Colloidal $LiYF_4$:Pr nanocrystals downsized to 10 nm – Part 2: spectroscopic properties

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Praseodymium doped fluoride crystals are well-known to be efficient laser media for the visible spectral range [1, 2]. Downsizing such crystals to the nanoscale promises additional degrees of freedom for novel composite photonic devices. However, scattering constitutes the limiting loss factor in such devices so that the size of the nanocrystals should be well below the wavelengths of the involved photons. The first part of our joint contribution is about the challenging synthesis of monodispersed colloidal $LiYF_4$:Pr nanocrystals with low doping concentrations between 0.7 and 1.47 at% . In this second part, we present the results of the extensive spectroscopic characterization of these nanocrystals. The absorption spectra are strongly broadened and exhibit fewer peaks than expected, c.f. Fig 1a). The emission spectra, however, show multiple narrow lines as expected from $LiYF_4$:Pr bulk crystals, see Fig 1b). This behavior contradicts the broadened absorption spectra because both spectra should be reciprocal according to McCumber theory. In addition, we compared the emission spectra of the nanocrystals with their bulk counterparts and observed an additional emission at 595 nm, see inset in Figure 1b). While the other visible emission occurs through spontaneous relaxation from the ^{3}P-manifold of the Pr-ions this emission originates from the subjacent $^1D_2$ energy level. We investigated the spontaneous emission characteristics of the ^{3}P-manifold. It exhibits excited state lifetimes between 15 and 18µs, which is about half of the lifetime of bulk crystals. Simultaneously, the quantum yield of the nanocrystals is below 5%, which seems to contradict their considerably high lifetimes. Surprisingly, the $^1D_2$ lifetime of the nanocrystals agrees very well with the respective lifetimes of the bulk crystals. Altogether, we observed contradicting spectroscopic behavior during the investigation of the nanocrystals. In our contribution, we will present a detailed spectroscopic investigation of these nanocrystals and discuss the role of involved quenching mechanisms to explain these contradictions. We will further present how the optical behavior of the nanocrystals' changes through downsizing to the 10nm range.

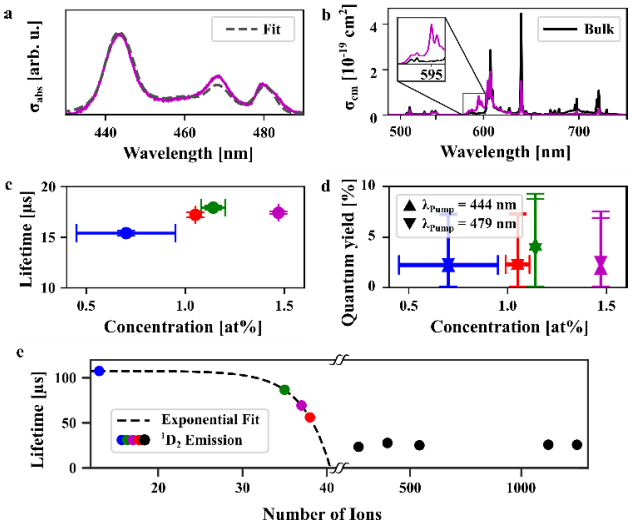

Fig 1: Results of spectroscopic investigations on $LiYF_4$:Pr nanocrystals. a) Absorption spectrum, b) Emission spectrum after excitation at 479 nm, c) Lifetimes of the $^3P_0$ level, d) Quantum yield, e) Lifetimes of the 595 nm transition after excitation at 479 nm.

Literature

[1] A. Richter, E. Heumann, E. Osiac, G. Huber, W. Seelert, A. Diening, "Diode pumping of a continuous-wave Pr^{3+}-doped $LiYF_4$ Laser", Opt. Lett. **29**, 2638 (2004)

[2] A. Richter, E. Heumann, G. Huber, V. Ostroumov, W. Seelert, "Power scaling of semiconductor laser pumped Praseodymium lasers, Opt. Exp. **15**, 5172 (2007)