Making red emitting phosphors with $\text{Pr}^{3+}$

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Basics

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

- Intersystem crossing ($f \rightarrow d$)
  - $4f5d$ 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
  - $\text{Pr}^{3+} + M^{n+} \rightarrow [\text{Pr}^{4+} + M^{(n-1)+}]$
Experimental

- Preparation of titanates, vanadates, niobates, tantalates
  - As crystalline powders by solid state reactions
  - As single crystals using the flux growth method
- $\text{Pr}^{3+}$ inserted in the rare earth or calcium sites
  - Only one site is available for the $\text{Pr}^{3+}$
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
- \[ \text{IVCT} = 31450[2.89 - \chi(M^{n+})] \]
- \(^3\text{P}_0: \sim 20400 \text{ cm}^{-1}\)
- IVCT: Energy mismatch < 7400 cm\(^{-1}\)
Predicting $^{3}P_{0}$ quenching

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

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Avg(Pr-M) [Å]</th>
<th>$\nu_{\text{max}}$ [cm$^{-1}$]</th>
<th>IVCT [cm$^{-1}$]</th>
<th>Red/(red + blue)</th>
<th>$\chi$(M*)/Avg(Pr-M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaYTiO$_4$</td>
<td>3.27</td>
<td>890</td>
<td>27,800</td>
<td>100%</td>
<td>0.627</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>3.31</td>
<td>639</td>
<td>26,700</td>
<td>100%</td>
<td>0.619</td>
</tr>
<tr>
<td>YVO$_4$</td>
<td>3.64</td>
<td>891</td>
<td>26,310</td>
<td>100%</td>
<td>0.550</td>
</tr>
<tr>
<td>LaVO$_4$</td>
<td>3.71</td>
<td>860</td>
<td>28,800</td>
<td>&gt;90%</td>
<td>0.540</td>
</tr>
<tr>
<td>CaNb$_2$O$_6$</td>
<td>3.67</td>
<td>904</td>
<td>32,800</td>
<td>&gt;80%</td>
<td>0.504</td>
</tr>
<tr>
<td>YNbO$_4$</td>
<td>3.73</td>
<td>830</td>
<td>33,600</td>
<td>&gt;80%</td>
<td>0.496</td>
</tr>
<tr>
<td>YTaO$_4$</td>
<td>3.72</td>
<td>825</td>
<td>34,480$^a$</td>
<td>&gt;50%</td>
<td>0.484</td>
</tr>
<tr>
<td>LaNbO$_4$</td>
<td>3.83</td>
<td>807</td>
<td>31,000$^a$</td>
<td>≈50%</td>
<td>0.476</td>
</tr>
<tr>
<td>LaTaO$_4$</td>
<td>3.81</td>
<td>810</td>
<td>35,000</td>
<td>≈50%</td>
<td>0.472</td>
</tr>
<tr>
<td>CaZrO$_3$</td>
<td>3.48</td>
<td>545</td>
<td>–</td>
<td>&lt;20%</td>
<td>0.459</td>
</tr>
</tbody>
</table>

$^a$ 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 $^{3}P_{0}$ quenching
Conclusions

- Low-lying IVCT can be used to quench the $^{3}P_0$ level
- Criterion: High ratio $R = \chi(M^{n+})/\text{Avg}(\text{Pr-M})$
- Red-emitting phosphors can be obtained by using the low cost Pr$^{3+}$ ion
  - Pr$_2$O$_3$: $\sim$ 80 €/kg
  - Eu$_2$O$_3$: $\sim$ 1200 €/kg