

Comparison of Yb, Ho Upconversion Energy Transfer in Different Fluoride Crystals

X. X. Zhang, M. Bass, and B. H. T. Chai

Center for Research in Electro-Optics and Lasers, University of Central Florida, Orlando, Florida 32826

R. E. Peale

Department of Physics, University of Central Florida, Orlando, Florida 32816

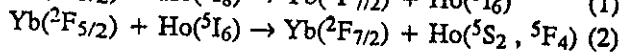
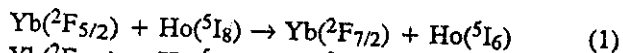
ABSTRACT

A detailed spectroscopic comparison of the Yb, Ho upconversion energy transfer in BaY_2F_8 , KYF_4 , and LiYF_4 is presented. Yb, Ho:KYF₄ is shown to be superior over the other two crystals and may have promise as a room temperature green upconversion laser.

INTRODUCTION

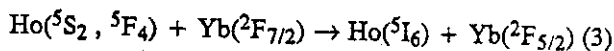
Recently, there is a renewed interest in obtaining short wavelength solid state lasers through upconversion schemes. Yb sensitized upconversion energy transfer is specially attractive for this purpose because of the ability of high power InGaAs diode lasers to pump Yb. Yb, Ho upconversion energy transfer is relatively simple compared to upconversion involving other rare earth ions. Although an Yb sensitized Ho green laser has been realized at 77 K in BaY_2F_8 [1], no such lasing has been achieved at room temperature. In searching for a more suitable host for the room temperature Yb, Ho green upconversion laser we have carried out a systematic spectroscopic study on the Yb, Ho upconversion processes in BaY_2F_8 (BYF), KYF_4 (KYF), and LiYF_4 (YLF). Based on the detailed absorption, emission and fluorescence decay data, KYF is shown to be a promising host.

Yb^{3+} ions transfer the excitation energy to the green emitting levels ($^5\text{S}_2$, $^5\text{F}_4$) of Ho^{3+} ions through the following two successive steps [2, 3, 4]



For efficient upconversion energy transfer to take

place it is important that the lifetimes of the intermediate state of Ho ($^5\text{I}_6$) as well as the excited state of Yb ($^2\text{F}_{5/2}$) are sufficiently long. However, this depends on the multiphonon relaxation rate and, therefore, critically on the phonon energy and the energy gap [5]. The energy mismatch between $\text{Yb}(^2\text{F}_{5/2})$ and $\text{Ho}(^5\text{I}_6)$ levels, which are involved in the nonresonant energy transfer step described by Eq. (1), is also important for upconversion. Back transfer from Ho to Yb can also take place through the following process [4, 6]



We have demonstrated such back transfer and shown that it is responsible for the drastic reduction of the upconversion green emission with increasing temperature [7, 8]. Therefore back transfer is also a very important factor to consider in attempting an Yb, Ho upconversion green laser.

CRYSTAL INFORMATION

Four Yb^{3+} , Ho^{3+} codoped samples were used in the upconversion comparison study. They are $\text{Ba}(\text{Y}_{0.799}\text{Yb}_{0.2}\text{Ho}_{0.001})_2\text{F}_8$, $\text{KY}_{0.799}\text{Yb}_{0.2}\text{Ho}_{0.001}\text{F}_4$, $\text{KY}_{0.798}\text{Yb}_{0.2}\text{Ho}_{0.002}\text{F}_4$, and $\text{LiY}_{0.798}\text{Yb}_{0.2}\text{Ho}_{0.002}\text{F}_4$. For the sake of convenience they will be referred to as BYF, KYF (1), KYF (2), and YLF respectively. The first two and the last two samples have equivalent doping. Also used in the experiments are three singly doped crystals: $\text{KY}_{0.8}\text{Yb}_{0.2}\text{F}_4$, $\text{LiY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ and $\text{KY}_{0.996}\text{Ho}_{0.004}\text{F}_4$. All these crystals were grown in the CREOL crystal growth laboratory by a modified Czochralski technique.

BYF [9] is a monoclinic and biaxial crystal. Its space group is C_{2h}^3 . Yb^{3+} and Ho^{3+} ions substitute for Y^{3+} sites which have a C_2 site symmetry. There is only one equivalent Y^{3+} site in the crystal. The crystallographic parameters are $a = 6.97 \text{ \AA}$, $b = 10.46 \text{ \AA}$, $c = 4.26 \text{ \AA}$, and $\beta = 99.7^\circ$. KYF [10] is a trigonal crystal with a D_3^5 space group symmetry. There are multiple inequivalent Y^{3+} sites which has the lowest site symmetry, C_1 . The lattice constants for KYF are $a = 14.06 \text{ \AA}$ and $c = 10.1 \text{ \AA}$. YLF has a tetragonal structure with a C_{4h}^6 space group. There is only a single crystallographic Y^{3+} site with S_4 symmetry [11]. The lattice constants are $a = 5.26 \text{ \AA}$ and $c = 10.94 \text{ \AA}$ [12]. Both YLF and KYF are uniaxial crystals. The comparison of crystal structures is summarized in Table 1.

Table 1. Comparison of Crystal Structures

| Crystals Studied | BaY ₂ F ₈ (BYF) | KYF ₄ (KYF) | LiYF ₄ (YLF) |
|-----------------------|---------------------------------------|------------------------|-------------------------|
| Crystal symmetry | monoclinic | trigonal | tetragonal |
| Optical class | biaxial | uniaxial | uniaxial |
| Space group | C_{2h}^3 | D_3^5 | C_{4h}^6 |
| Site symmetry | C_2 | C_1 | S_4 |
| Number of dopant site | single | multi-site | single |

EXPERIMENTAL RESULTS

Low temperature absorption and photoluminescence spectra have been measured by high resolution Fourier spectroscopy technique and reported by us in a separate paper [13]. Only the main results will be mentioned here. For almost every manifold of Ho^{3+} and Yb^{3+} the absorption spectra cover a wider range in KYF than BYF or YLF indicating the larger crystal field splitting. As a result, the energy mismatch between the lowest Stark level of $Yb^{3+} \ ^2F_{5/2}$ manifold and the highest Stark level of $Ho^{3+} \ ^5I_6$ manifold is the smallest in KYF. This mismatch is 1290, 1538, and 1492 cm^{-1} for KYF, BYF, and YLF respectively.

The upconversion green emission spectra at room temperature are shown in Fig. 1 for BYF, KYF, and YLF. The absorption spectra of Ho^{3+} ions in the green region in these crystals are also given in the same figure. The emission spectra were obtained by Ti:sapphire laser excitation into the peak absorption of Yb^{3+} in each crystal, and the integrated intensities of the green emission were measured for all samples and

are listed in Table 2 for comparison.

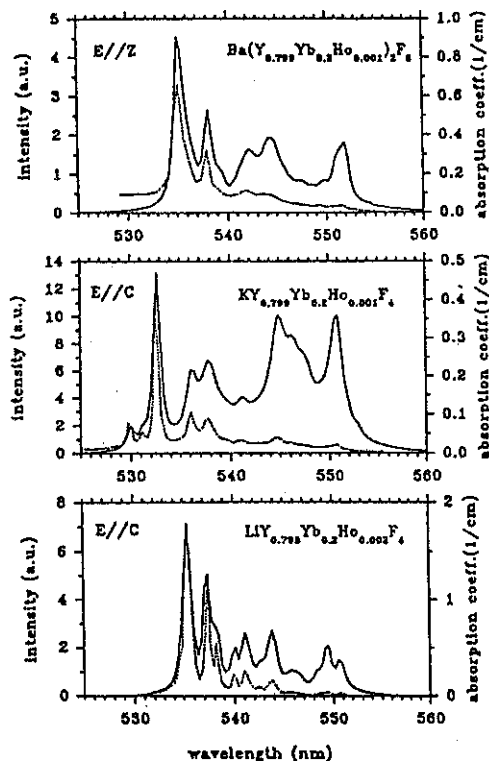


Figure 1. Room temperature upconversion emission (—) spectra and absorption (---) spectra in the green region for Yb, Ho codoped BYF, KYF, and YLF.

Table 2. Comparison of Yb to Ho transfer

| Sample | BYF | KYF(1) | KYF(2) | YLF |
|-------------------------------|------|--------|--------|------|
| I _{green} (a.u.) | 15.5 | 68 | 100 | 19.4 |
| τ (Yb) (ms) | 2.04 | 4.98 | 4.98 | 1.95 |
| τ (Yb, Ho) (ms) | 1.58 | 1.75 | 1.04 | 1.71 |
| W_{tr} (Yb→Ho) (s^{-1}) | 143 | 371 | 761 | 72 |
| η (Yb→Ho) (%) | 23 | 65 | 79 | 12 |

Table 3. Comparison of Ho to Yb transfer

| Sample | BYF | KYF | YLF |
|------------------------------------|--------------------|--------------------|--------------------|
| τ (Ho) (μs) (12K) | 546 | 351 | 240 |
| τ (Ho) (μs) (R.T.) | 407 | 220 | 110 |
| τ (Ho, Yb) (R.T.) (μs) | 11 | 30 | 7 |
| W_{tr} (Ho→Yb) (s^{-1}) | 8.84×10^4 | 2.88×10^4 | 1.34×10^5 |
| η (Ho→Yb) (%) | 97 | 86 | 95 |

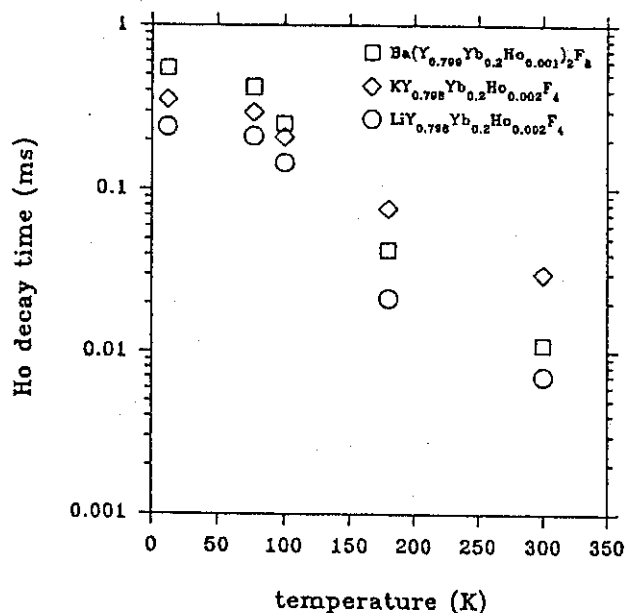


Figure 2. Decay time of Ho^{3+} green emitting levels ($^5\text{S}_2$, $^5\text{F}_4$) as a function of temperature in Yb, Ho codoped BYF, KYF, and YLF.

The Yb^{3+} decay times were measured at 12 K with a Q-switched Cr:LiSAF laser tuned to 920 nm and are listed in Table 2. Here, $\tau(\text{Yb})$ and $\tau(\text{Yb}, \text{Ho})$ in the table are the Yb^{3+} decay times without and with the presence of Ho^{3+} ions in the crystal. Since the decays are non-exponential, the decay time values in Table 2 were obtained by normalizing the initial intensity to one and integrating over the entire decay curve. $\tau(\text{Yb})$ for KYF and YLF were measured in singly doped samples, namely $\text{KY}_{0.8}\text{Yb}_{0.2}\text{F}_4$, and $\text{LiY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ respectively. $\tau(\text{Yb})$ for BYF is cited from Ref. 14 since no singly doped Yb^{3+} :BYF was available for the measurement.

The decay time of Ho^{3+} ($^5\text{S}_2$, $^5\text{F}_4$) was measured by exciting the samples with a frequency-doubled Q-switched Nd:YAG laser at 532 nm and the results are listed in Table 3. $\tau(\text{Ho})$ and $\tau(\text{Ho}, \text{Yb})$ in the table are the Ho^{3+} decay times without and with the presence of Yb^{3+} ions in the crystal. $\tau(\text{Ho})$ for KYF was measured in a singly doped sample, $\text{KY}_{0.996}\text{Ho}_{0.004}\text{F}_4$. At 12 K, the decays of Ho^{3+} in singly doped Ho^{3+} :KYF and in codoped Yb^{3+} , Ho^{3+} :KYF are the same and both are exponential. Singly doped Ho^{3+} :BYF and Ho^{3+} :YLF samples were not available for the $\tau(\text{Ho})$ data. However, since the decay of Ho^{3+} shows no difference between Ho^{3+} :KYF and Yb^{3+} , Ho^{3+} :KYF samples at 12 K, we used codoped BYF and YLF samples to obtain the $\tau(\text{Ho})$ for BYF and YLF at 12 K. The decay curves

are exponential for both samples, which indicates that indeed the presence of Yb^{3+} does not affect the decay time of Ho^{3+} in either crystal at 12 K and justifies the validity of the data. The room temperature $\tau(\text{Ho})$ for BYF was calculated from the 12 K decay time and the room temperature nonradiative decay rate cited from Ref. 15 and $\tau(\text{Ho})$ for YLF is cited from Ref. 16. At room temperature, the decay of Ho^{3+} in Yb^{3+} , Ho^{3+} codoped crystals, $\tau(\text{Ho}, \text{Yb})$, is drastically reduced compared to that in the singly doped crystals as seen in Table 2.

The temperature dependence of the Ho^{3+} decay time in Yb^{3+} , Ho^{3+} codoped crystals was also studied for BYF, KYF, and YLF. The results are given in Fig. 2.

DISCUSSIONS

It can be seen from Table 2 that the decay time of Yb^{3+} in KYF is particularly long compared to that in BYF and YLF. This is probably due to the weaker radiative transition strength in KYF since the decay time was found to change very slightly with temperature, i.e., the measured Yb^{3+} decay time is basically the radiative decay time. The weaker transition strength is evident from the lower absorption cross section of Yb^{3+} in KYF. The decay time of Ho^{3+} ($^5\text{S}_2$, $^5\text{F}_4$) in KYF, on the other hand, is not the longest compared to BYF and YLF. This is probably due to the smaller energy gap between Ho^{3+} ($^5\text{S}_2$, $^5\text{F}_4$) and the lower manifolds in KYF [13]. Since the decay time is limited by multiphonon transition between manifolds [5], and since the highest phonon energy is about the same in these three crystals as evidenced by the Raman spectra [17], smaller energy gap implies shorter decay time.

Examining the green emission and absorption spectra given in Fig. 2, one realizes that the potential lasing wavelength is near 550 nm due to the strong absorption to the shorter wavelength side of the emission band. It can be seen that the relative intensity of the 550 nm emission peak is particularly strong in KYF compared to either BYF or YLF, being $\approx 20\%$, $\approx 10\%$, and $< 10\%$ of the integrated intensity of the respective green emission band. In addition the absorption at this wavelength is lower in KYF than in BYF and YLF. This is very important for lasing because the green emission terminates in the ground state manifold.

It can be seen from Table 2 that Yb, Ho:KYF emits much more efficiently in the green than the equivalently doped BYF or YLF under the same excitation conditions. From the Yb^{3+} decay time data in Table 2, the energy transfer rate, $W_{\text{tr}}(\text{Yb} \rightarrow \text{Ho})$,

and the energy transfer efficiency, $\eta(\text{Yb} \rightarrow \text{Ho})$, from Yb^{3+} to Ho^{3+} were calculated using the following formulae:

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

$$\eta(\text{Yb} \rightarrow \text{Ho}) = 1 - \tau(\text{Yb}, \text{Ho})/\tau(\text{Yb}) \quad (5)$$

Table 2 presents the calculated results which demonstrate that the transfer is much more efficient in KYF. As mentioned above, Yb^{3+} ions transfer their excitation energy to Ho^{3+} ions through two successive steps, step one described by Eq. (1) and step two by Eq. (2). Step one is nonresonant which requires phonon assistance and step two is quasi-resonant. In order for the efficient green upconversion to take place it is crucial that transfer step one is efficient and lifetimes for Yb^{3+} ($^2F_{5/2}$) and Ho^{3+} (5I_6) are sufficiently long. The efficient upconversion in KYF therefore seems to correlate to the smaller energy mismatch between the lowest Stark level of Yb^{3+} $^2F_{5/2}$ manifold and the highest Stark level of Ho^{3+} 5I_6 manifold [13], which is favorable for the efficient transfer of step one, and the longer lifetime of Yb^{3+} $^2F_{5/2}$. However, the efficient upconversion in KYF is most importantly, we think, due to the nearness of adjacent Yb^{3+} sites in KYF: two YF_7 polyhedra of type I and II share one of their equatorial edges to form Y_2F_{12} groups [10] (The exchange interaction between Yb^{3+} and Ho^{3+} ions depends strongly on the overlap of Yb^{3+} and Ho^{3+} wavefunctions.)

It can be seen from Table 3 that the room temperature decay time of Ho^{3+} is drastically reduced in the presence of Yb^{3+} ions. This is due to energy transfer from Ho^{3+} to Yb^{3+} as described by Eq. (3) [7, 8]. From the Ho^{3+} decay data at room temperature, the energy transfer rate, $W_{\text{tr}}(\text{Ho} \rightarrow \text{Yb})$, and the energy transfer efficiency, $\eta(\text{Ho} \rightarrow \text{Yb})$, from Ho^{3+} to Yb^{3+} were calculated using the following formulae:

$$W_{\text{tr}}(\text{Ho} \rightarrow \text{Yb}) = 1/\tau(\text{Ho}, \text{Yb}) - 1/\tau(\text{Ho}) \quad (6)$$

$$\eta(\text{Ho} \rightarrow \text{Yb}) = 1 - \tau(\text{Ho}, \text{Yb})/\tau(\text{Ho}) \quad (7)$$

The calculated results, given in Table 3, show that the back transfer from Ho^{3+} to Yb^{3+} is the least efficient in KYF.

It can be seen from Fig. 3 that the decay time of Ho^{3+} in the codoped crystals decreases drastically with increasing temperature. When temperature is raised from 12 to 300 K, Ho^{3+} decay time is reduced by a factor of 49.6, 11.7, and 34.3 in codoped BYF, KYF, and YLF respectively. This indicates that the back transfer efficiency from Ho^{3+} to Yb^{3+} in these crystals increases with increasing temperature and that

the back transfer efficiency has the weakest temperature dependence in KYF.

CONCLUSIONS

In conclusion, we have shown that KYF is the most efficient host for Yb, Ho upconversion green emission compared to BYF and YLF. This is most likely attributed to the facts that KYF has the longest Yb^{3+} decay time, lowest phonon energy, the smallest energy mismatch between Yb ($^2F_{5/2}$) and Ho (5I_6), and edge-sharing adjacent sites. KYF has also been shown to have the lowest back transfer efficiency from Yb^{3+} to Ho^{3+} and the weakest thermal quenching of the decay time of Ho^{3+} due to the back transfer. In addition, KYF has unique spectroscopic properties (i.e. strong relative emission intensity and weak absorption) at the potential green lasing wavelength. We therefore conclude that Yb, Ho:KYF₄ may have promise as a room temperature green upconversion laser material.

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