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Title:

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Energy transfer between thulium and praseodymium ions in solids

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Abstract:

New thulium-to-praseodymium upconversion and cross-relaxation energy transfer mechanisms are observed. YLiF_4 has several subsets of dopant ions, which exhibit a variety of transfer efficiencies. Dual-pulse laser excitation of dimers in CsCdBr_3 is used to demonstrate a probable upconversion pathway.

1. Introduction

The application of energy-transfer phenomena to the design of devices which absorb and emit light at convenient wavelengths is increasing rapidly. If the ions that receive energy by the transfer are initially excited they may undergo "energy-transfer upconversion". This effect can be applied to the design of lasers which operate at a shorter wavelength than their pump source. The first example of this application was the 550 nm erbium laser which is pumped by energy transfer from ytterbium ions excited at 980 nm [1].

Direct pumping of upper states with visible lasers has demonstrated that praseodymium ions have several strong visible laser transitions from the $^3\text{P}_0$ and 1D_2 manifolds [2]. The potential for practical Pr^{3+} lasers has not yet been realized for need of an appropriate visible-laser-pump source and the lack of short-wavelength absorption that prevents efficient coupling to flashlamp excitation.

This paper presents the observation of new excitation mechanisms in which thulium-ion excitation in the UV or near-infra-red is transferred to

praseodymium ions. Because 800 nm thulium bands are ideal for excitation with GaAlAs semiconductor diode lasers these new mechanisms, which combine the convenient absorption of thulium with the strong emission of praseodymium, may be applicable to the design of new visible or infra-red lasers.

2. Experimental

The primary YLiF₄ sample for this investigation was a 5 mm cube doped with 1mol%Tm³⁺ and 0.5mol%Pr³⁺ that was grown by Sanders Associates, New Hampshire. Observations were confirmed in three codoped YLiF₄ samples grown by the laser-heated-pedestal-growth technique at the University of South Florida. CsCdBr₃ samples with dopant melt concentrations of 0.5mol%Tm³⁺ and 0.1mol%Pr³⁺ were provided by the University of Canterbury, New Zealand.

Laser spectroscopy was performed using 10 nsec pulses from Quanta-Ray PDL1 and PDL3 dye lasers pumped by DCR Nd:YAG lasers. The output of the two lasers was combined using dichroic mirrors. Fluorescence was collected with a SPEX 1402 1m monochromator and a Tektronix 11402 storage oscilloscope. A model 22C CTI closed-cycle refrigerator cooled samples to 12K.

3. Results

3.1 Energy transfer in YLiF₄

Tm³⁺ ions in YLiF₄ have a strong absorption at 355 nm due to the ³H₆ → ¹D₂ transition. This coincidence with the frequency-tripled Nd:YAG laser provides a simple excitation method for obtaining thulium emission spectra. Despite the lack of direct Pr³⁺ absorption in this region samples that are codoped with Tm³⁺ and Pr³⁺ show remarkably strong emission on the ³P₀ → ³H₅ (600 nm) and ³P₀ → ³H₄ (490 nm) praseodymium transitions. For 355 nm excitation the integrated emission from the latter, for example, is approximately twice as strong as the ¹G₄ → ³H₆ thulium emission in the same spectral region. This energy-transfer process may be applicable to the development of all-solid-state praseodymium lasers that are pumped by Nd:YAG lasers or flashlamps.

The observation of UV-to-visible conversion by thulium-to-praseodymium energy transfer lead us to examine the possibility of energy-transfer upconversion in the system. Blue (490 nm peak) and orange (604.5 nm peak) emission ($^3P_0 \rightarrow ^3H_4, ^3H_6$ respectively) from praseodymium was readily observable upon $^3H_6 \rightarrow ^3H_4$ near-infrared (791.5 nm peak) thulium excitation. The efficiency of the upconversion process varied greatly with the exact choice of pump wavelength.

Site selective upconversion excitation and emission spectroscopy revealed the presence of considerable spectral structure on both the Tm^{3+} and the Pr^{3+} transitions. Figure 1 clearly shows this structure on a small region of the $^3H_4 \rightarrow ^3P_0$ Pr^{3+} excitation region obtained by broad band monitoring of $^3P_0 \rightarrow ^3H_6$ emission. Site-selective laser spectroscopy was used to establish that 3P_0 lifetimes vary from 25 μ sec to 42 μ sec for these Pr^{3+} transitions. As the 3P_0 manifold comprises only a single level, each of the transitions must originate from a subset of Pr^{3+} ions that has a different local environment. Such perturbations on the large Pr^{3+} ion by the small Tm^{3+} ion, and vice versa, would account for the well defined structure that occurs on each of the Tm^{3+} and Pr^{3+} excitation and emission spectra in these codoped crystals. The "discrete" nature of the spectral perturbations suggests a non-random dopant ion distribution in which, presumably to minimize the lattice strain energy, the large Pr^{3+} and small Tm^{3+} ions prefer to closely associate with small ion separations that induce the relatively large energy level perturbations observed. Such a preference for clustering accounts for the variation in upconversion efficiency that depends on the choice of Tm^{3+} ion subset that is excited.

Laser-excitation spectroscopy was used to establish that four spectral properties of the subsets scaled consistently with observed increases in Tm^{3+} - pumped Pr^{3+} upconversion efficiency: (1) the 3H_4 (Tm^{3+}) pump state lifetime decreased dramatically. The unperturbed Tm^{3+} ion subset lifetime of greater than 1 msec at 12K decreased to 8 μ sec due to energy-transfer quenching by Pr^{3+} ions, in the center with greatest upconversion efficiency. A center with intermediate efficiency had a decay of 680 μ sec. (2) the upconverted 3P_0 (Pr^{3+}) decay time which reflects the 3H_4 Tm^{3+} feeding rate decreased. (3) Energy levels of Tm^{3+} that are doubly degenerate in the unperturbed site are

significantly split in the subsets that upconvert efficiently. For example, the $\Gamma_{3,4}$ level at 12643 cm^{-1} ($^3\text{H}_4$) in the isolated Tm^{3+} center [3] is split by 1.7 cm^{-1} and 5.9 cm^{-1} in centers of moderate and greatest upconversion respectively. (4) Pr^{3+} levels that are doubly degenerate in the perturbed sites are also split for the subsets with greatest upconversion efficiency. For example, the level at 79 cm^{-1} ($^3\text{H}_4$) in the isolated Pr^{3+} center [4] is split by 16.7 cm^{-1} into 2 levels for the subset with greatest perturbation.

3.2 Energy transfer in CsCdBr_3

Lanthanide ions form dimer centers in CsCdBr_3 that can result in very efficient energy transfer [5]. Because the pulsed laser energy absorbed by an ion will preferentially transfer to the other ion of its dimer, rather than to other dimers, this host was codoped with Tm^{3+} and Pr^{3+} to enhance the isolation of the energy transfer steps in the upconversion process.

Figure 2 demonstrates two laser spectroscopy experiments in the doubly doped system. Two 10 nsec laser pulses separated by 600 μsec are used to excite Tm/Pr dimers while monitoring the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ (Pr^{3+}) upconversion emission (490.1 nm). In Figure 2a both pulses excite the $^3\text{H}_6 \rightarrow ^3\text{H}_4$ (Tm^{3+}) transition at 799.5 nm. The weak peak observed upon the first pulse is due to energy transfer between dimers that should disappear in samples of low dopant concentration. The strong Pr^{3+} emission that occurs after the second pulse of Tm^{3+} indicates the requirement for two sequential energy-transfer steps from the Tm^{3+} $^3\text{H}_4$ level. Figure 2b shows the strong Pr^{3+} upconversion induced by a second pulse resonant with the $^1\text{G}_4 \rightarrow ^3\text{P}_2$ (Pr^{3+}) excited-state absorption transition at 803.0 nm. This observation demonstrates efficient population of the $^1\text{G}_4$ (Pr^{3+}) manifold, after the first pulse, from the $^3\text{H}_4$ (Tm^{3+}) manifold. This process was then confirmed directly by observation of a sharp dip in the $^1\text{G}_4$ (Pr^{3+}) emission transient at the time of the ESA pulse. Details of a temporal analysis that enables the extraction of relevant energy transfer rates from several dual-laser experiments will be published elsewhere.

4. Discussion

Figure 3 shows two possible energy-transfer upconversion mechanisms for Tm/Pr upconversion. Energy transfer between two Tm^{3+} ions may promote

one ion to the 1G_4 (Tm^{3+}) level which then transfers the energy to the 3P_0 (Pr^{3+}) level (Figure 3a). Alternatively, upconversion may occur within the Pr^{3+} ion via the 1G_4 (Pr^{3+}) level (Figure 3b). The presence of several distinct ion separations in $YLiF_4$ makes distinction between the two processes difficult. Dual laser experiments in $CsCdBr_3$, on the other hand, demonstrate that the process of figure 3a is the probable mechanism. Efficient emission from the 1G_4 (Pr^{3+}) after a single pulse that excites 3H_4 (Tm^{3+}), upconversion upon excitation with a second pulse resonant with Pr^{3+} ESA (Figure 2b) and the direct observation of 1G_4 population depletion with a second pulse demonstrate conclusively that the 1G_4 (Pr^{3+}) manifold is efficiently populated by energy transfer from the 3H_4 (Tm^{3+}) manifold. This information is essential to the design of new diode-pumpable laser and amplifier systems that use the 1G_4 , 3P_2 or 3P_0 (Pr^{3+}) manifolds as an initial state.

5. Conclusion

New Tm^{3+} to Pr^{3+} energy-transfer processes, which may be applicable to practical laser design, have been demonstrated in two hosts. These processes include UV-to-visible and near-IR-to-visible conversion. Tm^{3+} and Pr^{3+} dopant ions are found to preferentially cluster in $YLiF_4$ providing a few subsets that exhibit exceptionally efficient energy transfer. Pulsed laser spectroscopy of the simple dimers present in $CsCdBr_3$ was used to verify the importance of 1G_4 (Pr^{3+}) as an intermediate state in upconversion processes.

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Figure captions:

- Figure 1: Excitation spectrum of $^3\text{H}_4 \rightarrow ^3\text{P}_0$ Pr^{3+} transitions in Tm/Pr:YLiF_4 obtained by monitoring broad-band orange emission ($^3\text{P}_0 \rightarrow ^3\text{H}_6$ Pr^{3+}).
- Figure 2: Temporal form of $^3\text{P}_0 \rightarrow ^3\text{H}_4$ (Pr^{3+}) upconversion emission (490.1 nm) for dual-pulse excitation. The first pulse excites $^3\text{H}_6 \rightarrow ^3\text{H}_4$ (Tm^{3+}) (799.5 nm) and the second pulse, 600 μsec later, excites: (a) $^3\text{H}_6 \rightarrow ^3\text{H}_4$ (Tm^{3+}) and (b) $^1\text{G}_4 \rightarrow ^3\text{P}_2$ (Pr^{3+}) excited-state absorption (803.0 nm).
- Figure 3: Possible Tm^{3+} to Pr^{3+} energy-transfer upconversion schemes in YLiF_4 .

Fig 1

Fig 2

Fig 3

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