Optical Properties II: Emission of Light, Displays and Transparent Conductors

Chemistry 754
Solid State Chemistry
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Emission of Light

The optical properties of extended solids are utilized not only for their color, but also for the way in which they emit light.

Luminescence ? Emission of light by a material as a consequence of it absorbing energy. There are two categories:

? **Fluorescence:** Emission involves a spin allowed transition (short excited state lifetime)

? **Phosphorescence:** Emission involves a spin forbidden transition (long lived excited state).

Luminescence can also be classified according to the method of excitation:

? **Photoluminescence:** Photon excitation (i.e. fluorescent lights)

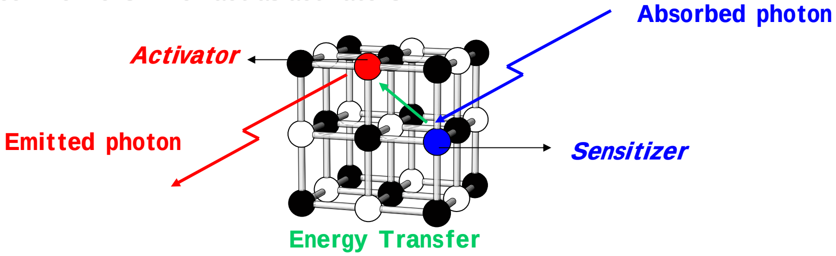
? **Cathodoluminescence:** Cathode rays (TV & Computer displays)

? **Electroluminescence:** Electrical injection of carriers (LEDs)

Sensitizers and Activators

Sensitizer ? Absorbs the incident energy (photon or excited electron). Often times the host lattice acts as the sensitizer.

Activator ? The site where the electron radiatively relaxes. Some common ions which act as activators:



Host Lattice ?Typically, the host lattice should have the following properties:

?**Large Band Gap** ? So as not to absorb the emitted radiation.

?**Stiff** ? Easily excited lattice vibrations can lead to non-radiative relaxation, which decreases the efficiency.

Common Luminescent Ions

Ion	Excited State	Ground State	ς_{max} Emission
Mn^{2+} ($3d^5$)	$t_2{}^4e^1$ ($^4T_1$)	$t_2{}^3e^2$ ($^6A_1$)	Green-Orange-Red*
Sb^{3+} ($5s^2$)	$5s^15p^1$	$5s^2$	Blue*
Ce^{3+} ($4f^1$)	$4f^05d^1$	$4f^15d^0$	Near UV to Red*
Eu^{2+} ($4f^7$)	$4f^65d^1$	$4f^75d^0$	Near UV to Red*
Tm^{3+} ($4f^{12}$)	$^1G_4$	$^3H_6$	450 nm (Blue)
Er^{3+} ($4f^{11}$)	$^4S_{3/2}$	$^4I_{15/2}$	545 nm (Green)
Tb^{3+} ($4f^8$)	$^5D_4$	$^7F_5$	545 nm (Green)
Pr^{3+} ($4f^2$)	$^3P_0$	$^3H_5$ ($^3F_2$)	605 (635) nm (Red)
Eu^{3+} ($4f^6$)	$^5D_0$	$^7F_2$	611 nm (Red)

*The energy of transitions involving d, p or s orbitals is very sensitive to the crystal field splitting induced by the lattice.

Conventional Fluorescent Lights

?**Excitation Source**

? Hg gas discharge ? UV Light (photoluminescence)

?**Sensitizer/Host Lattice**

? Fluoroapatite ? $Ca_5(PO_4)_3F$

?**Activators**

? Blue = Sb^{3+} ($5s^15p^1 \Downarrow 5s^2$) ς_{max} = 480 nm

? Orange-Red = Mn^{2+} ($t_{2g}^4e_g^1 \Downarrow t_{2g}^3e_g^2$) ς_{max} = 580 nm

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Tricolor Fluorescent Lights

Tricolor fluorescent lights are more commonly used today because they give off warmer light, due to more efficient luminescence in the red region of the spectrum. Such lights contain a blend of at least three phosphors.

?**Red Phosphor**

? **Host Lattice** = $(Y_{2-x}Eu_x)O_3$ x = 0.06-0.10 (Bixbyite structure)

? **Sensitizer =** O^{2-} 2p $\Downarrow$ Eu^{3+} 5d charge transfer (ς_{max} ~ 230 nm)

? **Activator =** $^5D_0 \Downarrow {}^7F_2$ transition on Eu^{3+} [f^6 ion] (ς_{max} ~ 611 nm)

?**Green Phosphor**

? **Host Lattice** = $(La_{0.6}Ce_{0.27}Tb_{0.13})PO_4$ (Monazite structure)

? **Sensitizer =** $4f^1 \Downarrow 5d^1$ excitation on Ce^{3+} [f^1 ion] (ς_{max} ~ 250 nm)

? **Activator =** $^5D_4 \Downarrow {}^7F_5$ transition on Tb^{3+} [f^8 ion] (ς_{max} ~ 543 nm)

?**Blue Phosphor**

? **Host Lattice** = $(Sr,Ba,Ca)_5(PO_4)_3Cl$ (Halophosphate structure)

? **Sensitizer =** $4f^75d^0 \Downarrow 4f^65d^1$ transition on Eu^{2+}

? **Activator =** $4f^65d^1 \Downarrow 4f^75d^0$ transition on Eu^{2+} (ς_{max} ~ 450 nm)

For a detailed yet very readable description of fluorescent light phosphors see: http://www.electrochem.org/dl/interface/sum/sum98/IF6-98-Page28-31.pdf

Cathode Ray Tube

The cathode ray tube is the technology used in most computer monitors and TV?s. The details of a typical commercial CRT?s are as follows.

?**Excitation Source**

Electron beam (cathodoluminescence)

?**Red**

Sensitizer/Host - YVO_4

Activator ? Eu^{3+}

?**Green**

Sensitizer/Host ? ZnS (CB)

Activator ? Ag^+

?**Blue**

Sensitizer/Host ? ZnS (CB)

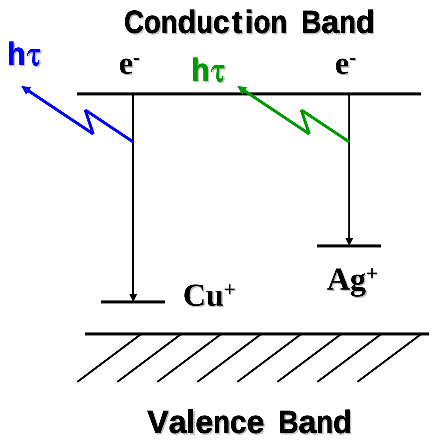
Activator ? Cu^+

Image taken from
http://www.howstuffworks.com/tv2.htm

Luminscence in ZnS

While the insulating red phosphor $(Y_{1-x}Eu_x)VO_4$ operates on a principle very similar to fluorescent light phosphors (with a different excitation source of course), the blue and green phosphors employ a different scheme for electronic excitation and luminescence.

The electronic excitation in ZnS (E_g = 3.6 eV) is from the valence band to the conduction band. While the relaxation that leads to the luminescence is from the conduction band to an impurity level in the band gap. Typically either Ag^+ or Cu^+, which are substitutional impurities. The energy of the emitted light can be tuned by changing impurities or changing the band gap of the semiconductor.



Electroluminescence

Flat Panel Displays

In electroluminescence an electron is directly injected into the phosphor (in the excited state) and it relaxes giving off a photon.

This diagram shows how by running current through a single row (absorbant back electrode) and a single column (transparent front electrode) it is possible to light up a single pixel.

Taken from the Planar systems website.
http://www.planar.com/technology/el.asp

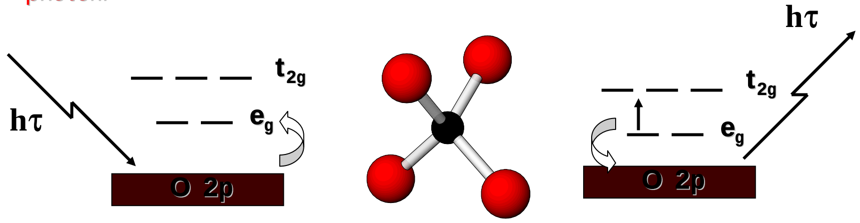
Self Luminescence in AWO$_4$

The AWO$_4$ (A= Ca, Sr, Ba) tungstates, based upon the scheelite structure with isolated tetrahedra, are self luminescent. Luminescence in these materials can be described by the following process.

1. WO$_4^{2-}$ group absorbs a UV photon via a charge transfer from oxygen to tungsten.

2. Excited state electron is in an antibonding state, weakens/lengthens the bond lowering the energy of the excited state.

3. Electron returns to the ground state giving off a longer wavelength photon.



Solid State Lasers

A Laser gives off light at a single wavelength. To achieve this the activator needs to have the following properties

- ? A long lived excited state
- ? A very narrow emission spectrum (localized luminescence centers)

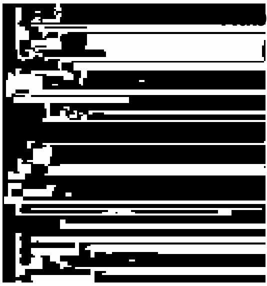
Nd:YAG laser

?Host = $Y_3Al_5O_{12}$ (Garnet)

?Activator = Nd^{3+} ($4f^3$)

?Lifetime = 10^{-4} s

? ς = 1064 nm



y laser

?Host = Al_2O_3

?Activator = Cr^{3+}

?Lifetime = 5 ms

? ς = 693.4 nm

Transparent Conducting Oxides

?**Characteristics of a transparent conducting oxide (TCO)**

- ? High transparency in the visible (E_g > 3.0 eV)
- ? High electrical conductivity (ω > 10^3 S/cm)

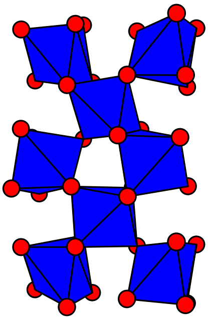
?**Applications of transparent conductors**

- ? Optoelectronic devices (LEDs, Semiconductor lasers, photovoltaic cells, etc.)
- ? Flat Panel Displays (liquid crystals, electroluminescent displays)
- ? Heat efficient windows (reflect IR, transparent to visible light)
- ? Smart windows and displays based on electrochromics
- ? Defrosting windows and antistatic coatings

?**TCO Materials**

- ? In_2O_3:Sn (ITO)
- ? SnO_2:Sb & $SnO_{2-x}F_x$
- ? ZnO:F & ZnO:M (M=Al, In, B, Ga)
- ? Cd_2SnO_4
- ? $CuAlO_2$ & $CuGaO_2$

TCO Structure Types I



In_2O_3
Bixbyite (Ia3)
6-coordinate In^{3+}
4-coordinate O^{2-}
Edge & Corner Sharing

Cd(CdSn)O_4
Inverse Spinel (Fd3m)
6-coordinate Sn^{4+}/Cd^{2+}
4-coordinate O^{2-}
Edge & Corner Sharing

$ZnSnO_3$
Ilmenite (R-3)
6-coordinate Sn^{4+}
6-coordinate Zn^{2+}
4-coordinate O^{2-}
Edge & Face Sharing

TCO Structure Types II

ZnO
Wurtzite ($P6_3mc$)
4-coordinate Zn^{2+}
4-coordinate O^{2-}
Corner Sharing

SnO_2
Rutile ($P4_2/mnm$)
6-coordinate Sn^{4+}
3-coordinate O^{2-}
Edge & Corner Sharing

Desirable Properties - TCO's

The following guidelines were put forward* as guidelines for the most desirable features of the electronic band structure for a TCO material. (*See Freeman, et al. in MRS Bulletin, August 2000, pp. 45-51)

?A highly disperse single s-band at the bottom of the conduction band.

    ? in order to give the carriers (electrons) high mobility
    ? To achieve this condition we need main group s^0 ions (Sn^{2+}, In^{3+}, Cd^{2+}, Zn^{2+})

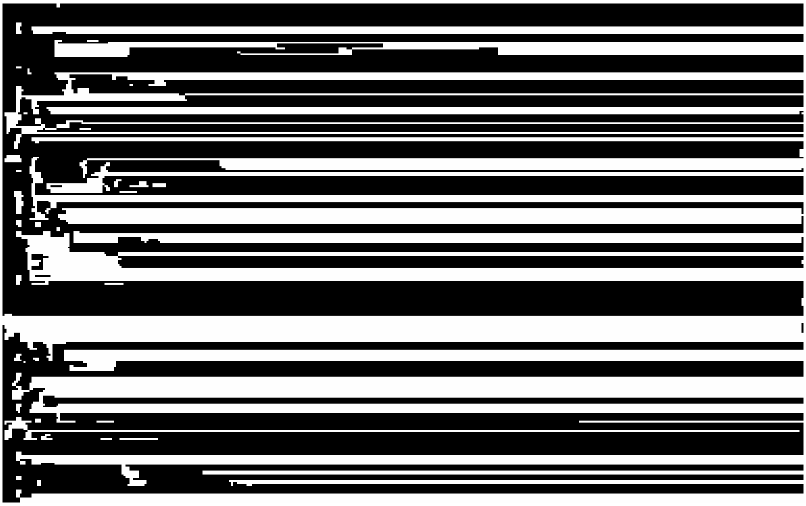
?Separation of this band from the valence band by at least 3 eV

    ? in order to be transparent across the visible spectrum
    ? We need the appropriate level of covalency so that the conduction band falls 3-4 eV above the O 2p band (Bi^{5+} & Pb^{4+} are too electronegative, In^{3+}, Zn^{2+}, Cd^{2+}, Sn^{4+} are of roughly the proper energy)

?A splitting of this band from the rest of the conduction band

    ? in order to keep the plasma frequency in the IR range
    ? Direct M ns - M ns interactions across the shared octahedral edge are useful to stabilize the s-band wrt the rest of the CB.

Electronic Structure In_2O_3



Taken from Freeman, et al. in MRS Bulletin, August 2000, pp. 45-51