Glass in energy

Glasses

for white light generation

MAT 498

Lehigh University

International Materials Institute for New Functionality in Glass

Lighting:

present situation

Roughly ~ 15 % of all electric energy consumed in the world is used for lighting (~ 22% in the US).

Conventional illumination, by means of incandescent light bulbs (W filament), is very inefficient since approximately 90% of the energy consumed is emitted as heat through the Joule effect, as an electrical current passes through a W filament. In addition, the average expected lifetime of a typical bulb is only of the order of 1 year.

Tungsten-halogen lamps, filled with a special halogen gas, are slightly more efficient, with energy savings of up to ~ 25%, also burn hotter and may increase the need for air conditioning.

In fluorescent lamps, on the other hand, a stream of electrons (produced by an electrical discharge in the fluorescent tube) excites Hg vapor atoms that emit ultra-violet light, which in turn excites a phosphor coating the inside of the tube to emit visible white light by means of *fluorescence.*

A fluorescent bulb produces less heat than normal light bulbs, so they can be four to six times more efficient. That's why a 15 W fluorescent bulb can produce the same amount of light as a 60 W incandescent bulb, for example. Although the compact fluorescent lamps (CFLs) are more efficient than traditional light bulbs, their light tone is not “warm” enough, which makes their light unpleasant to the human eye and they include toxic elements like Hg. Their lifetime is also limited.

Therefore, there is a need for alternatives to both the incandescent light bulbs and the CFLs.

For white light generation (WLG), the main approaches that have appeared as alternatives to the incandescent light bulbs so far, some of which include the use of glass in the active element (and not just as a housing or window) are:

A) Conversion of light into light (or PL), using glasses, or ceramic phosphors**:**

1) Typically, rare-earth (RE)-doped oxy-fluoride glasses and glass-ceramics (GCs) with low maximum phonon energies are used for up-conversion photoluminescence (PL), or down-conversion PL. Some examples are the works of Liu and Heo (2007) and P. Babu (2011), using melt quenched glasses, or by J. del-Castillo et al. using sol-gel (2009), all employing optical pumping (laser).

2) Different ceramic phosphors separately generate red, green and blue light components, which are then combined together for WLG (e.g. fluorescent light tube).

B) Conversion of electricity into light (the **White LED** approach):

3) Different LEDs (**L**ight **E**mitting **D**iodes) separately generate red, green and blue light components which are then mixed together for WLG.

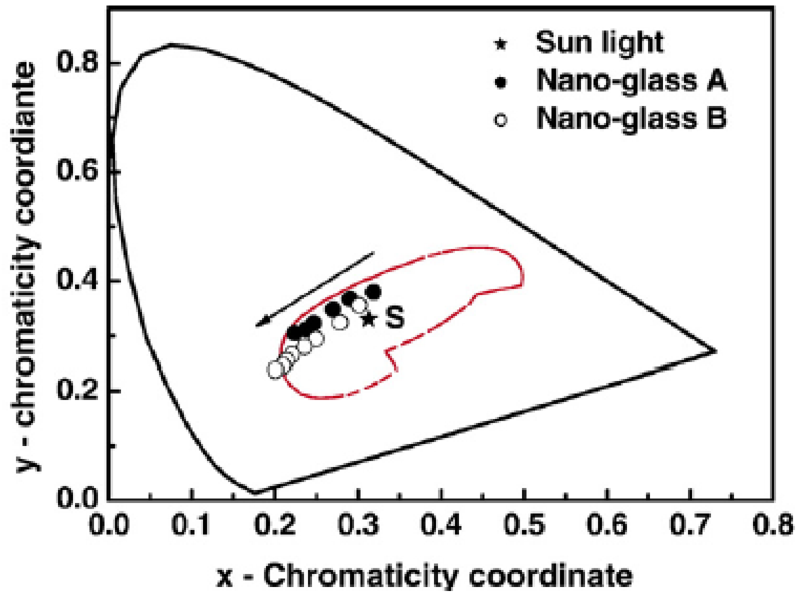
4) The light from a yellow phosphor like Ce^{3+}-YAG ($Y_3Al_5O_{12}$:Ce^{3+}) is combined with that of a blue LED pump (Shuji Nakamura). This has been the most successful approach so far. These White LEDs use less power and last longer than the other light sources (although they cost more) and they reduce energy use by up to 80%, such that a 12.5W LED can replace a 60 W incandescent bulb. Although no glass is involved in these white LEDs, phosphor–**glass** composites may be used in the future, as proposed by S. Yi and J.Heo. YAG-**Glass** Ceramic phosphors have also been proposed by S. Tanabe and co-workers.

The main approaches involving glasses are 1) and 4).

1) RE-doped oxy-fluoride glasses and glass-ceramics

It is worth mentioning the works of Liu and Heo (2007), P. Babu et al. (2011) and del-Castillo et al. (2009).

C. Liu and J. Heo (2007): generation of white light was achieved through simultaneous blue, green and red up-converted emissions by laser pumping at 900 nm, in oxy-fluoride nano GCs containing PbF_2 nanocrystals, doped with Ho, Tm and Yb. The host glass A, 30 SiO_2–15 GeO_2–15 $AlO_{1.5}$–3 TiO_2–5 YF_3–32 PbF_2 (in mol%), was prepared by melt quenching. RE fluoride dopants had molar concentrations of 0.2 TmF_3, 0.2 HoF_3 and 2.25 YbF_3.



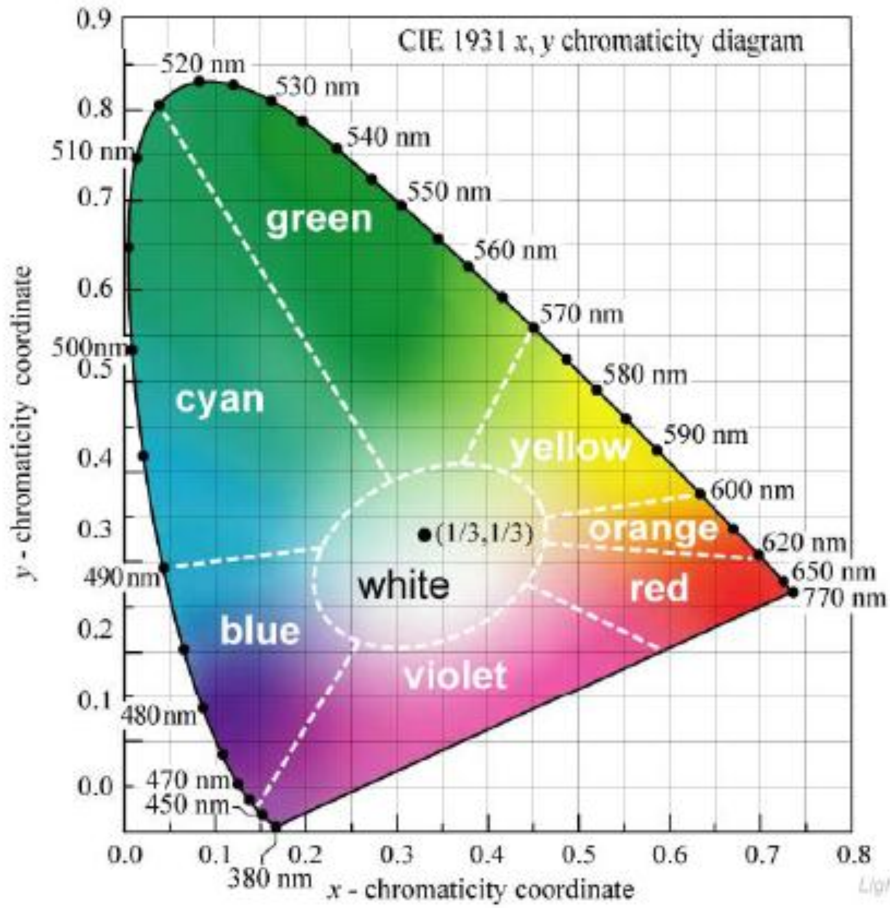
The position of white light emission from nano-glasses in the chromaticity diagram (CIE 1931) recorded at different pump powers. The area inside the dashed line shows the white light region, and the arrow indicates an increase in the pump power.

Adapted from: Chao Liu and Jong Heo, Mater. Lett. 61 (2007) 3751.

Key issue: a low phonon energy matrix is needed, such as fluoride nano-crystals.

The CIE Chromaticity diagram

CIE = COMMISSION INTERNATIONALE DE L'ECLAIRAGE
= INTERNATIONAL COMMISSION ON ILLUMINATION

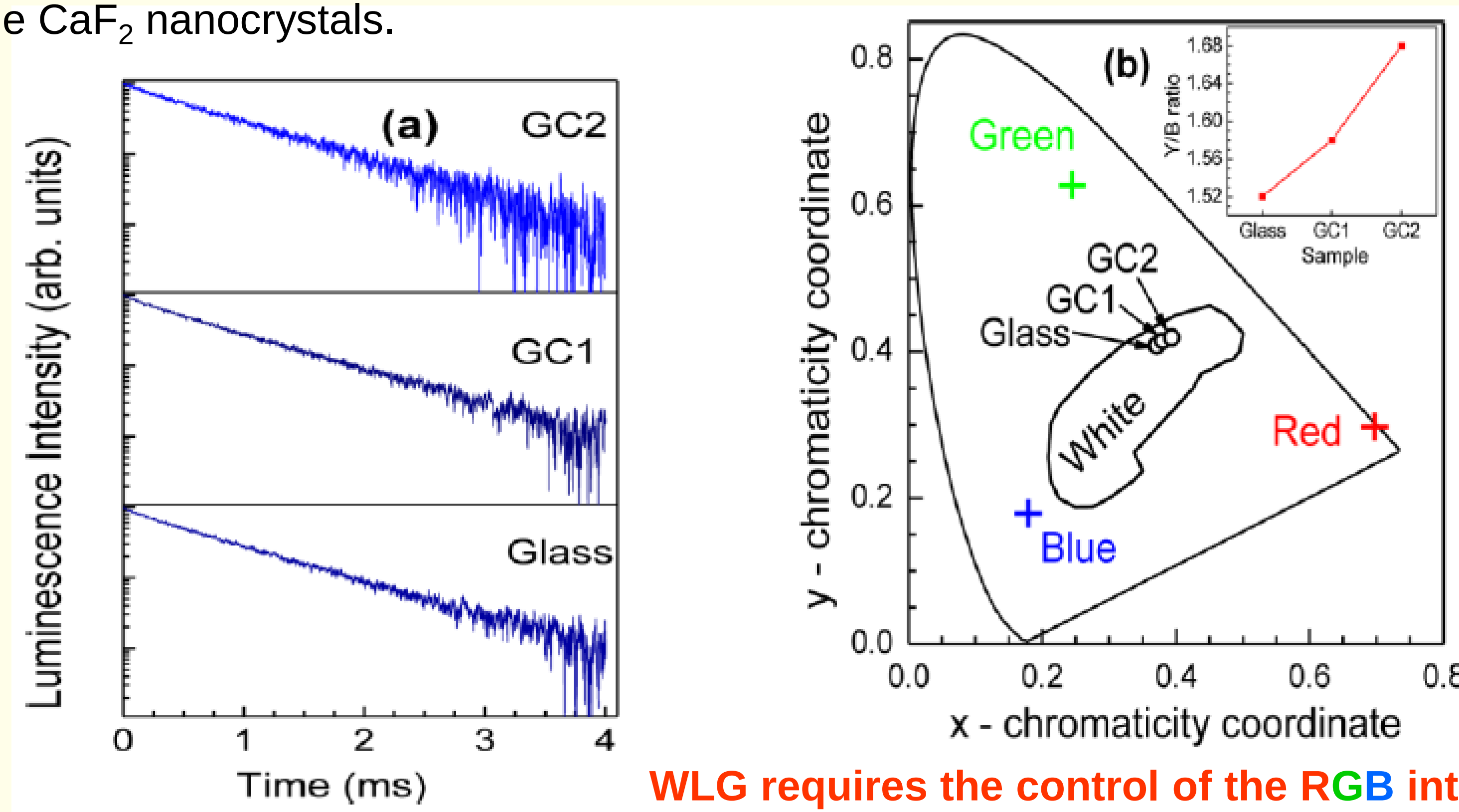


CIE 1931 (x, y) chromaticity diagram. Monochromatic colors are located on the perimeter. Color saturation decreases towards the center of the diagram. White light is located in the center. Also shown are the regions of distinct colors. The equal-energy point is located at the center and has the coordinates (x, y) = (1/3, 1/3).

Adapted from: http://bp.snu.ac.kr/Lecture/Energy_Materials/2-2-White%20LED(76)-101103.pdf (on 12 Jan 2012)

Any color can be expressed in terms of the two color coordinates x and y. The colors which can be obtained by combining a given set of three **primary colors** (such as blue, green and red) are represented on the chromaticity diagram by a triangle joining the coordinates for the three colors.

P. Babu et al. (2011): tried to achieve WLG by down-conversion in Dy^{3+}-doped oxyfluoride glass and transparent GCs containing CaF_2 nanocrystals, prepared by melt quenching. Special interest in Dy^{3+} visible luminescence is due to the existence of two intense bands in the **blue** and **yellow** regions that, combined, yield white light. The precursor glass composition was 45 SiO_2-20 Al_2O_3-10 CaO-24.9 CaF_2-0.1 DyF_3 (in mol%) and laser excitation was done at 451 nm. The Dy^{3+} ions were incorporated into the CaF_2 nanocrystals.



WLG requires the control of the RGB intensities!

(a) Luminescence decay curves of 0.1 mol % of Dy^{3+}:glass, GC1 and GC2 and (b) The CIE-1931 chromaticity color diagram showing the white light emission from the 0.1 mol % of Dy^{3+}:glass, GC1 and GC2. Inset shows the variation of Y/B with heat treatment temperature.

Adapted from: P. Babu et al., OPTICS EXPRESS Vol. 19 (2011) 1863.

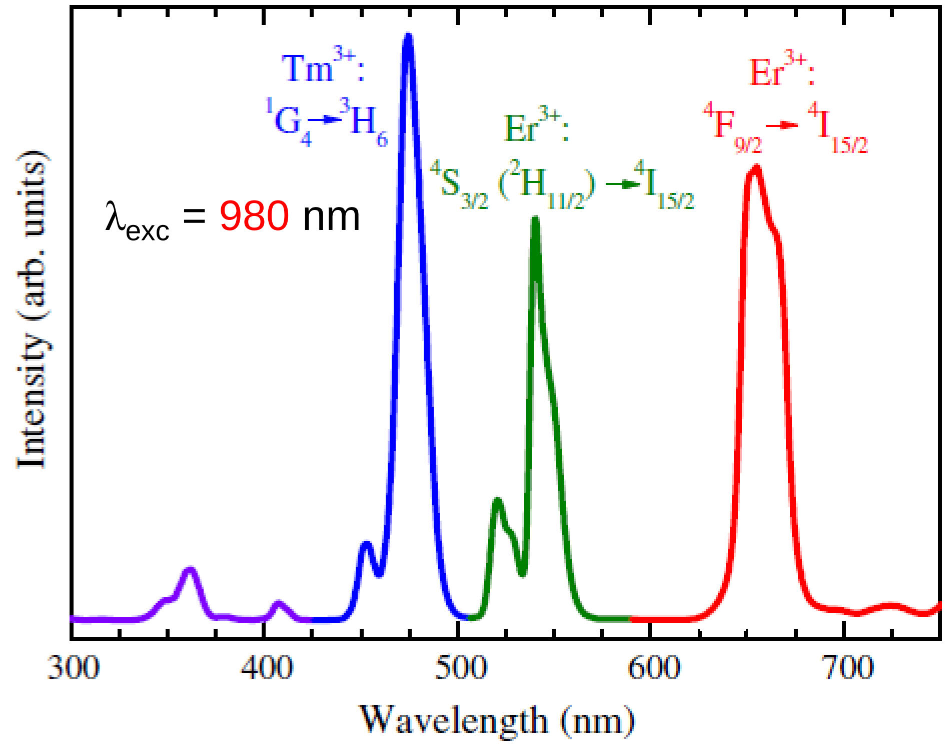
Other examples involving also melt-quenched glasses were:

R. Martinez-Martinez et al.: WLG through zinc metaphosphate glass activated by Ce^{3+}, Tb^{3+} and Mn^{2+} ions , J. Lumin. 129 (2009) 1276.

Here the RE ion down-conversion PL was investigated in $Zn(PO_3)_2$ glass. The blue and green emissions of Tb^{3+} ions and the red emission of Mn^{2+} ions were enhanced upon UV excitation through a non-radiative energy transfer from Ce^{3+}, to Tb^{3+} and Mn^{2+} ions. It was demonstrated that this glass activated with those three ions can generate white light emission under excitation at 254 nm, using an AlGaN-based LED for pumping.

Giri et al.: “White Light Up-conversion Emissions from Tm^{3+} + Ho^{3+} + Yb^{3+} co-doped Tellurite and Germanate Glasses on Excitation with 798 nm Radiation, J. Appl. Phys. 104, 113107 (2008).

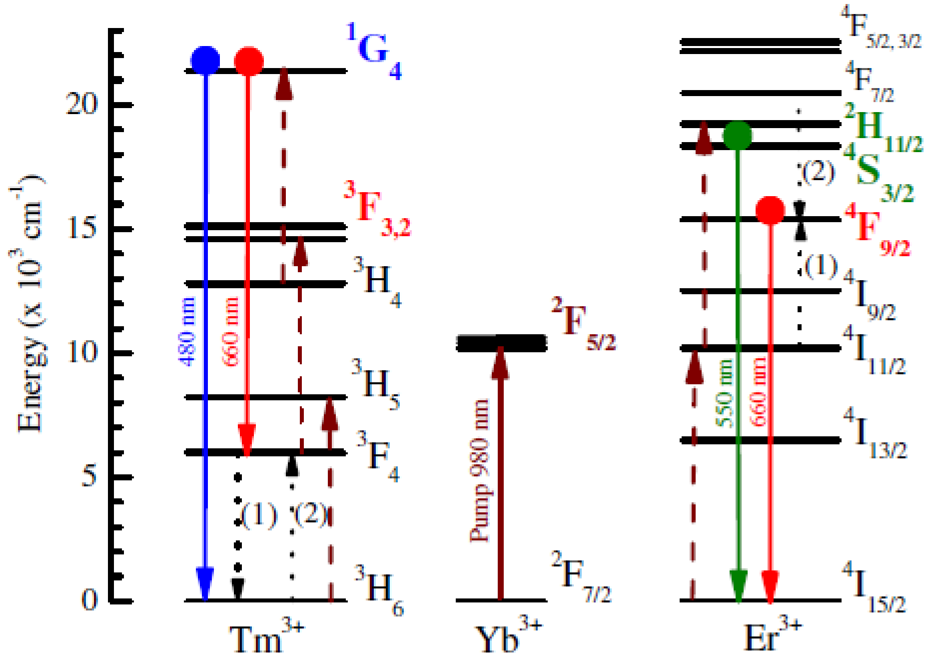
J. del-Castillo (2009): prepared low phonon energy, oxy-fluoride nano GCs doped with RE ions, for WLG by up-conversion, by sol-gel processing.



Simultaneous up-conversion emission of the three primary colours (blue, green and red) under infrared excitation at 980 nm with a power up to 200 mW of 94.5 SiO_2–5 LaF_3 tri-doped with 0.3 mol% Yb^{3+}, 0.1 mol% Er^{3+} and 0.1 mol% Tm^{3+} sol–gel derived nano-glass–ceramics (SOL-YET). Assignation of emission bands with corresponding transitions of rare-earth ions is indicated

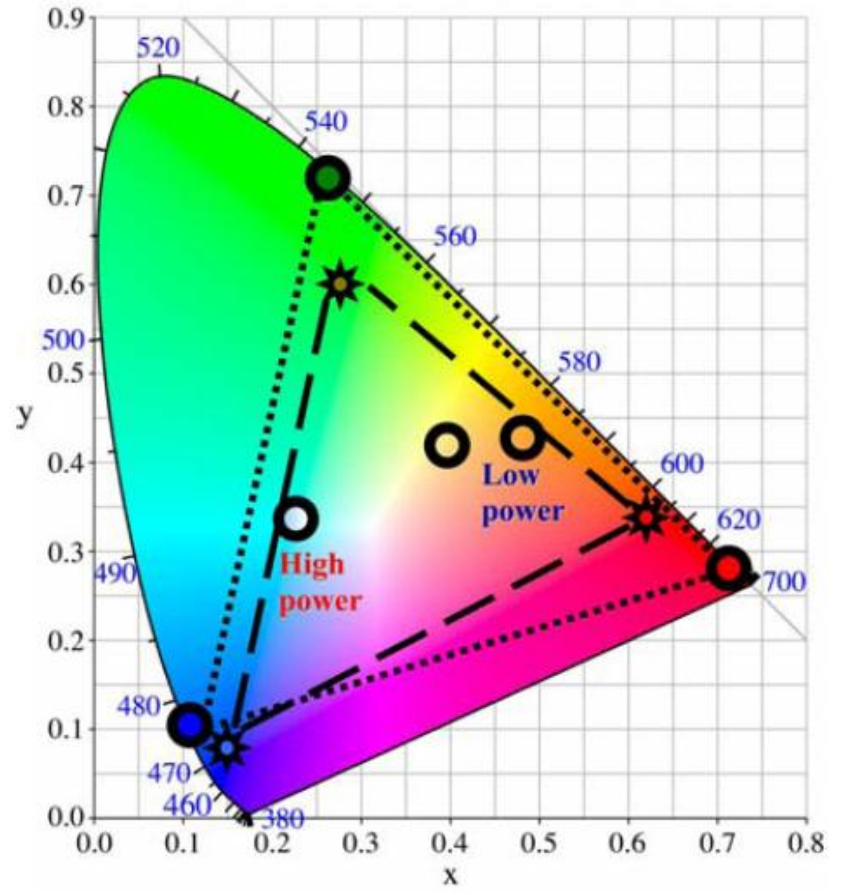
Adapted from: J. del-Castillo et al., J. Nanopart. Res. (2009) 11:879–884.

4f → 4f transitions



Energy level diagram of the Er^{3+}, Yb^{3+} and Tm^{3+} co-dopants. Solid arrows indicate pump and up-conversion emission transitions. Dash lines indicate 2- and 3-photon up-conversion processes. Dot lines labelled with (1) and (2) indicate energy transfer processes among Er^{3+} and Tm^{3+} ions responsible of the enhancement of the red emission

Adapted from: J. del-Castillo et al., J. Nanopart. Res. (2009) 11:879–884.



Comission Internationale d'Eclairage (CIE) coordinates of 94.5 SiO_2–5 LaF_3 doped with 0.3 mol% of Yb^{3+}, 0.1 mol% of Er^{3+} and 0.1 mol% of Tm^{3+} nano-glass–ceramic (SOL-YET) under excitation at 980 nm for different power intensities, from high power (200 mW) to low power (5 mW). Internal dotted triangle shows the wide colour gamut covered by the emission of sample. A comparison with gamut generated by commercial Dell monitor phosphor (P22) is included (dashed line triangle)

Adapted from: J. del-Castillo et al., J. Nanopart. Res. (2009) 11:879–884.

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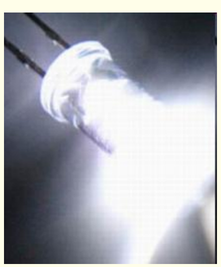
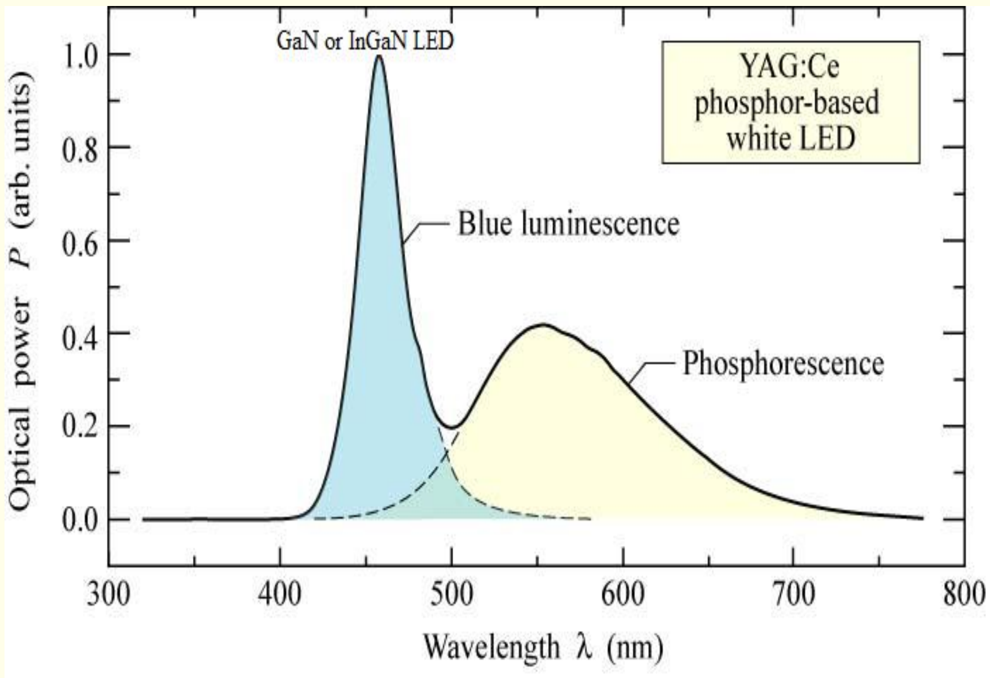
4) White LED:

- Fluorescent or **white LED** lamps are important for energy savings in lighting.
- **White LED**: high energy efficiency, very long lifetime, environmentally friendly…



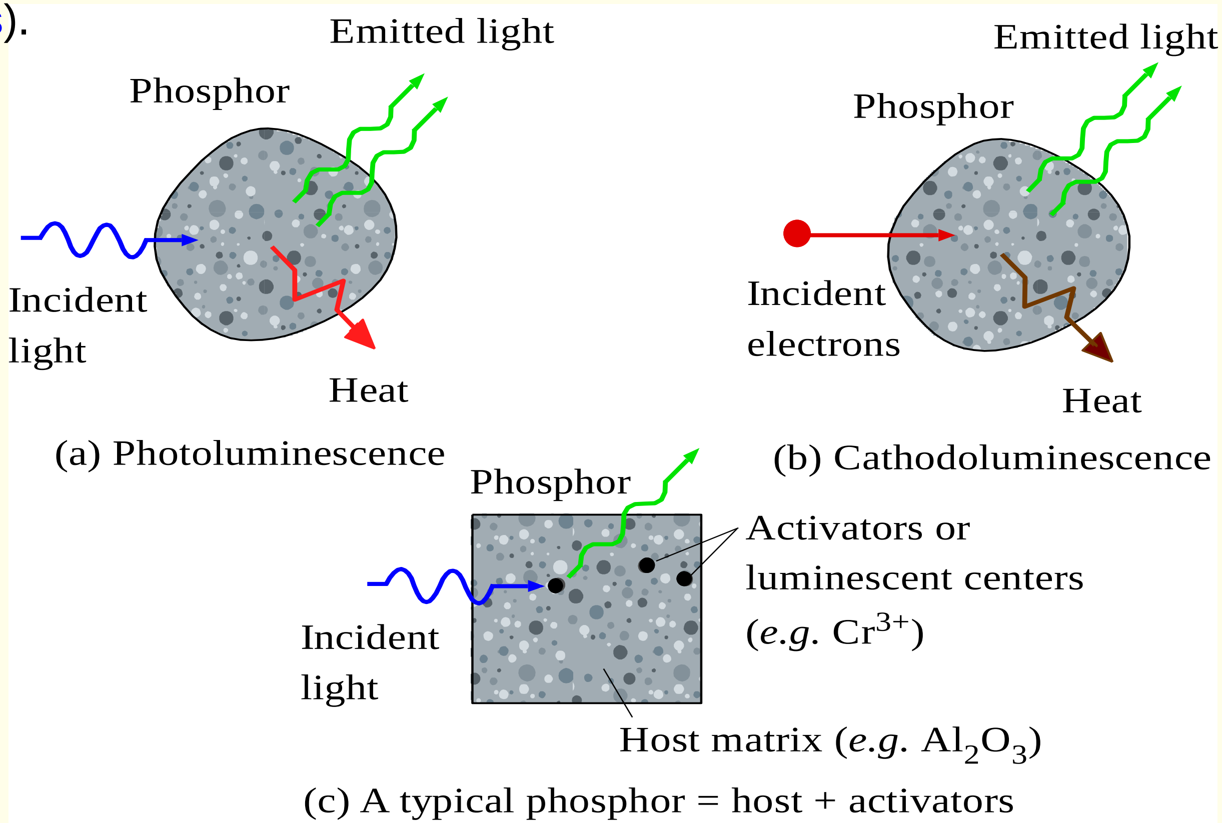


Ce:YAG: blue-excited white LED

5d → 4f transitions

Photoluminescence (PL) of phosphors

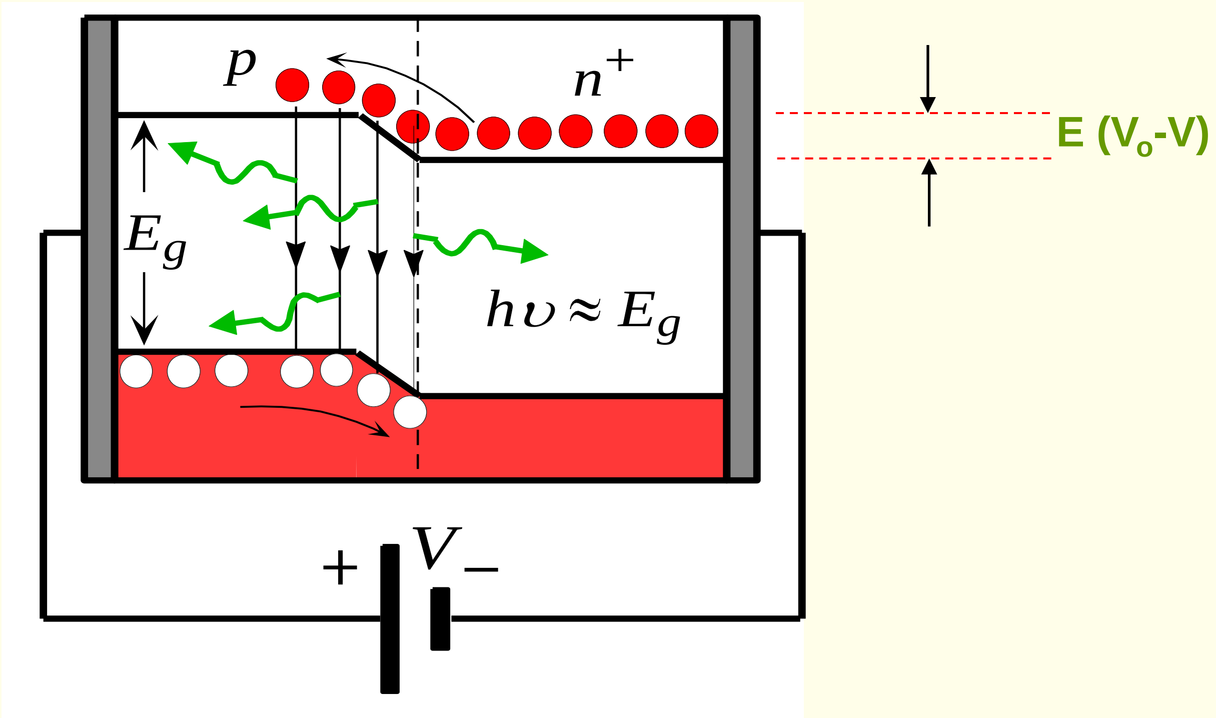
Luminescence is the emission of light by a material (called a *phosphor*), due to the absorption and conversion of energy into EM radiation of lower energy (**Stokes law**), typically visible or near IR light (the radiation emitted by the tungsten filament of a light bulb is called incandescence). **PL involves excitation by photons**, whereas **cathodoluminescence** is light emission due to bombarding of a phosphor with energetic **electrons** as in a CRT TV screen. **Electroluminescence** is light emission due to the passage of an **electric current** (as in LEDs).



Photoluminescence, cathodoluminescence and a typical phosphor

From: *Principles of Electronic Materials and Devices*, *Third Edition*, S.O. Kasap (© McGraw-Hill, 2005)

LED's



A **LED** is **a p-n junction diode** made from a **direct bandgap SC**, e.g. GaAs, in which electron-hole pair (EHP) recombination results in emission of a photon of energy hν ~ $\mathbf{E_G}$.

When a *forward* bias V is applied, the built-in voltage is reduced to V_o-V, allowing **electrons** from the n^+-side to diffuse and become **injected** into the p-side (figure-(b)). The ***recombination*** of electrons injected in the DR, **leads to photon emission**, designated by **injection electroluminescence**. The photons are emitted in random directions, as a result of ***spontaneous emission***.

From: *Principles of Electronic Materials and Devices*, *Third Edition*, S.O. Kasap (© McGraw-Hill, 2005)

The emission of light from a fluorescent tube is a *fluorescence* process where Ar and Hg gas atoms become excited by an electrical discharge and emit mainly UV light, which is absorbed by the fluorescent coating on the inside of the tube, emitting visible radiation. A number of different *phosphors* are used, in order to obtain "white" light from the tube (approach 2, slide #3). Also Red, blue and green LEDs based on indium gallium nitride (approach 3, slide #3) can outperform incandescent bulbs by reducing energy consumption by a factor of ten and enhancing lifetime 10 to 50 times over the standard incandescent bulb, which typically lasts one year.

RGB :

A combination of Red, Green and Blue phosphors or LEDs can generate white light.

WLG requires the control of the RGB intensities!

This flash light uses a white LED instead of an incandescent light bulb. The flash light can operate continuously for 200 hours and can project an intense spot over 30 feet.

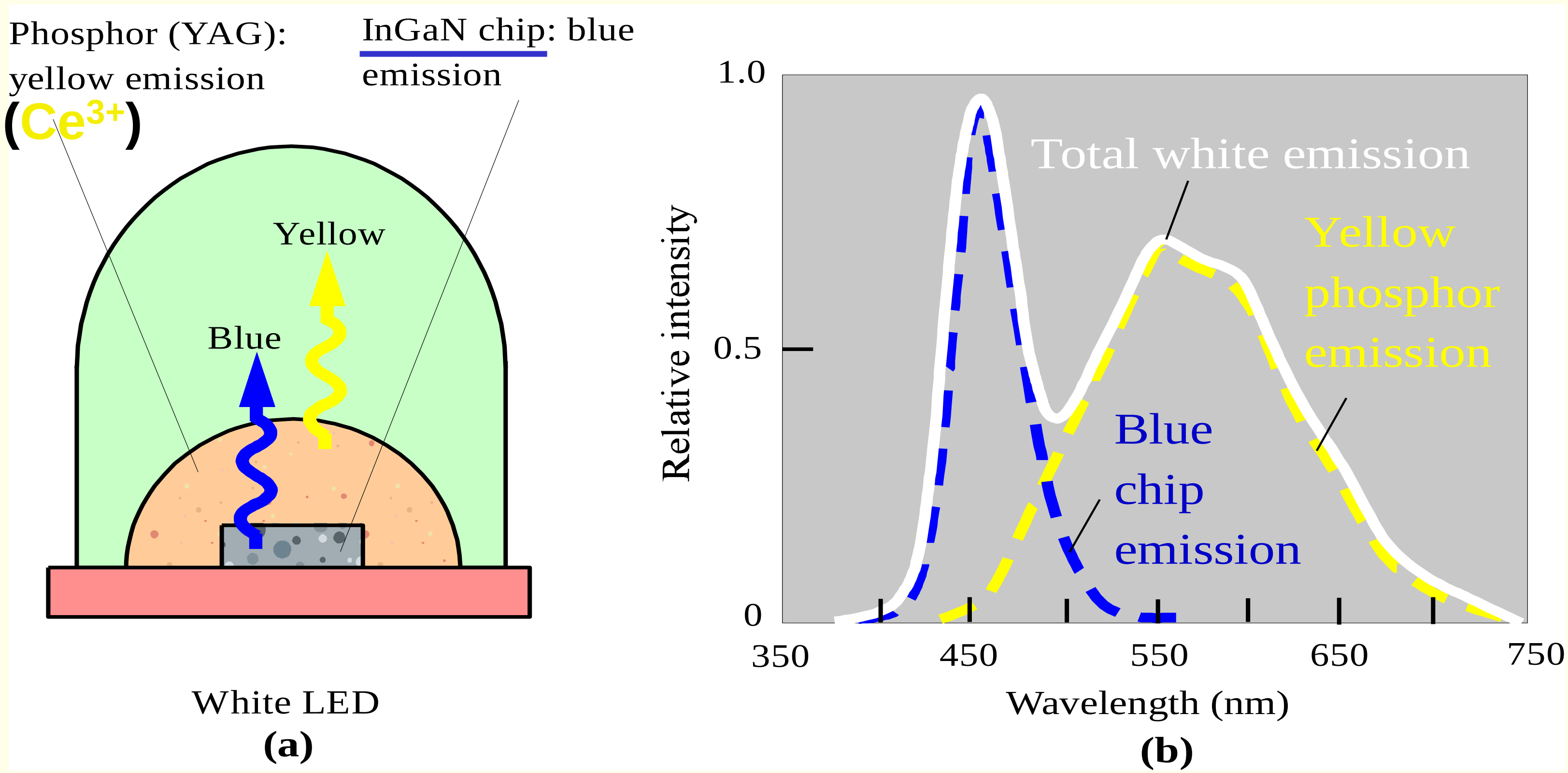
From: *Principles of Electronic Materials and Devices*, *Third Edition*, S.O. Kasap (© McGraw-Hill, 2005)

4) White LED approach: Mixing of the light emitted from a **yellow** phosphor like Ce^{3+}-YAG ($Y_3Al_5O_{12}$:Ce^{3+}) with that of a blue LED pump (Nakamura).

S. Nakamura, the inventor of the blue, green and white LED (~ 1996) and of the blue laser, had an impressive career as a researcher at Nichia Chemical Industries in Tokushima, Japan, before accepting an appointment to the College of Engineering at UC Santa Barbara. In approach 4 (slide #3), **white light LED's** have been developed, using a phosphor to generate **yellow** light when excited by the blue light emitted by a LED SC chip; the mixture of **blue** and **yellow** lights (complementary colors) appears **white.**

White LEDs are twice as bright as incandescent bulbs and will help preserve natural resources due to the use of non-toxic materials and to efficiency gains of InGaN-based LEDs.

White light LED structure



(a) A typical "white" LED structure. (b) The spectral distribution of light emitted by a white LED. Blue luminescence is emitted by the GaInN chip and "yellow" phosphorescence or luminescence is produced by a phosphor. The combined spectrum looks "white".

From: *Principles of Electronic Materials and Devices*, *Third Edition*, S.O. Kasap (© McGraw-Hill, 2005)

One disadvantage of YAG-based white LED as illumination source is its high color temperature (CT), typically higher than 6000 K; only "cool white" can be obtained. In order to decrease the CT of a white light source and to obtain "warm white" (the CT of a typical W light bulb is ~ 3,000 K), it is necessary to move the color coordinates to the right-hand side of the chromaticity diagram by increasing the intensity of the red component and decreasing that of the blue one. This can be achieved by increasing the powder content of YAG phosphor in typical YAG-based white LED packages.

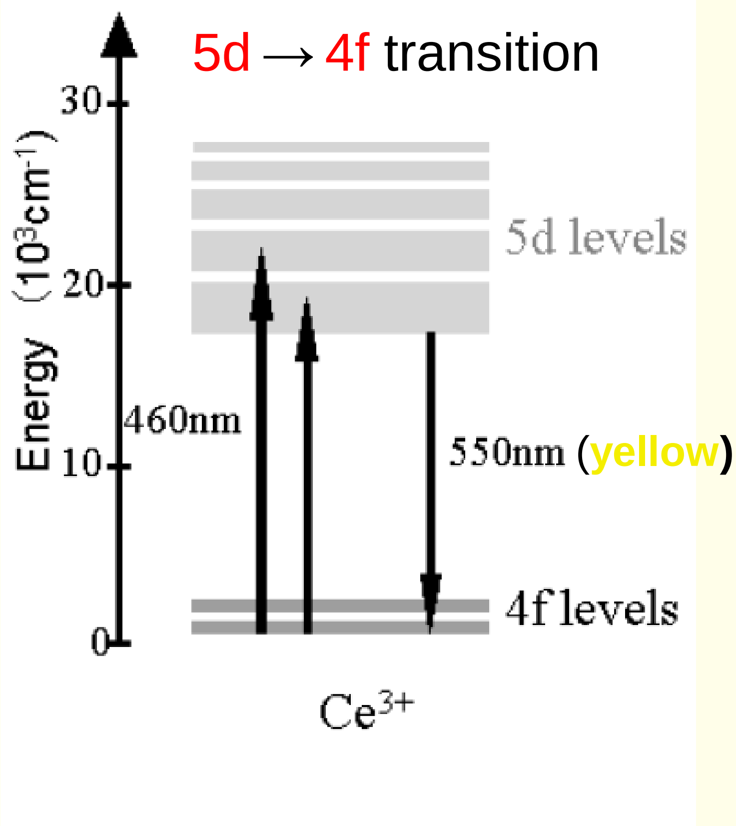
In the paper "**Phosphor-Glass Composites for White Light Generation from Blue LEDs**", presented at the 19th University Conference on Glass Science at RPI, Troy (NY), Aug. 3-5, 2011, by Seungryeol Yi*, Jong Heo, the possible use of phosphor-glass composites in the most common mode of white LED, the combination of blue LED and yellow phosphor pastes, has been proposed.

Since the polymer resin used for the phosphor paste is severely oxidized due to the high temperature and UV radiation during the operation, which adversely affects the optical properties of phosphors and since the efficiency of light extraction from blue LEDs and phosphors is also affected due to the low refractive index of the resin, attempts have been made to replace the resin with glass frits by dispersing the phosphor powder in glasses.

Commercial YAG:Ce^{3+} phosphor was mixed with glass frits of several different compositions and the thermal conditions for the viscous sintering of the composite materials was optimized. Optical properties of the composites were measured and chemical and optical stabilities of YAG:Ce^{3+} phosphors at the elevated temperatures were evaluated.

Ce:YAG-**Glass** ceramic phosphors have also been investigated by S. Tanabe and co-workers.

Ce^{3+}-doped glasses in the SiO_2-Al_2O_3-Y_2O_3 and SiO_2-Al_2O_3-Y_2O_3-Gd_2O_3 systems were prepared and the obtained glass was crystallized at temperatures ranging from T_x to T_x + 120 °C for a selected period of time (T_x was a typical ceramming temperature in this study).



Energy level diagram of Ce^{3+} ion.

The quantum efficiency of Ce^{3+} emission in the GC was estimated at ~ 30%, which was improved by increasing the ceramming temperature of mother glass. Red shift of the emission wavelength was observed for the samples with larger Gd_2O_3 content. The color coordinates of the composite LED were widely varied simply by changing the thickness of the GC plate. The Gd-substituted GC materials yield color coordinates closer to "warm white".

Q.

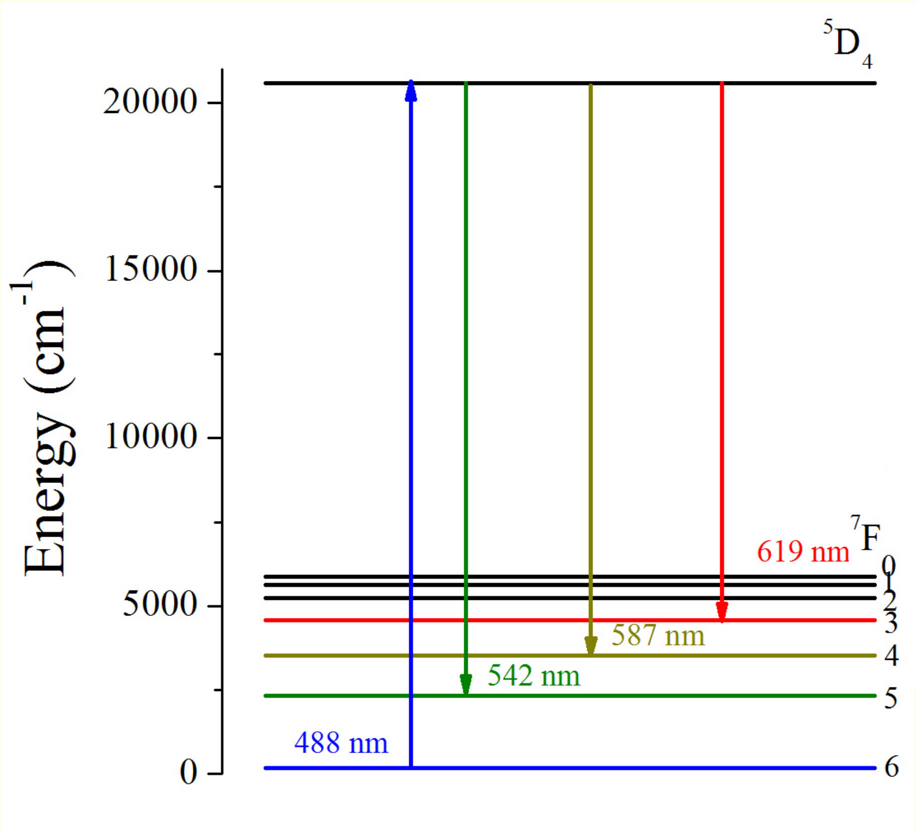
Adapted from: S. Tanabe et al., Fifth International Conference on Solid State Lighting, ed. by I.T. Ferguson et al., Proc. SPIE Vol. 5941 (2005).

Photonic crystal-assisted WLG by down-conversion

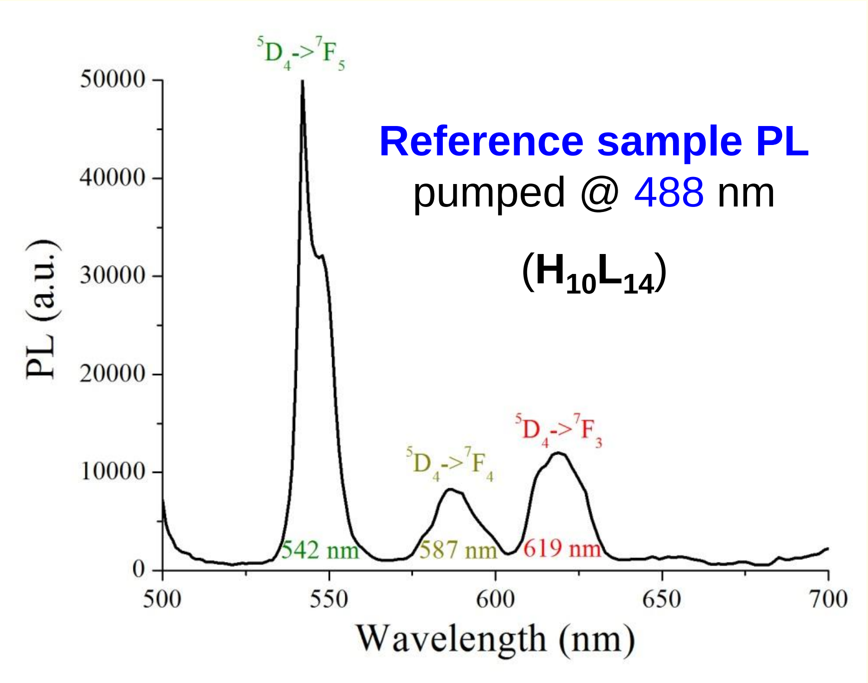
Photoluminescence from Tb-doped triple microcavity for WLG

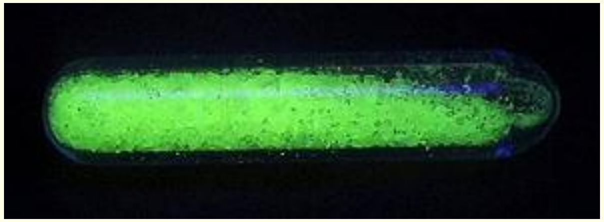
Yigang Li and Rui M. Almeida, J. Phys. D: Appl. Phys. 43 (2010) 455101.

Spontaneous PL emission from Tb^{3+}



Energy states of Tb^{3+}



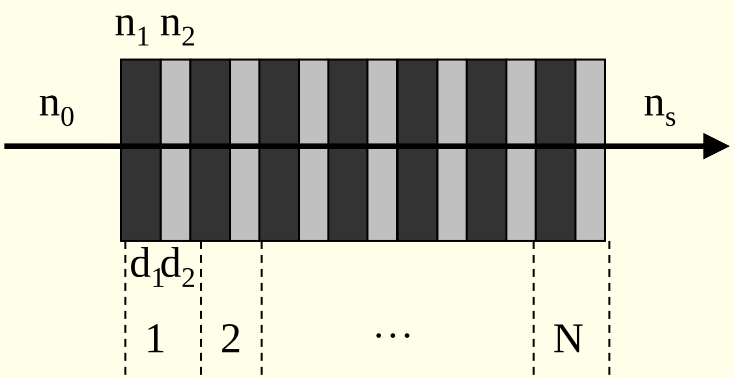


Photonic bandgap (PBG) structures may help.

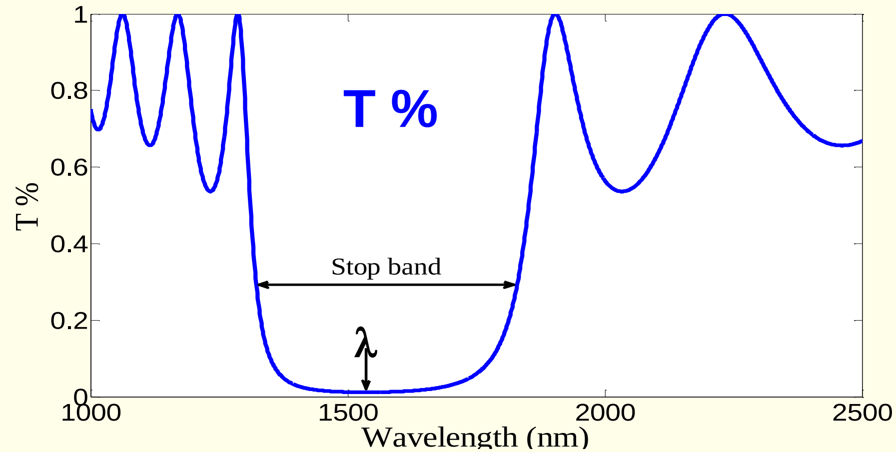
Adapted from: Yigang Li and Rui M. Almeida, J. Phys. D: Appl. Phys. 43 (2010) 455101.

Photonic crystal or Photonic Bandgap (PBG) structure

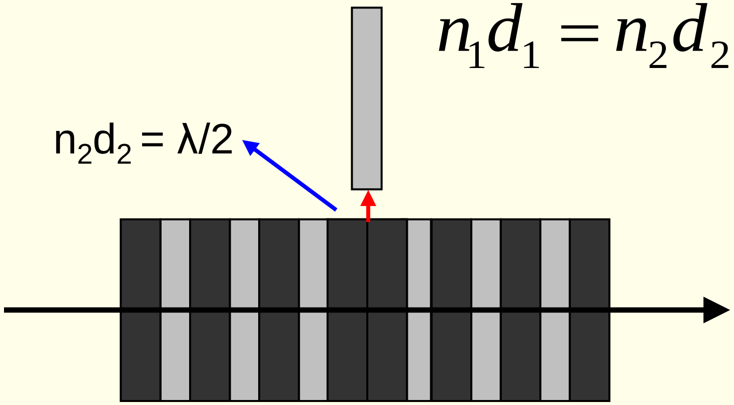
$n_1 \sim 1.44$ (Al silicate glass) $n_2 \sim 2.0$ (titania)



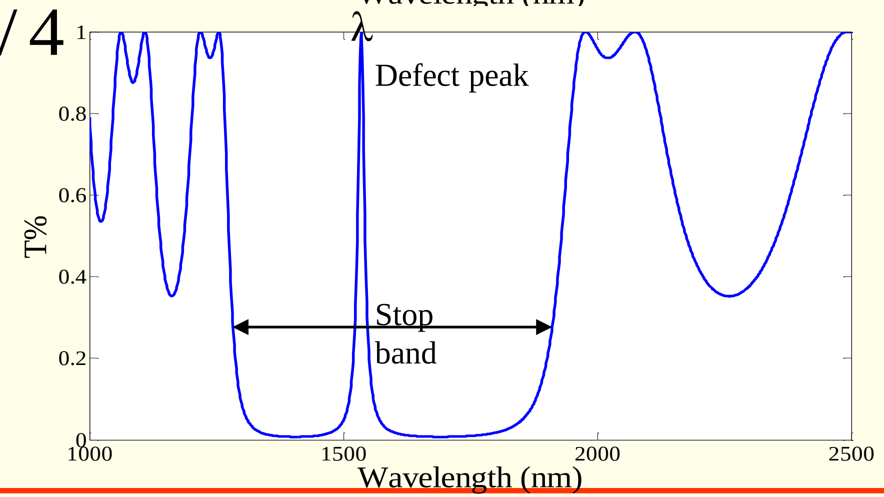
Distributed Bragg Reflector (Bragg mirror)



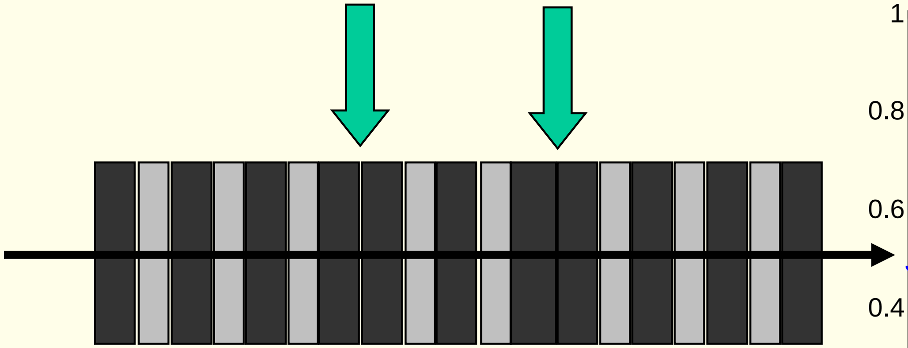
$$n_1 d_1 = n_2 d_2 = \lambda / 4$$

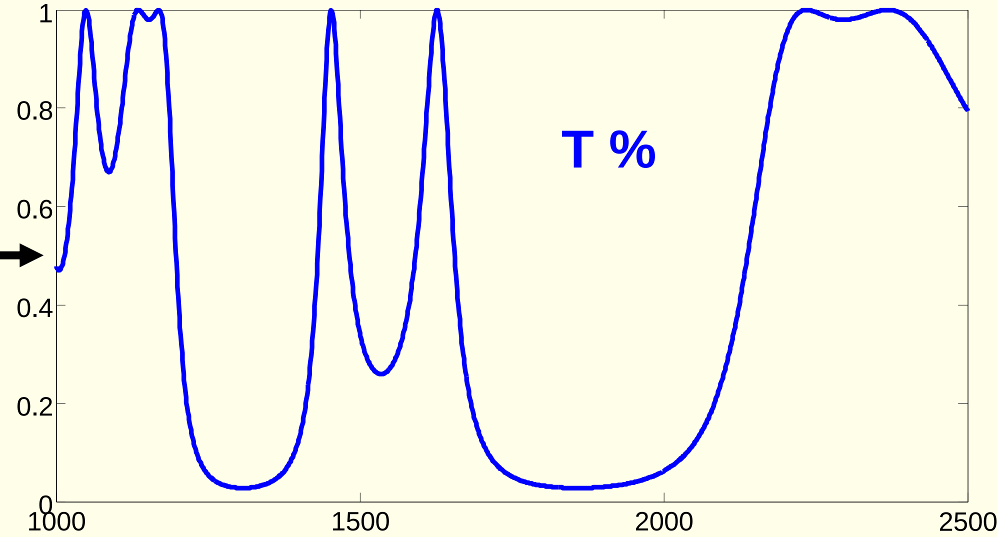


F-P microcavity

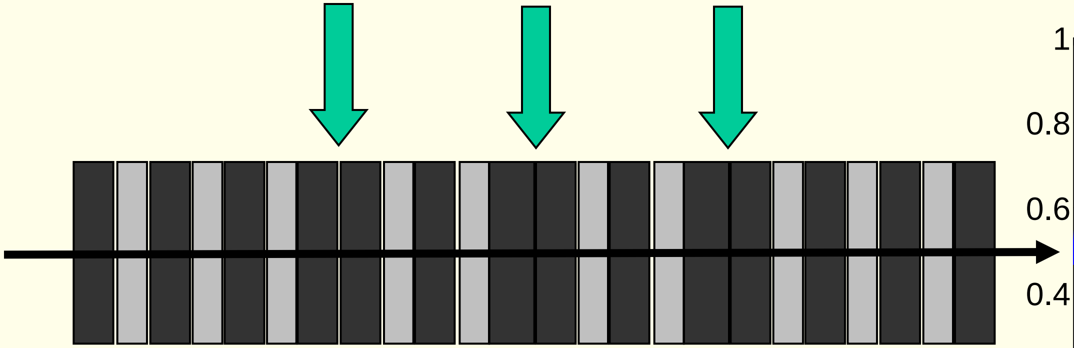


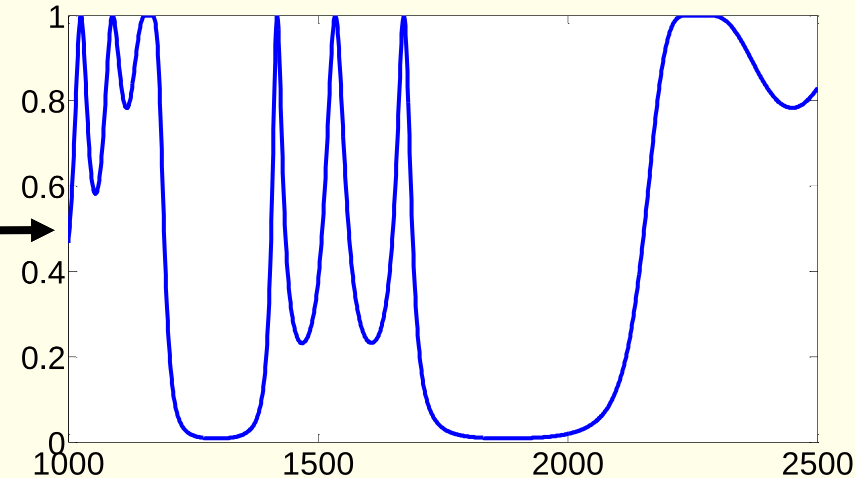
Coupled microcavity





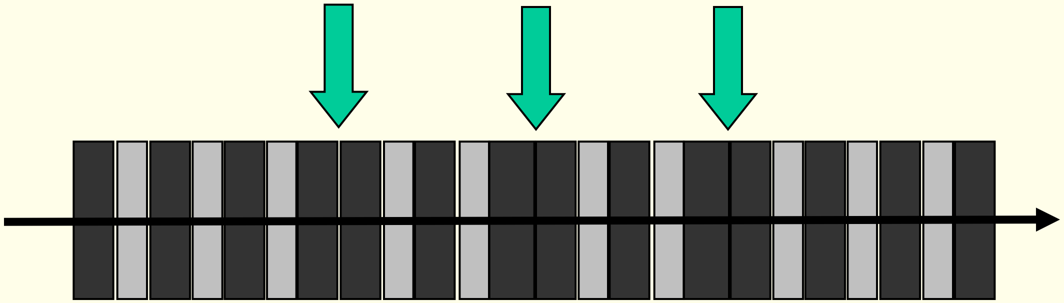
Double coupled microcavity





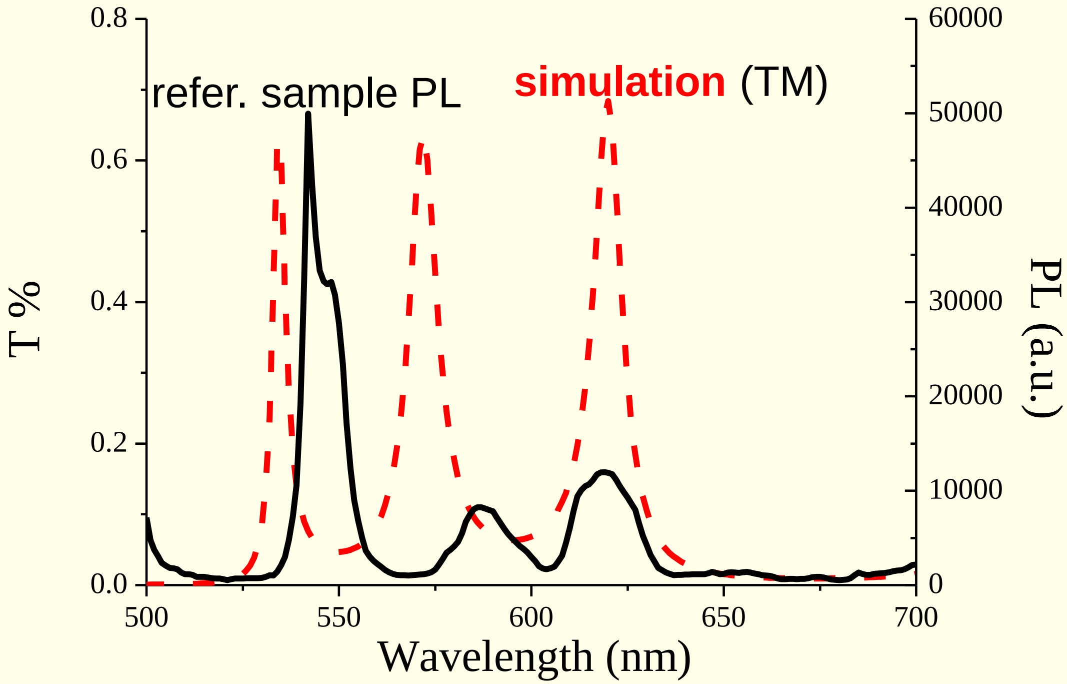
Triple coupled microcavity

Triple microcavity



$d_{silicate}$ ~ 110 nm (n = 1.44)

$d_{titania}$ ~ 50 nm (n = 2.0)

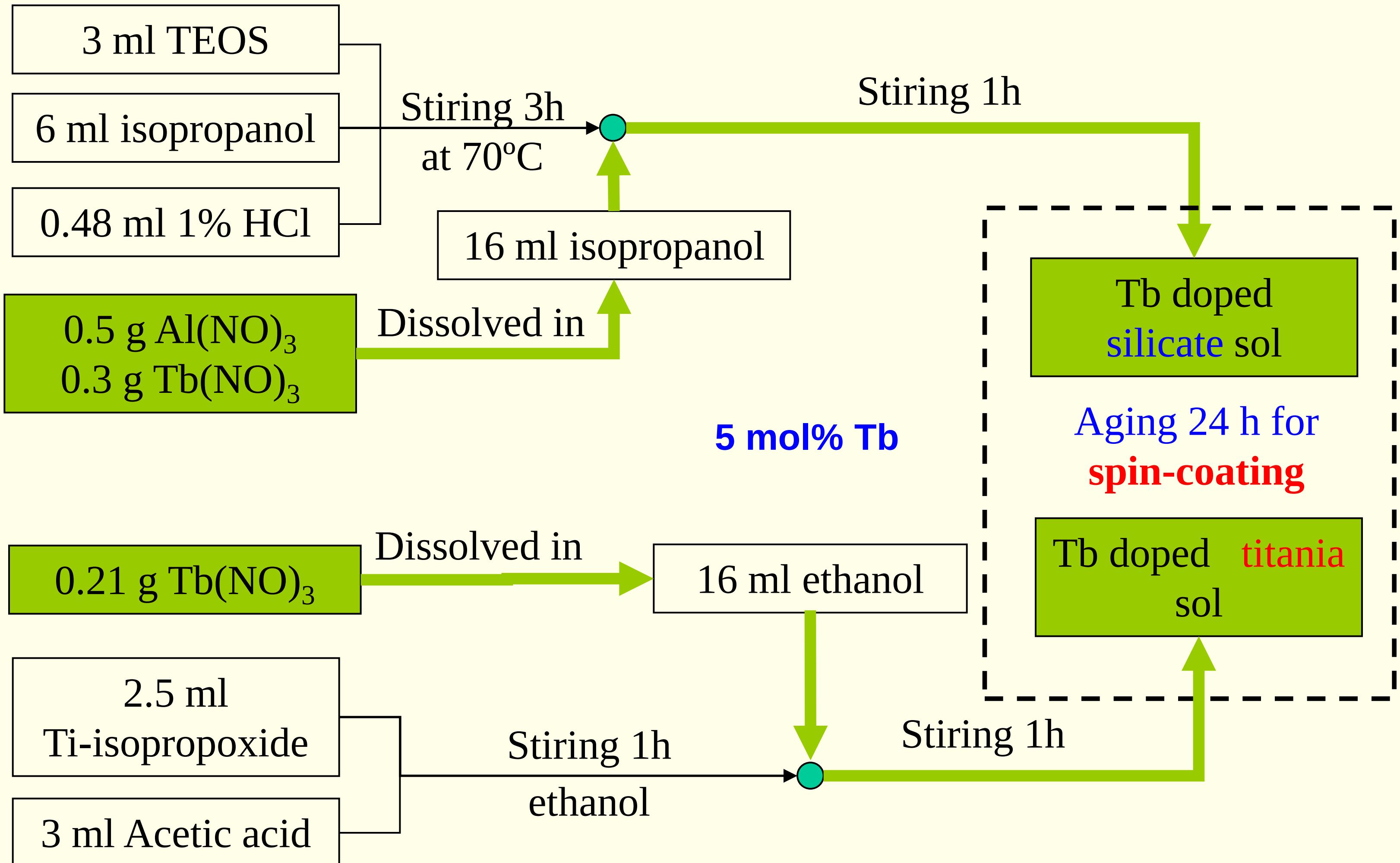


Aims:

- Broaden
- Balance
- Enhance

Q.

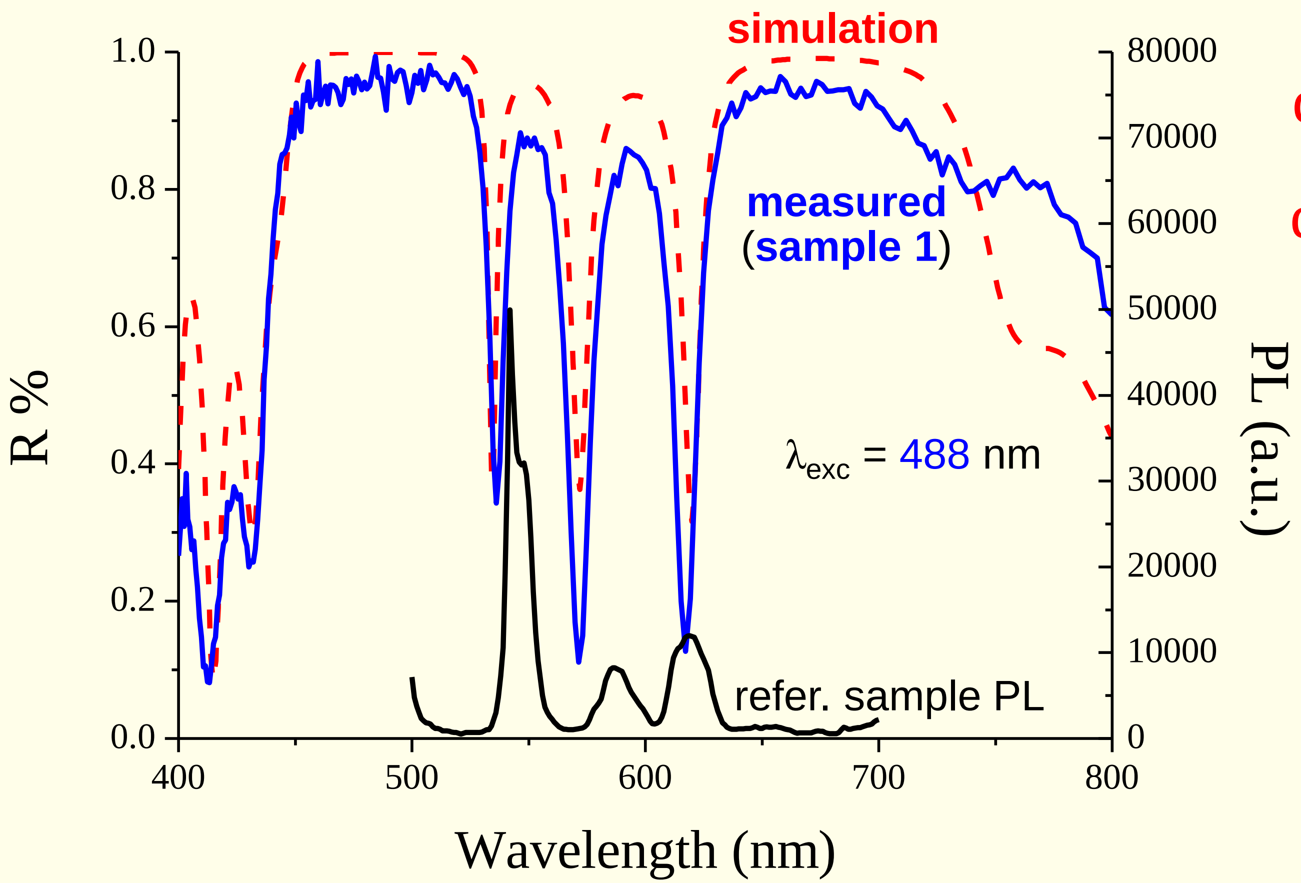
Fabrication process: sol-gel processing



Adapted from: Yigang Li, Luís M. Fortes, Andrea Chiappini, Maurizio Ferrari and Rui. M. Almeida, J. Phys. D: Appl. Phys. 42 (2009) 205104.

Reflection spectrum

Adapted from: Yigang Li and Rui M. Almeida, J. Phys. D: Appl. Phys. 43 (2010) 455101.



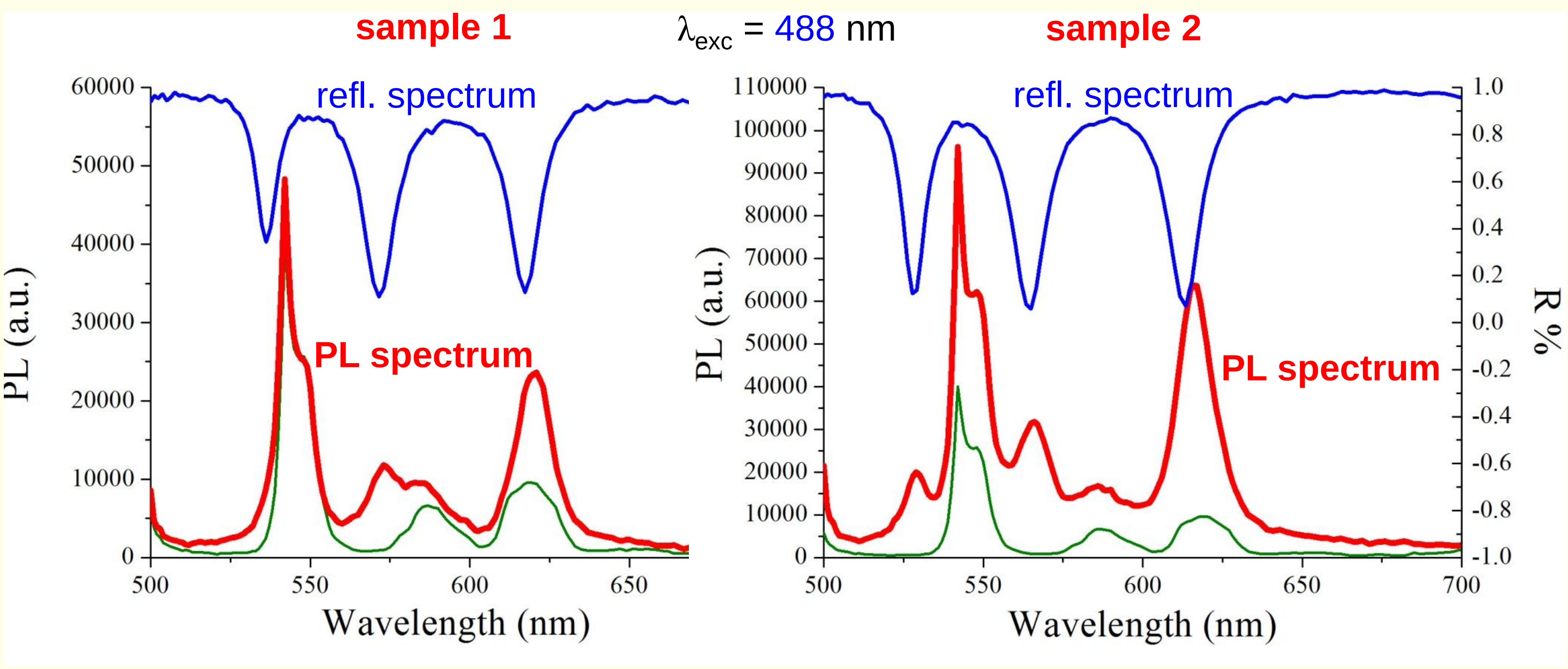
$d_{silicate}$ = 110 nm

$d_{titania}$ = 49.5 nm

$Q = \lambda/\Delta\lambda = 54$

The profile of the measured reflection spectrum coincided very well with the theoretical curve, including the stop band, the defect peaks and the fringes.

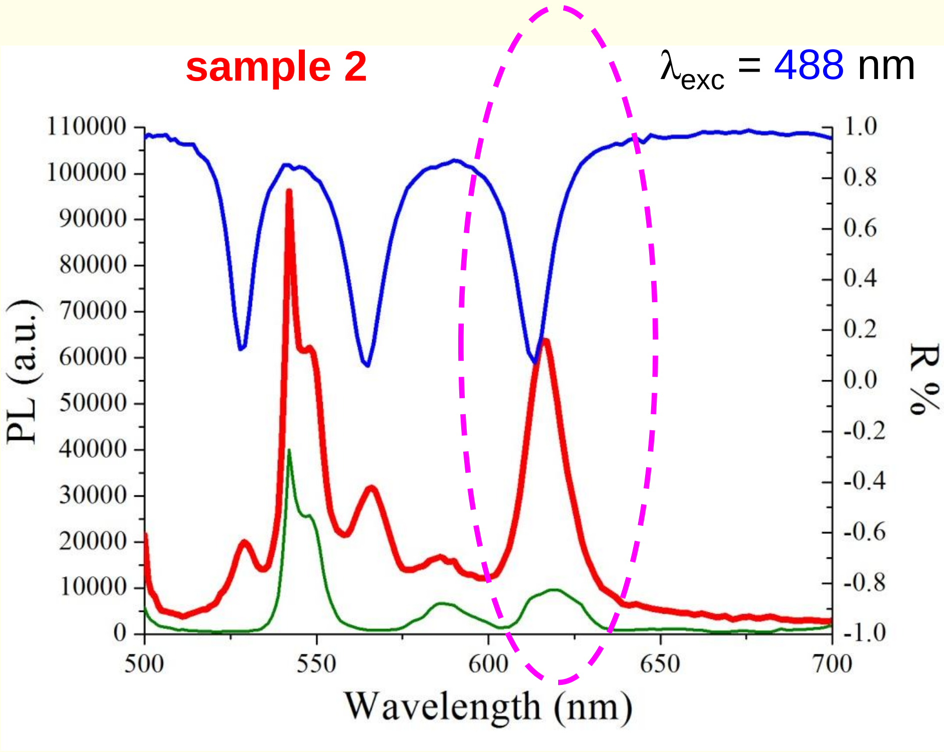
Broadened PL of two samples

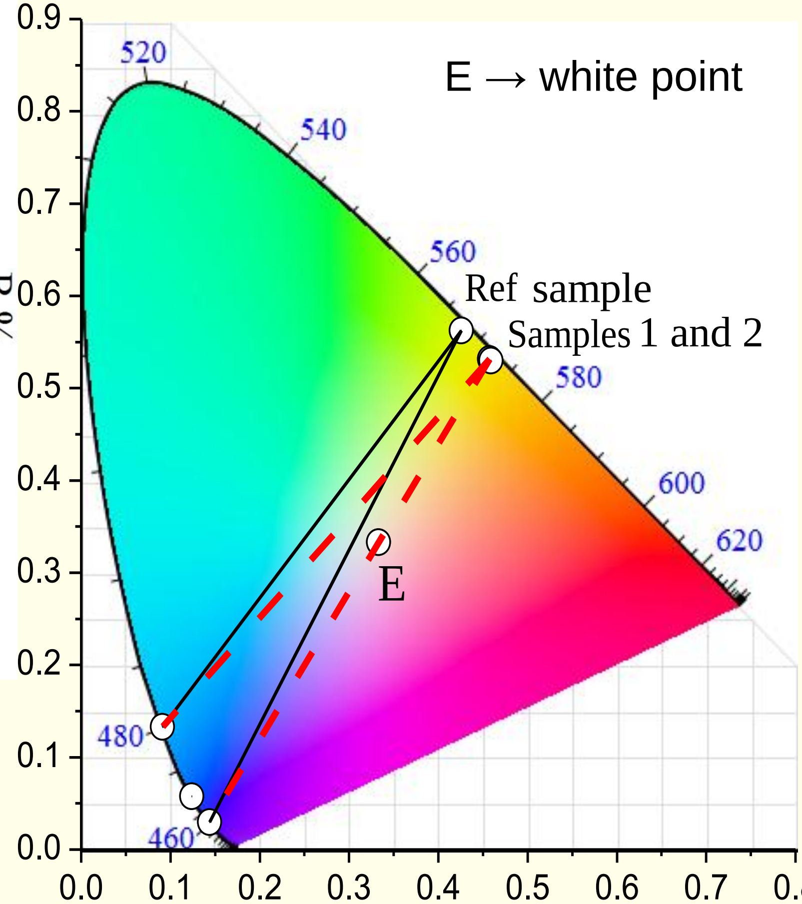


The three distinct PL peaks of Tb^{3+} ions were broadened to combine into a continuous fluorescence band.

Adapted from: Yigang Li and Rui M. Almeida, J. Phys. D: Appl. Phys. 43 (2010) 455101.

The balance between green and red



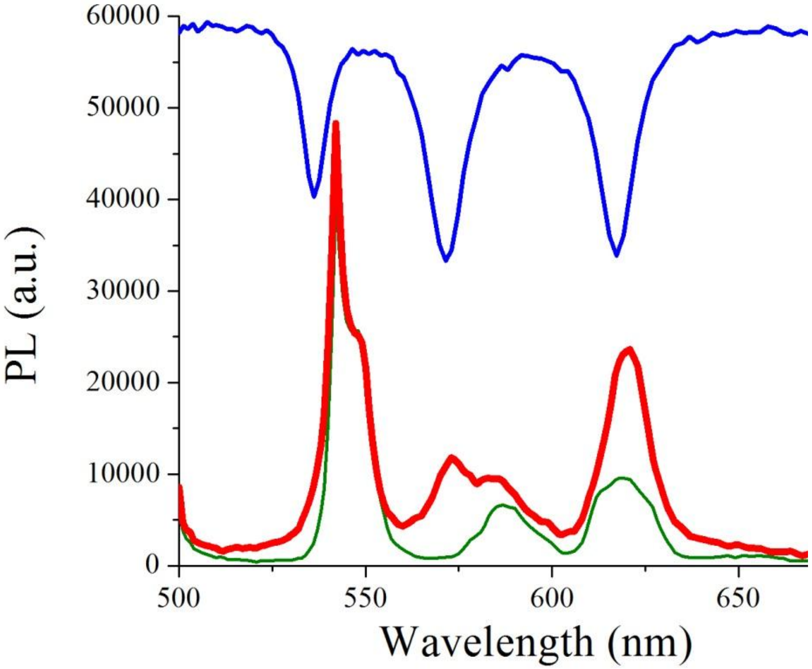


White light can almost be obtained by mixing the modified PL with the blue exciting light, while this is impossible for the PL of the reference sample.

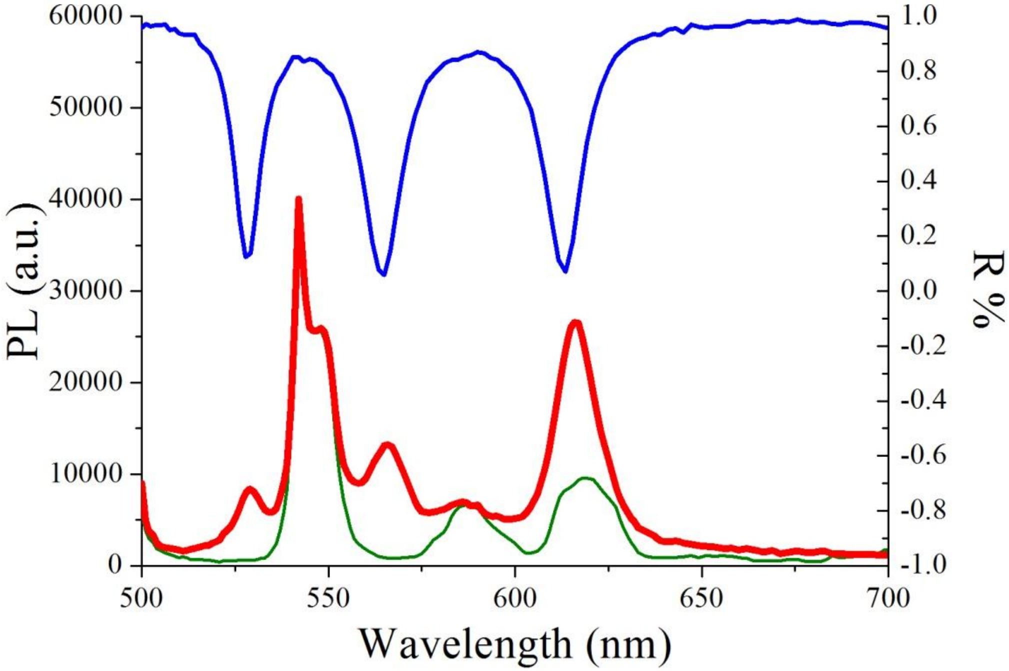
Adapted from: Yigang Li and Rui M. Almeida, J. Phys. D: Appl. Phys. 43 (2010) 455101.

Intensity enhancement

sample 1



sample 2



1.7 times enhancement (based on peak area)

1.9 times enhancement (based on peak area)

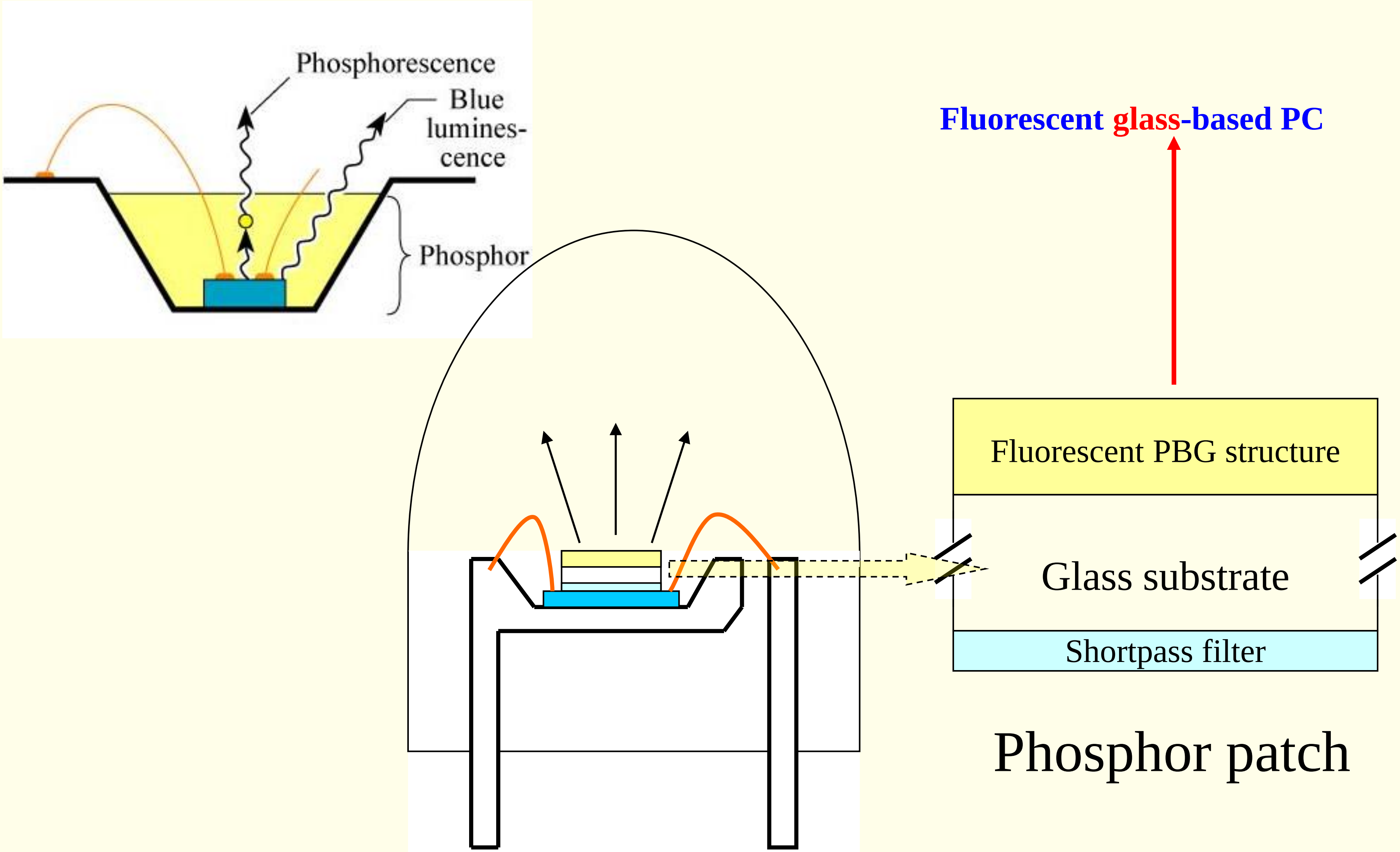
Summary

- Terbium-doped triple coupled microcavities were successfully prepared by sol-gel processing.

- The three distinct Tb^{3+} PL peaks were enhanced, balanced and broadened by the PBG structure and combined into a broad continuous fluorescence band.

How to apply the PBG structure to a white LED?

A new scheme for white LED



Adapted from: Yigang Li and Rui M. Almeida, J. Phys. D: Appl. Phys. 43 (2010) 455101.

Advantages

- This approach may enhance and modify the PL of current phosphors based on 5d→4f transitions.
- It enables the development of new phosphors based on 4f→4f transitions.
- It improves heat management and energy efficiency by avoiding the phosphor powder scattering.

Q.

2012 Global Glass Markets

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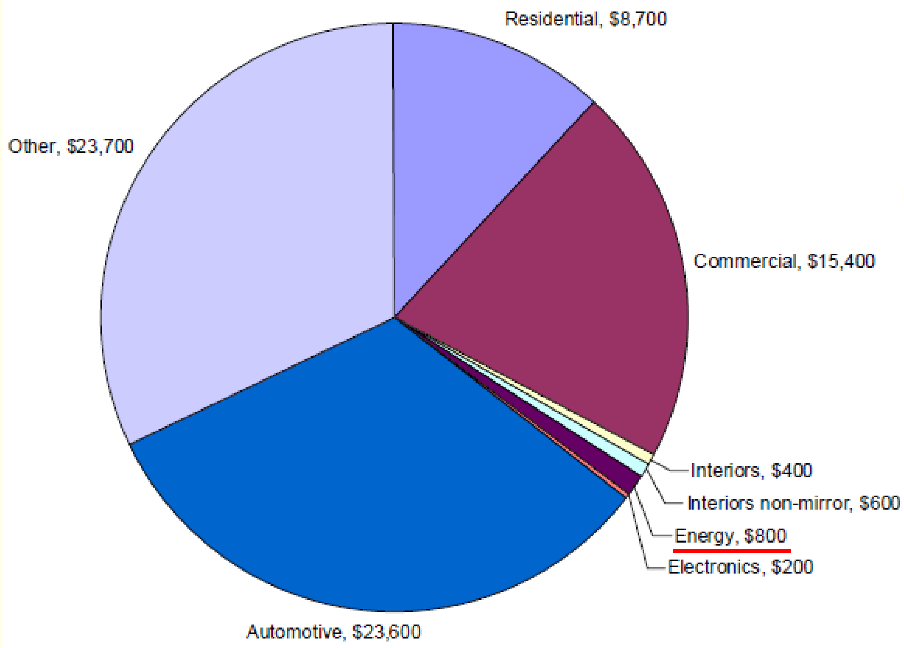
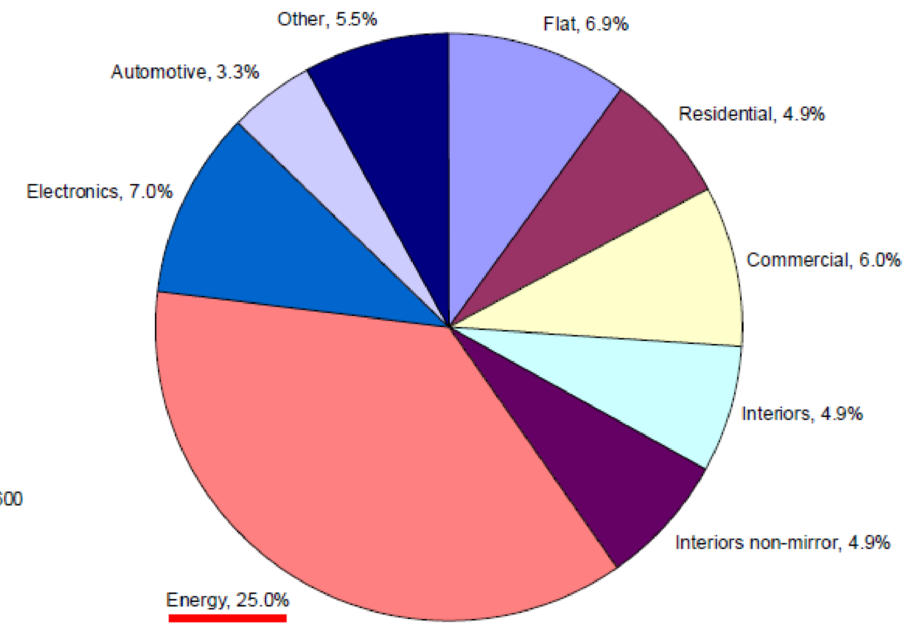
Total 2012 Global Available Market ($ mil)



Total 2012 Global Available Market - Annual Growth



Global energy glass consumption in 2012 will be 1.1% of total market

Adapted from: Solar market impact on the glass industry, Jim West (Guardian Industries), International Workshop on Glass for Harvesting, Storage and Efficient Usage of Solar Energy, Nov. 16-18, 2008, Pittsburgh, PA

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