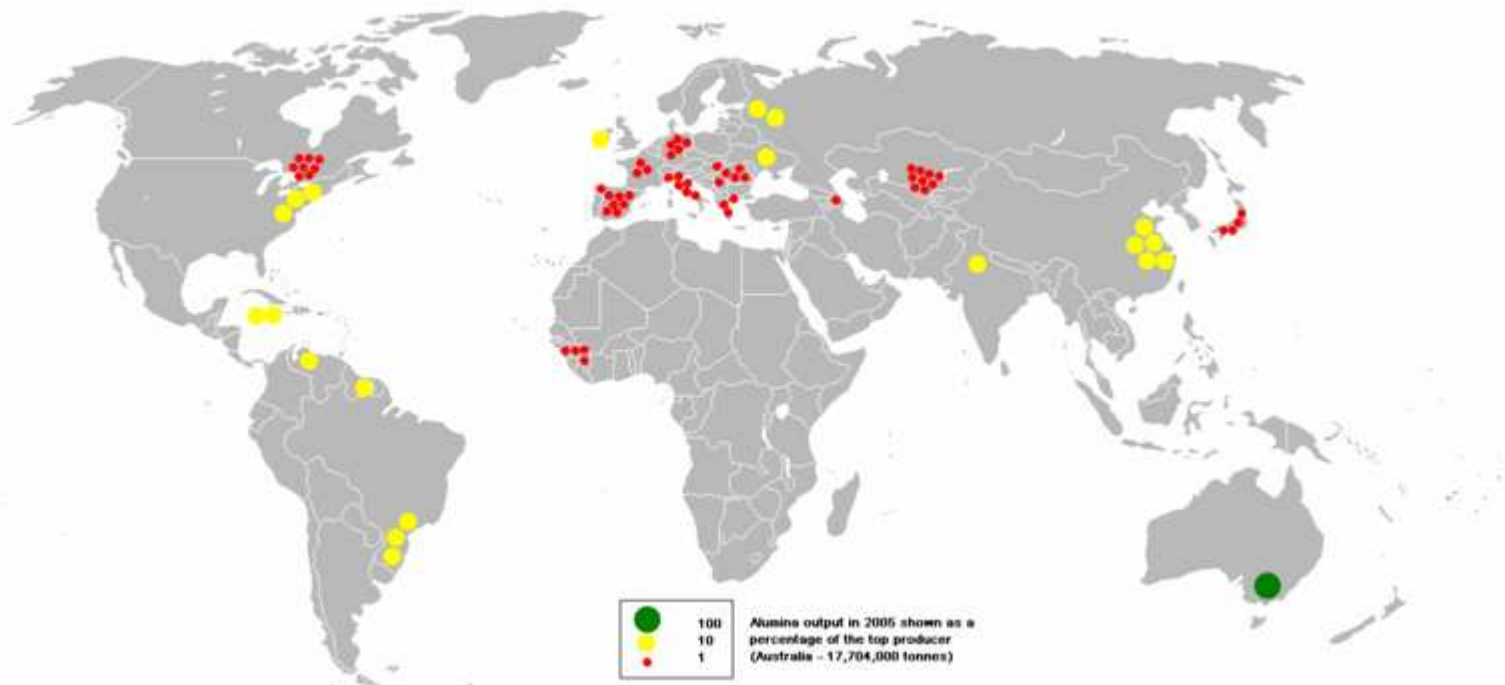

Zasto su rubini crvene boje?

Predavanje 4

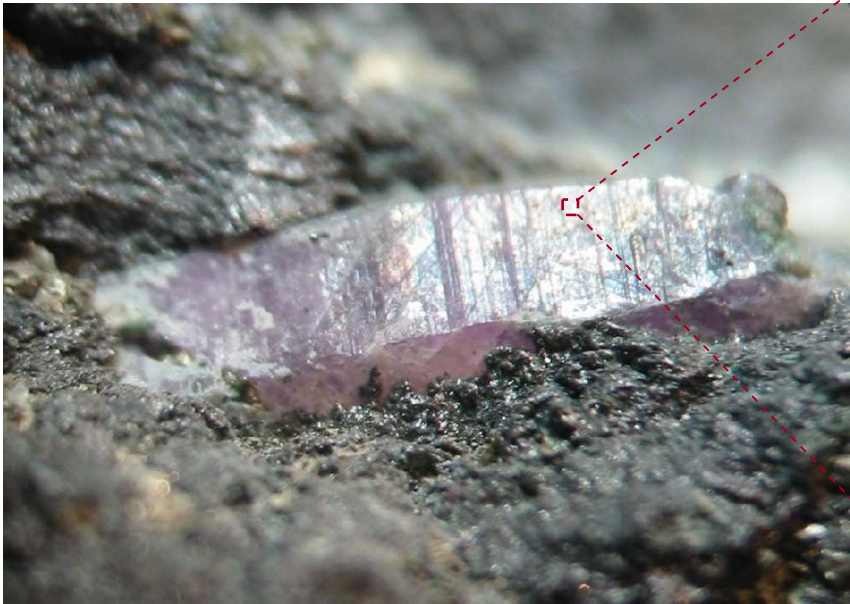
Al_2O_3 – aluminij oksid

- *korundum* (corundum)
 - sanskrit “kurivinda” (rubin)
 - hindu “kurand”
 - tamil “kurundam”
- bijeli ili bezbojni safir



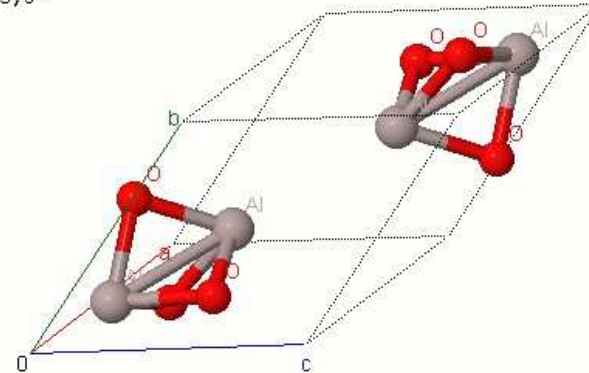
Al_2O_3 – aluminij oksid

- *korundum* (corundum)
 - sanskrit “kurivinda” (rubin)
 - hindu “kurand”
 - tamil “kurundam”
- bijeli ili bezbojni safir



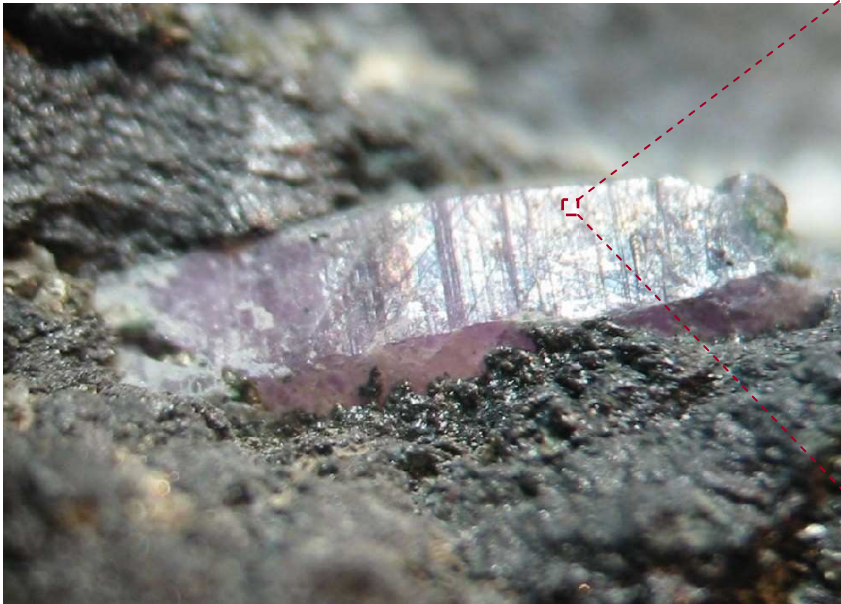
$\text{Al}_2\text{O}_3 =$ kompleksni ion ion koji sadrži središnji metalni kation vezan s jednim ili više iona ili molekula

R -3 c
a=5,120Å
b=5,120Å
c=5,120Å
 $\alpha=55,3^\circ$
 $\beta=55,3^\circ$
 $\gamma=55,3^\circ$

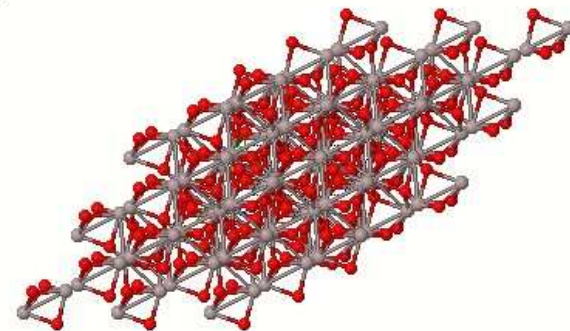


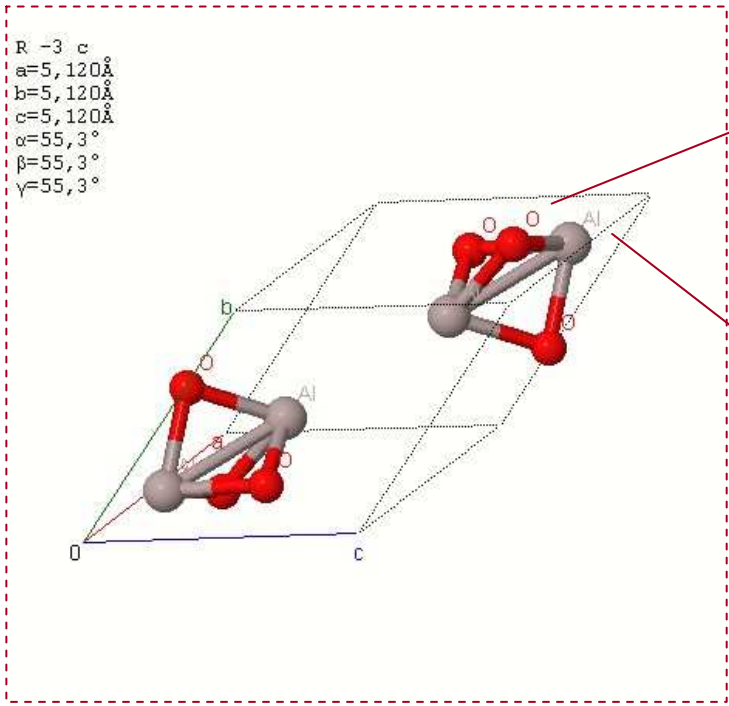
Al_2O_3 – aluminij oksid

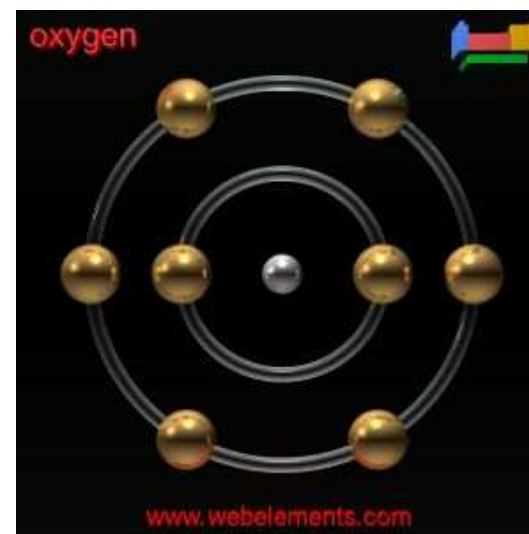
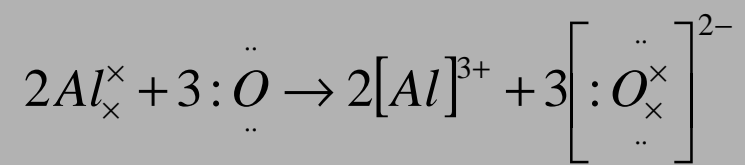
- *korundum* (corundum)
 - sanskrit “kurivinda” (rubin)
 - hindu “kurand”
 - tamil “kurundam”
- bijeli ili bezbojni safir

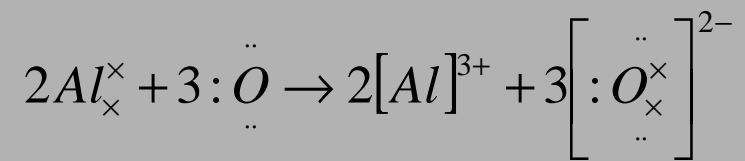


R -3 c
a=5,120Å
b=5,120Å
c=5,120Å
 $\alpha=55,3^\circ$
 $\beta=55,3^\circ$
 $\gamma=55,3^\circ$

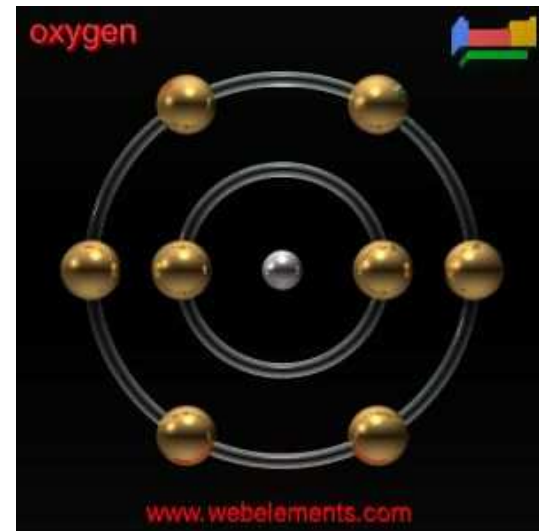


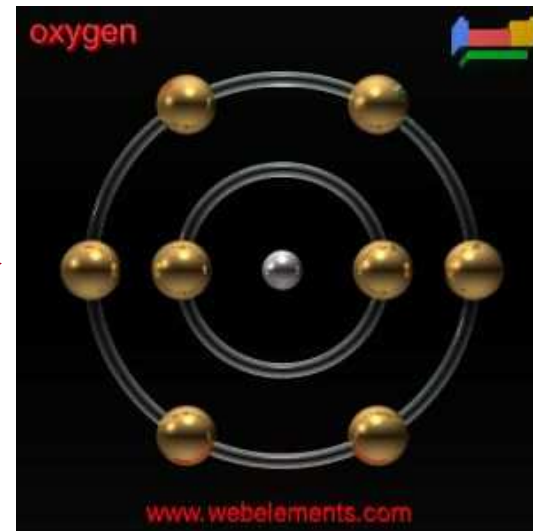
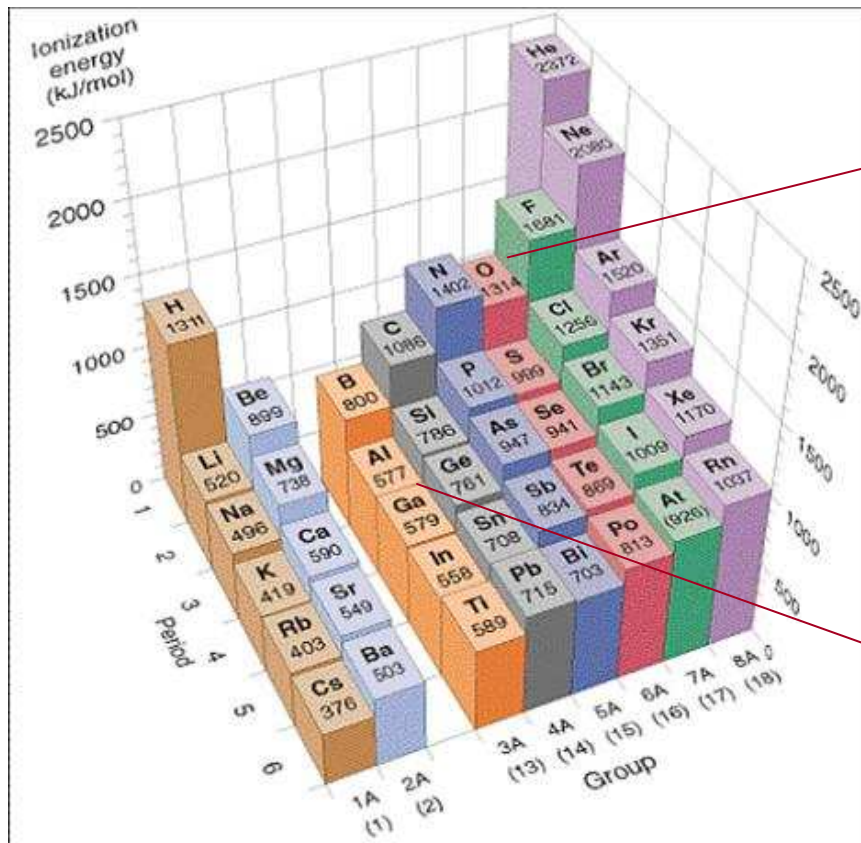


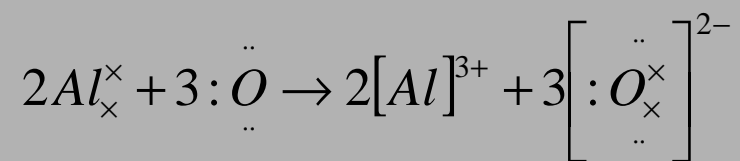




- svi elektroni su spareni
- potpuno popunjene ili prazne ljuske

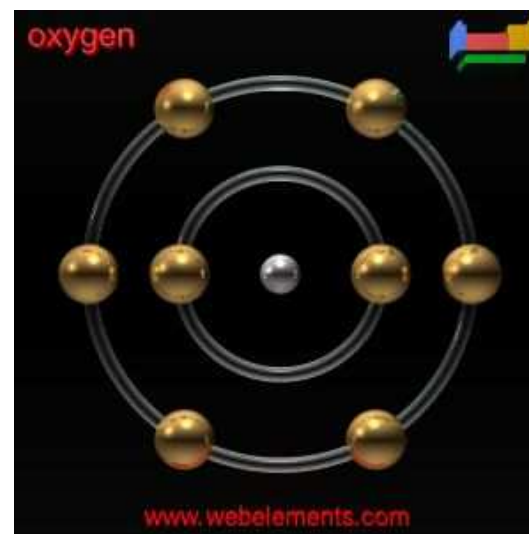


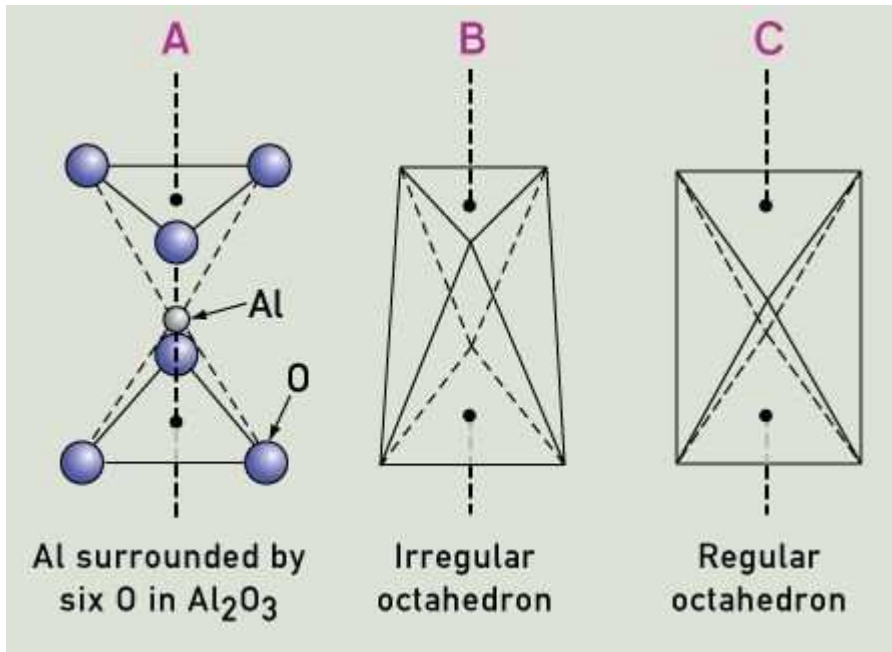




- svi elektroni su spareni
- potpuno popunjene ili prazne ljuske

- bezbojan (za vidljivi dio spektra)



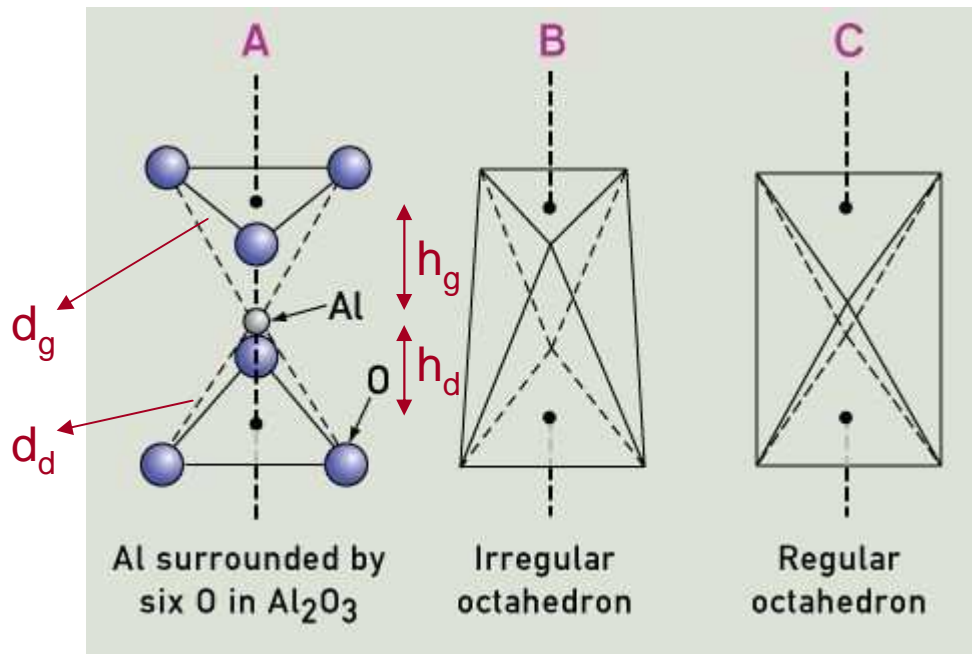


Kisik

- $R_{\text{ion}} = 2.8\text{\AA}$
- heksagonalno slozeni slojevi

Aluminij

- $R_{\text{ion}} = 1.1\text{\AA}$
- između slojeva kisika
- na svaka 2 od 3 mjesta



- $d_g < d_d$

- $h_g > h_d$ (50% Al)

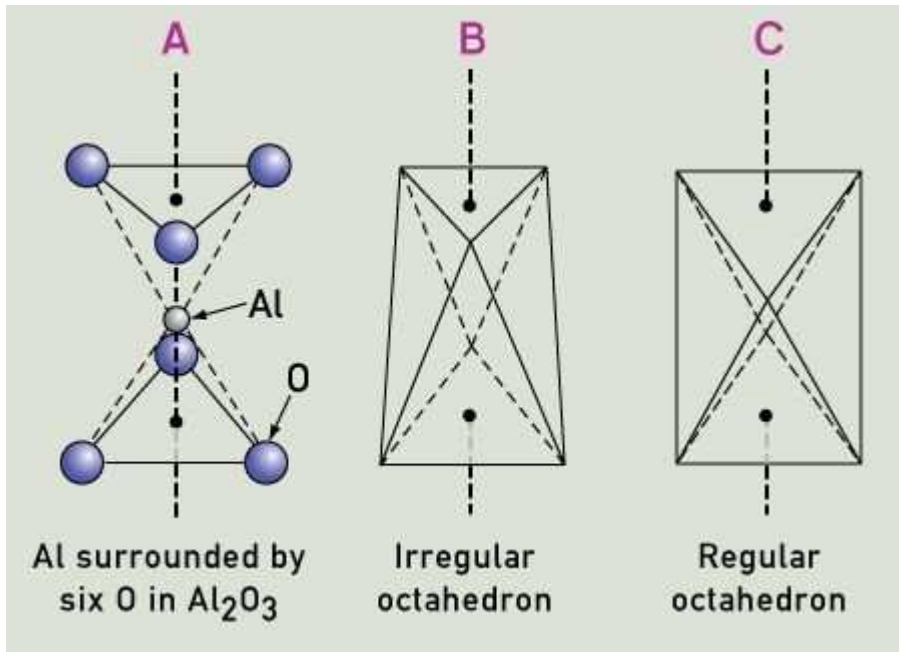
- $h_g < h_d$ (50% Al)

Kisik

- $R_{\text{ion}} = 2.8\text{\AA}$
- heksagonalno slozeni slojevi

Aluminij

- $R_{\text{ion}} = 1.1\text{\AA}$
- izmedu slojeva kisika
- na svaka 2 od 3 mjesta



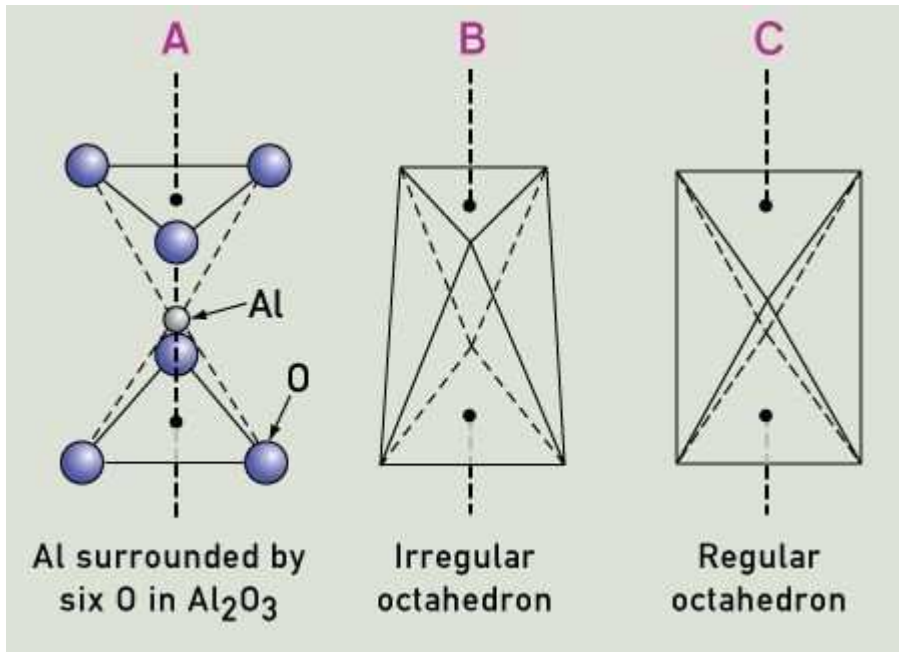
“Ionic point of view”

Aproksimacija:

kristalno polje → ion Al³⁺ u elektrostatskom polju iona O²⁻

simetrija

jakost
el. polja



ioni O^{2-} = *ligandi* = ioni ili molekule koji okružuju metalni ion u kompleksnom ionu

“General point of view”

Aproksimacija:

polje liganada →
elektrici naboji +
osobine vezanja

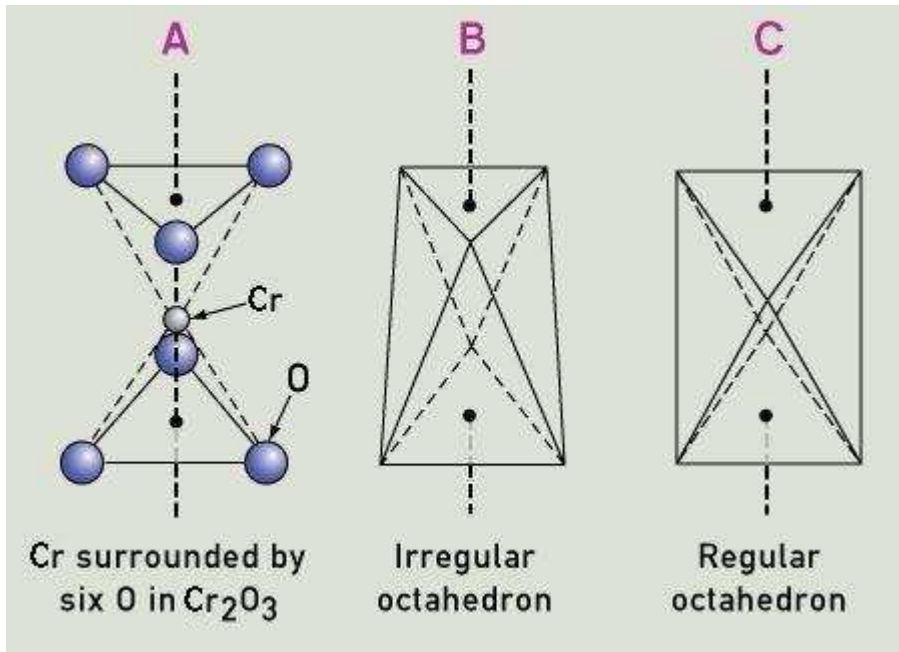
simetrija

jakost
polja
liganada

Teorija molekularnih orbitala

Teorija polja liganada

Teorija kristalnog polja

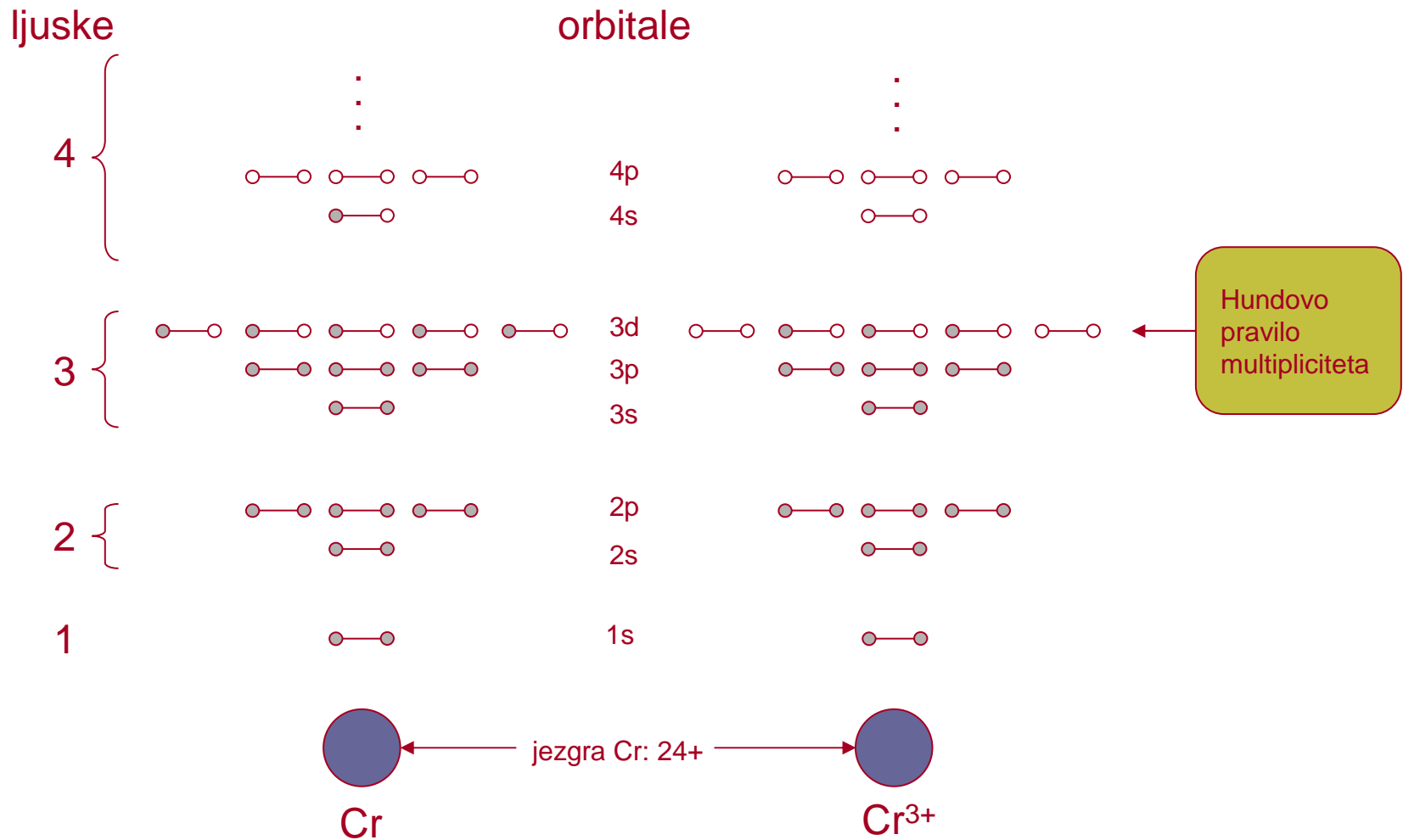


Rubin → lat. ruber =
“crveno”

- korundum
+ Cr umjesto Al (svaki stoti Al)
- 1% Cr₂O₃
- Al₂O₃:1%Cr ili
99Al₂O₃·1Cr₂O₃ ili
Al_{1.98}Cr_{0.02}O₃ ili
Al₂O₃:1%Cr₂O₃

$$R_{\text{Cr}^{3+}} = 1.2\text{\AA} \geq R_{\text{Al}^{3+}}$$

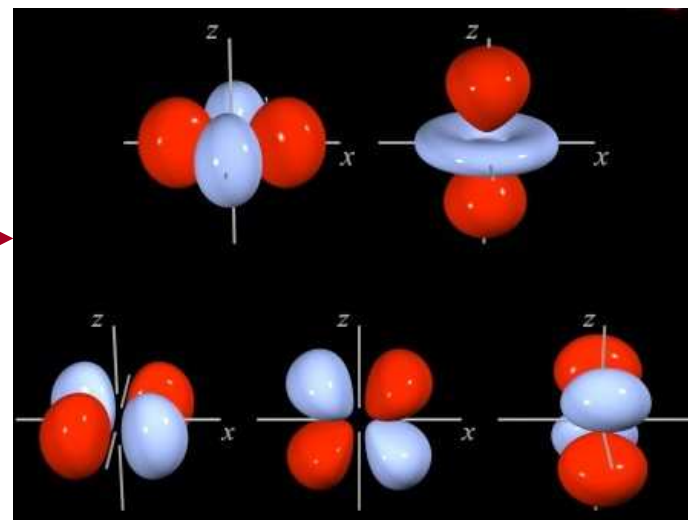
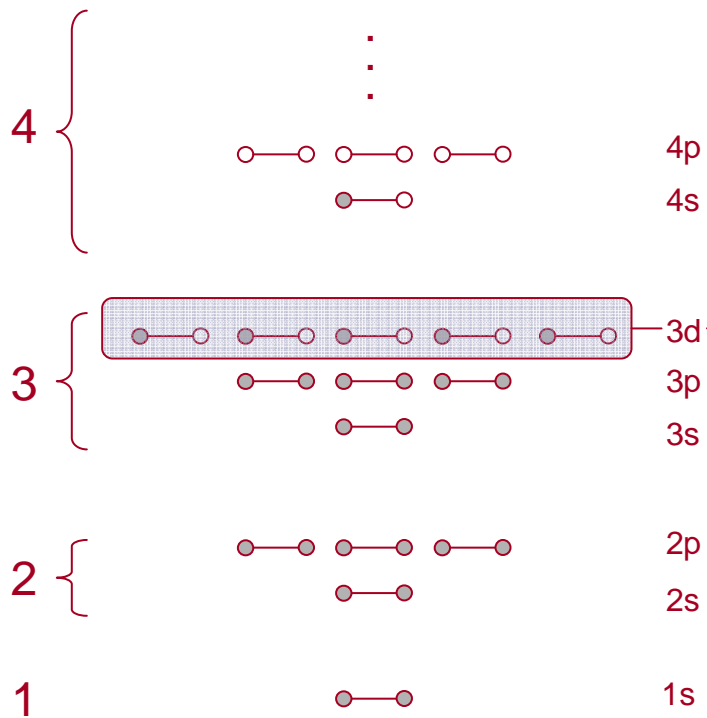
Elektronska konfiguracija osnovnog stanja atoma i iona kroma

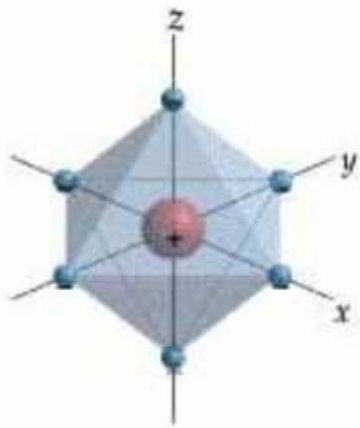


Elektronska konfiguracija osnovnog stanja atoma i iona kroma

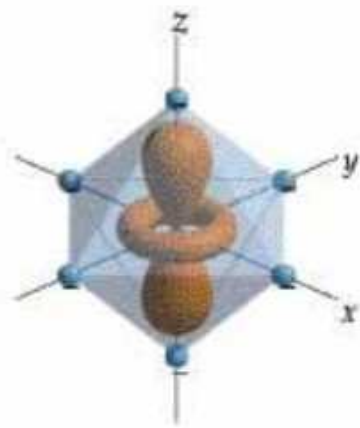
ljuske

orbitale



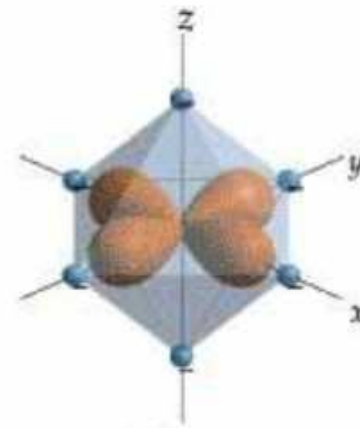


(a)



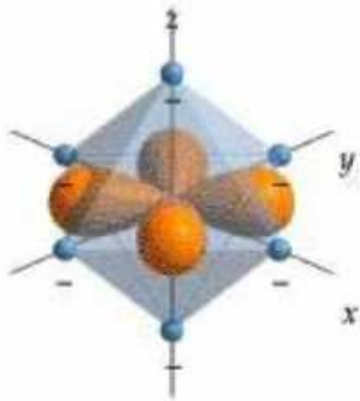
d_{z^2}

(b)

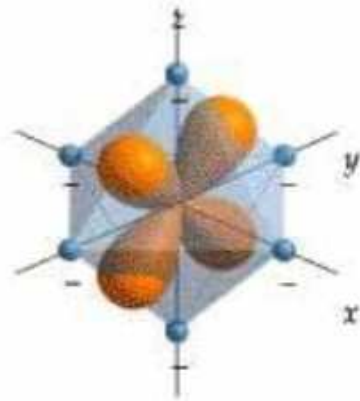


$d_{x^2 - y^2}$

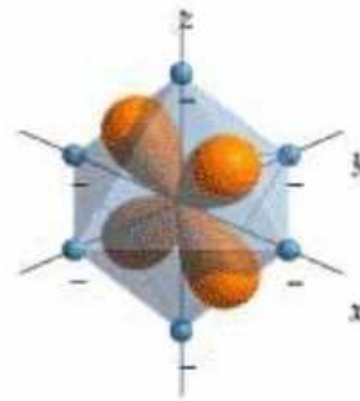
(c)



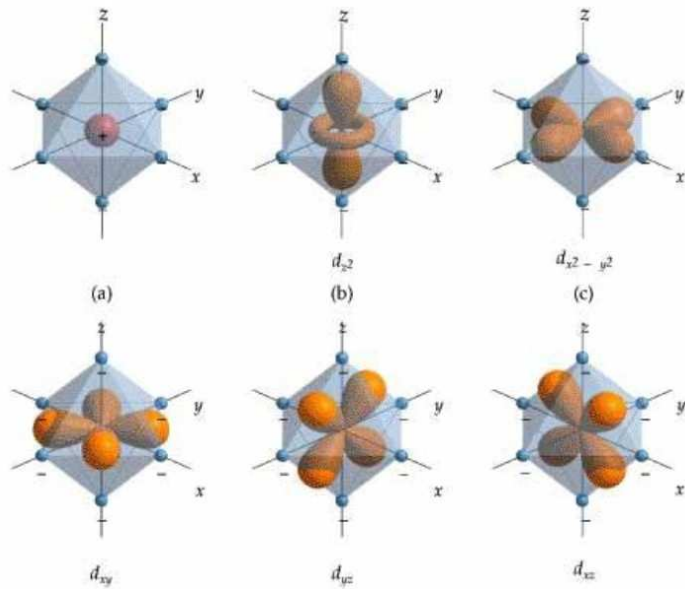
d_{xy}



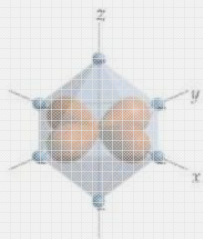
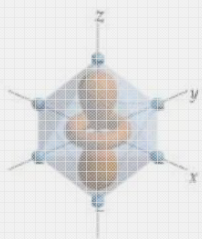
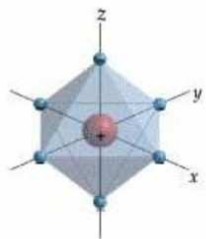
d_{yz}



d_{xz}



- e – e medudjelovanje liganada i d -orbitala
- jace odbijanje \rightarrow veca energija



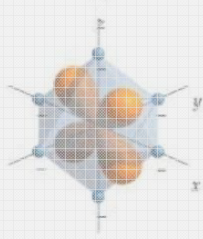
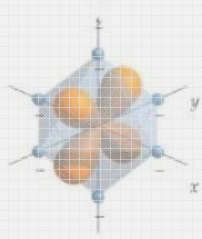
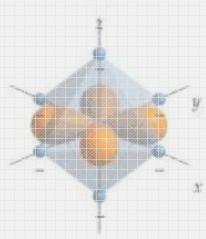
d_{z^2}

$d_{x^2 - y^2}$

(a)

(b)

(c)



d_{xy}

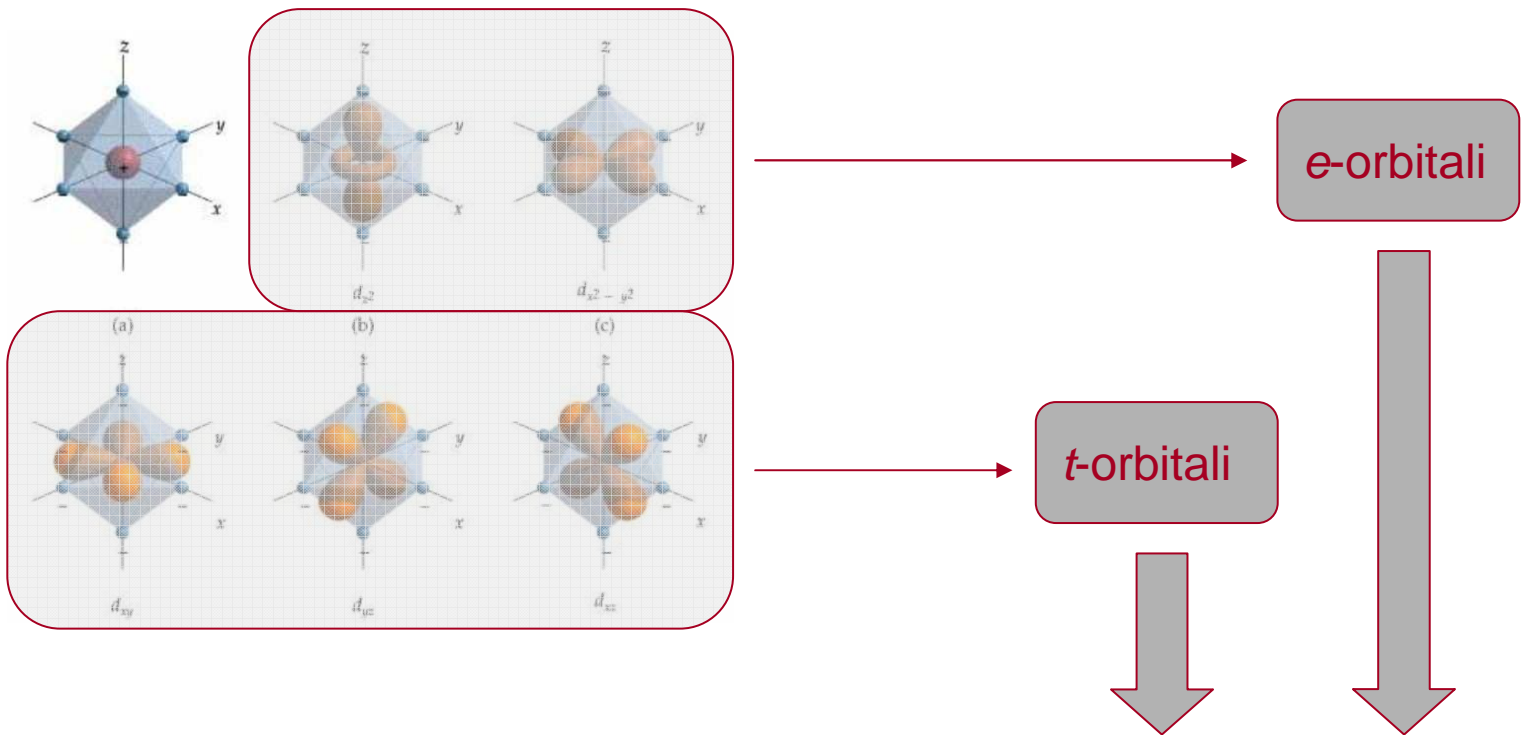
d_{xz}

d_{yz}

e-orbitali

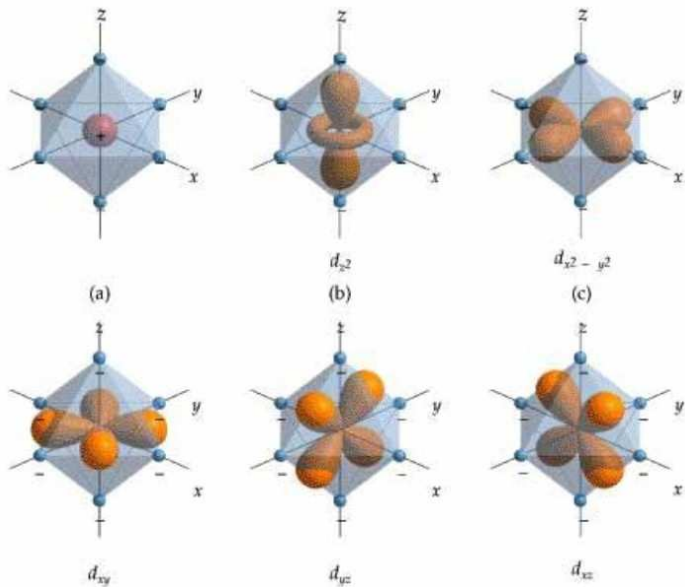
t-orbitali

- e – e međudjelovanje liganada i d-orbitala
- jace odbijanje → veca energija



- $e - e$ međudjelovanje liganada i d -orbitala
- jace odbijanje \rightarrow veca energija

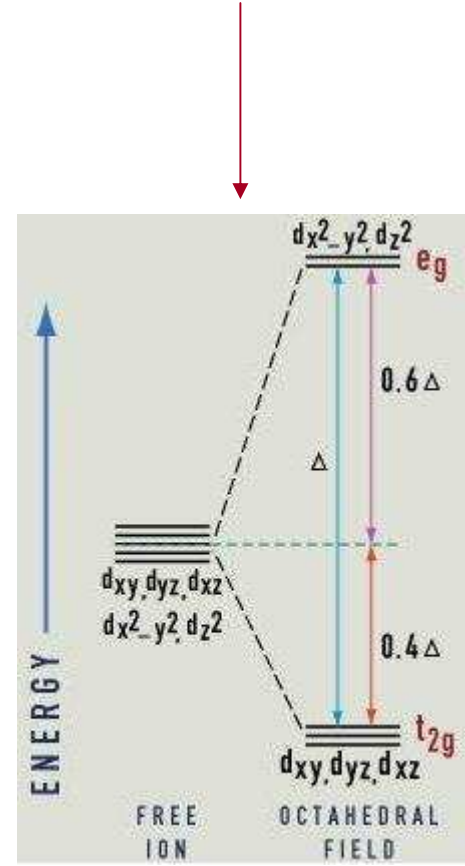
- $E_{e\text{-orbitala}} > E_{t\text{-orbitala}}$
- pojavljuje se rascjep u energijskim nivoima, $\Delta_o = \text{rascjep polja liganada}$

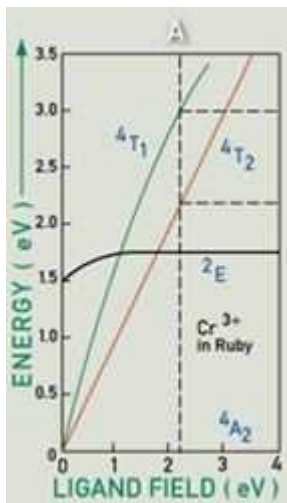


rascjep polja liganada, Δ_o
(*ligand field splitting*)

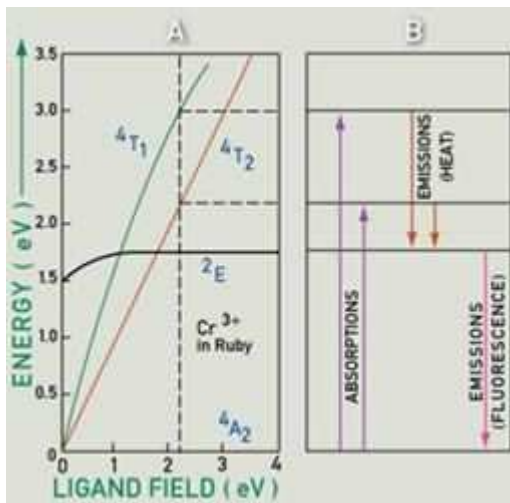
Δ_o ovisi o:

- simetriji kompleksnog iona
- jakosti polja liganada



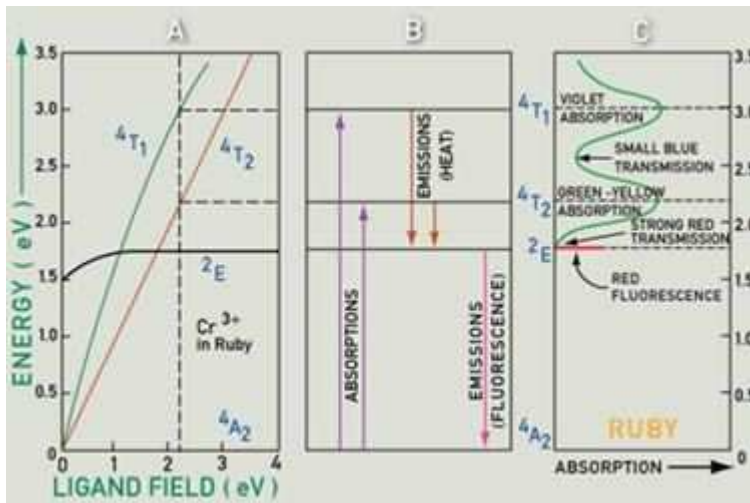


Energijski nivoi
Cr³⁺ u
trigonalno
pomaknutom
oktaedarskom
okruzenju



Energijski nivoi Cr^{3+} u trigonalno pomaknutom oktaedarskom okruženju

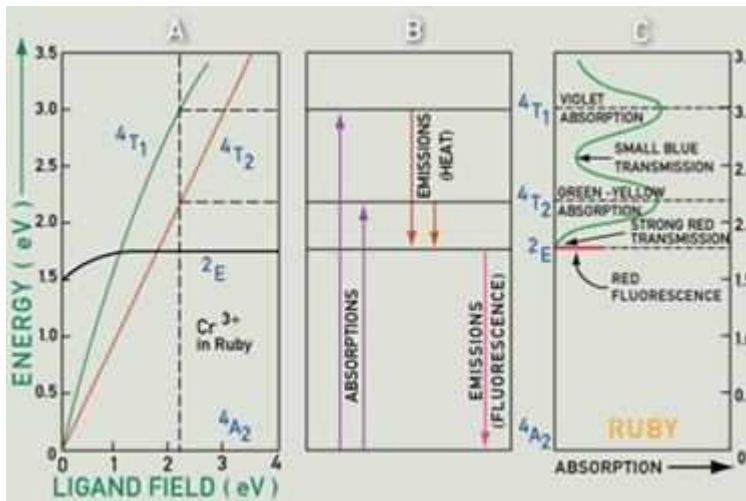
Prijelazi između energijskih nivoa u rubinu



Energijski nivoi Cr³⁺ u trigonalno pomaknutom oktaedarskom okruženju

Prijelazi između energijskih nivoa u rubinu

Absorpcijski spektar i fluorescencija u rubinu



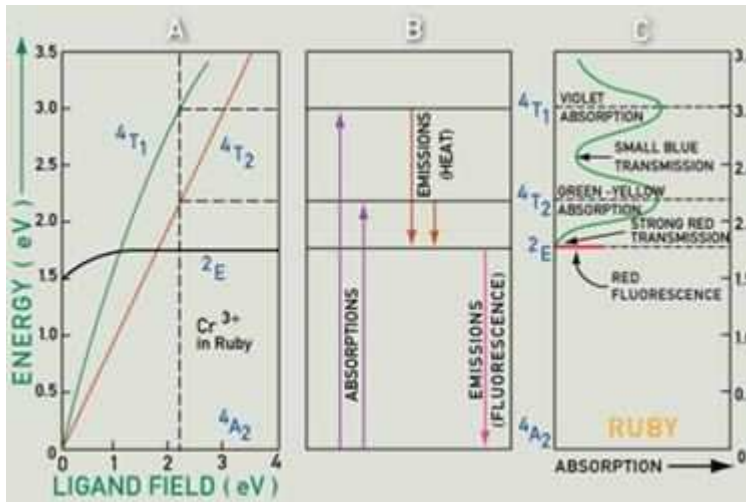
Absorpcije u rubinu:

- ${}^4A_2 \rightarrow {}^4T_2$ 2.2 eV (zuto-zelena)
- ${}^4A_2 \rightarrow {}^4T_1$ 3.0 eV (ljubicasta)
- nemala u plavom dijelu spektra
- **nula u crvenom dijelu spektra**
- utjecaj vibracija → spektralne vrpce

Energijski nivoi Cr³⁺ u trigonalno pomaknutom oktaedarskom okruzenju

Prijelazi između energijskih nivoa u rubinu

Absorpcijski spektar i fluorescencija u rubinu



Absorpcije u rubinu:

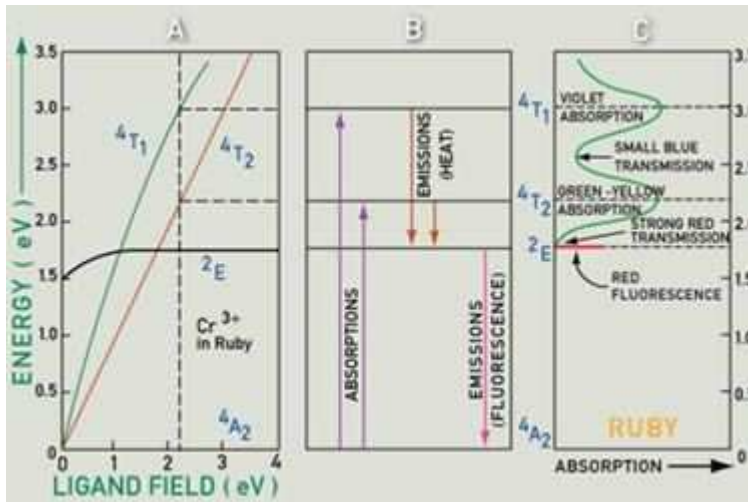
- ${}^4A_2 \rightarrow {}^4T_2$ 2.2 eV (zuto-zelena)
- ${}^4A_2 \rightarrow {}^4T_1$ 3.0 eV (ljubicasta)
- nemala u plavom dijelu spektra
- **nula u crvenom dijelu spektra**
- utjecaj vibracija → spektralne vrpce

Energijski nivoi Cr^{3+} u trigonalno pomaknutom oktaedarskom okruženju

Prijelazi između energijskih nivoa u rubinu

Absorpcijski spektar i fluorescencija u rubinu





Elektroni ne mogu dugo ostati u pobudenim stanjima

Emisije u rubinu

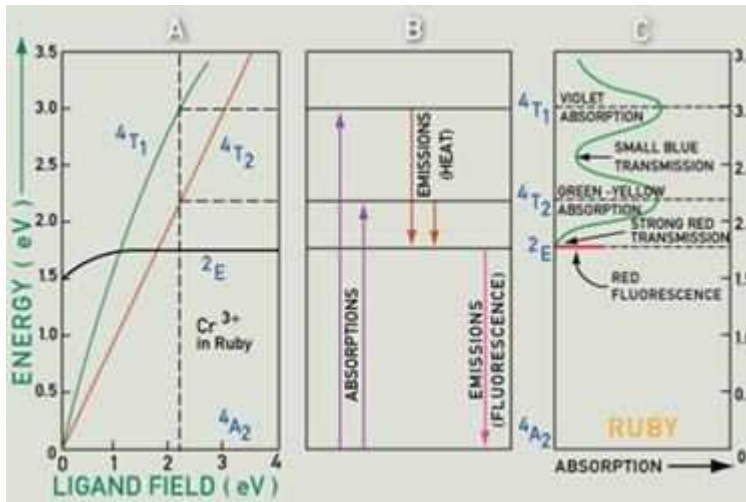
Nedozvoljene (zasto?):

- $4T_1 \rightarrow 4A_2$
- $4T_2 \rightarrow 4A_2$

Dozvoljene:

- $4T_1 \rightarrow 2E$ 1.2 eV
- $4T_2 \rightarrow 2E$ 0.4 eV

toplina



Elektroni ne mogu dugo ostati u pobudenim stanjima

Emisije u rubinu

Nedozvoljene (zasto?):

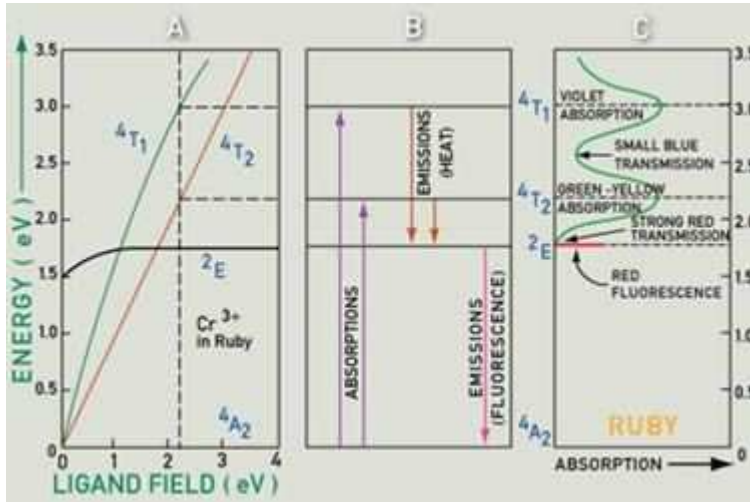
- $4T_1 \rightarrow 4A_2$
- $4T_2 \rightarrow 4A_2$

Dozvoljene:

- $4T_1 \rightarrow 2E$ 1.2 eV
- $4T_2 \rightarrow 2E$ 0.4 eV
- $2E \rightarrow$ osn. stanje 1.79 eV

toplina

fluorescencija



Fluorencencija u rubinu

- R₁ linija → 693.5 nm
- R₂ linija → 692.3 nm

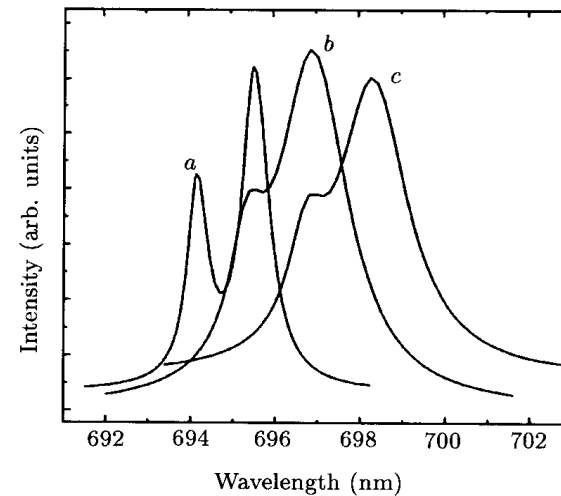
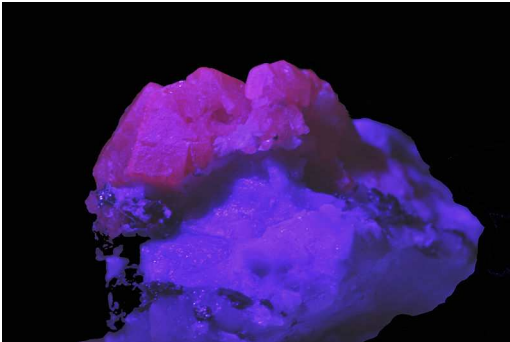
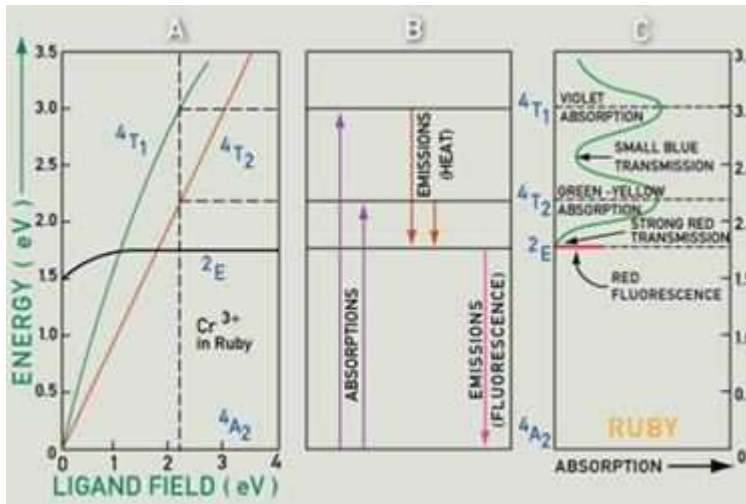
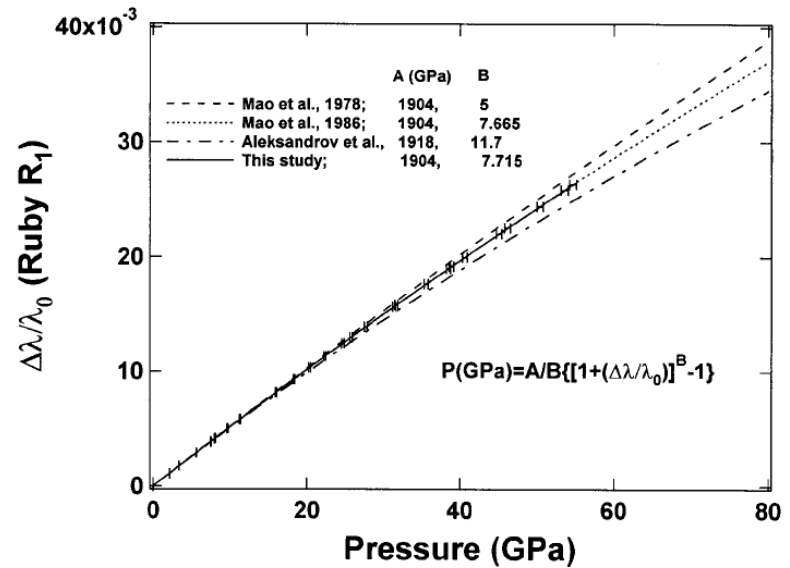
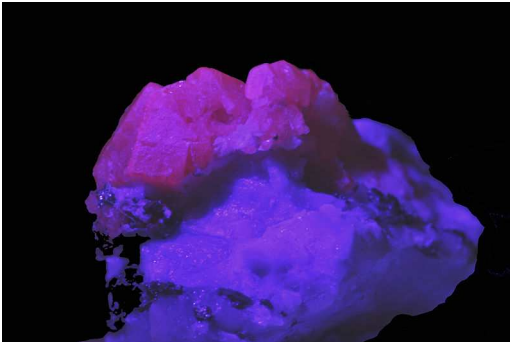


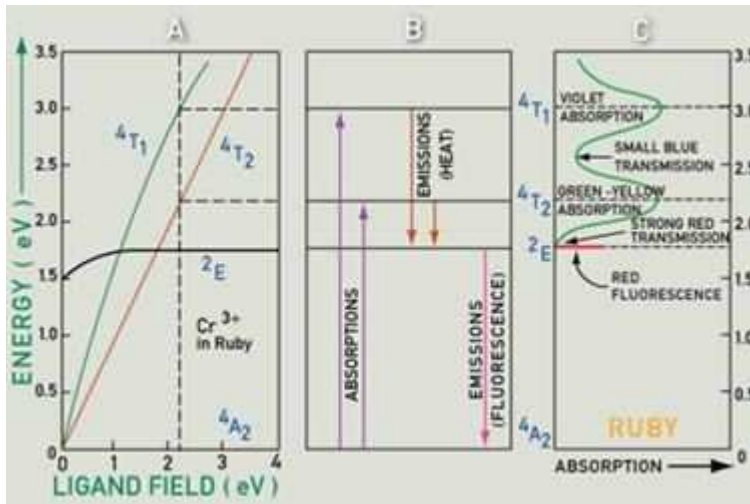
Fig. 2. Ruby fluorescence spectra measured in CaSO₄ powder at room temperature, showing broadening due to pressure. *a*: Ambient, *b*: $P = 2.7$ GPa, *c*: $P = 11.1$ GPa.



Fluorescencija u rubinu

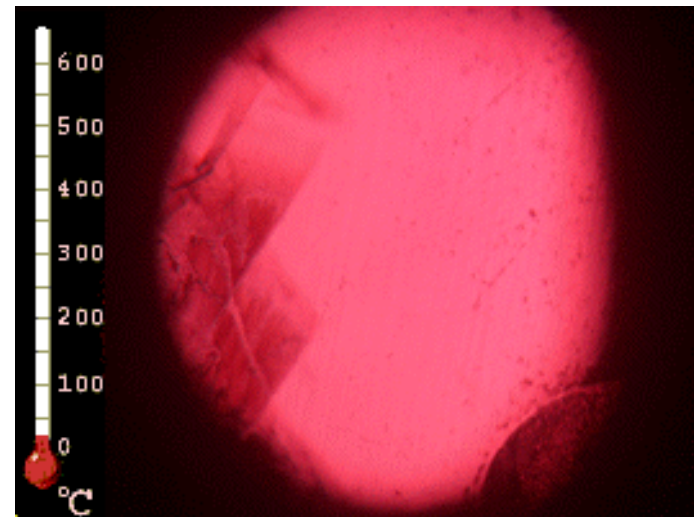
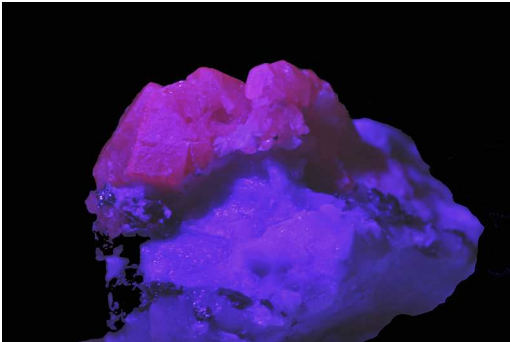
- R₁ linija → 693.5 nm
- R₂ linija → 692.3 nm

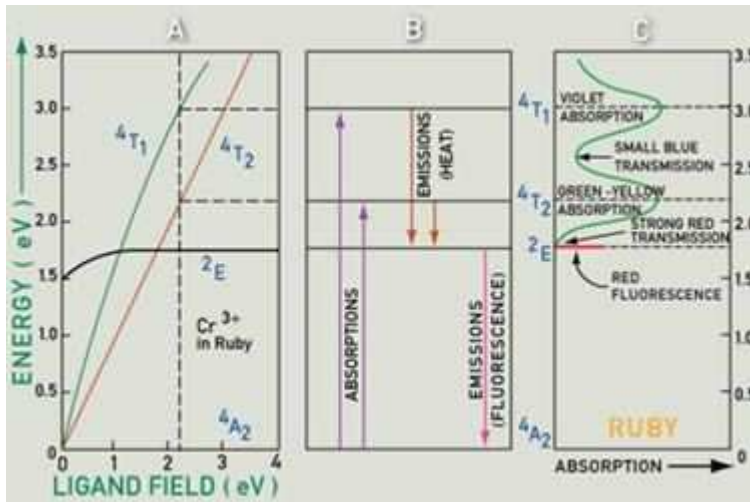




Fluorencencija u rubinu

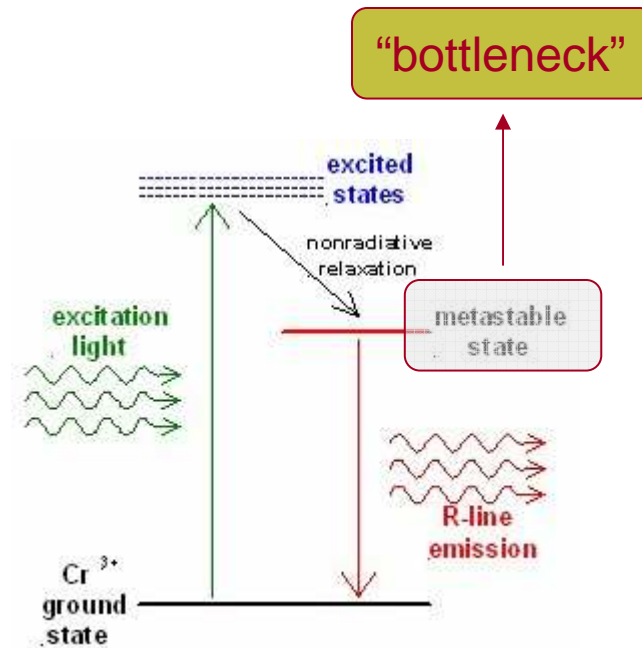
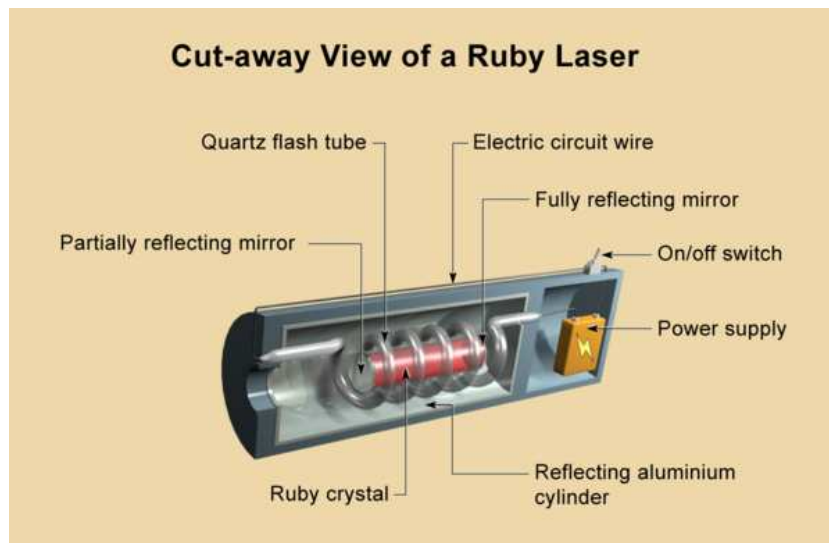
- R_1 linija \rightarrow 693.5 nm
- R_2 linija \rightarrow 692.3 nm

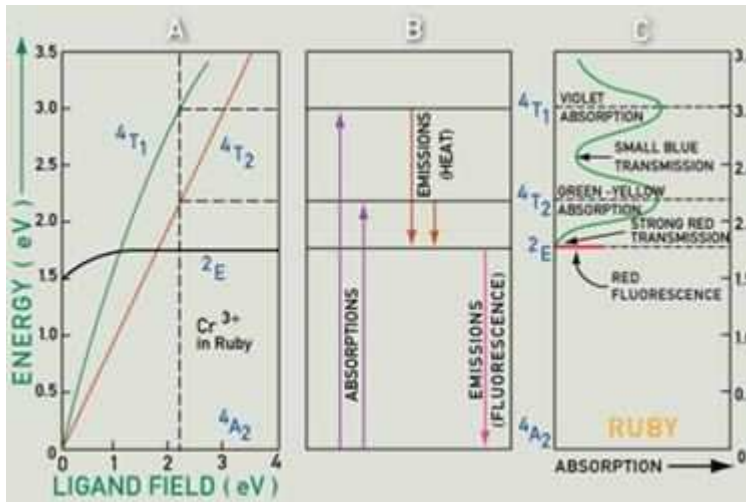




Fluorescencija u rubinu

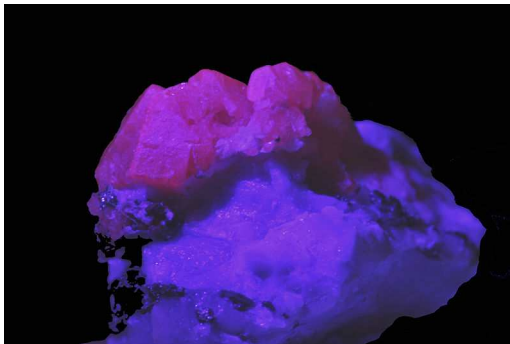
- R₁ linija → 693.5 nm
- R₂ linija → 692.3 nm





Fluorescencija u rubinu

- R₁ linija → 693.5 nm
- R₂ linija → 692.3 nm
- Fe nečistoce → suzbijanje fluorescencije

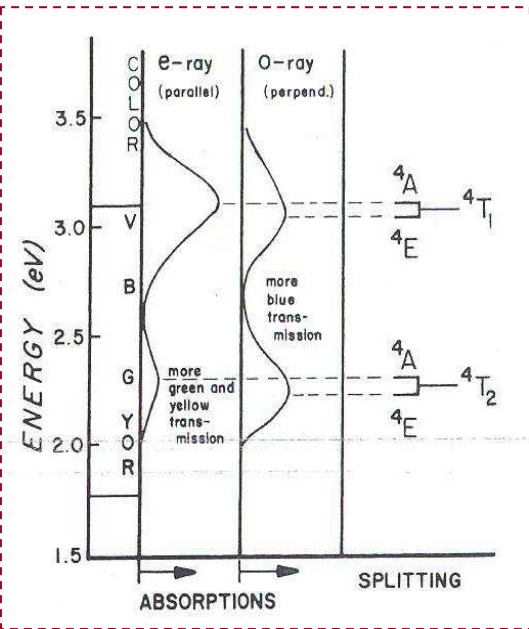
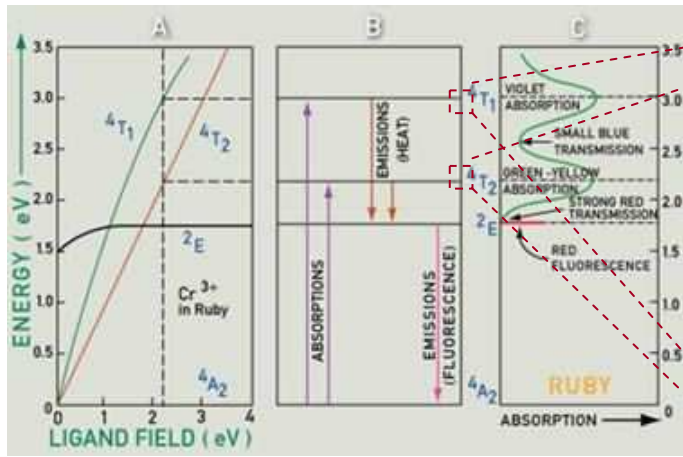


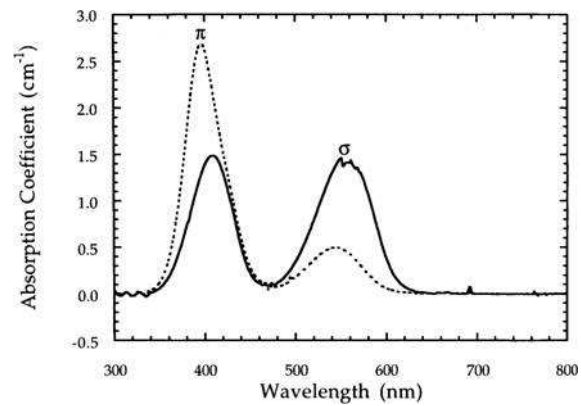
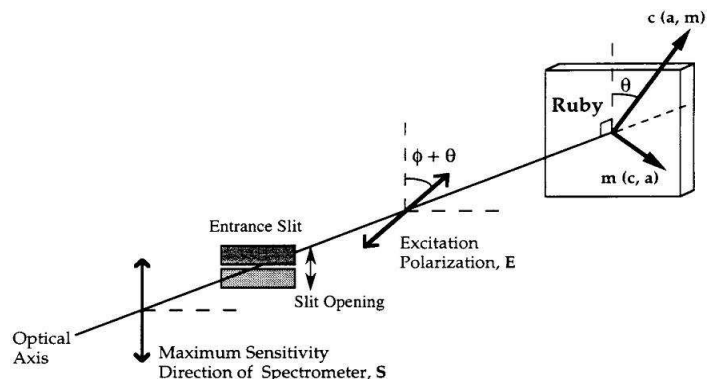
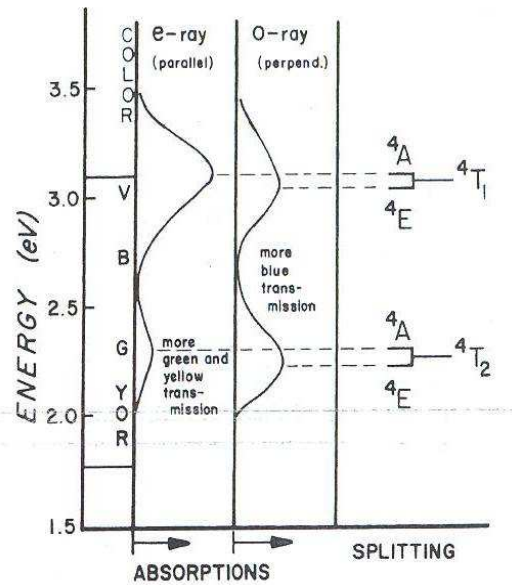
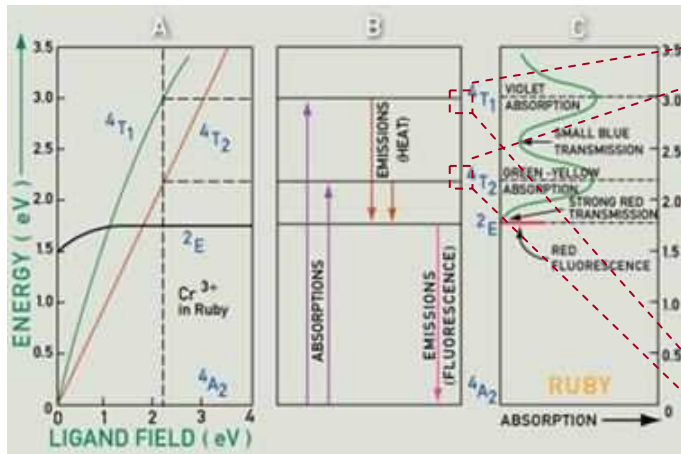
• apsorpcijski spektar

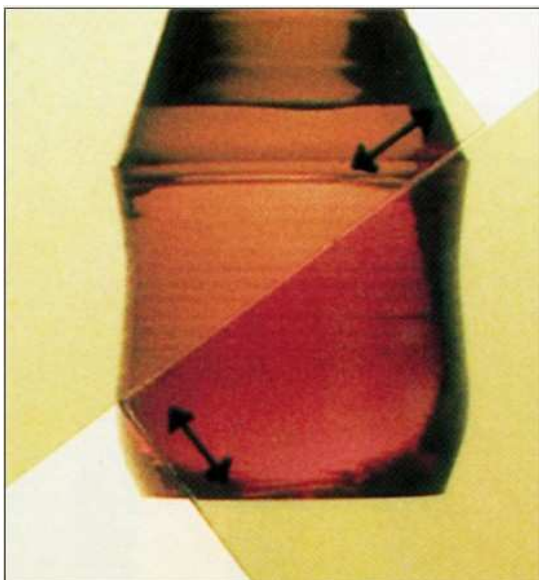
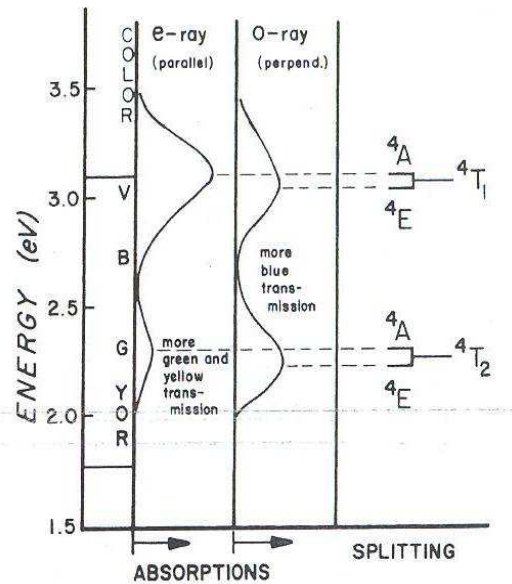
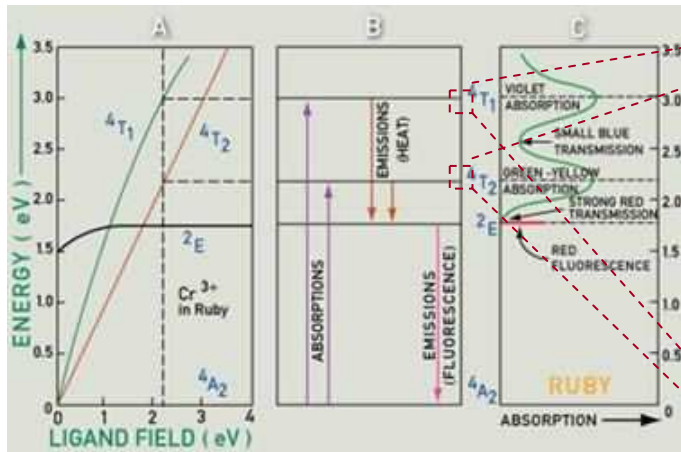
• fluorescencija

crvena boja

Slučajnosti!

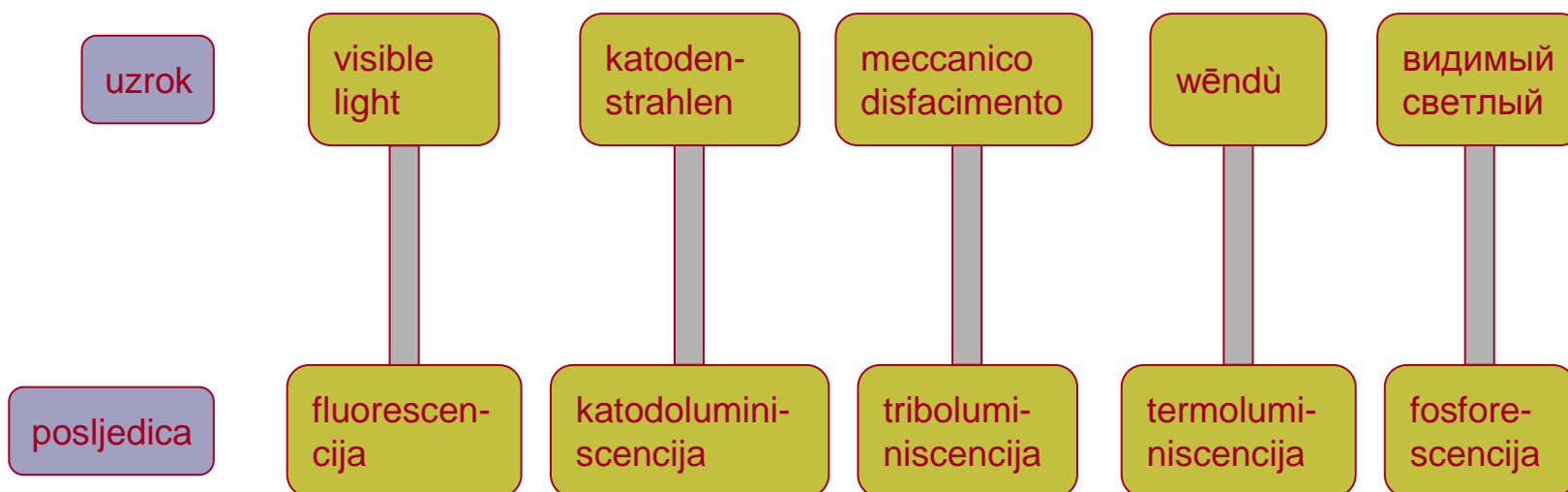






“pleokroizam”
(visebojnost)

Luminiscencija u rubinu



smaragd (emerald) – gr.
σμάραγδος (smaragdus;
"green gem")



smaragd (emerald) – gr.
σμάραγδος (*smaragdos*;
"green gem")

- *necistoca* → Cr^{3+}
- *okolina* → trigonalno pomaknuti oktaedri
- Cr^{3+} zamjenjuje Al^{3+}

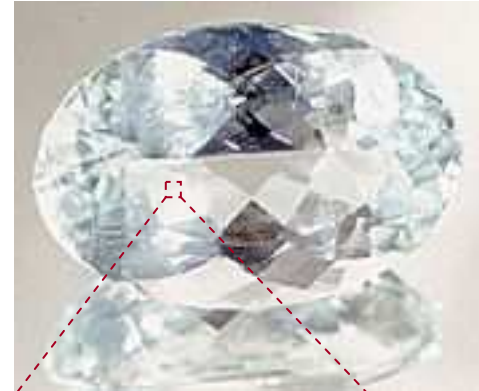


smaragd (emerald) – gr.
σμάραγδος (smaragdos;
"green gem")

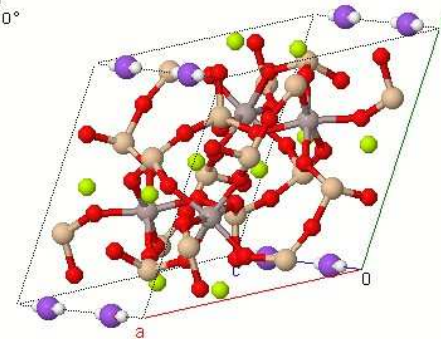
- necistoca → Cr^{3+}
- okolina → trigonalno pomaknuti oktaedri
- Cr^{3+} zamjenjuje Al^{3+}

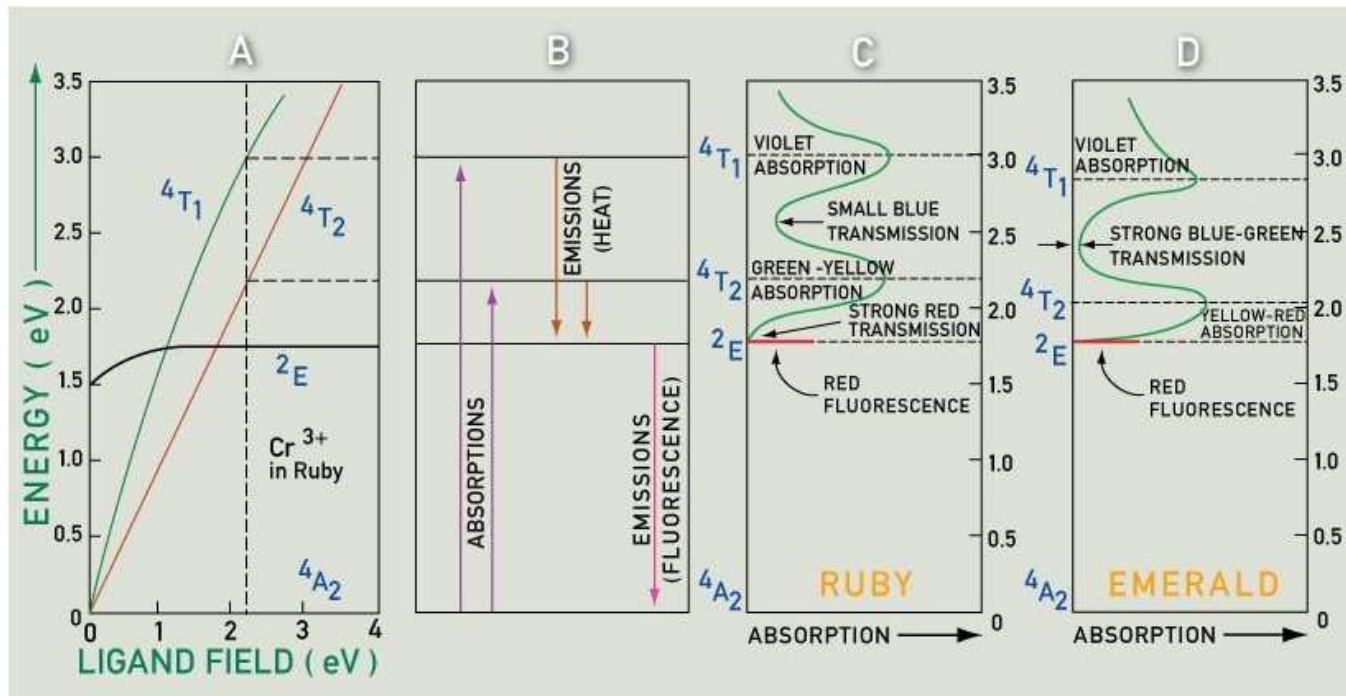
beril = smaragd bez
necistoca ("goshenite")

- "beryllium aluminum silicate"
- $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ili $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$



P 6/m c c
a=9,218Å
b=9,218Å
c=9,197Å
α=90,0°
β=90,0°
γ=120,0°





krizoberil – gr. χρυσός
chrysos i βήρυλλος beryllos
= "a gold-white spar"

"beryllium aluminate" =
 $\text{BeO} \cdot \text{Al}_2\text{O}_3$ ili BeAl_2O_4



krizoberil – gr. χρυσός
chrysos i βήρυλλος beryllos
= "a gold-white spar"

krizoberil + necistoca Cr^{3+}
→ *aleksandrit*



krizoberil – gr. χρυσός
chrysos i βήρυλλος beryllos
= "a gold-white spar"

krizoberil + necistoca Cr^{3+}
→ *aleksandrit*



efekt aleksandrita →
nije pleokroizam, nego
psihofizioloski
fenomen



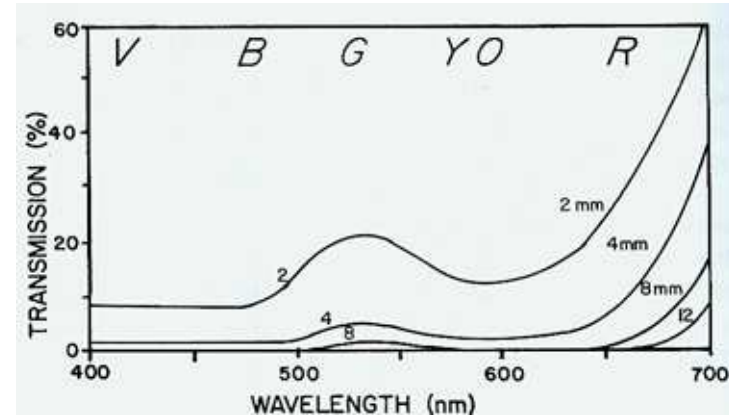
Dolina Umba, Usambara, Tanzanija
A. Halvorsen, B. B. Jensen, *Journal of Gemmology*
(London), 25(5), 325-330 (1997)



Photo Copyright © Mario Pauwels

turmalin → sinhalezanski turamali ili toramali = “different gemstones found in Sri Lanka”

- kompleksna borosilikatna grupa (barem 13 razlicitih minerala)
- $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, gdje su:
 - X = Ca, Na, K, praznina
 - Y = Li, Mg, Fe^{2+} , Mn^{2+} , Zn, Al, **Cr^{3+}** , **V^{3+}** , Fe^{3+} , Ti^{4+} , praznina
 - Z = Mg, Al, Fe^{3+} , **Cr^{3+}** , **V^{3+}**
 - T = Si, Al, B
 - B = B, praznina
 - V = OH, O
 - W = OH, F, O



2 – 4 mm → zuto-zelena

8 mm → zuta

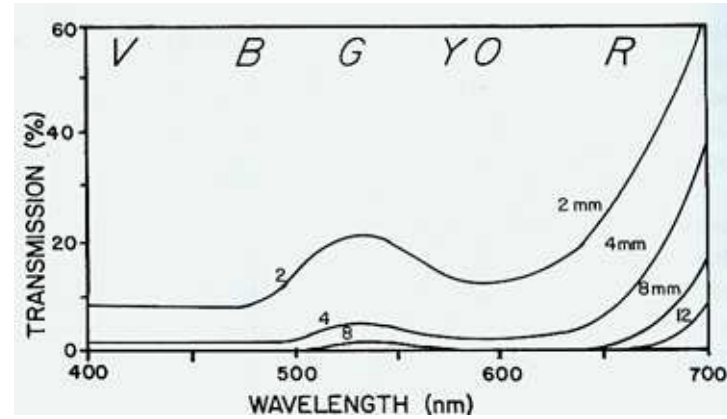
8 – 10 mm → narandzasta

12 mm → crvena

Photo Copyright © Mario Pauwels



Photo Copyright © Mario Pauwels



Efekti:

- usambara efekt – ne vidi se pod svjetlima u kojima nema crvenih valnih duljina
- pleokrozizam
- aleksandrit efekt

Literatura

- Kurt Nassau, "The Physics and Chemistry of Color: The Fifteen Causes of Color", 2nd ed., John Wiley & Sons, Inc., New York (2001)
 - Raymond Chang, "Chemistry" 2nd ed., Random House, Inc., New York (1984)
 - <http://www.mindat.org>
 - <http://www.webexhibits.org>
 - <http://www.chem1.com/acad/webtext/chembond/cb09.html>
 - <http://www.webelements.com>
 - <http://www.docstoc.com/docs/22046079/CHEM-160-General-Chemistry-II-Lecture-Presentation-Coordination>
 - L. W. Xu, R. Z. Che, C. Q. Jin, Chin. Phys. Lett. **17**, 555 (2000)
 - <http://www.jjkent.com/articles/precious-stones-guide-vol7/index.htm>
 - <http://www.gemselect.com/other-info/paste-gems.php>
 - C.-S. Zha, Ho-k. Mao, R. J. Hemley, PNAS **97**, 13494 (2000)
 - <http://www.nordskip.com/usambara.html>
-