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# The microscopic interaction parameter for Tm-to-Ho resonant energy transfer in LiYF<sub>4</sub>

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## Abstract

Absorption and luminescence measurements on Tm<sup>3+</sup> and Ho<sup>3+</sup> ions in LiYF<sub>4</sub>:Tm<sup>3+</sup>, LiYF<sub>4</sub>:Ho<sup>3+</sup>, and LiYF<sub>4</sub>:Tm<sup>3+</sup>, Ho<sup>3+</sup> crystals were carried out. The data collected were used to determine the Ho<sup>3+</sup> absorption coefficient integral for <sup>5</sup>I<sub>8</sub> → <sup>5</sup>I<sub>7</sub> transition, and the integral for the overlap between the normalized Tm<sup>3+</sup> luminescence spectrum due to the <sup>3</sup>F<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transition and the Ho<sup>3+</sup> absorption band due to <sup>5</sup>I<sub>8</sub> → <sup>5</sup>I<sub>7</sub> transition. The relevant critical transfer distance ( $R_0$ ) that gives a measure of the Tm<sup>3+</sup>–Ho<sup>3+</sup> coupling was determined by considering a Förster-type interaction between the ions. It was found to be 22.5 Å at 300 K with the overlap integral  $6.8 \times 10^{-19} \text{ cm}^5$ , which is 4.41 times higher at 77 K.

## 1. Introduction

Energy-transfer processes are very important in solid-state laser systems because they can cause an enhancement of the luminescence emission, but also they can greatly reduce it. This is usually achieved by the introduction of an ion of a different type, called a sensitizer or donor, into the laser host material in addition to the ion, called an activator or acceptor, which is responsible for the laser emission. The donor ion absorbs strongly at the pumping source energy, and transfers this excitation energy to the acceptor.

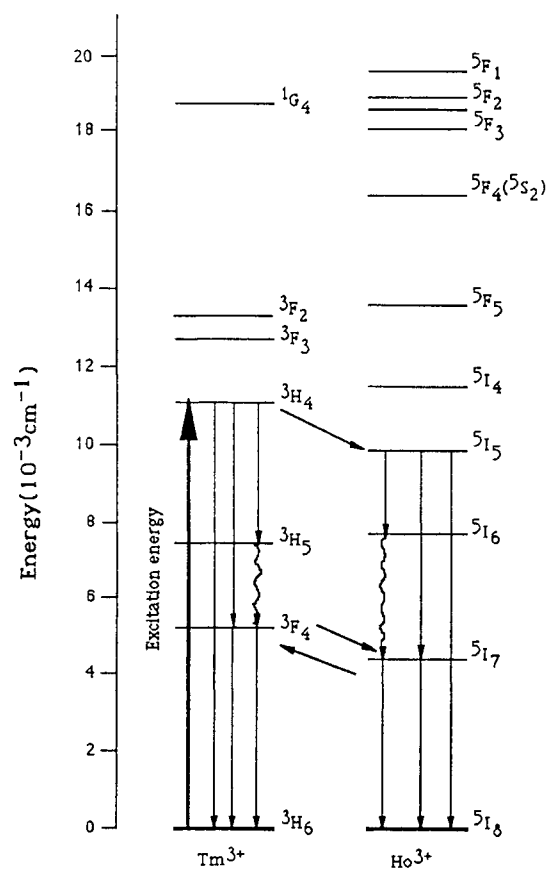
Most of the research on LiYF<sub>4</sub>-based (YLF-based) crystals has addressed problems such as the laser threshold, output energy versus input energy curve, and laser pulse characteristics [1–14]. For example, some laser systems including YLF:Ho<sup>3+</sup> and YLF:Tm<sup>3+</sup> have been described [15], and also pulsed room temperature laser action at 2.06 μm has been reported using YLF:Ho<sup>3+</sup> sensitized with Er<sup>3+</sup> and Tm<sup>3+</sup> [16].

A systematic study of the excited-state dynamics of Tm<sup>3+</sup> ions and (Tm)<sup>3</sup>F<sub>4</sub> → (Ho)<sup>5</sup>I<sub>7</sub> energy transfer at room temperature in YLF samples with different Ho<sup>3+</sup> concentrations was first reported by Brenier *et al* [17, 18]. Recently, Walsh *et al* [19] have reanalysed the room temperature branching ratios, cross-sections, and radiative lifetimes of Tm<sup>3+</sup> and Ho<sup>3+</sup> ions in YLF. An investigation of the concentration effects on the infrared luminescent channels in the Ho<sup>3+</sup>-doped YLF showed that the luminescence quenching does not occur for Ho<sup>3+</sup> concentrations less than 10–15% [20]. Microscopic interaction parameters for non-resonant

energy-transfer processes in YLF:Tm, Ho crystal at room temperature have also been reported [21]. The authors of [21] proposed a method that enables the calculation of the overlap integral from fundamental cross-section spectra of non-resonant energy transfer involving multiphonon generation at both donor and acceptor sites. According to their model, the value of the critical interaction distance,  $R_0$ , for the  $(\text{Tm})^3\text{F}_4$ -to- $(\text{Ho})^5\text{I}_7$  energy transfer if no phonon is involved in the process equals 20.5 Å. Their result also shows that 68% of the Tm-to-Ho energy transfer does not need the assistance of phonons, i.e. is resonant transfer. The effect of co-dopant concentrations and the excitation conditions on the 2 μm luminescence dynamics in YLF:Tm, Ho crystals at room temperature under short-pulse laser excitation tuned to 792 nm has also been reported [22].

In this study, the microscopic interaction parameter for the  $\text{Tm}^{3+}$ -to- $\text{Ho}^{3+}$  resonant energy transfer that enhances the 2.1 μm luminescence of  $\text{Ho}^{3+}$  in  $\text{LiYF}_4:\text{Tm}^{3+}, \text{Ho}^{3+}$  crystal was determined as a function of temperature assuming that the mechanism responsible for the energy transfer is of dipole-dipole type. This crystal has the following advantages over the other host materials for substituting rare-earth impurities: (i) the rare-earth ions can be substituted at the  $\text{Y}^{3+}$  sites without charge compensation [23]; (ii) the electronic levels of the dopants have longer lifetime since YLF has a low phonon cut-off energy. This gives a better energy-storage capability for the laser [24, 25].

The energy levels of Tm and Ho in YLF are shown in figure 1. The interaction between the rare-earth ions and the crystal field of the host lattice is not strong, but does affect the



**Figure 1.** Energy levels of  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  in  $\text{LiYF}_4$ .

energy-transfer process for two reasons. First, in many cases the energy-transfer process is assisted by phonons, whose frequency and population at a certain temperature depend on the host. Second, thermal vibrations may also affect the positions and widths of sharp levels; even if such effects are small, they may be important in the case of resonant transfer.

## 2. Experimental procedure

The experiments were carried out for three samples: YLF:Tm<sup>3+</sup>(0.5%), YLF:Ho<sup>3+</sup>(1%), and YLF:Tm<sup>3+</sup>(5%), Ho<sup>3+</sup>(0.2%). The crystals were grown by the Czochralski technique [4].

The absorption spectra of the samples were obtained to find out whether any additional levels appear for the doubly doped sample due to the interactions between Tm<sup>3+</sup> and Ho<sup>3+</sup> ions. The spectra show that the spectrum of the doubly doped sample is simply the superposition of the absorption spectra of the Tm<sup>3+</sup> and Ho<sup>3+</sup> ions in this host. As noted before [26], the luminescence spectra of the samples were obtained in the 500–2200 nm wavelength region. The spectra of the singly doped samples were measured by using a tungsten lamp as the exciting source. The luminescence spectrum of the doubly doped sample was measured by exciting just the Tm<sup>3+</sup> ions into their <sup>3</sup>H<sub>4</sub> level with the diode laser tuned at 795 nm. The spectrum is simply the overlap of the spectra of the (Tm)<sup>3</sup>F<sub>4</sub> → <sup>3</sup>H<sub>6</sub> and the (Ho)<sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> transitions. This is evidence for the energy transfer from the Tm<sup>3+</sup> ion to the Ho<sup>3+</sup> ion.

## 3. Discussion

The rate of energy transfer between a donor ion and an acceptor ion,  $W$ , depends on the separation between the ions,  $R$ . This dependence can be expressed in a multipolar expansion as follows [27]:

$$W(R) = \frac{C^{(6)}}{R^6} + \frac{C^{(8)}}{R^8} + \frac{C^{(10)}}{R^{10}} + \dots \quad (1)$$

where the first three terms correspond to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. If there is a dominant multipolar interaction, then the transfer rate assumes the simpler form

$$W(R) = \frac{C^{(n)}}{R^{(n)}} \quad (2)$$

and an energy-transfer radius,  $R_0$ , can be defined as follows:

$$W(R) = \frac{C^{(n)}}{R^{(n)}} = \frac{1}{\tau_0} \left( \frac{R_0}{R} \right)^n \quad (3)$$

with  $C^{(n)} = R_0^{(n)}/\tau_0$ . In this expression,  $\tau_0$  is the effective decay time of the donor ion in the absence of an acceptor ion and  $R_0$ , called the critical distance, is the separation between these ions at which the energy-transfer rate is equal to the decay rate of the donor ion. In the case of the resonance electric dipole–dipole interaction mechanism, Förster [28] has developed a theory, and has shown that the critical energy-transfer distance ( $R_0$ ) for such energy transfer between the donor and the acceptor ions depends on the spectral overlap integral of the normalized absorption spectrum of the acceptor ions and the normalized luminescence spectrum of the donor ions as well as the integrated absorption cross-section of the donor ions as given by the relation

$$R_0^{(6)} = \varepsilon \frac{3\pi e^2 c^2 h^5}{2m} f_A \int f_{em}(E) f_{abs}(E) \frac{dE}{E^4} \quad (4)$$

with

$$f_A = \frac{mcn}{2\pi^2 e^2 c_A} \int \sigma_A(w) dw$$

where  $\varepsilon$  is the quantum efficiency of the donor luminescence in the absence of acceptors and is given by  $\varepsilon = w_{rad}/(w_{rad} + w_{nrad})$  ( $w_{rad}$  and  $w_{nrad}$  are the probabilities of the radiative and non-radiative decays, respectively).  $e$  is the charge of an electron,  $m$  is the mass of an electron,  $h$  is the Planck constant,  $n$  is the refractive index of the sample, and  $c_A$  is the concentration of the acceptor ions.  $f_{em}(E)$ ,  $f_{abs}(E)$ , and  $\sigma_A(w)$  are the normalized spectral functions of the donor luminescence and the acceptor absorption, and the absorption cross-section or oscillator strength of the acceptor ion.

Equation (4) can also be written as follows:

$$R_0^6 = \frac{3n}{2^6 \pi^5 c_A} \int \frac{1}{\lambda^2} \sigma_A(\lambda) d\lambda \int \lambda^6 f_{em}(\lambda) f_{abs}(\lambda) d\lambda. \quad (5)$$

The characteristic energy transfer radius,  $R_0$ , defined in equation (5) can be determined by two different methods with the assumption that the mechanism responsible for the energy transfer is of dipole–dipole type. One method uses measured spectral data such as the absorption cross-section integral or the oscillator strength:

$$\int \frac{1}{\lambda^2} \sigma_A(\lambda) d\lambda$$

of the  $\text{Ho}^{3+}$  ion, and the overlap integral:

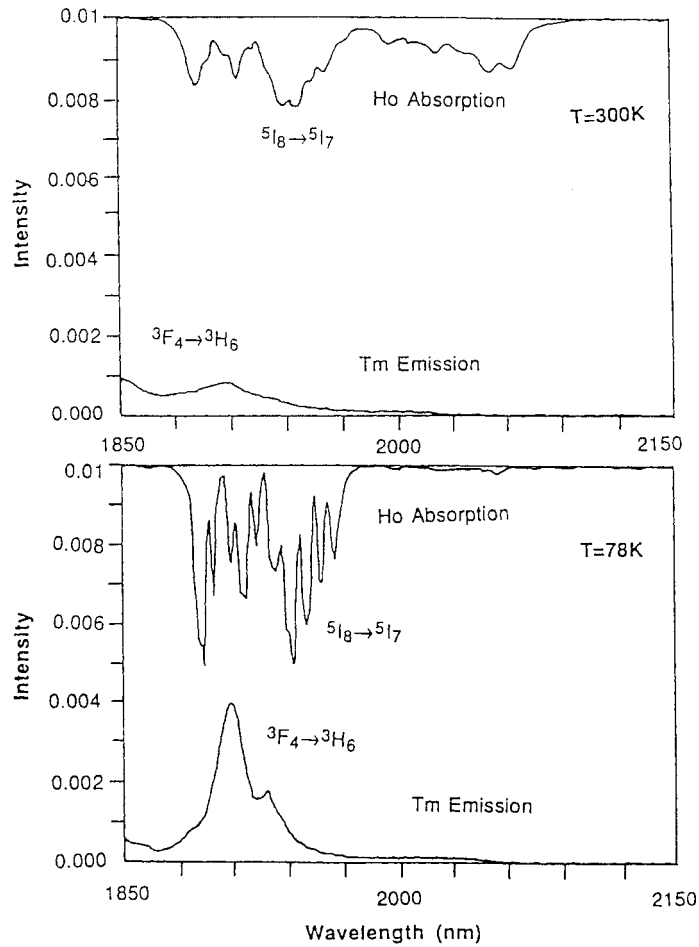
$$\int \lambda^6 f_{em}(\lambda) f_{abs}(\lambda) d\lambda$$

for the normalized  $\text{Tm}^{3+}$  emission due to the  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition and the  $\text{Ho}^{3+}$  absorption due to the  ${}^5\text{I}_8 \rightarrow {}^5\text{I}_7$  transition. The other method uses the measured decay curves of  $\text{Tm}^{3+}$  ions in the presence of  $\text{Ho}^{3+}$  to fit with the model developed by Inokuti and Hirayama. In this work, the critical distance,  $R_0$ , and the microscopic interaction parameter,  $C^{(6)}$ , were determined using the experimental data collected for the YLF: $\text{Tm}^{3+}$  and YLF: $\text{Ho}^{3+}$  samples.

The spectral overlap between the normalized  $\text{Tm}^{3+}$  emission due to the  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition and the  $\text{Ho}^{3+}$  absorption due to the  ${}^5\text{I}_8 \rightarrow {}^5\text{I}_7$  transition for these samples measured at 78 and 300 K are presented in figures 2(a) and 2(b). The temperature dependence of the oscillator strength for the  $\text{Ho}^{3+}$  absorption and the overlap integral are given in table 1. There are significant changes in the shape of the  $\text{Tm}^{3+}$  emission and  $\text{Ho}^{3+}$  absorption; therefore the spectral overlap changes drastically between 77 and 220 K, and the change becomes slower as the temperature is raised above 220 K. This shows that the resonant energy-transfer mechanism is dominant at low temperatures while the thermalization effect becomes more important as the temperature of the sample increases [26].

The value of the characteristic energy-transfer radius,  $R_0$ , determined using these spectral data in equation (5) was found to be temperature dependent as shown in figure 3 and table 2. The microscopic interaction parameter in equation (3) was calculated from  $R_0$  and is also reported in table 2 together with the effective lifetime of  $\text{Tm}^{3+}$  emission in the absence of  $\text{Ho}^{3+}$  ions.

In determining the source of the temperature dependence of the microscopic interaction parameter, it should be noted that  $C^{(6)}$  depends on three quantities: the radiative decay rate of  $\text{Tm}^{3+}$ , the absorption oscillator strength of  $\text{Ho}^{3+}$ , and the Tm–Ho spectral overlap integral. The oscillator strength is eventually independent of temperature, so the temperature dependence of  $C^{(6)}$  should be due to the other two factors. Their temperature dependences are presented in figure 4. As can be seen in this figure, the overlap integral shows a rapid decrease by a

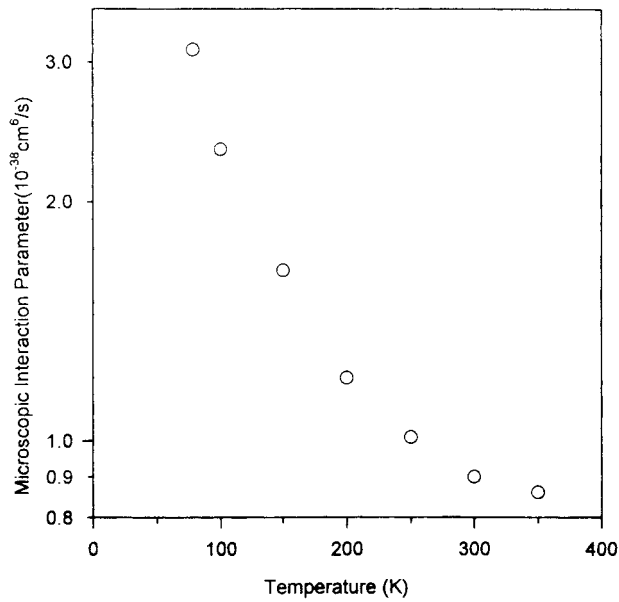


**Figure 2.** Spectral overlap between the normalized luminescence spectrum of LiYF<sub>4</sub>:Tm<sup>3+</sup> and the normalized absorption spectrum of LiYF<sub>4</sub>:Ho<sup>3+</sup>.

**Table 1.** The temperature dependence of the absorption integral for the Ho<sup>3+</sup> absorption, and the overlap integral for the normalized luminescence spectrum of Tm<sup>3+</sup> and the absorption of Ho<sup>3+</sup> in LiYF<sub>4</sub> crystal.

$T$ (K)	$\int \lambda^{-2} \sigma_A(\lambda) d\lambda$ ( $10^3 \text{ cm}^{-2}$ )	$\int \lambda^6 f_{em}(\lambda) f_{abs}(\lambda) d\lambda$ ( $10^{-19} \text{ cm}^5$ )
78	0.126	30
100	0.125	22
150	0.124	14
200	0.124	12
250	0.122	8.4
300	0.121	6.8
350	0.121	6.3

factor of 4.41 over the temperature range 77 and 300 K, while the decay rate of the Tm<sup>3+</sup> emission changes by a factor of 1.3. Consequently the rate of decrease of the microscopic



**Figure 3.** The temperature dependence of the microscopic interaction parameter for the Tm-to-Ho energy transfer in LiYF<sub>4</sub>.

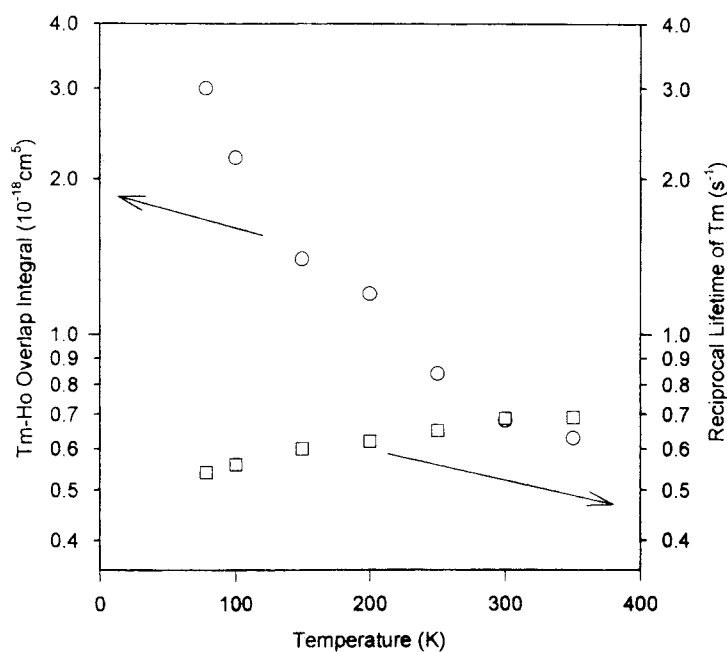
**Table 2.** The temperature dependence of the critical interaction radius,  $R_0$ , the microscopic interaction parameter for Tm-to-Ho energy transfer,  $C^{(6)}$ , and the reciprocal lifetime of Tm<sup>3+</sup> luminescence,  $\tau^{-1}$ , in the absence of Ho<sup>3+</sup> ions in LiYF<sub>4</sub> crystal.

$T$ (K)	$R_0^6$ ( $10^{-40} \text{ cm}^6$ )	$R_0$ (Å)	$C^{(6)}$ ( $10^{-38} \text{ cm}^6 \text{ s}^{-1}$ )	$\tau^{-1}$ ( $\text{s}^{-1}$ )
78	5.74	28.8	3.11	0.54
100	4.13	27.3	2.33	0.56
150	2.72	25.5	1.64	0.60
200	1.92	24.0	1.20	0.62
250	1.55	23.2	1.01	0.65
300	1.31	22.5	0.9	0.686
350	1.24	22.3	0.86	0.69

interaction parameter with temperature for a resonant energy-transfer mechanism of dipole–dipole type is due primarily to the decreasing spectral overlap between the Tm<sup>3+</sup> emission and Ho<sup>3+</sup> absorption in this host.

#### 4. Conclusions

The resonant transfer due to electric dipole–dipole interactions appears to be one of the mechanisms of Tm-to-Ho energy transfer in LiYF<sub>4</sub> crystal. The values of the critical interaction distance,  $R_0$ , and the microscopic interaction parameter,  $C^{(6)}$ , for the doubly doped sample were determined assuming that the interaction is of Förster type; they were found to be 22.5 Å and  $9 \times 10^{-40} \text{ cm}^6 \text{ s}^{-1}$  at room temperature, respectively. These values agree well with those reported in reference [21]. The temperature dependence of the microscopic interaction parameter between 77 and 350 K was found to be primarily due to the temperature dependence of the spectral overlap.



**Figure 4.** The temperature dependence of the spectral overlap between the Tm<sup>3+</sup> luminescence and Ho<sup>3+</sup> absorption in the 1850 and 2150 nm wavelength regions, and the reciprocal lifetime of the Tm<sup>3+</sup> emission.

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