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Abstract
Upon excitation at 796 nm, Nd³⁺-doped $BaCl_2$ single crystals show several upconverted fluorescence bands in the visible spectral range, with the most intense bands at 530, 590 and 660 nm, in addition to the typical fluorescence bands in the infrared spectral range. The power dependence of the infrared fluorescence and the two-photon upconversion fluorescence intensities as well as the corresponding radiative lifetimes have been investigated. No 'saturation' of the fluorescence intensities was observed upon increasing the excitation power.

1. Introduction

Low phonon energy glasses are desirable hosts for rare-earth (RE) ions such as Er, Ho, Nd, Pr and Tm because they enable emission from RE energy levels that would be quenched in high phonon energy glasses [1].

Upconversion occurs when the active RE ion is optically excited to emit visible light by the sequential absorption of two low energy infrared photons. Of particular importance to the upconversion efficiency is the intermediate energy level lifetime of the RE ion, which depends on the phonon frequency of the host material.

Fluorozirconate glasses (FZ) are characterized by low phonon energies (<580 cm^{-1}) [2], a critical parameter leading to reduced non-radiative losses and increased upconversion efficiencies. However, the phonon frequency is not only dependent on the composition of the matrix the RE ion is incorporated into but also by the size of the matrix; in nanocrystals only low phonon frequencies are found [3]. Upconversion emissions are of particular interest for upconversion lasers, and also for photovoltaic applications where the efficiency of bifacial solar cells could be vastly improved by an upconverting back layer [4]. In order to get enhanced upconversion efficiency we wish to develop a class of fluorozirconate glass ceramics in which the RE is incorporated into the glass as well as in $BaCl_2$ nanocrystals formed therein, after appropriate thermal annealing [5, 6].

Nd³⁺ belongs in the category of trivalent RE ions. The RE ions are characterized by an incompletely filled 4f shell, i.e. 4f³ for Nd³⁺. The 4f orbital lies inside the ion and is shielded from the surroundings by the filled 5s and 5p orbitals. Absorption and emission spectra are characterized by transitions between states within the 4f³ configuration. The influence of the host lattice on the optical transitions is small but essential.

In [7] an enhanced upconverted fluorescence was found in Nd³⁺-doped fluorozirconate glasses which were additionally doped with chlorine ions. During the thermal processing, some of the Nd³⁺ ions enter the nanocrystals leading to additional splitting of the infrared fluorescence spectra and to increased upconverted fluorescence intensities. In order to get a better understanding of the upconversion mechanism in Nd³⁺-doped $BaCl_2$ nanocrystals, an investigation of the processes in the corresponding bulk material is essential.

2. Experimental details

2.1. Samples

Nd³⁺-doped single crystals of orthorhombic $BaCl_2$ were grown at the University of Paderborn crystal growth laboratory using

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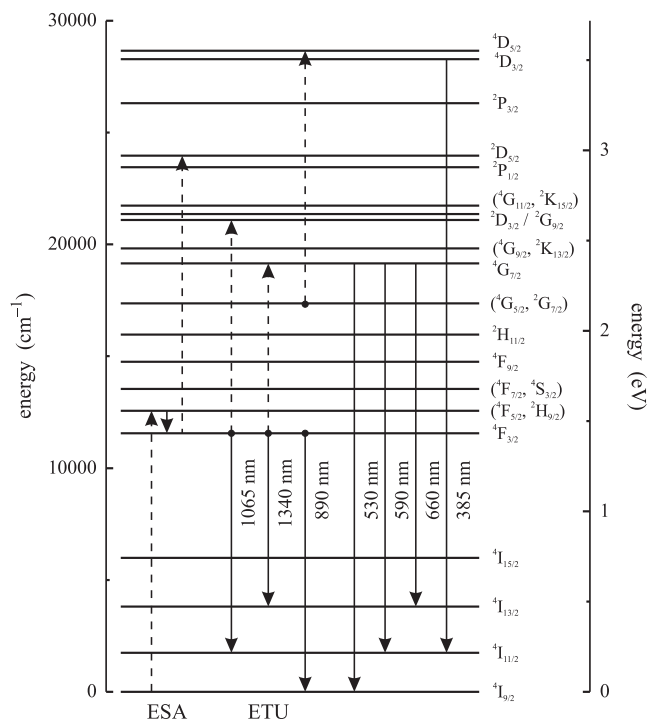[4] Author to whom any correspondence should be addressed.

Figure 1. Energy level diagram of Nd^{3+} in $BaCl_2$: the infrared and upconversion emissions (solid arrows) and possible upconversion routes (dashed arrows) are indicated. The diagram was drawn in analogy to that of Nd^{3+} in FZ glasses [9–11].

Figure 2. Normalized fluorescence spectra of (a) 0.01 mol% and (b) 1 mol% Nd^{3+}-doped $BaCl_2$. The fluorescence was recorded under CW infrared laser excitation at 796 nm. Parts of the fluorescence spectra (dotted curves) are blown up as indicated.

the Bridgman technique. To prepare the samples, 0.01 and 1 mol% of $NdCl_3$, respectively, were added to $BaCl_2$ powder in a quartz glass ampoule with an $SiCl_4$ atmosphere. Prior to crystal growth the $BaCl_2$ powder was dried in vacuum with subsequent melting in the $SiCl_4$ atmosphere to reduce oxygen contamination. The procedure was completed by slow cooling through the cubic–orthorhombic phase transition near 920 °C for $BaCl_2$. The stable phase of $BaCl_2$ at room temperature has the orthorhombic $PbCl_2$ structure [8].

2.2. Energy level diagram of Nd^{3+}

Figure 1 shows the energy level diagram of Nd^{3+} in $BaCl_2$. Possible upconversion routes and assignments of the main infrared and upconversion emissions are shown as well. The diagram was drawn in analogy to that of Nd^{3+} in FZ glasses [9–11].

2.3. Set-up

Fluorescence and fluorescence excitation spectra were recorded using a single-beam spectrometer in which a 0.22 m (Spex 1681) and a 0.55 m (Horiba Jobin Yvon iHR550) monochromator were available for excitation and emission. The excitation was carried out with a xenon lamp, a halogen lamp or a continuous wave (CW) infrared laser diode (Toptica Photonics #LD-0795-0150-2); the fluorescence was detected in the visible spectral range with a cooled photomultiplier (Hamamatsu R943-02) and in the infrared spectral range with a cooled germanium detector (Edinburgh Instruments).
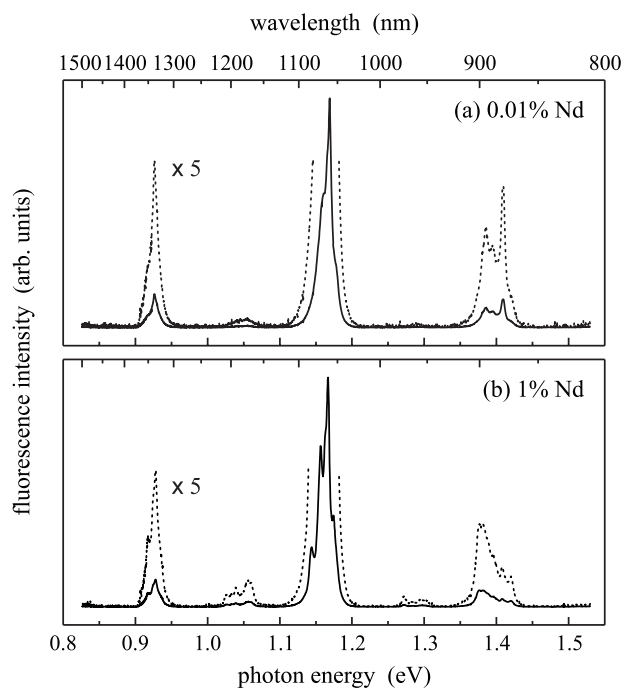
The spectra were not corrected for spectral sensitivity of the experimental set-up. The fluorescence spectra comparing the intensity of the single-photon fluorescence with the upconverted fluorescence were recorded with a high-speed silicon detector (Thorlabs DET110) and corrected for the spectral sensitivity of the detector.

For the fluorescence lifetime measurements, the infrared laser diode was switched on and off with a square wave signal from a generator (Rhode & Schwarz AFS). The fluorescence signal was detected with the photomultiplier and recorded with a digital oscilloscope (Tektronix TDS 1012B). For the power dependence measurements of the fluorescence and upconverted fluorescence intensities a power meter (Thorlabs PM300E) with a silicon sensor (Thorlabs S121B) was used to measure the excitation power.

3. Results

3.1. Infrared fluorescence

Figure 2 shows the infrared fluorescence spectra of 0.01 and 1 mol% Nd^{3+}-doped $BaCl_2$ single crystals. The observed emissions at 890, 1065 and 1340 nm are typical for Nd^{3+} and can be assigned to $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ transitions, respectively. The blown-up spectrum of the 1 mol% sample clearly shows additional emission bands at approximately 960 and 1190 nm; these line groups are barely observable in the 0.01 mol% doped sample. They are probably caused by $^4F_{5/2}$ to $^4I_{11/2}$ and $^4F_{5/2}$ to $^4I_{13/2}$ transitions, respectively. All infrared Nd^{3+} emissions are more or less split by the crystal field [12].
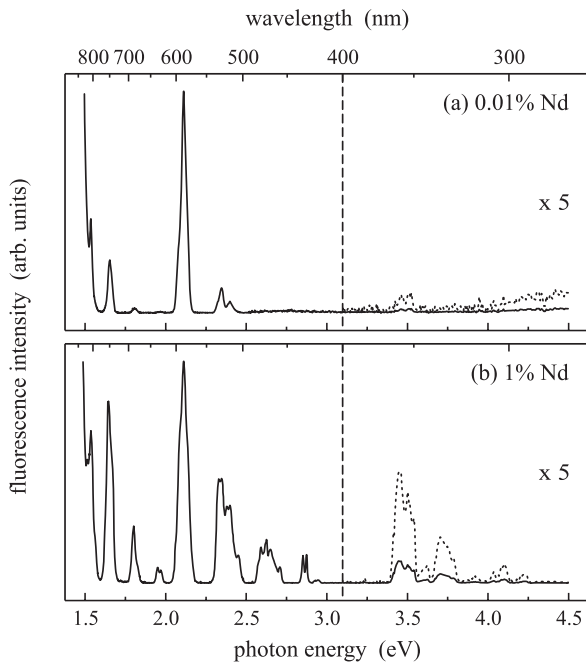
Figure 3. Normalized excitation spectra of (a) 0.01 mol% and (b) 1 mol% Nd^{3+}-doped $BaCl_2$. The emission was detected at 880 nm. All transitions start from the $^4I_{9/2}$ ground level. Parts of the excitation spectra (dotted curves) are blown up as indicated.

The corresponding excitation spectra (figure 3), recorded at 880 nm for the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition, depend clearly on the Nd^{3+} concentration. The relative intensity ratio of the excitation bands of the 1 mol% sample differs significantly from that of the 0.01 mol% sample: the spectrum of the 1 mol% doped sample shows numerous excitation bands over the whole visible and ultraviolet spectral range. In contrast, the excitation spectrum of the 0.01 mol% sample is relatively simple, with one dominating excitation band at 590 nm which can be assigned to $^4I_{9/2} \rightarrow ({}^4G_{5/2}, {}^2G_{7/2})$ transitions. Note that, for wavelengths longer than approximately 750 nm, scattered excitation light starts to enter the spectra.

For upconversion processes, the lifetime of the intermediate energy levels is of particular importance. Thus, lifetime measurements of the $^4F_{3/2}$ level have been performed at a wavelength of 880 nm (figure 4) which corresponds to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. These measurements yielded different lifetimes for different Nd^{3+}-doping levels: the measured lifetime of the 0.01 mol% sample is (280 ± 1) μs, while the lifetime for the 1 mol% doping level is (49 ± 1) μs. This result was expected since energy transfer processes between neighbouring Nd^{3+} ions lead to a shorter lifetime for the sample with the higher Nd^{3+} concentration.

3.2. Upconverted fluorescence

Upconversion in the visible range was observed at room temperature under CW infrared laser excitation at 796 nm. Figure 5 shows the upconverted fluorescence spectrum for 0.01 and 1 mol% Nd-doped $BaCl_2$ in the 340–750 nm spectral range. Note that, at about 750 nm, scattered excitation light
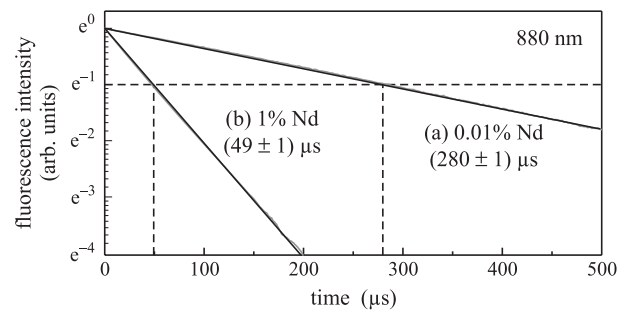

Figure 4. Fluorescence decay of Nd^{3+} in $BaCl_2$ doped with (a) 0.01 mol% and (b) 1 mol% $NdCl_3$. The fluorescence was detected at 880 nm and excited at 796 nm with a pulsed infrared laser diode.
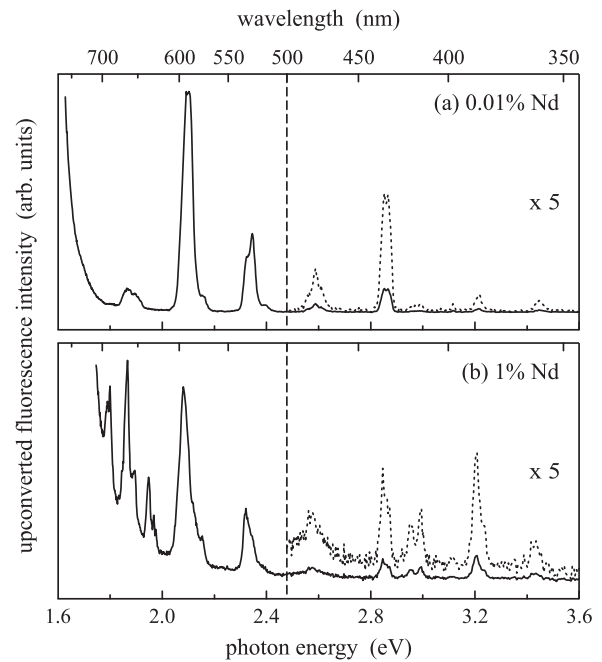

Figure 5. Normalized upconverted fluorescence spectra of (a) 0.01 mol% and (b) 1 mol% Nd^{3+}-doped $BaCl_2$ under CW infrared laser excitation at 796 nm. Parts of the upconverted fluorescence spectra (dotted curves) are blown up as indicated.

starts to enter the spectrum. The most intense emission bands are located in the green (530 nm), yellow (590 nm) and red (660 nm) region. They arise from the ^4G multiplets [10]. The ^4G multiplets, comprised of the $^4G_{9/2}$, $^4G_{7/2}$ and $^4G_{5/2}$ states, produce overlapping emission bands and are therefore the strongest in the spectrum. The ^4G multiplets are energetically accessible with two 796 nm photons (figure 1). The weak bands in the blue spectral range originate from the $^2P_{1/2}$ excited state. The two bands at 635 and 690 nm found in the 1 mol% Nd-doped sample are tentatively assigned to transitions from the excited states $^2H_{11/2}$ and $^4F_{9/2}$, respectively, to the $^4I_{9/2}$ ground state.

The upconverted fluorescence bands at approximately 360, 385 and 415 nm are accessible with three photons (figure 1). The highest energy band at 360 nm arises from a $^4D_{3/2}$ to $^4I_{9/2}$ transition; the 385 nm emission is from the same excited state, but to the $^4I_{11/2}$ ground state. The 415 nm
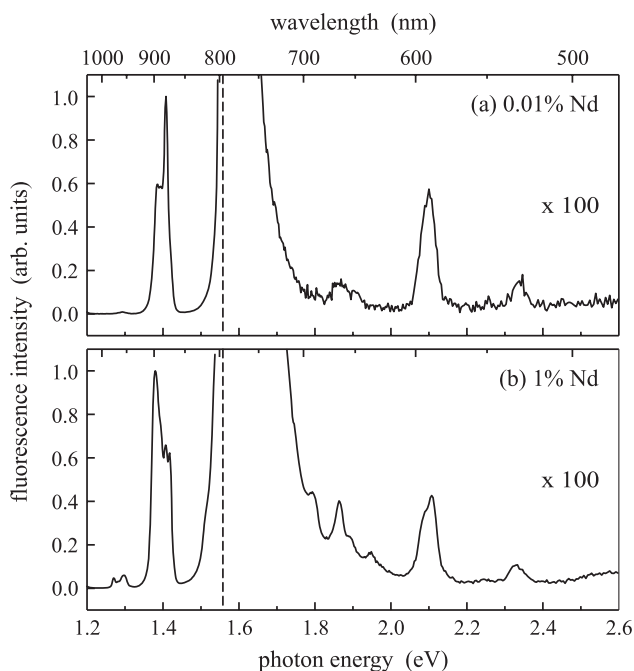
Figure 6. Fluorescence spectra of (a) 0.01 mol% and (b) 1 mol% Nd^{3+}-doped $BaCl_2$ under CW infrared laser excitation at 796 nm (dashed line). The spectra are normalized to the $^4F_{3/2} \rightarrow \, ^4I_{9/2}$ transition at 890 nm, while the upconverted fluorescence parts ($\lambda < 800$ nm) are blown up as indicated.

Figure 7. Upconverted fluorescence decay of Nd^{3+} in $BaCl_2$ doped with (a) 0.01 mol% and (b) 1 mol% $NdCl_3$. The fluorescence was detected at 590 nm and excited at 796 nm with a pulsed infrared laser diode.

Figure 8. Power dependence (on a double-logarithmic scale) of the fluorescence and upconverted fluorescence intensity in (a) 0.01 mol% and (b) 1 mol% Nd^{3+}-doped $BaCl_2$, recorded at the wavelengths indicated under CW laser diode excitation at 796 nm.

emission can be attributed to a transition from the $^4D_{3/2}$ excited state to the $^4I_{13/2}$ ground state.

Figure 6 shows a direct comparison between the single-photon fluorescence and the upconverted fluorescence. The 890 nm fluorescence intensity arising from the $^4F_{3/2} \rightarrow \, ^4I_{9/2}$ transition is approximately 200 times higher for both doping levels than the intensity of the strongest two-photon upconverted fluorescence at 590 nm.

To complete the picture on energy level lifetime we also performed lifetime measurements on the two-photon upconverted fluorescence. Again, the lifetime measurements did not allow analysis of the temporal behaviour but give a rough idea how the system behaves. The Nd^{3+}-doped $BaCl_2$ single crystals were excited with a CW laser diode operating at 796 nm and the upconverted fluorescence decay was detected at 590 nm (figure 7). As expected and already observed for the infrared fluorescence lifetime, the measurements yielded different lifetimes for different Nd^{3+}-doping levels: the lifetime of the two-photon upconverted fluorescence at 590 nm is (19 ± 0.5) μs and (9.5 ± 0.5) μs for the 0.01 and 1 mol% sample, respectively.

Figure 8 shows the dependence of the emission intensity on the 796 nm excitation power for the infrared fluorescence band at 880 nm and the most intense upconverted fluorescence band at 590 nm. The power dependence was measured by inserting different optical filters (e.g. neutral density filters) in the pump beam. Fluorescence spectra were recorded over several orders of magnitude of excitation power, e.g. from approximately 130 mW (maximal laser diode output power) down to a few μW. For the emission at 880 nm, the slope is
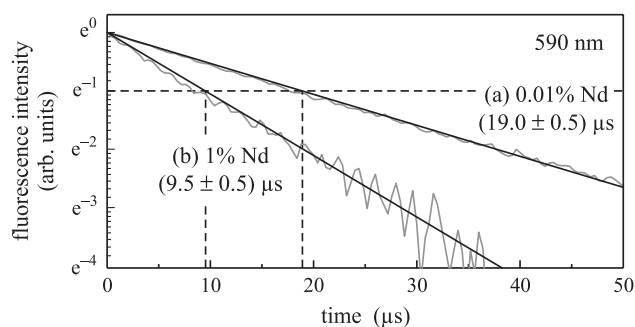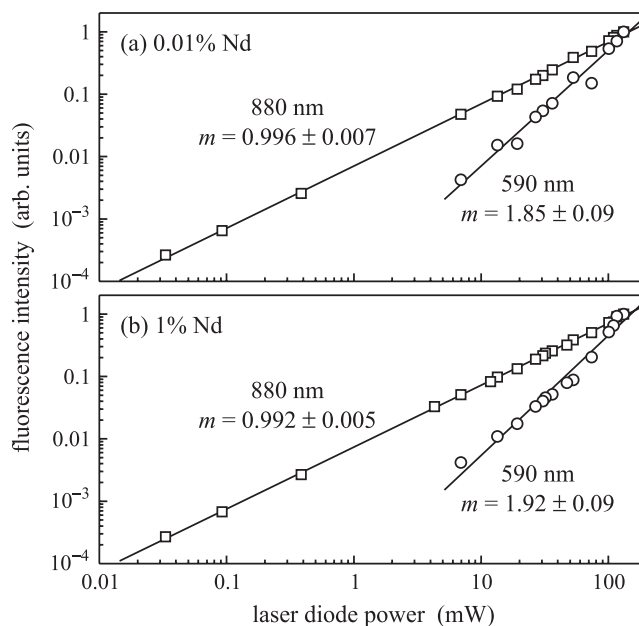
0.996 and 0.992 for a Nd^{3+}-doping level of 0.01 and 1 mol%, respectively, e.g. an almost perfect linear dependence on the excitation power without any saturation effects. Upconversion spectra were recorded for excitation powers in the range from 130 down to 7 mW. For the upconverted fluorescence band at 590 nm, the slope is 1.85 and 1.92 for 0.01 and 1 mol%, respectively.

4. Discussion

Infrared fluorescence and upconverted fluorescence spectroscopy show that Nd^{3+} can be incorporated into $BaCl_2$ single crystals and elucidates therein its characteristic optical properties, in particular, an intense upconversion effect upon excitation with a laser diode operating at 796 nm.

The upconversion spectrum of figure 5 suggests that the most important excited states for upconversion fluorescence

are $^4D_{3/2}$, $^2P_{1/2}$ and the ^4G multiplets. The 796 nm photons are strongly absorbed and excite ions into the $^4F_{5/2}$ level from which they relax non-radiatively to the relatively long lived $^4F_{3/2}$ level. The ^4G multiplets can be populated by excited state absorption (ESA) and/or energy transfer upconversion (ETU). In the ESA process a second 796 nm photon raises the ion from the $^4F_{3/2}$ to $^2D_{5/2}$, for which there is a good energy match for 796 nm photons; this would be followed by non-radiative relaxation into the $^2P_{1/2}$ level and into the various ^4G states. In the ETU process, each ion is separately excited into the $^4F_{3/2}$ state. From that level de-excitation of one ion can result in excitation of the other. The range of this can be sufficiently large that this transfer mechanism can be more effective than ESA. The Nd level scheme provides a number of such possibilities. Close energy matching is obtained with excitation from $^4F_{3/2}$ to $^4G_{9/2}$ accompanied by de-excitation to $^4I_{11/2}$ and also with excitation to $^4G_{7/2}$ and de-excitation to $^4I_{13/2}$.

Excitation to the $^4D_{3/2}$ state clearly requires the energy of three 796 nm photons. However, it is difficult to identify the excitation mechanism without more detailed information on the energy levels beyond those depicted in figure 1. An ESA process could occur to these higher levels from one of the ^4G levels, which are known to be significantly populated by two-photon excitation followed by non-radiative relaxation. Alternatively an energy transfer mechanism could operate as shown in figure 1 with an ion in a $^4G_{5/2}$ state interacting with a neighbour in a $^4F_{3/2}$ state, resulting in excitation of one ion to $^4D_{5/2}$ accompanied by de-excitation to $^4I_{9/2}$. The $^4D_{5/2}$ state would rapidly relax to populate $^4D_{3/2}$, giving rise to the observed emissions.

In principle, for low excitation powers one would expect a quadratic dependence of the two-photon upconverted fluorescence at 590 nm on the excitation power [13]. The power dependence shown in figure 8 yields, however, exponents of 1.85 and 1.92 for 0.01 and 1 mol%, respectively. This experimentally observed decrease is determined by the competition between linear decay and upconversion processes for the depletion of the intermediate excited states. The shorter fluorescence lifetime, i.e. the faster depletion of the $^4F_{3/2}$ state in the case of the 1 mol% doped sample, leads to a larger slope (on a double-logarithmic scale) in the upconverted intensity versus excitation power dependence. The intensity of upconverted fluorescence that is excited by the sequential absorption of n photons has a dependence on absorbed excitation power $P_{\text{exc.}}$, which may range from $P_{\text{exc.}}^n$ in the limit of infinitely small upconversion rates down to $P_{\text{exc.}}^1$ for the upper state and less than $P_{\text{exc.}}^1$ for the intermediate states in the limit of infinitely large upconversion rates [13]. The fact that the deviation from $n = 2$ is small in the case of 0.01 and 1 mol% Nd^{3+}-doped $BaCl_2$ indicates that we are in these systems far away from the point where 'saturation' effects will play a role.

Acknowledgments

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