Nanostructure of $(Yb_xY_{1-x})_2O_3$ Films Revealed With BF and HAADF STEM

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Materials for High-Power Lasers

- Solid-state lasers have reached >10-kW-grade power in one or a few transverse modes.
- The maximum average power is limited by overheating and thermal fracture:
  - Need laser architecture with efficient cooling
  - Need for materials with a high thermal shock parameter

$$R_t = \frac{K_{th}(1-\nu)}{\alpha E} S_t$$

K_{th}: thermal conductivity
v: Poisson coefficient,
α: thermal expansion coefficient [ºC-1] E: Young Modulus [Pa], S_t: fracture limit [Pa]

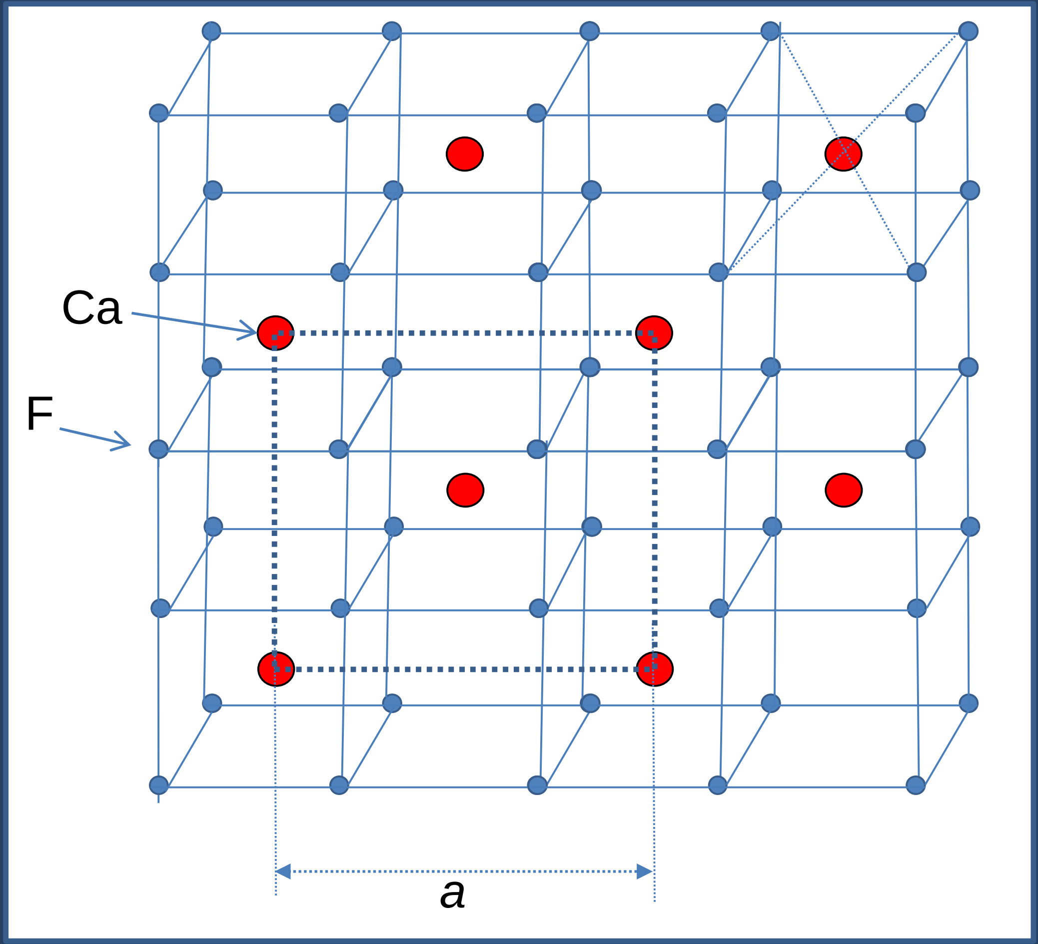
State-of-the-art crystalline material is: $Yb^{3+}:Y_3Al_5O_{12}$

Y_2O_3 : a Great Host for High-Power Lasers

- Low phonon energy (550 cm^{-1} vs 700 cm^{-1} for YAG) => helps reduce non-radiative multiphonon relaxation;
- High density of rare-earth substitution sites (twice as YAG)
- High melting point: 2430ºC (YAG: 1930ºC): Difficult to grow using traditional methods (Chrochralskii)
- Cubic material (optically isotropic): can be made transparent in the polycristalline form using the ceramic process or thin-film deposition techniques

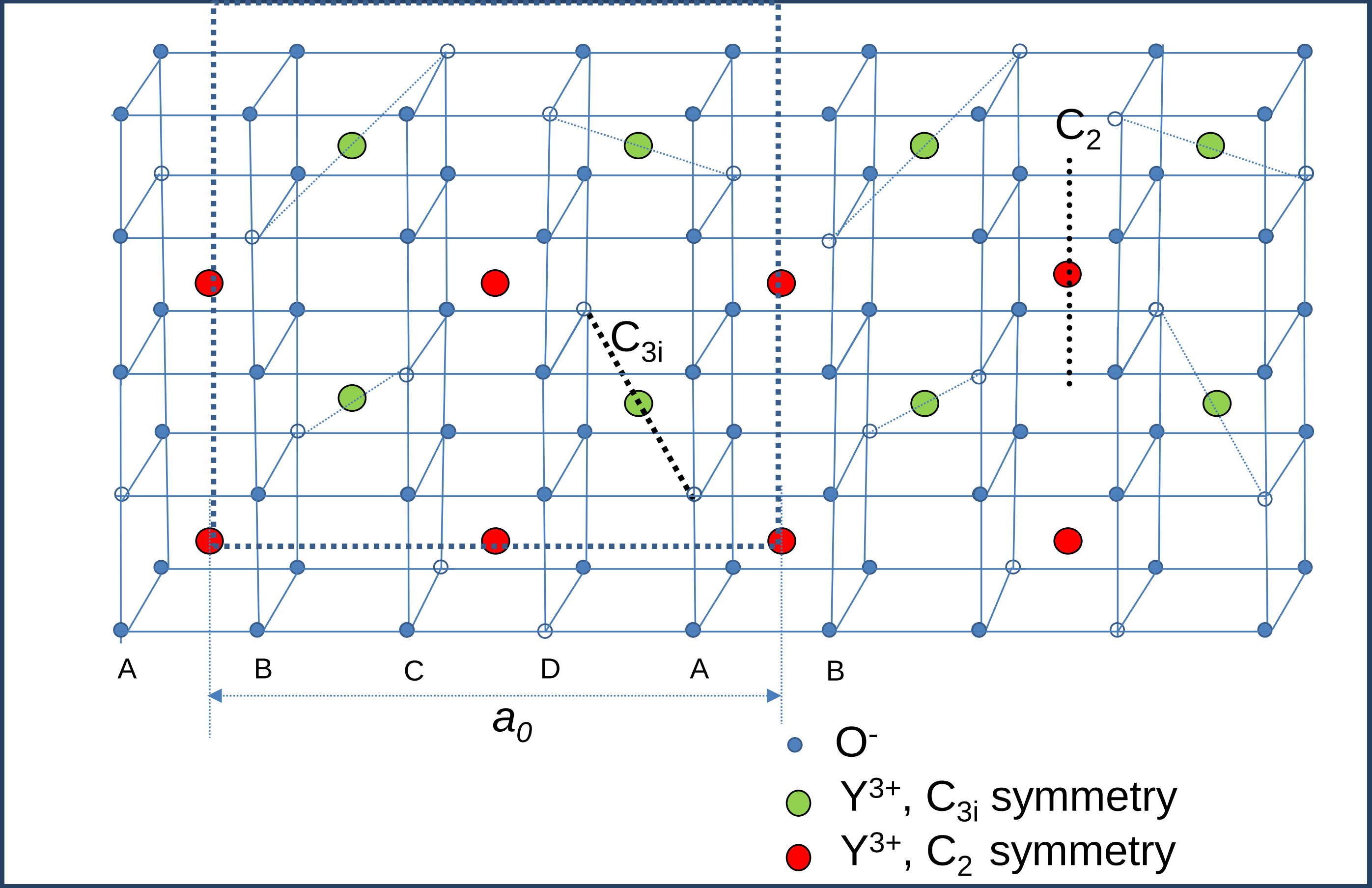
Crystallographic Structure of Y_2O_3

Similar to CaF_2



The CaF_2 lattice is face-centered-cubic (FCC).

Crystallographic Structure of Y_2O_3



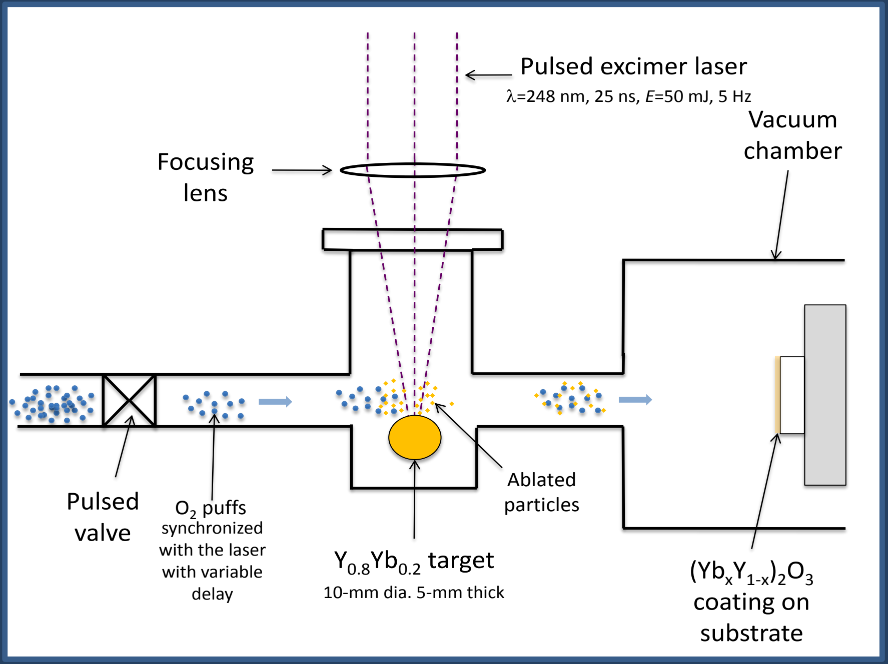
Similar to CaF_2 but with one fourth of the O^{2-} removed

$Y_{32}O_{48}$: 48 O^{2-} sites = 64 -16 ''vacancies'' ; 32 Y^{3+} sites= $24C_2+8C_{3i}$

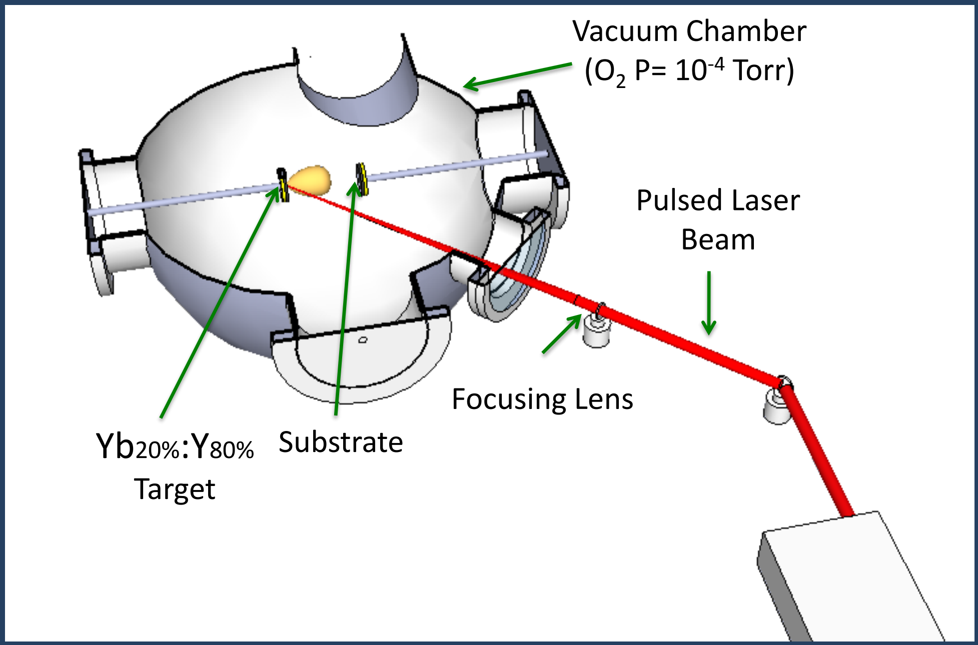
Bravais lattice: BCC; T_h^7 (206)

Thin-Film Synthesis

Reactive cross-beam laser ablation



Pulsed laser deposition



STEM

- 70-nm-thick specimens prepared by focused ion beam.
- JEOL 2200FS (200 kV, I_p=150 pA), probe dia.=0.12 nm, Depth of field : 10 nm

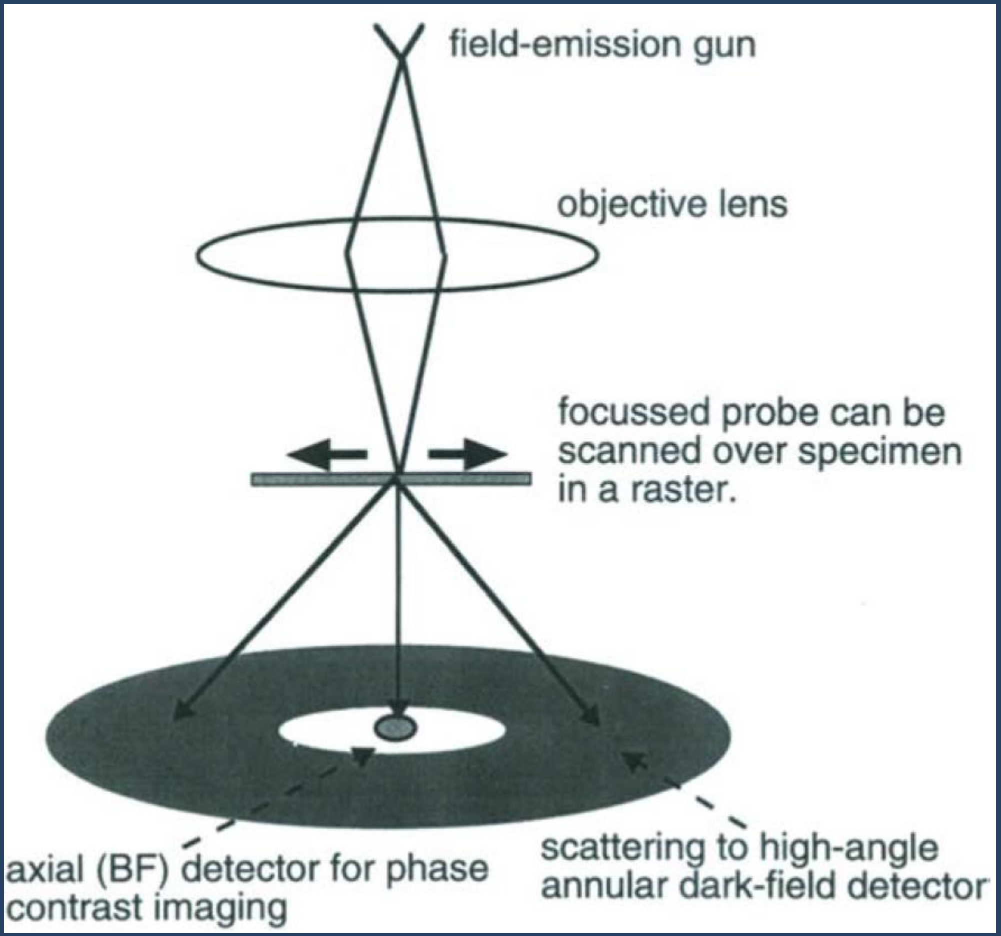
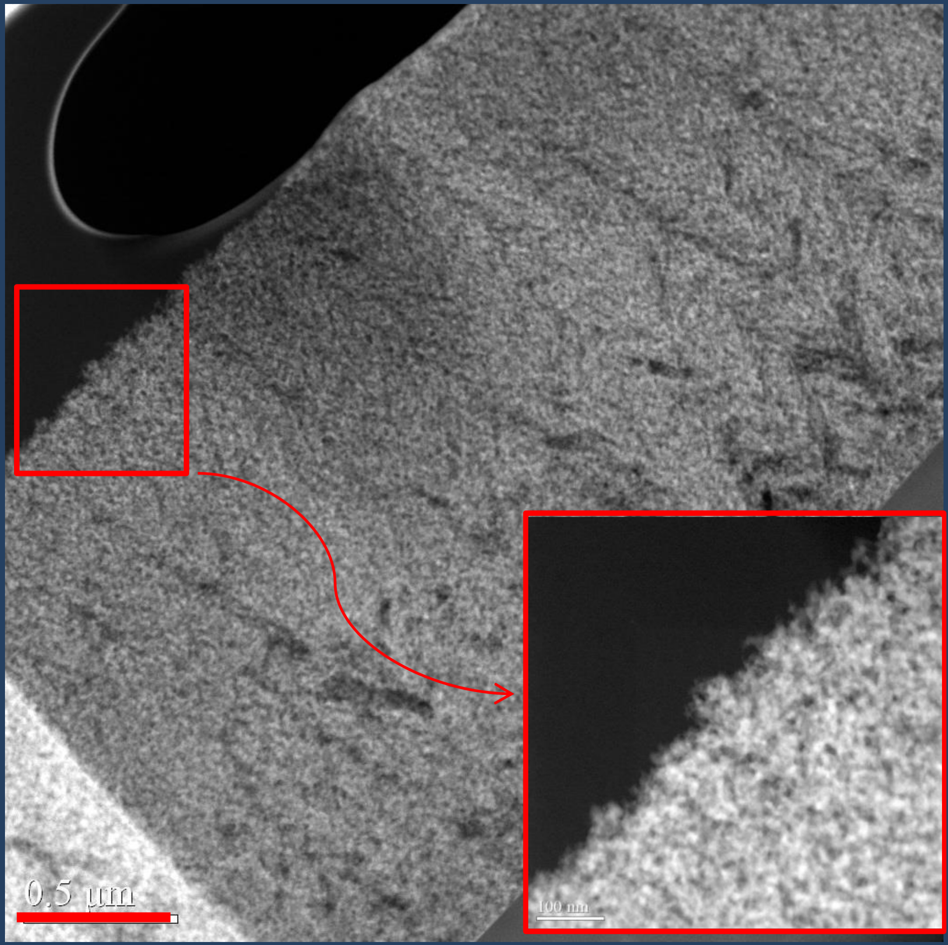


Image taken from Nellist et al., Adv. Imaging Electron. Phys. 113, 2000

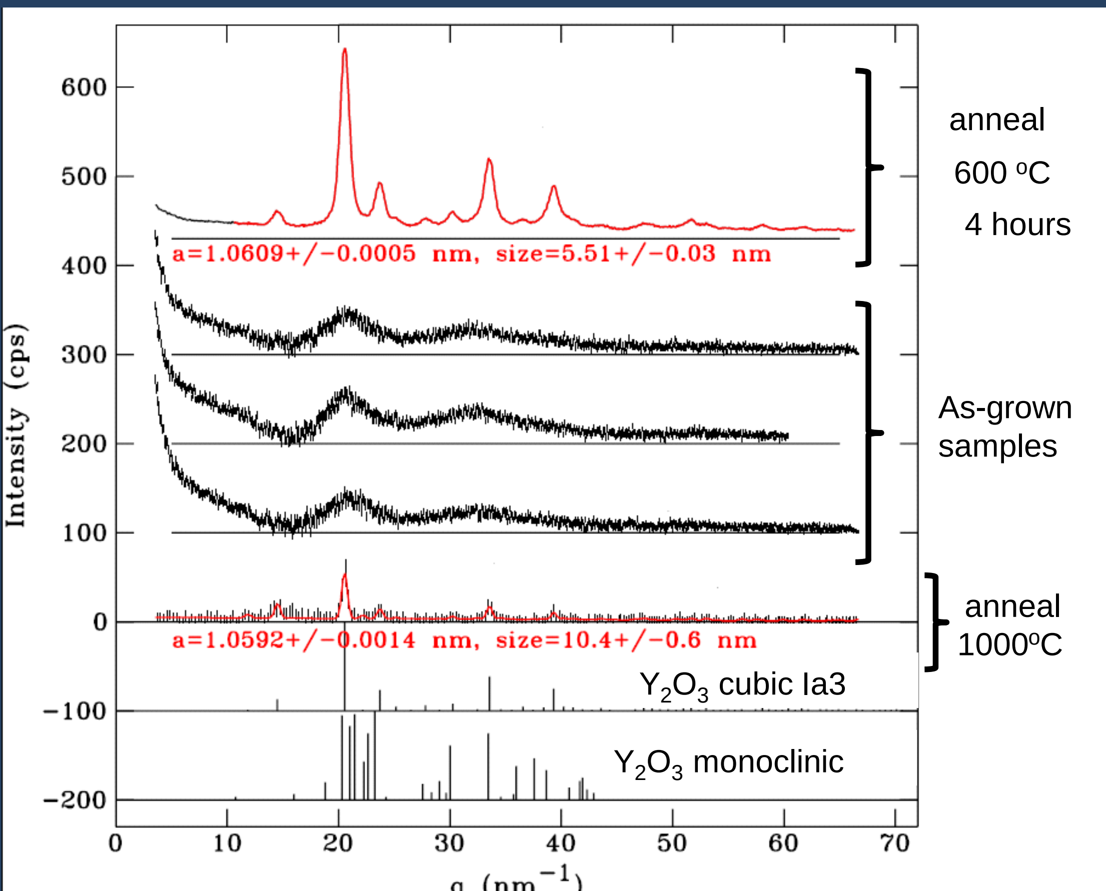
- BF contrast is based on interference between diffraction orders at the detector (coherent) imaging.
- HAADF contrast :
  - Detection angle: 100 and 170 mrad.
  - Intensity proportional to Z^{α}, where α=1.7
  - Higher signal for Y (Z=39) or Yb (Z=70) than O (Z=8).

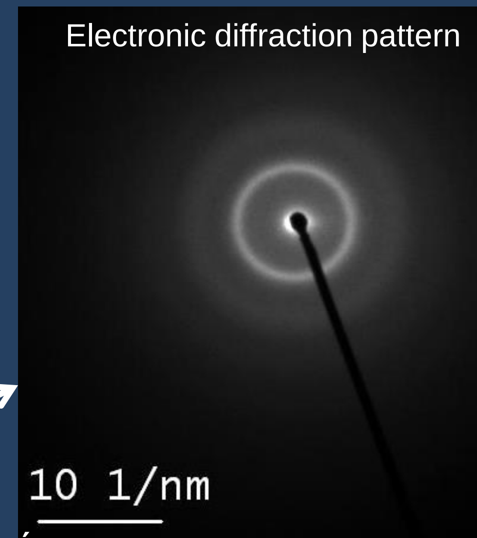
STEM-HAADF Picture of As-Grown Coatings



0.5 µm

X-ray diffraction patterns with various annealing conditions





Échelle de nombre d'onde $q/2\pi$

- As-grown samples: amorphous
- Annealed samples: Y_2O_3
  - 600 °C / 4 hours => L_c= 5 nm;
  - 1000 °C / 4 hours => L_c=10 nm.

Measured by Ralf Bruening, Univ. Mount-Alison

GCMP

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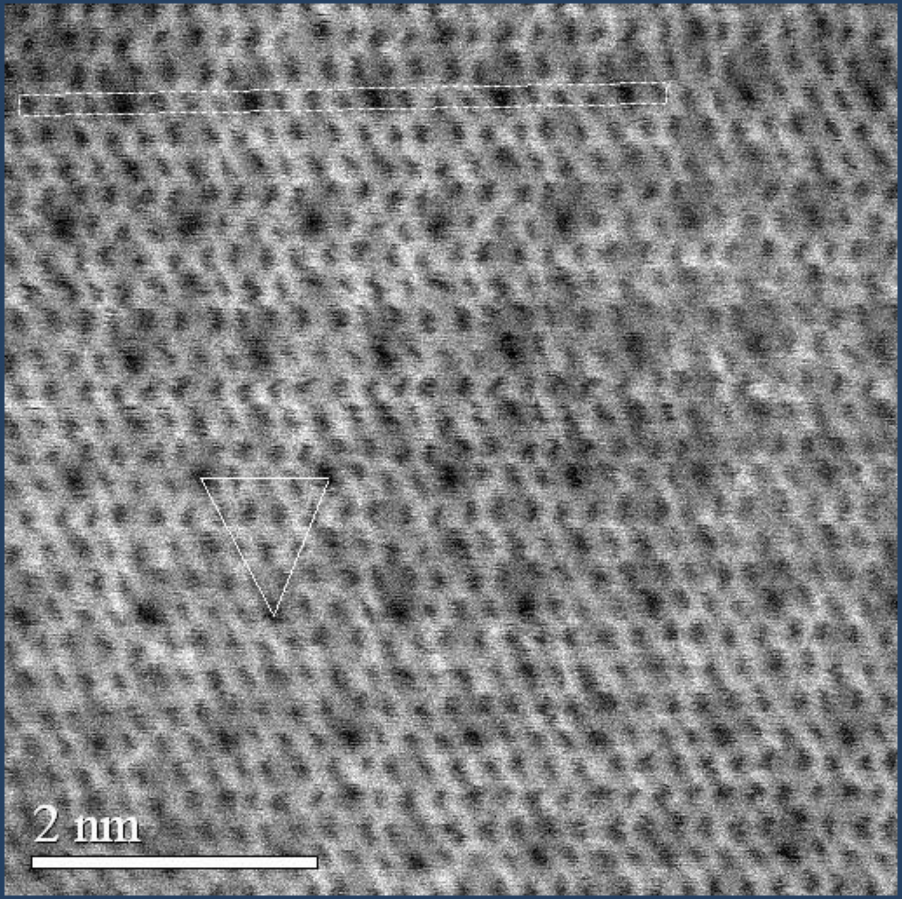
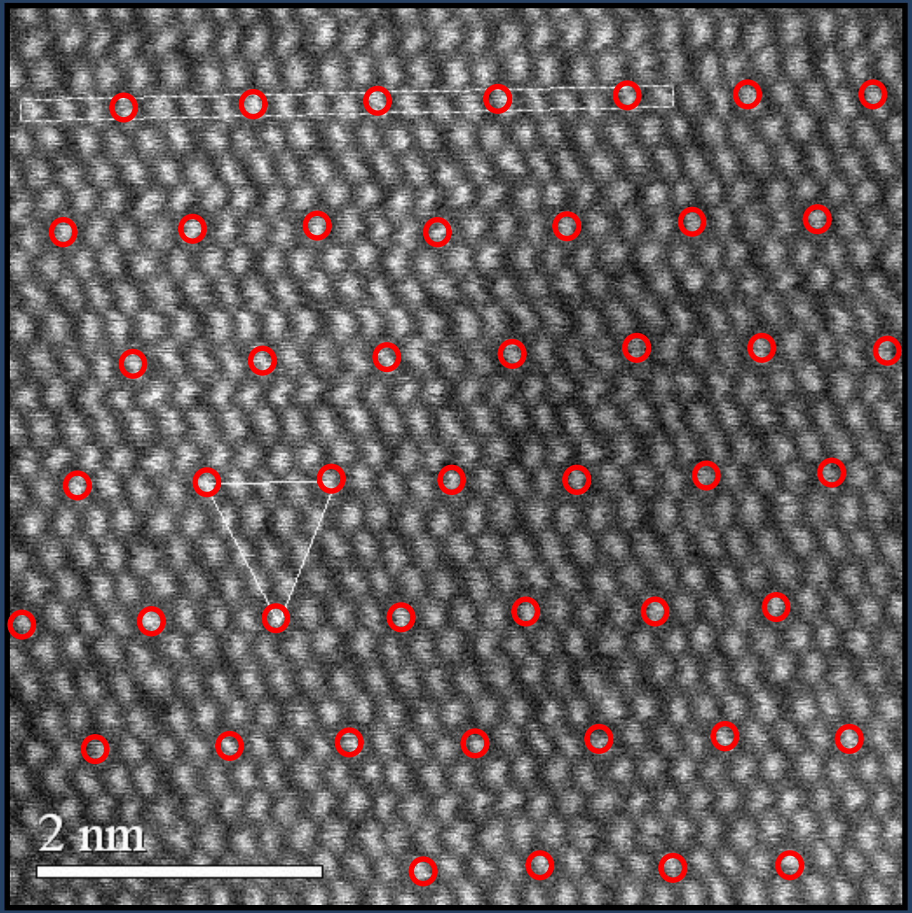
BF and HAADF images, <111> Zone axis

Bright-Field STEM

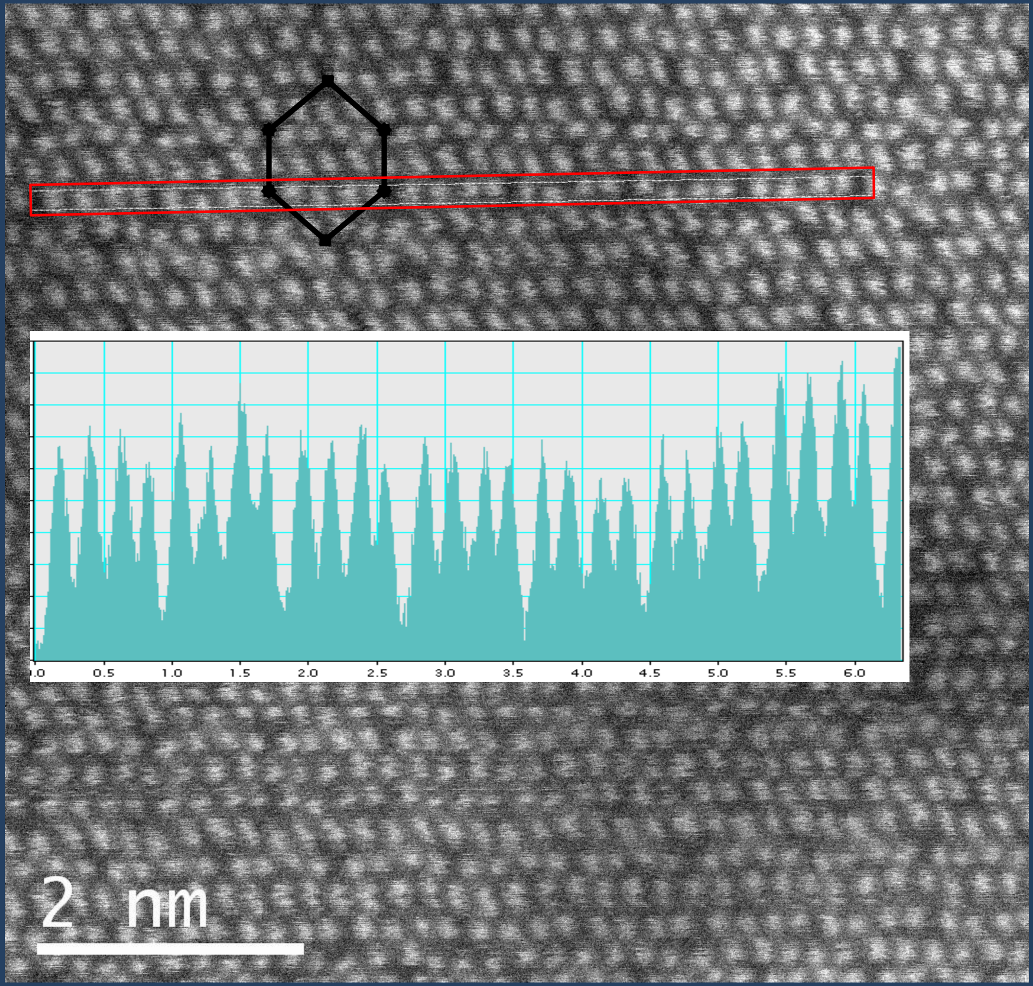


HAADF STEM



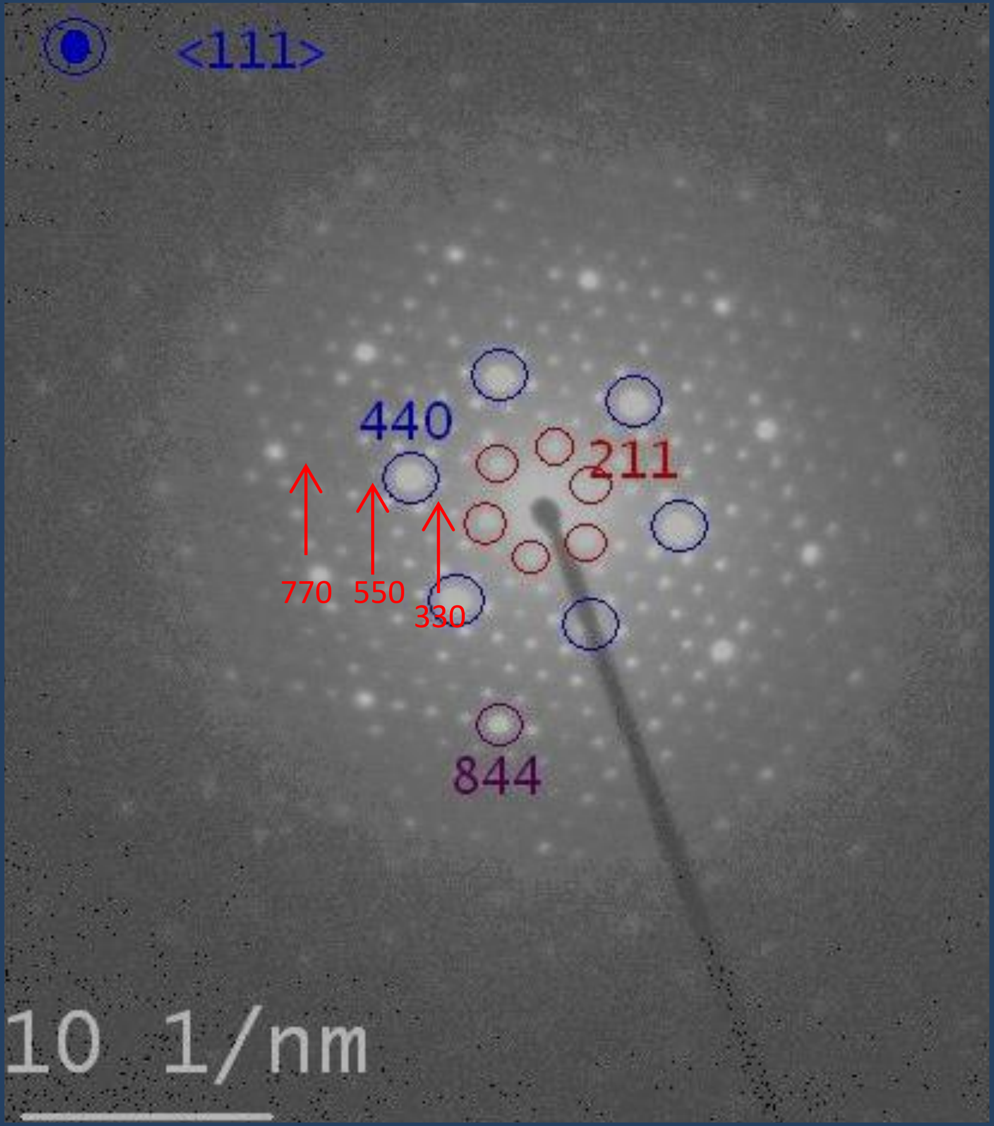
BF image suggests the presence of vacancies with long-range order, but these are absent in the HAADF image.

Different Long-Range Order in HAADF Images



Is this the conventional structure of Y_2O_3?

Electron Diffraction Pattern <111>



($2p$+1, $2q$+1,0) peaks forbidden for the Y_2O_3 bixbyite structure

Different crystallographic structure?
or
Effect of secondary elastic scattering?

Simulation of the Y_2O_3 Structure

Ion sites	Wyckoff position	Number of sites in elementary cell	Coordinate x/a	Coordinate y/a	Coordinate z/a
Y^{3+}	b (sym. C_{3i})	8	1/4	1/4	1/4
	d (sym. C_2)	24	x_A	0	1/4
O^{2-}	e	48	$3/8 + x_O$	$1/8 + y_O$	$3/8 + z_O$

$a=1.06$ nm, $x_O = 0.0157$, $y_O = 0.0270$, $z_O = 0.0054$, $x_A = -0.0327$

Ref: Hanic et al., Acta Cryst B40 : 76-82, 1984

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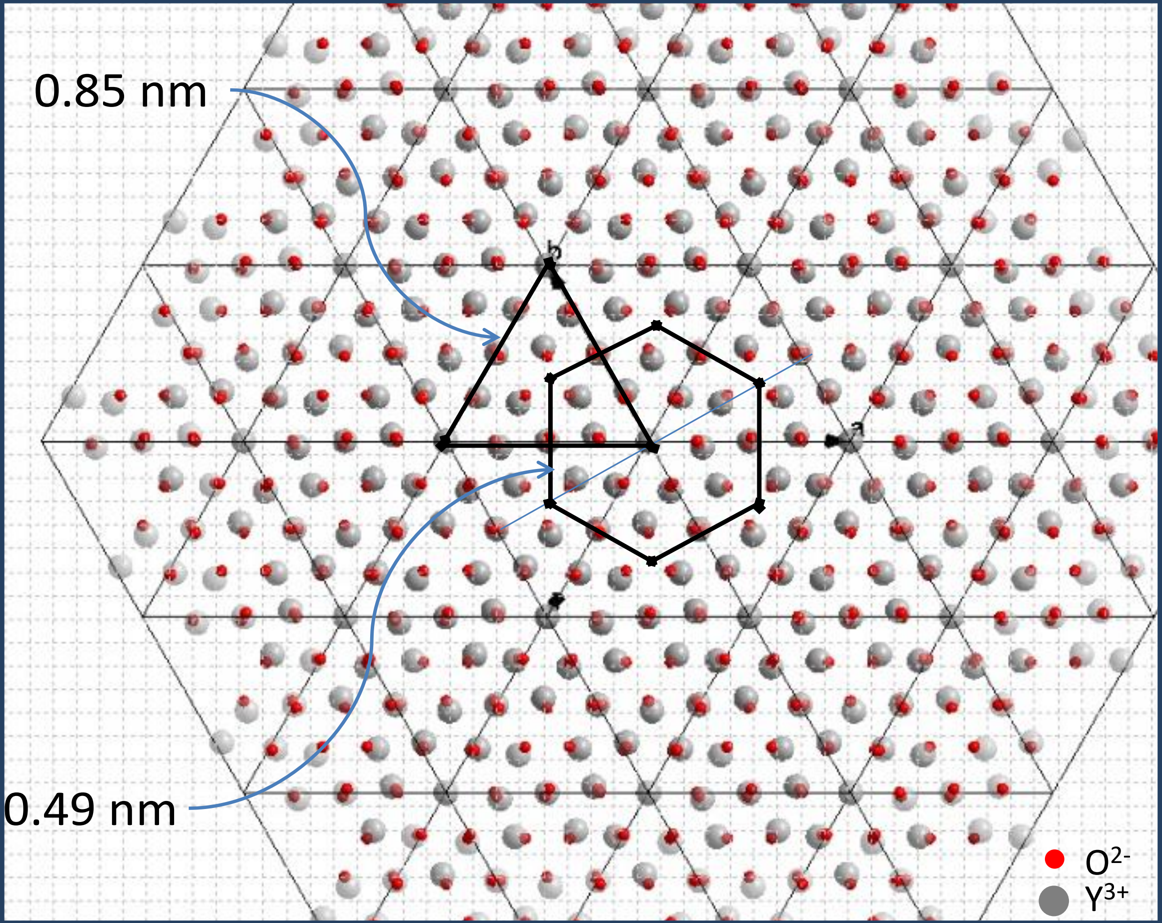

1) Dark spots in BF coincide with the absence of oxygen ions;
2) Dark spots HAADF correspond a distortion of the cationic network.

Summary

- BF and HAADF images of Yb: Y_2O_3 thin films reveal complimentay informations, each revealing a different pattern of dark spots organized in a honeycomb structure:
  - HAADF images show periodic distortion of the cationic columns; O^{2-} was not detected.
  - BF images reveal the absence of oxygen ions at specific crystallographic columns;
  - Combining BF and HAADF modes makes it possible to get a comprehensive picture of the atomic structure of a material.

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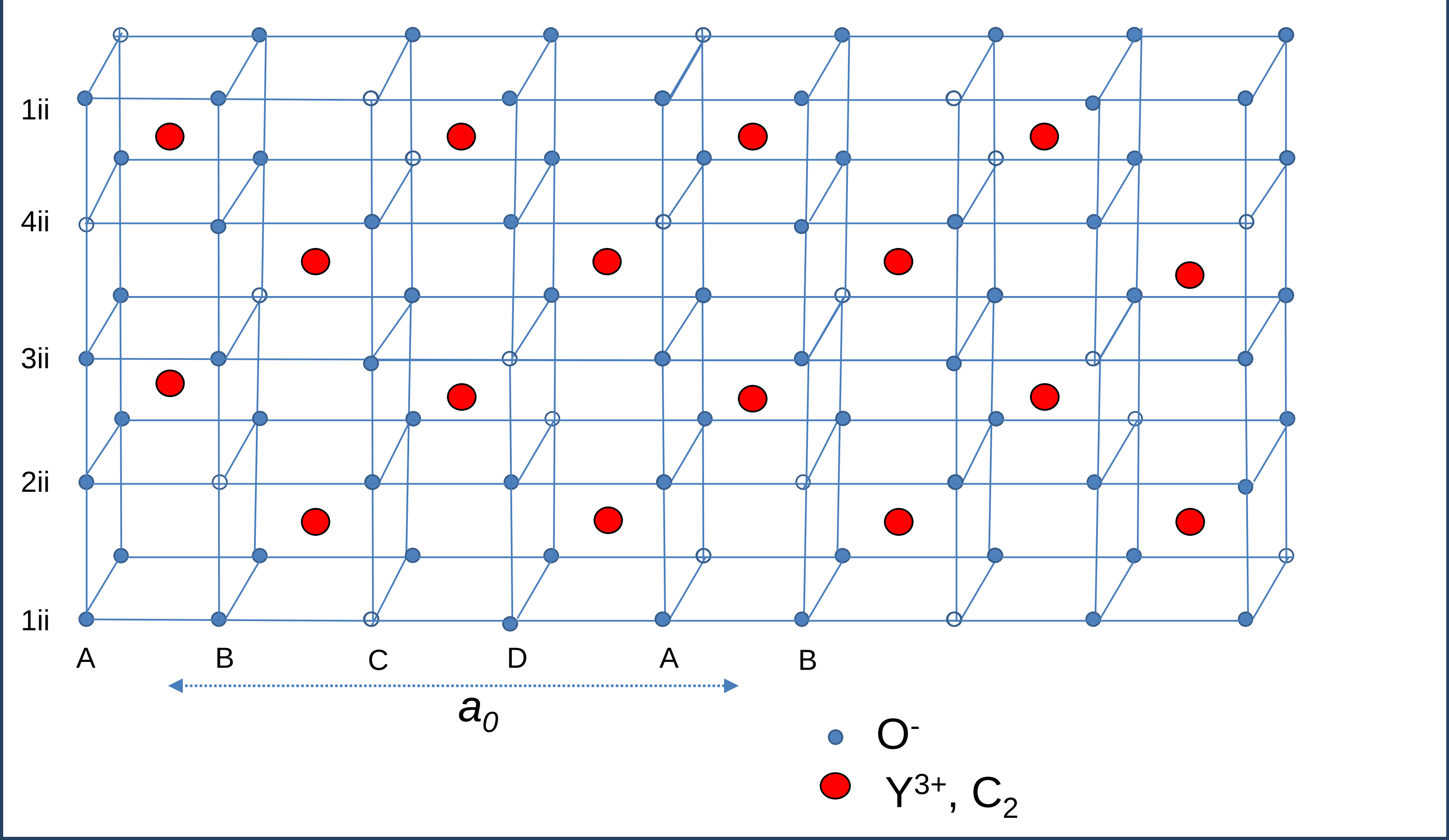
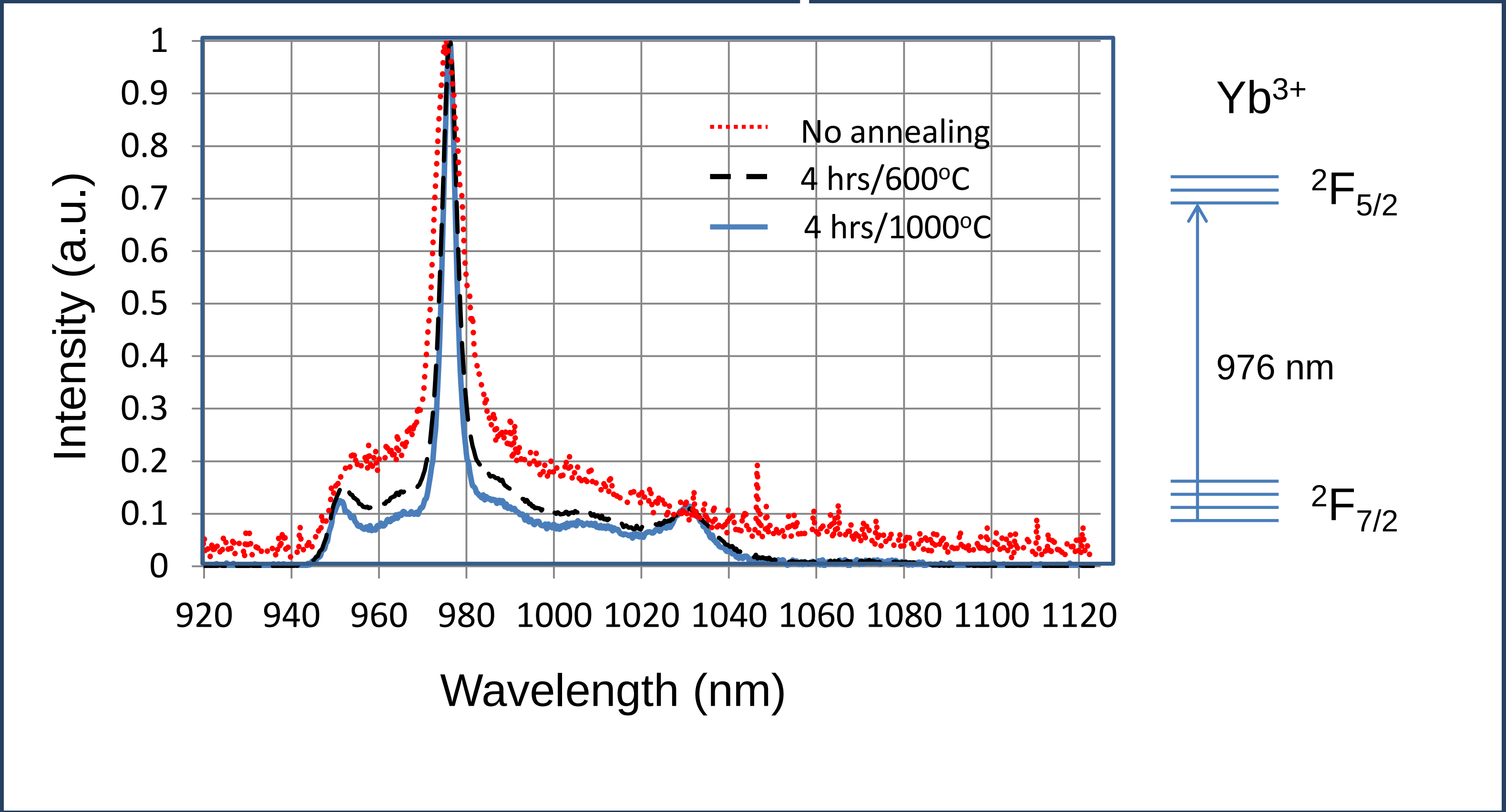
Crystallographic Structure of Y_2O_3

$Y_{32}O_{48}$ 32 Y^{3+} sites= $24C_2+8C_{3i}$ 48 O^{2-} sites = 64 -16 ''vacancies''

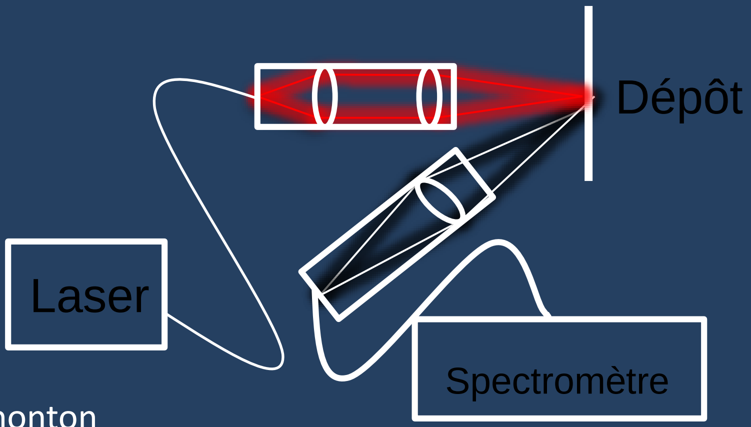


Bravais lattice: body centered cubic; T_h^7 (206) space group

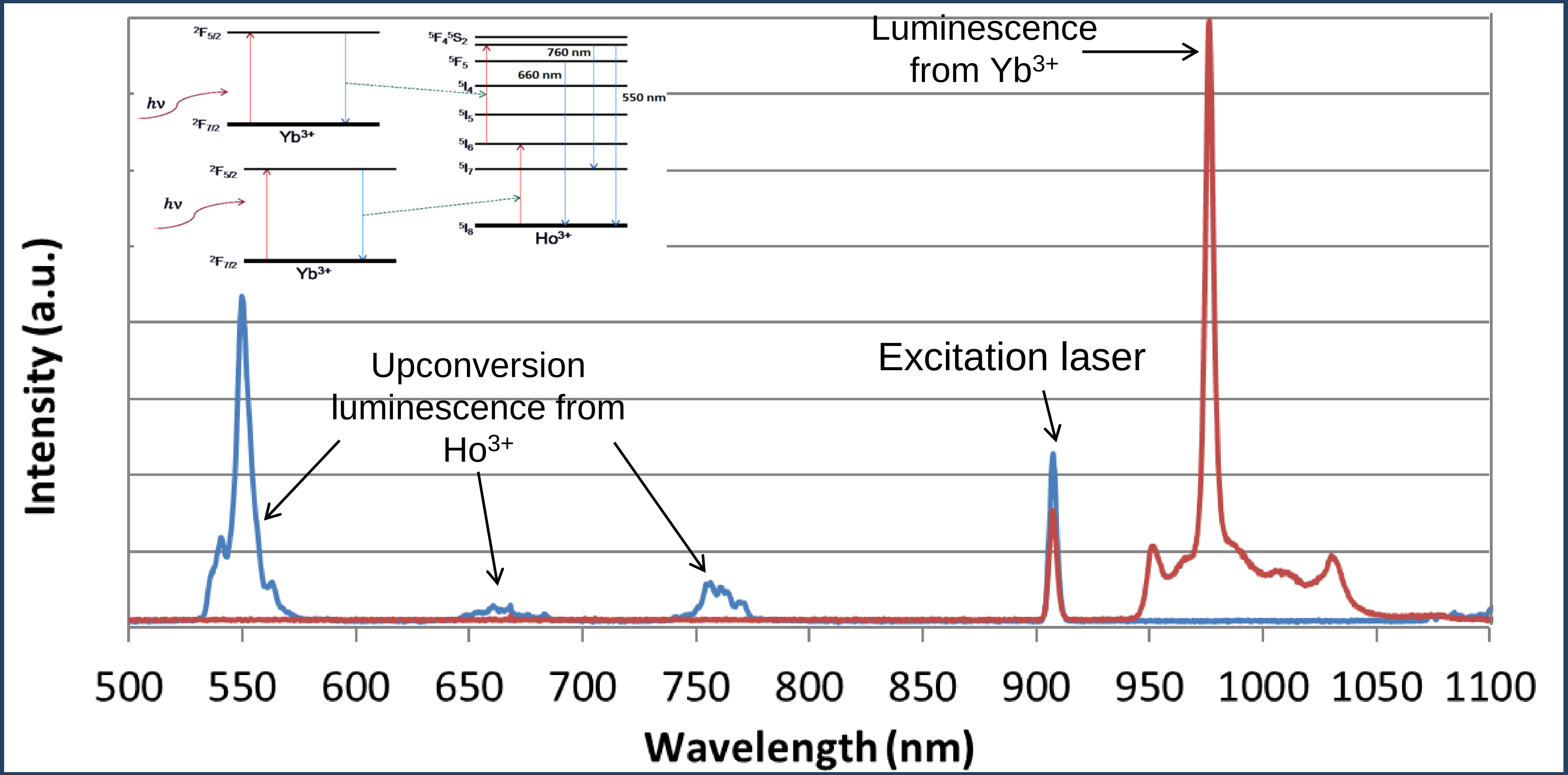
Luminescence Spectra from Yb^{3+}



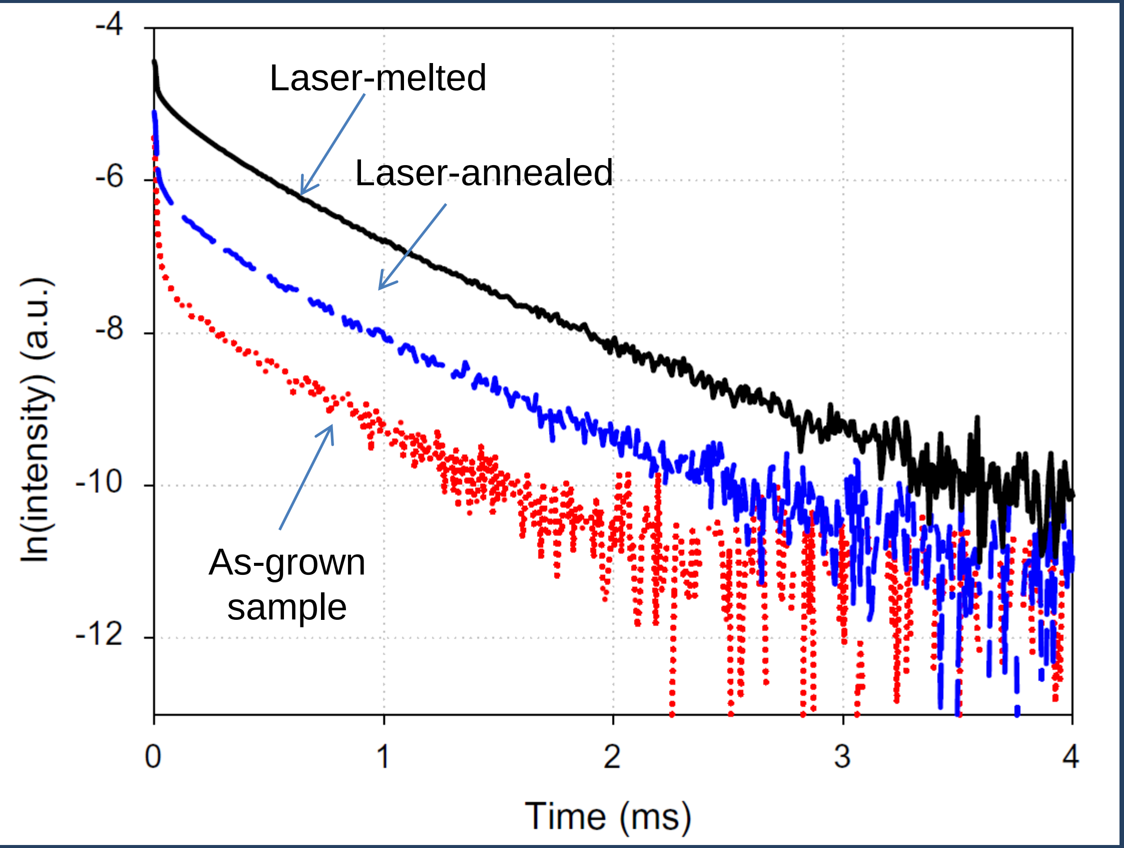
1. Significant broadening and little structure for the amorphous material => Suggests that the crystal field around Yb ions is inhomogeneous
2. Spectra narrow as the size of the crystallites increases



Upconversion Luminescence From Other Trivalent Rare-Earth Ions



Luminescence Decay Curves



- Non-exponential decay: can be explained by the presence of randomly distributed traps in the material (Cf. J.F. Bisson, JOSA B, 32(5). 757-766, 2015);
- Important jump in luminescence intensity after melting the material;
- Lifetime at long times in the order of : τ=0.93 ms (about the same for all cases).