

# Intrinsic chromatic switching of visible luminescence in $\text{Yb}^{3+}, \text{Er}^{3+}:\text{CsCdBr}_3$

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Bistability is reported in sensitized  $\text{Er}^{3+}$  luminescence driven by an  $\text{Yb}^{3+}$  transition that previously revealed an  $\text{Yb}^{3+}$  luminescent instability. To our knowledge this is the first report of bistable energy transfer between different rare-earth ions. © 2003 Optical Society of America

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The intrinsic bistability of luminescence in compounds doped with  $\text{Yb}^{3+}$  ions<sup>1–4</sup> has attracted widespread interest because of its relevance for all-optical logic, computation, and control of light by light itself<sup>5</sup> and because of its puzzling origin. However, all reports of bistable luminescence to date have described abrupt changes in emission *intensity* caused by alterations of excitation rate or external temperature. In the present work we extend such observations to a case in which resonant pumping of  $\text{Yb}^{3+}$  ions in a crystal of  $\text{Er}^{3+}, \text{Yb}^{3+}:\text{CsCdBr}_3$  not only causes the second dopant species ( $\text{Er}^{3+}$ ) to exhibit bistable switching of luminescent intensity but also causes dramatic changes in emission *spectra* as well. We refer to this phenomenon as chromatic switching and report sudden jumps in resonant energy transfer from Yb to Er, high-contrast switching and hysteresis, and evidence for participation of only a few Stark sublevels in the process. We establish the importance of doubly resonant transfer of energy from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  ions in a two-photon sensitization of Er and explain the sudden shift of emission color from yellow to green. Because similar chromodynamics have been reported at room temperature in rare-earth-doped nano-oxides,<sup>6</sup> we expect the present results for a well-characterized crystal to provide a basis for understanding optically controlled chromaticity in more practical luminescent materials.

In earlier work, sudden jumps of luminescent intensities in  $\text{Yb}^{3+}:\text{CsCdBr}_3$  and other heavy metal halides were analyzed in terms of temperature-dependent couplings between populations and other degrees of freedom in the equations of motion for optically driven dopant ion pairs. A couple of theoretical models successfully reproduced experimental findings with regard to hysteresis loop width, height, and position versus intensity and temperature.<sup>2</sup> Site-selective spectroscopy<sup>4</sup> revealed an extremely narrow range of excitation energies ( $\Delta\nu \sim 30$  GHz) within the inhomogeneous  ${}^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(2')$  absorption transition of  $\text{Yb}^{3+}$  that yielded bistability. No bistability was observed at immediately adjacent excitation wavelengths with higher absorption, implying that a thermal nonlinearity was not responsible for this phenomenon. However, subsequent research in Yb-doped glasses at room temperature<sup>7</sup> revealed a more complex situation

that was challenging to reconcile with earlier work, and experiments on non-pair-forming compounds<sup>8</sup> suggested an alternative explanation of bistable luminescence based purely on temperature-dependent absorption. More recently, bistable emission was reported in Cr-doped crystals<sup>9</sup> and analyzed in terms of the nonlinear temperature dependence of the non-radiative decay of  $\text{Cr}^{3+}$  ions. So among the mechanisms for luminescent bistability proposed to date one finds temperature-dependent local field effects, absorption, and nonradiative relaxation. In this Letter we report a new type of luminescent instability that may provide a fresh testing ground for these nonlinear switching mechanisms.

For the present experiments, single crystals of  $\text{Er}, \text{Yb}:\text{CsCdBr}_3$  (1% Yb,  $\sim 0.001\%$  Er) were mounted in an open-cycle cryostat. A simple cold finger failed to maintain an adequate cooling rate for observations of bistability in this material, whereas when the sample was placed directly in the helium gas flow, high-contrast bistability and hysteresis were readily observed. The intensities of infrared and visible upconversion emission from both Yb and Er were recorded versus incident power at constant temperature. The sample temperature was controlled actively at each set point to better than  $\pm 0.1$  K. A programmable attenuator simultaneously adjusted intensity levels and suppressed intensity fluctuations of the  $\text{Ti}:\text{Al}_2\text{O}_3$  laser below  $\pm 0.4\%$ . Dwell times exceeded 6 s per point for scans of 250 points. Tuning in the range 940–980 nm was effected with a three-plate intracavity birefringent filter. Examples of bistable intensity and hysteresis of  $\text{Er}^{3+}$  visible luminescence observed when incident radiation was tuned to the  $10\,602\text{-cm}^{-1}$  absorption of Yb are shown in Fig. 1 for various intensities and temperatures.

The Er emission behavior shown in Fig. 1 was obtained under the same tuning and power conditions as in earlier experiments with singly doped  $\text{Yb}^{3+}:\text{CsCdBr}_3$ . There, intensity switching of Yb emission was observed over a remarkably narrow range on the  ${}^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(2')$  pump transition of  $\text{Yb}^{3+}$  at  $10\,602\text{ cm}^{-1}$ .<sup>4</sup> Here instead, Er luminescence was monitored upon resonant excitation of Yb transitions. No Er luminescence was detected in pure  $\text{Er}^{3+}:\text{CsCdBr}_3$  excited at this wavelength, so it was

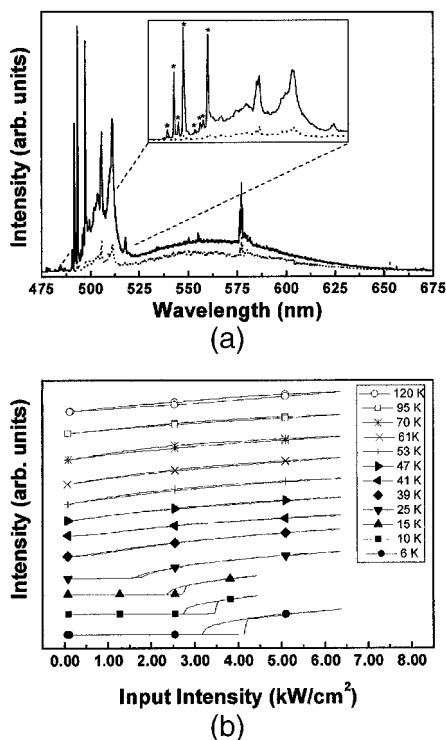


Fig. 1. (a) Emission spectra of Er,Yb:CsCdBr<sub>3</sub> at input powers of 170 mW (dotted curve, magnified by 1.7) and 185 mW (solid curve) with  $\lambda_{\text{ex}} = 10602 \text{ cm}^{-1}$ . Inset, enlarged for 485–520 nm. Asterisks denote Er transitions. Almost all features in the 495–520-nm range are Yb cooperative pair transitions. (b) Luminescence intensity versus input intensity at various temperatures in Er,Yb:CsCdBr<sub>3</sub> ( $\lambda_{\text{ex}} = 10602 \text{ cm}^{-1}$ ).

evident that in the codoped crystal Er emission was the result of energy transfer from Yb to Er. To our knowledge, the data in Fig. 1 therefore constitute the first report of bistable, sensitized luminescence in any system. Er transitions  ${}^4I_{15/2}(1) \rightarrow {}^4I_{11/2}(0')$  and  ${}^4I_{11/2}(4) \rightarrow {}^4F_{7/2}(0')$ , which are resonant within experimental error with Yb relaxation on transition  ${}^2F_{5/2}(0') \rightarrow {}^2F_{7/2}(0)$  ( $\Delta E \sim 3 \text{ cm}^{-1}$  and  $\Delta E \sim 0 \text{ cm}^{-1}$ , respectively) and can account for this process, are shown schematically in Fig. 2. The excitation spectrum of Fig. 2(a) confirms that Er luminescence results from Yb absorption. Excitation on  $(0 \rightarrow 0')$  and  $(0 \rightarrow 1')$  transitions similarly produces Er luminescence but no switching. To determine whether the bistable Er luminescence merely reflects a nonlinearity of strongly pumped Yb ions or is somehow independent in origin, we recorded emission spectra in the neighborhood of the intensity setting at which switching took place. At intensities below the switching threshold the sample appeared yellow-green, whereas above it the emission was predominantly blue-green, as shown in the comparative spectra of Fig. 1(a) at 15 K. On the lower branch, only Yb cooperative emission from 494 to 520 nm appeared, accompanied by a broad, low-intensity feature from 525 to 610 nm. The latter emission was presumed to originate from an impurity-related color center, since it was too broad to be hotband emission from Er, Yb, or a complex of these

two, and it invariably disappeared when the temperature of the sample rose above  $\sim 20 \text{ K}$ , regardless of excitation intensity. On the upper branch, blue-green transitions of Er<sup>3+</sup> suddenly appeared and dominated the spectrum [Fig. 1(a)], exhibiting hysteresis [as indicated in Fig. 1(b)]. Consistent with these spectroscopic changes, the sample changed from yellow to green for a small increase of the incident intensity.

The upconversion mechanism was tested through measurements of temporal decay and the dependence of emission on temperature, input intensity, and wavelength. The temporal decay curves for Yb and Er luminescence that are shown in Fig. 3 are typical of results obtained with low-intensity, pulsed excitation via any of the absorptive transitions of Yb. The curves reveal that Er emission is sustained not just over the short lifetime<sup>10</sup> of the  ${}^4F_{7/2}$  level of Er ( $2.1 \times 10^{-4} \text{ s}$ ) but over a longer interval very close to half the lifetime<sup>11</sup> of isolated Yb ions in the  ${}^2F_{5/2}(0')$  level ( $7.8 \times 10^{-4} \text{ s}$ ). The decay rates for Er emission and Yb cooperative luminescence are both within 5% of that expected for processes depending quadratically on Yb excited-state occupation ( $\tau_{\text{Er}} \sim 4.11 \times 10^{-4} \text{ s}$  and  $\tau_{\text{Yb-Yb}} \sim 3.62 \times 10^{-4} \text{ s}$ ). In Fig. 3, the Er emission intensity (fitted with the solid curve) is found to depend quadratically on input intensity, confirming the two-quantum aspect of the sensitization scheme. This dependence shows that Er emission results from a double Yb  $\rightarrow$  Er transfer as in Fig. 2. We did not attempt to distinguish sensitization by cooperative

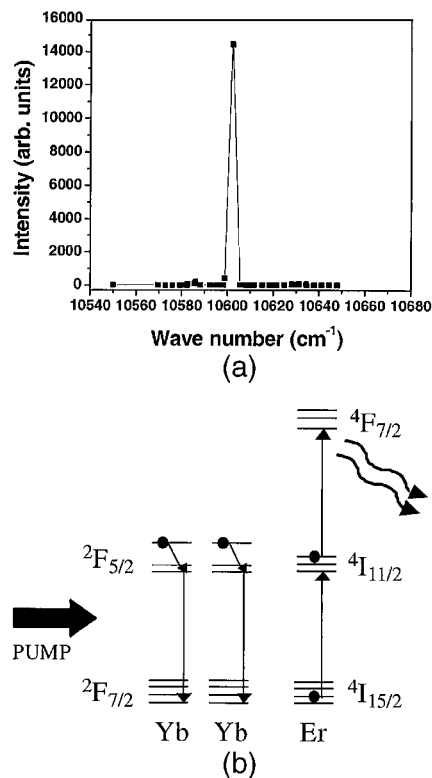


Fig. 2. (a) Excitation spectrum of visible Er luminescence in Er,Yb:CsCdBr<sub>3</sub> and (b) proposed sensitization mechanism via two resonant, thermally activated Yb  $\rightarrow$  Er transfers at  $10122 \text{ cm}^{-1}$ .

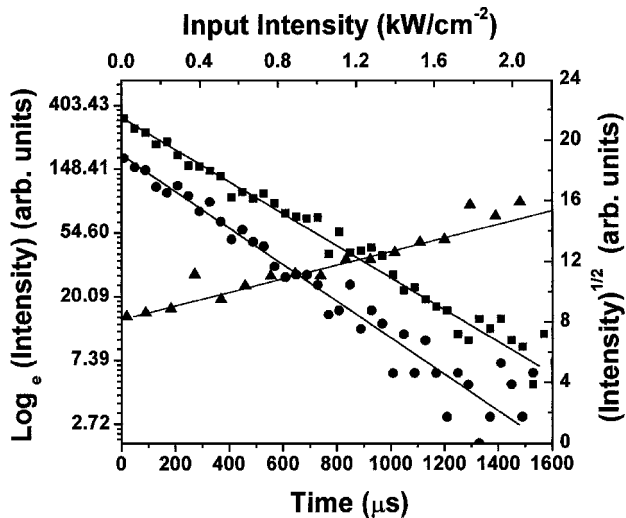


Fig. 3. Temporal decay of Yb (circles) and Er (squares) intensities excited at  $\lambda_{\text{ex}} = 10\,602\text{ cm}^{-1}$ , recorded on pair [ $^2F_{7/2}(i', j') \rightarrow ^2F_{5/2}(i, j)$ ] and single-ion [ $^4F_{7/2}(0') \rightarrow ^4I_{15/2}(2)$ ] transitions at 505.1 and 493.2 nm, respectively, in  $\text{CsCdBr}_3$  (bottom and left-hand scales), together with Er upconversion dependence on input intensity (triangles, top and right-hand scales). Pair indices at 505.1 nm are (1, 0)  $\rightarrow$  (0, 3), (1, 0)  $\rightarrow$  (3, 0), and (2, 0)  $\rightarrow$  (3, 3).

upconversion from two sequential transfers in view of the proximity to resonance.

We considered the possibility of two-photon excitation of Er causing bistability on its own. Direct excitation of Er at  $10\,157\text{ cm}^{-1}$  or  $10\,122\text{ cm}^{-1}$  (transitions [ $^4I_{15/2}(0) \rightarrow ^4I_{11/2}(0')$ ] plus [ $^4I_{11/2}(2) \rightarrow ^4F_{7/2}(0')$ ] or [ $^4I_{15/2}(1) \rightarrow ^4I_{11/2}(0')$ ] plus [ $^4I_{11/2}(3, 4, 5) \rightarrow ^4F_{7/2}(0')$ ], respectively, with net detunings<sup>12</sup> of  $<6\text{ cm}^{-1}$  each) produced intense green Er luminescence by two-photon absorption at liquid helium temperatures, but neither set of transitions yielded bistability. Consequently, the possibility that the observed chromatic switching was somehow mediated purely by nonlinear absorption of Er ions when the incident laser was coincidentally tuned near Yb absorptions was ruled out.<sup>13</sup> However, the double transfer from Yb was evidently very effective, since upconversion intensities via this route were comparable to those achieved with direct, resonant excitation of Er. Note that the two resonant transfers shown in Fig. 2 should be highly temperature sensitive because of the intermediate, endothermic step. The second transfer requires

thermal activation and should respond exponentially to increasing temperature. Consistent with this, we found that only when the Yb  $^2F_{5/2}(2')$  level was pumped, causing heating and intensity switching, did chromatic switching take place. Absorptions on other transitions of Yb led to the same downward, one-photon transitions (individually resonant with Er absorptions within  $\sim 3\text{ cm}^{-1}$ ) but did not yield chromatic switching. Finally, the range over which chromatic switching of Er was observed [Fig. 1(b)] was the same as the range of Yb intensity switching. These findings collectively indicate that the Yb-driven, thermally activated, doubly resonant sensitization process depicted in Fig. 2, rather than any electronic nonlinearity of Er ions alone, accounts for high-contrast, chromatic switching in Er, Yb:CsCdBr<sub>3</sub>.

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