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Phonon-assisted cooperative energy transfer and frequency upconversion in a Yb^{3+}/Tb^{3+} codoped fluoroindate glass

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We report large thermal enhancement of the frequency upconversion (UC) process due to cooperative energy transfer (CET) in a Yb^{3+}/Tb^{3+} codoped fluoroindate glass obtained by heating the sample from 308 to 530 K. To study the influence of multiphonon transitions in the UC process we chose anti-Stokes quasiresonant excitation of Yb^{3+} ions which were used as sensitizers. UC of radiation at 1064 nm into blue and green light was obtained. Various emission lines of Tb^{3+} were observed between 400 and 700 nm due to CET from Yb^{3+} to Tb^{3+} ions. A rate equation model was used to describe the temperature dependence of the UC emission intensities and the theoretical results are in good agreement with the experimental data.
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I. INTRODUCTION

Frequency upconversion (UC) of infrared-to-visible light in rare-earth (RE) doped solids has been for years the subject of many studies mainly because it is possible to exploit UC for various photonic applications.[1] One such application is, for example, the realization of UC lasers[2] operating at the visible that are pumped by infrared diode lasers. Fluoride glasses have been investigated as a candidate for such devices, because they combine good mechanical stability with superior chemical properties which allows large concentrations of RE to be incorporated into the host matrix. Of particular importance is the fact that fluoride hosts have low cut-off phonon energies compared with, for example, most oxide hosts. This characteristic enhances the UC emission by the suppression of nonradiative channels.

Among existing fluoride hosts, fluoroindate glasses (FIGs)[3] are particularly interesting because of their stability against moisture in the atmosphere, large transparency windows that extend from 0.25 up to 8 μm, and low cut-off phonon energy ($\sim 507\,cm^{-1}$).[4] Various UC processes that involve different RE ions have been demonstrated and indicate that FIG is a promising host material for UC based devices.[5–10]

Besides choosing a good host material for RE ions, the efficiency for infrared-to-visible and ultraviolet light conversion can be improved if one uses a sensitizer to increase near-infrared absorption. In this case, the ytterbium (Yb^{3+}) ion has been used because it contains only one electronic transition inside the 4*f* subshell, which guarantees a large ground-state absorption cross section.[11] Then, energy transfer from excited Yb^{3+} ions to other RE ion species (UC emitters) follows, resulting in improvement of the UC fluorescence.[12–16] This effect was recently exploited in different codoped systems such as Yb^{3+}/Er^{3+},[13] Yb^{3+}/Pr^{3+},[14] Yb^{3+}/Tb^{3+},[15] and Yb^{3+}/Tm^{3+}.[16]

In the early stages of research on new UC processes resonant excitation schemes was mainly considered; however, nonresonant absorption can be advantageous in many ways. Extensive work on phonon-assisted (PA) processes in RE doped materials was reported in Refs. 17–20 where the authors show that it is possible to observe UC fluorescence in RE-doped solids even if the energy mismatch between the electronic transition and the excitation photons is larger than the host cut-off phonon energy. Furthermore, it was shown that PA processes involve not only cut-off phonons, all phonon modes participate in a way which is determined by the phonon density of states of the matrix. Accordingly, the concept of ''effective phonon mode'' (EPM), which is roughly a kind of phonon energy weighted average, was introduced.

PA processes have proved to be useful in applications such as temperature sensors,[21,22] UC lasers,[23] laser cooling of solids,[24,25] and phase-conjugated mirrors.[26] It was also shown that the laser threshold of a fiber laser could be reduced as well as its output power enhanced using a PA excitation scheme.[27] The thermal enhancement of UC processes in FIGs doped with Yb^{3+}/Pr^{3+} (Ref. 28) and Nd^{3+} (Ref. 29) was recently exploited.

In this work, we used a laser operating at 1064 nm to nonresonantly excite Yb^{3+} ions in a FIG sample codoped with terbium (Tb^{3+}) ions. Phonon-assisted transitions were exploited and many UC emission lines from Tb^{3+} ions were observed due to energy transfer from Yb^{3+} ions. Amongst the many UC lines observed we decided to study the blue emission at 417 nm and the green emission at 545 nm as a function of the sample temperature. Both UC emissions experienced large enhancement when the temperature was varied from 308 to 530 K.

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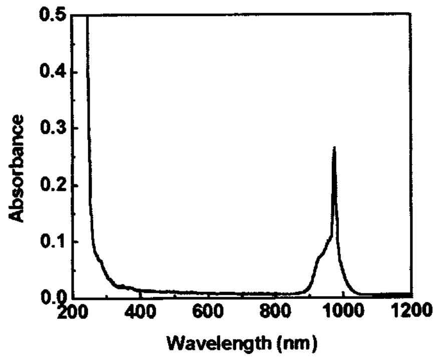

FIG. 1. Absorption spectrum. The strong band at ~980 nm is associated with Yb^{3+} ions. Absorption bands of Tb^{3+} are located between 350 and 550 nm but they are too weak to be observed with the present Tb^{3+} concentration. Sample thickness: 2 mm.

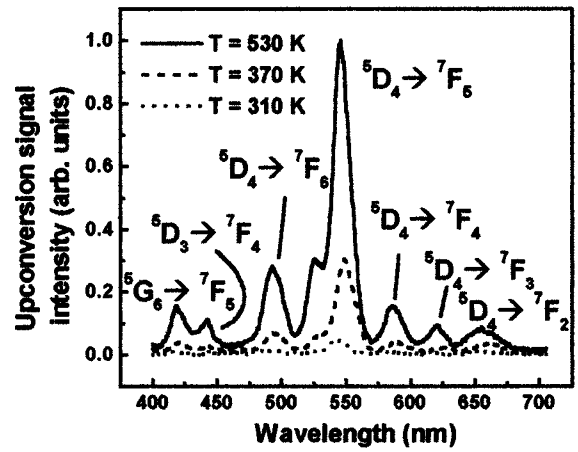

FIG. 2. Energy upconversion spectra of the Yb^{3+}/Tb^{3+} codoped fluoroindate sample at 310 (dotted line), at 370 (dashed line), and at 530 K (solid line) under excitation with 1.3 W at 1064 nm. The peaks observed correspond to Tb^{3+} transitions, which are shown.

The present results demonstrate the possibility of thermal enhancement of frequency upconversion mediated by cooperative energy transfer processes that involve three and four RE ions when the sample's temperature is raised above room temperature.

II. EXPERIMENTAL DETAILS

The FIG sample studied has the following composition in mol %: $37\,InF_3-20\,ZnF_2-20\,SrF_2-14.5\,BaF_2-2\,NaF-4\,GaF_3-0.5\,TbF_3-2\,YbF_3$. Details of the preparation procedure are described in Ref. 3. The linear absorption spectrum was measured from 200 to 1200 nm using a double beam spectrophotometer. The UC measurements were performed using a mode-locked Nd:YAG laser (76 MHz, 80 ps) emitting at 1064 nm (average power: 1.3 W) as the excitation source. The laser beam was focused onto the sample using a 30 cm focal length lens and its beam waist at the sample position was estimated as ~70 μm. The temperature of the sample was controlled using a hot plate and UC fluorescence, collected in direction perpendicular to the excitation beam, was sent to a 0.25 m monochromator attached to a photomultiplier tube. The electronic signal was analyzed using a lock-in amplifier connected to a personal computer for signal processing. During the experiments the temperature was kept below the onset of crystallization of the glass.[3]

III. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of the sample. The band centered at ~980 nm can be identified by transitions that originate from the Yb^{3+} ground multiplet $^2F_{7/2}$ to the excited multiplet $^2F_{5/2}$. The large bandwidth observed is characteristic of inhomogeneously broadened RE transitions in glasses. Very weak bands due to Tb^{3+} are located between 350 and 550 nm.

Figure 2 shows the UC emission in the range 400–700 nm for 310, 370, and 530 K under laser irradiation of 1.3 W at 1064 nm. Note that the signal intensities increased with the temperature. The emission bands, assigned in previous reports,[15,30,31] are associated to Tb^{3+} transitions which are centered at 417 nm ($^5D_3,{}^5G_6\rightarrow{}^7F_5$), 442 nm ($^5D_3\rightarrow{}^7F_4$), 492 nm ($^5D_4\rightarrow{}^7F_6$), 545 nm ($^5D_4\rightarrow{}^7F_5$), 585 nm ($^5D_4\rightarrow{}^7F_4$), 621 nm ($^5D_4\rightarrow{}^7F_3$), and 654 nm ($^5D_4\rightarrow{}^7F_2$). Details of two of the more intense emission lines in the blue and green regions of the spectrum, e.g., at 417 and 545 nm, were investigated. For both lines we have measured the dependence of the fluorescence intensity as a function of the laser intensity. As shown previously[15] a quadratic (cubic) dependence indicates that the green (blue) line is due to the absorption of a two (three) laser photons. These results, together with the fact that Tb^{3+} does not absorb in the near infrared, led us to propose the excitation scheme depicted in Fig. 3. Accordingly, initially a pump photon at 1064 nm induces PA excitation of Yb^{3+} ions from multiplet $^2F_{7/2}$ to excited multiplet $^2F_{5/2}$. Then, two excited Yb^{3+} ions eooperatively transfer their energies to a neighboring Tb^{3+} ion in the ground multiplet, exciting this ion to the $^5D_4$ multiplet. Transition $^5D_4\rightarrow{}^7F_5$ generates fluorescence at 545 nm. This process has been previously observed in Yb^{3+}/Tb^{3+} -doped crystals[32,33] and in FIG samples[15] but the Yb^{3+} ions were resonantly excited in those cases. Here

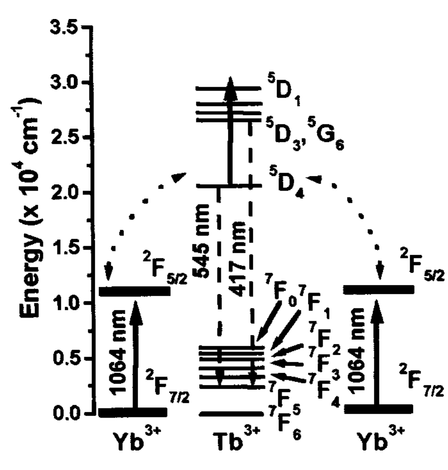

FIG. 3. Energy level scheme of the two Yb^{3+} sensitizers and the Tb^{3+} activator ions that participate in the process of phonon-assisted cooperative energy transfer and frequency UC. The dashed lines represent cooperative energy transfer from Yb^{3+} to Tb^{3+} ions. The photonic energy mismatches are compensated for by absorption or emission of phonons.

phonons are involved to compensate for laser frequency detuning to the $^2F_{5/2}$ level. Besides this process the excited Tb^{3+} ion can absorb one more laser photon at 1064 nm, being promoted from $^5D_4$ to $^5D_1$. The excess energy is transfer to the lattice through phonon excitation. The existence of several energy levels between $^5D_1$ and ($^5D_3$,$^5G_6$) shown in Fig. 3 implies fast nonradiative decay to lower-lying levels, finally reaching levels ($^5D_3$,$^5G_6$), from which the Tb^{3+} ions can emit radiation at 417 nm. Another possible way to populate the ($^5D_3$,$^5G_6$) levels would be, instead of absorbing a laser photon, energy transfer from another excited Yb^{3+} to the already excited Tb^{3+} ion. This has been attributed as the main contribution in Ref. 30 for fluorophosphate glasses with concentrations of YbF_3 larger than 16 % mol. For the low Yb^{3+} concentration used here we do not expect a large contribution due to a third excited Yb^{3+} donor. In fact, this excitation path has an energy mismatch of more than $10^3\,\mathrm{cm}^{-1}$ which reduces the probability of its occurrence. Also recall that blue emission of very low intensity was observed in previous work where resonant excitation at 976 nm with laser power of 40 mW was used.[15] Due to the low laser intensity achieved the poor signal-to-noise ratio in that experiment did not allow characterization of the process of blue emission. The blue signal observed in the present work is clearly seen although the same sample is used. Thus, we conclude that the presence of the strong laser beam contributes to enhancing the probability of laser excitation of Tb^{3+} ions at $^5D_4$ to levels above ($^5D_3$, $^5G_6$) levels.

To corroborate the proposed scheme of PA absorption and cooperative energy transfer, we measured the dependence of the integrated fluorescent emissions at 417 and 545 nm as a function of the temperature. The results presented in Fig. 4 show 76-fold enhancement of the blue emission and 20-fold enhancement of the green emission when the temperature of the sample was raised from 308 to 530 K. The solid lines represent theoretical results obtained using a temperature dependent rate equation model, which takes into account the energy levels relevant for the generation of the UC emissions described by

$$\dot{n}_g = -R_1(T)n_g + \gamma_e n_e, \tag{1}$$

$$\dot{n}_e = R_1(T)n_g - \gamma_e n_e - C_1 n_e^2 n_1 + C_2 n_g^2 n_2, \tag{2}$$

$$\dot{n}_1 = -C_1 n_e^2 n_1 + \gamma_5(T) n_5, \tag{3}$$

$$\dot{n}_2 = -\gamma_2 n_2 + C_1 n_e^2 n_1 - C_2 n_g^2 n_2 - R_2(T) n_2, \tag{4}$$

$$\dot{n}_3 = R_2(T) n_2 - \gamma_3(T) n_3, \tag{5}$$

$$\dot{n}_4 = \gamma_3(T) n_3 - \gamma_4 n_4, \tag{6}$$

$$\dot{n}_5 = \gamma_2 n_2 + \gamma_4 n_4 - \gamma_5(T) n_5, \tag{7}$$

where the energy levels are labeled g ($^2F_{7/2}$) and e ($^2F_{5/2}$) for Yb^{3+} ions and 1 ($^7F_6$), 2 ($^5D_4$), 3 ($^5D_1$), 4 ($^5D_3$,$^5G_6$), and 5 ($^7F_5$) for Tb^{3+} ions. The pumping rates are given by $R_1(T) = \sigma_{ge}(T)\Phi$ and $R_2(T) = \sigma_{23}(T)\Phi$, where Φ is the photon flux (given by the ratio of the laser intensity and the excitation photon energy) and $\sigma_{ij}(T)$ denotes the temperature dependent absorption cross section between levels i and j, given by

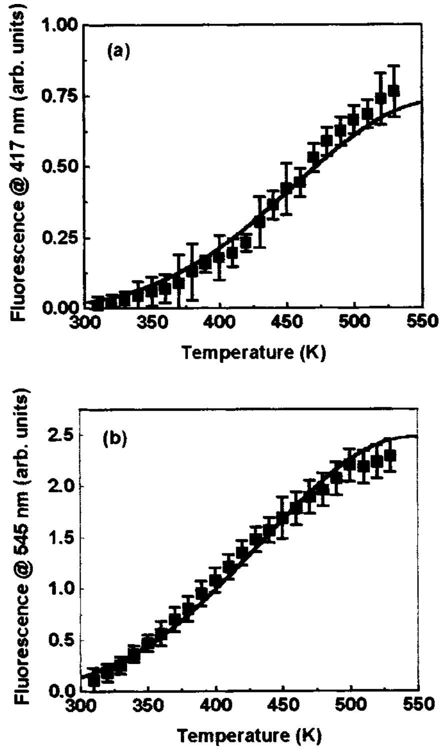

FIG. 4. Temperature dependence of the integrated UC signals at (a) 417 and (b) 545 nm (pump power: 1.3 W). The solid lines represent the best fit for populations in the steady state using C_2 (the energy back-transfer rate) as the fitting parameter.

$$\sigma_{ij}(T) = \sigma_{ij}\left\{\exp\left[\frac{hv_{\text{phonon}}}{k_B T} - 1\right]\right\}^{-q_{ij}}, \tag{8}$$

where σ_{ij} is the absorption cross section between levels i and j at room temperature. Based on the absorption data shown in Fig. 1 and on Judd–Ofelt theory[34–36] we found that $\sigma_{ge} \cong \sigma_{23} \sim 0.2\,\mathrm{pm}^2$. The EPM energy, hv_{phonon}, in FIGs is $310\,\mathrm{cm}^{-1}$,[29] and q_{ij} is the number of EPMs participating in the process ($q_{ge}=3, q_{23}=1$). Parameters C_1 and C_2 are, respectively, the cooperative energy transfer and back-transfer rates. The total decay rate from level i is given by $\gamma_i(T) = \Sigma_j A_{ij} + W_{\text{nr}}(T) = \gamma_i^{\text{rad}} + W_i^{\text{nr}}(T)$, where A_{ij} is the radiative decay rate. The temperature dependent nonradiative decay rate is given by

$$W_i^{\text{nr}}(T) = W_i^{\text{nr}}(T_0)\left[\frac{1-\exp(-hv_{\text{phonon}}/k_B T)}{1-\exp(-hv_{\text{phonon}}/k_B T_0)}\right]^{-p}, \tag{9}$$

where p represents the number of EPMs involved in the relaxation of level i to the closest lower-lying energy level and T_0 is room temperature. For this particular case we have $p=1$. The radiative decay rates were estimated using Judd–Ofelt theory and $W_i^{\text{nr}}(T_0)$ was calculated using the energy-gap law.[35]

The data shown in Fig. 4 were fitted using the steady state solution of Eqs. (1)–(7) for the population of states $^5D_4$ and ($^5D_3$,$^5G_6$) as a function of the temperature. Considering that $C_1 = 1650$ Hz as determined in Ref. 15 we are left with only one fitting parameter, i.e., C_2. It was found that the best fit occurs for $C_2 = 850$ Hz as illustrated in Fig. 4. Hence, the present experiment indicates that the energy backtransfer, ruled out in first approximation,[15] contributes to the dynamics of PA processes.

IV. CONCLUSIONS

An investigation of thermally enhanced frequency UC due to cooperative energy transfer in Yb^{3+}/Tb^{3+} codoped fluoroindate glass excited at 1064 nm was performed. The results demonstrate that PA processes may enhance the UC fluorescence efficiency of FIGs if they are suitably exploited. A 76-fold (20-fold) enhancement of the blue (green) upconverted emission at 417 nm (545 nm) when the temperature of the sample was raised from 308 to 530 K was observed. A set of rate equations was written and their solutions are in good agreement with the experimental results. By using the effective phonon mode energy of $310\,\mathrm{cm}^{-1}$ determined in previous work[29] as well as the direct energy transfer rate calculated in Ref. 15, it was possible to determine the energy back-transfer rate from Tb^{3+} to Yb^{3+} ions.

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