Rare-earth photoluminescence in sol-gel derived confined glass structures

An IMI Video Reproduction of Invited Lectures from the 17th University Glass Conference

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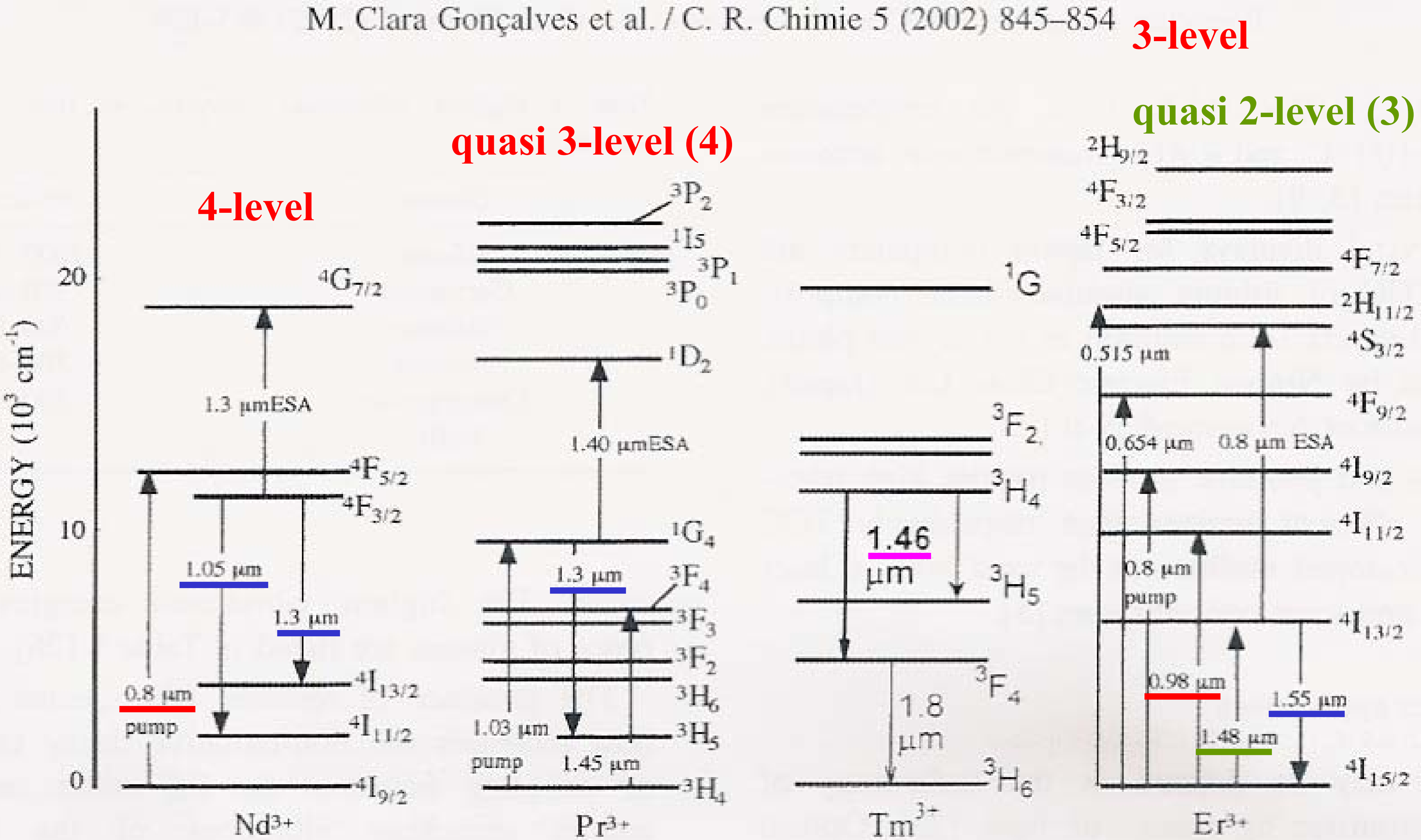
Outline

- **Er^{3+} - doped sol-gel (SG) planar waveguides**
  - Silicate glasses as Er^{3+} hosts: effects of TiO_2 and HfO_2 additions on the structure and photoluminescence (PL) spectra
  - Effects of Ag^o nanoparticles on the Er^{3+} PL intensity
- **Er^{3+}/ Yb^{3+} - doped Fabry - Perot microcavities (by SG)**
- **Conclusions**

Possible RE ion (active) dopants for glassy hosts

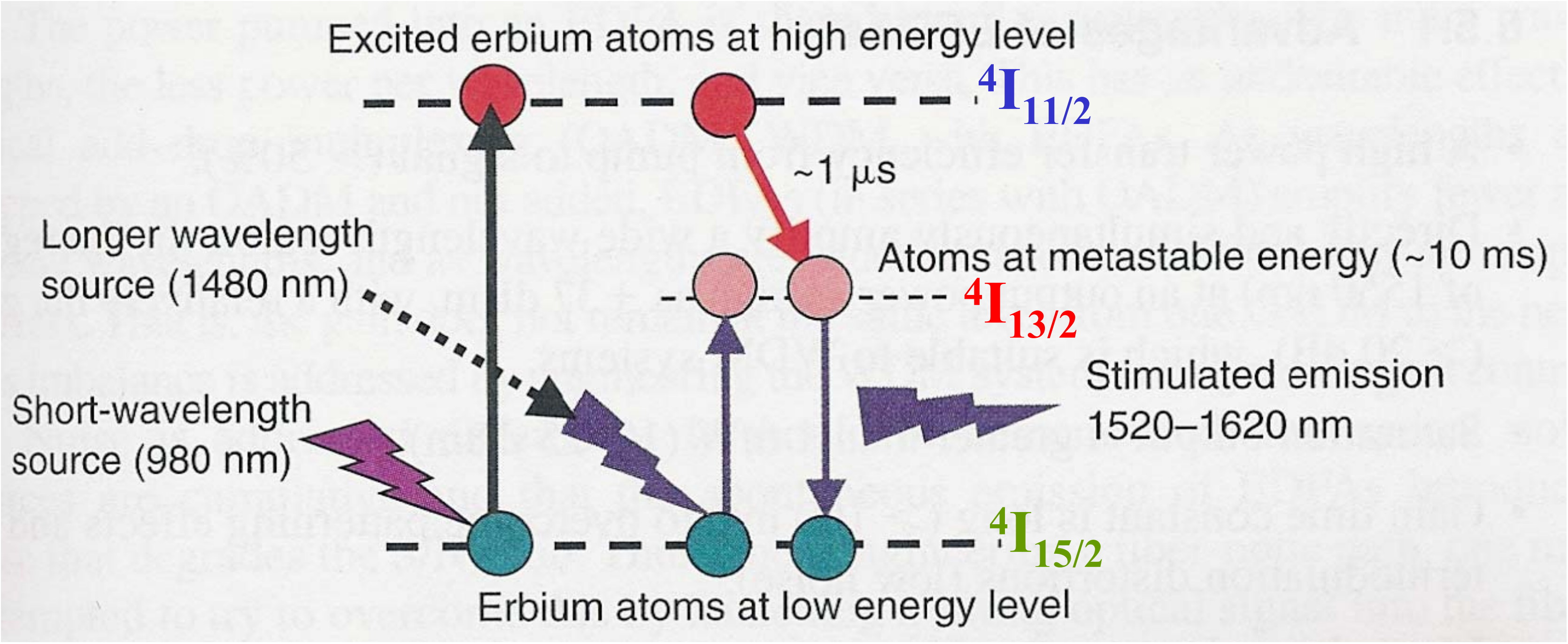


second window (~ 1.3 µm) **third window (~ 1.5 µm)**

The **Erbium Doped Fiber Amplifier (EDFA)** operates as a 3- level system when pumped at 980 nm and as a quasi 2-level system when pumped at 1480 nm to the long-lived (metastable) $^4I_{13/2}$ level.

The signal photons at ~ 1.5 μm stimulate emission of Er^{3+} at ~ 1520-1620 nm, amplifying the original signal, while maintaining its frequency and phase.

Electronic energy levels of Er^{3+}

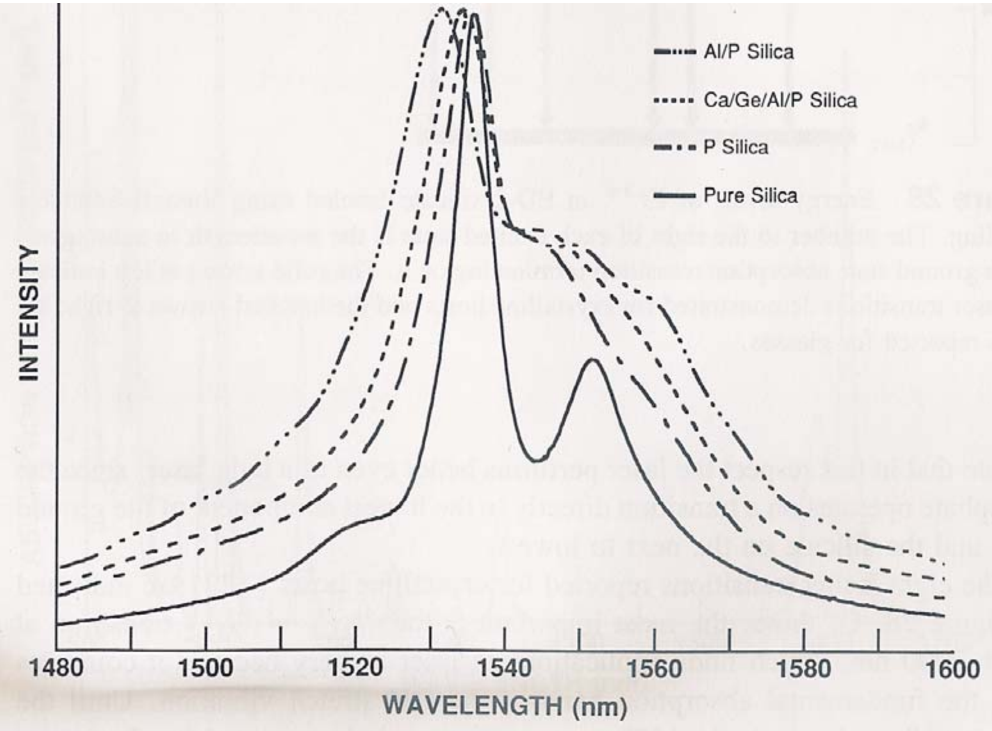


(Adapted from: *Introduction to DWDM Technology*, S.V. Kartalopoulos, IEEE Press, 2000)

Er^{3+} PL spectrum @ ~ 1.5 µm

The $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission of Er^{3+} spans the **third window** of fiberoptic communications. In the case of Al/P doped silica glass fibers, it fully covers the C band, from 1530-1565 nm. (FWHM ~ 50 nm).

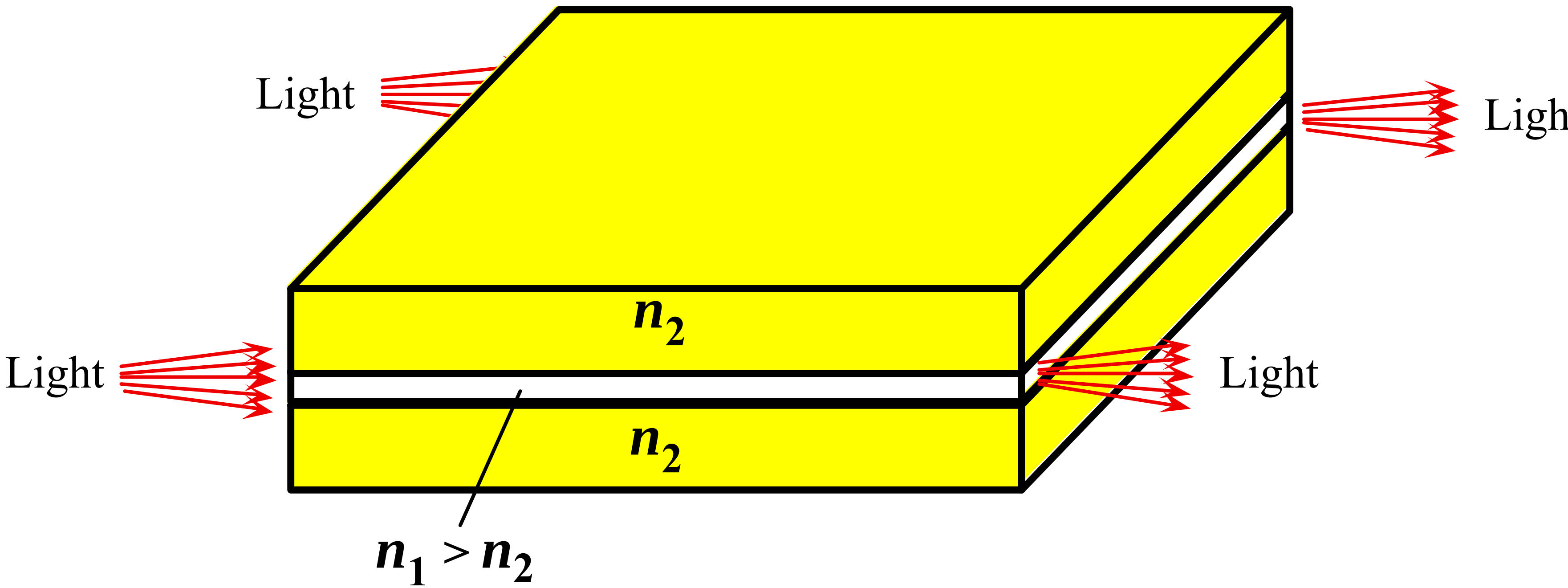
The Dense Wavelength Division Multiplexing (DWDM) systems also include the S (short, 1450-1530 nm) and L (long, 1560-1620 nm) wavelength ranges.



Emission spectrum of Er^{3+}-doped silica fibers.

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel Dekker, 1993)

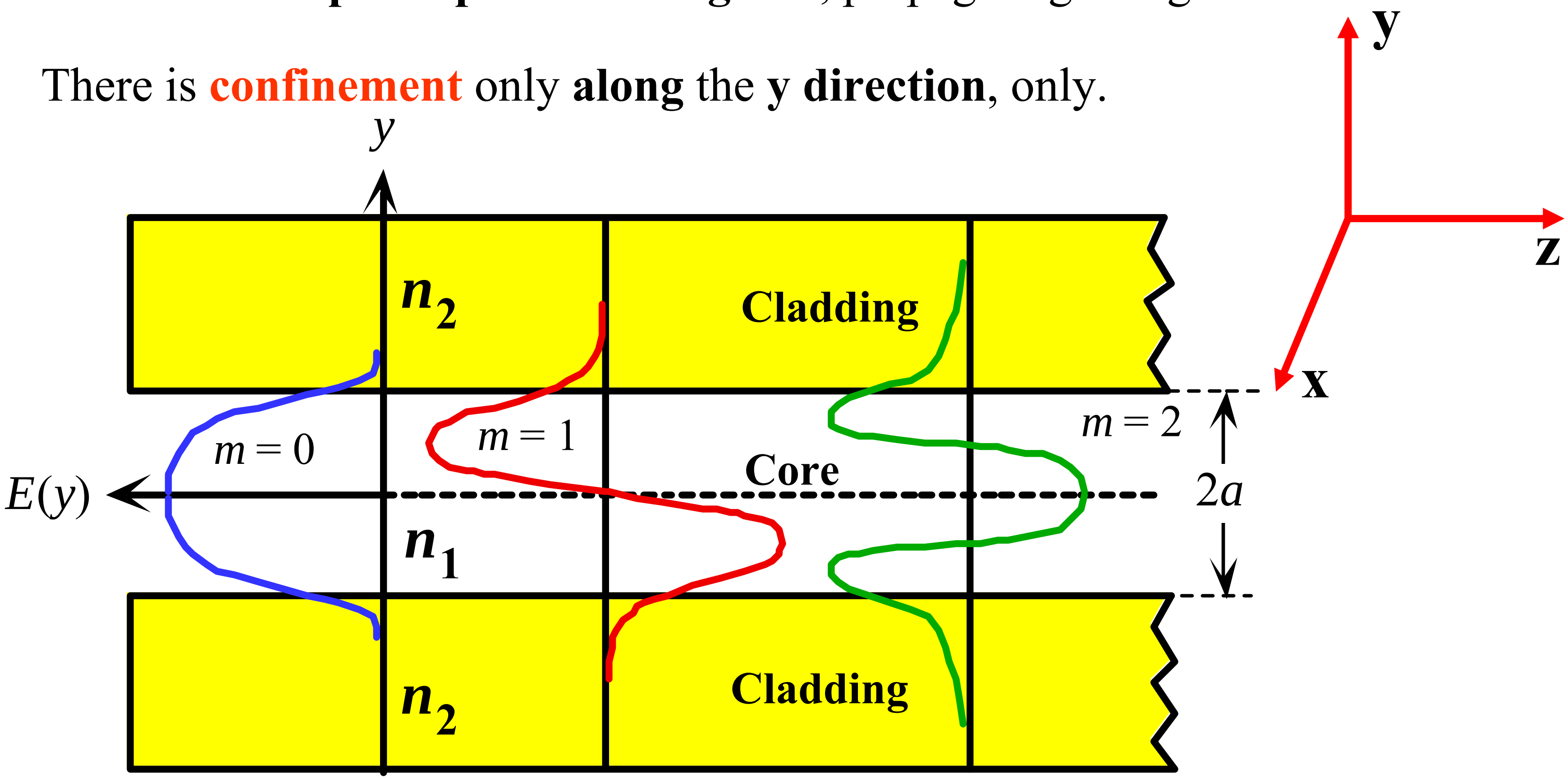
Planar waveguides



A planar dielectric waveguide has a central rectangular region of higher refractive index n_1 than the surrounding region which has a refractive index n_2. It is assumed that the waveguide is infinitely wide and the central region is of thickness $2a$. It is illuminated at one end by a monochromatic light source.

Modes in an optical planar waveguide, propagating along the z direction.

There is **confinement** only **along** the **y direction**, only.



The electric field patterns of the first three modes ($m = 0, 1, 2$) traveling wave along the guide. Notice different extents of field penetration into the cladding. (Evanescent field increases with mode order and λ).

Silicate glasses as Er^{3+} hosts

- **<u>Incorporation of Er^{3+} ions in silica-based sol-gel planar waveguides, for integrated optical amplification</u> @ 1.5 µm:**

  Er^{3+} can also act as a **sensitive probe** of the structure of the host material:

  - the disordered structure of **glass** and **amorphous films** leads to site-to-site variations in the local bonding

    ⬇

    inhomogeneous broadening of spectral features

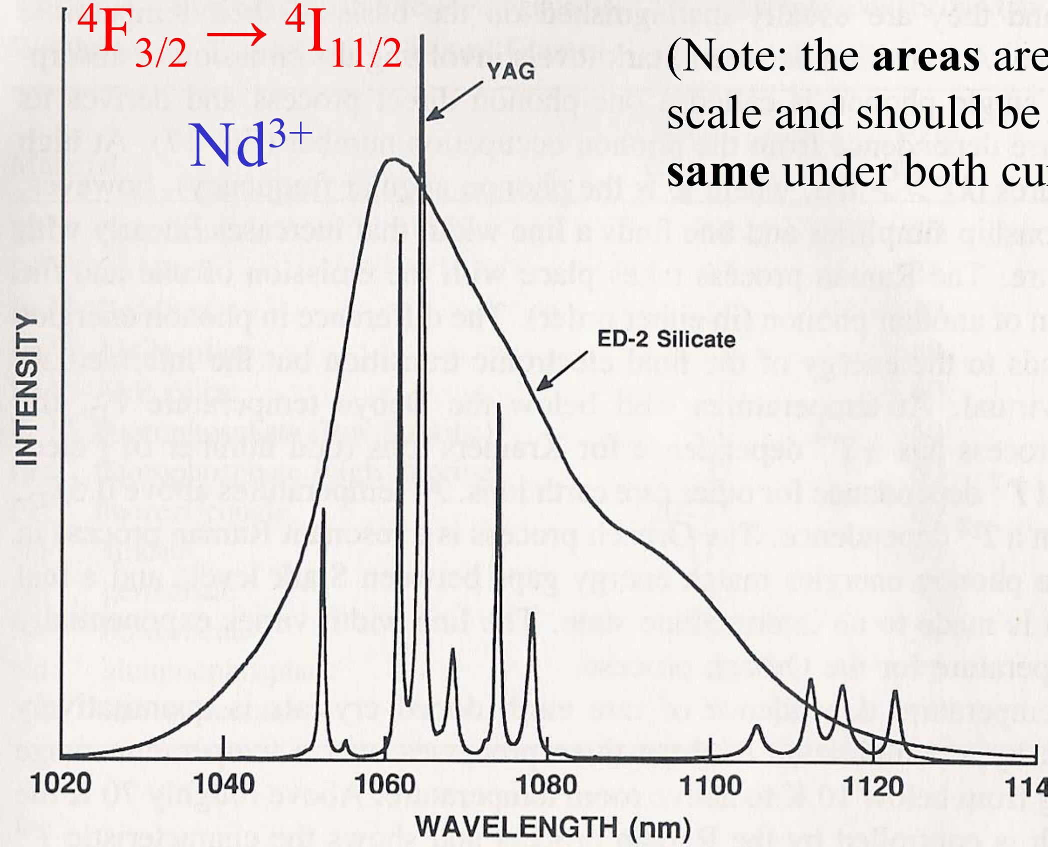
  - possible splitting of Stark components when Er^{3+} is in the neighborhood of crystallites within the glass matrix *(Strohhofer et al. 1998)*

Transitions between individual **Stark components of** different **J multiplets** can be observed as discrete lines in RE-doped crystals, but not in glasses. Crystalline hosts provide high cross sections at nearly discrete wavelengths; glass hosts have lower cross sections over a broad range of wavelengths.

$^4F_{3/2} \rightarrow {}^4I_{11/2}$

Nd^{3+}

(Note: the **areas** are off-scale and should be the **same** under both curves).



Comparison of the emission spectra for Nd^{3+}-doped YAG and Nd^{3+}-doped ED^{-2}silicate glass.

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcell-Dekker, 1993)

Nanostructuring of planar waveguides

incorporation of Ag° nanoparticles into Er^{3+}-doped silica-based waveguides

surface plasmon resonance of noble metal nanoparticles

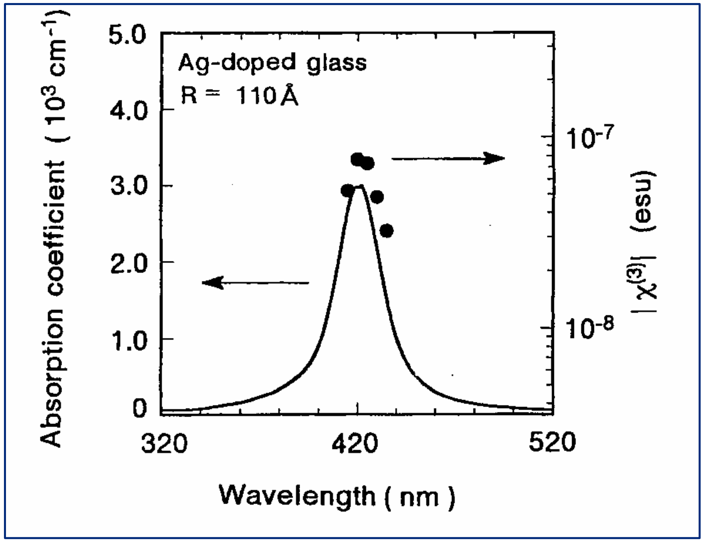
- enhancement of third-order optical nonlinear susceptibility ($\chi^{(3)}$) of the composite
- increase in local electric field strength at (and near) the metal particles

Local field factor:

$$f_{loc} = E_{loc} / E =$$

$$= 3\varepsilon_g / (\varepsilon_m + 2\varepsilon_g)$$

$$@ \text{ SPR freq.: } f_{loc} >> 1$$



(Yamane and Asahara, *Glasses for photonics*)

Viable systems for 1.5 μm applications:

Er^{3+}-doped SiO_2 - TiO_2 → long fluorescence lifetimes

(Almeida et al. 1999, Orignac et al. 1999, Almeida et al. 2003)

Er^{3+}-doped SiO_2 - HfO_2 → intense Er^{3+} PL signal

(Gonçalves et al. 2003)

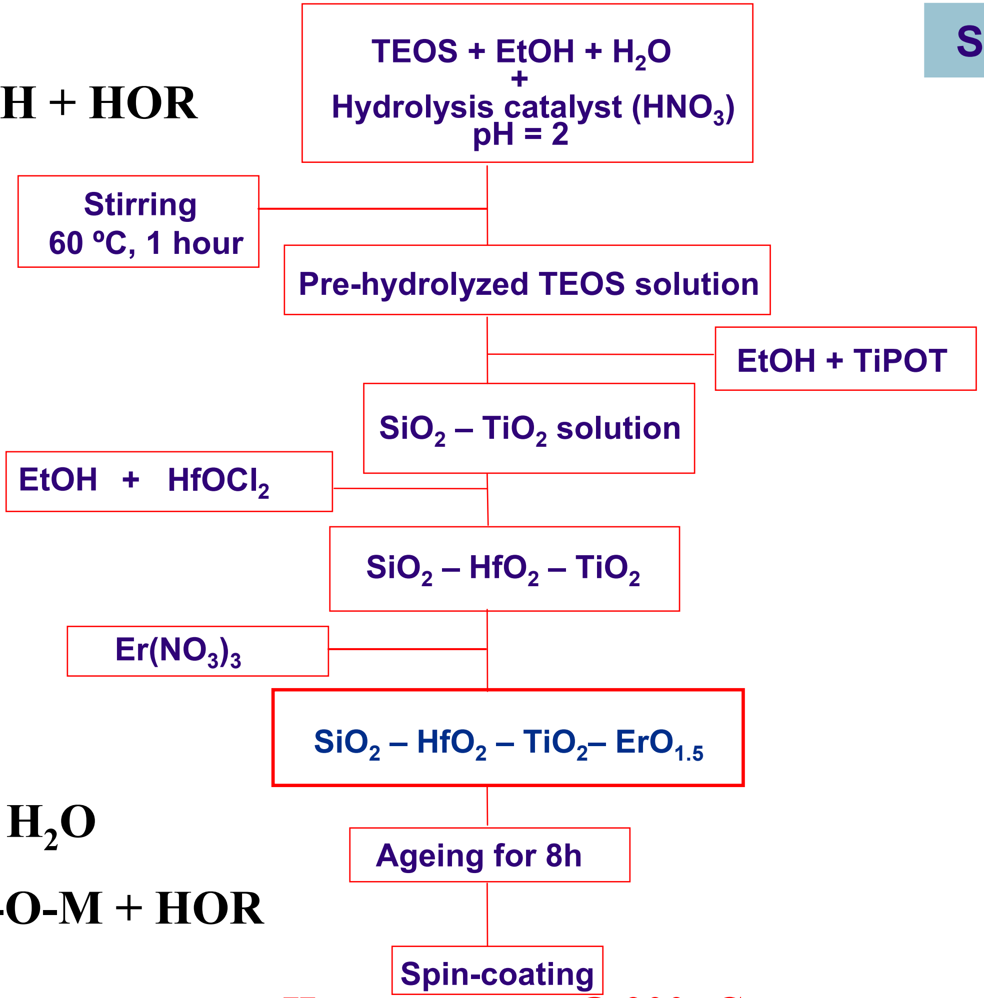
Both have:

- Significant refractive index contrast (waveguiding)
- Transparency over a wide wavelength range
- Led to the preparation of good optical quality waveguides

Sol-gel processing of Er^{3+}-doped silica-based films and waveguides

Hydrolysis:

$$M\text{-}OR + H_2O \rightarrow M\text{-}OH + HOR$$



Heat treatment @ 900 ºC

SiO_2-HfO_2-TiO_2-$ErO_{1.5}$

(100-x-y)**S-yH-xT-Er**

x = **mol% TiO_2**

y = **mol% HfO_2**

e.g.: 75S-20H-5T-Er

($R_E = n_{EtOH}/n_{TEOS+TPOT} = 18$)

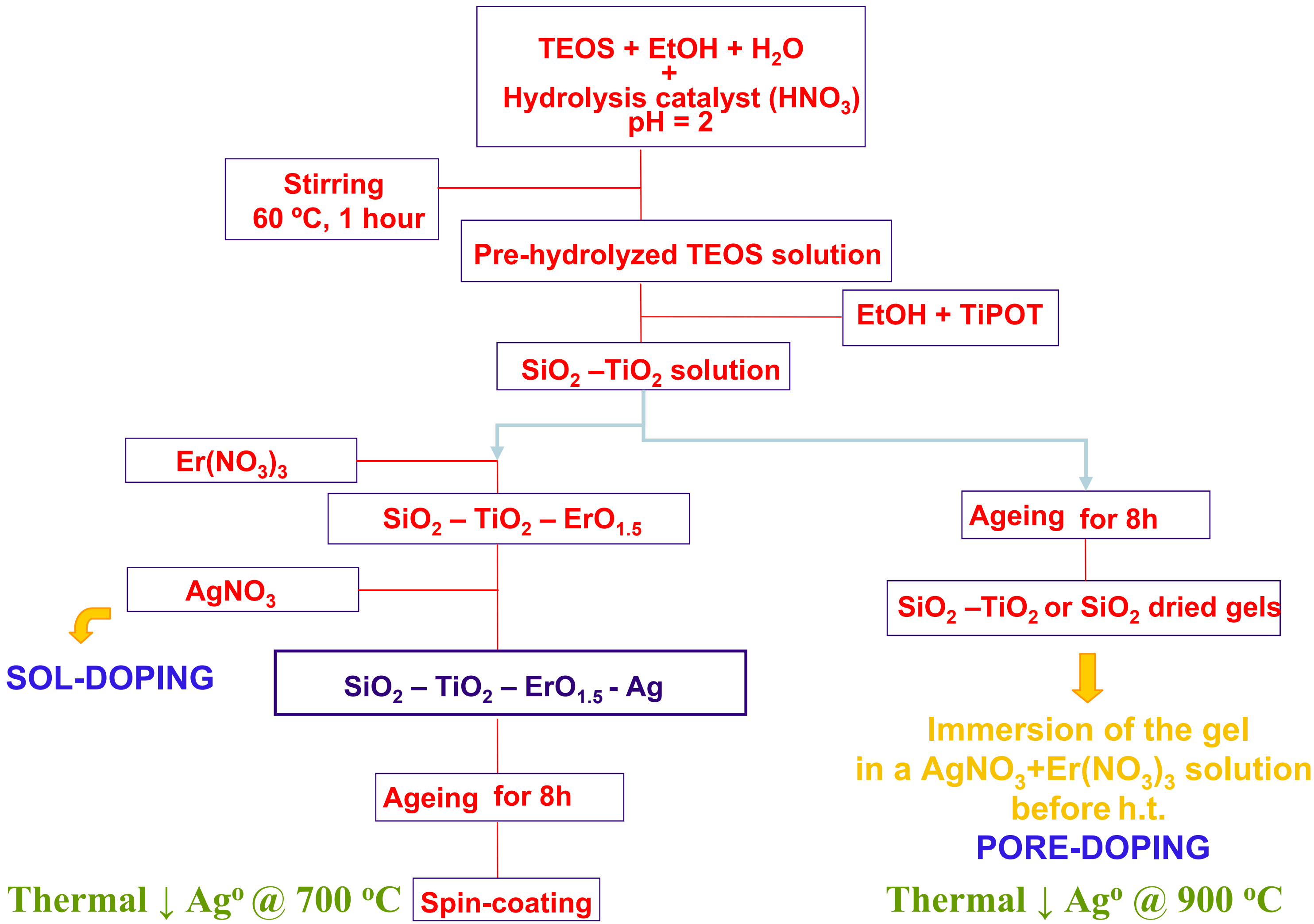
($R = n_{H2O}/n_{TEOS+TPOT} = 4$)

Condensation:

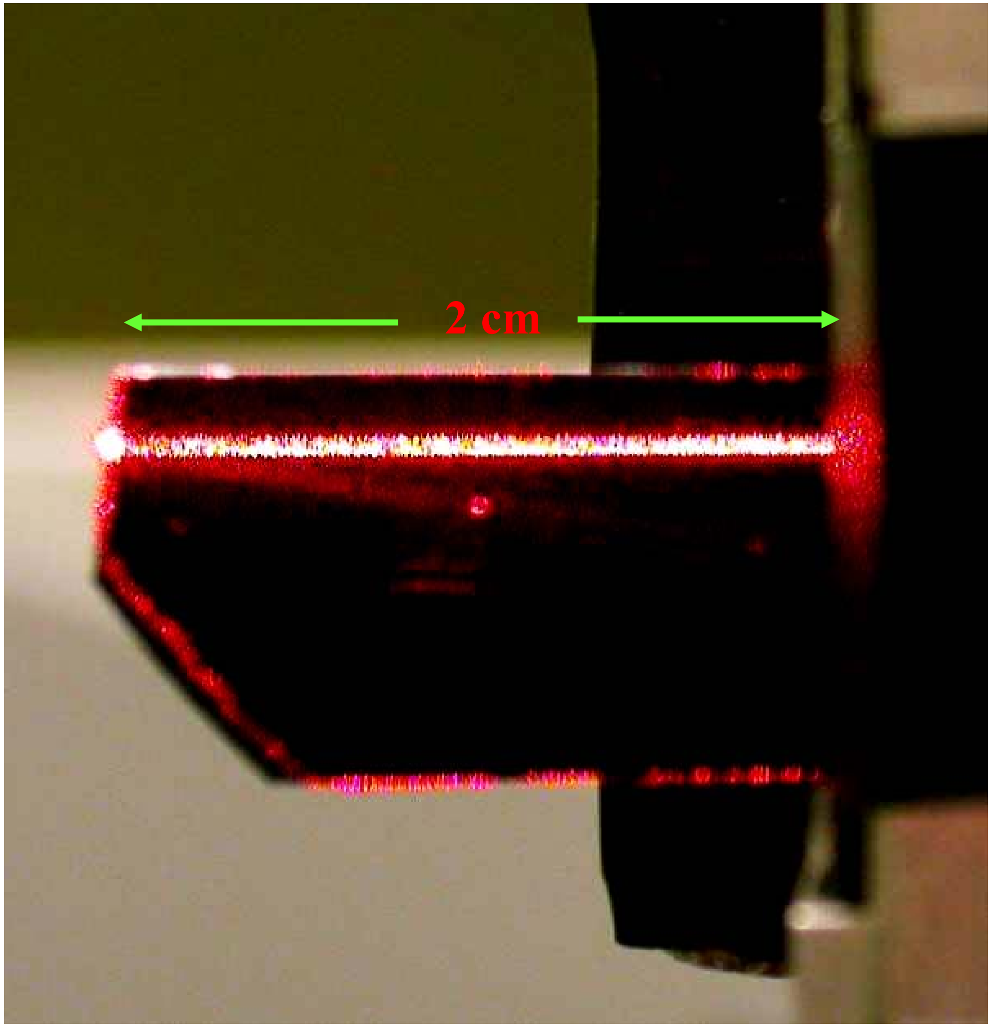
$$2\ M\text{-}OH \rightarrow M\text{-}O\text{-}M + H_2O$$

$$M\text{-}OH + M\text{-}OR \rightarrow M\text{-}O\text{-}M + HOR$$

Sol-gel processing of Er / Ag-doped, silica-based glasses and waveguides



Waveguiding



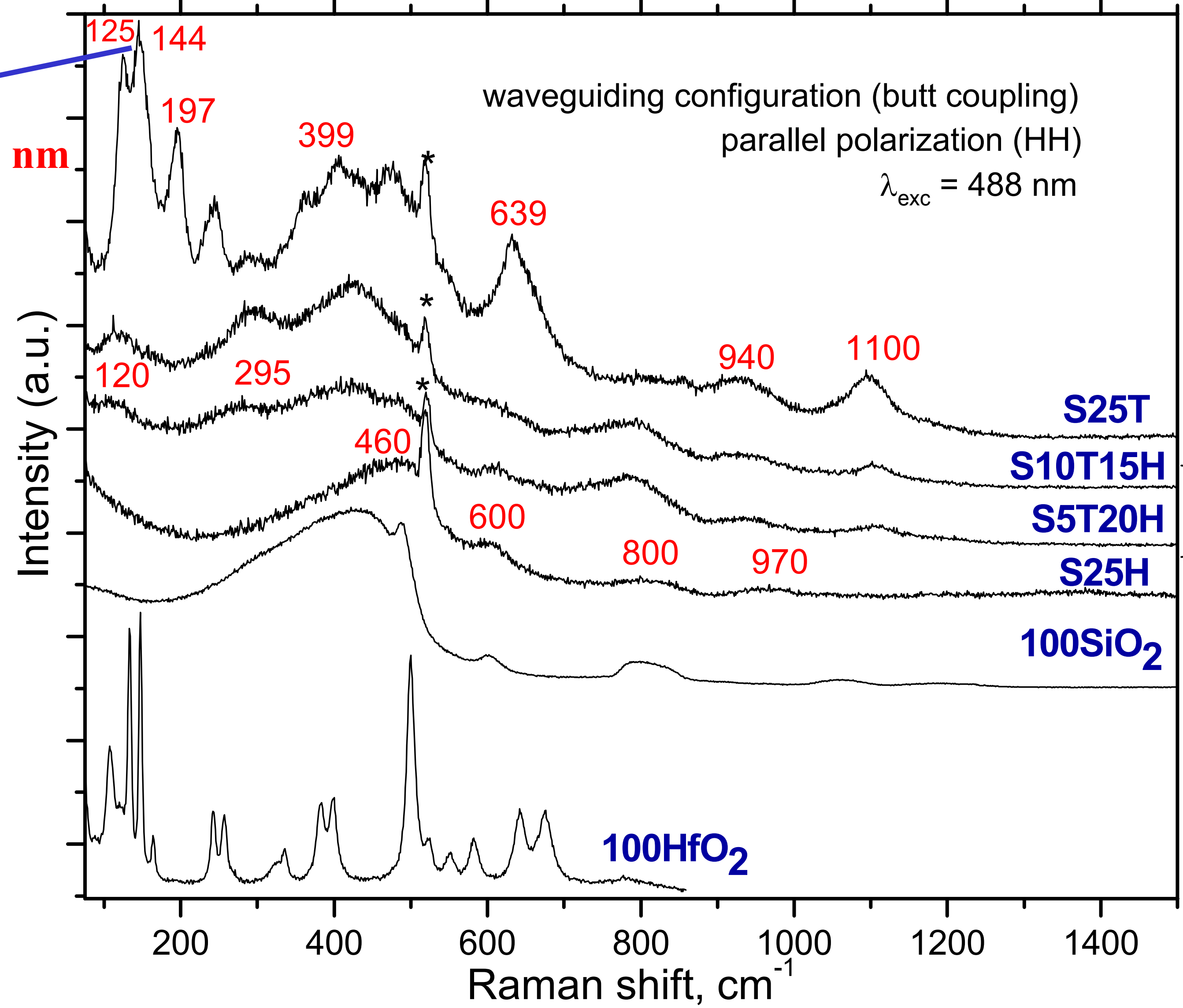
He-Ne laser light (@ **633 nm**) being guided by a SiO_2-TiO_2-Al_2O_3 optical planar waveguide on SOS, by means of prism coupling. Loss ~ 0.2 dB/cm.

Polarized Waveguide Raman Spectroscopy

Waveguide Raman spectroscopy (WRS): structural study of the films

I_{125} / I_{144} :

$t_{anatase} \sim$ 3-4 nm



120 - 300 cm^{-1}

Ti-O-Hf
Hf-O-Hf
bending
modes

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X-ray diffraction

and

Er^{3+} photoluminescence (PL)

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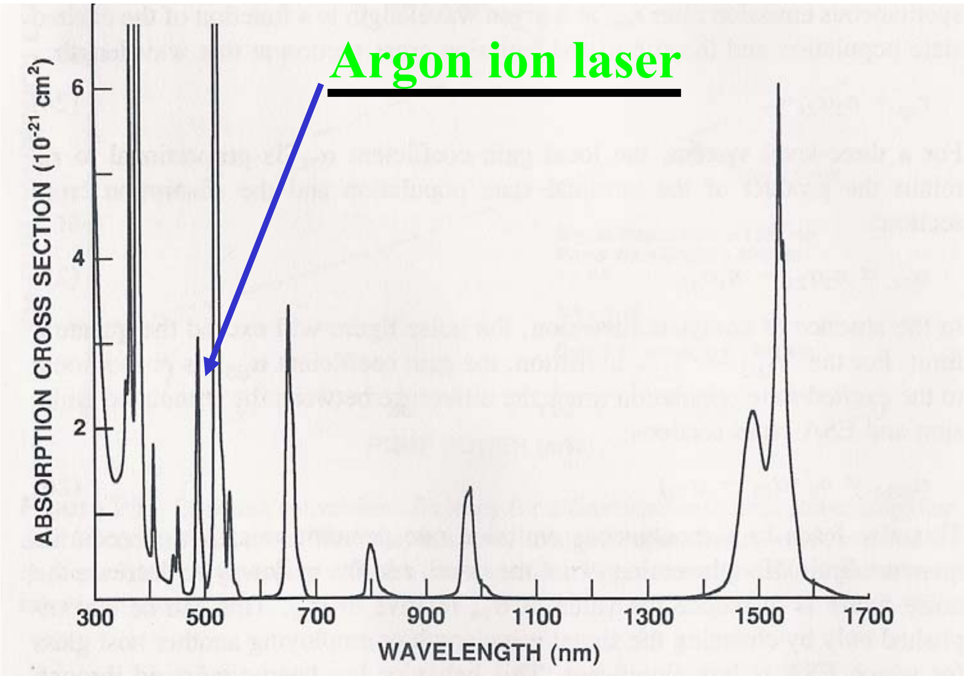
Pumping of Er^{3+} ions

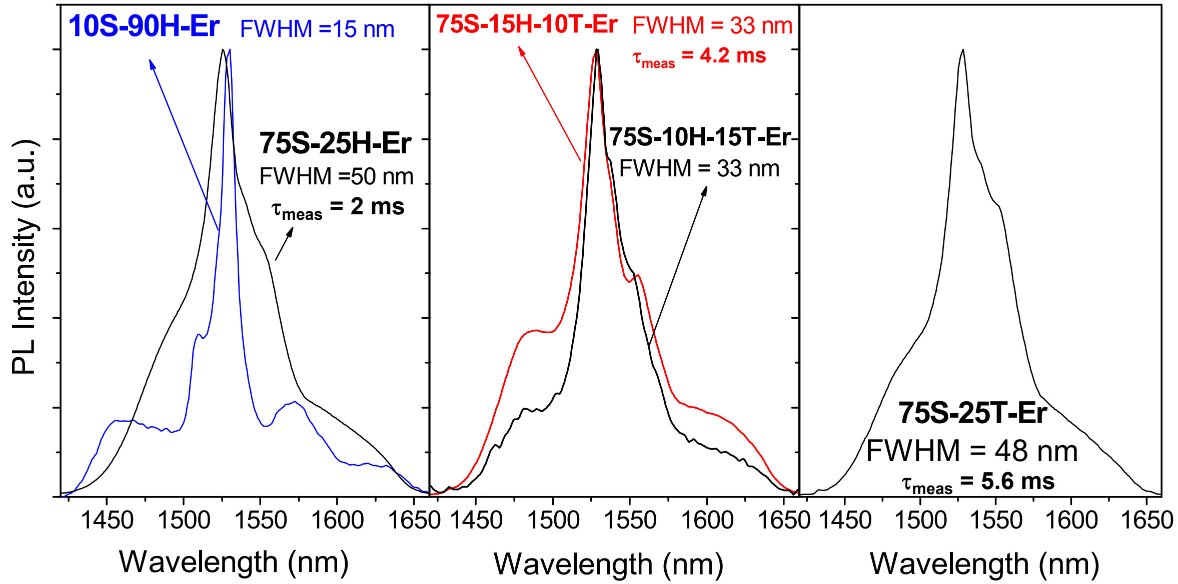
Absorption spectrum of Er^{3+} in a silicate glass.

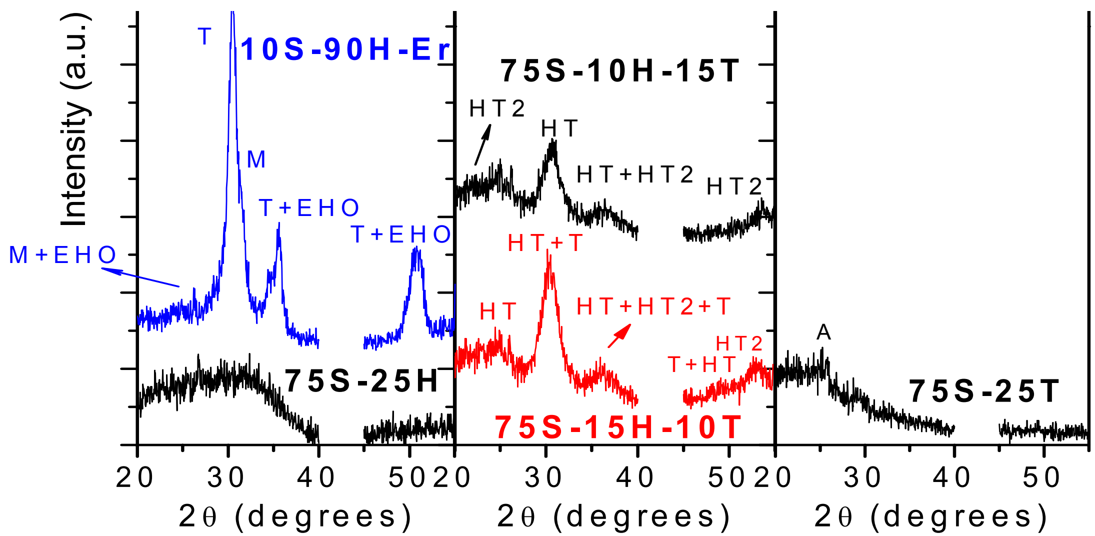


Absorption cross section spectrum of Er^{3+}-doped ED-2 silicate glass. The peaks of the strong bands at 380 and 520 nm are 28 and 19 × 10^{-21} cm^2, respectively.

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel Dekker, 1993)

Er^{3+} ($^4I_{13/2}$-$^4I_{15/2}$) PL spectra and XRD patterns for silica-based planar waveguides (0.5% Er)





T- HfO_2 (tetragonal)

M- HfO_2 (monoclinic)

A - TiO_2 (anatase) ~ **3 - 4 nm**

HT - $HfTiO_4$ ~ **4 - 5 nm**

HT2 - $HfTi_2O$

EHO - $Er_2Hf_2O_7$ or $Er_4Hf_3O_{12}$

Effects of Ag^{o} *nanoparticles* on the Er^{3+} PL intensity

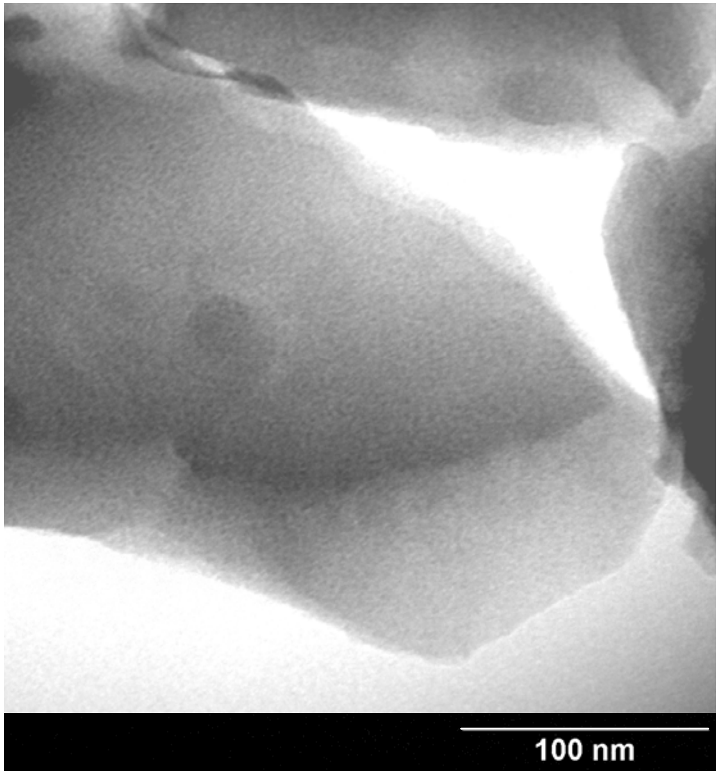
TEM, visible absorption spectroscopy

and

Er^{3+} PL of the nanocomposites

Sol-doping of planar waveguides

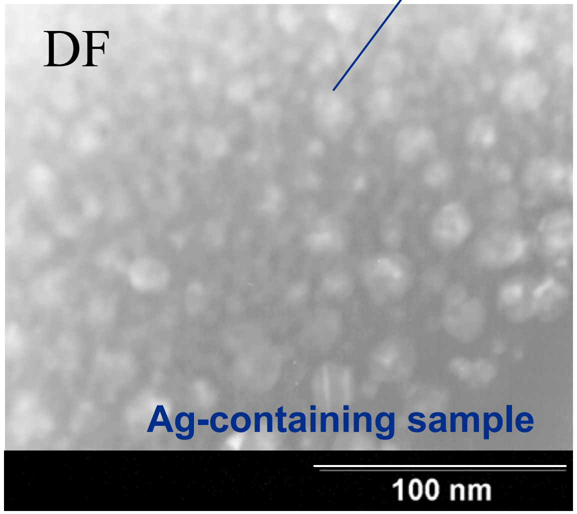
Transmission electron microscopy



$80\%\ SiO_2 – 20\%\ TiO_2 – 0.5\%\ Er$

3 h at 600º C

Agº nanocrystallites (2r~10-20 nm)

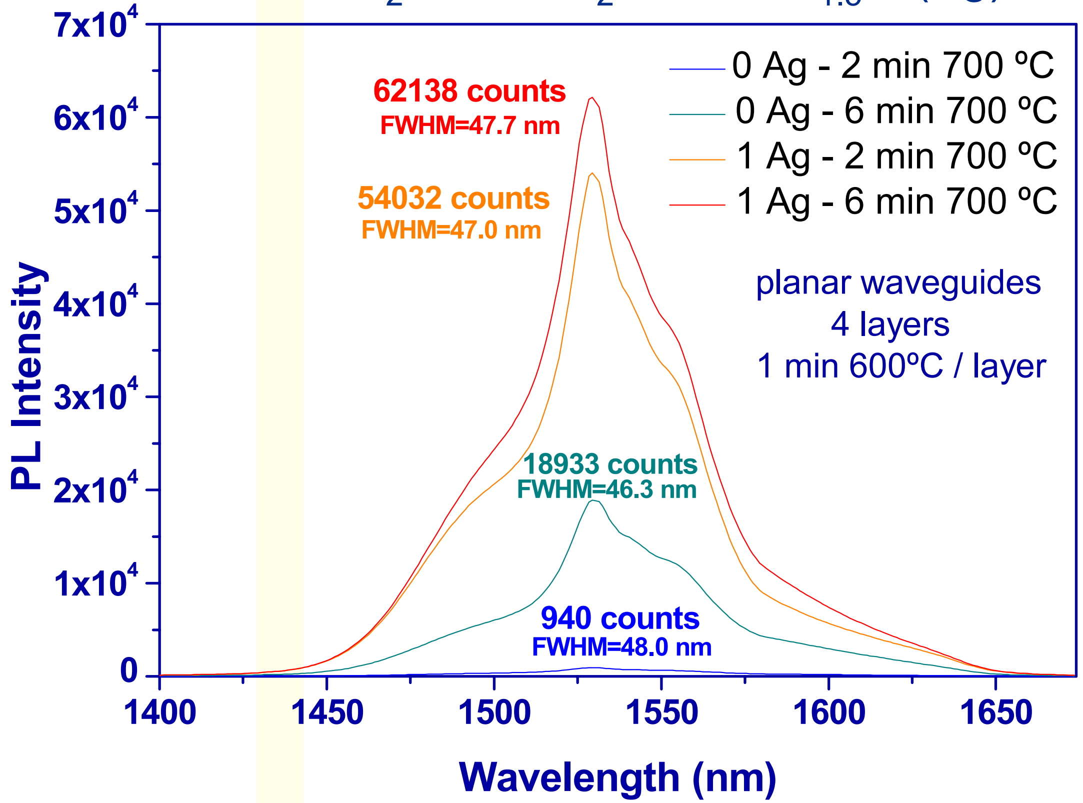


$77.25\%\ SiO_2 – 19.25\%\ TiO_2 – 0.5\%\ Er – 3\%\ Ag$

1 h at 600º C

Influence of silver on the Er^{3+} PL intensity: sol doping of waveguides with Ag^+

80 SiO_2 – 20 TiO_2 - 0.5 $ErO_{1.5}$ - (Ag)

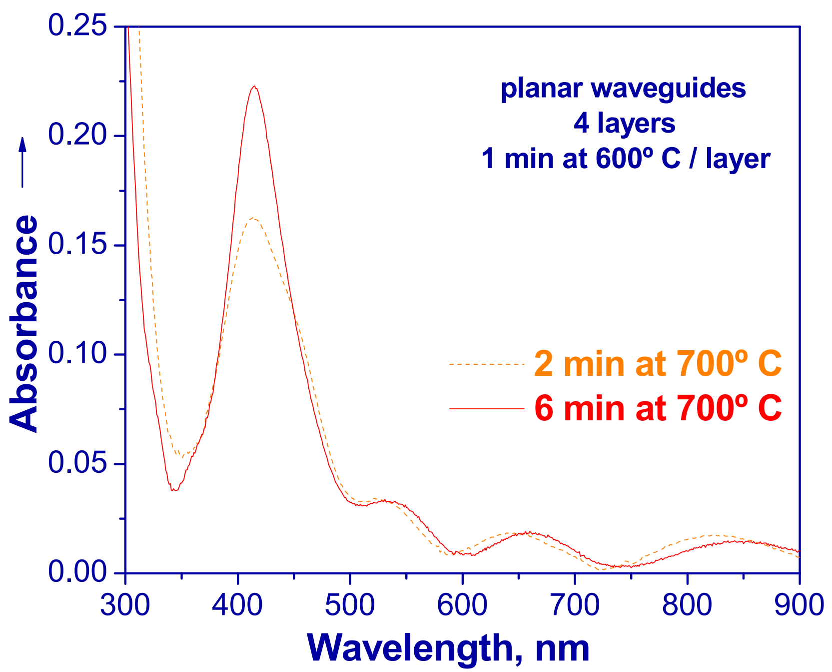


Ag^o absorption

$$2r = \nu_F^{Ag} / FWHM(\omega)$$

$$2r \sim 2 - 4 \text{ nm}$$

78.8% SiO_2 - 19.7% TiO_2 - 0.5% $ErO_{1.5}$ - 1% Ag



Sol-doping with 1% Ag, 2 min @ 700 ºC

~ 60 times PL enhancement

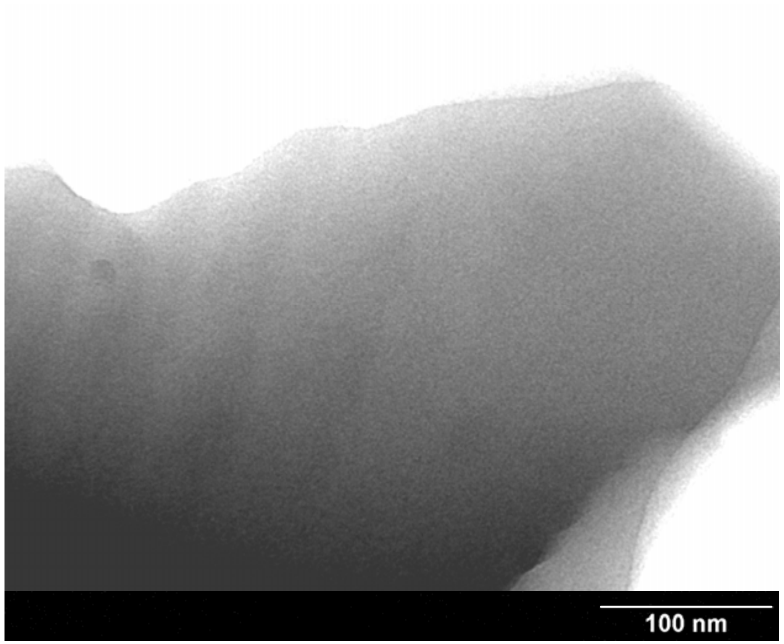
λ_{pump} = 514.5 nm

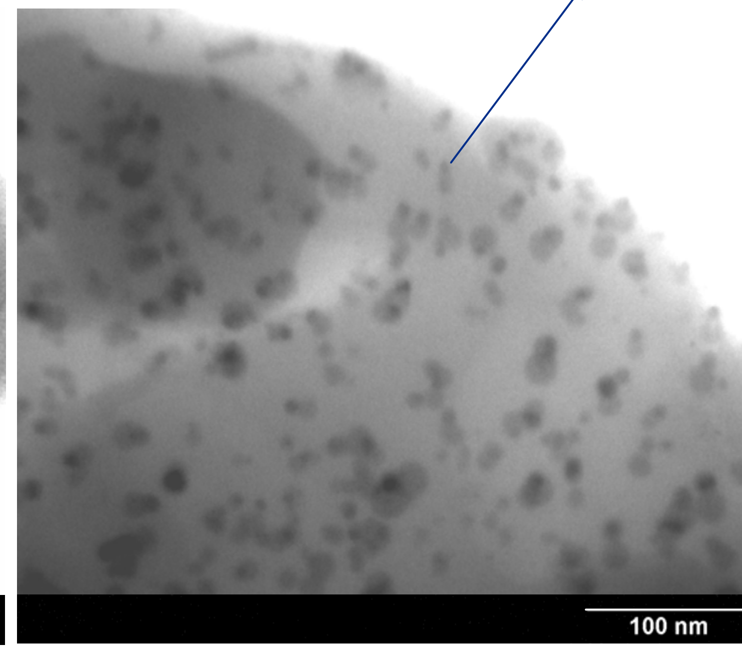
Pore-doping of bulk silica gels

Transmission electron microscopy

bulk silica gel samples treated for 5 h at 900º C

Agº nanocrystallites (2r~10-15 nm)





(Ag-containing sample, Er1Ag2)

Er^{3+}-doped bulk silica glass (prepared by pore-doping with a $Er(NO_3)_3$ solution)

Er^{3+} / Ag^{o}-doped bulk silica glass (prepared by pore-doping with a $Er(NO_3)_3$ + $AgNO_3$ solution)

Influence of silver on the Er^{3+} PL intensity: pore doping of bulk silica gels with Er^{3+} and with Er^{3+}/Ag^{+}

100% SiO_2 (bulk samples)

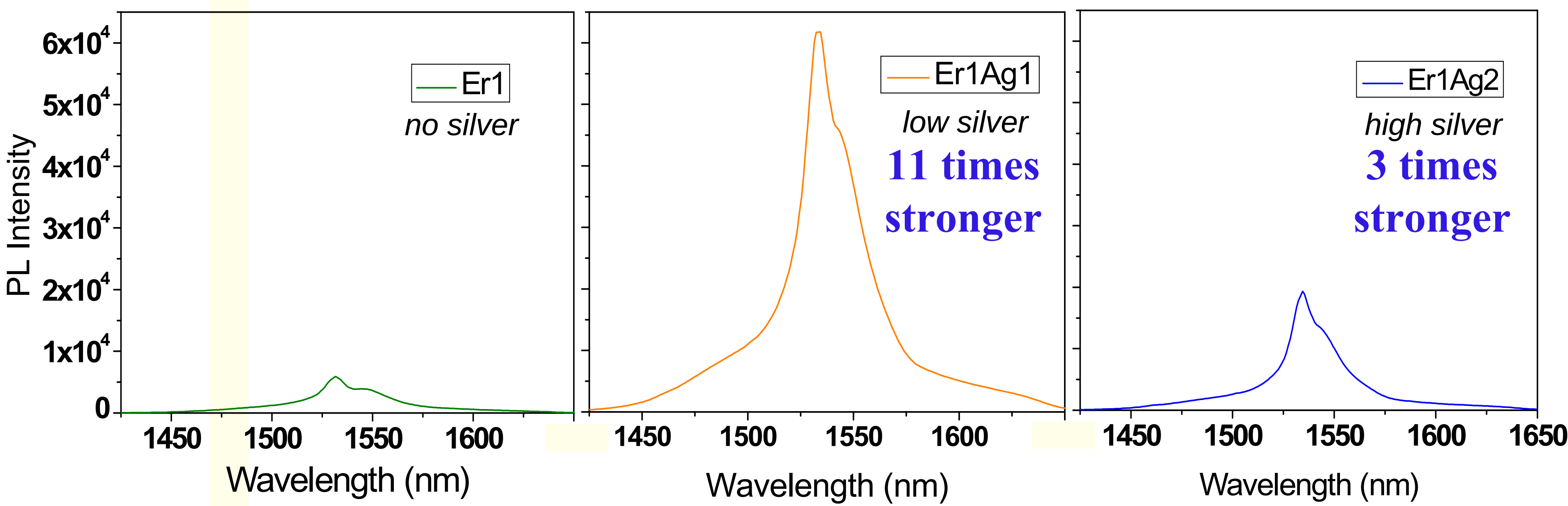
pore doping with Er

immersion for 30 h in a 0.15M $Er(NO_3)_3$ solution

pore doping with Er and Ag

immersion for 30 h in a 0.15M $Er(NO_3)_3$ + 0.15 M $AgNO_3$ solution

immersion for 30 h in a 0.15M $Er(NO_3)_3$ + 0.25 M $AgNO_3$ solution



no silver

FWHM=33 nm

less silver and smaller nanoparticles, d ~ 3nm

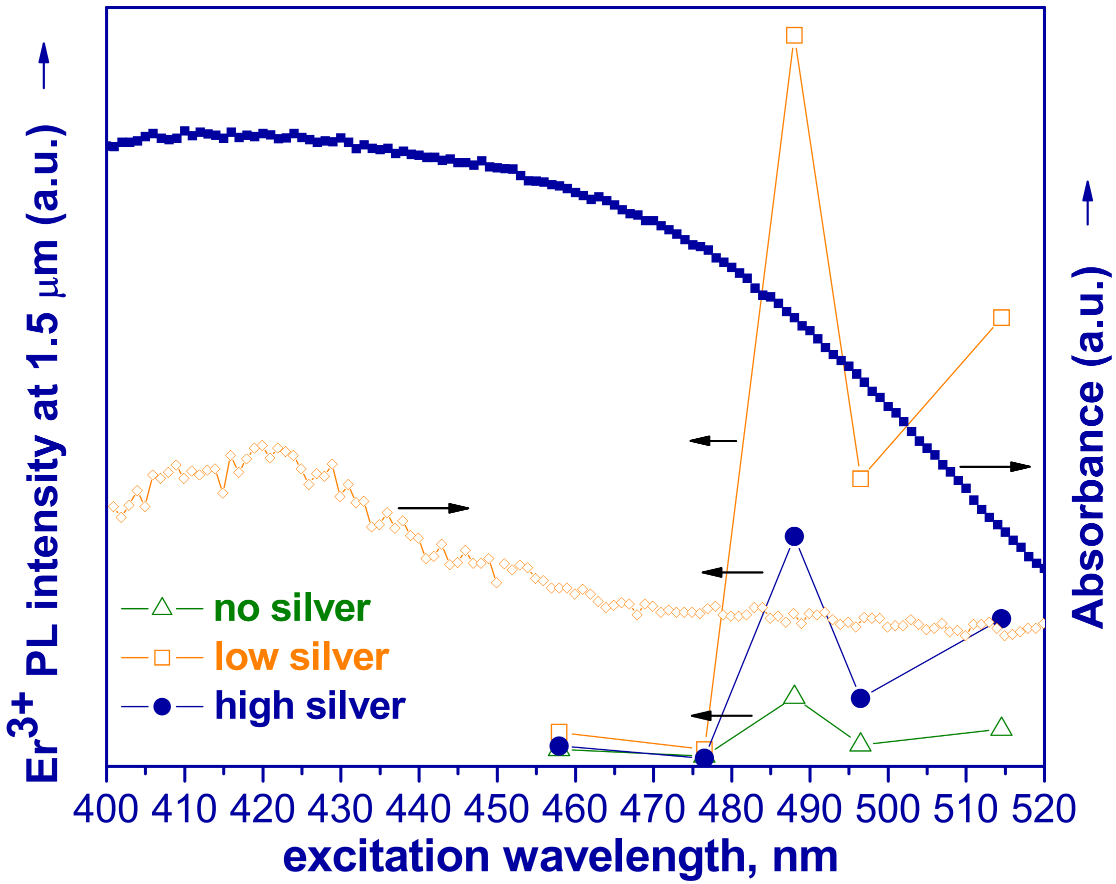
FWHM=27 nm

larger Ag° nanopart. ~10-15 nm

FWHM=24 nm

λ_{pump} = **488 nm**

Ag° optical absorption and Er^{3+} PL intensity at 1.5 μm
(bulk glass samples prepared by pore-doping of gels)



Er^{3+} PL enhancement (~ 11 times) occurs only for resonant excitation

(when λ_{exc} is absorbed by the Er^{3+} ions @ 488, 497, 515 and not @ 458, 477 nm)

⬍

Local electric field enhancement around Er^{3+}, due to SPR of Ag° nanoparticles

▪ Effects of TiO_2 and HfO_2 additions to SiO_2 based optical waveguides, prepared by sol-gel:

Conclusions

→ The structure and spectroscopic properties of these RE-doped sol-gel materials were found to be strongly connected:

- the appearance of **hafnia** and **hafnia-titania mixed crystals** in SiO_2-HfO_2-TiO_2 waveguides led to a significant **narrowing of the Er^{3+} PL peak**, with the formation of **well resolved Stark components**.

Effects of the incorporation of **Ag° nanoparticles into SiO_2-based sol-gel optical waveguides**:

Conclusions

→ The **presence of ~2-15 nm Ag° nanoparticles** in silica glasses and silica-titania planar waveguides caused a **significant enhancement of the Er^{3+} PL at 1.5 µm (~ 3-60 X)**, irrespective of the method used for Ag or Er^{3+} incorporation.

→ The **dominant mechanism** responsible for the observed PL increase in Ag-containing samples is proposed to involve a **local electric field enhancement around the Er^{3+} ions, due to SPR of the Ag° nanoparticles.**

Rare-earth doped Fabry-Perot microcavities

PHOTONIC BANDGAP STRUCTURES

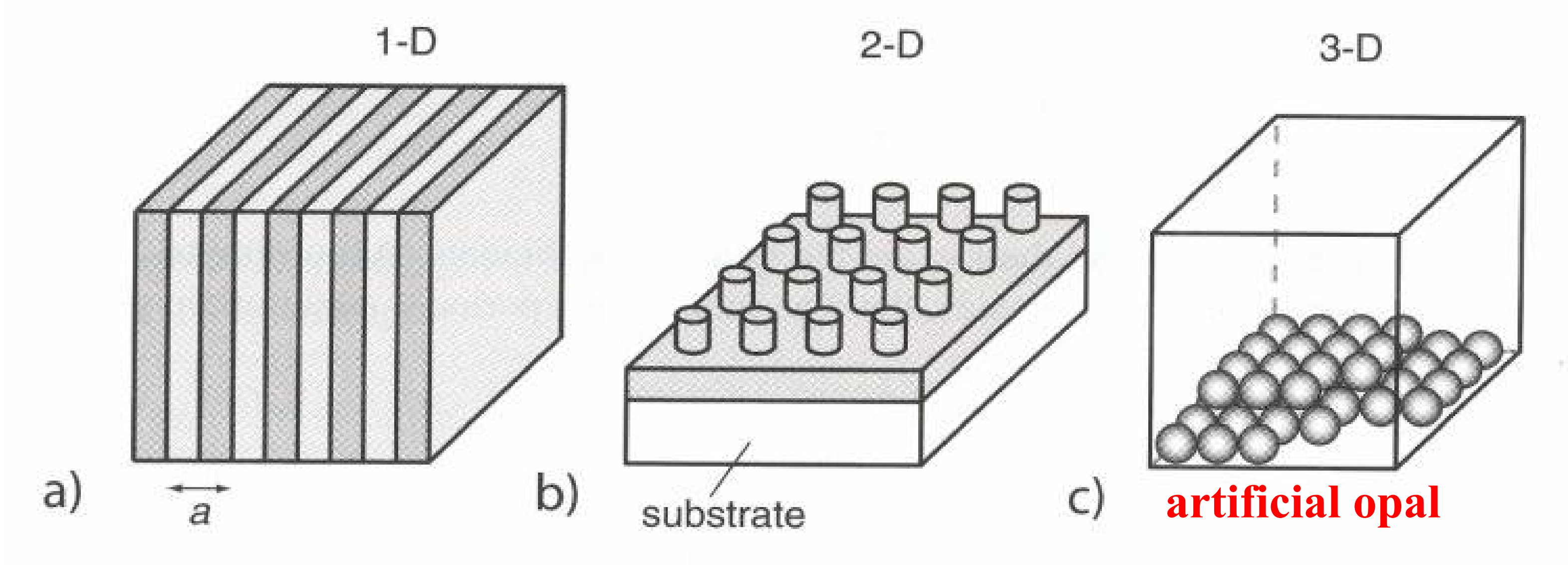
Also called photonic crystals, the optical analogues of semiconductors.

Structures whose refractive index is periodic on a length scale ~ λ in the optical region of the electromagnetic spectrum.

Light is prevented from propagating by Bragg reflection:

$$\lambda = 2d\sqrt{n_{eff}^{2} - \sin^{2}\theta}$$

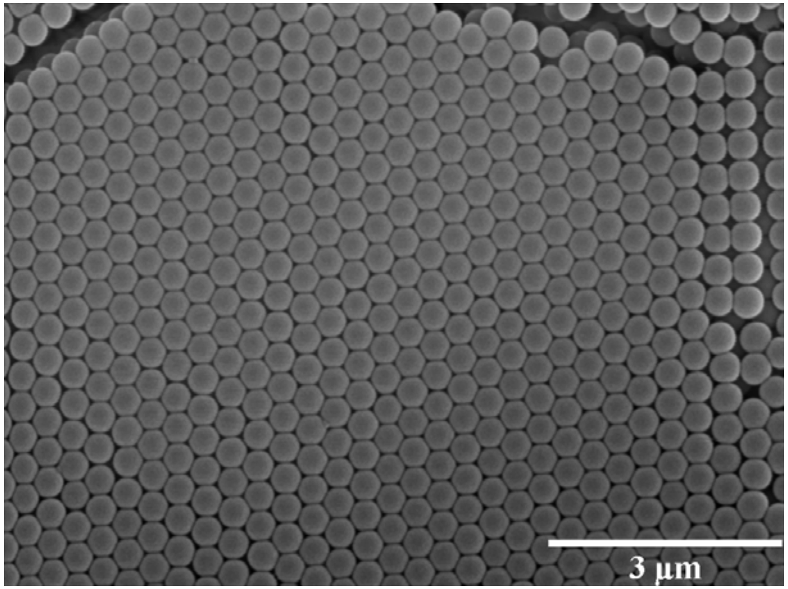
1-D, 2-D and 3-D photonic crystals



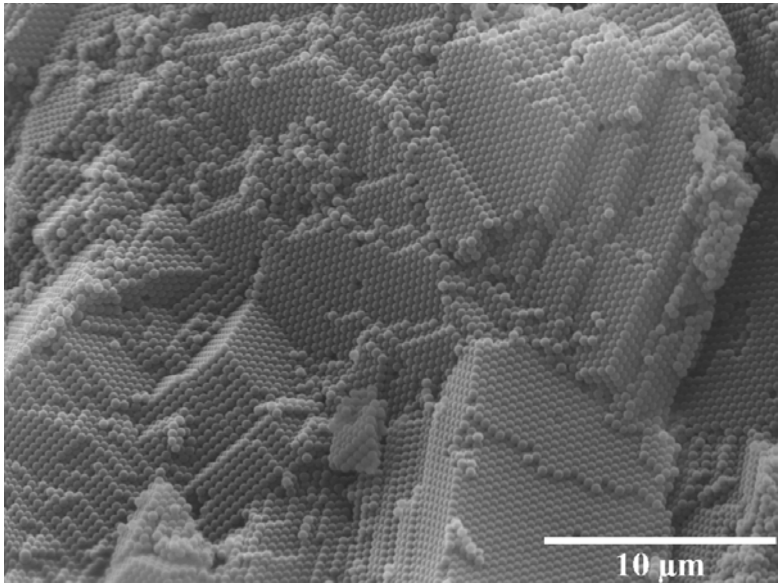
Schematic of 1-, 2-, and 3-D periodic lattices consisting of two materials of different dielectric constants. The lattice constant is denoted **a**.

Artificial opal prepared by convective self-assembly

SEM micrographs of an opal made of 460 nm diameter PS spheres, by convective self-assembly: (a) top view of {111} plane; (b) cleaved edge showing {100} and {111} planes of the *fcc* structure.



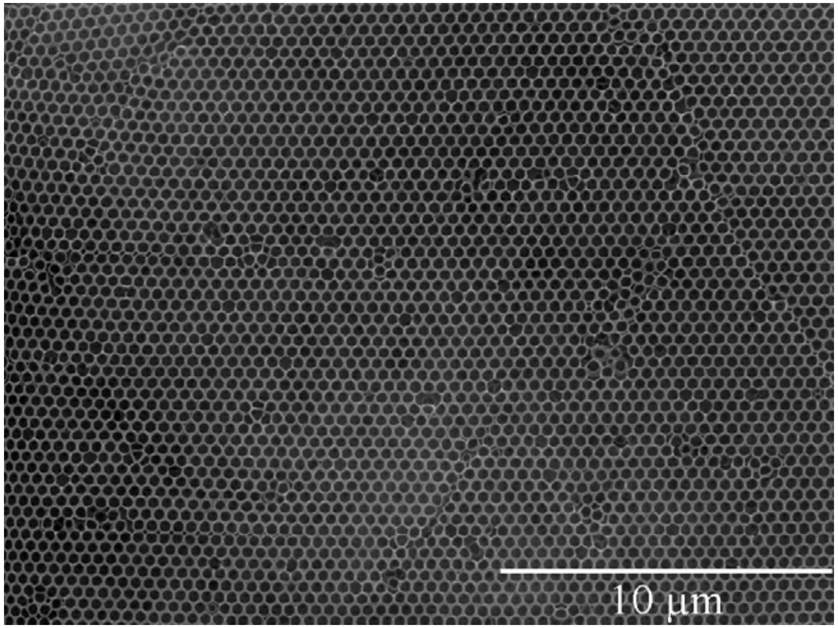
(a)

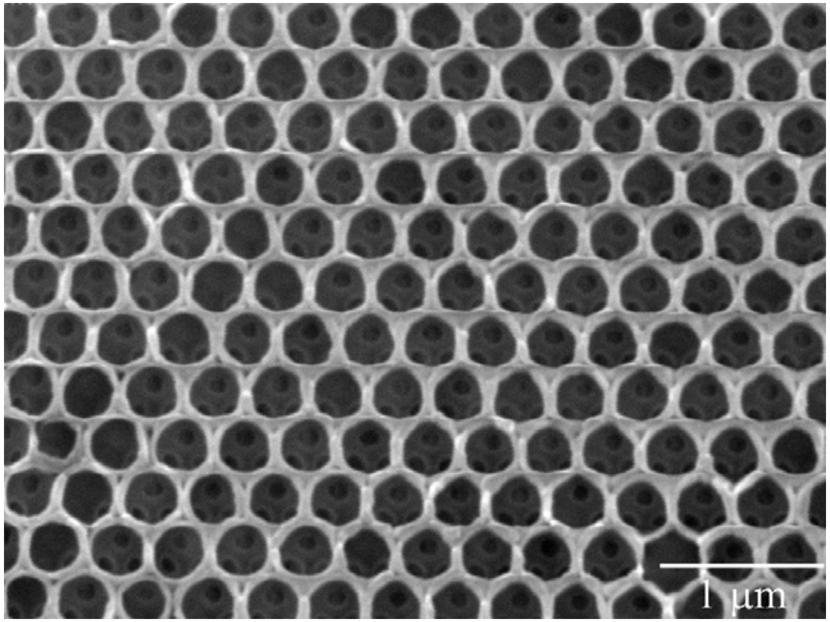


(b)

Titania inverted opal

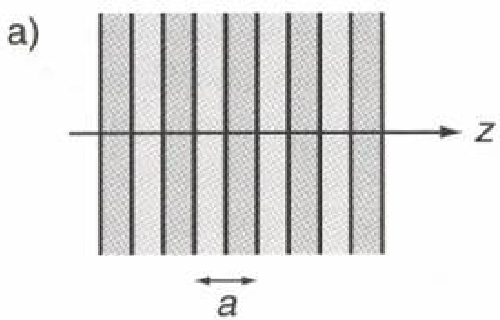
SEM micrographs of a titania / air inverted opal structure, prepared by convective self-assembly of PS templates, at different magnifications.



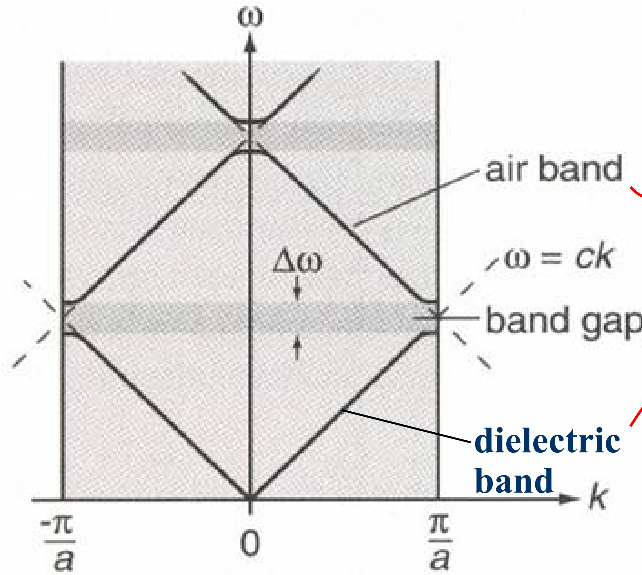


Interference filter

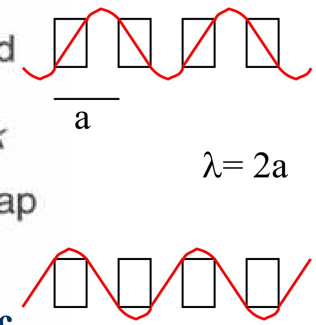
(also called a Distributed Bragg Reflector, or simply a Bragg mirror)



Interference filter as 1-D photonic crystal



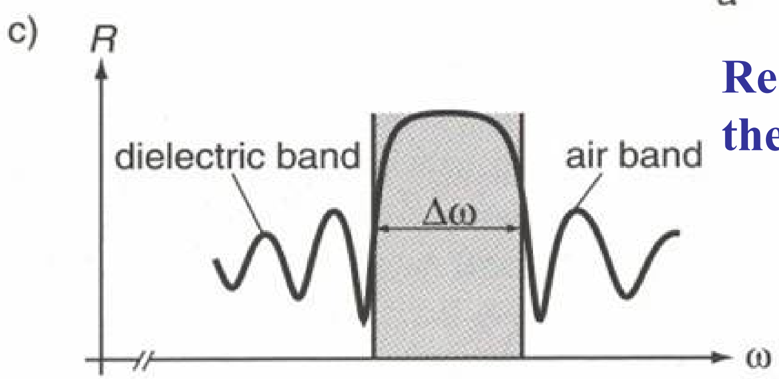
$$\omega_a = \frac{c_0}{n_a} k$$



$\lambda = 2a$

$$\omega_d = \frac{c_0}{n_d} k$$

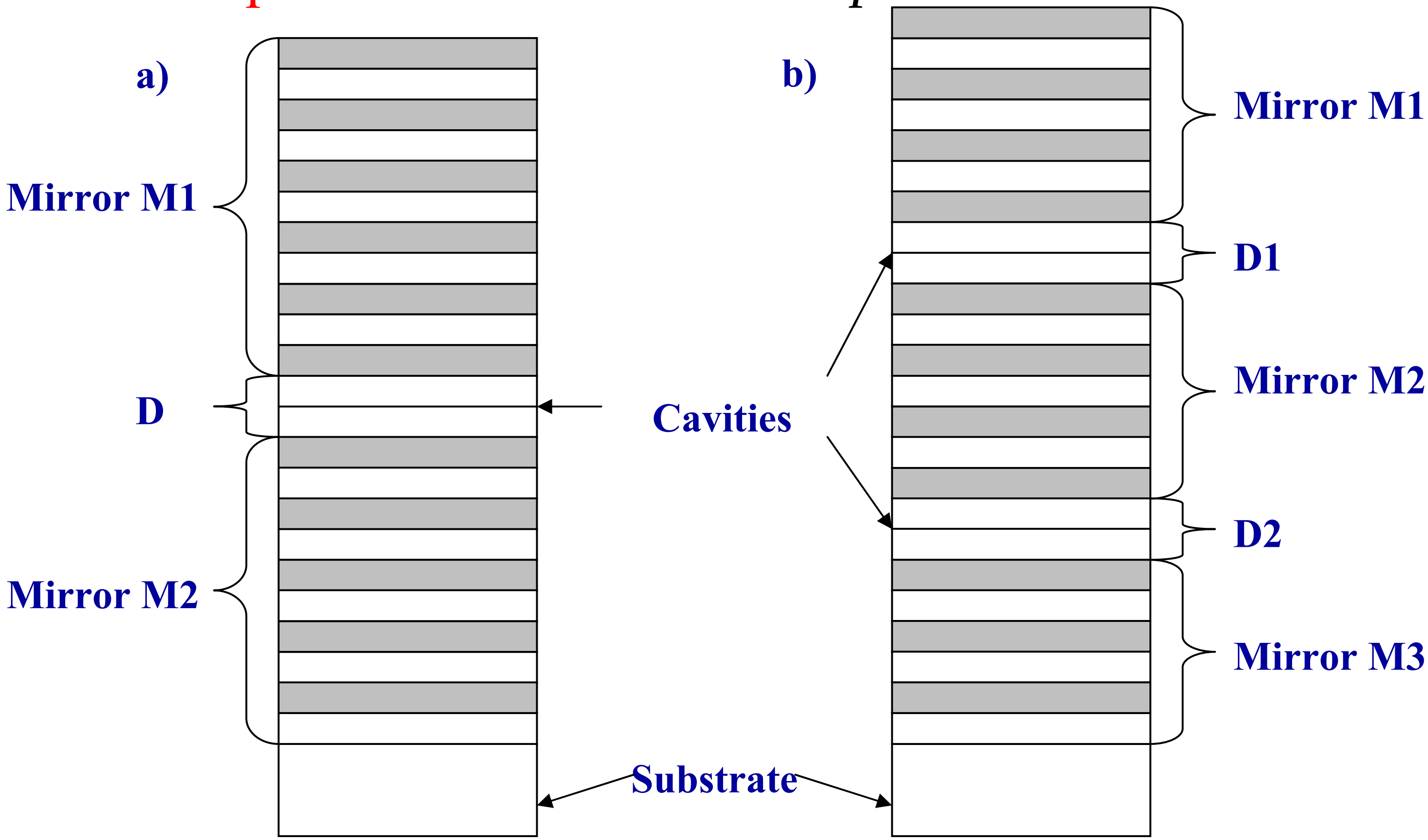
Reduced zone scheme for the dispersion relation



Typical filter characteristics with "stop band"

Microcavities prepared from SiO_2 and TiO_2 sol-gel layers

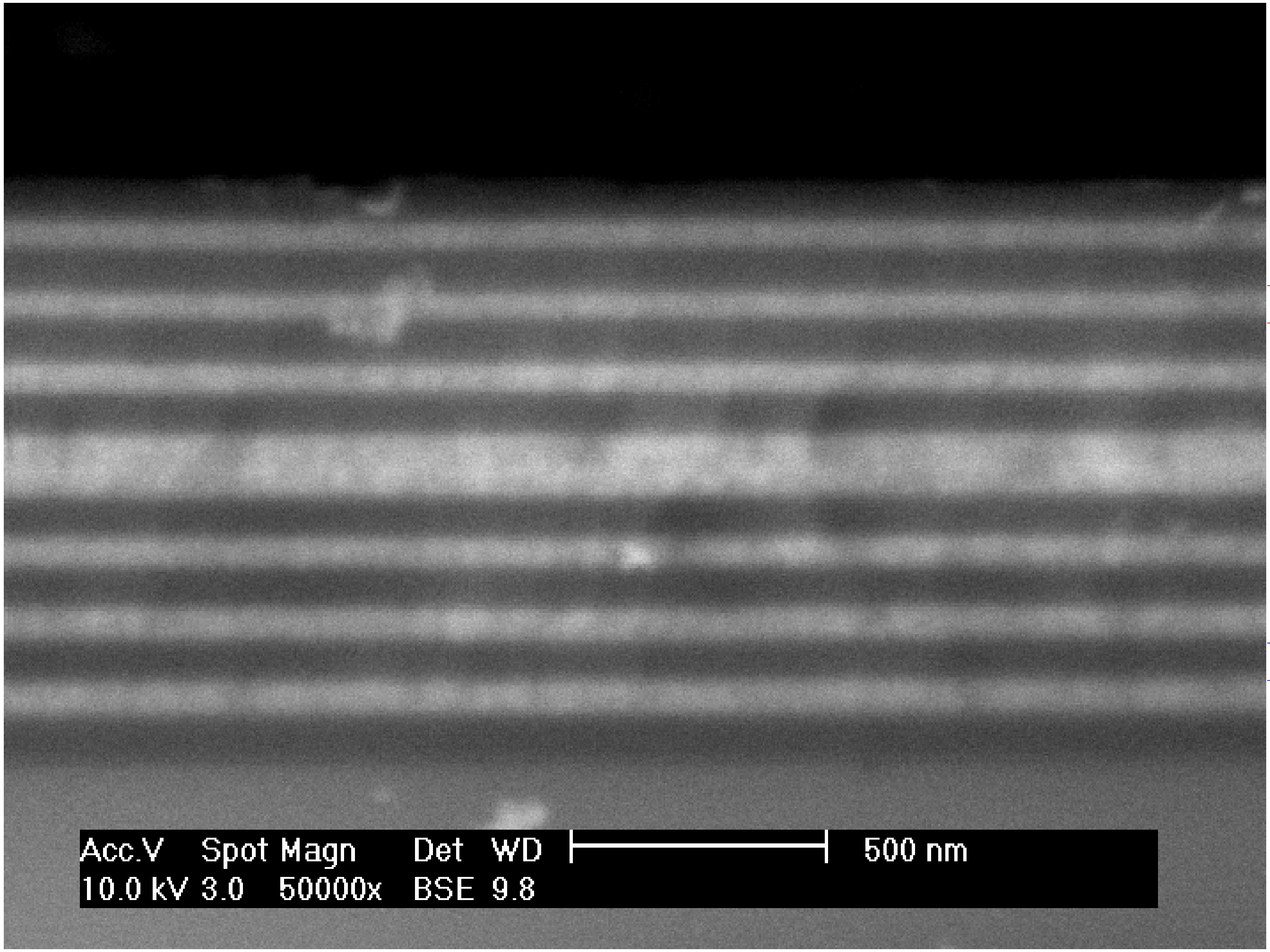
Bragg mirrors: "quarter-wave" stacks of *optical* thickness: **$nx = \lambda/4$**



Schematics of 1-D PBG structures: → (a) microcavity of silica;
→ (b) coupled microcavities of silica.

TiO_2 layers are gray and **SiO_2 layers** are the open rectangles.

Microcavity with a TiO_2 defect layer



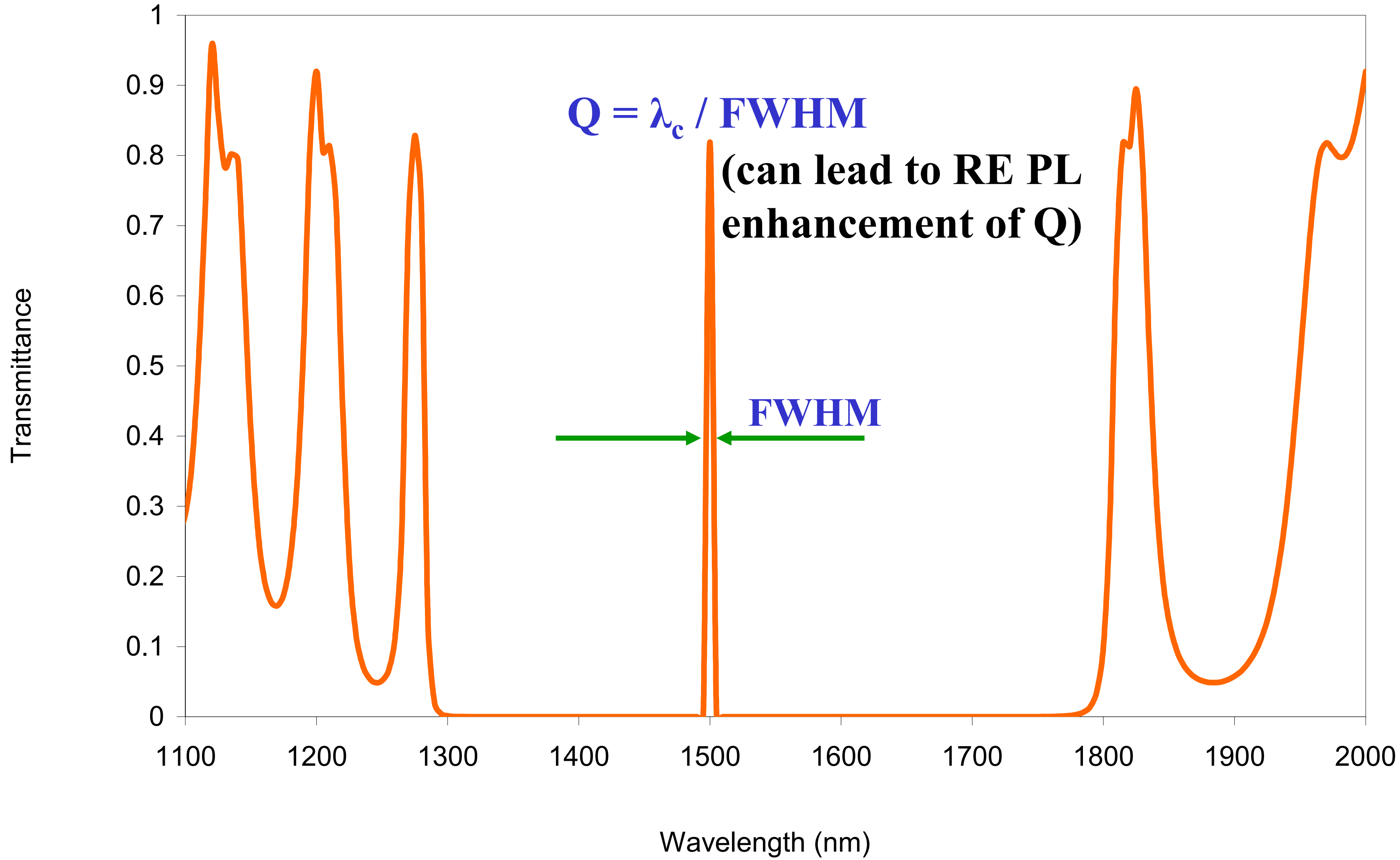
] H ~ 50 nm

} H ~ 100 nm

] L ~ 80 nm

Cross-section FEG-SEM micrograph of a microcavity, with a **titania defect** layer. (Backscattered electron mode).

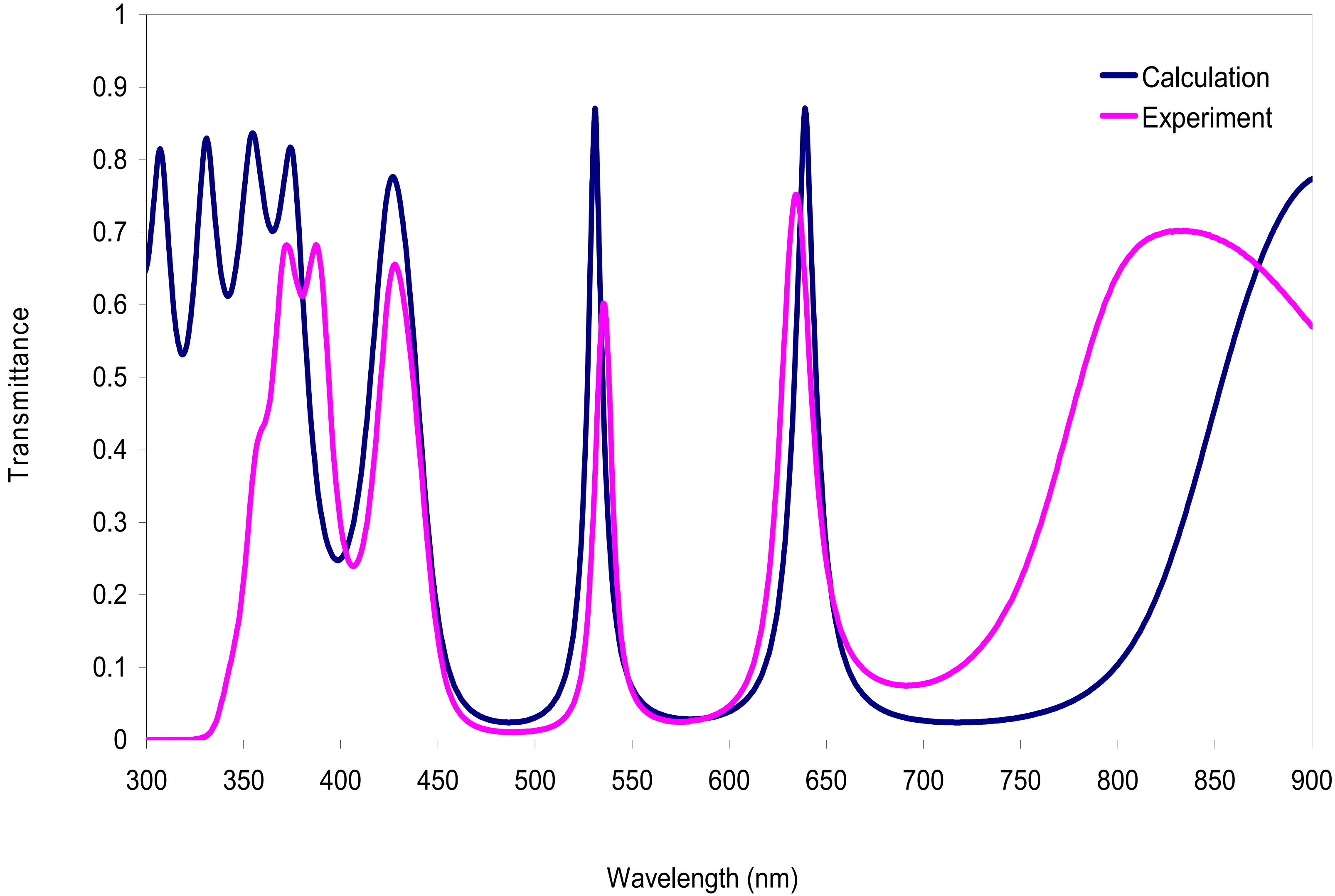
Simulation of F-P microcavity by transfer matrix method



(LH)10 L (LH)10 **Q = 284**

L=SiO_2 (nL=1.45, eL=258 nm); H=TiO_2 (nH=2.3, eH=163 nm)

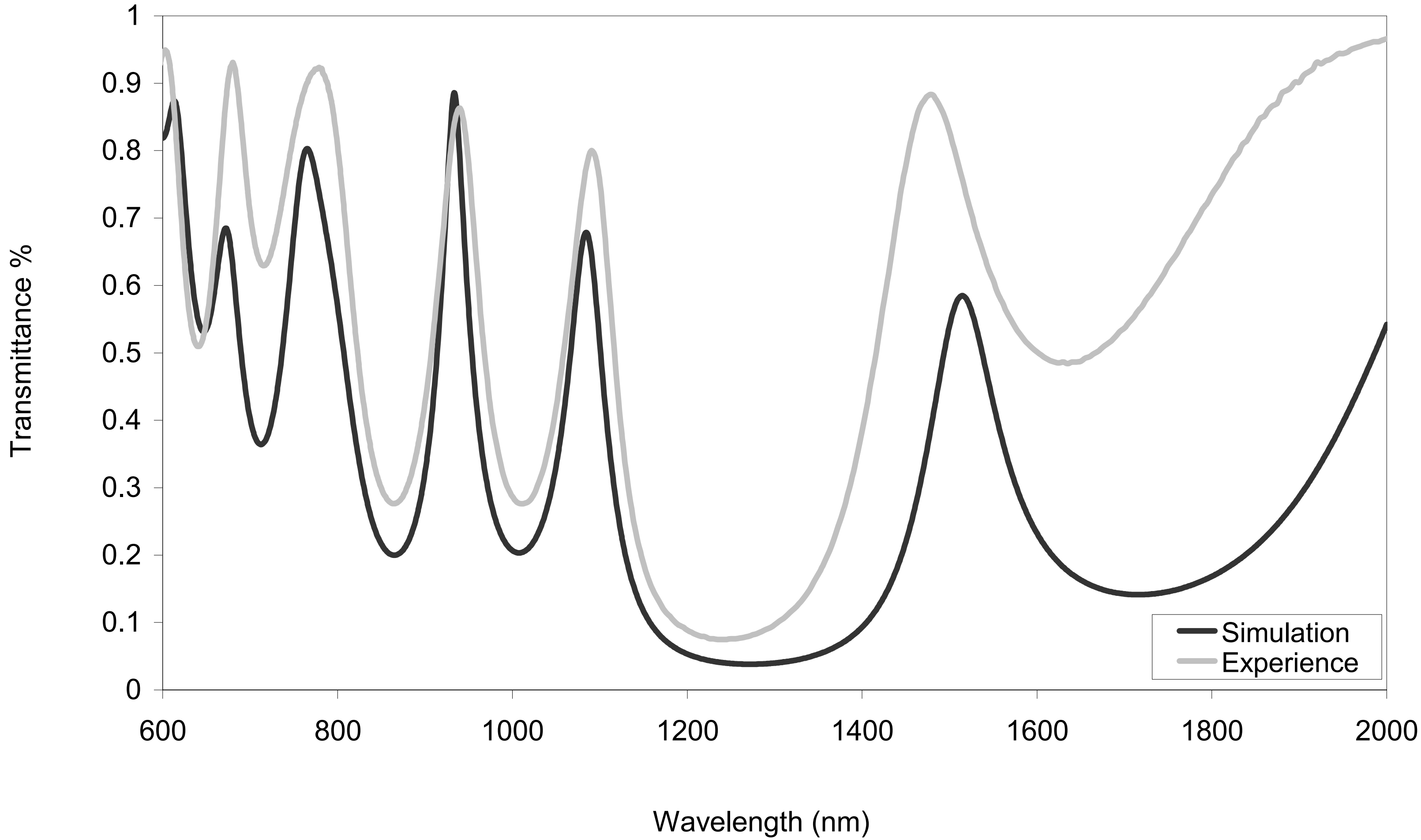
Coupled cavities in the Visible region



(LH)3 L (LH) L (LH)3

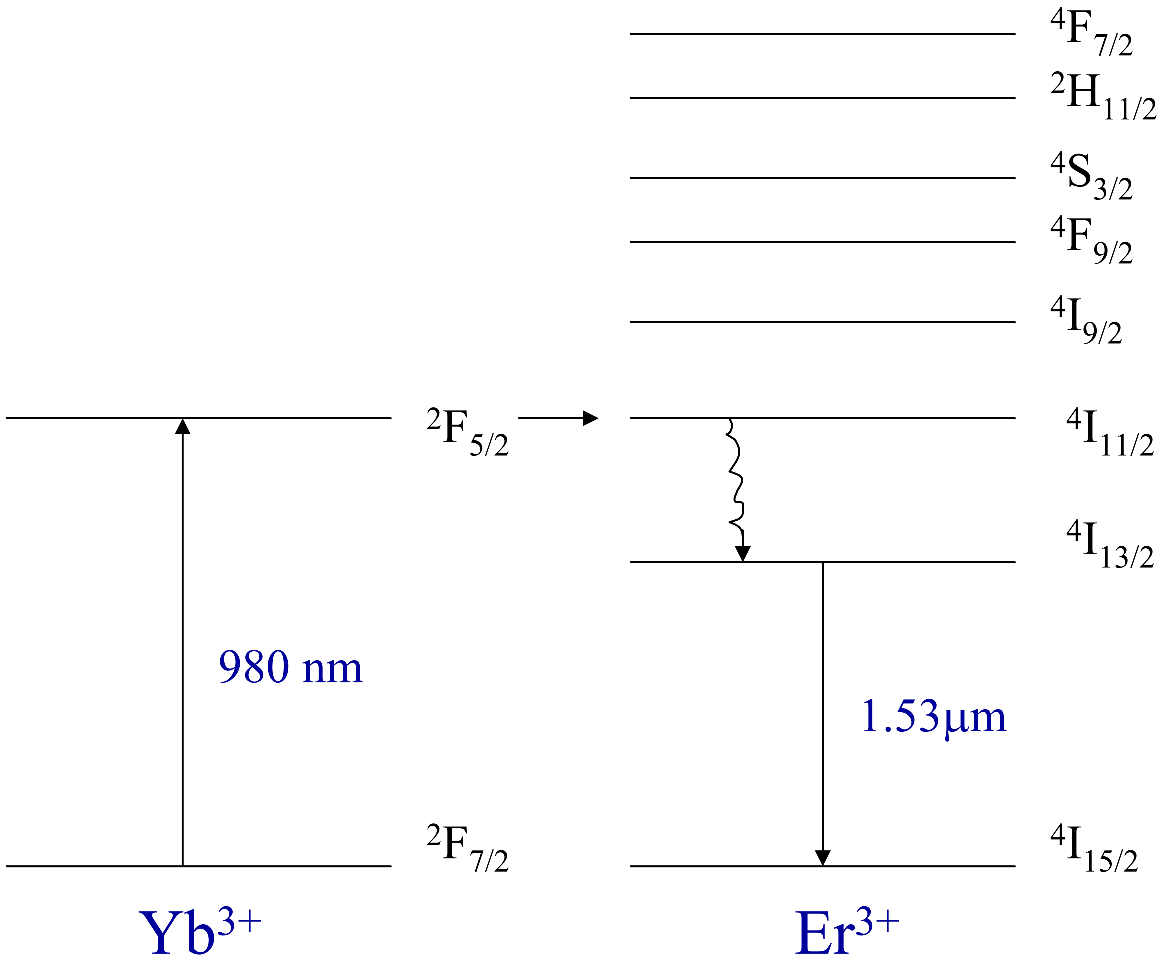
L=SiO2 (n=1.45, e=100 nm) H=TiO2 (n=2.3 e= 63 nm)

Coupled cavities in the NIR region



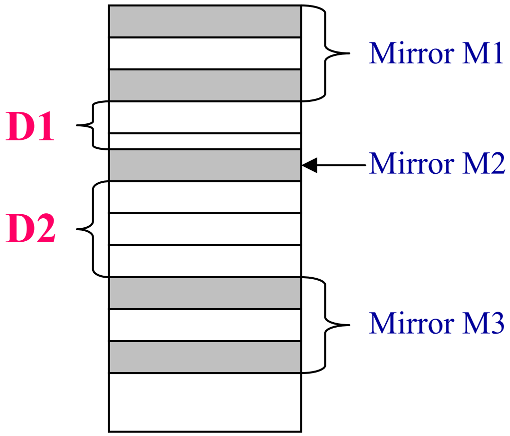
Comparison between experimental and simulated optical transmission of a coupled microcavity with the structure (LH)2L3/2(LH)L3HLH where L stands for SiO_2 and H for TiO_2.

Antenna (or sensitizing) effect



Energy level diagram of Er^{3+} and Yb^{3+} ions ("antenna" effect).

Doped coupled microcavities



A → D1 (Er^{3+}, Yb^{3+}); D2 (Er^{3+}, Yb^{3+});

B → D1 (Yb^{3+}); D2 (Er^{3+});

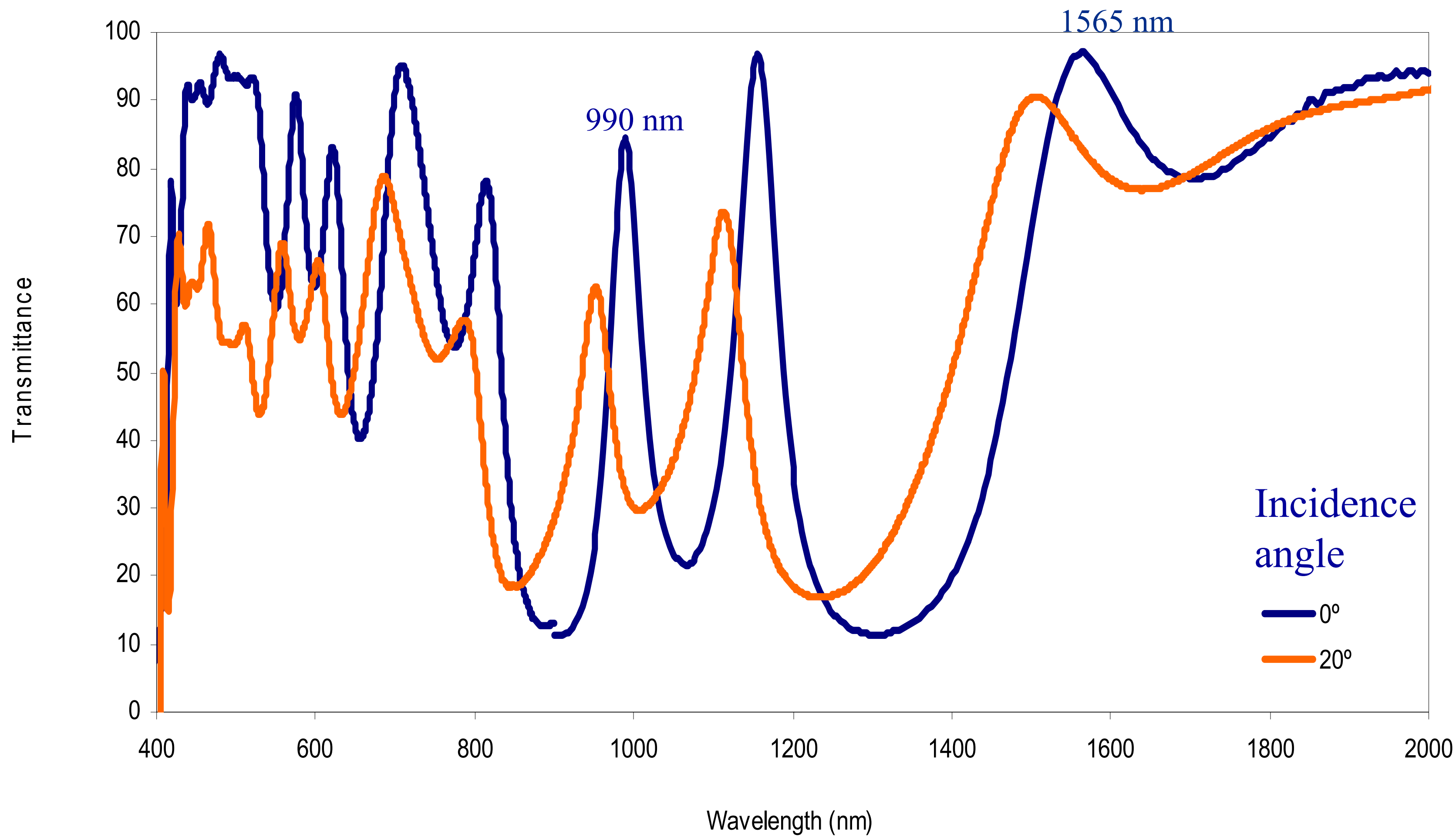
C → D1 (); D2 (Er^{3+});

$[Er^{3+}]$ = 0.5 mol% in SiO_2

$[Yb^{3+}]$ = 2.0 mol% "

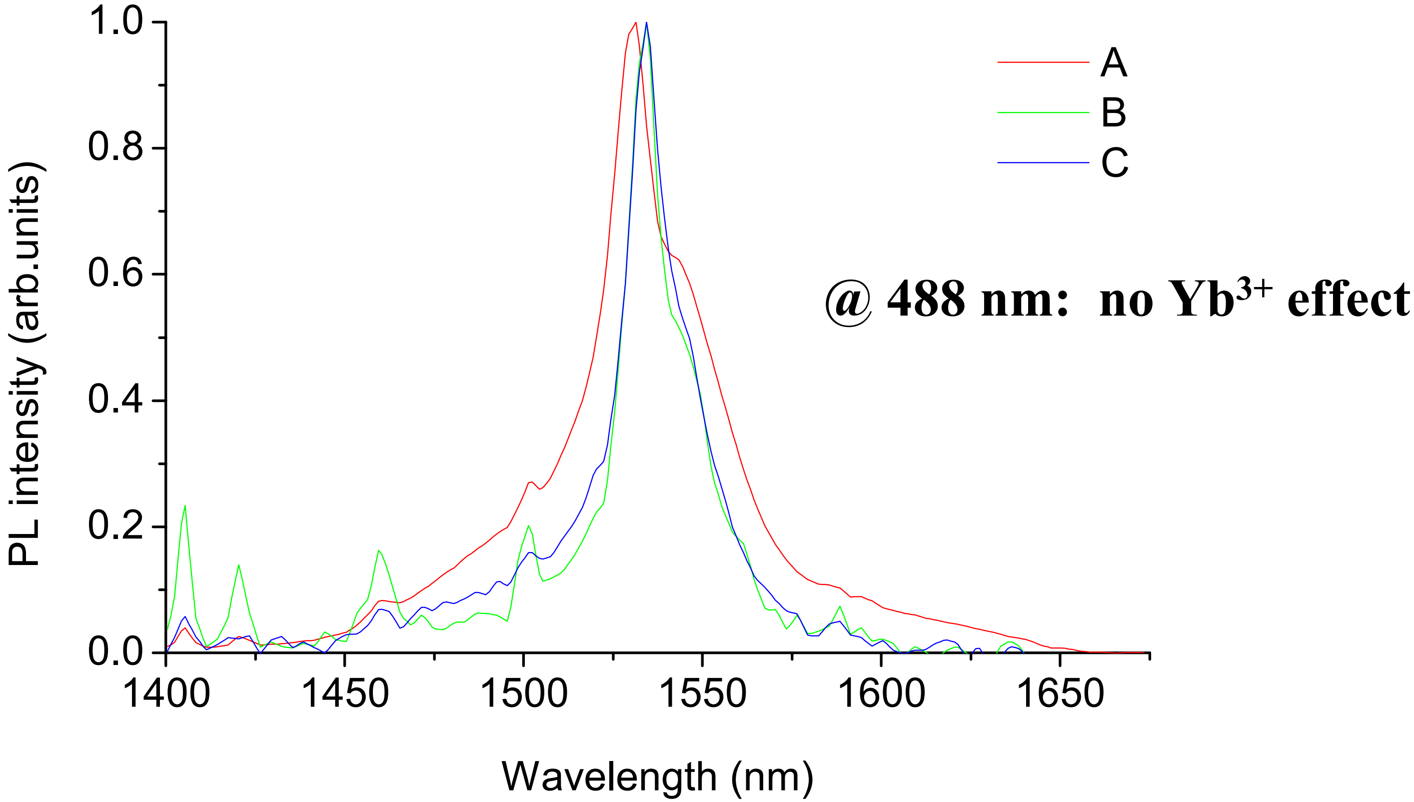
(Sample A has 50% more Er^{3+} than B or C)

Transmission of cavity A



"Transmission" (1-R%) spectra of cavity A at different incident angles.

Normalized PL of A, B and C (excited @ 488 nm)



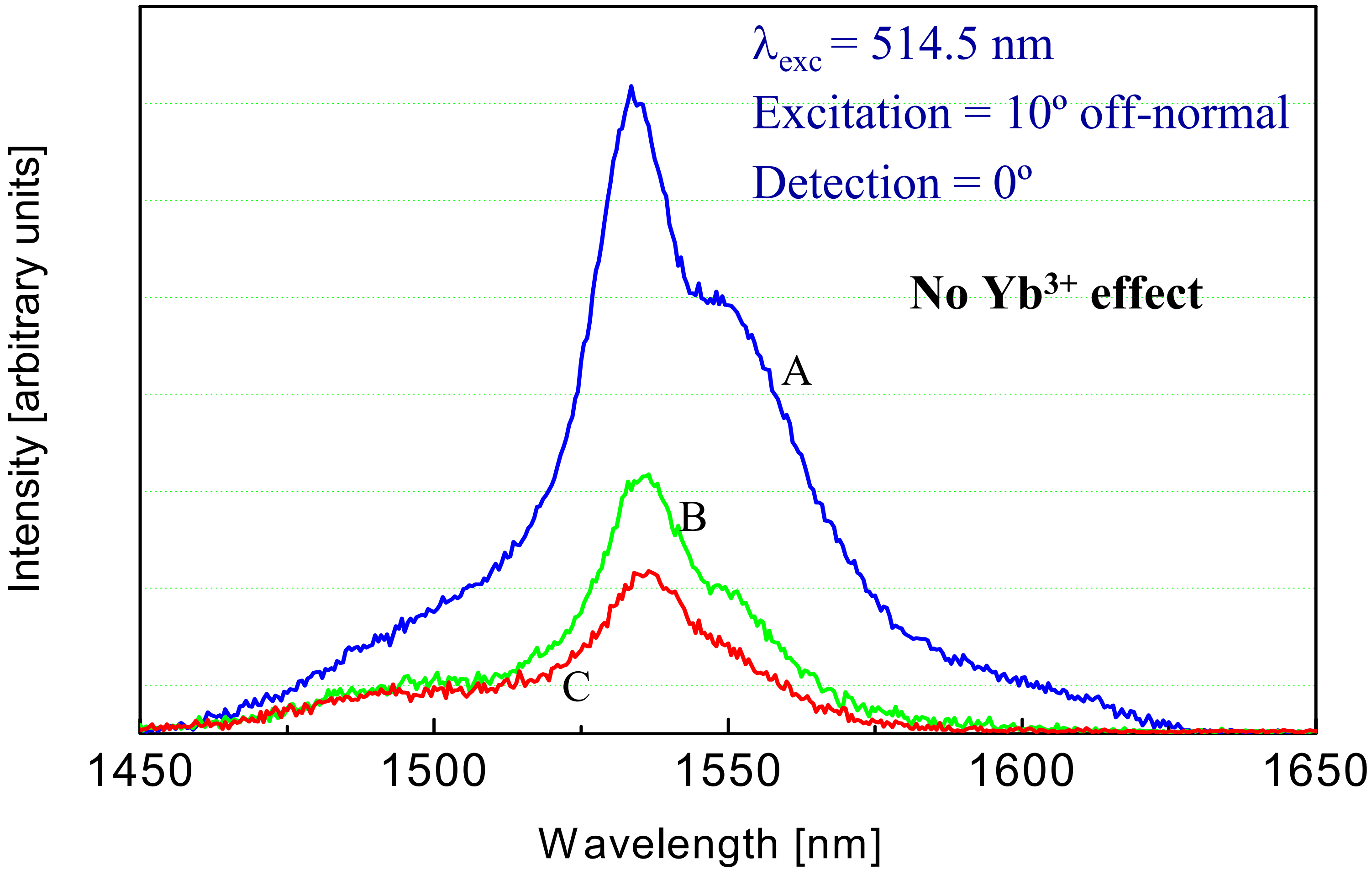
Normalized Er^{3+} photoluminescence spectra of coupled microcavities, excited at 488 nm, at normal incidence.

A: both cavities co-doped with Er^{3+} and Yb^{3+};

B: D1 doped with Yb^{3+} and D2 doped with Er^{3+};

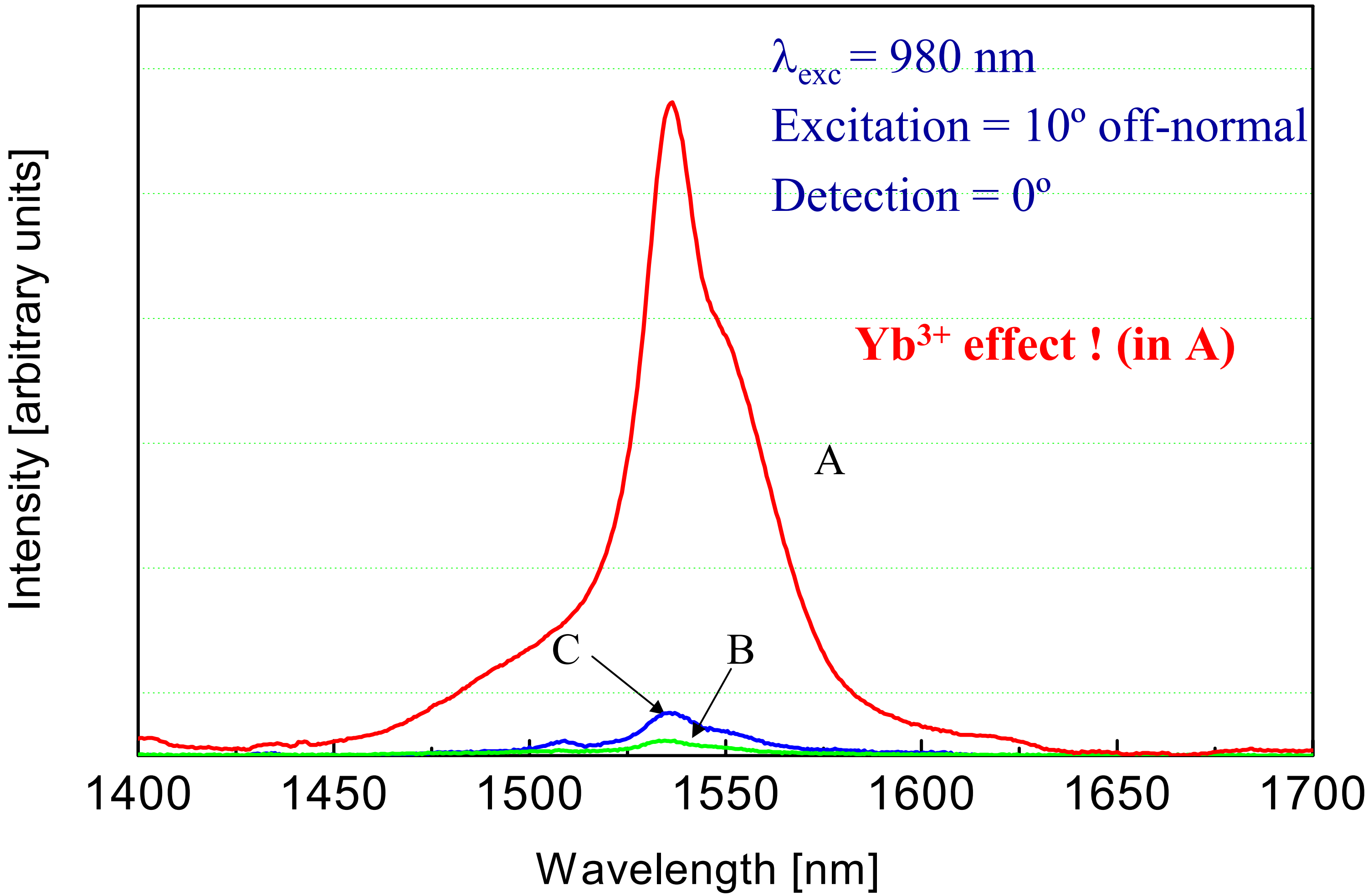
C: only cavity D2 doped with Er^{3+}.

PL of A, B and C (excited @ 514.5 nm)



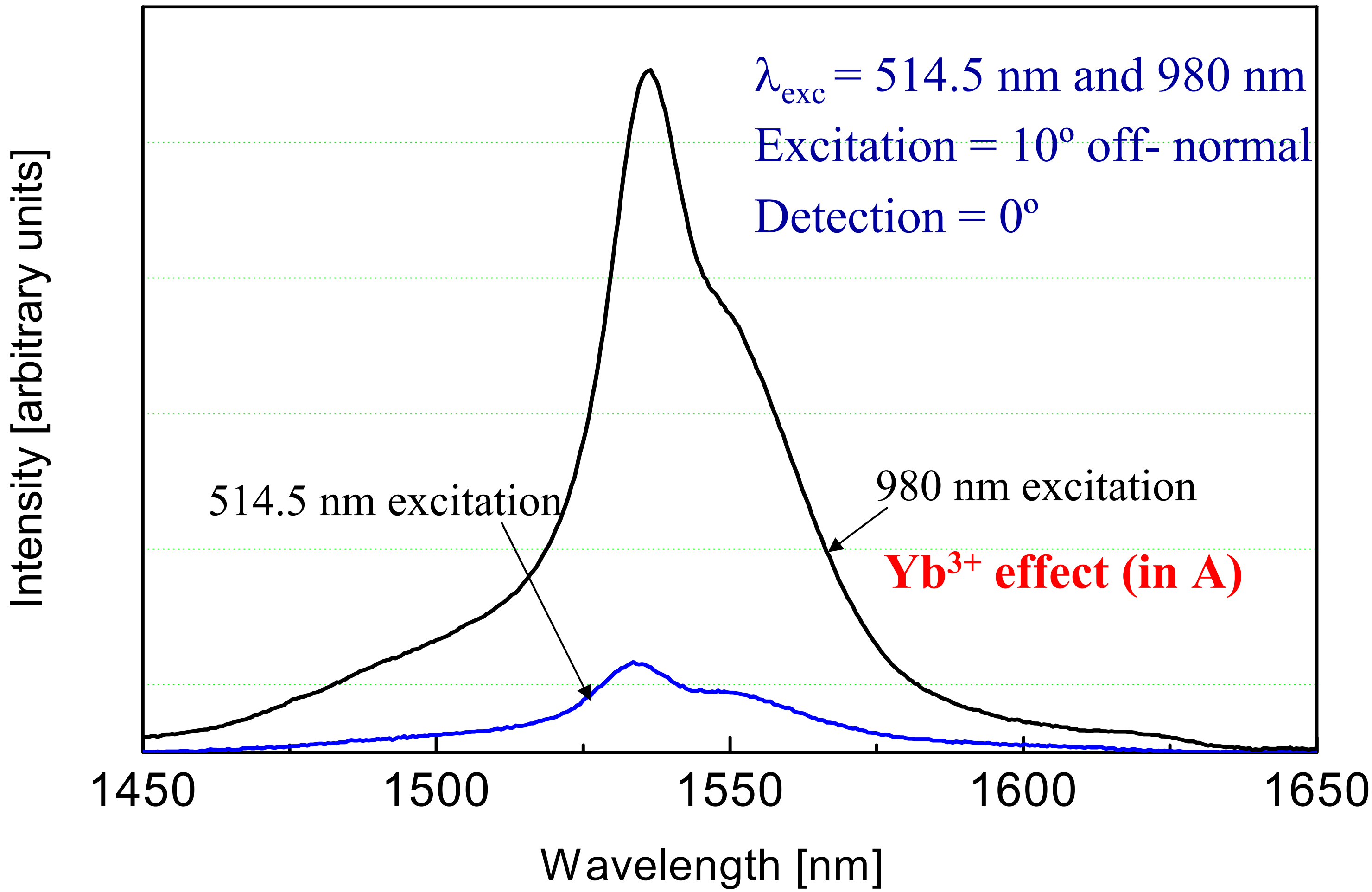
Comparison of Er^{3+} photoluminescence spectra of coupled microcavities A, B and C, excited at 514.5 nm (TE).

PL of A, B and C (excited @ 980 nm)



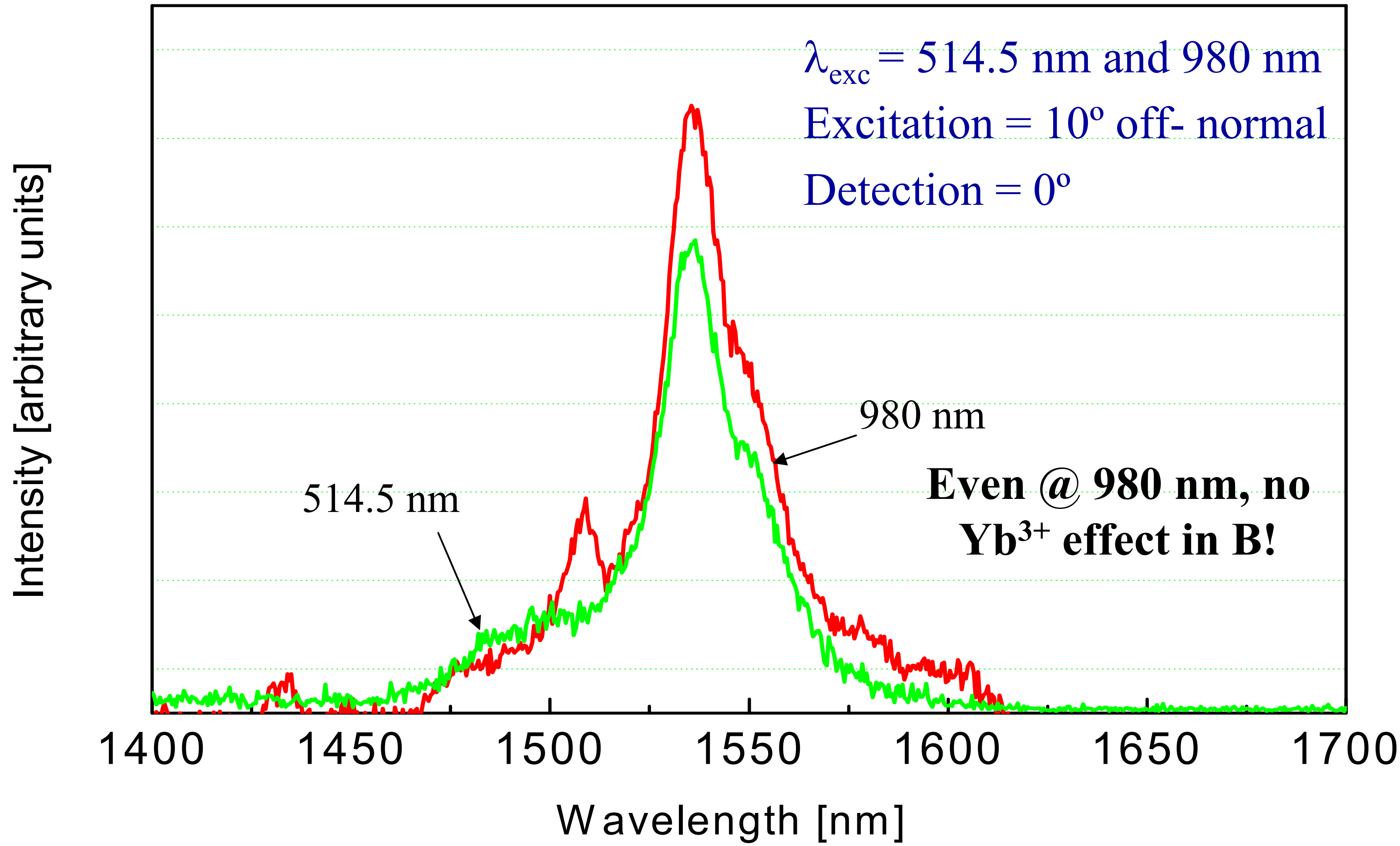
Comparison of Er^{3+} photoluminescence spectra of coupled microcavities A, B and C, excited at 980 nm (TE).

PL of A (excited @ 514.5 nm and 980 nm)



Comparison of Er^{3+} photoluminescence spectra of coupled **microcavity A**, excited at 514.5 nm and 980 nm (TE).

PL of B (excited @ 514.5 nm and 980 nm)



Comparison of Er^{3+} photoluminescence spectra of coupled **microcavity** B, excited at 514.5 nm and 980 nm (TE).

Conclusions:

- 1-D single and coupled Fabry-Perot microcavities can be prepared by sol-gel processing, with Q factors up to 35, using silica and (anatase) titania alternating layers.

- The silica cavity (defect) layers can be doped with Er^{3+} and / or Yb^{3+} ions.

- **The presence of Er in both cavity layers of coupled microcavities led to an increase of the PL signal width and intensity** , compared to Er present only in one of the cavities (after correcting for the total Er concentration).

- **A significant sensitizing ("antenna") effect was observed, when exciting Er^{3+} with 980 nm light in the presence of Yb^{3+}, as long as the two types of ions were present simultaneously in the same cavity**.

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