Making red emitting phosphors with Pr^{3+}

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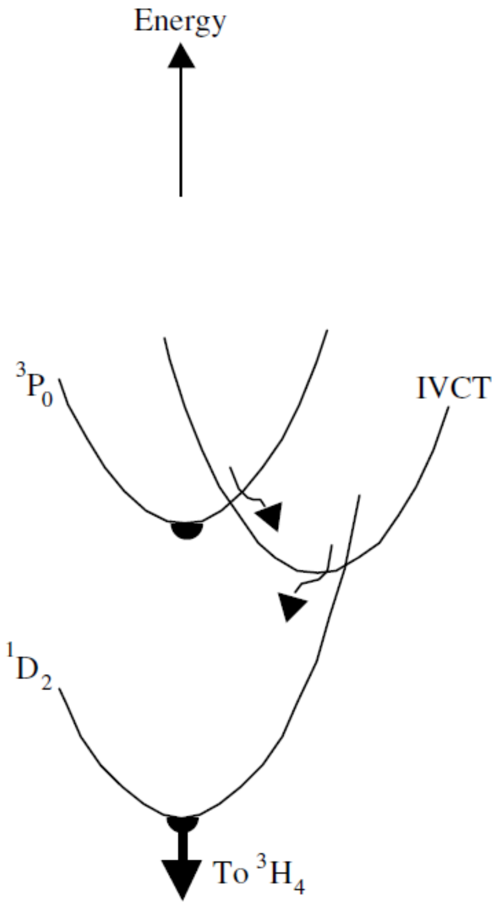
Basics

- Pr^{3+} activated phosphors containing closed-shell transistion metal ions show red luminescence
  - Titanates, vanadates, niobates
- UV excitation
- $^3P_0$ level (greenish-blue emission) quenched by intervalance charge transfer state (IVCT)
- $^1D_2$ -> $^3H_4$: red emission

Quenching of $^3P_0$

- Intersystem crossing (f⟶d)
  - 4f5d band is too high in energy ($60000\ cm^{-1}$)
- Cross relaxation
  - Limited due to doping < 0.2 mol-%
- Multiphonon relaxation
  - Only weak contribution (Dijk-Schuurman equation)
- IVCT
  - $Pr^{3+} + M^{n+} \longrightarrow [Pr^{4+} + M^{(n-1)+}]$

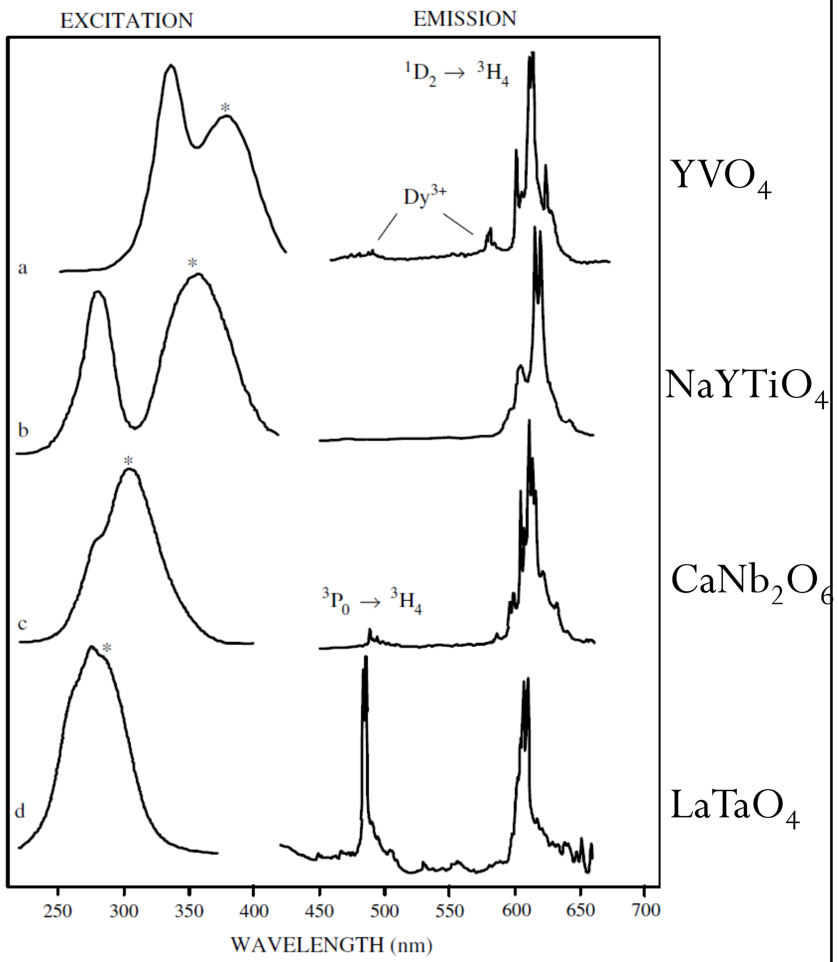


Experimental

- Preparation of titanates, vanadates, niobates, tantalates
  - As crystalline powders by solid state reactions
  - As single crystals using the flux growth method
- Pr^{3+} inserted in the rare earth or calcium sites
  - Only one site is available for the Pr^{3+}

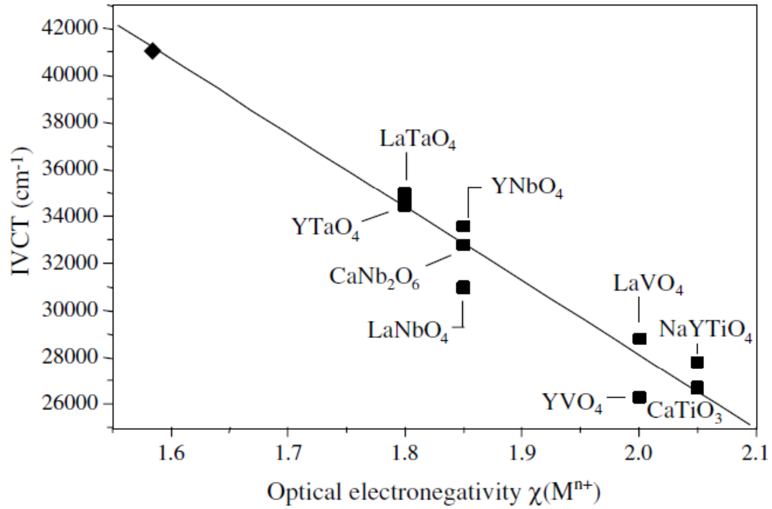
Excitation and emission

- Two excitation bands
  - Host absorption (higher energy)
  - IVCT absorption (lower energy)



IVCT and optical electronegativity

- Energetic position of the IVCT is roughly linear with the optical electronegativity
- IVCT = 31 450[2.89-$\chi(M^{n+})$)
- $^3P_0$: ~20 400 cm^{-1}
- IVCT: Energy mismatch < 7400 cm^{-1}



Predicting $^3P_0$ quenching

Structural, vibrational and optical characteristics of closed-shell transition metal lattices containing Pr^{3+}

Lattice	Avg(Pr–M) [Å]	$\hbar\omega_{max}$ [cm^{-1}]	IVCT [cm^{-1}]	Red/(red + blue)	$\chi(M^{n+})$/Avg(Pr–M)
$NaYTiO_4$	3.27	890	27,800	100%	0.627
$CaTiO_3$	3.31	639	26,700	100%	0.619
YVO_4	3.64	891	26,310	100%	0.550
$LaVO_4$	3.71	860	28,800[a]	>90%	0.540
$CaNb_2O_6$	3.67	904	32,800	>80%	0.504
$YNbO_4$	3.73	830	33,600	>80%	0.496
$YTaO_4$	3.72	825	34,480[a]	>50%	0.484
$LaNbO_4$	3.83	807	31,000[a]	≅50%	0.476
$LaTaO_4$	3.81	810	35,000	≅50%	0.472
$CaZrO_3$	3.48	545	–	<20%	0.459

[a] The value is not accurate, Avg = average.

- Average distance (Avg(Pr-M)) between Pr and metal is also important
- Smaller distance leads to higher quenching rates
- Ratio of optical electronegativity and average distance is a simple criterion for predicting $^3P_0$ quenching

Conclusions

- Low-lying IVCT can be used to quench the $^3P_0$ level
- Criterion: High ratio $R = \chi(M^{n+})/\mathrm{Avg}(\text{Pr-M})$
- Red-emitting phosphors can be obtained by using the low cost Pr^{3+} ion
  - Pr_2O_3: ~ 80 €/kg
  - Eu_2O_3: ~ 1200 €/kg