Lecture 33:

RE Doped Glasses III – Decay Rates and Efficiency

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Quantum efficiency

The quantum efficiency of a photoluminescence (emission) process is given by the ratio between the number of emitted photons and the number of incident (pump) photons.

This ratio is also equal to the ratio between the radiative decay rate and the total (radiative + non-radiative) decay rate:

$$\eta_Q = W_{rad} / (W_{rad} + W_{nr}) = \tau_{meas} / \tau_{rad} \leq 1$$

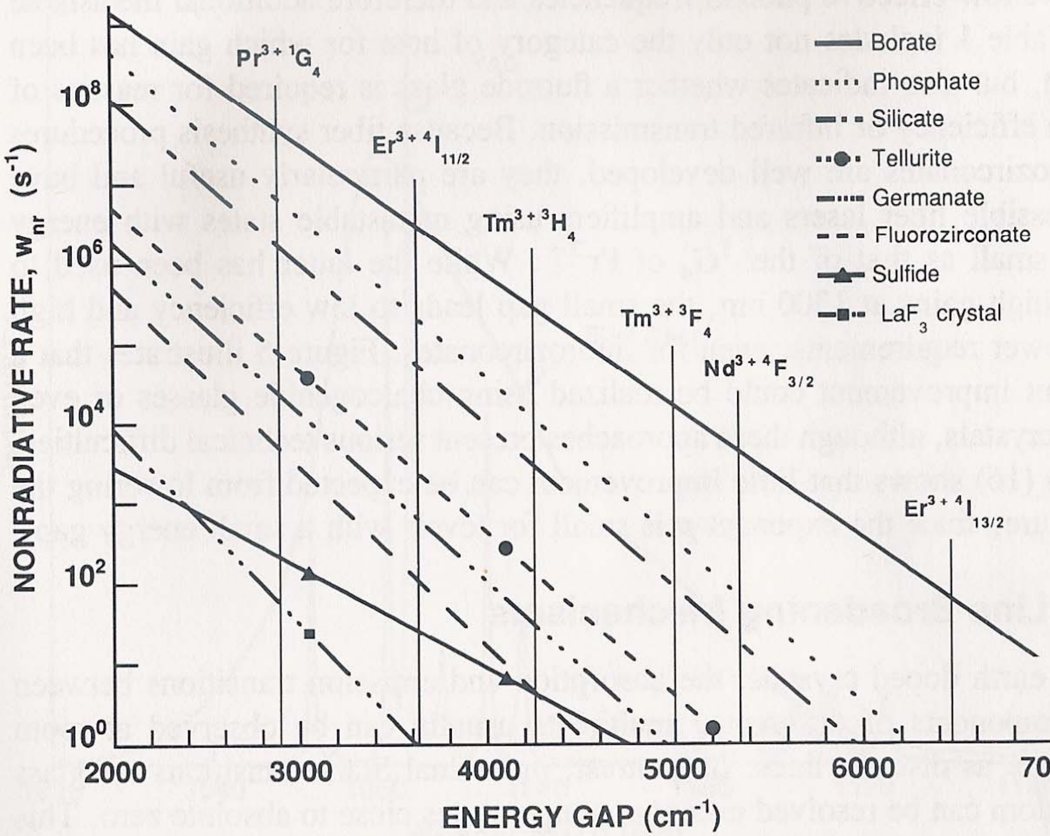
The non-radiative decay rate can be further divided into multiphonon (MP) decay (due to the matrix "phonons", i.e., intrinsic, or due to impurity vibrations) and concentration quenching (due to ion-ion interactions):

$$W_{nr} = W_{MP} + W_{CQ}$$

For gaps much larger than the energy of the phonons involved, the non-radiative MP decay rate, W_{MP}, is inversely proportional to the exponential of the energy gap, ΔE:

$$W_{MP} = C\,[n(T) + 1]^{p} \exp(-\alpha\,\Delta E)$$

where C and α are host-dependent parameters, p is the number of phonons needed to bridge the gap and n(T) is the Bose-Einstein phonon occupation number:



Nonradiative relaxation rate as a function of energy gap for the indicated glasses.

$n(T) = [\exp(h\nu/kT)-1]^{-1}$

$\nu \rightarrow$ phonon frequency

Electronic energy term notation: $^{2S+1}L_J$

L, S $\rightarrow$ total angular momentum and spin;

J = L + S (Russell-Saunders coupling)

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel Dekker, 1993)

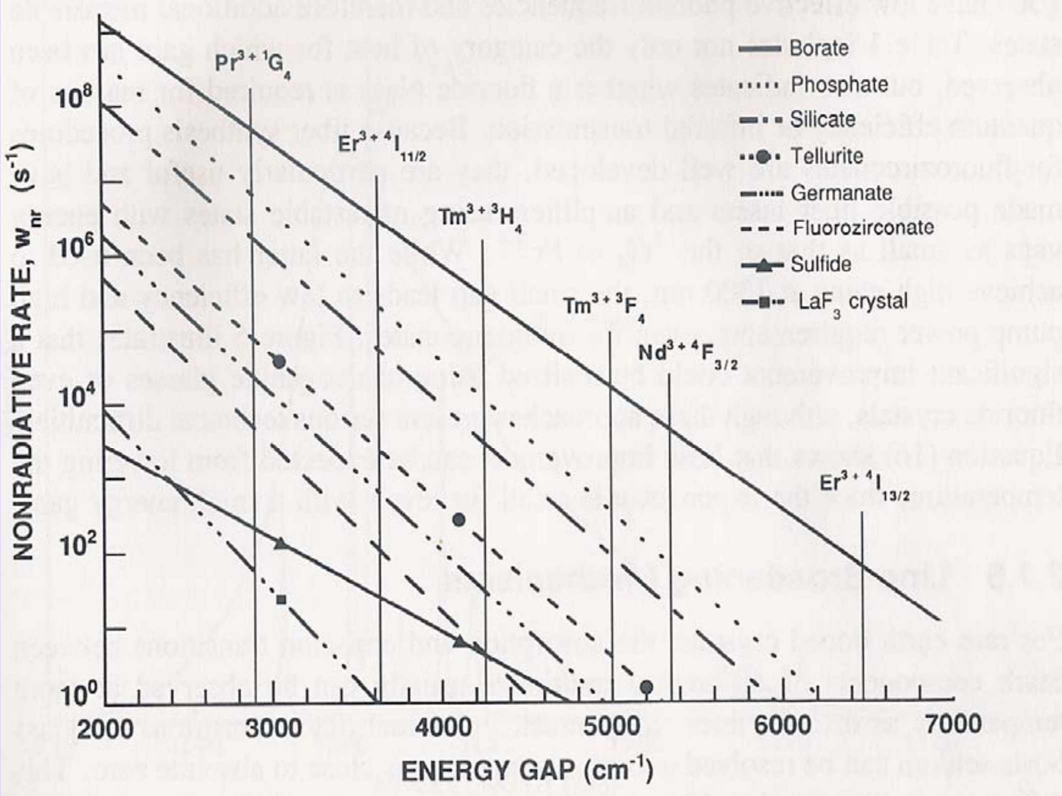
Due to the [n(T)+1] factor, the MP non-radiative decay rate decreases with decreasing temperature. In practice, C, α and p (or hν) are regarded as empirical parameters, which are host dependent but insensitive to the particular RE ion and energy levels, obtained by fitting the "energy gap law" equation to the measured W_{MP} values obtained for different ions (and thus different gaps) in the same host.

Parameters Describing the Nonradiative Relaxation of Rare Earth Ions in Glass

Host	C (s^{-1})	α (10^{-3} cm)	$\hbar\omega$ (cm^{-1})
Borate	2.9×10^{12}	3.8	1400
Phosphate	5.4×10^{12}	4.7	1200
Silicate	1.4×10^{12}	4.7	1100
Germanate	3.4×10^{10}	4.9	900
Tellurite	6.3×10^{10}	4.7	700
Fluorozirconate	1.59×10^{10}	5.19	500
Sulfide	10^{6}	2.9	350
LaF_3 (crystal)	6.6×10^{8}	5.6	350

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel Dekker, 1993)

This figure was obtained using the parameters in the previous table and the equation for W_{MP}. Oxides have larger W_{MP} because of their higher vibrational frequencies, when compared to halides and chalcogenides. For glasses, the vibrations causing non-radiative relaxation are the high frequency, localized stretching modes of their fundamental polyhedral structural units.



Nonradiative relaxation rate as a function of energy gap for the indicated glasses.

E.g., the 6500 cm^{-1} energy gap below the $^4I_{13/2}$ level of the Er^{3+} emission at 1.5 μm is large enough that W_{MP} is only significant for **borates** (or also phosphates), but the presence of impurity OH groups in any host (hν ~ 3300 cm^{-1}) will significantly increase W_{MP}. The first excited state of Tm^{3+}, $^3F_4$, has low radiative yield even in silica glass, but this improves in tellurites, germanates and fluorides, which have lower vibrational energies.

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel Dekker, 1993)

Pr^{3+} : *Multiphonon relaxation rates from the Pr^{3+} : $^1G_4$ to the $^3F_4$ state and quantum efficiency in various oxide and non-oxide glass [Reprinted from D. R. Simons, A. J. Faber, F. Simonis and H. de Waal, 8th International Symposium on Halide Glasses, Perros-Guirec (1992) 448, with permission from Centre National d'Etudes des Telecommunications (CNET)]*

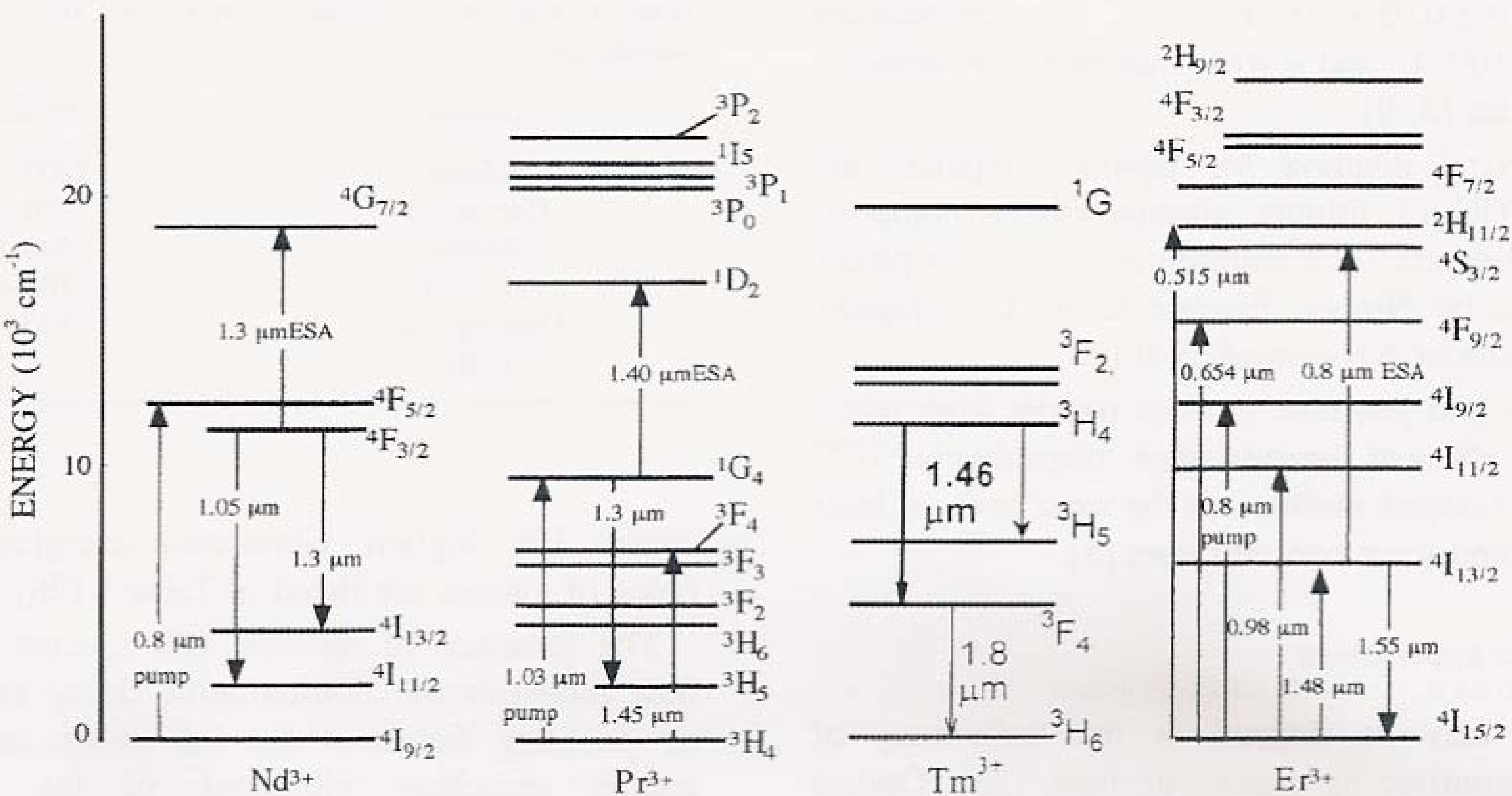
Glass	Composition	Energy gap, ΔE (cm^{-1})	Phonon energy, $\hbar\omega_{ph}$ (cm^{-1})	Relaxation rate, W_{nr} (s^{-1})	Quantum efficiency, η
Oxide	borate	2950[a]	1400	3.9×10^7	7.8×10^{-6}
	phosphate	2950[a]	1200	5.2×10^6	6.0×10^{-5}
	silicate	2950[a]	1100	1.3×10^6	2.3×10^{-4}
	germanate	2878	900	2.7×10^4	1.1×10^{-2}
	tellurite	2950	700	6.9×10^4	4.5×10^{-3}
Fluoride	fluoroberyllate	2950[a]	500	1.3×10^4	2.3×10^{-2}
	fluorozirconate	2941	500	6.4×10^3	4.6×10^{-2}
Sulfide	Al(Ga)–La–S	2950[a]	350	1.0×10^3	2.3×10^{-1}

[a]estimated value.

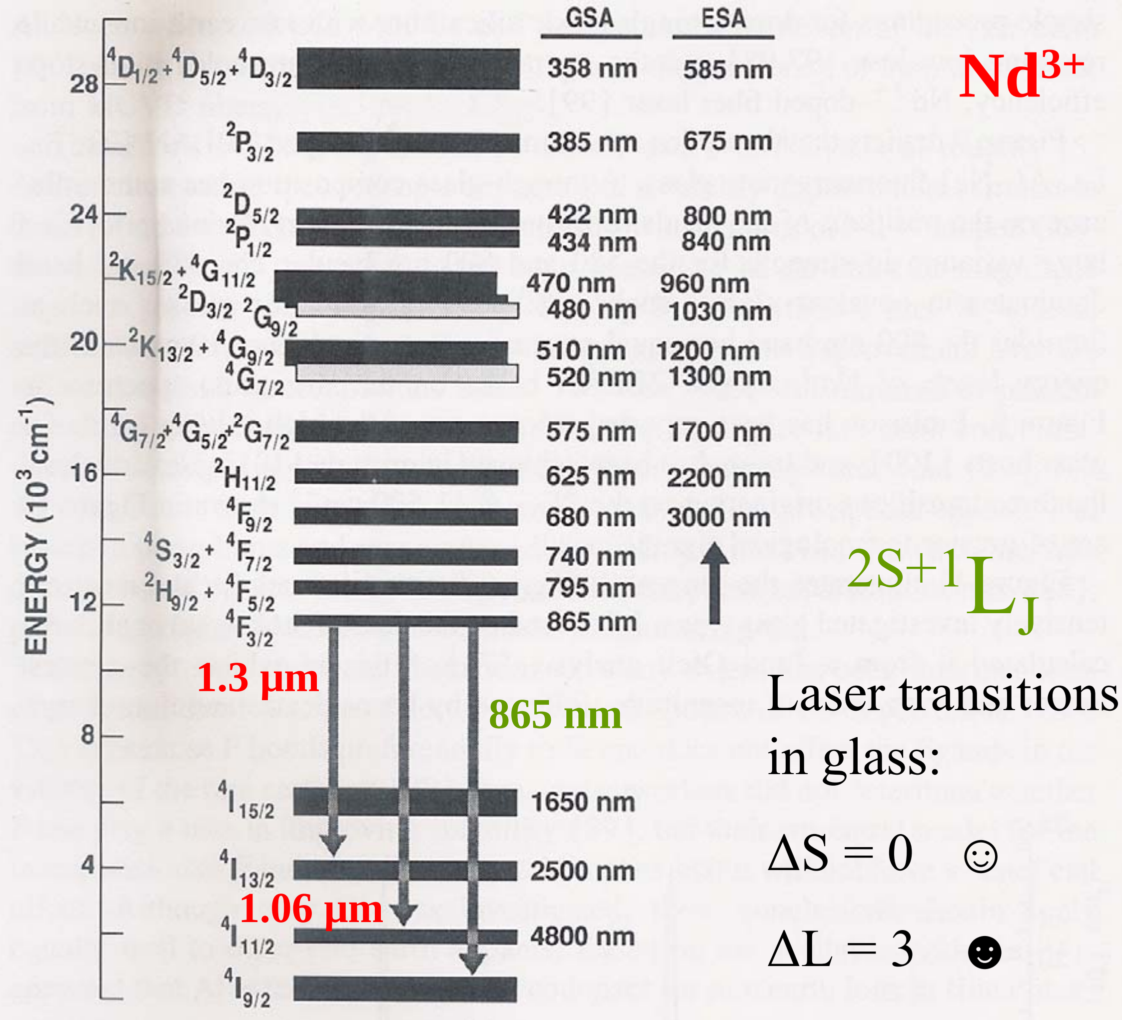
(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

Possible RE ion dopants for glassy hosts

M. Clara Gonçalves et al. / C. R. Chimie 5 (2002) 845–854



Simplified electronic energy level diagrams of three different RE ions and relevant transitions for pumping and emission.



Nd^{3+}

$^{2S+1}L_J$

Laser transitions in glass:

$\Delta S = 0$ ☺

$\Delta L = 3$ ☻

Energy levels of Nd^{3+} in ZBLAN fluorozirconate labeled using Russell–Saunders coupling. Downward arrows indicate laser transitions demonstrated for glass hosts. The first number to the right of each excited state (GSA column) is the wavelength of the ground state absorption transition terminating on it. The second number (ESA column) is the wavelength of the ESA transition originating on the $^4F_{3/2}$ and terminating on the labeled level.

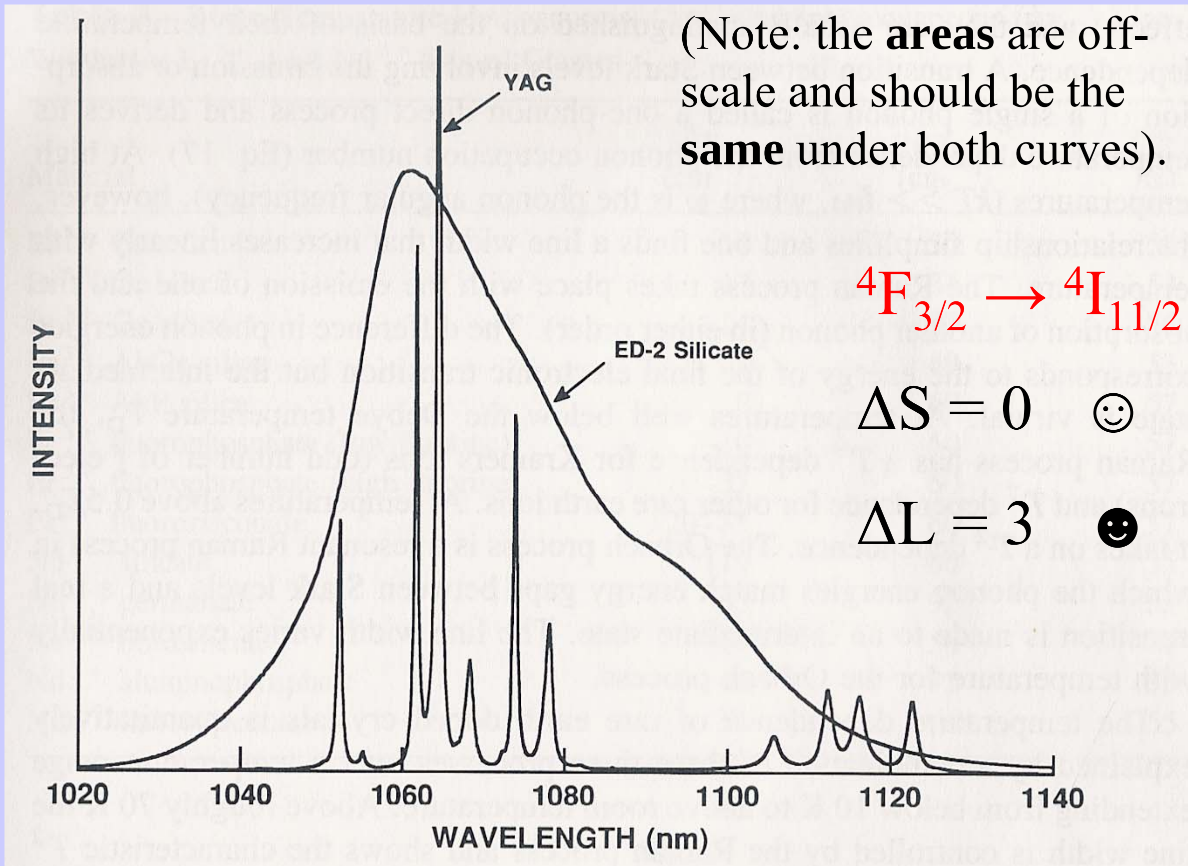
(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel-Dekker, 1993)

1.06 μm . *Range of spectroscopic properties for the $^4F_{3/2}$–$^4I_{11/2}$ transition of Nd^{3+} observed in different glasses at 295 K [Reprinted from M. J. Weber, J. Non-Cryst. Solids* **123** *(1990) 208, copyright (1990) with permission from Elsevier Science]*

Nd^{3+} Host glass	Refractive index n_d	Cross section σ_p (pm^2)	Peak wavelength λ_p (μm)	Effective linewidth $\Delta\lambda_{eff}$ (nm)	Radiative lifetime τ_R (μs)
Oxide					
silicate	1.46–1.75	0.9–3.6	1.057–1.088	35–55	170–1090
germanate	1.61–1.71	1.7–2.5	1.060–1.063	36–43	300–460
tellurite	2.0–2.1	3.0–5.1	1.056–1.063	26–31	140–240
phosphate	1.49–1.63	2.0–4.8	1.052–1.057	22–35	280–530
borate	1.51–1.69	2.1–3.2	1.054–1.062	34–38	270–450
Halides					
beryllium fluoride	1.28–1.38	1.6–4.0	1.046–1.050	19–29	460–1030
aluminium fluoride	1.39–1.49	2.2–2.9	1.049–1.050	28–32	540–650
heavy metal fluoride	1.50–1.56	2.5–3.4	1.048–1.051	25–29	360–500
chloride	1.67–2.06	6.0–6.3	1.062–1.064	19–20	180–220
Oxyhalides					
fluorophosphate	1.41–1.56	2.2–4.3	1.049–1.056	27–34	310–570
chlorophosphate	1.51–1.55	5.2–5.4	1.055	22–33	290–300
Chalcogenides					
Sulfide	2.1–2.5	6.9–8.2	1.075–1.077	21	64–100
oxysulfide	2.4	4.2	1.075	27	92

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

The absorption and emission transitions between the individual Stark components of different J multiplets can usually be observed at room temperature as discrete lines in RE-doped crystals, but not in glasses. While crystalline hosts provide high cross sections at nearly discrete wavelengths, glass hosts have lower cross sections over a broad range of wavelengths.



(Note: the **areas** are off-scale and should be the **same** under both curves).

$^4F_{3/2} \rightarrow {}^4I_{11/2}$

$\Delta S = 0$ ☺

$\Delta L = 3$ ☻

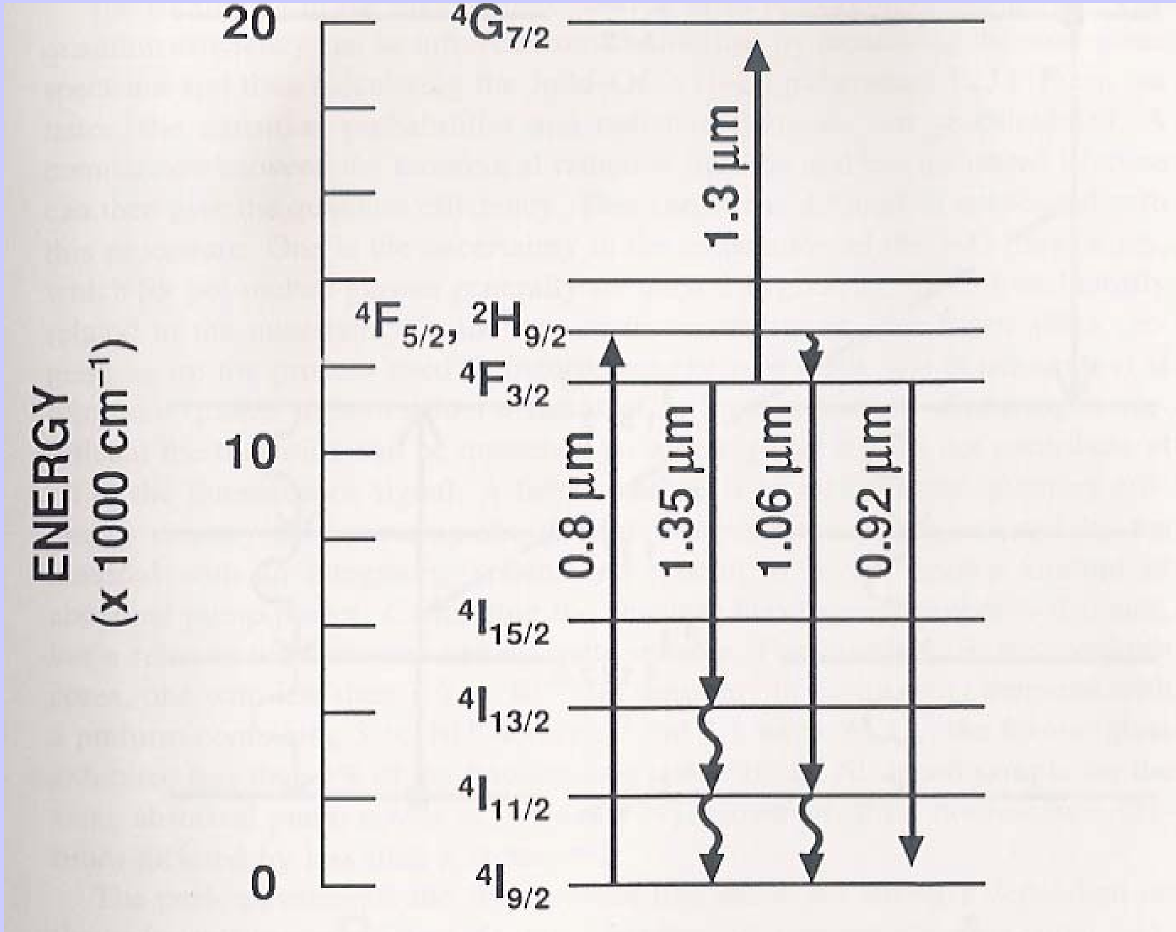
Comparison of the emission spectra for Nd^{3+}-doped YAG and Nd^{3+}-doped ED^{-2}silicate glass.

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcell-Dekker, 1993)

The *homogeneous broadening* of the transitions between the Stark components of different J multiplets is caused by lifetime broadening in both crystals and glasses, dominated by rapid phonon-induced transitions between the individual Stark components within a given multiplet. Such transitions occur on a ~ ps time scale at low temperature, but become much faster at room temperature, causing homogeneous broadening to increase significantly with temperature.

In addition to homogeneous line broadening, a glass host will also cause the so-called *inhomogeneous broadening*, due to site-to-site variations in the local structure around the different RE ions present.

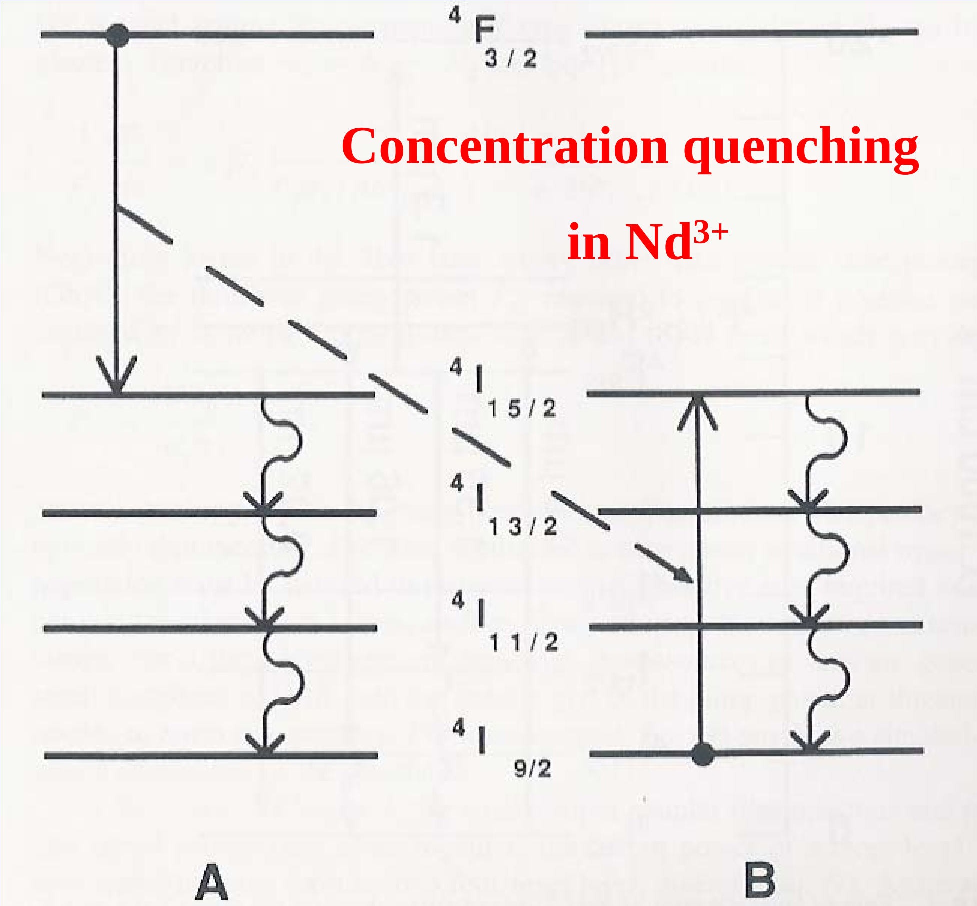
Relaxation of the $^4F_{3/2}$ level of Nd^{3+} is primarily radiative for all the more common glasses, with the exception of the high vibrational energy borates, which have high non-radiative relaxation rates, leading to $^4F_{3/2}$ excited state lifetimes as short as 45 μs ($\eta_Q \sim$ 10-15 %) . The presence of impurity OH groups can also be a problem, for any glass host.



Energy level diagram of Nd^{3+}-doped silica showing the pump band at 0.8 μm and the fluorescence transitions near 0.92, 1.06, and 1.35 μm. Nonradiative transitions are indicated by wavy arrows.

(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel-Dekker, 1993)

Quantum efficiency of fluorescence, for a given RE-glass system, sets the upper limit of the RE concentration, limited by *concentration quenching*. The figure shows *cross-relaxation* between an excited ion A and a neighboring ion B in the ground state, with both ions making non-radiative transitions to the intermediate $^4I_{15/2}$ state, from which they decay non-radiatively to the ground state. *Cooperative up-conversion* (already discussed) is another possible mechanism for concentration quenching.



(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel Dekker, 1993)