

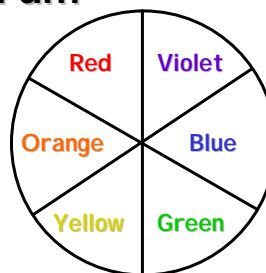
Optical Properties I: Color ? Pigments and Gemstones

Chemistry 754
Solid State Chemistry
Lecture #21
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Electromagnetic Radiation and the Visible Spectrum

UV	100-400 nm	12.4 - 3.10 eV
Violet	400-425 nm	3.10 - 2.92 eV
Blue	425-492 nm	2.92 - 2.52 eV
Green	492-575 nm	2.52 - 2.15 eV
Yellow	575-585 nm	2.15 - 2.12 eV
Orange	585-647 nm	2.12 - 1.92 eV
Red	647-700 nm	1.92 - 1.77 eV
Near IR	10,000-700 nm	1.77 - 0.12 eV



If absorbance occurs in one region of the color wheel the material appears with the opposite (complimentary color). For example:

- ? a material absorbs violet light ↓ Color = Yellow
- ? a material absorbs green light ↓ Color = Red
- ? a material absorbs violet, blue & green ↓ Color = Orange-Red
- ? a material absorbs red, orange & yellow ↓ Color = Blue

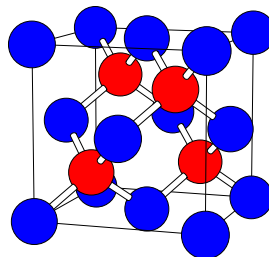
$$E = hc/\zeta = \{(4.1357 \times 10^{-15} \text{ eV}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})\}/\zeta$$
$$E \text{ (eV)} = 1240/\zeta(\text{nm})$$

Color in Extended Inorganic Solids

- ? **Intratatomic (Localized) excitations**
 - ? Cr^{3+} Gemstones (i.e. Cr^{3+} in Ruby and Emerald)
 - ? Blue and Green Cu^{2+} compounds (i.e. malachite, turquoise)
 - ? Blue Co^{2+} compounds (i.e. Al_2CoO_4 , azurite)
- ? **Charge-transfer excitations (metal-metal, anion-metal)**
 - ? $\text{Fe}^{2+} \downarrow \text{Ti}^{4+}$ in sapphire
 - ? $\text{Fe}^{2+} \downarrow \text{Fe}^{3+}$ in Prussian Blue
 - ? $\text{O}^{2-} \downarrow \text{Cr}^{6+}$ in BaCrO_4
- ? **Valence to Conduction Band Transitions in Semiconductors**
 - ? WO_3 (Yellow)
 - ? CdS (Yellow) & CdSe (Black)
 - ? HgS (Cinnabar - Red)/ HgS (metacinnabar - Black)
- ? **Intraband excitations in Metals**
 - ? Strong absorption within a partially filled band leads to metallic lustre or black coloration

Band to Band Transitions Optical Properties of Semiconductors

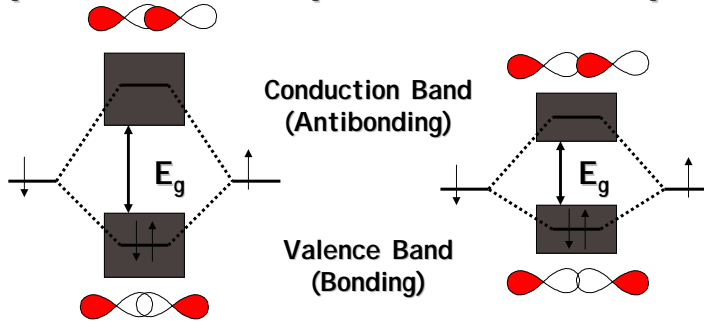
We can examine the relationship between bonding (spatial and energetic overlap) and optical properties by considering the band-gaps of those compounds which adopt the Sphalerite structure, with all ions in tetrahedral coordination (see figure to the right).



Since electronic transitions from the valence to conduction band span a fairly large range of energies, semiconductors act as sort of a long pass filter (only reflecting light with energy less than the band gap). This can give rise to only certain colors.

<u>Band Gap (eV)</u>	<u>Color</u>	<u>Example</u>
> 3.0	White	ZnO
3.0-2.5	Yellow	CdS
2.3-2.5	Orange	GaP
1.8-2.3	Red	HgS
< 1.8	Black	CdSe

Spatial Overlap and Band Gap (E_g)

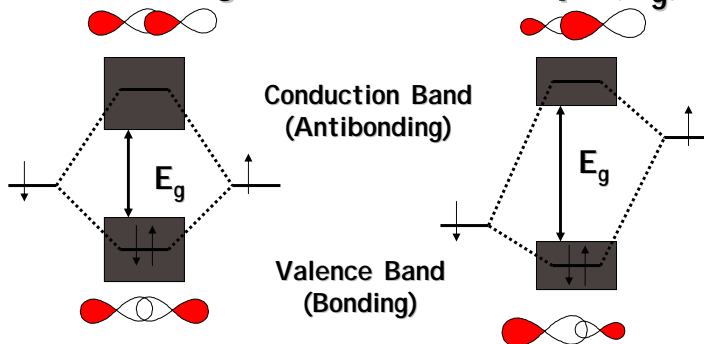


What are the effects of increasing the spatial overlap? Van-Vechten & Phillips assumed spatial overlap is proportional to $d^{-2.5}$ (where d is the bond distance).

Primary Effect: Increases the overall energy level of the conduction band (more highly antibonding) [$E_g \Rightarrow$]

Secondary Effect: Increases the bandwidth [$E_g \Leftarrow$]

Ionicity and Band Gap (E_g)




What are the effects of increasing the electronegativity difference between the elements?


Primary Effect: Increases the separation of the valence and conduction bands (the bonds become more ionic) [$E_g \Rightarrow$]

Secondary Effects: Decreases the bandwidth [$E_g \Leftarrow$] and reduces the covalent antibonding destabilization [$E_g \Leftarrow$]

Energetic & Spatial Overlap

				Al	Si	P		
				Zn	Ga	Ge	As	Se
				Cd	In	Sn	Sb	Te

 **Constant Spatial Overlap**
Increasing Ionicity ($E_g \Rightarrow$)

	Si	d=2.35 ? + θ =0	AIP	d=2.37 ? + θ =0.62		
	Ge	d=2.44 ? + θ =0	GaAs	d=2.45 ? + θ =0.43	ZnSe	d=2.45 ? + θ =0.90
	Sn	d=2.81 ? + θ =0	InSb	d=2.80 ? + θ =0.31	CdTe	d=2.81 ? + θ =0.61

Decreasing Spatial Overlap ($E_g \Leftarrow$)
Slowly Decreasing Ionicity ($E_g \Leftarrow$)

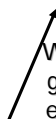
Experimental Band Gaps

Si	1.12 eV	AIP	2.45 eV		
Ge	0.67 eV	GaAs	1.42 eV	ZnSe	2.8 eV
Sn	0.08 eV	InSb	0.17 eV	CdTe	1.4 eV

Colored Semiconductors

CdS ($E_g=2.42$ eV)

CdTe ($E_g=1.50$ eV)

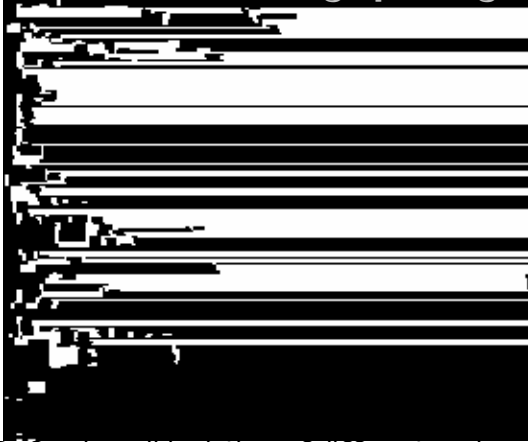

 We see that as the band gap decreases as either electronegativity of the anion decreases (CdS \downarrow CdTe, ZnS \downarrow ZnSe) or the overlap decreases (ZnS \downarrow CdS).

ZnS ($E_g=3.6$ eV)

ZnSe ($E_g=2.58$ eV)

Also note that colored compounds only result when $1.8 < E_g < 3.0$. Larger gaps give white/transparent & smaller gaps give black.

Bandgap Engineering



The GaAs ($E_g=1.4$ eV, $a=5.65\text{\AA}$) :
 AlAs ($E_g=2.1$ eV, $a=5.66\text{\AA}$) is
 among the most important for
 optoelectronic devices, because of
 the excellent lattice matching.

Figures taken from "Semiconductor
 Optoelectronic Devices", by P. Bhattacharya

By forming solid solutions of different semiconductors electrical engineers are able to design materials and junctions with specific band gaps. This approach often called band gap engineering is used to fabricate a number of devices, such as LEDs, semiconductor (diode, heterojunction, quantum well) lasers, photodetectors, solar cells, etc. In this field it is important to consider (a) the band gap of the two end members, (b) the lattice match between materials, (c) direct vs. indirect gap materials.

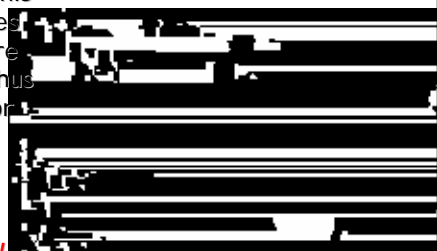
Light Emitting Diodes



Forward bias at a p-n junction forces minority carriers across the junction. This causes electrons to fall into vacant holes radiatively, giving off light. Dopants are important sites for localizing carriers, thus transitions are often CB \downarrow acceptor, or donor \downarrow VB

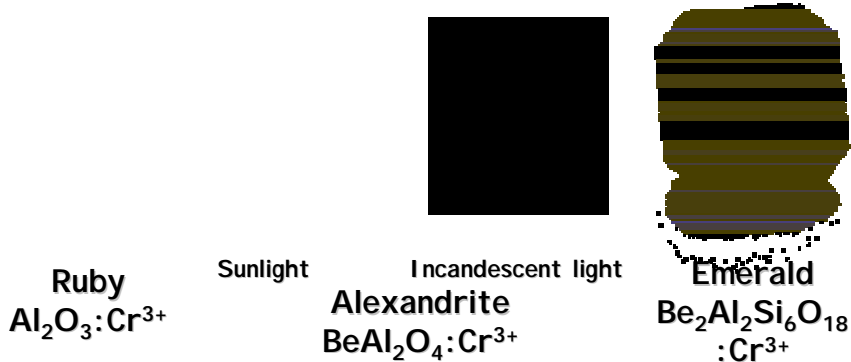
Common LED materials

- GaAs ($E_g=1.43$ eV) \downarrow Near IR
- GaP:N ($E_g = 2.25$ eV) \downarrow Yellow
- GaP:Zn,O ($E_g = 2.25$ eV) \downarrow Red
- GaN, SiC \downarrow Blue



Cr³⁺ Gemstones

Excitation of an electron from one d-orbital to another d-orbital on the same atom often times gives rise to absorption in the visible region of the spectrum. The Cr³⁺ ion in octahedral coordination is a very interesting example of this. Slight changes in its environment lead to changes in the splitting of the t_{2g} and e_g orbitals, which changes the color the material. Hence, Cr³⁺ impurities are important in a number of gemstones.



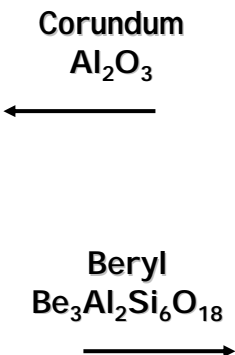
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	Ruby	Alexandrite	Emerald
Host	Corundum Al ₂ O ₃	Chrysoberyl BeAl ₂ O ₄	Beryl Be ₃ Al ₂ Si ₆ O ₁₈
t _{2g} e _g Splitting	2.23 eV	2.17 eV	2.05 eV
Color	Red	Blue-Green (Daylight) Red (Candlelight)	Green

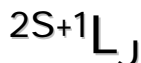
Cr³⁺ Gemstones-Host Structures

In each of the three gemstones Cr³⁺ impurities substitute for Al³⁺ on an octahedral site.



Term Symbols

Term symbols are shorthand notation for representing the electron configuration of a localized ion.



- ? S = The total spin quantum # of the atom/ion (keep in mind that each electron has a spin angular momentum of +? or -?)
- ? L = The total angular momentum quantum #
- ? J = L+S

See any advanced inorganic chemistry text for a description of term symbols. We will concentrate on the spin value, as it can easily be interpreted to determine the number of unpaired electrons.

Transitions where the total spin changes require at least one electron to reverse its spin. Such transitions are called spin forbidden transitions. They are very weak transitions.

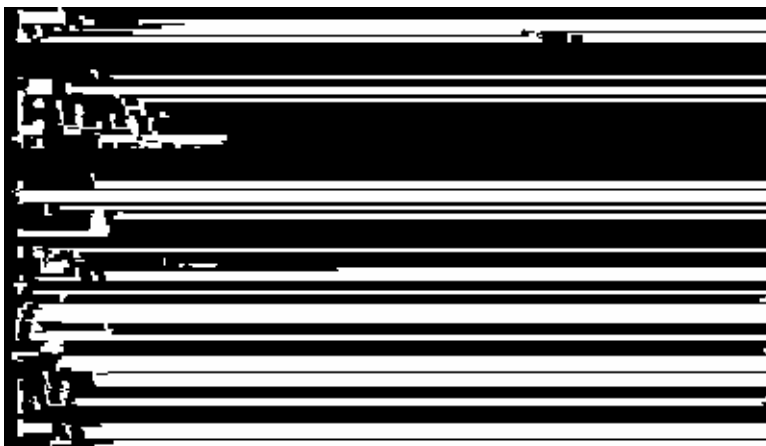
Tunabe-Sugano Diagram Cr³⁺

The Tunabe-Sugano diagram below shows the allowed electronic excitations for Cr³⁺ in an octahedral crystal field (${}^4A_2 \downarrow {}^4T_1$ & ${}^4A_2 \downarrow {}^4T_2$). The dotted vertical line shows the strength of the crystal field splitting for Cr³⁺ in Al₂O₃. The ${}^4A_2 \downarrow {}^4T_1$ energy difference corresponds to the splitting between t_{2g} and e_g



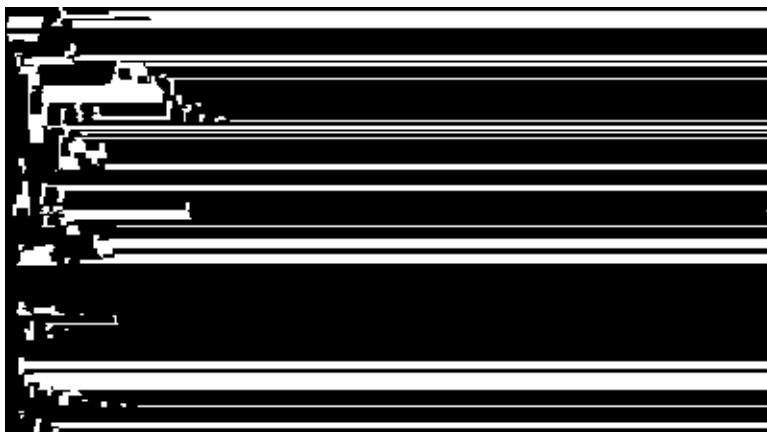
Ruby Red

This figure (taken from ?The Physics and Chemistry of Color, by Kurt Nassau) shows the two spin allowed transitions for Cr³⁺ in ruby give rise to absorption in the violet and the green. Since the transmission in the red is much more than the transmission in the blue rubies are red. The ${}^2E \downarrow {}^4A_2$ fluorescence adds to the deep red color of a ruby.



Emerald Green

This figure (also taken from "The Physics and Chemistry of Color", by Kurt Nassau) shows the transitions for Cr^{3+} in beryl. The crystal field splitting is a little bit smaller than ruby, so that the lower energy absorption is shifted to lower energy taking out much of the reflectance of red light and changing the color to green.



The Alexandrite Effect

Alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) has a crystal field splitting, 2.17 eV, intermediate between ruby (Al_2O_3 - 2.23 eV) and Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ - 2.07 eV). Thus it has some transmittance in the red and a fairly large transmittance in the blue-green region of the spectrum. This leads to very interesting color and optical properties.

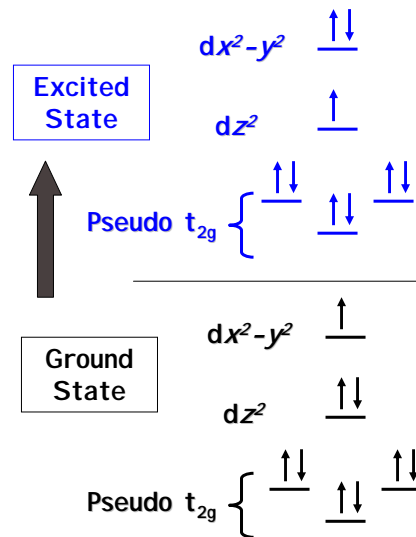
In the presence of reddish light, as from a candle or an incandescent light source, it is deep red in color. Resembling a ruby.

In the presence of light with a major component in the blue/UV region of the spectrum, such as sunlight or fluorescent light, the reflectance in the blue-green region of the spectrum dominates and alexandrite resembles an emerald.

Cu²⁺ Transitions

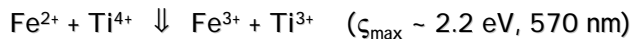
The d⁹ configuration of Cu²⁺, leads to a Jahn-Teller distortion of the regular octahedral geometry, and sets up a fairly low energy excitation from dx²-y² level to a dz² level. If this absorption falls in the red or orange regions of the spectrum, a green or blue color can result. Some notable examples include:

Malachite (green) →
Cu2CO3(OH)2
Turquoise (blue-green)
CuAl6(PO4)(OH)8*4H2O
Azurite (blue)
Cu3(CO3)2(OH)2 →



Charge Transfer in Sapphire

The deep blue color the gemstone sapphire is also based on impurity doping into Al₂O₃. The color in sapphire arises from the following charge transfer excitation:



The transition is facilitated by the geometry of the corundum structure where the two ions share an octahedral face, which allows for favorable overlap of the dz² orbitals.

Unlike the d-d transition in Ruby, the charge-transfer excitation in sapphire is fully allowed. Therefore, the color in sapphire requires only ~ 0.01% impurities, while ~ 1% impurity level is needed in ruby.

In the mineral ilmenite, FeTiO₃, all of the Al³⁺ has been replaced by Fe²⁺/Ti⁴⁺. The absorption band broadens out and the color becomes black.

Anion to Metal Charge Transfer

Normally charge transfer transitions from an anion (i.e. O^{2-}) HOMO to a cation LUMO fall in the UV region of the spectrum and do not give rise to color. However, d^0 cations in high oxidation states are quite electronegative lowering the energy of the transition metal based LUMO. This moves the transition into the visible region of the spectrum. The strong covalency of the metal-oxygen bond also strongly favors tetrahedral coordination, giving rise to a structure containing isolated MO_4^{n-} tetrahedra. Some examples of this are as follows:

$Ca_3(VO_4)_2$ (tetrahedral V^{5+})	Color = White
$PbCrO_4$ (tetrahedral Cr^{6+})	Color = Yellow
$CaCrO_4$ & K_2CrO_4 (tetrahedral Cr^{6+})	Color = Yellow
$PbMoO_4$ (tetrahedral Mo^{6+})	Color = Yellow
$KMnO_4$ (tetrahedral Mn^{7+})	Color = Maroon