Critical Materials in Optoelectronics

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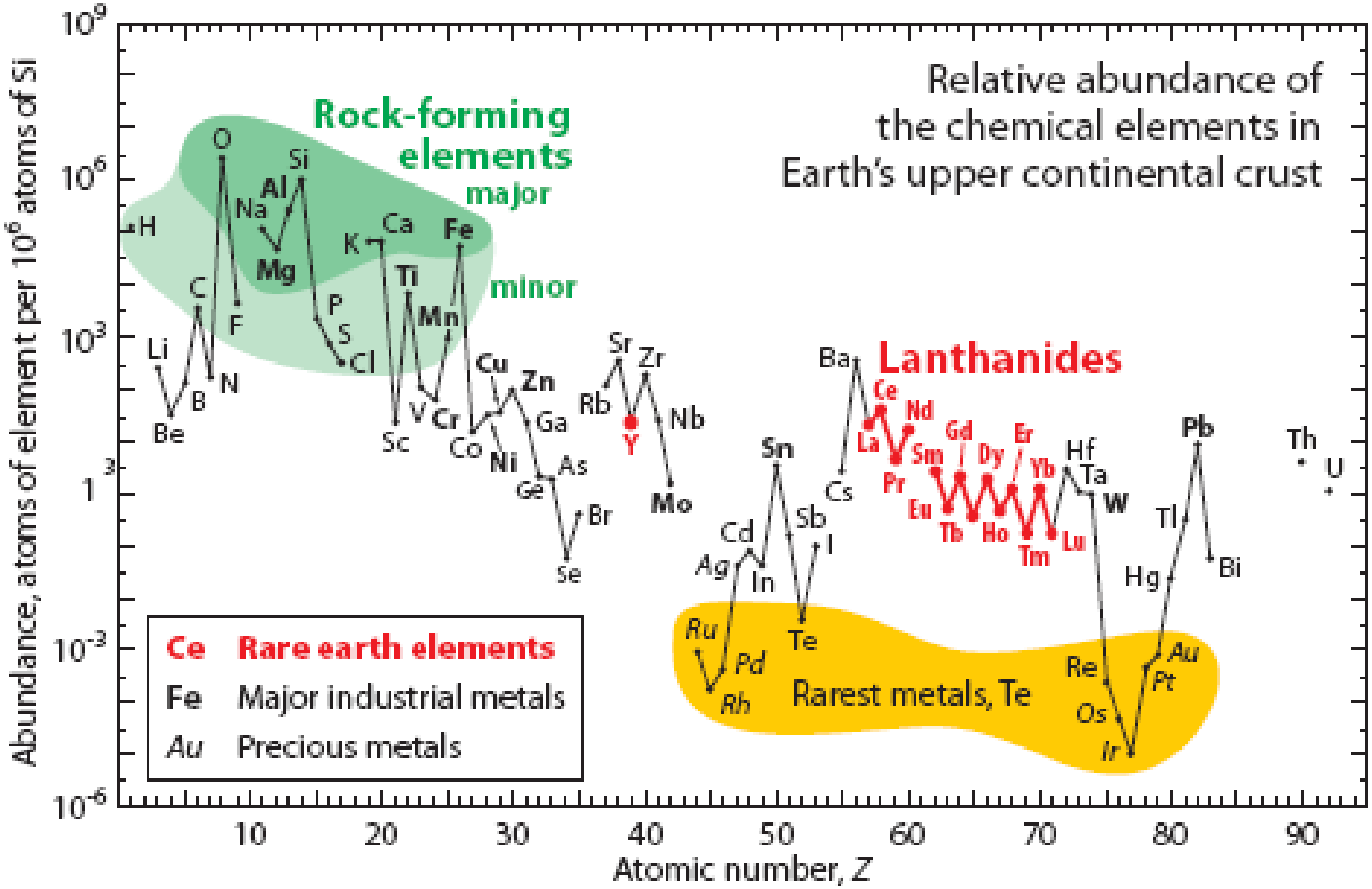
HAPPY NEW (5772) YEAR!

Outline

1. Intro. Critical materials: Some lesser-known facts?
2. Eu red phosphors, mostly Eu:Y_2O_3
3. Er-doped fiber amplifiers (EDFA).
4. Nd-, Er-, & Ho-doped yttrium aluminum garnet (YAG) lasers
5. Indium in III-V devices $(In_{1-w}Ga_w)(N_{1-x-y-z}As_xP_ySb_z)$, inc. white LEDs
6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries
7. Heavy and rare earth metal atom (e.g., Pd, Pt, Ir, and Eu) chelates for the display & SSL industries
8. Concluding remarks

1. Intro. Critical materials: Some lesser-known facts?

Item: Rare Earths (Y & Lanthanides)



K. A. Gschneidner, Jr., Material Matters 6, 32 (Sigma-Aldrich, 2011)

1. Intro. Critical materials: Some lesser-known facts? (cont.)

"As seen in Figure 1 the rare earth elements are reasonably abundant and lie between the 25th and 75th percentiles of natural abundance of the elements, with cerium being the most abundant rare earth and lutetium the least... It is not that the rare earths are only found in China; viable deposits are known to be located in almost any corner of the world. China has about 31% of the known reserves, while the USA has one of the best minable deposits in the world—Mountain Pass, California, which is about 75 miles west of Las Vegas on Interstate 15, about 5 miles inside the California/Nevada border. If this is the situation, how did we (the ROW) get into this dilemma? And how will the ROW extract itself?"

K. A. Gschneidner, Jr., Material Matters 6, 32 (Sigma-Aldrich, 2011)

1. Intro. Critical materials: Some lesser-known facts? (cont.)

"In 1970, China had 75% of the known rare earth reserves and, based on this, started to demonstrate a strong presence in the rare earth markets. However, in the subsequent 30 years, the percentage of Chinese reserves dropped to about 30% because of the discovery of new deposits all over the world, even though the absolute amount of the known Chinese reserves grew by about 290%. Recently, China has changed its approach to the rare earth market, and they have introduced production quotas, export quotas and export taxes, enforced environmental legislation, and granted no new rare earth mining licenses. Furthermore, China has stated that they will no longer export rare earth-finished products, because of rapid growth of internal markets and limited reserves, especially the heavy rare earths (Gd through Lu). As a result, the price for rare earth materials and products containing rare earths has risen to a level at which the ROW mining companies and producers can be competitive and make a profit. The non-Chinese production of rare earth oxides (REO) per year was estimated to be 4 ktons in 2009. There is another important source of rare earth materials: those that are smuggled out of China…"

K. A. Gschneidner, Jr., Material Matters 6, 32 (Sigma-Aldrich, 2011)

1. Intro. Critical materials: Some lesser-known facts? (cont.)

“It is noted that only about 43% of the cerium mined today is utilized, and if it were completely utilized cerium′s share of the market would be nearly 50%. Even though cerium is relatively inexpensive to separate compared to the other rare earths—a simple oxidation/reduction process—it must be first removed from the flow stream in order to begin the processing of the other rare earths by a counter current liquid/liquid extraction process… There is also a second penalty: it must be stored (about 50 kton per year). The rare earth industry would greatly welcome new, large (tens of ktons) cerium applications. If the cerium market were balanced, it would significantly reduce the costs of the other rare earth elements.”

K. A. Gschneidner, Jr., Material Matters 6, 32 (Sigma-Aldrich, 2011)

1. Intro. Critical materials: Some lesser-known facts? (cont.)

If we separate the REs into "surplus," "balanced," and "tight" supply categories,

- **Tight: Nd, Tb, Dy**
- **Balanced: Y, Mischmetal, La, Pr, Sm, Eu, Gd, Er, Tm, Yb, Lu**
- **Surplus: Ce, Ho**

Solution?

- **Increased mining**
- **Training of workforce**

K. A. Gschneidner, Jr., Material Matters 6, 32 (Sigma-Aldrich, 2011)

1. Intro. Critical materials: Some lesser-known facts? (cont.)

Item: Indium, mostly due to indium tin oxide (ITO)

http://www.metalprices.com/pubcharts/Public/Indium_Price_Charts.asp

1. Intro. Critical materials: Some lesser-known facts? (cont.)

Item: Indium, mostly due to indium tin oxide (ITO)

Supply:

- **Produced only as byproduct of zinc; future growth in supply could be limited by slower demand growth for zinc, which is contingent upon macroeconomic conditions in China, Canada, Korea and Japan.**
- **China dominant producer (50% of global), but mines in Canada, Japan, Korea, Peru, Belgium, Russia produce & could expand.**
- **Due to environmental concerns, China has closed many smaller/polluting smelters, restricting output.**
- **Annual production is ~900 tons. Primary is ~600 tons, balance is from recycled ITO and stockpiles.**

Demand:

- **Last year, 85% of all In went to ITO. This demand is predicted to grow 15%/yr for next 3 yrs.**
- **Emerging uses: CIGS (copper-indium-gallium-selenium) solar cells, electrode-less lamps, Hg alloy replacements, control rods for nuclear reactors.**
- **Global demand exceeded production in 2008-2010, leading to a market in disequilibrium.**

Recent Headlines: Tighter Availability of Crude Indium in China –August 2, 2011
"…Supply of In tightens due to widespread crackdown by Chinese gov't on smaller lead and zinc refiners amid environmental concerns. . . The situation has led the US price spread to tighten to $720-770/kg from $690-770 /kg. "Its more supply driven than demand. It seems like the Chinese crackdown on smaller producers is now having an impact," said one US trader, noting that prices could test $800 /kg in the coming weeks. "The major producers that do have material are not willing to sell at lower prices. So the market is now in stronger hands." Trade sources said that prices could now start to rise steadily as China appears determined to impose the new regulations and demand looks set to improve as the market moves towards the traditional autumn buying period. "The Chinese government's attempts to crackdown on these facilities has happened in fits and starts over the last several years. But it now seems to be steadily imposing these rules," said the trader."

MinorMetals, Aug 2011

2. Eu red phosphors, mostly Eu:Y_2O_3.

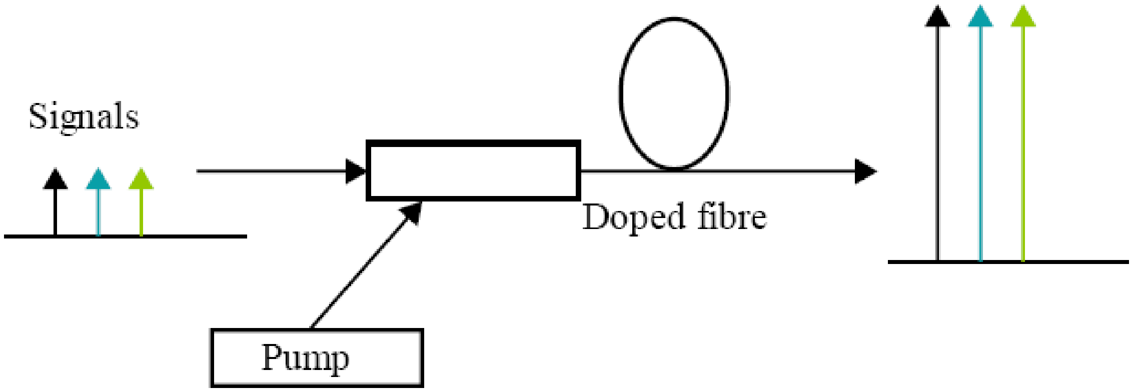
Item: Eu is 0.3% of mined REs, balanced @ 400 tons oxide/yr
Y is 6% of mined REs, balanced @ 8.5 ktons oxide/yr

- **4% – 6.5% Eu:Y_2O_3 emits intense red phosphorescence @ 611 nm, used extensively in ~~TVs~~, fluorescent lamps, & CFLs** (http://www.sylvania.com/BusinessProducts/MaterialsandComponents/LightingComponents/Phosphor/FluorescentLamps/)
- **CFL volume rising strongly, but so are RE reserves.**
- **Hot on the heels of CFLs: White LEDs and OLEDs rapidly developing for SSL.**

3. Er-doped fiber amplifiers (EDFA)

Item: Er is 0.5% of mined REs, balanced @ 700 tons oxide/yr

- **Apps: fiber optics signal amplifiers, coloring agent, Er-stabilized ZrO_2 for jewelry.**
- **EDFA are critical components of the repeaters in optical fiber networks, where the carrier wavelength is 1.55 μm.**
- **This critical need may slowly wane as wireless communications steadily grow.**



http://en.wikipedia.org/wiki/Optical_amplifier#Doped_fiber_amplifiers

3. Nd-, Er-, & Ho-doped YAG lasers

Nd: 16% of mined REOs, slightly tight @ 23 ktons
(2.8 ktons metal for wind turbines)
Er: 0.5% of mined REOs, balanced @ 700 tons oxide/yr
Ho: 0.1% of mined REOs, surplus @ 100 tons oxide/yr
Y: 6% of mined REOs, balanced @ 8.5 ktons oxide/yr

- **Powerful Nd:YAG lasers (λ = 1064 nm, with frequency doubling to 532 nm and tripling to 355 nm) used extensively in spectroscopy**
- **The long-pulse (200-350 ms) Ho:YAG laser (λ = 2.12 μm) used extensively in urology for laser lithotripsy**

(G. J. Vassar et al., J. Endourology. 13, 181 (1999).;
K. F. Chan et al., J. Endourology. 15, 257 (2001);
http://www.yoururologyhealth.com/holmium_lithotripsy)

5. Indium in III-V devices $(Al_{1-v-w}Ga_vIn_w)(N_{1-x-y-z}P_xAs_ySb_z)$, inc. white LEDs for SSL

- **The strategic material, if any, is In.**
- **Current street lighting market is $327M/yr**
- **Estimated compound growth rate (CAGR) for LED street- and area-lighting for 2010 - 215 : 28% on units, 12% on revenue**

  (LED Magazine, Sep 2011)

Retrofitting to LEDway streetlights, City of Anchorage will reduce energy costs by ~50%, saving ~$360k /yr.

5. Indium in III-V devices $(In_{1-w}Ga_w)(N_{1-x-y-z}As_xP_ySb_z)$, inc. white LEDs for SSL (cont.)

LEDway streetlights with 60 LEDs, Type III medium optics with backlight control, 700mA, Color Temperature: 4300K

LEDway streetlights replaced 100- and 150-watt high-pressure sodium fixtures

- By retrofitting to LEDway streetlights, Anchorage will reduce energy costs by 50%, saving ~$360k/yr.
- LEDway fixtures 10^5 h life > 7x that of high-pressure sodium (HPS) lamps, reducing maintenance costs.
- Visibility is dramatically improved through superior uniformity and control.

http://ledway-px.rtrk.com/RuudLedWay/media/RuudLedWayMediaLibrary/Case-Studies/Anchorage-Case-Study.pdf

6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries

Item: Current state of OLED technology & commercialization.

Samsung Galaxy smart phones: OLED sales > $1B/yr

Sony 11" OLED TV

LG 17" OLED TV

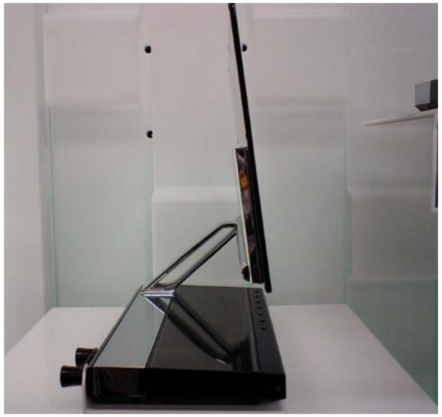
Osram White OLED (WOLED) lighting products

6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries

Item: Current state of OLED technology & commercialization (cont.)

Sony 11" OLED TV. Debuted 12/2007, $2,500

Contrast ratio 10^6:1



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Item: Current state of OLED technology & commercialization (cont.)

30 cm x 30 cm WOLED Panels, ~20 lm/W @ 1000 Cd/m^2.

(Kido et al., Science <u>310</u>, 1762 (2005))

6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries

Item: Current state of OLED technology & commercialization (cont.)

Osram WOLED lighting products

1.8 mm → 1.4 mm → 0.7 mm

Transparent WOLEDs or panels that convert to mirrors when off

Also flexible OLEDs on 0.1 mm-thick stainless steel

State-of-the-art: 87 lm/W @ 1,000 cd/m^2 (nits)

Target: 300 lm/W, CCT = 3000 K, CRI > 80

1 lumen (lm) = 1.46 mW @ 555 nm.

1 candela (cd) = 1 lm/steradian

If emission profile is Lambertian

(angular dependence is cosine),

then 1 cd/m^2 = π lm/m^2

6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries

Item: Current state of OLED technology & commercialization (cont.)

Competing WOLED developers

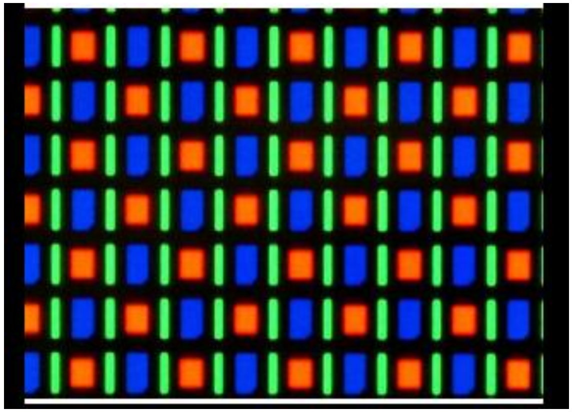
Siemens Osram

GE Global research

Lumiotec (Japan)

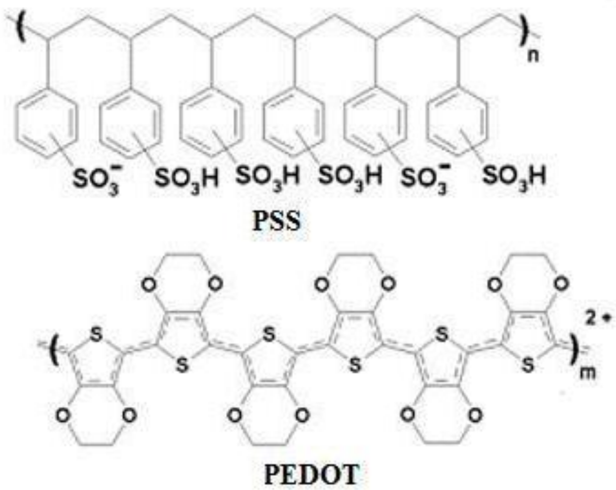
Phillips Lumileds

Universal Display Corp (UDC) (US)



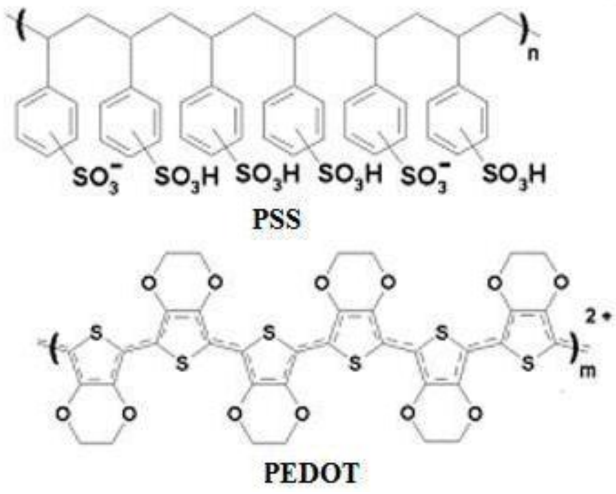
6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries

- ITO is the preferred transparent conducting electrode in thin film PVs.
- It's still the ***only*** transparent conducting electrode in all commercial LCDs and OLEDs.
- Major progress in developing ZnO & AlZnO as alternatives, but not sufficient.
- Other alternatives under investigation:
  Conducting polymers, carbon nanotubes (CNTs), graphene, thin metal~~s~~ layers, printable metal grids.
- One of the most promising alternatives:
  poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)
- PEDOT:PSS explored for > 10 yrs
  The key is the recent development of a process to fabricate ***multilayered*** PEDOT:PSS
  (Y. H. Kim et al., Adv. Func. Mater. 21, 1076 (2011);
  M. Cai et al., Appl. Phys. Lett. (in press))
- Process involves blending with polyethylene glycol (PEG), immersing in PEG, & annealing.



6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries (cont.)

Materials	Thickness (nm)	Transmittance (%)	Sheet resistance (Ω/square)
Treated PEDOT:PSS	36	91	226
	72	87	115
	114	82	72
	149	79	55
ITO	140	92	14



M. Cai, T. Xiao, R. Liu, Y. Chen, R. Shinar, and J. Shinar, Appl. Phys. Lett. (in press)

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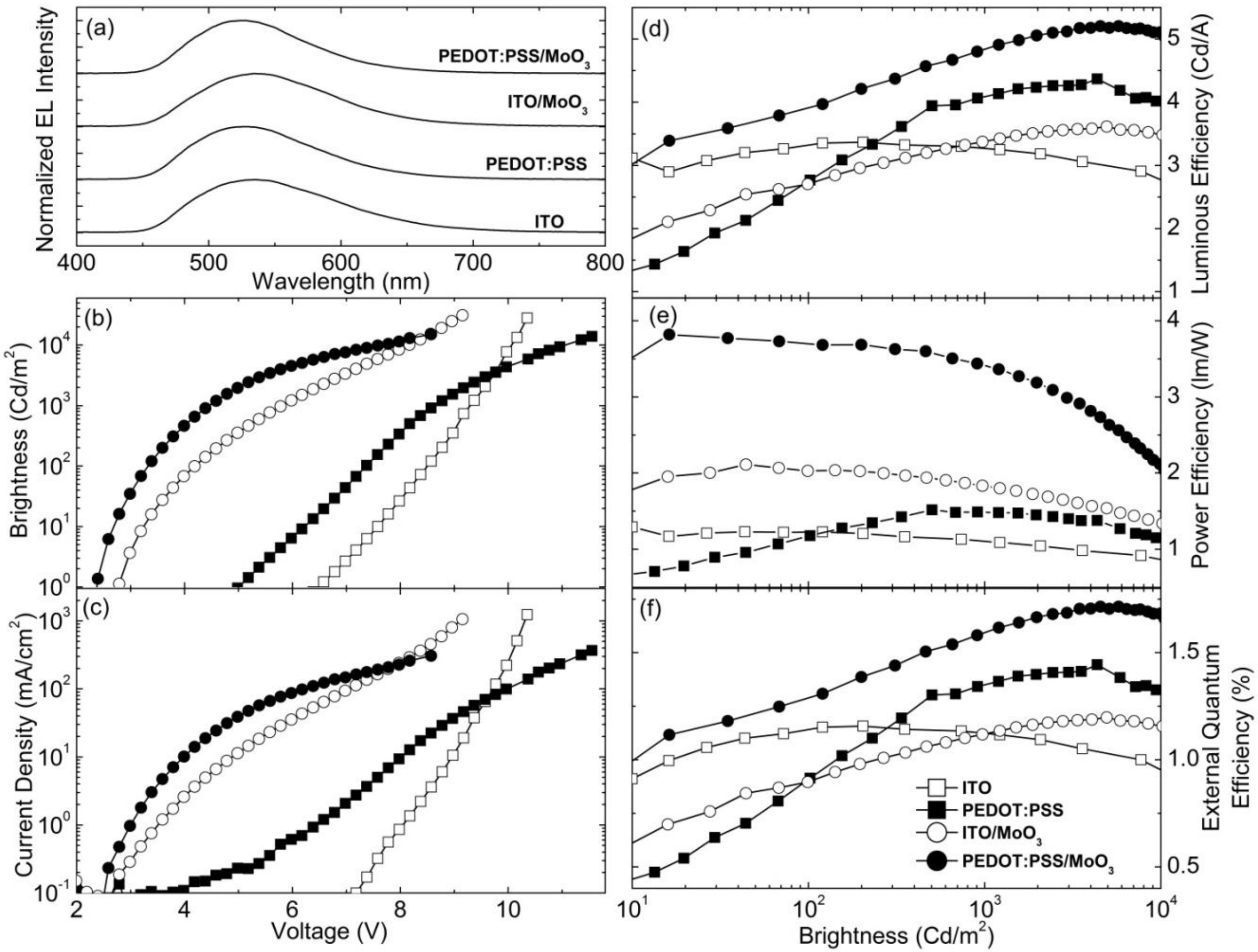

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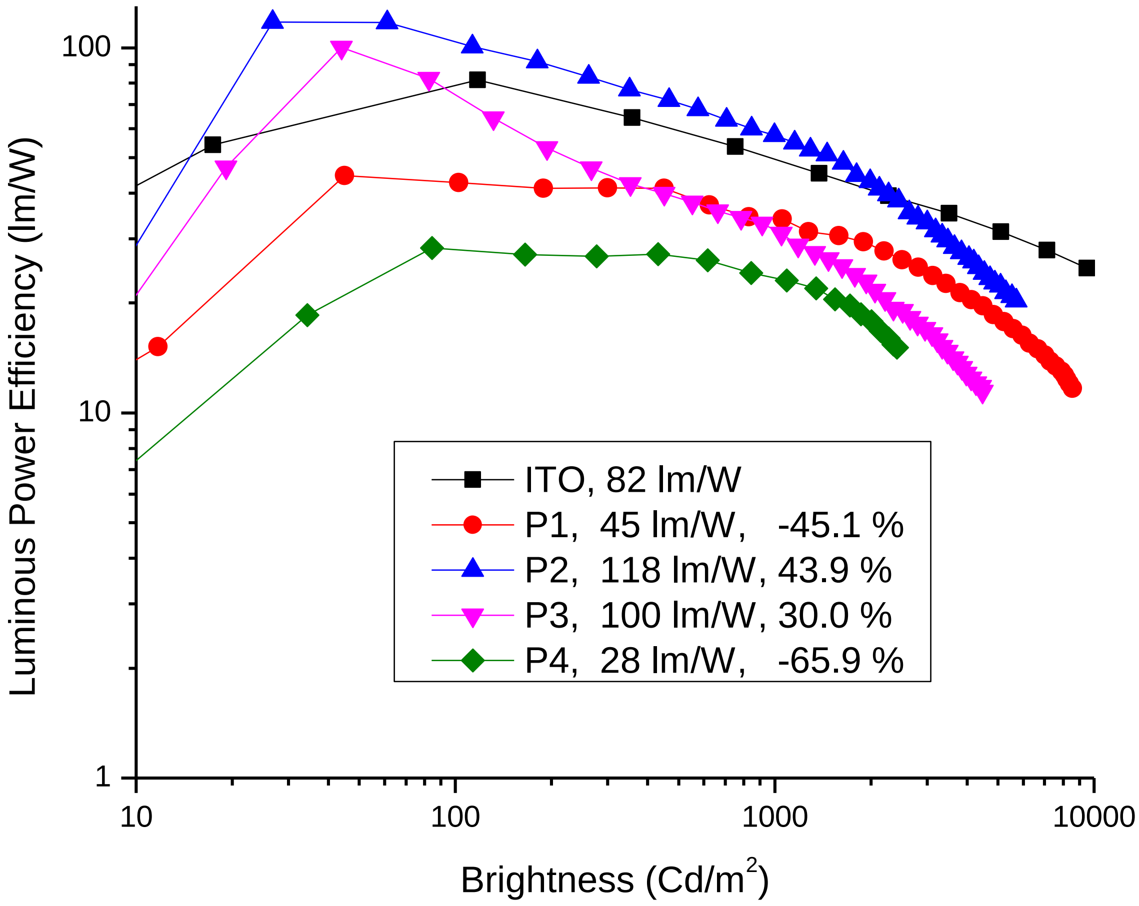
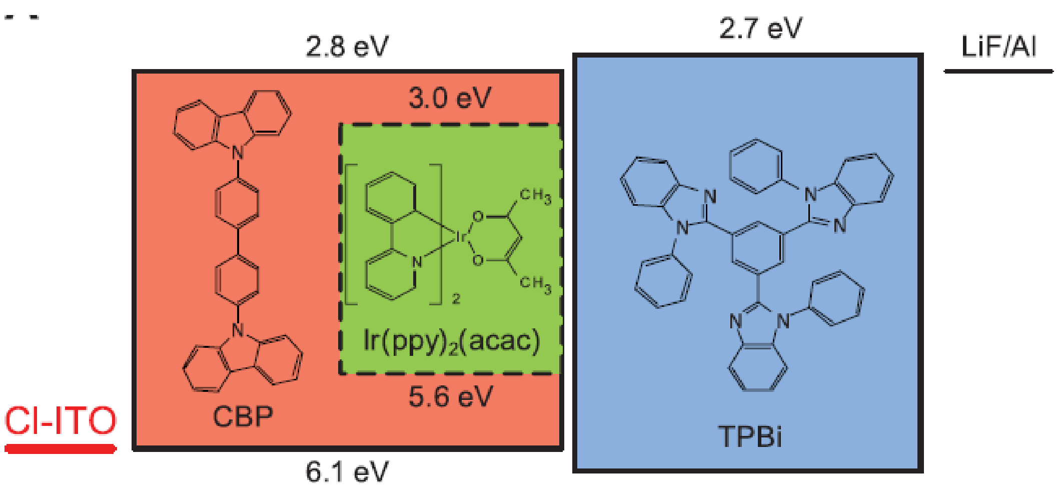
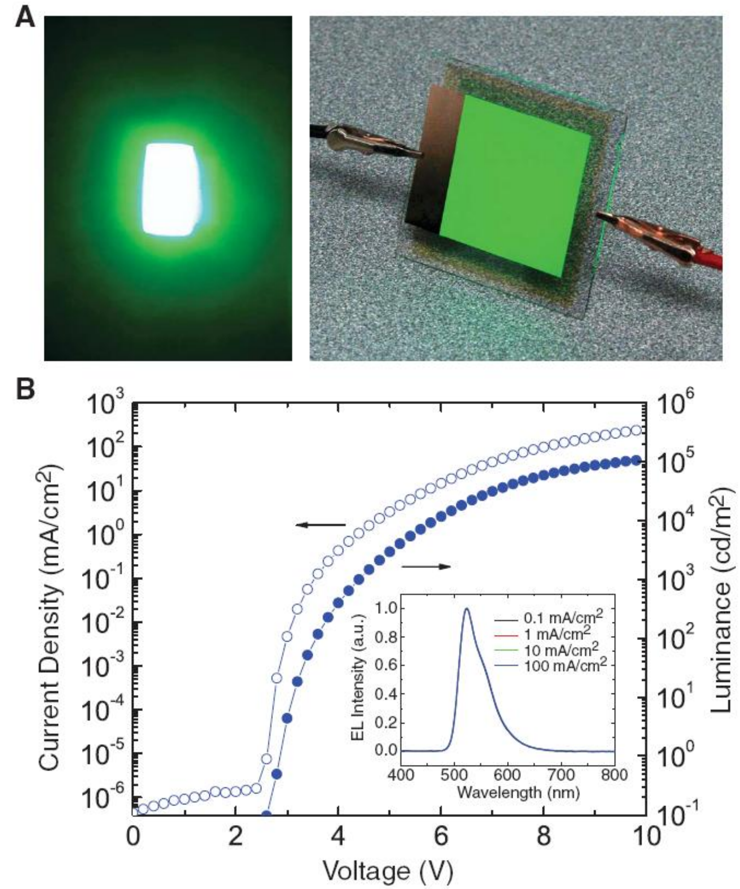


M. Cai, T. Xiao, R. Liu, Y. Chen, R. Shinar, and J. Shinar, to be published

6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries (cont.)

- **But ITO is a moving target: Recent report on chlorinated ITO-based OLEDs with impressive record efficiency.**





Device performance of OLEDs with Cl-ITO electrode. (A) (Left) image of 1x2 mm^2 device operating @ 5000 cd/m^2 and (right) 50x50 mm^2 pixel (B) Current density & luminance vs bias. The inset shows the EL spectra

M. J. Helander et al., Science 332, 944 (2011)

6. Indium tin oxide (ITO) in photovoltaics (PV), the display, and solid state lighting (SSL) industries (cont.)

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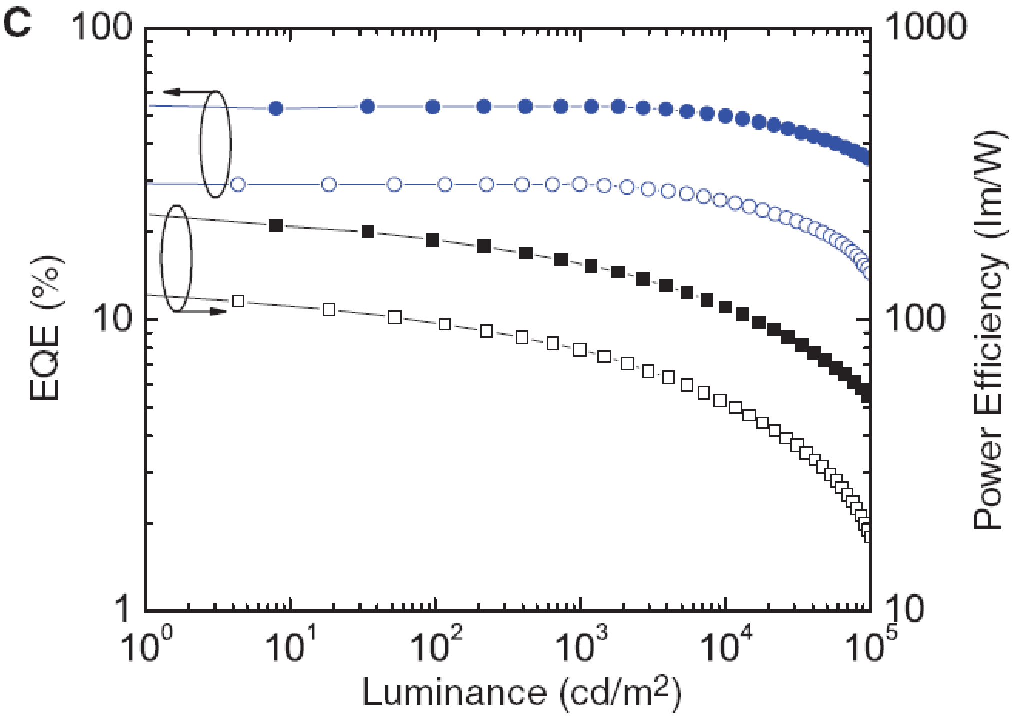
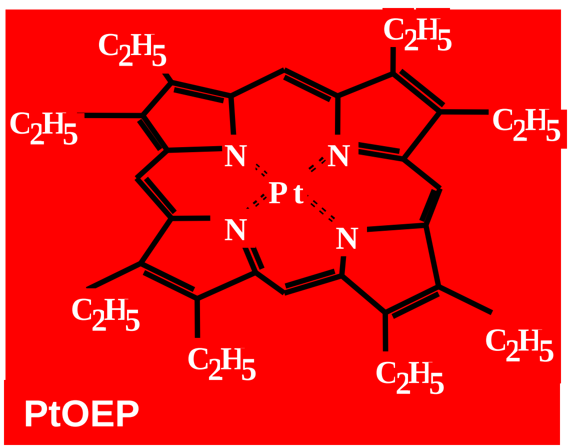


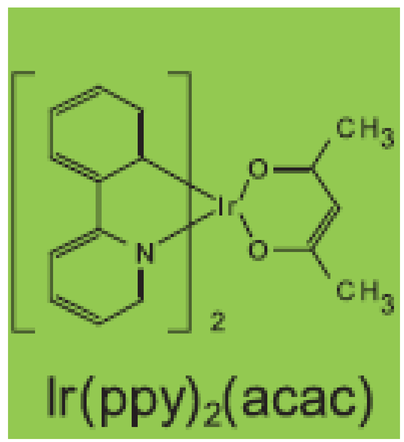
(C) EQE and power efficiency as a function of luminance. The open symbols are w/o outcoupling enhancement, the solid symbols are w/lens-based outcoupling enhancement.

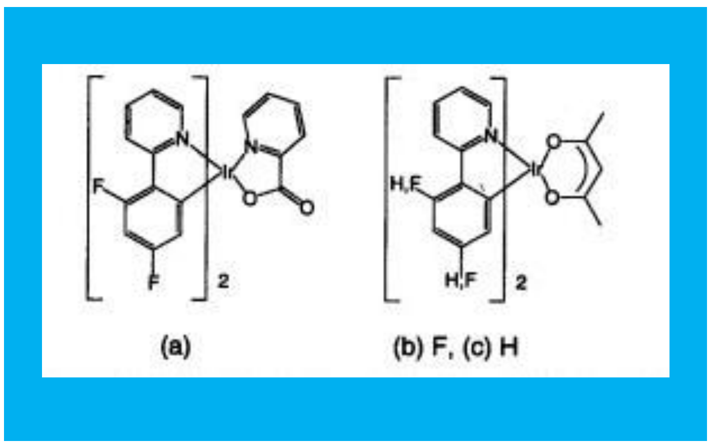
M. J. Helander et al., Science 332, 944 (2011)

7. Heavy and rare earth metal atom (e.g., Pd, Pt, Ir, and Eu) chelates for the display & SSL industries

- In all OLEDs, carrier injection into the emitting layer results in 25% singlet excitons (SEs), 75% triplet excitons (TEs).
- In fluorescent OLEDs, only the SEs are radiative, so max internal quantum efficiency IQE_{max} ~ 25%.
- So phosphors, in which the TEs are radiative, are crucial for high IQE_{max}.
- These phosphors are heavy-metal chelates.

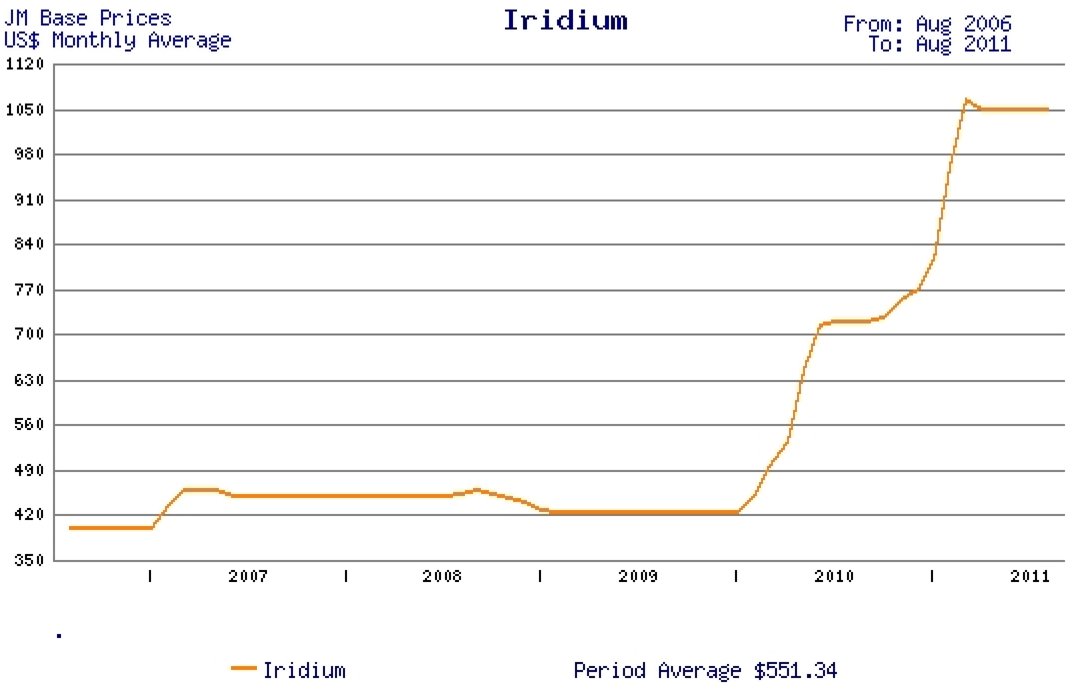






(a) bis(2-phenylpyridinato-*N*,$C^{2'}$)iridium(acetylacetonate) [$ppy_2Ir(acac)$]
(b) bis[4, 6-di-fluorophenyl!-pyridinato-*N*, $C^{2'}$]iridium(acetylacetonate) [Fir(acac)]
(c) iridium(III)bis[4,6-di-fluorophenyl)-pyridinato-*N*,$C^{2'}$]picolinate (FIrpic)

7. Heavy and rare earth metal atom (e.g., Pd, Pt, Ir, and Eu) chelates for the display & SSL industries (cont.)



Price of Iridium per Ounce (in USD)

http://www.ebullionguide.com/price-chart-iridium-last-5-years.aspx

7. Heavy and rare earth metal atom (e.g., Pd, Pt, Ir, and Eu) chelates for the display & SSL industries (cont.)

Supply:

- **Iridium is the rarest of all the Platinum Group Metals (PGMs).**
- **The major commercial sources of this element are found in pyroxenite and the sulfide ore laurite in South Africa, and pentlandite from nickel mining regions in Russia and Canada.**
- **Iridium is difficult to refine and is only produced in small quantities.**
- **Supplies of iridium expanded, largely drawing down refined stocks, to meet new demand in 2010.**

Demand:

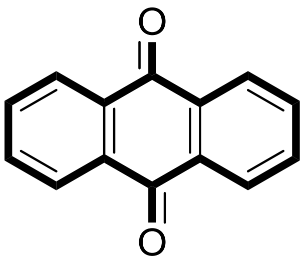
- **Iridium demand increased to 334,000 oz in 2010 from 81,000 oz the previous year. Much of this demand was for iridium crucibles employed in backlit LED televisions.**
- **Growth in the worldwide automotive sector in 2010 also led to increased demand for iridium-tipped spark plugs.**
- **The sharp increase in demand in the small, relatively illiquid market of iridium had a significant impact on the price, which traded on average 51% higher than in 2009 at $642.**

Recent Headlines: Iridium Soars on High-Tech Gadget Demand –May 16, 2011
By Jack Farchy in London
The popularity of smartphones, tablets and flatscreen televisions has triggered a 150% jump in the price of Ir. Demand more than quadrupled last year, according to Johnson Matthey. The sudden rush of buying in the tiny market has sent the price soaring to an all-time high >$1,000/troy ounce. The 150% surge in prices since the start of 2010 dwarfs the rallies in silver, gold, platinum and palladium. The market for iridium is very small, less than $500m/year, compared with $30bn for Ag and $10bn for Pt, but the metal is crucial for some new technologies. "Iridium crucible manufacture expanded suddenly and rapidly during 2010, driving up demand," said the refiner. "The small size of the Ir market helped amplify movements in the price as industrial buyers built their stocks of working metal in response to technology changes." The jump in prices is a boon for the few, almost exclusively South African, producers. However, iridium's golden age may be just beginning. The drive for environmentally friendly lighting in homes, streets and cars could spur a rush for the metal.

MinorMetals, Aug 2011

7. Heavy and rare earth metal atom (e.g., Pd, Pt, Ir, and Eu) chelates for the display & SSL industries (cont.)

Anthraquinone (AQ)



- **Heavy-metal-free Room-temp phosphors: A viable alternative?**

  Example: Anthraquinone

  M. Montalti, A.Credi, L. Prodi, M. T. Gandolfi, Editors, *Handbook of Photochemistry. 3rd Ed., p. 93* (CRC Press-Taylor & Francis, Boca Raton, 2006).

  But at 295 K, phosphorescence quantum yield is very low. Should we be initiating efforts in this direction?

- **Exploit TE + TE → SE to increase IQE_{max} well beyond 25%?**

8. Concluding Remarks

- **For optoelectronics, the "critical" in critical resources is questionable.**
- **There is no single silver bullet, b/c the situation is much better:**

  There are many potential silver bullets for the different problems.
- **Stay tuned.**