CROSS-RELAXATION OF ELECTRONIC EXCITATION IN LANTHANIDE-DOPED CRYSTALS AND GLASSES

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Cross-relaxation due to dipole-dipole electrostatic interaction between electric dipole moments of lanthanide ions decreases the fluorescence quantum yield and shortens excited state lifetime. Despite that, cross-relaxation is important because it enables sensitized fluorescence, which is useful when emitting ions can't absorb the excitation light. Gain media is therefore co-doped with another type of lanthanide ions, which absorb the excitation light and transfer the electronic excitation to the ions, which produce fluorescence. This kind of gain media is used in solid-state lasers and optical fiber amplifiers.

KRIŽNA RELAKSACIJA ELEKTRONSKE VZBUDITVE V KRISTALIH IN STEKLIH DOPIRANIH Z LANTANIDI

Elektrostatična interakcija med električnimi dipolnimi momenti lantanidnih ionov omogoča križno relaksacijo elektronske vzbuditve. Ta zmanjša fluorescenčni izkoristek in skrajša življenjski čas vzbujenega stanja. Kljub temu je pomembna, saj omogoča posredovano fluorescenco, ki je uporabna, če aktivni ioni ne morejo absorbirati vzbujevalne svetlobe. Ojačevalno sredstvo zato dopiramo z drugimi lantanidnimi ioni, ki absorbirajo vzbujevalno svetlobo in prenesejo elektronsko vzbuditev na primarne ione, ki nato fluorescirajo. Takšna ojačevalna sredstva uporabljamo v trdninskih laserjih in optičnih vlakenskih ojačevalnikih.

1. Introduction

Lanthanides are chemical elements that are generally not well-known, but nevertheless very important. Due to their electronic configuration, they have large magnetic moments. This is why they are used as contrast agents for magnetic resonance imaging (MRI) and in permanent magnets. Although these applications are of higher importance, the majority of produced lanthanide elements is used as chemical catalysts or additives, e.g., in metallurgy and production of glass and ceramics [1].

Besides their special magnetic properties, lanthanides also have unique photophysical properties, which will be discussed in this article. Lanthanides are widely used in optoelectronics, e.g. as wavelength converters in spontaneous and stimulated emission. But we will focus on the application of lanthanide ions as gain media in solid-state lasers and optical fiber amplifiers. The desired qualities for a gain media are strong absorption bands for pumping and high fluorescence quantum yield for laser transition [2]. Lanthanide ions embedded in appropriate crystals or glasses fulfil these conditions. Most commonly used lanthanides for this purpose are neodymium, erbium, and ytterbium, followed by thulium and holmium.

2. Lanthanides

The lanthanide series consists of 15 chemical elements from lanthanum with atomic number 57 to lutetium with atomic number 71. They are often called "rare earths" although they are not rare, just very dispersed in the soil and rarely found in larger amounts [4].

Most lanthanide ions are fluorescent, which means that they emit light upon relaxation from an excited energy level to a lower energy level. Their emission spectra feature multiple narrow lines over a wide wavelength range. Their spectral positions are relatively independent of the host matrix [4]. To better understand lanthanide fluorescence, we have to analyse their electronic energy levels and radiative and nonradiative transitions between them.

Figure 1. Lanthanides in the periodic table. Reproduced from [5].

2.1 Electronic structure

All lanthanide elements except lanthanum are part of the f-block in periodic table, as shown in Figure 1, which means the 4f electron shell is being filled. The electron configuration of all lanthanides is $[Xe]\,4f^n\,5d^1\,6s^2$ or $[Xe]\,4f^{n+1}\,6s^2$, where n = 0˘14 is the number of electrons for individual lanthanide, and $[Xe] = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^6$ is electron configuration of xenon [4]. Although filled 5s and 5p orbitals are energetically lower than 4f orbitals, there is a large probability that 4f electrons are closer to the core than the 5s and 5p electrons. Consequently, 5s and 5p orbitals shield 4f orbitals from the chemical environment, so all lanthanides have very similar chemical properties. The most common oxidation state for all lanthanides is trivalent cation Ln^{3+}, where the symbol Ln is used to indicate any lanthanide [4]. Their electron configuration is $[Xe]\,4f^n$ which means they all have valence electrons in 4f orbitals.

2.2 Energy levels

From now on we will focus only on lanthanide ions Ln^{3+} embedded in a suitable crystal or glass matrix, as they are relevant for the applications we are interested in. There are several interactions within the ion that cause the splitting of degenerate f-orbital energy level. They are represented in Figure 2a using europium ion Eu^{3+} as an example. The electron configuration is first divided into terms due to Coulomb interaction, which acts as repulsion between the electrons within the 4f orbital.

Spin-orbit coupling is a consequence of electromagnetic interaction between the electron's magnetic dipole, its orbital motion, and the electric field of the positively charged nucleus. Because of the spin-orbit coupling, each term is split further into J-levels, which represent free ion levels. They are described with the symbol $^{2S+1}L_J$, where S is the total spin angular momentum, L marks the total orbital angular momentum (L = 0, 1, 2, 3, 4, ..., represented with letters S, P, D, F, G, ...) and J is the total angular momentum of the f electrons [4].

When a lanthanide ion is doped into a crystal or glass, the J-levels split into several sublevels, because the ion is affected by the electric field of the matrix usually referred to as the crystal field [4]. This is called the Stark effect and leads to 2J+1 sublevels if the total angular momentum J is an integer, or into $J + \frac{1}{2}$ sublevels if J is not an integer (Kramers theorem) [6]. These splittings are relatively small because the 4f electrons are shielded from the environment.

Figure 2. a) Diagram representing the splitting of the electronic energy levels of Eu^{3+} ion, due to different interactions, reproduced from [4]; b) fluorescence spectra of Eu^{3+} ions in different environments, adapted from [7]. The third graph in figure b) was produced in a different experiment than the first and second graphs, therefore the units aren't comparable, and the third graph is normalised to 1.

Figure 2b shows an example of europium ion's emission spectra in different environments. As already said, the crystal field splitting is very small. For this reason, the narrow emission lines, which correspond to transitions between sublevels, merge into larger emission bands. These emission bands correspond to transitions between J-levels. Their spectral positions are negligibly influenced by the matrix. On the other hand, transitions between sublevels are much more sensitive to the environment. In disordered systems, like glasses, or in this case water, there is an inhomogeneous broadening due to different strength of the local crystal field at the lanthanide ion's positions. Inhomogeneous broadening can be seen in the first graph of Fig. 2b, where we can't distinguish individual emission lines. In crystals, however, almost all ions have identical surroundings, and therefore the same crystal field splitting. Emission lines are broadened homogeneously and can be seen as the fine structure of the emission bands (third graph of Fig. 2b). The intensities of the emission lines also heavily depend on the environment, which can be seen in the emission lines, induced by the transition $^5D_0 \rightarrow\,^7F_2$.

3. Electronic excitation and relaxation

Electronic excitation is a process where the electron system receives an appropriate amount of energy to get elevated from the ground state to any other quantum state. The absorbed energy has to be the same as the energy difference between the original and the final energy level. This can happen, e.g., upon absorption of a photon.

Electronic relaxation is the inverse process of the excitation. The excited electron system relaxes to a lower energy level by radiative (photon emission) or nonradiative energy transfer.

3.1 Radiative transitions

Radiative transitions involve the emission or absorption of photons. Spectroscopic selection rules define if a given transition is allowed or forbidden. In centro-symmetric systems, each quantum state has defined parity, which can be odd or even [3]. In these systems, electric dipole transitions within the same electron orbitals are formally forbidden, because they conserve parity. Electric dipole (ED) transitions in free lanthanide ion, which is a centro-symmetric system, cause redistribution of electrons within the 4f sub-shell [4]. For this reason, they are formally forbidden.

In a host matrix, however, the non-centrosymmetric part of the crystal field mixes some odd-parity configurations (e.g., $[\text{Xe}]\,4\text{f}^{\text{n}-1}\,5\text{d}^1$) into the $[\text{Xe}]\,4\text{f}^{\text{n}}$ configuration. In these systems, spectroscopic selection rules don't apply that strictly. The formally forbidden f-f ED transitions thus become "partly allowed" or "induced" transitions.

Besides the electric dipole transitions, magnetic dipole and electric quadrupole transitions are also possible in the discussed systems, but are much less probable, despite that ED transitions are only "partly allowed".

3.2 Nonradiative transitions

Nonradiative transitions in lanthanide ions, embedded in crystals and glasses, arise mostly due to multiphonon relaxation, whereby the electronic excitation energy is converted into vibrations of the surrounding matrix [6].

The probability rate for multiphonon relaxation decreases approximately exponentially with the number of phonons, $p = \frac{\Delta E}{h\nu}$, that fit into the energy gap ΔE between the initial and final electronic state. It is given by

$$W_p = C(n(T) + 1)^p e^{-\alpha h \nu p}, \tag{1}$$

where h is the Planck's constant and ν is the phonon frequency. The Bose-Einstein occupation number of the phonon mode is given by $n(T) = (e^{h\nu/k_B T} - 1)^{-1}$, where T is temperature and k_B is Boltzmann constant. The host matrix determines the phonon spectrum as well as constants C and α. In glasses the energy of phonons goes up to 0.2 eV [6], while the value of $k_B T$ at room temperature is around 25 meV.

From Eq. 1, it follows that, for a given energy gap ΔE, the probability rate W_p will be the highest for the smallest possible number of phonons p, and therefore for phonons with the highest energy $h\nu$. For this reason, nonradiative transitions over larger energy gaps are usually less probable than radiative transitions because they require multiple phonons. On the other hand, nonradiative transitions over small energy gaps are often more probable than radiative ones, especially when the latter are only "partly allowed".

As a result of the above, the observed radiative transitions originate mainly from a few excited states, which have a sufficiently large energy gap ΔE to the lower-lying levels. For example, in Figure 2 we can see that all observed emission lines of Eu^{3+} ion originate from level $^5\text{D}_0$, which has a large energy gap, of approximately 1.5 - 2 eV, to the levels $^7\text{F}_\text{J}$.

On the other hand, when the ion is in any other energy state, which has a smaller energy gap to the next lower-lying level, it usually undergoes multiphonon relaxation because the radiative probability rate is negligible. Therefore the emission lines of levels $^5\text{D}_1$, $^5\text{D}_2$, ... are not visible. The energy gaps between levels $^5\text{D}_\text{J}$ are around 0.1 - 0.3 eV.

3.3 Lifetime and quantum yield

The lifetime of an excited state refers to the average time the ion remains in this state before it undergoes relaxation. The population of the excited level $N(t)$ decays with time due to radiative and nonradiative processes as described by the differential equation

$$\frac{\mathrm{d}N(t)}{\mathrm{d}t} = -(k_r + k_{nr})N(t), \tag{2}$$

where k_r is radiative probability rate and k_{nr} is nonradiative probability rate. The resulting decay of the excited state is exponential

$$N(t) = N_0 e^{-t/\tau}, \tag{3}$$

where N_0 is the initially excited population of lanthanide ions and τ is the excited-state lifetime, equal to the reciprocal of the total decay rate

$$\tau = (k_r + k_{nr})^{-1}. \tag{4}$$

The excited-state lifetime is a quantity we can measure, and it depends on the probability rates of both radiative and nonradiative transitions. This can be expressed with the radiative lifetime, $\tau_r = \frac{1}{k_r}$, which refers to the lifetime in the absence of nonradiative transitions,

$$\frac{1}{\tau} = \frac{1}{\tau_r} + k_{nr}. \tag{5}$$

k_{nr} heavily depends on the environment, for example, temperature, concentration, etc., while τ_r doesn't.

An important parameter is also the fluorescence quantum yield, which is defined as the ratio of the number of emitted photons and the number of absorbed photons

$$Q_F = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} = \frac{k_r}{k_r + k_{nr}}. \tag{6}$$

Evidently, nonradiative transitions decrease the fluorescence quantum yield. The term "quenching" indicates the reduction of the fluorescence quantum yield due to different processes. In solid materials, these processes include multiphonon relaxation and concentration quenching, due to cross-relaxation.

4. Cross-relaxation

Let us consider lanthanide ions doped into a crystalline or glass host matrix. At a sufficiently high doping concentration, we have to consider also interactions between the lanthanide ions. Electrostatic interaction between a lanthanide ion and its nearest neighbours is usually too weak to cause additional energy level splitting, but it may enable nonradiative transfer of electronic excitation [6]. This process is called cross-relaxation and is schematically illustrated in Figure 3.
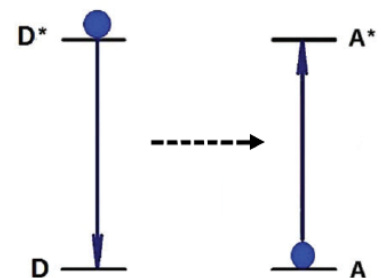
Figure 3. Nonradiative energy transfer between an excited donor (D*) and non-excited acceptor ion (A), called cross-relaxation. Adapted from [8].

The initially excited ion is called a donor D*. It relaxes non-radiatively to its ground state D and transfers the excitation to a nonexcited ion, called an acceptor. This ion gets elevated from the

ground state A to the excited state A*. Generally, the distance between the ions is large enough that cross-relaxation can be described by the dipole-dipole energy transfer mechanism. Exceptionally, when the distances are comparable with ion's sizes, electric multipole interactions must be considered [8]. Note that cross-relaxation shouldn't be confused with emission and reabsorption of a photon since it is a fundamentally different process.

The probability rate for cross-relaxation, derived using quantum theory, is given as

$$W_{DA} = \frac{1}{\tau_r} \left(\frac{R_0}{r} \right)^s,$$ (7)

where τ_r is the radiative lifetime of the donor excited state (D*), r is the distance between donor and acceptor, R_0 is the Förster radius, $s = 6$ for dipole-dipole interactions, $s = 8$ for dipole-quadrupole interactions and $s = 10$ for quadrupole-quadrupole interactions [8].

In addition to multiphonon relaxation, cross-relaxation also reduces the fluorescence quantum yield (Eq. 6) and decreases the excited-state lifetime (Eq. 5).

4.1 Concentration quenching

Probability for cross-relaxation increases with the concentration of lanthanide ions (Eq. 7). When the concentration is sufficiently high, the electronic excitation can migrate across the host until it

reaches a defect or impurity where it is dissipated [6]. For this reason, the fluorescence quantum yield is further reduced, and the excited-state lifetime decreased. This process is called concentration quenching.

An example of decreasing excited-state lifetime with increasing concentration of Sm^{3+} ions is presented in Figure 4.

In a laser gain media, long excited-state lifetimes are desired to achieve population inversion. The concentration of lanthanide ions must thus be kept below a few percent [10]. This can present a problem, because the absorption coefficient is directly proportional to the concentration.
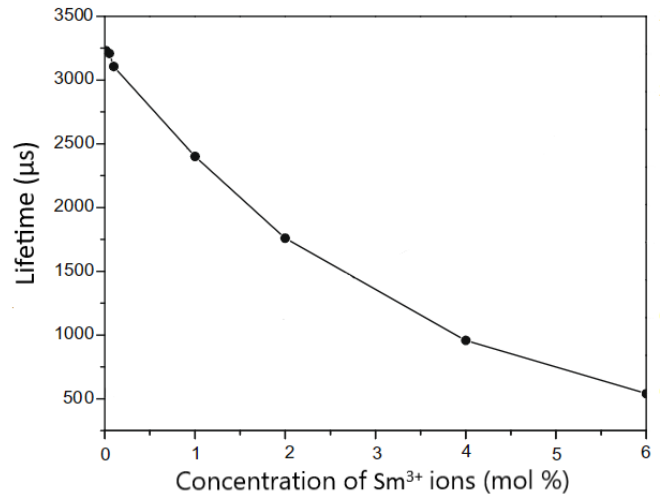
Figure 4. Excited-state lifetime for $^4G_{5/2}$ level of Sm^{3+}-doped PKFBA glass. Adapted from [11].

4.2 Phonon-assisted cross-relaxation

The Förster radius R_0 in Eq. 7 determines the distance between the ions at which the W_{DA} will be considerable. In the 1950's it was calculated by an American physicist David L. Dexter [9] to depend critically on the spectral overlap

$$R_0^6 \propto \frac{\int f_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda}{\int f_D(\lambda) d\lambda},$$ (8)

of the emission spectrum of the donor $f_D(\lambda)$ and the absorption spectrum of the acceptor $\epsilon_A(\lambda)$, where λ is the wavelength that corresponds to the energy difference of the given transitions.

This resonance condition demands that $f_D(\lambda)$ and $\epsilon_A(\lambda)$ must overlap for the probability rate W_{DA} to be significant.

Later on, it turned out that in many cases, the resonance condition for cross-relaxation is not that strict. Absorption or emission of phonons can, namely, take care of the conservation of energy, as illustrated in Figure 5 [8]. The phonon-assisted cross-relaxation, therefore, enables a transfer of electronic excitation between different kinds of lanthanide ions. The temperature and the phonon spectra of the host matrix dictate how large energy difference between the excited states of the donor (D*) and acceptor (A*) $\delta E_{D^*A^*}$ can the phonons compensate.
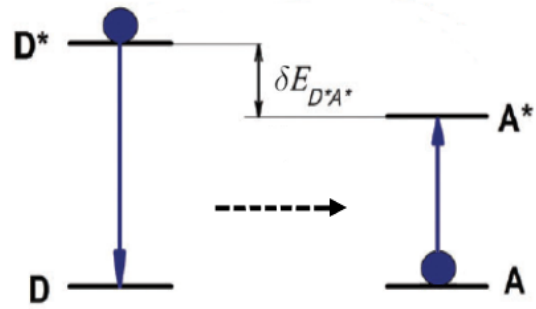
Figure 5. Phonon-assisted cross-relaxation between Ln^{3+} ions. Reproduced from [8].

4.3 Sensitized fluorescence

Sensitized fluorescence is a concept, where the donor or sensitizer ion absorbs the energy from excitation light and transfers the electronic excitation to a different kind of lanthanide ion by cross-relaxation. The acceptor or emitter ion then relaxes radiatively by emitting light with a different wavelength. The unique feature of sensitized fluorescence is that the excited-state lifetime of sensitizer ions depends on the concentration of emitters [6].

From Eq. 7 we see that the probability rate for cross-relaxation from the sensitizer to an emitter ion decreases quickly with their distance. Because of that, cross-relaxation between the sensitizer ions can be beneficial, as it enables the migration of electronic excitation closer to the emitter ions, even though the initially excited sensitizer ions are far from them. This enhances the fluorescence because more emitter ions get excited, as opposed to concentration quenching. To balance both processes, the concentration of both sensitizer and emitter ions must be optimised for individual application and specifically for each host matrix.

The sensitized fluorescence is important when the emitter ions don't absorb the excitation light in a given region of the spectrum, for example, visible or UV. Then, suitable sensitizer ions can be used to absorb this light and transfer the excitation to the emitter ions. The most commonly used sensitizer ion is ytterbium ion Yb^{3+} because it has a large absorption cross-section for NIR light. In addition, its simple energy scheme consists of only one excited state with a huge energy gap to the ground state, which reduces the possibility for undesired nonradiative relaxation of the excited state and results in long excited-state lifetime. Most frequently used emitter ions compatible with Yb^{3+} are Er^{3+}, Tm^{3+} and Ho^{3+}.

5. Co-doped Yb-Er glass gain media

One example of the above is Yb-sensitized Er-activated glass gain media, whose pumping process is illustrated in Figure 6. Non-excited ytterbium ions absorb near-infrared light from 860 nm to 1020 nm by transitioning to the level $^2F_{5/2}$. Because the energy difference between this state and ground state $^2F_{7/2}$ is large, the probability for multiphonon relaxation is very small. Therefore, a significant part of ytterbium ions relaxes by cross-relaxation, and transfer the excitation to erbium ions (a), which get elevated from ground state $^4I_{15/2}$ to excited state $^4I_{11/2}$. From there, they quickly relax via multiphonon relaxation to the upper laser energy level, $^4I_{13/2}$. Afterwards, they relax to the ground state, primarily radiatively, causing the emission at 1,54 μm.

When a significant amount of erbium ions get excited in order to reach population inversion, some erbium ions in the excited state $^4I_{13/2}$, can again receive excitation from ytterbium ions via cross-relaxation (b) [6]. They get elevated to the state $^4F_{9/2}$, because the energy difference for this transition is similar to the energy difference between $^2F_{7/2}$ and $^2F_{5/2}$ in the ytterbium ion. From $^4F_{9/2}$ erbium ions relax back to the upper laser level $^4I_{13/2}$ by sequential multiphonon relaxation. In this case, the excitation energy of one ytterbium ion is dissipated in the form of vibrations to the host matrix, which is undesired.

Cross-relaxation is also possible between two excited erbium ions in the state $^4I_{13/2}$. One of them relaxes to the ground state $^4I_{15/2}$, and the other gets elevated to the higher excited state $^4I_{9/2}$, from which it again relaxes by sequential multiphonon relaxation back to the level $^4I_{13/2}$ [6]. This process is called nonlinear quenching and is undesired because the excitation energy of one ytterbium ion is also dissipated in the form of vibrations. Nonlinear quenching is not very likely due to small concentrations of excited erbium ions.

Figure 6. Energy level diagram of Er-Yb system. Black solid line represents optical pumping at 980 nm, dashed lines correspond to cross-relaxation, wavy lines represent multiphonon relaxation and red solid line illustrates emission at 1,54 μm. Adapted from [12].

5.1 Erbium glass laser

A scheme of a typical solid-state laser is presented in Figure 7a. Optical amplification in the gain media is reached, when the population of the upper energy level of laser transition is higher than the population of the lower energy level. To achieve this, the gain media is optically pumped with an external light source, which excites active ions into higher energy levels. The problem is that the absorption cross-section of erbium ions in the region of visible and UV light is very small. To excite enough erbium ions, a very high concentration of them would be necessary, which is not possible due to concentration quenching. Therefore, the erbium glass laser takes advantage of the sensitized fluorescence via ytterbium ions, which are added in a high amount. Typical concentration of Yb^{3+} is thus around 20 %, while the concentration of Er^{3+} is below 2 %. Figure 7b shows how the erbium glass gain media looks like.

One important feature of erbium glass laser is its relative eye-safety because the absorption of 1,54 μm light in water is precisely right so that the energy of the incident light is homogeneously absorbed across the eye and doesn't damage the sensitive retina. The maximal permissible exposure of pulsed 1,54 μm laser radiation hitting a human eye is five orders of magnitude larger than that for 1,06 μm Nd:YAG lasers [10].

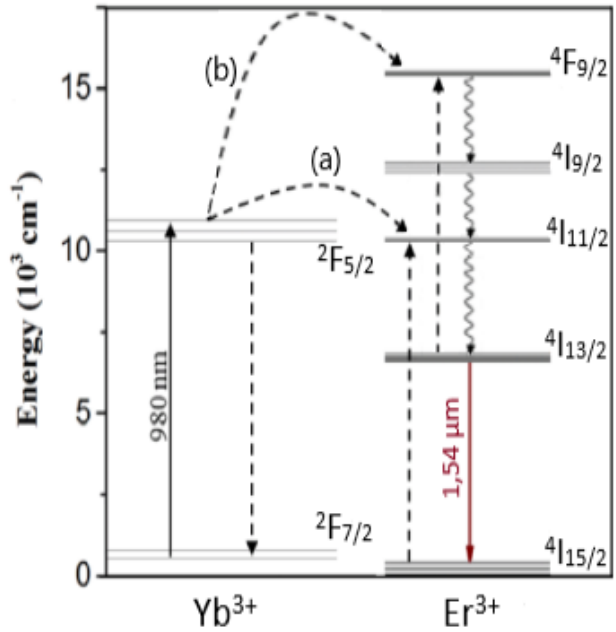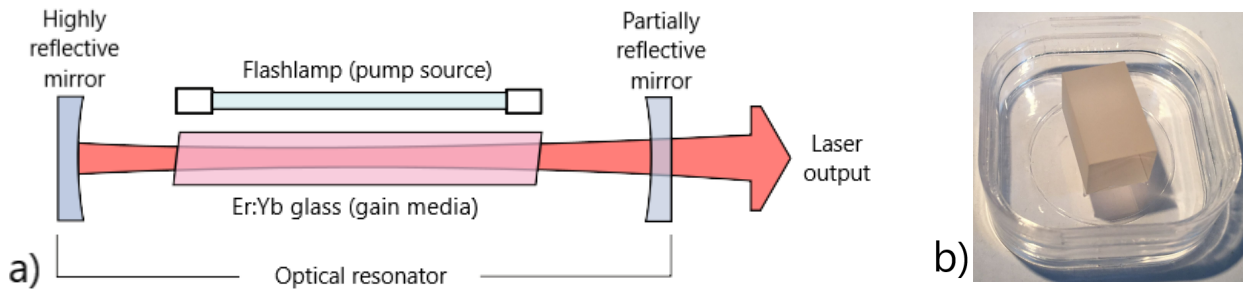**Figure 7.** a) Schematic setup of a solid state laser, showing optical resonator, gain media and pump source, adapted from [13]; b) erbium glass gain media, reproduced from [14].

One of the important applications is the use of erbium glass laser as the source for optical telecommunications because the optical fibers have minimum dispersion and losses right around the $1,5$ μm wavelength. Because of their eye-safety, erbium glass lasers are used for measuring distances to the target, e.g., as rangefinders in the military or as tacheometers in geodesy. Erbium glass lasers can also be used in medicine, especially for healing scars, because they heat the tissue, but don't damage it.

5.2 Erbium fiber amplifier

Another important application of erbium-doped gain media are optical amplifiers for long-range fiber communications. They efficiently amplify light in the $1,5$ μm wavelength region, where optical fibers have minimum losses and dispersion.

A typical setup of an erbium fiber amplifier is illustrated in Figure 8. The source of light, that travels through the fiber, is erbium glass laser, therefore, the wavelength of this light is 1540 nm. The main part of a fiber amplifier is the active fiber (green part), which is actually a section of glass fiber, co-doped with ytterbium and erbium. This gain media provides optical amplification when it is pumped with an external light source, e.g., laser diodes. This light excites ytterbium ions Yb^{3+}, which transfer the excitation to erbium ions Er^{3+}, which get excited to the state ${}^4I_{13/2}$ (Fig. 6), same as in the erbium glass laser. The excited erbium ions then amplify the light in the $1,5$ μm region via stimulated emission back to the ground state ${}^4I_{15/2}$.
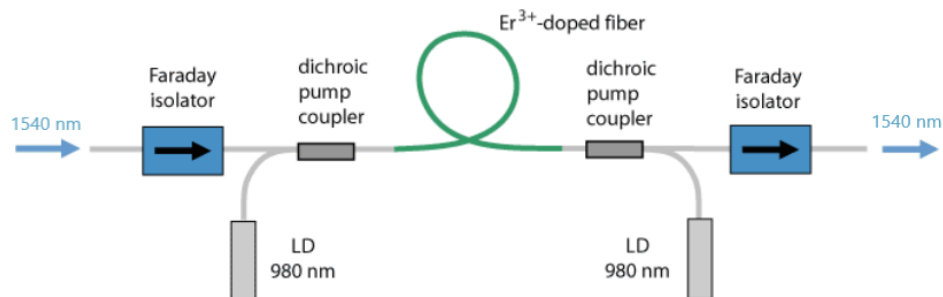
Figure 8. Schematic setup of an erbium-doped optical amplifier. LD are laser diods, used for optical pumping. Faraday isolators prevent back-reflections. Dichroic couplers couple the pump light from the laser diodes into the active fiber. Reproduced from [15].

Erbium fiber amplifiers are used, e.g., as optical repeaters in the undersea cables, which carry telecommunication signals over large distances. Their advantage is that they don't need electricity to operate and that they amplify an optical signal directly without converting it into an electrical signal first.

6. Conclusion

Cross-relaxation of electronic excitation occurs due to the coupling of electric dipole moments of lanthanide ions, doped into crystals or glasses. Cross-relaxation decreases fluorescence quantum yield and shortens the excited-state lifetime. On the other hand, cross-relaxation is useful because it enables sensitized fluorescence, e.g., in Yb-Er glass gain media. Namely, erbium ions don't absorb the excitation light in the visible and UV region, and their required concentration is limited by concentration quenching. Therefore, the pumping process takes place via co-doped ytterbium ions, which transfer the excitation to erbium ions.

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