Time-Resolved Fourier Spectroscopy of Energy Transfer in (Ho^{3+},Yb^{3+}):KYF_4

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Abstract

Time-resolved Fourier-transform spectroscopy is applied to a near infrared energy transfer problem in an optically activated insulator for the first time. Two $Ho^{3+} \rightarrow Yb^{3+}$ channels in the up-conversion laser crystal (Ho^{3+},Yb^{3+}):KYF_4 are studied in luminescence with simultaneous temporal and spectral resolution. A simple rate equation model fit to the data confirms a previous analysis for transfer from Ho^{3+} $^5F_4$, $^5S_2$ levels but suggest a more complex picture for transfer from Ho^{3+} $^5F_5$ levels.

Key Words

Energy transfer, Spectroscopy-Fourier transform, Spectroscopy- time-resolved, Rare-earth doped materials

Introduction

Event-locked time-resolved Fourier-transform spectroscopy is a new method of obtaining spectra in the time and frequency domains simultaneously[1-5]. It is applied here for the first time to the study of energy-transfer phenomena in the near-IR luminescence of a multiply-doped multi-site laser crystal. The system studied is (Ho^{3+},Yb^{3+}):KYF_4, an IR-pumped upconversion laser crystal of recent interest[6-8].

Experiment

Single crystals of (Ho^{3+},Yb^{3+}):KYF_4 were grown by the Czochralski method in the CREOL crystal-growth facility by Prof. B. H. T. Chai. Samples were cooled to 80 K using a cold-finger cryostat. Photoluminescence was excited using a frequency doubled Nd:YAG laser (Spectra Physics) or a YAG-pumped dye-laser with a flowing dye-cell amplifier. Spectra were collected using event-locked Fourier spectroscopy [1-5] over the frequency range 8,500 to 15,000 cm^{-1} without averaging . A spectral resolution of 4 cm^{-1} was sufficient to resolve the lines, and a few spectra at 1 cm^{-1} were taken to confirm this. Temporal resolution was 1 μs. Signal modulated by the interferometer-spectrometer was detected using a Si photodiode. The unmodulated reference signal was collected with a cooled InGaAs detector.

Results

532 nm excitation

Fig. 1 presents the energy levels of Ho^{3+} and Yb^{3+} ions. The thick upward arrow indicates 532 nm excitation of Ho^{3+}. The downward arrows represent all emission bands observed. The diagonal line represents energy transfer to Yb^{3+}.

Fig. 2 is a waterfall plot of time- and frequency-resolved luminescence. Time increases from back to front in 11 μs steps starting with an initial time delay of 8 μs. Identities of individual lines were established from spectra of singly-doped crystals. Major Ho^{3+} and Yb^{3+} lines are indicated. All observed Ho3+ lines originate from the $^5F_4$, $^5S_2$ levels. The Ho^{3+} lines decay monotonically while the Yb^{3+} lines

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initially grow and then decay with a long time constant. Since Yb^{3+} is not excited by 532 nm radiation, Yb^{3+} emission arises via energy transfer from Ho^{3+}.

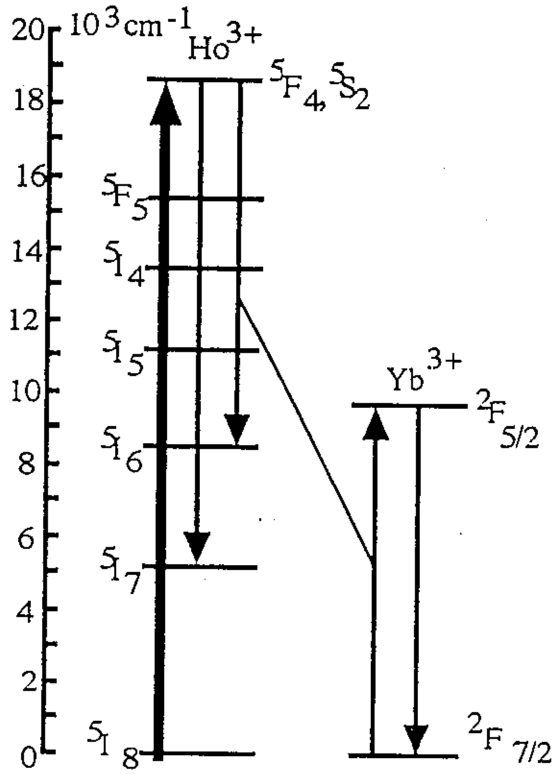

Figure 1 Energy levels and observed transitions for 532 nm pumping.

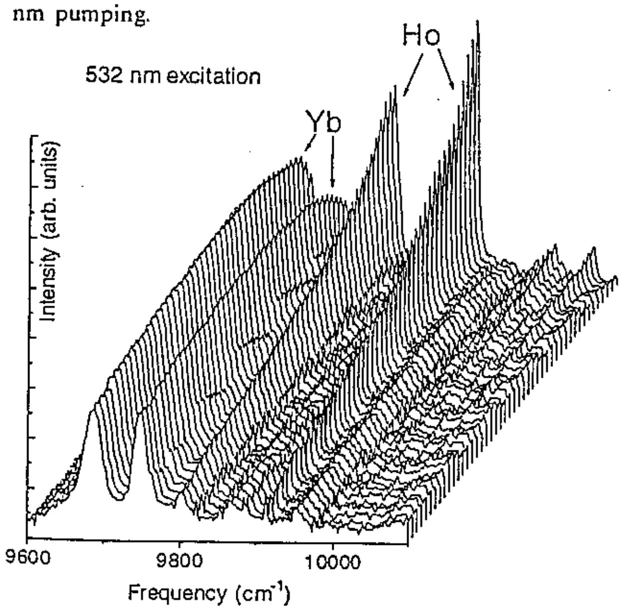

Figure 2. Time-resolved Fourier spectroscopy of luminescence from (Ho,Yb):KYF_4 for 532 nm excitation. Time increases forward in 11 μs steps.

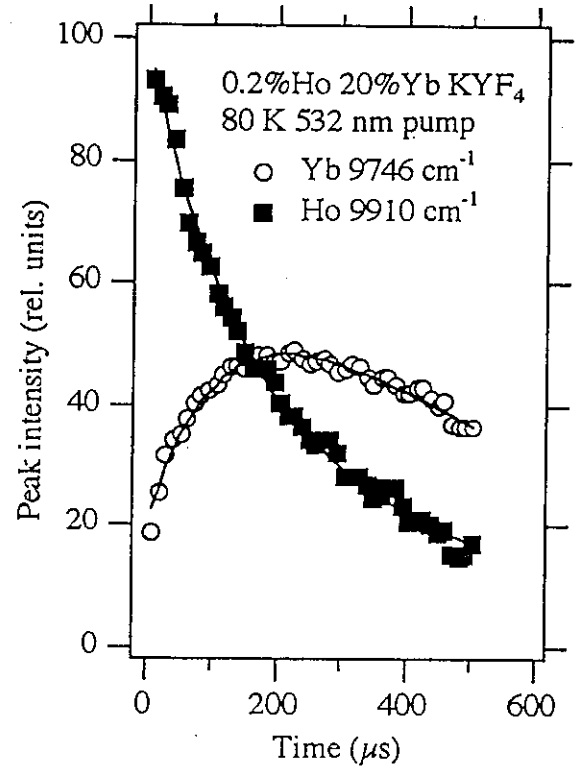

Figure 3. Intensity vs. time for 0.2%Ho 20%Yb KYF_4.

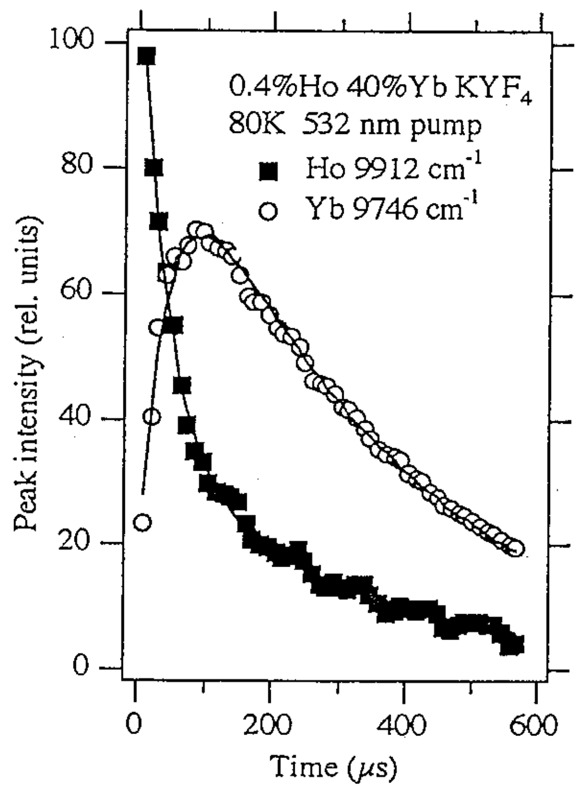

Figure 4 Intensity vs. time for 0.4%Ho 40%Yb KYF_4.

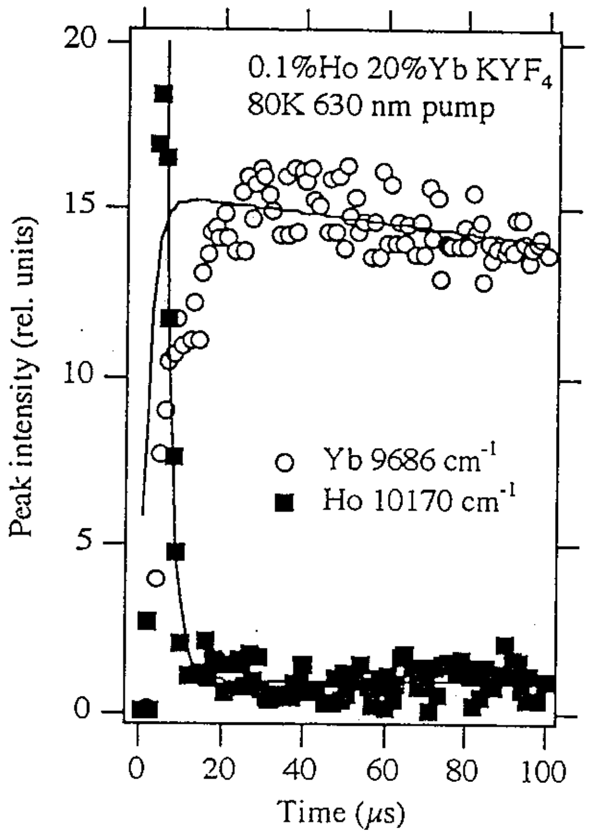

Figure 7. Intensity vs. time for 0.1% Ho 20% Yb KYF_4.

In these equations τ_{Ho} is the lifetime of the Ho excited state in the absence of energy transfer, τ_{tr} is the transfer time, and τ_{Yb} is the luminescence lifetime of Yb^{3+} ions. The solution gives the time dependence of the luminescence from each ion as

$$I_{Ho}(t) = a \exp\left[-\frac{t}{\tau^*}\right]$$

$$I_{Yb}(t) = b\left\{\exp\left[-\frac{t}{\tau_{Yb}}\right] - \exp\left[-\frac{t}{\tau^*}\right]\right\}$$

where τ^* is given by

$$\frac{1}{\tau^*} = \left(\frac{1}{\tau_{Ho}} + \frac{1}{\tau_{tr}}\right).$$

This model is an oversimplification since Ho^{3+} emission in the presence of Yb^{3+} is known to be non-exponential[6,7]. However, it is justified as a first approximation since the transfer phenomena studied here occur at early times when the Ho^{3+} emission is approximately exponential and since at longer times the weak Ho^{3+} emission is anyway masked by the wings of Yb^{3+} lines. The method of finding τ_{tr} from τ_{Ho} and τ^* is identical to that of [6,7] though the method of finding τ_{Ho} and τ^* and their resulting values differ.

Because Yb^{3+} and Ho^{3+} lines partially overlap in our study, a superposition of I_{Ho} and I_{Yb} was taken when fitting peak intensities vs time. Determination of the fitting parameters a, b, τ^* and τ_{Yb} was done as follows. An Yb^{3+} peak was used to first determine all four parameters. A Ho^{3+} peak was then fit holding τ_{Yb} fixed. The Yb^{3+} peak was then refit holding both τ_{Yb} and τ_{Ho} fixed. Hence, in the final formulas only the coefficients a and b differ for the chosen lines.

Discussion

Figs. 3 and 4 indicate that our model and fitting procedure are adequate for the 532 nm pump data. However, for pumping the $^5F_5$ level, the fit is poor because the Yb^{3+} emission rises considerably slower than the Ho^{3+} emission is observed to decay. This suggests that intermediate levels are involved in the transfer process. Reasonable possibilities are the ^5I levels, as indicated in Fig. 5, since these are easily accessible from $^5F_5$ via relaxation and since several close spectral overlaps with Yb^{3+} occur. The apparent unimportance of other levels in the transfer from $^5F_4$, $^5S_2$ may result from the relatively larger gap separating $^5F_4$, $^5S_2$ from lower levels. These observations support the $Ho^{3+}[^5F_4, {}^5S_2] \rightarrow Yb^{3+}$ energy transfer studies of [6,7] where it was implicitly assumed that other pathways are unimportant.

Acknowledgment

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References and Note

[1]. H. Weidner and R. E. Peale, "Time resolved Fourier spectroscopy for activated optical materials", accepted by Applied Optics, 12/95.