Optical and Photonic Glasses

Lecture 34:

RE Doped Glasses IV – Erbium Doping

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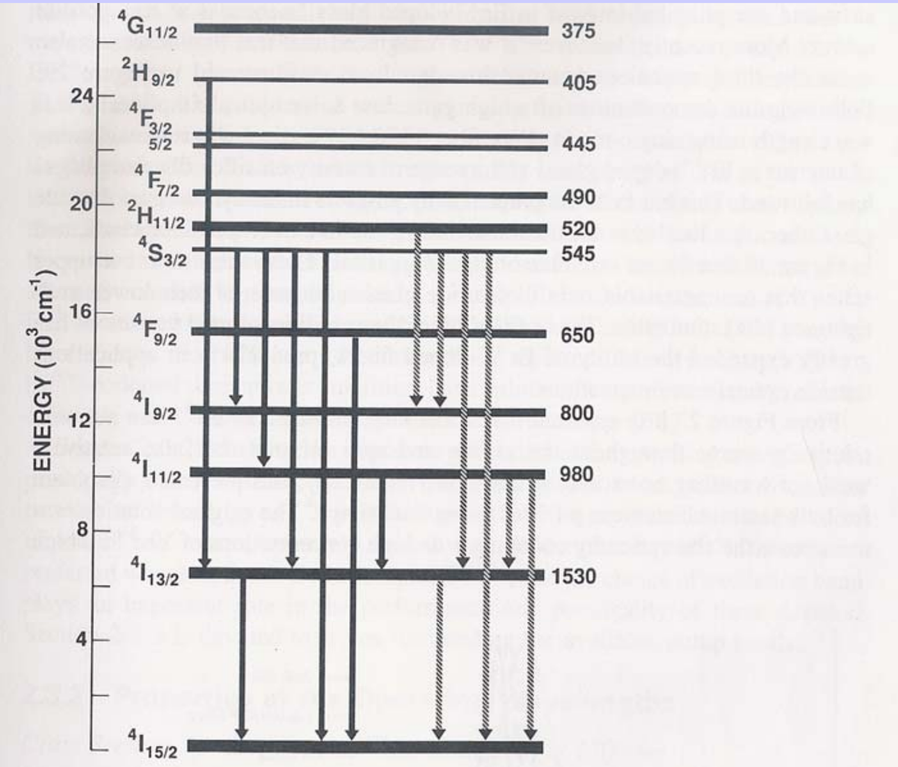
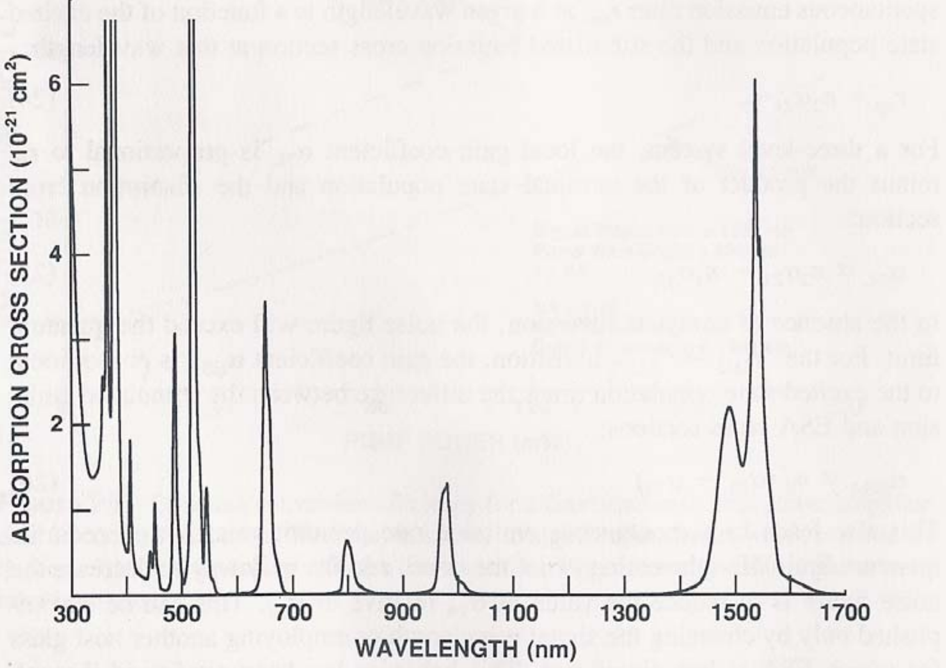
After Nd^{3+}, the most extensively studied RE ion has been Er^{3}+, which has 11 f electrons. Below are the corresponding energy levels in a silicate glass. E.g., the $^4I_{15/2}$ ground state corresponds to 3 unpaired f electrons (S=3/2), L=6 and J=L+S=15/2, whereas $^4I_{9/2}$ corresponds to J=L-S=9/2. The laser transitions which do not originate on the $^4I_{13/2}$ are possible only in HMFG or ChG, where they use upper states which are metastable only in these glasses, due to their low vibrational energies and multiphonon decay rates.



[redacted] Energy levels of Er^{3+} in ED-2 silicate labeled using Russell–Saunders coupling. The number to the right of each excited state is the wavelength in nanometers of the ground state absorption transition terminating on it. The solid arrows at left indicate the laser transitions demonstrated for crystalline hosts and the hatched arrows at right are those reported for glasses.

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

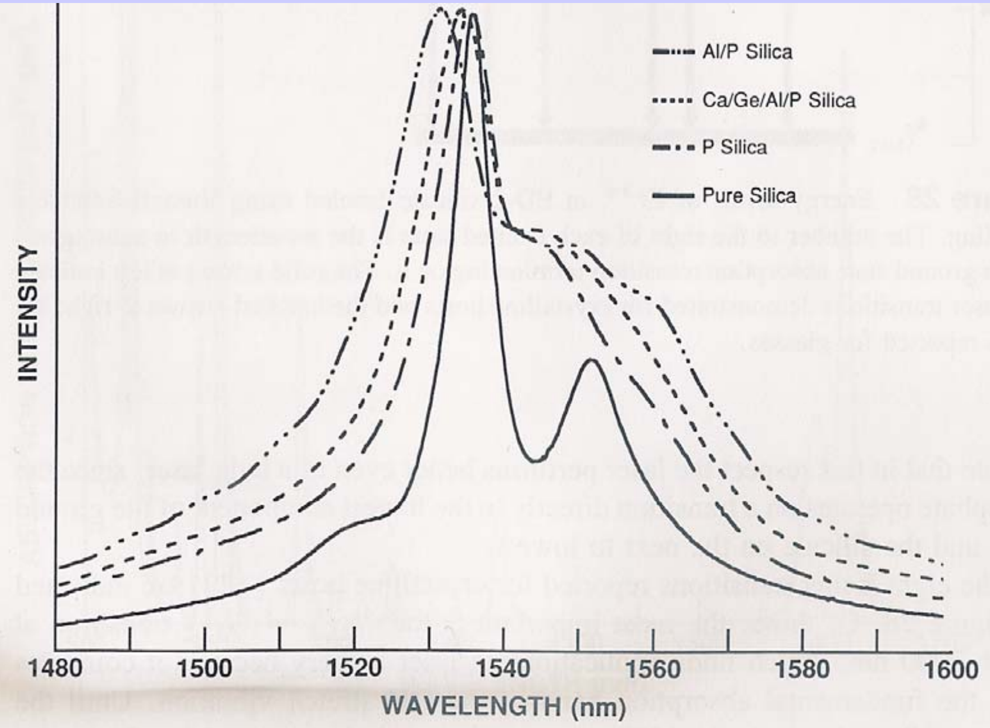
The figure shows the absorption spectrum of Er^{3+} in the same glass. The first Er^{3+}-doped glass laser was demonstrated by Snitzer and Woodcock in 1965, for the $^4I_{13/2} \rightarrow {^4I_{15/2}}$ transition at ~ 1530 nm. Despite being a 3-level lasing system with a weak cross section at 980 nm, this laser could operate at room temperature due to its co-doping with Yb^{3+}, a sensitizer ion with a strong absorption at ~ 975 nm, which transferred this energy to the Er^{3+} ions by the so-called *antenna efect*. The ~ 1530 nm transition is very important for amplification in the third window of fiberoptics telecommunications. The $^4I_{11/2} \rightarrow {^4I_{13/2}}$ transition at ~ 2.8 μm is also very useful for laser surgery, because it coincides with the fundamental OH stretching absorption.



Absorption cross section spectrum of Er^{3+}-doped ED-2 silicate glass. The peaks of the strong bands at 380 and 520 nm are 28 and 19 × 10^{-21} cm^2, respectively.

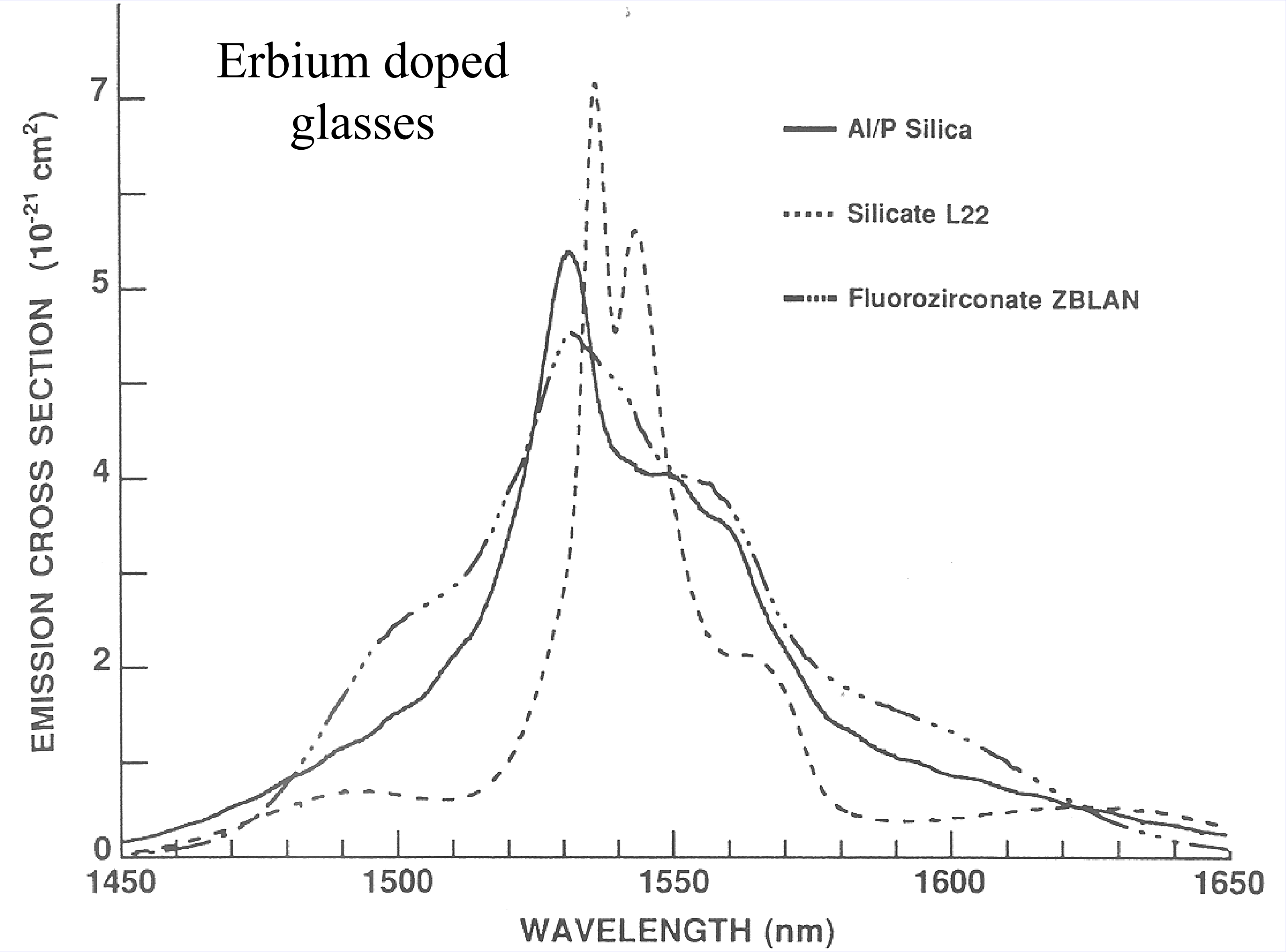
(Adapted from: *Rare earth doped fiber lasers and amplifiers*, ed. M.J.F. Digonnet, Marcel Dekker, 1993)

Since the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission of Er^{3+} spans the third window of fiberoptic communications, especially in the case of Al/P doped silica glass fibers, where it fully covers the so-called C (center) band, from 1530-1565 nm, this led to the development of the Erbium Doped Fiber Amplifiers (EDFA's). In the case of the present Dense Wavelength Division Multiplexing (DWDM) systems, which also include the S (short, 1450-1530 nm) and the L (long, 1560-1620 nm) wavelength ranges, Tm or Er doped fluoride or tellurite glass fiber amplifiers can be used. (Raman amplification is also possible in all cases).



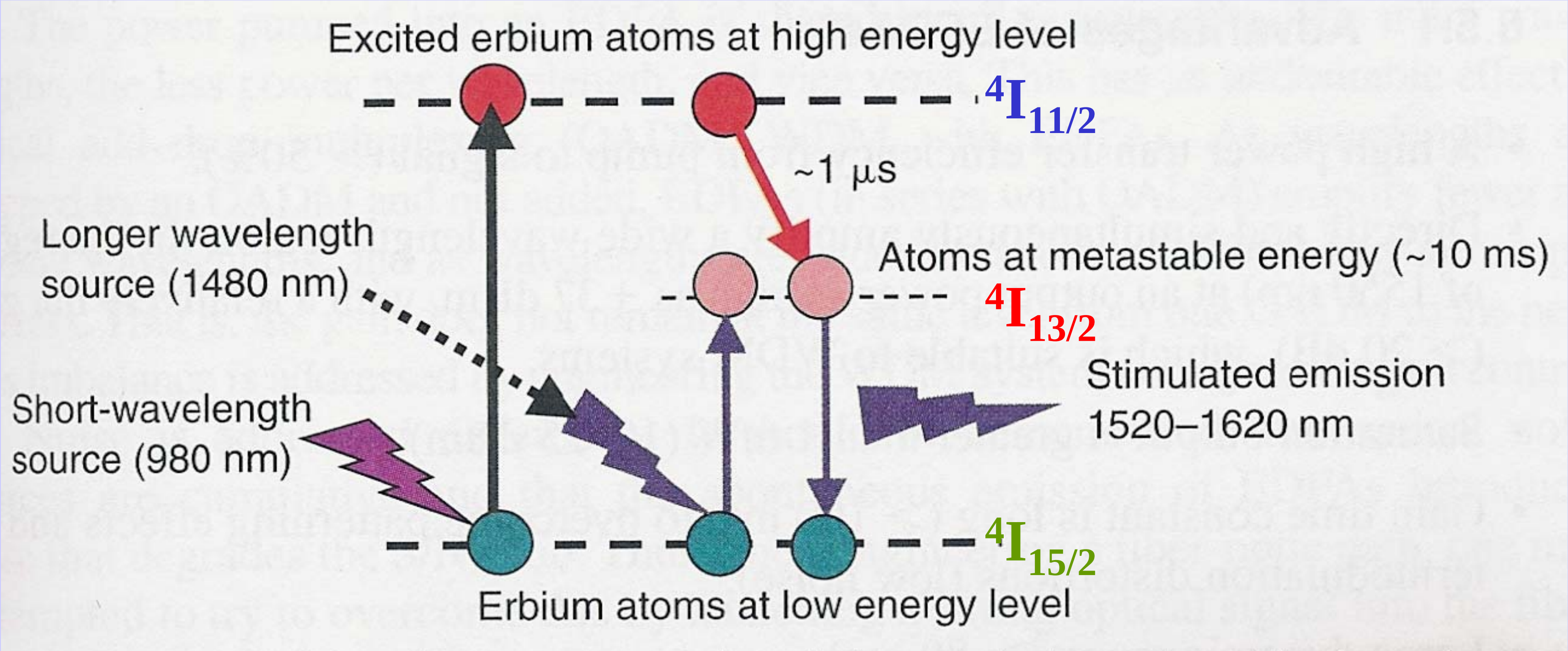
Emission spectrum of Er^{3+}-doped silica fibers.

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



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

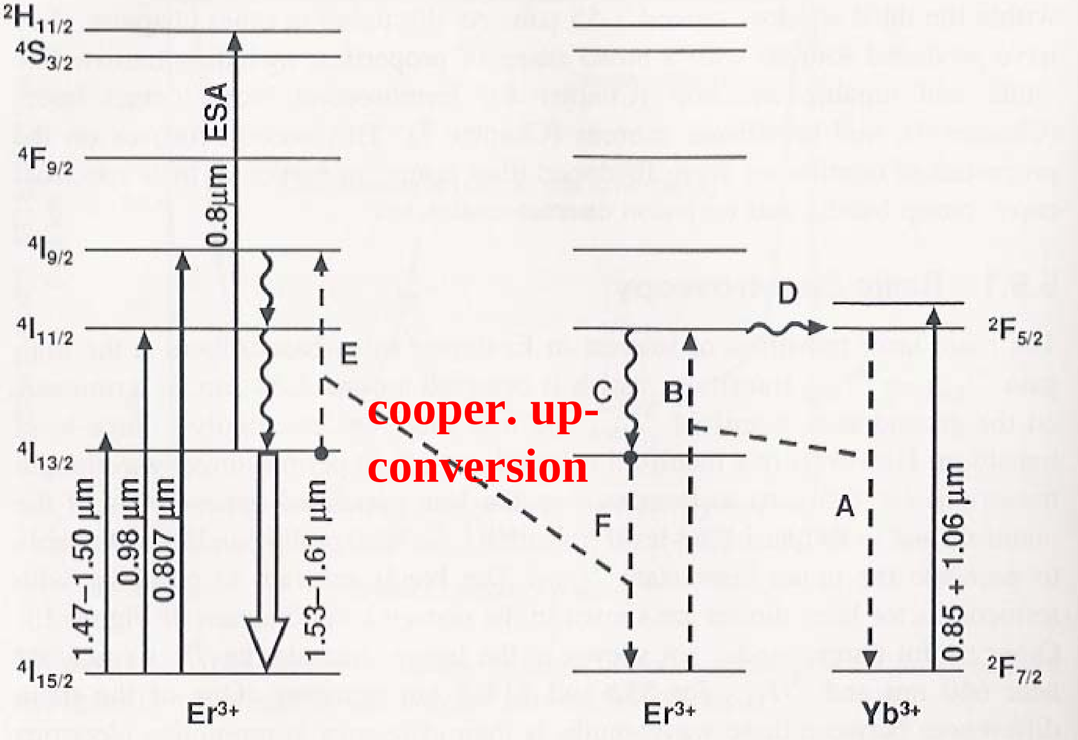
The principles on which the EDFA is based are illustrated below. This operates as a 3-level system when pumped at 980 nm (with possible Yb co-doping) and as a quasi 2-level system when pumped at 1480 nm to the long-lived (metastable) $^4I_{13/2}$ level. The signal photons at ~ 1.5 µm (the third operating window of fiberoptic communications) stimulate emission of the Er^{3+} ions in the EDFA at ~ 1520-1620 nm, therefore amplifying the original signal.



Principles of spontaneous emission of erbium; only the two lowest levels are shown.

(Adapted from: *Introduction to DWDM Technology*, S.V. Kartalopoulos, IEEE Press, 2000)

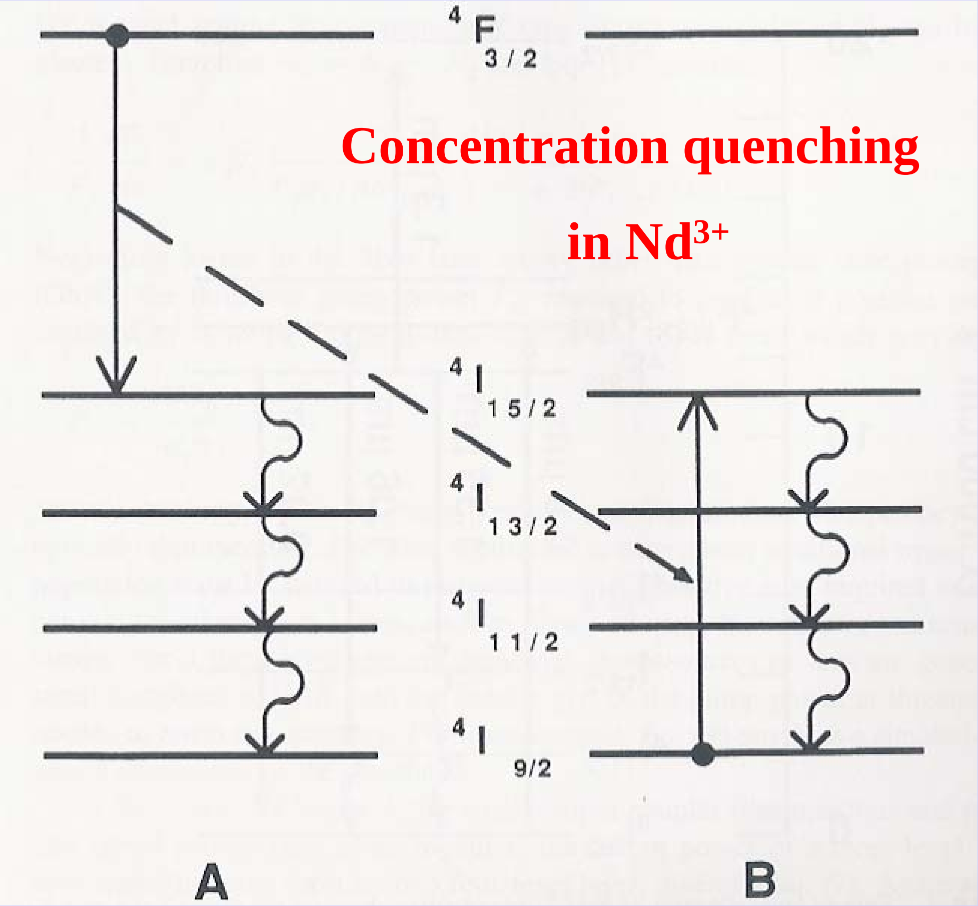
In addition to cross relaxation, which is an important mechanism of *concentration quenching* in Nd^{3+}, but not in Er^{3+} (which has no levels between the $^4I_{13/2}$ and $^4I_{15/2}$ states) another mechanism important in Er^{3+} is *cooperative up-conversion*, which causes concentration quenching, as opposed to Excited State Absorption (ESA) up-conversion, which also causes quenching, but involves only one Er^{3+} ion. Both cases are illustrated below. As cooper. up-conv. requires two interacting ions in the excited state, it is not evident at low pumping levels.



Energy level diagram for Er^{3+} ions in silica and the various processes relevant to laser oscillation around 1.55 μm. Also illustrated is the effect of the Yb^{3+}/Er^{3+} in fibers sensitized with Yb^{3+}

(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)

Concentration quenching is the reduction in quantum efficiency of a RE ion as its concentration increases. It generally manifests itself by a shortening of the measured metastable level lifetime and occurs mostly through cross relaxation or co-operative up-conversion processes. The empirical formula which relates the measured lifetime to the ion concentration, c, is:

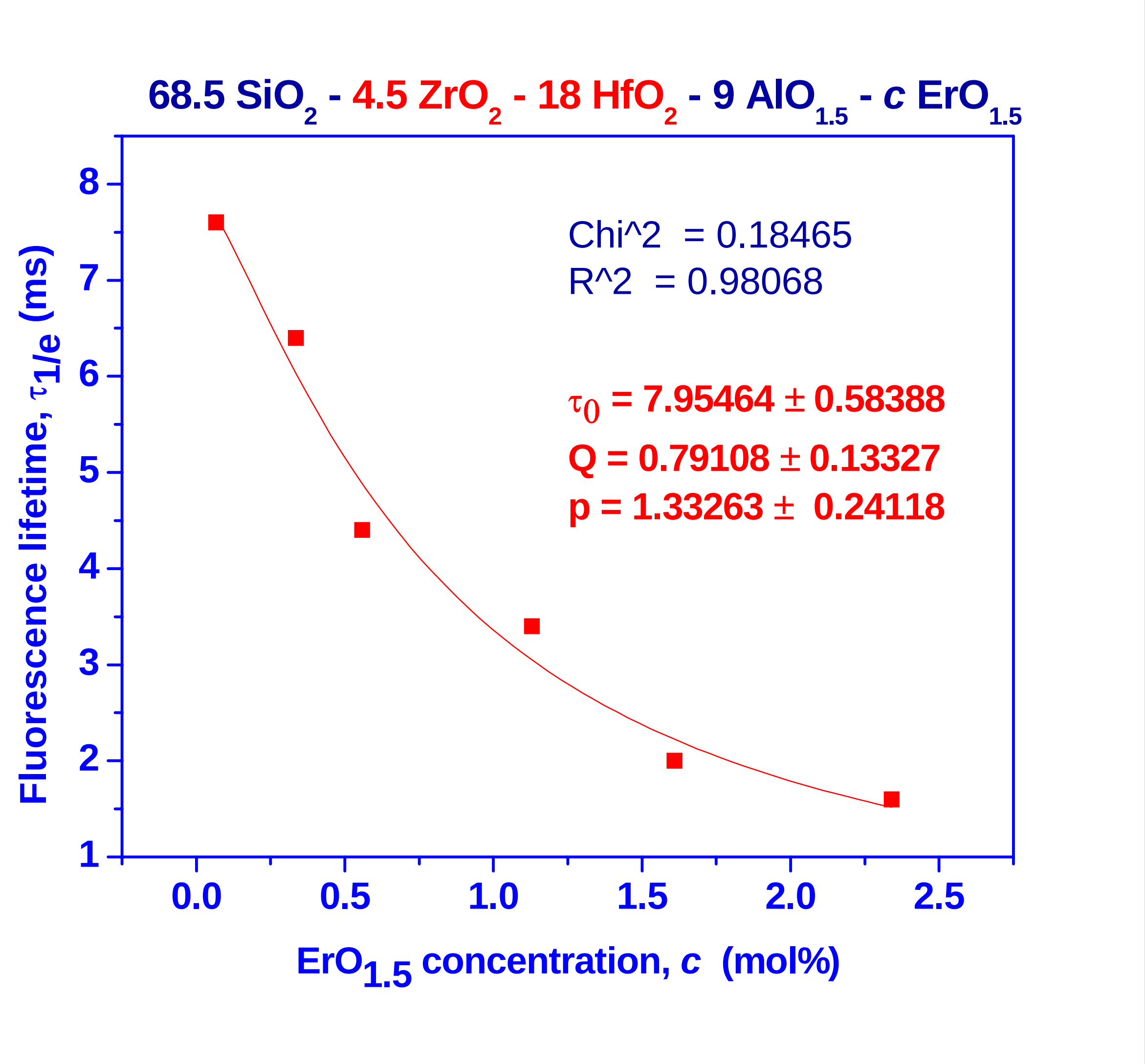
$$\tau_{meas} = \tau_o / [1 + (c/Q)^p]$$

where τ_o is the lifetime in the limit of zero concentration and Q is the *quenching concentration*, at which $\tau_{meas} = \tau_o/2$. In the case of Nd^{3+}, e.g., the phenomenological parameter p is found to be ~ 2, which has suggested a two-ion crosss relaxation mechanism for the concentration quenching. In silicate glasses, Q for Nd^{3+} has been determined at $(4 – 6) \times 10^{20}$ cm^{-3}. This analysis assumes that RE ion *clustering* does not occur. In pure silica glass, however, RE solubility is generally very low and ionic concentrations must be kept below ~ 5×10^{19} cm^{-3}. In fiber devices, in fact, the RE concentrations are kept below 10^{19} cm^{-3}, although co-doping with Al and P increases the RE solubility.

Another very effective PL quenching mechanism is energy transfer to OH groups in the glass, which is strictly no longer a form of concentration quenching, but rather of MP non-radiative relaxation.

Er^{3+} fluorescence lifetime as a function of ion concentration:

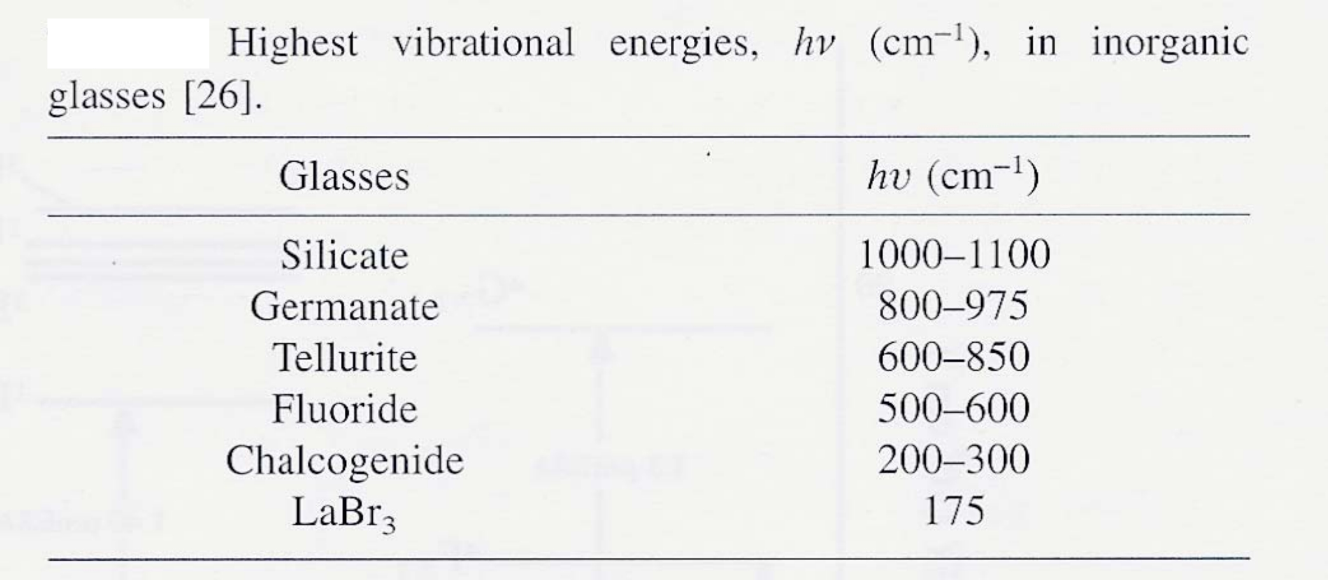
fits to the equation: $\tau = \tau_o / [1+(c/Q)^p]$



RE doping of fluoride and chalcogenide glasses

Fluoride glasses, in particular HMFG and ChG are highly suitable for rare-earth element doping for active optical applications, such as lasers or amplifiers, in bulk, fiber, or thin film from.

The main reasons are: (1) the large solubility of RE elements in these glasses, especially in fluoride glasses, much higher than in oxide glasses like the silicates (tellurite glasses, based on TeO_2, have also large RE solubility); (2) the low vibrational frequencies of the HMFG and ChG matrix first order modes, when compared to most oxide glasses, which reduces non-radiative multiphonon relaxation and favors radiative (PL) emission.



Highest vibrational energies, $h\nu$ (cm^{-1}), in inorganic glasses [26].

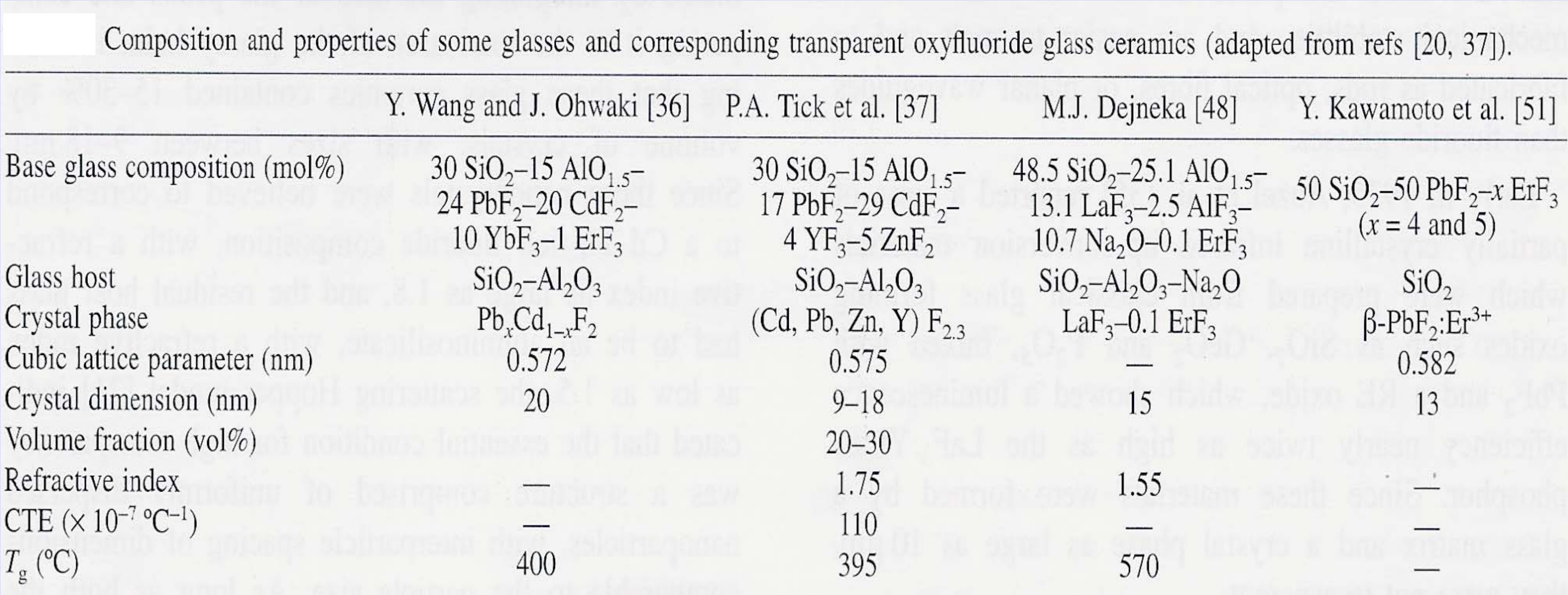
Glasses	$h\nu$ (cm^{-1})
Silicate	1000–1100
Germanate	800–975
Tellurite	600–850
Fluoride	500–600
Chalcogenide	200–300
$LaBr_3$	175

(Adapted from: M.C. Goncalves et al., *C.R. Chimie*, 5 (2002) 24)

RE-doped transparent glass-ceramics (TGC)

There is much interest in Pr-doped oxyfluoride TGC for the second window (1.3 μm) of optical communications. These contain fluoride nanocrystals ~ 15 nm in diameter, embedded in a primarily oxide glass matrix which has good chemical and mechanical stabilities. A quantum efficiency well higher than the 2.4 % in FZ host was measured for SiO_2-Al_2O_3-CdF_2-PbF_2-YF_3 TGC, due to Pr being primarily incorporated in fluoride nanocrystals. Similar TGC have been doped with Er,Yb, Tm and Eu, for possible frequency up-conversion application.

TGC can be obtained under conditions where the achievement of low optical absorption and scattering are possible. For example, crystals with sizes < ~ 30 nm will present negligible Rayleigh scattering in the visible region, as long as the refractive index difference between the crystals and the amorphous phase does not exceed ~ 0.1. However, according to a model due to Hopper (1985), crystal sizes of 30 nm and a Δn of up to 0.3 is still acceptable, provided the crystal spacing is not more than 6 times the average crystal size (≤ ~ 180 nm).



Composition and properties of some glasses and corresponding transparent oxyfluoride glass ceramics (adapted from refs [20, 37]).

	Y. Wang and J. Ohwaki [36]	P.A. Tick et al. [37]	M.J. Dejneka [48]	Y. Kawamoto et al. [51]
Base glass composition (mol%)	30 SiO_2–15 $AlO_{1.5}$–24 PbF_2–20 CdF_2–10 YbF_3–1 ErF_3	30 SiO_2–15 $AlO_{1.5}$–17 PbF_2–29 CdF_2–4 YF_3–5 ZnF_2	48.5 SiO_2–25.1 $AlO_{1.5}$–13.1 LaF_3–2.5 AlF_3–10.7 Na_2O–0.1 ErF_3	50 SiO_2–50 PbF_2–x ErF_3 (x = 4 and 5)
Glass host	SiO_2–Al_2O_3	SiO_2–Al_2O_3	SiO_2–Al_2O_3–Na_2O	SiO_2
Crystal phase	$Pb_xCd_{1-x}F_2$	(Cd, Pb, Zn, Y) $F_{2.3}$	LaF_3–0.1 ErF_3	β-PbF_2:Er^{3+}
Cubic lattice parameter (nm)	0.572	0.575	—	0.582
Crystal dimension (nm)	20	9–18	15	13
Volume fraction (vol%)		20–30		
Refractive index	—	1.75	1.55	—
CTE (× 10^{-7} °C^{-1})	—	110	—	—
T_g (°C)	400	395	570	—

(Adapted from: M.C. Goncalves et al., C.R. Chimie 5 (2002) 845.)