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X. X. Zhang

University of Central Florida

P. Hong

University of Central Florida

M. Bass

University of Central Florida

B. H. T. Chai

University of Central Florida

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Blue upconversion with excitation into Tm ions at 780 nm in Yb- and Tm-codoped fluoride crystals

X. X. Zhang,* P. Hong, M. Bass,[†] and B. H. T. Chai[‡]

CREOL—Center for Research and Education in Optics and Lasers, University of Central Florida, Orlando, Florida 32826

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Strong blue emissions have been observed in fluoride crystals, such as LiYF₄, BaY₂F₈, and KYF₄, codoped with Tm³⁺ and Yb³⁺ when excited into the Tm³⁺ ³F₄ state at ~780 nm. Energy transfer from Tm³⁺ to Yb³⁺ ions followed by the transfer from Yb³⁺ to Tm³⁺ was demonstrated to be responsible for the upconversion process. A pumping scheme is proposed based on this upconversion mechanism for blue-laser applications using these materials.

Tm³⁺ ions are attractive for blue lasing because they offer transitions at ~455 and ~480 nm in crystals. Lasing in the blue has been demonstrated at both wavelengths.¹⁻⁶ There are two approaches to achieve blue lasing in crystals: one using crystals doped with only Tm³⁺ ions and the other doped with both Tm³⁺ ions as the emitting species and Yb³⁺ ions as sensitizer. When only Tm³⁺ ions are used, two pump sources (e.g., ~780 and ~650 nm) are usually required¹⁻⁵ to achieve upconversion blue lasing. Besides the inconvenience of using two pump sources, this approach also suffers the disadvantages of pump inefficiency and pump wavelength sensitivity. Ytterbium-sensitized upconversion lasers have the advantage of using a single pump source (e.g., ~960 nm).⁶ They also offer higher pump efficiency than the single-active-ion upconversion lasers, since high Yb³⁺ ion concentrations can be used to achieve strong absorption of the pump light. However, we have demonstrated^{7,8} that energy back transfer from Tm³⁺ to Yb³⁺ ions depletes the populations not only of the blue emitting levels but also of the intermediate levels. Similar energy back transfer has been shown⁹ to be responsible for the thermal quenching of the upconversion green emission and the failure to achieve room-temperature lasing in Yb³⁺-sensitized Ho³⁺ crystals. We report the first observation, to the best of our knowledge, of strong blue emissions under a single excitation source at ~780 nm in Yb³⁺- and Tm³⁺-codoped fluoride crystals. We show that these upconversion blue emissions result from the forward and backward energy transfer between Tm³⁺ and Yb³⁺ ions. Discussions are presented on the potential application for this upconversion mechanism to serve as a pump scheme for blue upconversion lasers.

Three fluoride crystals, LiYF₄ (YLF), BaY₂F₈, and KYF₄, were studied. They were either singly doped with Tm³⁺ or codoped with Yb³⁺ and Tm³⁺ ions. An argon-ion-laser-pumped, tunable Ti:sapphire laser was used for the steady-state luminescence study. A Q-switched Cr³⁺:LiSrAlF₆ (LiSAF) tunable laser (pulse width ~80

ns) and a Q-switched Cr³⁺:Alexandrite laser (pulse width ~100 ns) were used to study the luminescence dynamics. The visible steady-state luminescence spectra were recorded with a Si detector. The luminescence dynamics of Tm³⁺ and Yb³⁺ ions were detected by a Hamamatsu R1464 and a Hamamatsu R632 photomultiplier tube, respectively, and recorded by a Tektronix 300 MHz digital oscilloscope.

When samples doped with both Yb³⁺ and Tm³⁺ ions were excited into the Tm³⁺ ³F₄ absorption at ~780 nm, strong blue emissions were observed. The room-temperature emission spectra obtained with a cw Ti:sapphire laser are given in Fig. 1. It is important to note that exciting the same crystals doped only with Tm³⁺ ions at the same wavelength did not result in any detectable blue emissions. The blue emission dynamics at ~480 nm, obtained from a Yb³⁺- and Tm³⁺-codoped YLF crystal under excitation by the Q-switched Alexandrite laser at ~780 nm, are given in curve (a) of Fig. 2. Under the same excitation condition, emission from Yb³⁺ ions at ~1 μm was also observed. The temporal evolution of this emission in Yb³⁺, Tm³⁺:YLF is shown in Fig. 3. Also given in Fig. 3 are the emission decays of the Tm³⁺ ³F₄ states at ~800 nm in YLF samples with and without Yb³⁺ ions. Similar results have been observed for the other two crystals. We also studied the intensities of the blue emissions as a function of excitation power. The results are given in Fig. 4 for a 20% Yb³⁺, 0.5% Tm³⁺:YLF with different excitation wavelengths. We observed that the intensities of the ~483 and ~455 nm emissions increase with excitation density to the power of 1.6 and 2.2, respectively, and that these dependences did not change with excitation wavelengths in the vicinity of ~780 nm.

For comparison we also give in Fig. 2 curve (b) the ~480 nm blue emission dynamics obtained under excitation into Yb³⁺ ions at ~960 nm (using the Q-switched Cr:LiSAF laser). The steady-state emission spectra obtained with such an excitation wavelength were almost

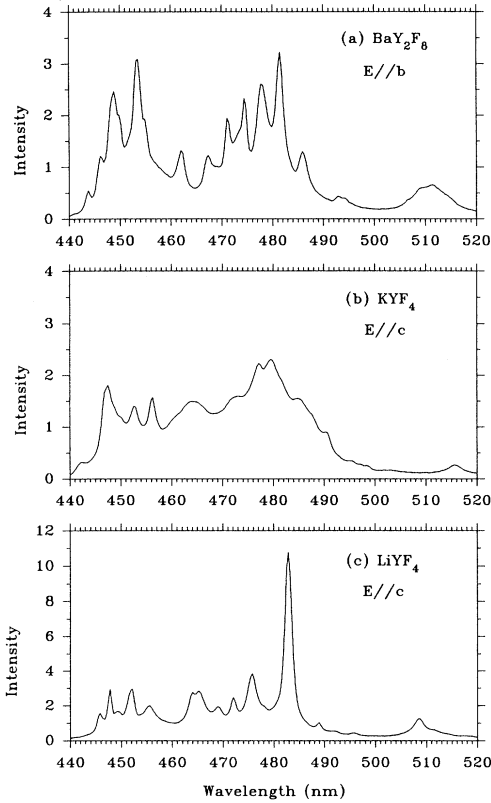


FIG. 1. Room-temperature emission spectra of fluoride crystals codoped with Tm^{3+} and Yb^{3+} ions under excitation at ~ 780 nm: (a) BaY_2F_8 , (b) KYF_4 , and (c) LiYF_4 . The ordinate axes are in arbitrary units.

exactly the same as those given in Fig. 1.

In order to understand the blue upconversion mechanism under the Tm^{3+} excitation, we first review the upconversion processes under excitation into Yb^{3+} ions. The energy levels of Yb^{3+} and Tm^{3+} are illustrated in Fig. 5. When codoped with Tm^{3+} ions in crystals, Yb^{3+} ions absorb the near-infrared radiation and transfer their excitation energies to Tm^{3+} ions. The Tm^{3+} ions are excited into the 1G_4 blue emitting level through three successive energy-transfer steps:¹⁰ (1) a Tm^{3+} ion is excited into the 3H_5 level by energy transfer from the first excited Yb^{3+} ion, and this Tm^{3+} ion then relaxes into its 3H_4 level; (2) the same Tm^{3+} ion is further excited into the 3F_2 level by the second excited Yb^{3+} ion and then relaxes into the lower metastable state, 3F_4 ; (3) the third excited Yb^{3+} ion transfers its excitation energy to this Tm^{3+} ion and excites it from the 3F_4 to the 1G_4 state. These processes can be described by the following equations and are illustrated in Fig. 5(a):

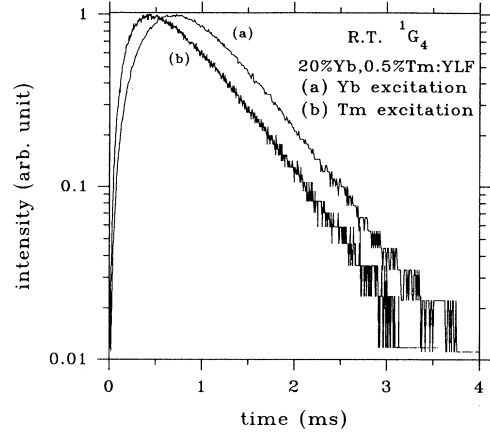
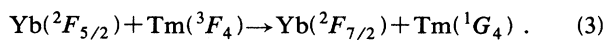
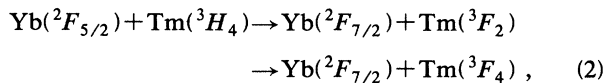
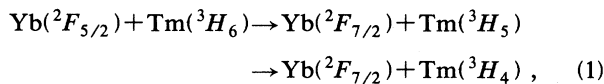


FIG. 2. Blue emission dynamics at ~ 480 nm in 0.5% Tm, 20% Yb:YLF under different excitations conditions: (a) Yb excitation at ~ 960 nm, and (b), Tm excitation at ~ 780 nm.

The Tm^{3+} ion can be further excited by similar processes into higher excited states such as 1D_2 . The $^1G_4 \rightarrow ^3H_6$ and $^1D_2 \rightarrow ^3H_4$ transitions of Tm^{3+} ions result in blue emissions peaked at ~ 480 and ~ 455 nm, respectively.

It is easily seen that sufficient populations on the intermediate levels such as 3F_4 are needed in order to achieve efficient upconversion blue emission. However, once Tm^{3+} ions are excited into these levels they can transfer their excitation energies back to Yb^{3+} ions, therefore depleting the populations. This energy transfer from the 3F_4 state of Tm^{3+} ions to Yb^{3+} ions is demonstrated in Fig. 3. Comparing curve (a) to (b), one can see that the decay of Tm^{3+} luminescence originating from the 3F_4 state is much faster in the presence of Yb^{3+} ions. The faster decay is indicative of energy transfer from Tm^{3+} to Yb^{3+} ions. This energy transfer is clearly demonstrated in YLF by the presence of Yb^{3+} luminescence under the excitation of Tm^{3+} , as shown in curve (c) in Fig. 3. Yb^{3+} emission in this case increases in the early time and reaches its maximum about $600 \mu\text{s}$ after the cessation of Tm^{3+} excitation. This time delay is due, in large part, to

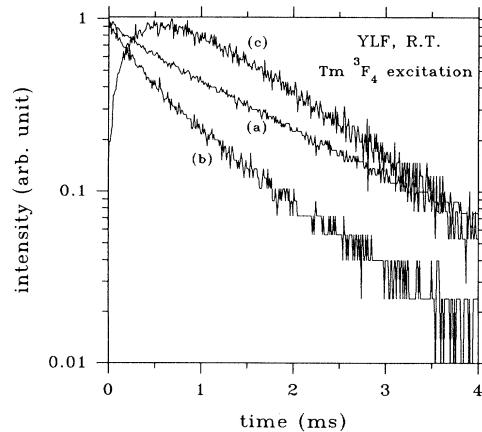


FIG. 3. Emission dynamics of Tm^{3+} and Yb^{3+} ions in YLF under the excitation into $\text{Tm}^{3+} \ ^3F_4$ level: (a) $\text{Tm}^{3+} \ ^3F_4$ emission in 1% Tm:YLF, (b) $\text{Tm}^{3+} \ ^3F_4$ emission in 1% Tm, 10% Yb:YLF, and (c) Yb^{3+} emission in 1% Tm, 10% Yb:YLF.

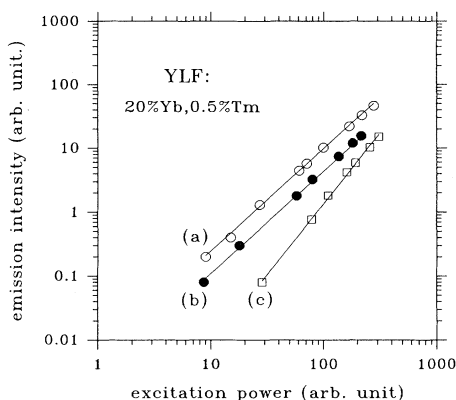


FIG. 4. Blue emission intensities as a function of excitation density at two excitation wavelengths in 20% Yb, 0.5% Tm:YLF: (a) emission at 483 nm and excitation at 794.3 nm, (b) emission at 483 nm and excitation at 786 nm, and (c) emission at 455 nm and excitation at 794.3 nm.

the finite transfer time between Tm^{3+} and Yb^{3+} ions. The energy transfer from the $\text{Tm}^{3+} {}^3F_4$ state to Yb^{3+} ions is also demonstrated by the similar results observed in the other two fluoride crystals, BaY_2F_8 and KYF_4 . As will be shown, energy transfer from the $\text{Tm}^{3+} {}^3F_4$ to the $\text{Yb}^{3+} {}^2F_{5/2}$ level is critical in understanding the blue up-conversion mechanism under Tm^{3+} excitation.

The energy transfer rate from Tm^{3+} to Yb^{3+} ions, $W_{\text{Tm-Yb}}$, can be calculated from the Tm^{3+} decay times obtained in samples with and without Yb^{3+} ions:

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

where τ_{Tm} and $\tau_{\text{Tm,Yb}}$ are the emission decay times of the $\text{Tm}^{3+} {}^3F_4$ state without and with the presence of Yb^{3+} ions in the crystals, respectively. In the case where the decay curve is nonexponential, the decay time is obtained by normalizing the luminescence intensity at time equal to zero and then integrating over the entire decay curve. τ_{Tm} was found to be 1.34 ms for 1% Tm:YLF at room temperature. $\tau_{\text{Tm,Yb}}$ was 0.71 and 0.57 ms for 10% Yb,

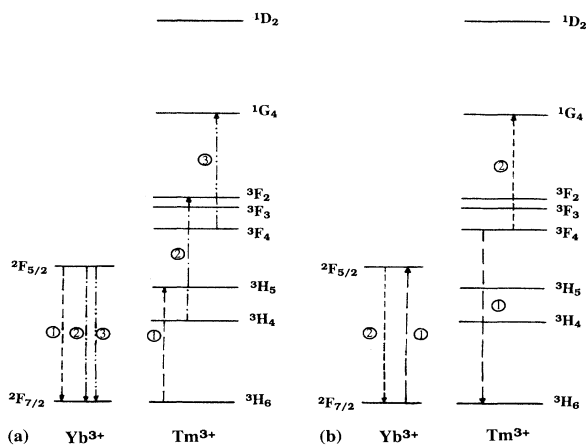


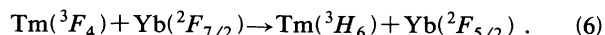
FIG. 5. Energy levels of Yb^{3+} and Tm^{3+} ions. Circled numbers illustrate the sequential steps of energy transfer after (a) Yb^{3+} ions or (b) Tm^{3+} ions are excited which result in the excitation of Tm^{3+} ions into the 1G_4 blue emitting level.

1% Tm:YLF and 20% Yb, 1% Tm:YLF, respectively. As a result, the room-temperature transfer rate was found to be ~ 660 and $\sim 1020 \text{ s}^{-1}$ for 10% Yb, 1% Tm:YLF and 20% Yb, 1% Tm:YLF, respectively. The energy-transfer efficiency η from the $\text{Tm}^{3+} {}^3F_4$ state to Yb^{3+} can also be calculated using

$$\eta = 1 - \tau_{\text{Tm,Yb}}/\tau_{\text{Tm}}, \quad (5)$$

and was found to be 47% and 57% in YLF samples containing 10% and 20% Yb^{3+} , respectively. It can be seen that the energy-transfer efficiency from the $\text{Tm}^{3+} {}^3F_4$ state to Yb^{3+} ions is quite high and that the transfer efficiency increases with Yb^{3+} concentration.

It was found that the energy-transfer rate from the $\text{Tm}^{3+} {}^3F_4$ state to Yb^{3+} ions decreases as the temperature is lowered and reaches a finite value as the temperature approaches zero. This indicates that the energy-transfer process is accompanied by the emission of phonons. Examining the energy diagram of Tm^{3+} and Yb^{3+} ions, one can easily see that such an energy-transfer process can only take place through the relaxation process



As mentioned earlier, when fluoride crystals codoped with Tm^{3+} and Yb^{3+} were excited into the $\text{Tm}^{3+} {}^3F_4$ level at $\sim 780 \text{ nm}$, strong blue emissions at both ~ 455 and $\sim 480 \text{ nm}$ were observed. Since the blue emissions were not observed in Tm^{3+} singly doped crystals under the same excitation condition, they must result from the interaction between Tm^{3+} and Yb^{3+} ions. After Tm^{3+} ions are excited into the 3F_4 level they can transfer their excitation energies to Yb^{3+} ions very efficiently through Eq. (6), as demonstrated above. Once Yb^{3+} ions are excited they can, in principle, transfer their excitation energies back to Tm^{3+} ions and give rise to the blue emission through the processes described by Eqs. (1)–(3). The transfer efficiency of each of these individual steps depends, of course, on the relative populations of the relevant states, 3H_6 , 3H_4 , and 3F_4 . However, in the case of Tm^{3+} excitation the 3F_4 level is directly populated. As a result, the sensitization of Tm^{3+} by Yb^{3+} ions can now take place directly through process (3). That is, the blue emitting level, 1G_4 , can be populated efficiently through two sequential energy-transfer processes described by Eqs. (6) and (3) when one pumps into the $\text{Tm}^{3+} {}^3F_4$ level. This upconverting process, as illustrated in Fig. 5(b), is expected to be faster than that through excitation of Yb^{3+} ions since the former involves two energy-transfer steps and the latter three steps. Comparing the blue emission dynamics in Fig. 2, one indeed sees that the blue emissions reach their maximum intensities earlier with excitation into Tm^{3+} ions than into Yb^{3+} ions.

The facts that the 1G_4 blue emission intensity increases with the excitation density to the power of 1.6 in YLF and that this dependence is insensitive to excitation wavelength, as shown in Fig. 4, seem to further confirm that the upconversion process to the $\text{Tm}^{3+} {}^1G_4$ state under $\text{Tm}^{3+} {}^3F_4$ excitation is a two-step energy-transfer process in Tm^{3+} - and Yb^{3+} -codoped crystals.

Blue upconversion by exciting into Tm^{3+} at $\sim 780 \text{ nm}$ through the mechanism discussed above offers some ad-

vantages over the conventional approach of exciting into Yb^{3+} at ~ 960 nm and therefore is, potentially, a pumping scheme for laser application. First, the upconversion efficiency is expected to be higher for the former than the latter, e.g., the maximum conversion efficiency to 483 nm emission is $\sim 66\%$ for Yb^{3+} excitation at ~ 960 nm and $\sim 81\%$ for Tm^{3+} excitation at ~ 780 nm. Second, high-power, cheap diode lasers at ~ 780 nm are much more readily available than the 960 nm diode lasers. Pumping at ~ 780 nm is feasible since Tm^{3+} ions have adequate absorptions at this wavelength. Since Tm ions are directly pumped, the ground state can be depleted and therefore the transition between 1G_4 and 3H_6 , the ground state, at ~ 483 nm can be lased using ground-state depletion¹¹ or pump-resonant excitation¹² methods. When Yb^{3+} ions are excited the depletion of the ground state is not as easily achieved because of the efficient back transfer described by Eq. (6). The advantage of lasing through the transition between 1D_2 and 3H_4 levels at ~ 455 nm is even more obvious because it uses only one pump source at 780 nm in this case, unlike previous reports¹⁻⁵ which used two pump sources. In addition, after Yb^{3+} ions are excited through Eq. (6), they can transfer to Tm^{3+} ions not only through Eq. (3) but also through (2), as mentioned above. This latter energy-transfer step depletes the population of 3H_4 and should make population inversion between 1D_2 and 3H_4 levels easier to achieve. This effect should be even more significant under intense pumping conditions since then the relative population of the $\text{Tm}^{3+} {}^3H_4$ level will be higher and so will the efficiency of transfer process (2). Knüpfner *et al.*⁵ recently observed the positive effect of Yb^{3+} on the lasing performance between $\text{Tm}^{3+} {}^1D_2$ and 3H_4 levels in YLF when pumping with 780 and 650 nm sources. They commented, however, that they did not understand this positive effect. Their result is explained by our model.

We caution that both Yb^{3+} and Tm^{3+} concentrations must be optimized for laser applications. On one hand, higher Yb^{3+} concentration is more desirable for efficient blue upconversion through processes described by Eqs. (6) and (3). On the other hand, higher Yb^{3+} concentration will more rapidly deplete the population of the $\text{Tm}^{3+} {}^1G_4$ state, since Tm^{3+} ions also transfer their energies to Yb^{3+} ions from the 1G_4 state.⁷ For example, when excited by the frequency-doubled, Q-switched Cr:LiSAF laser

tuned at ~ 480 nm the decay time of the $\text{Tm}^{3+} {}^1G_4$ level was found to be 218, 200, and 180 μs in YLF samples containing 1% Tm^{3+} , 1% Tm^{3+} and 10% Yb^{3+} , and 1% Tm^{3+} and 20% Yb^{3+} , respectively. The energy-transfer efficiency from this level to Yb^{3+} ions is then 8% and 17% in YLF samples containing 10% and 20% Yb^{3+} , respectively. The energy-transfer efficiency obviously increases with Yb^{3+} concentration in the sample. Although this energy-transfer efficiency is much lower than that out of the 3F_4 level, this energy-transfer process imposes a loss mechanism to the 1G_4 level when building a lasing inversion of this level with respect to the ground state. No noticeable reduction of decay time in YLF was observed for the 1D_2 level in the presence of Yb^{3+} ions, indicating that the energy back transfer from this level is negligible in this crystal. A weak energy-transfer process from the 1D_2 level was also observed in both KYF_4 and BaY_2F_8 . For the laser transition between the 1G_4 and 3H_6 levels, a low Tm^{3+} concentration is required to minimize self-absorption losses. A higher Tm^{3+} concentration is more desirable for better pump efficiency. High Tm^{3+} concentration can, however, cause cross relaxation among Tm^{3+} ions and therefore reduce the emission decay times of the blue emitting levels as well as the intermediate levels. This could reduce the quantum efficiencies of the blue emitting levels as well as the upconversion efficiency. Detailed modeling is in progress to help determine the optimal Yb^{3+} and Tm^{3+} concentrations for lasing applications.

In conclusion, we have demonstrated strong blue emissions in Yb^{3+} - and Tm^{3+} -codoped fluoride crystals by exciting the Tm^{3+} ions using a single source at ~ 780 nm. The upconversion mechanism under such excitation is shown to be dominantly a two-step energy-transfer process in a YLF crystal containing 20% Yb^{3+} and 0.5% Tm^{3+} : Tm^{3+} to Yb^{3+} energy transfer described by Eq. (6) followed by Yb^{3+} to Tm^{3+} energy transfer described by Eq. (3). We suggest that this upconversion process may serve as a pump mechanism enabling blue laser emission. The Yb^{3+} and Tm^{3+} concentrations need to be optimized for this to be possible.

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*FAX: (407) 658-6880. Electronic address: ZHANG@LASER.CREOL.UCF.EDU

†Also at Depts. of Physics and Electrical and Computer Engineering, University of Central Florida, Orlando, FL 32816.

‡Also at Depts. of Physics, Electrical and Computer Engineering and Mechanical Engineering, University of Central Florida, Orlando, FL 32816.

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