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Emission Cross Sections and Energy Extraction for the Mid-infrared Transitions of Er, Tm, and Ho in Oxide and Fluoride Crystals

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Abstract

Emission cross sections have been measured for the transitions between the two lowest spin orbit multiplets of Er, Tm, and Ho in several fluoride and oxide crystals. Properties affecting energy extraction efficiency are summarized and pulsed extraction performance is calculated for several of these quasi-three-level laser media.

I. Introduction

The first excited spin-orbit multiplets of Er, Tm, and Ho have long lifetimes, on the order of 10 ms, in many crystals. For this reason, these ions are potentially attractive for laser diode pumping in energy storage laser applications in the mid-infrared spectral region. Very few measurements of emission cross sections have been made for these ions, however, so their suitability for efficient fast-pulse amplification and Q-switching has not been explored in a systematic and quantitative fashion. In this paper we summarize measurements of emission cross sections and lifetimes of these ions in a number of oxide and fluoride crystals. The physics of energy extraction in quasi-three-level media is developed, and some examples of pulsed energy extraction for three of the most favorable media are presented.

II. Cross section measurements

Emission cross sections were measured using two methods. The primary method was to measure absorption cross sections and rare earth concentrations and then to make use of the reciprocity between absorption and emission cross sections. This leads to

the following relationship for the effective emission cross section spectrum, σ_{eff} , and the measured quantities

$$\sigma_{\text{eff}}(\nu) = \frac{\alpha(\nu)}{N_0} \frac{Z_g}{Z_e} \exp[E_0 - h\nu]/kT \quad (1)$$

In Eq. (1), $\alpha(\nu)$ is the measured absorption coefficient, N_0 is the rare earth concentration, Z_e and Z_g are the partition functions of the upper and lower crystal field split spin-orbit manifolds defined with different zeros of energy (at the lowest crystal field level of each manifold), $E_0 = h\nu_0$ is the energy separating the lowest crystal field levels of the upper and lower manifolds, and ν is the optical frequency. This notation is summarized in Fig. 1, which is a generic energy level diagram for these rare earth transitions. This method does not rely on any questionable assumptions for its validity. It does, however, require a knowledge of the energies and degeneracies of all of the crystal field levels of both manifolds.

Figure 1. Generic energy level diagram of excited and ground spin-orbit multiplets of Er^{3+} , Tm^{3+} , and Ho^{3+} .

The second method we used to obtain emission cross sections is the Füchtbauer-Ladenberg formula, with which the cross section is calculated from the emission spectrum and radiative lifetime, τ_{rad} . It must be assumed that τ_{rad} is the measured emission lifetime, which for new, poorly characterized materials, which may not be the case. We found, however, that the two sets of cross sections agreed within the experimental errors for all but two of the materials that we measured.

The measurements and their dependence on rare earth ion and crystal structure are discussed in detail in a forthcoming publication [1], so only a brief qualitative summary of the spectra will be given here. Several cross section spectra for materials of interest are shown in Figs. 2-5. The emission cross sections are given by the dashed curves, and the absorption cross sections are the solid curves. The entire set of crystals for which cross sections were measured is given in Table 1.

Table 1. Selected set of emission cross sections and corresponding values of ΔE

Host	Er		Tm		Ho		Coord: Number
	σ_{eff}	ΔE	σ_{eff}	ΔE	σ_{eff}	ΔE	
$\text{Y}_3\text{Al}_5\text{O}_{12}$	0.45	470	0.22	580	0.98	460	8
LiYF_4	0.42	350	0.33	360	1.20	280	8
BaY_2F_8	0.27	280	0.11	310	1.07	310	8
LaF_3	0.37	220	0.25	210	0.33	320	~9
KCaF_3	0.12	260	0.15	250	0.28	300	6
YAlO_3	0.31	450	0.50	460	0.82	460	12
$\text{La}_2\text{Be}_2\text{O}_5$	0.23	250	0.23	450	0.42	340	~10

σ_{eff} values in units of 10^{-20} cm^2
 ΔE in cm^{-1}

Figure 2. Emission (dashed) and absorption cross sections of Ho^{3+} :YAG.

Figure 4. Emission and absorption cross sections of Er^{3+} :YAG.

Figure 3. Emission and absorption cross sections of Ho^{3+} :YLF.

Figure 5. Emission and absorption cross sections of Tm^{3+} :YAG.

The three oxides and four fluorides have coordination numbers ranging from 6 to 12. They therefore cover a range of crystal field environments, and they should be representative of the full range of properties expected for these ions in crystalline hosts.

III. Energy extraction in quasi-three-level laser media

Nonradiative transitions between the crystal field levels of each of the rare earth multiplets in Fig. 1 occur [2] at a rate of about 10^{12} s^{-1} . It can be assumed, therefore, that each multiplet will achieve thermal equilibrium in a few picoseconds, and the assumption of thermal equilibrium is good for pumping and extraction pulses longer than 10 ps or so. Ground state depleted pumping of rare earths has been discussed in detail in a previous publication [3], so only the extraction terms in the rate equations will be discussed here.

We define the excited fraction as β and the total rare earth concentration as N_0 and consider extraction pulses much shorter than the $\sim 10 \text{ ms}$ lifetimes of the upper multiplet, so that pumping and radiative decay can be neglected. Referring to Fig. 1, the rate of change of the excited manifold population, $N_0\beta$, at a particular time and position in the laser medium is given by

$$\frac{d(N_0\beta)}{dt} = -\frac{\Phi}{h\nu} \sigma_{if}(N_i g_f - N_f g_i)$$

where Φ is the laser flux at a wavelength resonant with the i-f transition, and σ_{if} is the cross section for the transition between levels i and f with degeneracies g_i and g_f . This equation is easily rearranged to give

$$\frac{d\beta}{dt} = -\frac{\Phi}{\Gamma_s(1-\beta_{\min})}(\beta-\beta_{\min}) \quad (2a)$$

where

$$\beta_{\min} = \left[1 + \frac{Z_g}{Z_e} \exp(\Delta E/kT) \right]^{-1}, \quad (2b)$$

$$\Delta E = E_f - E_i = E_0 - h\nu, \quad (2c)$$

$$\sigma_{\text{eff}} = \frac{\sigma_{if} N_i g_f}{\beta N_0} = \frac{\sigma_{if}}{Z_e} g_i g_f \exp(-\bar{E}_i/kT), \quad (2d)$$

$$\Gamma_s = hc/\lambda \sigma_{\text{eff}}. \quad (2e)$$

Similarly, the equation for the growth of the laser flux is

$$\frac{\partial \Phi}{\partial z} + \frac{n}{c} \frac{\partial \Phi}{\partial t} = (N_i g_f - N_f g_i) \sigma_{if} \Phi - \alpha \Phi$$

and, with the above substitutions, this becomes

$$\frac{\partial \Phi}{\partial z} + \frac{n}{c} \frac{\partial \Phi}{\partial t} = \left(\frac{N_0 \sigma_{\text{eff}} \Phi}{1-\beta_{\min}} \right) [\beta - \beta_{\min}] - \alpha \Phi \quad (3)$$

Note that σ_{eff} is the emission cross section obtained from the measurements, and α is an assumed non-saturable passive loss due to scattering and absorption in the laser medium. Additional terms can be added to Eq. (2) to account for radiative and nonradiative decay and pumping.

Eqs. (2) and (3) differ from those of a four level laser because of the nonzero value of $\beta_{\min}$, which is the minimum inversion required for net gain on the laser transition (i.e., it is the fractional inversion that gives $N_i = N_f$). $\beta_{\min}$ is also the minimum inverted fraction that will remain in the medium after an extraction pulse of arbitrarily large fluence. If the initial inversion before extraction is β_0 , the maximum value of the initial stored energy that can be extracted is

$$\eta_{\max} = \frac{\beta_0 - \beta_{\min}}{\beta_0} = 1 - \frac{\beta_{\min}}{\beta_0} \quad (4)$$

Since the optical transitions of these rare earths are homogeneously broadened in crystalline environments, the fraction $\eta_{\max}$ can, in principle, be extracted at any wavelength for which there is a finite emission cross section. Of course, $\eta_{\max}$ increases with wavelength, because ΔE increases with wavelength. The dependence of $\eta_{\max}$ on ΔE is illustrated in Fig. 6 for three values of β_0 . The ratio of partition functions was taken to be unity, since it does not vary strongly from that value for

Figure 6. Dependence of $\eta_{\max}$ on ΔE for several values of the initial inversion, β_0 .

different ions and crystals. For high extraction efficiency, it is obviously desirable to extract at wavelengths as long as possible, provided that the emission cross section is large enough that the

saturation fluence is below the optical damage threshold, which is an increasing function of pulse duration. This selection of operating wavelength will clearly depend on the pulse duration, but, for most of the materials surveyed, it is possible to identify some optimum operating wavelengths that provide the best combination of large ΔE and high σ_{eff} for fast pulse (ns- μ s range) extraction. These choices are indicated on Figs. 2-5 and in Table 1.

IV. Discussion

The spectra of Ho^{3+} in Figs. 2 and 3 show that it has a very favorable distribution of oscillator strength in eightfold coordination. The strongest transitions have large values of ΔE . The Er^{3+} :YAG spectrum in Fig. 4 is the most favorable for that ion, since it gives the largest cross sections at large ΔE . Unfortunately, most of the strongest transitions of Er^{3+} are at $\Delta E \sim 0$ (which is the reason why Er in glass has essentially two-level extraction). The peak Er^{3+} cross sections at large ΔE are at most 50% as large as those of Ho^{3+} , partly because of the distribution of transition strength, but also because of the more pronounced broadening of the upper crystal field levels of the ground manifold by emission of phonons. The spectra of Tm^{3+} :YAG in Fig. 5 are typical of Tm^{3+} in all of the crystals investigated. Tm^{3+} tends to have its strongest transitions at $\Delta E < 0$, like the ones labeled A in the inset, rather than those labeled B, which are favorable for high extraction efficiency. In addition, the phonon broadening of Tm^{3+} is large at large values of ΔE . In general, we found that the fluoride crystals gave poorer properties than the oxides because of a combination of smaller crystal field splittings (yielding smaller ΔE) and more severe broadening of the crystal field levels due to phonon emission, which might be ascribed in part to the smaller phonon frequencies, which lead to higher phonon densities of states in fluorides.

The data in Table 1 show that Ho:YAG, Ho:YLF, and Er:YAG offer the best combinations of σ_{eff} and ΔE for these ions. We used numerical solutions of Eqs. (2) and (3) with the operating points identified in Figs. 2-4 to evaluate the extraction performance for multipass amplifiers based on those three media. The doping density-length products of these amplifiers were all chosen, somewhat arbitrarily, to give the same initial single pass gain of $e^2 = 7.39$. Using the first term on the right in Eq. (3), which gives the gain, this condition can be written

$$\frac{(\beta_0 - \beta_{\min})}{(1 - \beta_{\min})} N_0 \sigma_{\text{eff}} \ell = 2. \quad (5)$$

The single pass gain could be several times larger than this without encountering very serious amplified spontaneous emission losses, but, as we shall demonstrate, the output fluences would then become uncomfortably high for short-pulse applications. A value of $\beta_0 = 0.5$ was chosen for all three cases, and uniform pumping was assumed. Eq. (5) then determines the doping density-length product $N_0 \ell$. Other reasonable parameter choices are a distributed passive loss in the medium of $\alpha \ell = 10^{-2}$ and a single-pass cavity loss of 5%. A summary of the amplifier parameters is given in Table 2. Noteworthy differences

Table 2.
Parameters for amplifier media evaluated in Figs. 7-9

	$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Er}^{3+}$	$\text{LiYF}_4:\text{Ho}^{3+}$	$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ho}^{3+}$
λ (μm)	1.64	2.06	2.10
σ_e (10^{-20} cm^2)	0.45	1.20	0.94
Γ_e (J/cm^2)	27.3	8.04	10.1
ΔE (cm^{-1})	470	282	458
Z_0/Z_e	0.94	0.81	0.62
$\beta_{\min}$	0.10	0.24	0.15
β_0	0.50	0.50	0.50
$\eta_{\max}$	0.80	0.52	0.70
N_0 (cm^{-2})	10.0×10^{18}	4.9×10^{18}	5.2×10^{18}
ℓ (cm)	10	10	10
E_{stored} (J/cm^2)	61.3	23.6	24.6

between the media are: 1) the small cross section of Er:YAG, which leads to a very large saturation fluence, high stored energy density, and high output fluence compared with the Ho^{3+} media; 2) the smaller ΔE of Ho:YLF, which yields a large $\beta_{\min}$ and small $\eta_{\max}$.

The calculated extraction efficiencies and output fluences for the three media are given as functions of the input fluence in Figs. 7-9. Both Ho^{3+} media are capable of high extraction efficiencies at modest output fluences ($< 10 \text{ J/cm}^2$). Er^{3+} , on the other hand, requires fluences of several tens of J/cm^2 for efficient extraction, which is a stressing limitation for nanosecond pulse applications. Er^{3+} may also have excited state absorption at large ΔE in YAG and several of the other crystals. The Er^{3+} concentration given in Table 2 may be below the level where upconversion significantly reduces the lifetime of the upper laser level [4], but this must be investigated at higher excited state densities than were used in Ref. 4. For all three of these low cross section materials, the importance of multipass extraction for achieving high stage gains at moderate output fluences is apparent from Figs. 7-9. High stage gains for single pass operation can be achieved by increasing the single pass gain, but then the stored energy becomes too large for reliable, efficient, short-pulse extraction.

V. Conclusions

Emission cross sections of Er, Tm, and Ho were measured in seven fluoride and oxide crystals providing a range of crystal field environments. This survey of cross sections was undertaken not only to obtain cross sections for Er, Tm, and Ho in well-known laser media, such as YAG and YLF, but primarily to search for new media with possibly better properties for diode-pumped energy storage applications. The data also give some idea of the behavior of the cross section spectra in various host environments. It is apparent from Table 1 that none of the other media investigated offers better values of σ_{eff} and ΔE than YAG and YLF. In general, our results show that the best spectroscopic properties are found in oxide crystals, which yield narrower lines and larger crystal field splittings than fluorides.

The emission cross sections are on the low side for all three ions, although reasonably high extraction efficiencies appear to be possible in pulsed operation, particularly for multipass amplifiers and Q-switched operation.

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Figure 7. Extracted fraction and output fluence vs. input fluence for a Ho^{3+} :YAG amplifier for up to three passes.

Figure 8. Extracted fraction and output fluence for Ho^{3+} :YLF.

Figure 9. Extracted fraction and output fluence for Er^{3+} :YAG.

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