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Ho³⁺ to Yb³⁺ back transfer and thermal quenching of upconversion green emission in fluoride crystals

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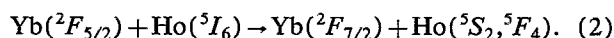
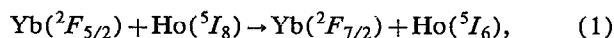
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Energy transfer from Ho³⁺ to Yb³⁺ has been demonstrated in fluoride crystals such as KYF₄, BaY₂F₈, and LiYF₄. This transfer was found to occur above a certain temperature and its efficiency increases with temperature. It accounts for the thermal quenching of green emission from upconverted Ho³⁺ and partly explains the failure, to date, to obtain room temperature, Yb³⁺ sensitized Ho³⁺ upconversion lasers in these three hosts. Low Yb³⁺ concentration is suggested for future attempts to achieve room temperature Yb³⁺, Ho³⁺ upconversion green laser operation of these crystals.

Demand has increased for compact visible laser sources in a variety of applications including color displays, optical recording, reprographics, biomedical diagnostics, and underwater optical communication. Upconversion lasers potentially provide practical all-solid-state sources at wavelengths from ultraviolet to red.¹ Yb³⁺ sensitized upconversion energy transfer is especially attractive for this purpose because compact high-power InGaAs diode lasers are available to directly pump the Yb³⁺ absorption band near 970 nm. Yb³⁺, Ho³⁺ upconversion energy transfer is relatively simple compared to upconversion involving other rare-earth ions. Although a Yb³⁺ sensitized Ho³⁺ green upconversion laser has been realized at 77 K in BaY₂F₈,² no such lasing has been achieved at room temperature. Our recent comparison study of the Yb³⁺, Ho³⁺ upconversion energy transfer in different fluorides³ showed that KYF₄ is potentially a better host for this purpose. A recent lasing experiment succeeded at 77 K⁴ but failed at room temperature in KYF₄ samples containing either 10% or 20% Yb³⁺. To understand the failure, to date, to obtain Yb³⁺ sensitized Ho³⁺ upconversion green lasers above cryogenic temperature, we investigated the temperature dependence of the upconversion processes in Yb³⁺, Ho³⁺ codoped KYF₄(KYF), BaY₂F₈ (BYF), and LiYF₄ (YLF) crystals between 12 and 300 K. The results, presented in this letter, reveal a drastic decrease in the intensity of the upconversion green emission with increasing temperature in all three hosts. This is shown to be due, in large part, to the back transfer of energy from Ho³⁺ to Yb³⁺.

Yb³⁺ ions are excited to the excited state (²F_{5/2}) upon the absorption of infrared radiation. Following excitation Yb³⁺ ions transfer their excitation energy to the green emitting levels (⁵S₂, ⁵F₄) of Ho³⁺ ions through the following two successive steps.⁵⁻⁷



The transition between (⁵S₂, ⁵F₄) levels and the ground states (⁵I₈) of Ho³⁺ gives rise to the green emission.

Room temperature and 77 K upconversion green emission spectra of 20% Yb³⁺, 0.2% Ho³⁺: KYF are given in Figs. 1(a) (reproduced here from Ref. 3 for completeness) and 1(b), respectively. The spectra were obtained by exciting the sample with a Ti:sapphire laser tuned to 972 nm. The room temperature absorption spectrum of Ho³⁺ in the green region is also given in Fig. 1(a). It is easily seen from Fig. 1(a) that the potential lasing wavelength is near 551 nm since the self-absorption of this peak is the weakest. Attention was therefore confined to this peak. The temperature dependence of its integrated intensity in 20% Yb³⁺, 0.4% Ho³⁺: KYF is given in Fig. 2. The results were obtained by exciting the sample at 923 nm because at this wavelength the absorption did not change significantly with temperature. The intensity decreases by a factor of ≈50 between 12 and 300 K. Similar results were obtained for similarly doped BYF and YLF.

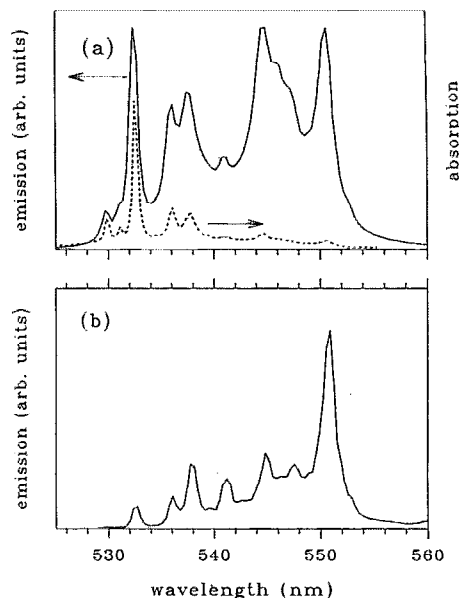


FIG. 1. (a) Upconversion green emission (solid line) and absorption (dash line) spectra at room temperature, and (b) upconversion green emission spectrum at 77 K in 20% Yb³⁺, 0.2% Ho³⁺:KYF₄.

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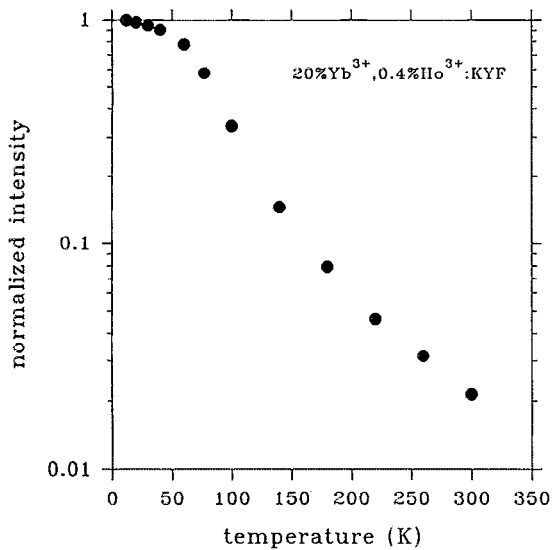
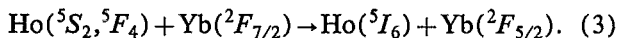


FIG. 2. Temperature dependence of the integrated intensity of the 551 nm peak in 20% Yb³⁺, 0.4% Ho³⁺: KYF₄ with 923 nm excitation.

In addition to radiative decay, Ho³⁺ ions in (⁵S₂, ⁵F₄) levels can also transfer their excitation energy to Yb³⁺ ions through the following cross-relaxation process:^{5,8}



The existence of the transfer process given in Eq. (3) is evidenced by studying the luminescence dynamics of the system. When the Ho³⁺(⁵S₂, ⁵F₄) levels in 20% Yb³⁺, 0.4% Ho³⁺:KYF were excited at 300 K with a 532 nm Q-switched, frequency-doubled Nd:YAG laser, Yb³⁺ luminescence was observed. Under these conditions the Ho³⁺ luminescence decay from the (⁵S₂, ⁵F₄) levels was nonexponential with a much shorter decay time than that in 0.4% Ho³⁺:KYF. The shortening of the Ho³⁺ decay time and its nonexponential decay characteristics in the codoped crystals are caused by energy transfer from Ho³⁺ to Yb³⁺.

The dynamics of the Yb³⁺ luminescence, when pumping the Ho³⁺ at 532 nm, consists of a rise at early times and an exponential decay at later times. The decay time at the later times (≈ 0.37 ms) is much shorter than in 20% Yb³⁺:KYF (≈ 4.6 ms), but is almost the same as that in 20% Yb³⁺, 0.4% Ho³⁺:KYF when pumping the Yb³⁺ at 923 nm. This indicates that rapid energy transfer from Yb³⁺ to Ho³⁺ occurs following the back transfer from Ho³⁺ to Yb³⁺.

The decay times of the Ho³⁺ (⁵S₂, ⁵F₄) levels in 0.4% Ho³⁺:KYF, τ_{Ho} , and in 20% Yb³⁺, 0.4% Ho³⁺:KYF, $\tau_{\text{Ho,Yb}}$, are plotted as a function of temperature in Fig. 3, curves (a) and (b), respectively. Since the decay of Ho³⁺ in 20% Yb³⁺, 0.4% Ho³⁺:KYF is nonexponential, $\tau_{\text{Ho,Yb}}$ was calculated by normalizing the initial intensity of the decay curve to 1 and then integrating over the entire decay curve. It can be seen from Fig. 3 that, from 12 to 300 K, the Ho³⁺ (⁵S₂, ⁵F) decay time is reduced by only a factor of ≈ 1.6 in Ho³⁺-doped KYF, but by a factor of ≈ 12 in Ho³⁺, Yb³⁺-codoped KYF. The Ho³⁺ (⁵S₂, ⁵F) decay

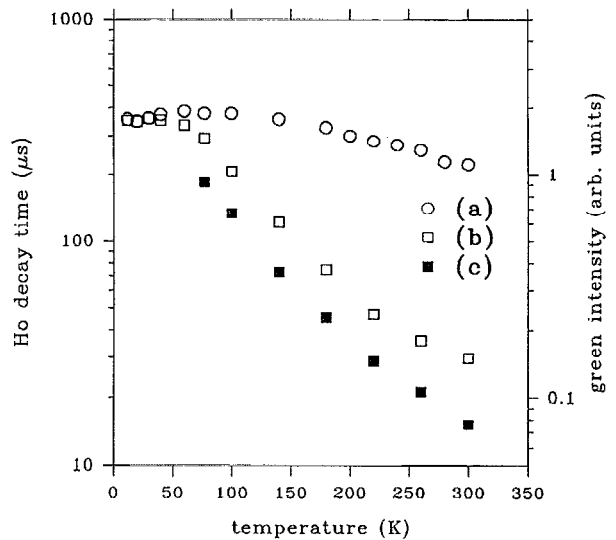


FIG. 3. The decay times of the Ho³⁺(⁵S₂, ⁵F₄) levels (a) in 0.4% Ho³⁺:KYF₄, (b) in 20% Yb³⁺, 0.4% Ho³⁺:KYF₄, and (c) the calculated integrated intensity of the green emission band in 20% Yb³⁺, 0.4% Ho³⁺:KYF₄ as a function of temperature.

time decreases by a factor of ≈ 1.3 and ≈ 2.2 in Ho³⁺-doped BYF and YLF, respectively, over the same temperature range. It decreases by a factor of ≈ 50 and ≈ 34 , respectively, in the codoped BYF and YLF. The additional reduction of the decay time of Ho³⁺ in the codoped crystals is due to the energy transfer from Ho³⁺ to Yb³⁺ described by Eq. (3).

The energy transfer rate from Ho³⁺ to Yb³⁺, $W_{\text{tr}}(\text{Ho-Yb})$, can be calculated from τ_{Ho} and $\tau_{\text{Ho,Yb}}$ as defined in the preceding paragraph using the following formula:⁹

$$W_{\text{tr}}(\text{Ho-Yb}) = 1/\tau_{\text{Ho,Yb}} - 1/\tau_{\text{Ho}}. \quad (4)$$

Figure 4 presents $W_{\text{tr}}(\text{Ho-Yb})$ as a function of temperature in 20% Yb³⁺, 0.4% Ho³⁺: KYF. It can be seen that

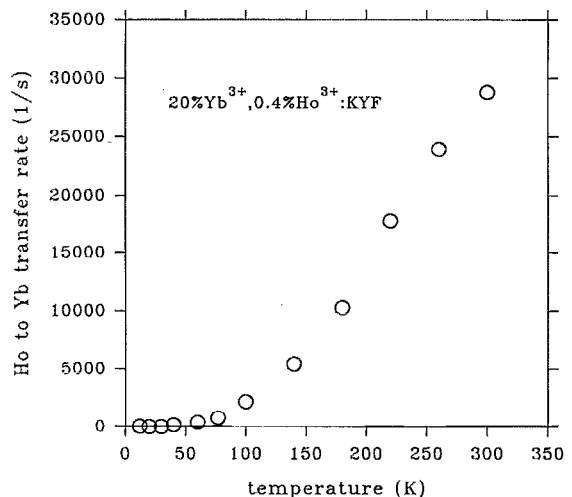


FIG. 4. Ho³⁺ to Yb³⁺ energy transfer rate as a function of temperature in 20% Yb³⁺, 0.4% Ho³⁺:KYF₄.

the energy transfer rate from Ho^{3+} to Yb^{3+} is almost zero below 50 K and increase drastically with increasing temperature at temperatures above 77 K.

To correlate the Ho^{3+} to Yb^{3+} back transfer with the thermal quenching of the upconversion green emission, we compare the temperature dependences of the Ho^{3+} ($^5S_2, ^5F_4$) decay time and integrated intensity of the entire green emission band [the integrated intensity of the 551 nm peak alone varies with temperature, even when the intensity of the entire band is constant, because of the Boltzmann population redistribution within the ($^5S_2, ^5F_4$) manifolds, as seen by comparing Figs. 1(a) and 1(b)]. The ratio between the integrated intensities of the 551 nm peak (I_1) and the entire band (I_g) can be written empirically as

$$I_1(T)/I_g(T) = 1/[1 + g \exp(-\Delta E/kT)], \quad (5)$$

where T is temperature, k the Boltzmann constant, ΔE the effective energy separation between the 551 nm emitting level and the higher levels, and g the effective degeneracy of the higher levels. The ratios at 77 and 300 K were measured to be 0.44 and 0.20, respectively, from the emission spectra. Parameters ΔE and g can be obtained by solving Eq. (5) at two temperatures using the measured ratios. They were calculated to be 83 cm^{-1} and 5.94, respectively. The integrated intensity of the green emission band between 77 and 300 K can then be estimated from that of the 551 nm peak intensity, ΔE , and g using Eq. (5). The results, in arbitrary units, are plotted as a function of temperature in Fig. 3, curve (c). It decreases by a factor of ≈ 15 from 77 to 300 K in 20% Yb^{3+} , 0.4% Ho^{3+} : KYF_4 .

The Ho^{3+} green intensity I_g is proportional to the product of the excitation intensity, excitation efficiency, and quantum efficiency of the green emitting levels ($^5S_2, ^5F_4$). The quantum efficiency is, in turn, proportional to the fluorescent decay time of that emitting level in the presence of nonradiative processes such as the energy transfer described by Eq. (3). Therefore, at any temperature T , the relation between I_g and the decay time of ($^5S_2, ^5F_4$) levels, $\tau_{\text{Ho}, \text{Yb}}$, in $\text{Yb}^{3+}, \text{Ho}^{3+}$ codoped samples can be written as

$$I_g(T) = K(T)\tau_{\text{Ho}, \text{Yb}}(T), \quad (6)$$

where $K(T)$ includes the contribution from both the excitation intensity and excitation efficiency, and its temperature dependence results from those of these two parameters. Comparing curves (c) to (b) in Fig. 3, one can see that the green intensity (I_g) and the decay time ($\tau_{\text{Ho}, \text{Yb}}$) follow almost exactly the same temperature dependence (i.e., they decrease by almost the same factor when the temperature is raised from 77 to 300 K). It is therefore clear, according to Eq. (6), that the reduction of the green intensity at higher temperatures is due, in large part, to the decrease of the decay time of Ho^{3+} green emitting levels. In the preceding discussion we interpreted the decrease of the decay time of the Ho^{3+} green emitting levels ($^5S_2, ^5F_4$) as caused by back transfer from Ho^{3+} to Yb^{3+} through the process described in Eq. (3). We therefore conclude that

the reduction of the upconverted green intensity at higher temperature is mainly caused by the back transfer from Ho^{3+} to Yb^{3+} .

Back transfer of energy from Ho^{3+} to Yb^{3+} has been demonstrated in fluoride crystals designed to serve as upconversion green emitters. This process, which reduces the population in the Ho^{3+} green emitting levels ($^5S_2, ^5F_4$), must be taken into account in the design of upconversion materials for use as lasers and phosphors. For example, since the upconversion green emission was shown to be quadratically dependent on Yb^{3+} concentration,¹⁰ the Yb^{3+} concentration for efficient upconversion was chosen to be as high as possible without encountering concentration quenching. In fact, $\text{Yb}, \text{Ho}:\text{BaY}_2\text{F}_8$, the first upconversion green laser,² which operated only at 77 K, used a 30 at. % Yb^{3+} concentration. As a consequence of the present observation of back transfer this choice must be revisited. Recent work showed that the back transfer rate from Ho^{3+} to Yb^{3+} increases superlinearly with increasing Yb^{3+} concentration.¹¹ This dependence of the back transfer rate on Yb^{3+} concentration taken together with its temperature dependence (see Fig. 4) leads to the suggestion that low Yb^{3+} concentration should be used in crystals designed for $\text{Yb}^{3+}, \text{Ho}^{3+}$ room temperature, upconversion green lasers.

The mechanism governing back transfer may be resonant or nonresonant energy transfer depending in large part on the degree of overlap between the Yb^{3+} absorption and the Ho^{3+} emission spectra in the $1 \mu\text{m}$ region. Studies of these spectra and modeling of the back transfer process are in progress. They will be reported subsequently. Preliminary data indicate that similar back transfer processes occur in the Yb^{3+} sensitized Er^{3+} and Tm^{3+} upconversion systems. Therefore, back transfer should also be taken into account when designing materials for green and blue upconversion lasers using these systems.

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