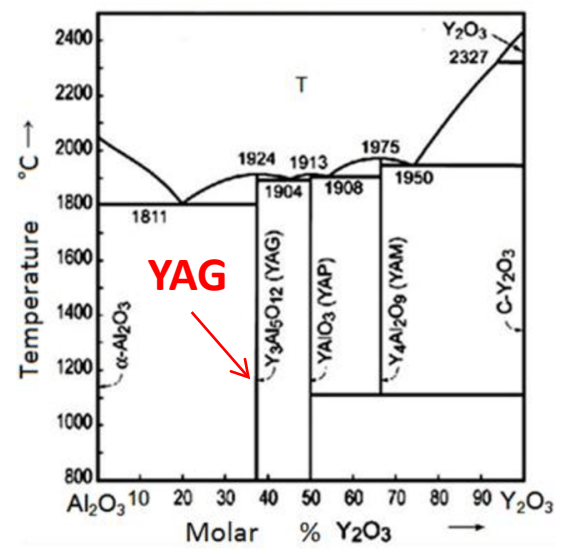
GGG



YIG



### Phase diagram



- ▀  $Y_3Al_5O_{12}$  (YAG) is always as a line compound
- ▀ Ns YAG - melt crystallisation, single crystal.
- ▀ Solid solution with  $x < 0.03$  ( $Y_{3+x}Al_{5-x}O_{12}$ )

# Highly non-stoichiometric YAG

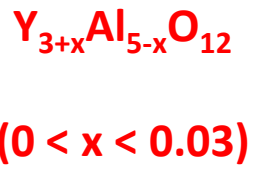
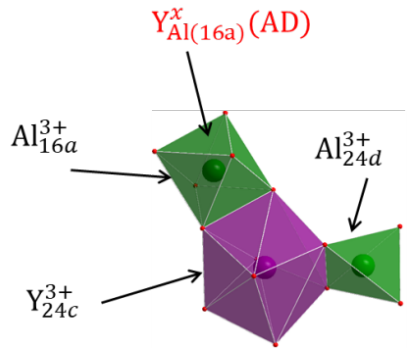
“anti-site defect”

Highly non-stoichiometric YAG

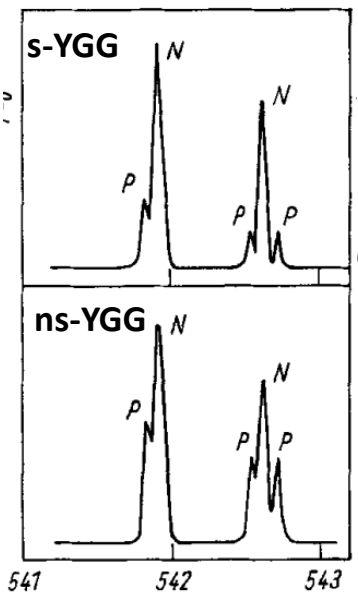
Weiwei Cao, Ana Isabel Becerro, Victor Castaing, Xue Fang et al. *Adv. Funct. Materi*, (2023), 23, 14

1% excess Y occupies Al<sub>oc</sub>

YGG: Er<sup>3+</sup>



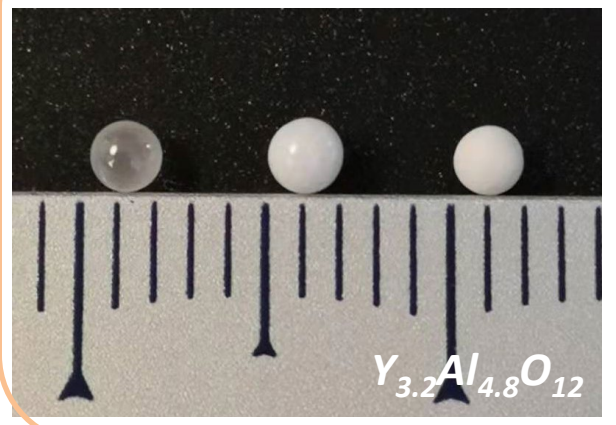
@A. Patel. *Appl. Phys. Lett.* (2008)



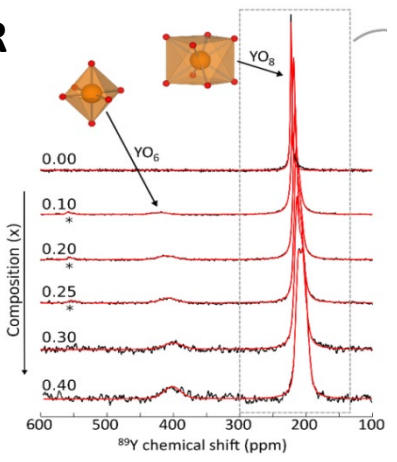
M. K. Ashurov. *Phys. stat. sol.* (1977)

06/10/2023

ADL synthesis

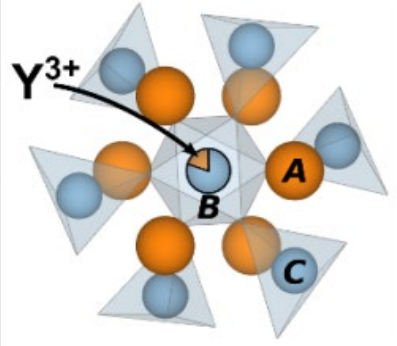
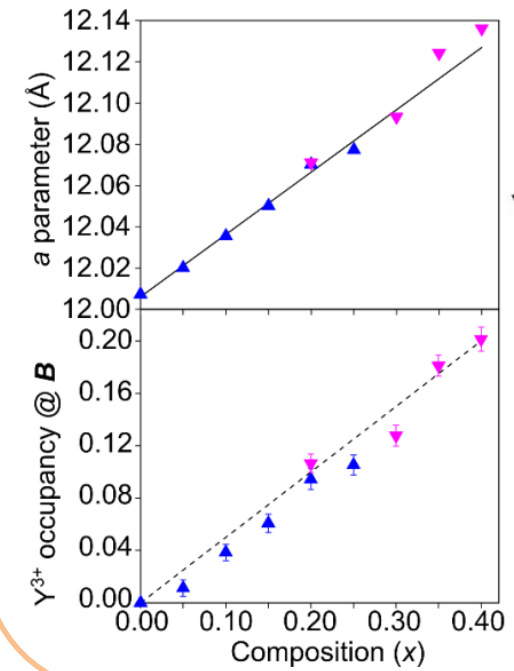


Y NMR



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SPD



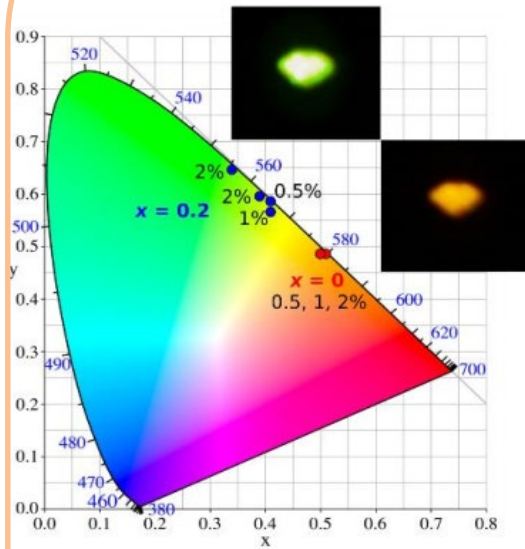
$Y_{3+x}Al_{5-x}O_{12}$  ( $0 < x < 0.4$ ) !!!

20% B is occupied by Y<sup>3+</sup>

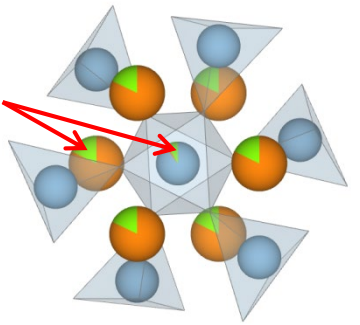
# Highly non-stoichiometric GAG

## Modification of Luminescence Properties

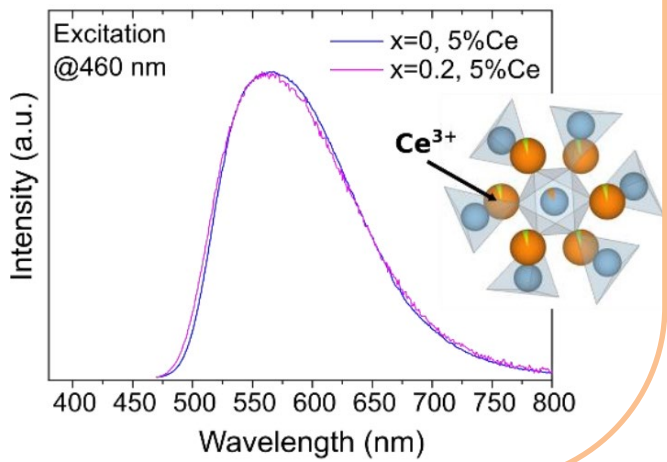
### Up-conversion YAG: Er<sup>3+</sup>/Yb<sup>3+</sup>



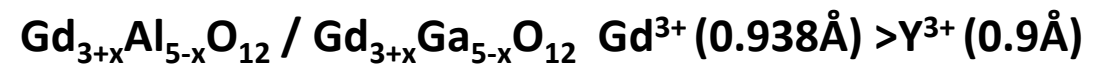
### Er<sup>3+</sup>/Yb<sup>3+</sup>



### Down-conversion YAG: Ce<sup>3+</sup>



## Highly non-stoichiometric GAG/GGG



???Question:

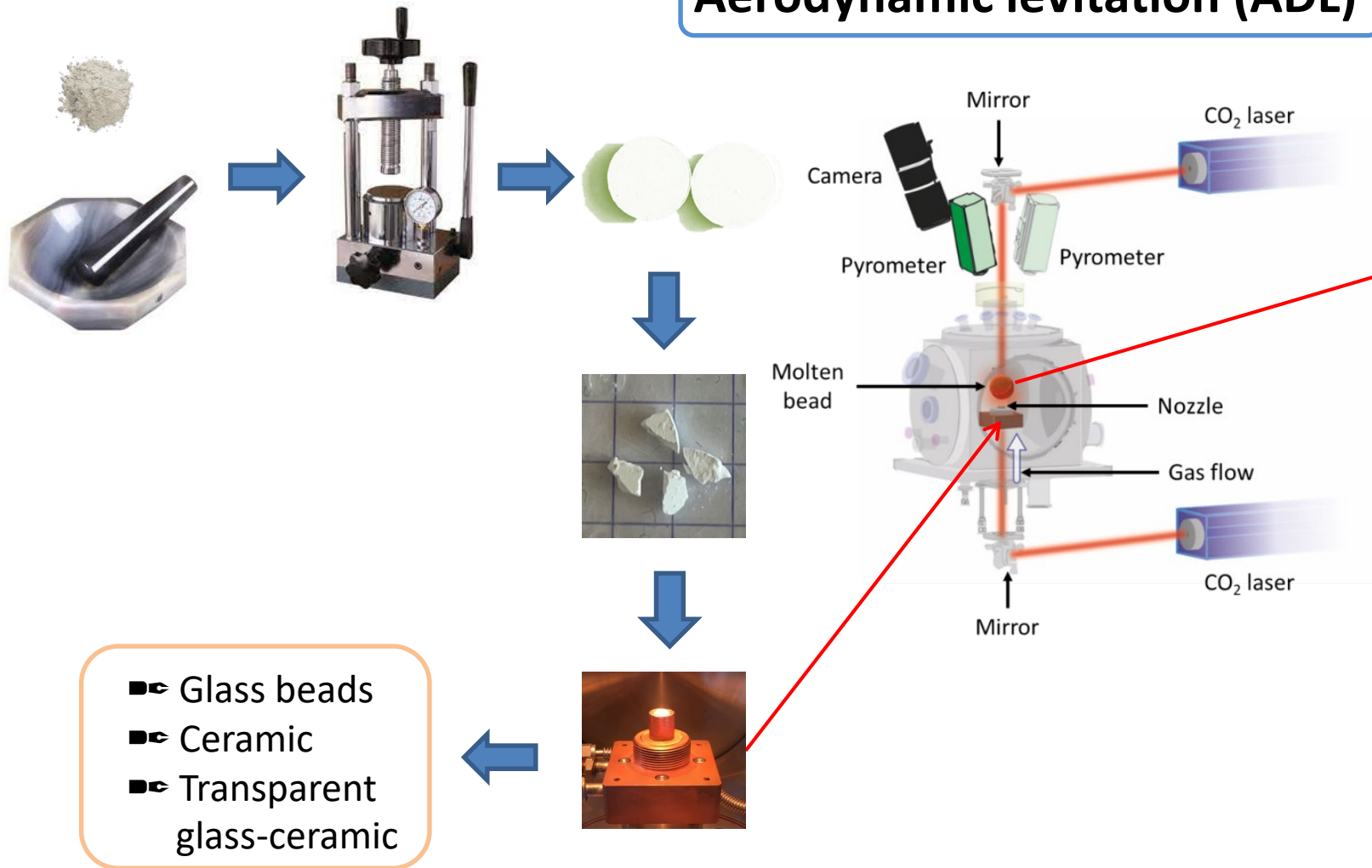
- ① Other highly nonstoichiometric garnet? (ADL synthesis)
- ② Range of solid solution (x < ?) (SPD)
- ③ Which dopant? Ce<sup>3+</sup>, Tb<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup> occupy the B site to form a new luminescent site.
- ④ How the luminescence performance respond to new BO<sub>6</sub> site? (Luminescence spectrum)

$Gd_{3+x}Al_{5-x}O_{12}$  !!



# Aerodynamic levitation

## Aerodynamic levitation (ADL)

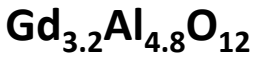


- Glass beads
- Ceramic
- Transparent glass-ceramic

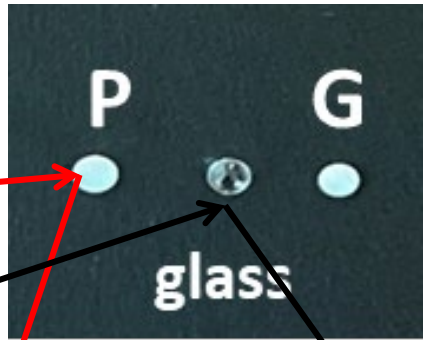
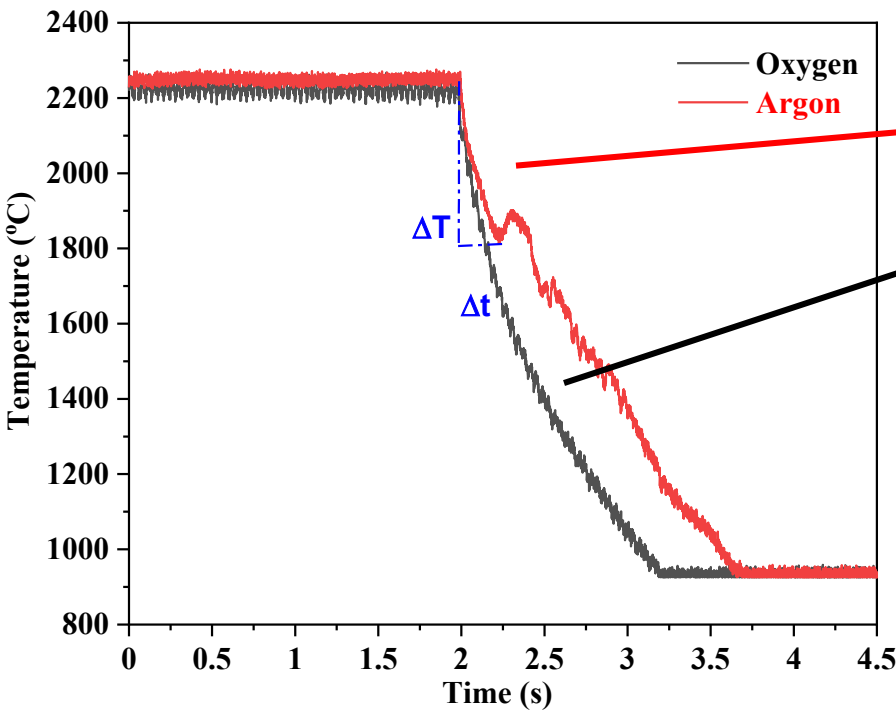
- ### ADL - ADVANTAGES
1. Extreme high temperature > 2000 °C
  2. Avoid heterogeneous nucleation
  3. Fast cooling rate
  4. Easy and fast fabrication
  5. Homogeneous

# Synthesis-crystallization from glass

## ① Other highly nonstoichiometric garnet? (ADL synthesis)



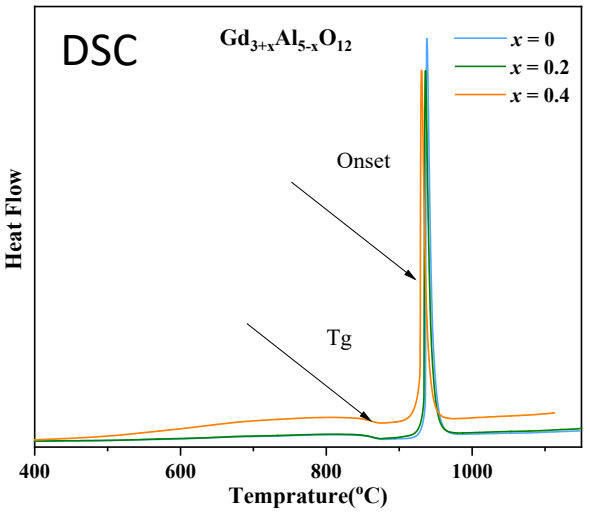
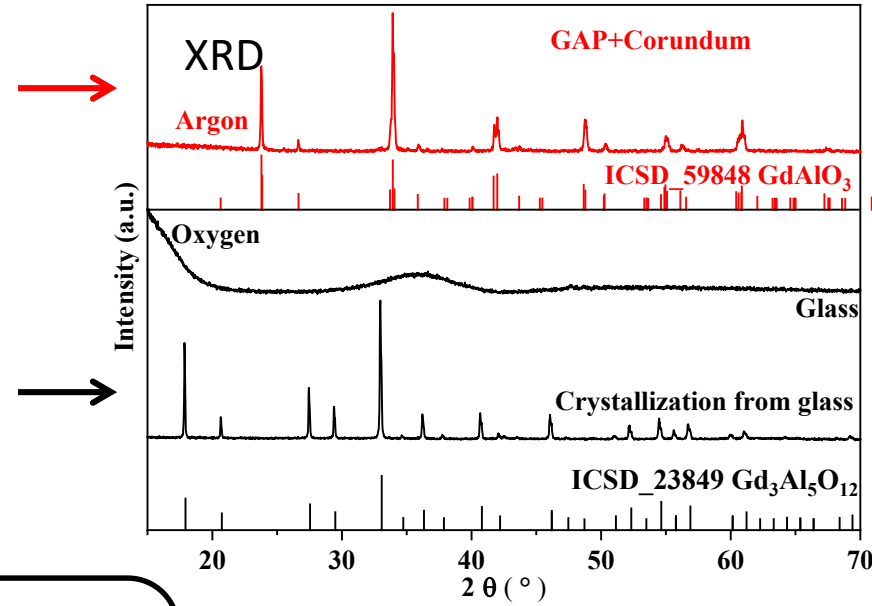
Cooling rate



Crystallization from melt



Oxygen-faster cooling rate

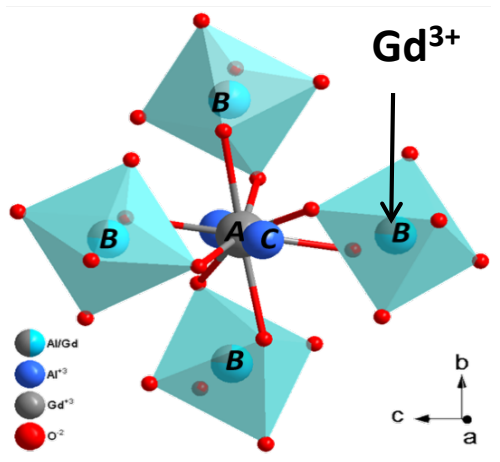
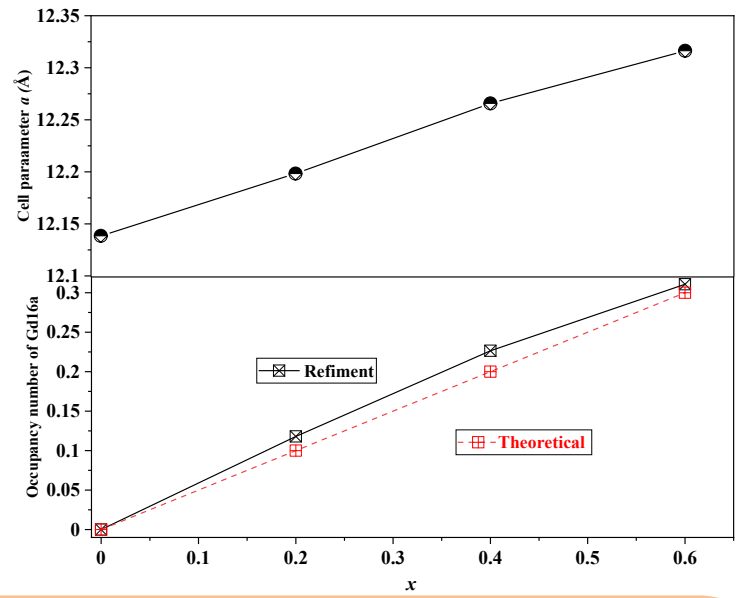
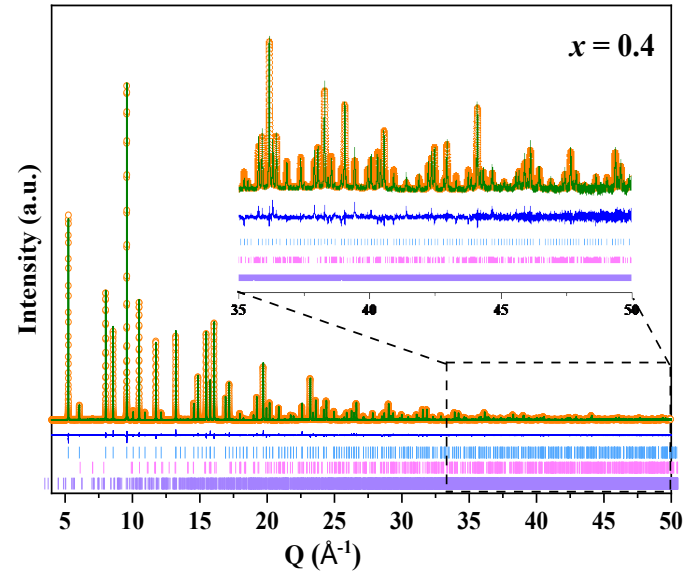
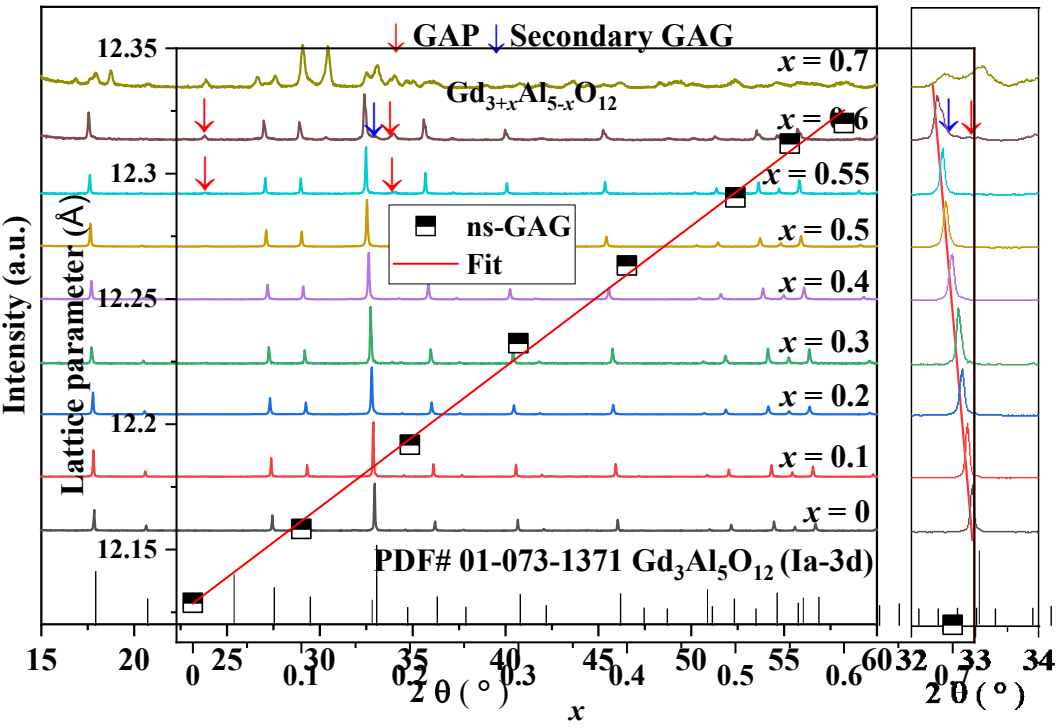
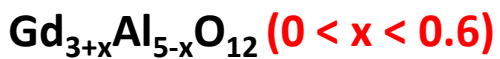


# Average structure analysis by powder diffraction

② Range of solid solution ( $x < ?$ ) (SPD)

SPD refinement

X-Ray diffraction

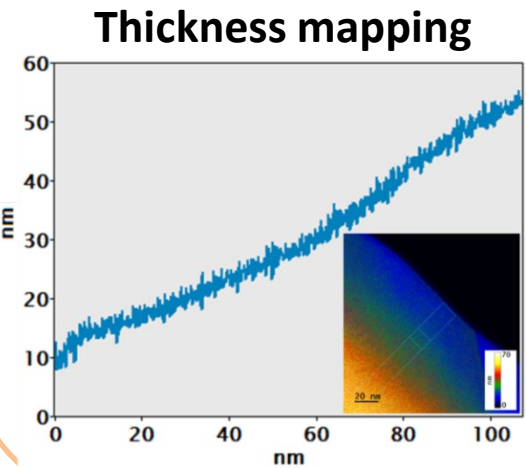
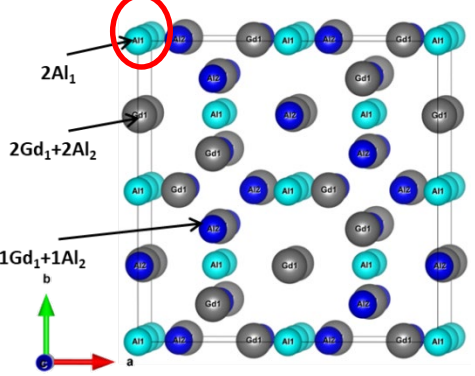
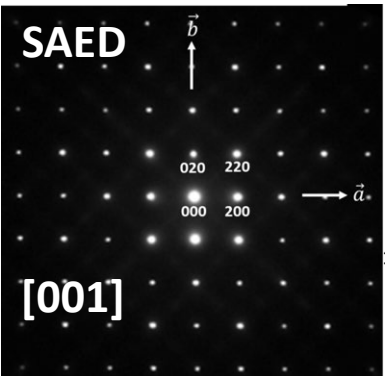
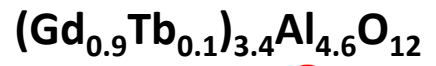


- ▣ Solid solution  $0 \leq x \leq 0.6$
- ▣ Up to 30% of the octahedrally-coordinated  $Al^{3+}$  at the B sites was substituted by  $Gd^{3+}$
- ▣ More Gd ( $x = 0.6$ ) occupies the octahedral site compared to Y ( $x = 0.4$ ), although Gd is larger than Y.

# Local structure analysis by STEM

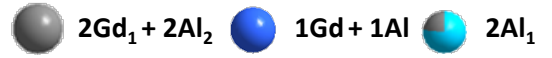
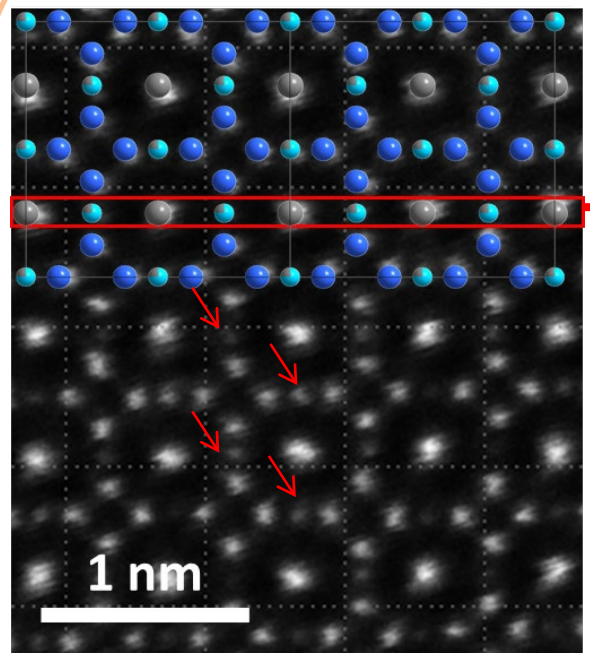
Cécile Genevois

③ Which dopant?  $Tb^{3+}$  occupy the B site to form a new luminescent site? (STEM)  $Gd^{3+}$  (0.938Å)  $Tb^{3+}$  (0.932Å)

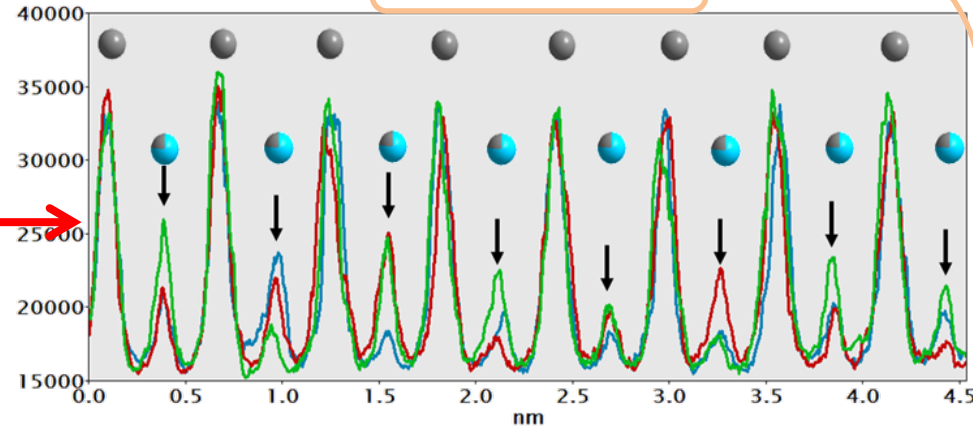


Thickness < 15 nm

## STEM-HAADF



## Intensity profile



### Z-contrast

$$I \propto \sum_i (m_i Z_i^n)$$

$Z_{Gd} = 64$   
 $Z_{Al} = 13$   
 $Z_{Tb} = 65$

I: intensity Z: atomic number of the element

Occupation of the B site by  $Gd^{3+}$



# Where is the dopant Tb? STEM-EDS

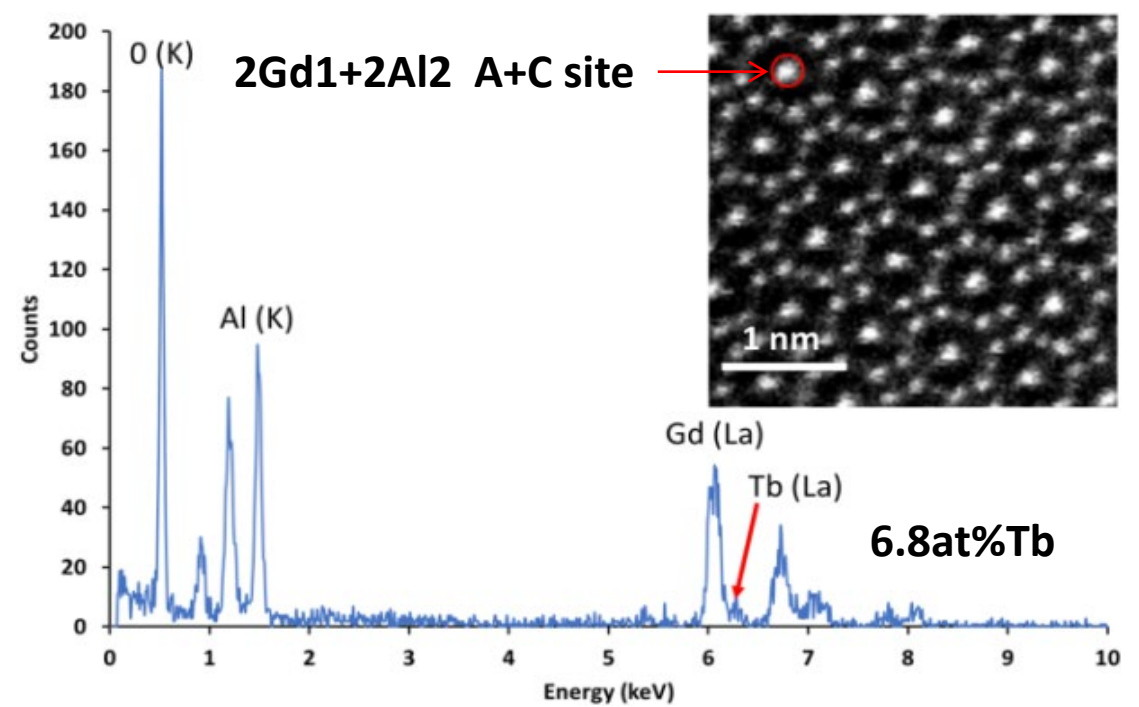
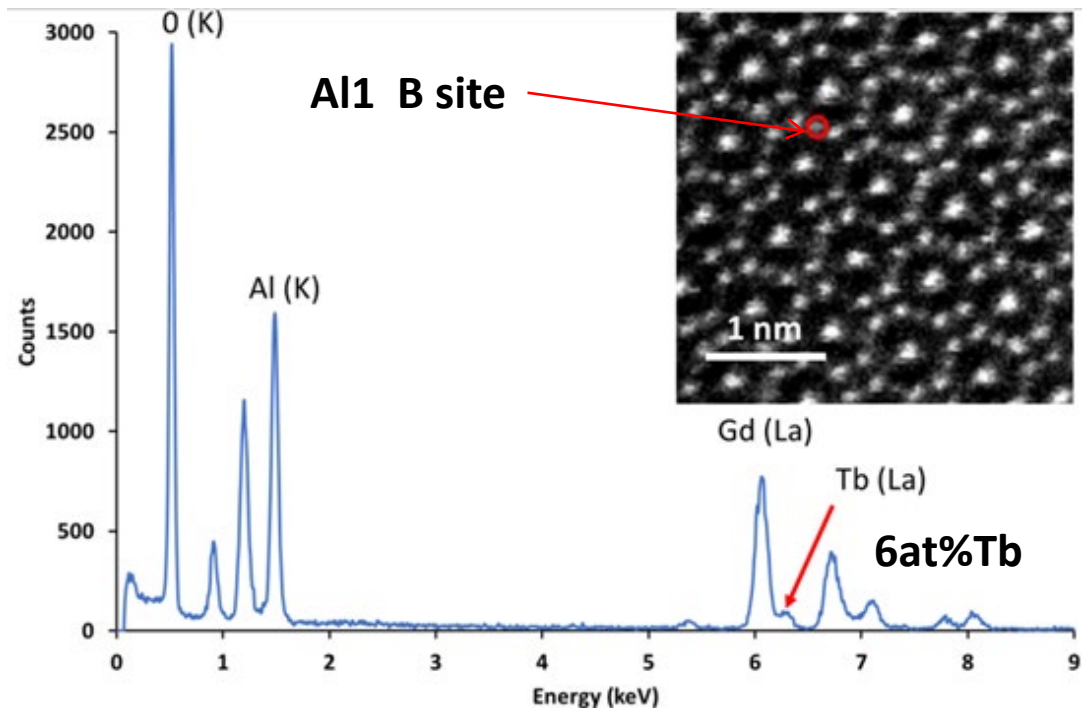
Cécile Genevois

STEM-EDS spectra at atom scale - L rays

► Tb<sup>3+</sup> distribute at A and B site

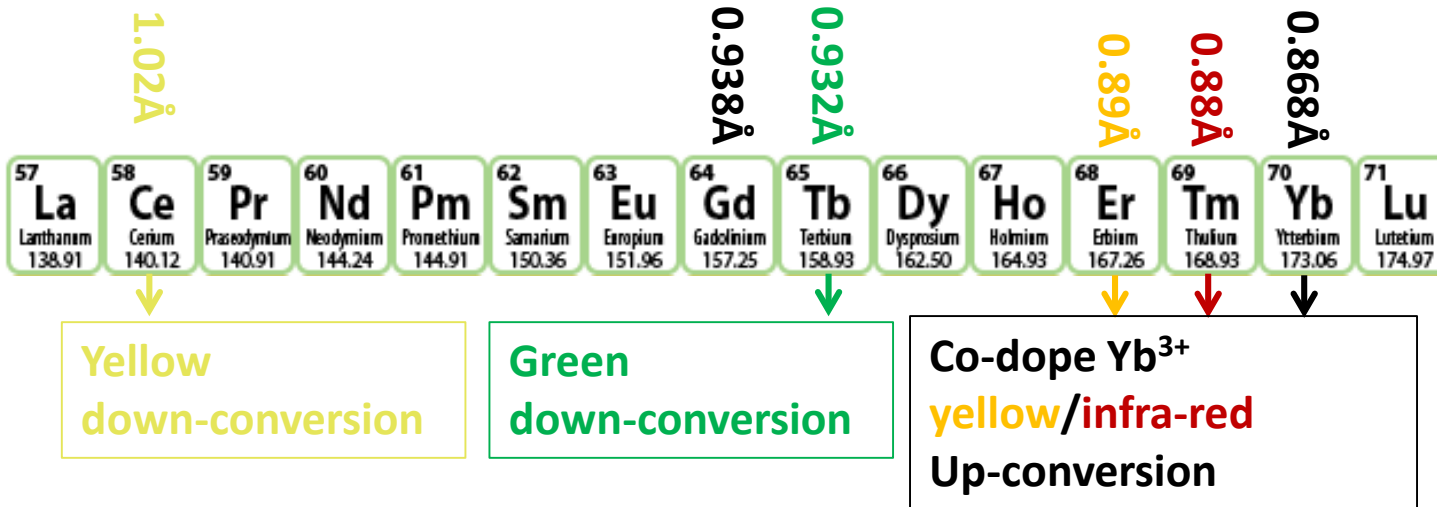
B site?

A site?



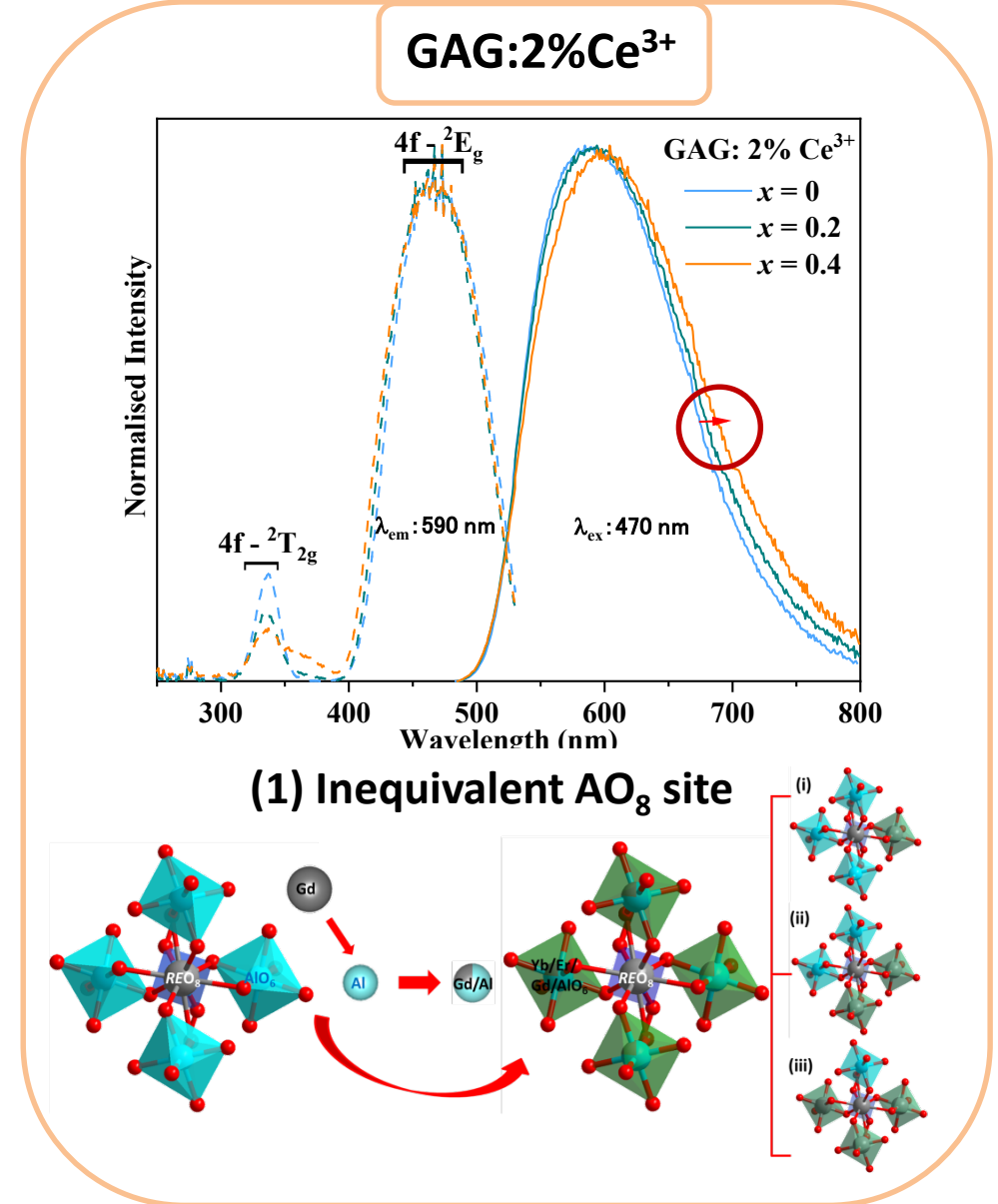
# Luminescence properties

④ How the luminescence properties respond to new  $\text{BO}_6$  site?  
(Luminescence spectrum)



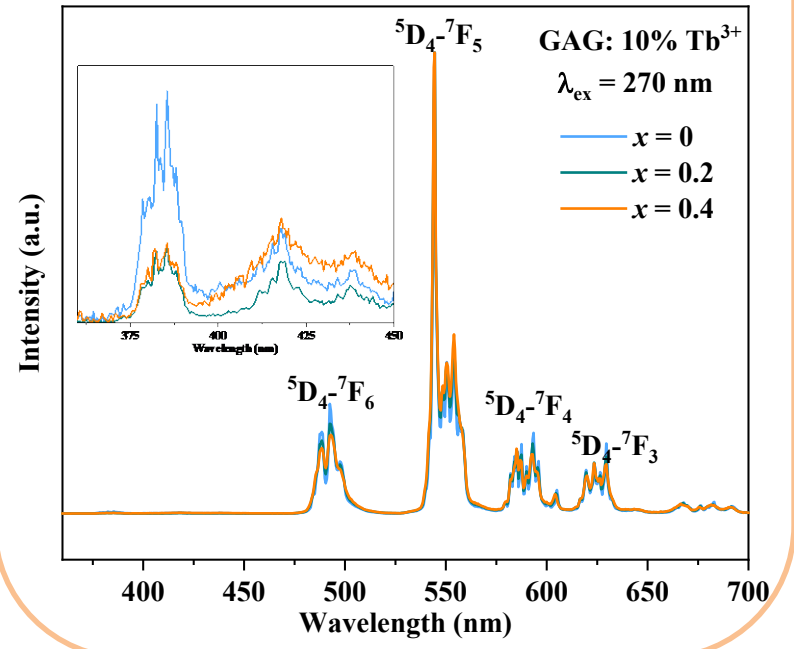
$\text{Ce}^{3+}$  : f-d transition is sensitive to environmental change  
 $\text{Tb}^{3+}$  : f-f transition is insensitive to environmental change  
 $\text{Tm}^{3+}$  :  $^3\text{H}_4$ - $^3\text{H}_6$  of  $\text{Tm}^{3+}$  is hypersensitive transition  
 $\text{Er}^{3+}$  :  $^2\text{H}_{11/2}$  -  $^4\text{I}_{15/2}$  of  $\text{Er}^{3+}$  is hypersensitive transition

Ana Becerro and Victor Castaing

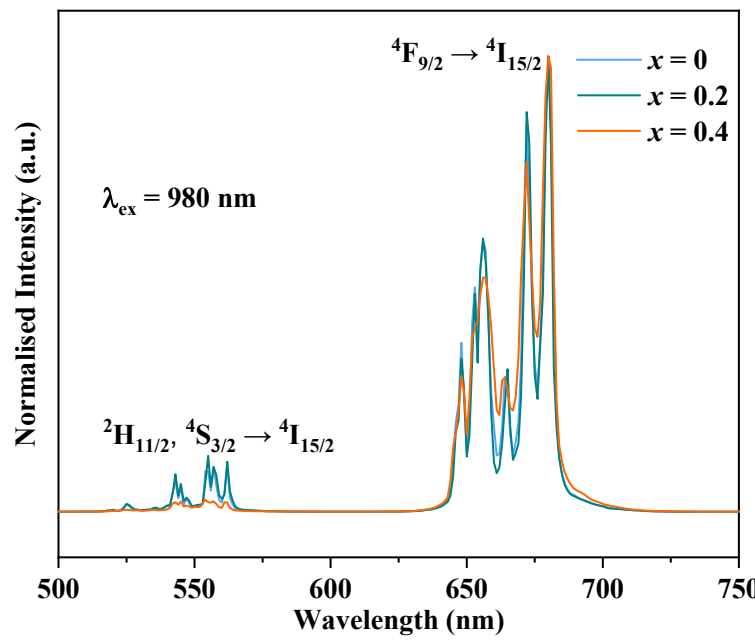


# Luminescence properties

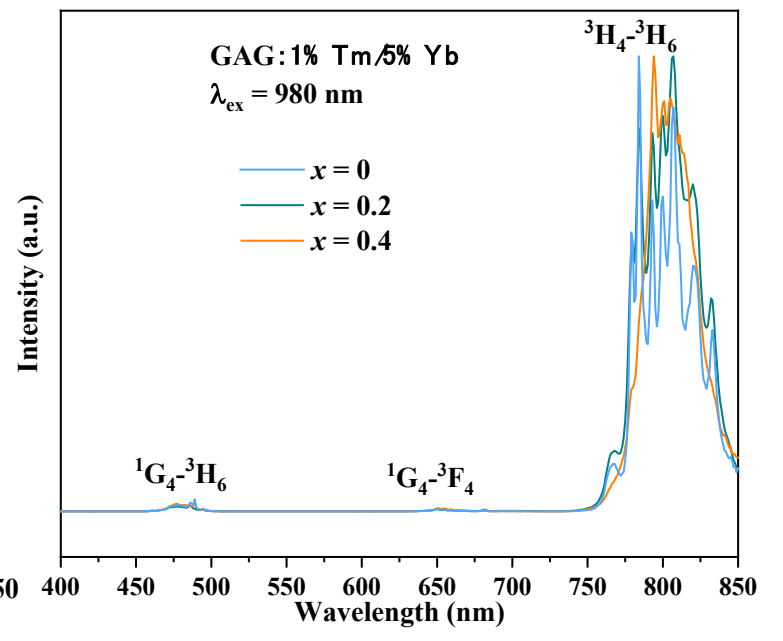
**GAG:10%Tb<sup>3+</sup>**



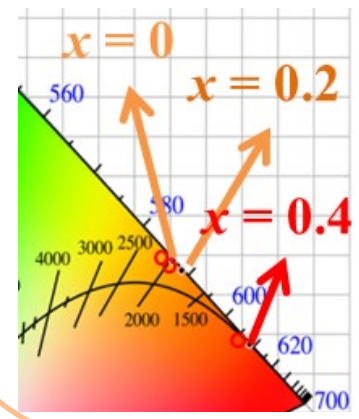
**GAG:2%Er<sup>3+</sup>/20%Yb<sup>3+</sup>**



**GAG:1%Tm<sup>3+</sup>/10%Yb<sup>3+</sup>**

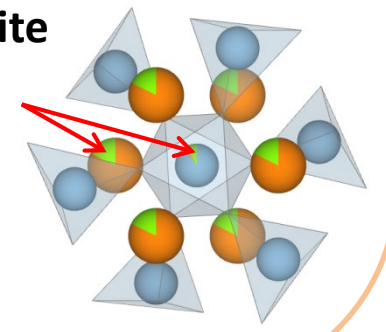


The f-f transitions of most rare earth ions are little influenced by their surroundings due to the shielding effect of the <sup>5</sup>S<sub>2</sub> and <sup>5</sup>P<sub>6</sub> shell.

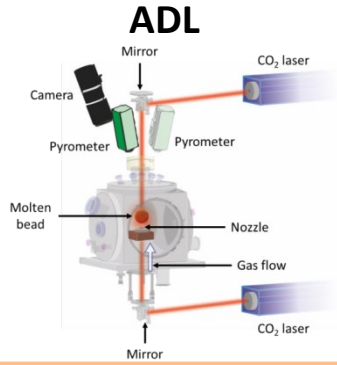


■ Hypersensitive transition  
<sup>2</sup>H<sub>11/2</sub> - <sup>4</sup>I<sub>15/2</sub> of Er<sup>3+</sup> and <sup>3</sup>H<sub>4</sub> - <sup>3</sup>H<sub>6</sub> of Tm<sup>3+</sup> are sensitive to BO<sub>6</sub> site

(2) AO<sub>8</sub>+BO<sub>6</sub> site



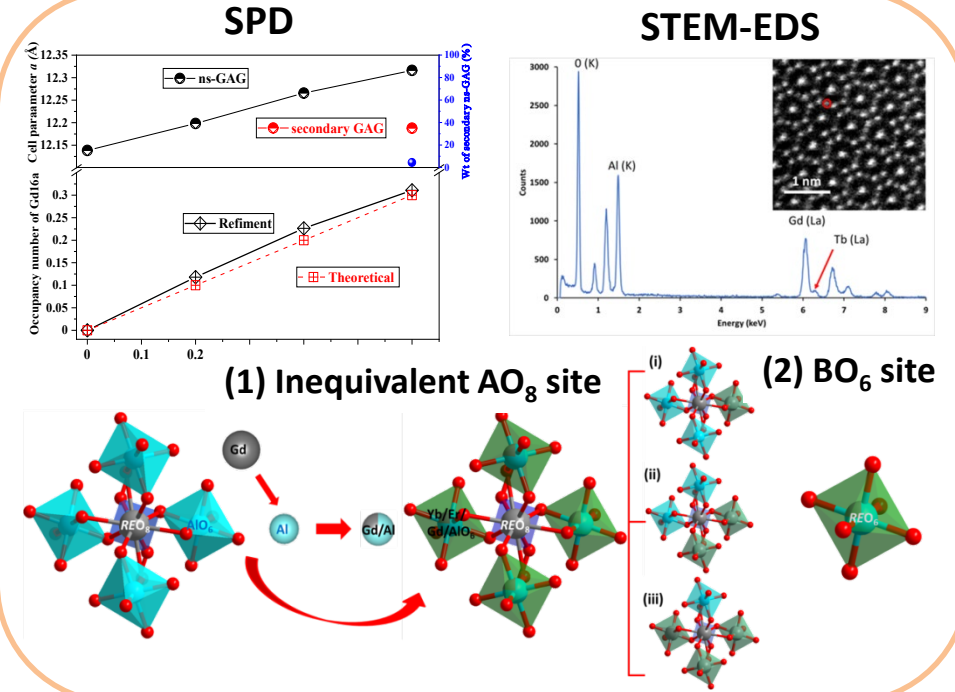
# Conclusions



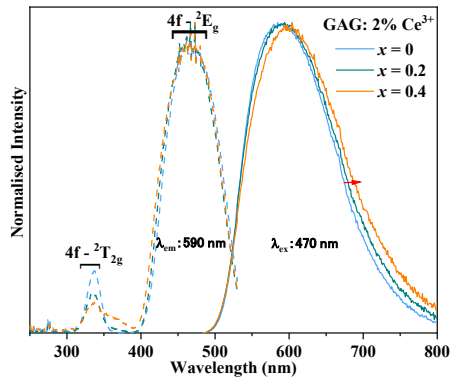
Synthesis

Highly nonstoichiometric GAG

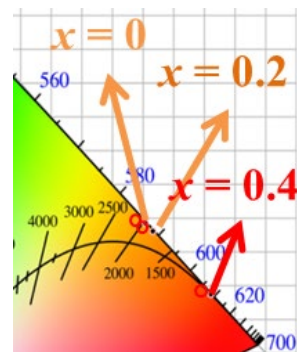
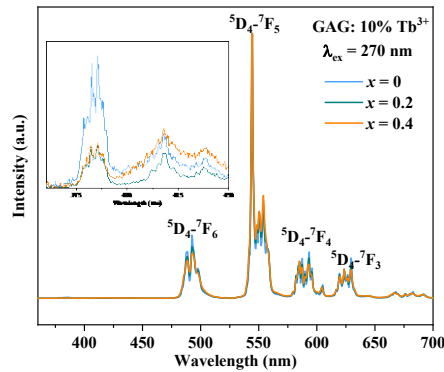
Structure



(1) Inequivalent  $AO_8$  site  
f – d transition of  $Ce^{3+}$



(2)  $BO_6$  site  
f – f Hypersensitive transition ( $Er^{3+}/Tm^{3+}$ )

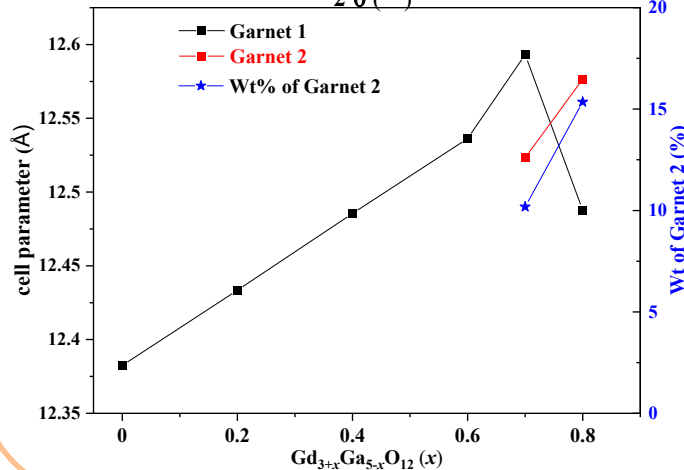
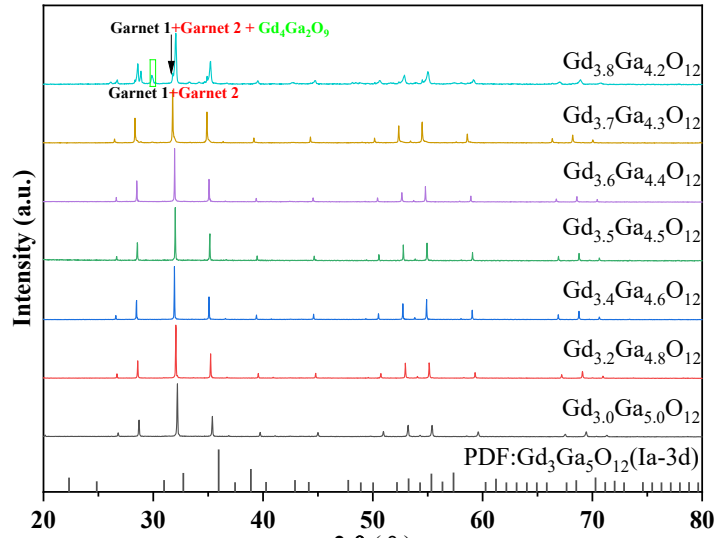


Luminescence

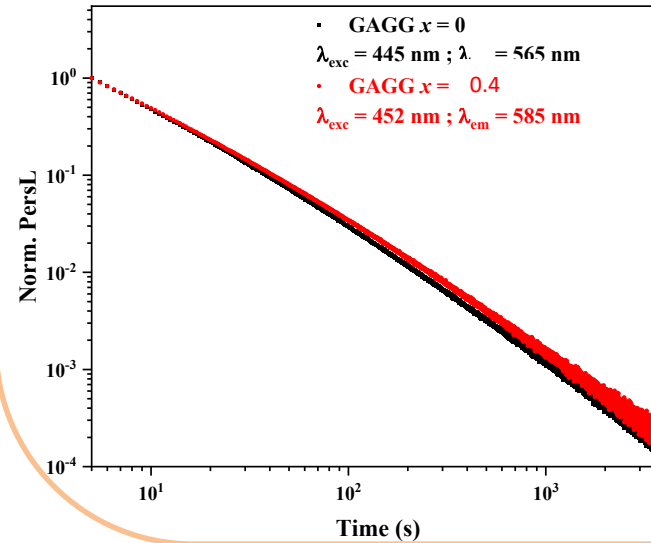
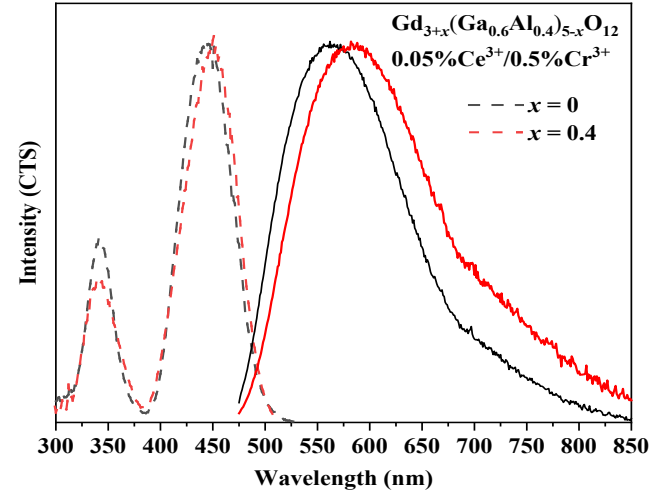


# Perspectives

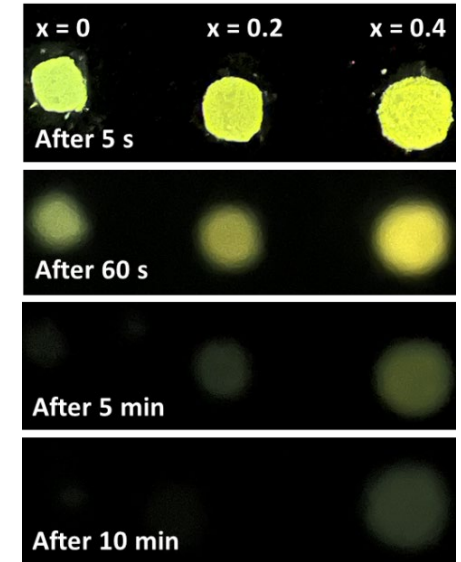
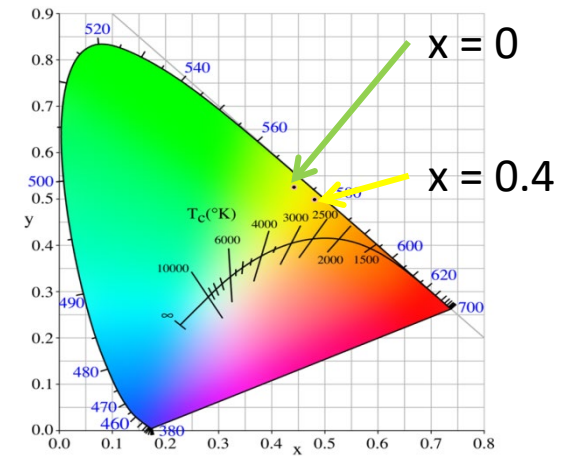
## Highly nonstoichiometric GGG



## Highly nonstoichiometric GAGG



## Persistent luminescence : $Gd_{3+x}(Al_{0.2}Ga_{0.3})_{5-x}O_{12}:0.05\%Ce^{3+}/0.5\%Cr^{3+}$





# Postdoctoral position

[fangxue1207@163.com](mailto:fangxue1207@163.com)  
[xue.fang@cncrs-orleans.fr](mailto:xue.fang@cncrs-orleans.fr)

- **Development of new functional materials**
  - **New energy**
  - **Glass-ceramics**



- **Solid chemistry**
- **Crystallography**



- **Solid state reaction**
- **Non-equilibrium synthesis**



- **Rietveld refinement**  
**(TOPAS)**  
**XRD/SPD/NPD**



- **Local structure**  
**NMR /EXAFS/ STEM**



- **Properties analysis**  
**AC impedance**  
**Luminescence spectroscopy**

*Thank you very much*

# Acknowledgements



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CERAM group  
 CEMHTI group  
 CNRS group



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Ana Isabel Becerro  
 Victor Castaing  
 Matthew S. Dyer



THANKS FOR  
 YOUR ATTENTION