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Infrared-to-visible upconversion luminescence in neodymium-doped bismuth–borate glass

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The upconversion luminescence in Nd^{3+}-doped bismuth–borate glass, excited by 0.8 μm light, was studied in the visible spectral region. Four distinct emission bands were found. From their kinetics, two mechanisms can be shown to be responsible for all four lines: energy-transfer upconversion, slightly dominating, and excited state absorption.

1 Introduction Bismuth–borate glasses have recently attracted considerable interest as host materials for laser-active ions like Er^{3+} [1, 2] or Nd^{3+} [3, 4]. Glasses of this type exhibit a high refractive index, widely adjustable in the range from 1.8 to 2.5 by the appropriate glass composition [5]. Detailed absorption and emission spectra for different glass compositions [2, 3] and different dopant concentrations [1, 4] have been measured; based on a Judd–Ofelt analysis [6, 7] of these absorption spectra the relevant spectroscopic parameters, like e.g. the radiative lifetime of excited states or the stimulated emission cross section, are obtained.

Very few, however, is known about upconversion luminescence in doped bismuth–borate glasses. This type of emission could be demonstrated in the past for Er^{3+}-doping [2]. For Nd^{3+}-doping it was investigated only for other hosts like germanate [8, 9], oxyfluoride [10, 11], fluoroindate [12] or chalcohalide glasses [13]. Knowledge about the upconversion processes is important due to various reasons. On the one hand, upconversion emission is the basis for potential applications in the visible spectral region like frequency converting phosphors. On the other hand, at higher excitation, upconversion processes may deplete excited states thus decreasing the radiative efficiency of the corresponding one-electron transitions, important, e.g., for laser action.

In this work, we present first results on upconversion luminescence in Nd^{3+}-doped bismuth–borate glass. Using 0.8 μm laser excitation, emission in the visible spectral region is generated. From an accurate evaluation of the decay kinetics, the dominant upconversion mechanisms are identified.

2 Experimental Neodymium-doped bismuth–borate glass samples $(Nd_2O_3)_y((Bi_2O_3)_x(B_2O_3)_{1-x})_{1-y}$ with the composition $x = 0.5$, $y = 0.025$ were fabricated from oxide melts with the same composition. The melts were thoroughly homogenized at a temperature of ≈1000 K in a platinum crucible and then cooled down to room temperature at a rate of 100 K per hour.

The luminescence measurements were performed in reflection geometry on platelet samples cut and polished. For the upconversion spectra a 0.8 μm laser diode was used for excitation, a photomultiplier for detection. The necessary spectral resolution und the suppression of normal infrared luminescence was achieved using a Jobin–Yvon TRIAX 180 spectrometer. To render the dependence on excitation intensity, the laser intensity could be varied; to render time dependences, the laser was modulated by an appropriate square wave signal. For the measurement of the lifetime of the $^4G_{7/2}$ level, a pulsed frequency-doubled Nd:YAG laser at 0.53 μm with a pulse duration of 10 ns was used.

3 Results and discussion The upconversion luminescence spectrum measured at room temperature is shown in Fig. 1. It consists of four broad emission bands – centered at 0.44, 0.54, 0.61, 0.66 μm. The corresponding tran-

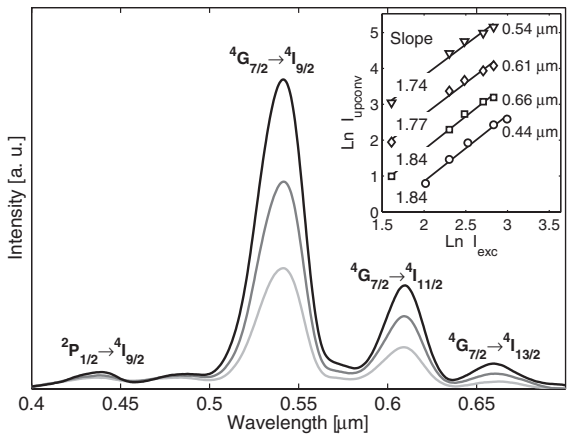

Figure 1 Upconversion spectrum of Nd^{3+}-doped bismuth–borate glass excited by 0.8 μm laser light. The inset shows the pump power dependence of the line intensities.

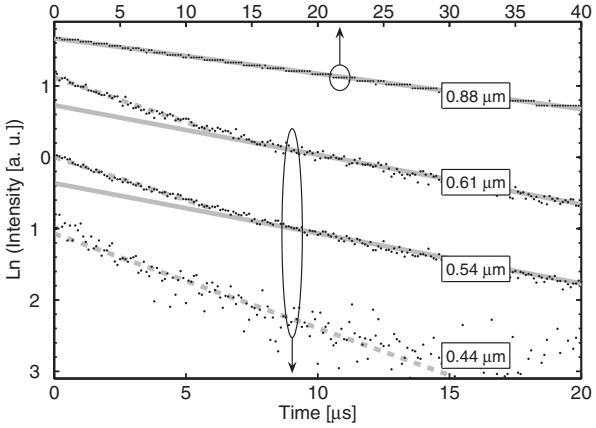

Figure 3 Decay curves after switch-off of the 0.8 μm pump laser for the 0.88 μm fluorescence and the upconversion emission bands indicated (the band at 0.66 μm, omitted here, shows identical behavior as the bands at 0.54 and 0.61 μm). Dots denote measured data, solid and dashed gray lines are mono-exponential fits in the respective time ranges.

sitions are indicated (see energy level diagram Fig. 2). The form and the intensity ratios of the bands do not depend on the excitation intensity, this is confirmed by the intensity dependence on pump power shown in the inset. The double-logarithmic plots reveal nearly identical slopes near 1.8 which indicate that for each of the upconversion transitions a two-photon process should be responsible.

According to the results known from other host materials mainly two mechanisms for upconversion must be considered, energy-transfer upconversion (ETU) and excited-state absorption (ESA). These mechanisms are sketched in the energy-level diagram of Nd^{3+} shown in Fig. 2 (energies according to Ref. [14]).

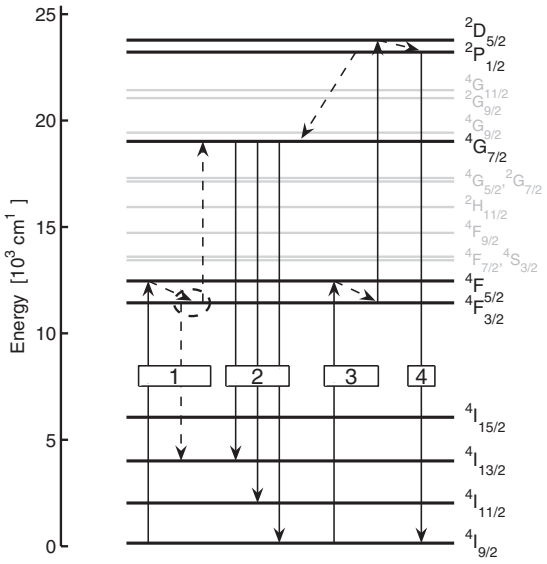

Figure 2 Energy-level diagram of Nd^{3+} in glass. Solid arrows denote radiative transitions, dashed arrows nonradiative ones. 2 and 4 indicate the transitions responsible for the four upconversion emission bands, 1 describes ground-state absorption of two photons followed by energy-transfer upconversion, 3 describes ground-state absorption followed by excited-state absorption.

To distinguish between the different upconversion mechanisms, the kinetics of the different emission bands after a fast switch-off of the exciting laser was investigated. The results are summarized in Fig. 3. The time decays of three relevant upconversion bands are plotted, and in addition – as a measure for the occupation of the $^4F_{3/2}$ level – the time decay of the 0.88 μm infrared fluorescence, arising from the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. From the latter, strictly mono-exponential decay, a total lifetime of 41 μs for this level is derived.

The upconversion bands arising from the $^4G_{7/2}$ level (0.54, 0.61, and 0.66 μm) show two distinct time constants, identical for each of these bands. The slower one, approximately 14 μs, can be related to ETU from the $^4F_{3/2}$ level. This ETU rate should be proportional to the respective occupation, N_1, times a transition rate, W, which is a function of the mean distance, $R \propto N_1^{-1/3}$, to neighbouring excited sites. W may be expanded into a series in R with the first element $\propto R^{-n}$. For dipole–dipole interaction involved, $n = 6$ [15]. Putting this together, we arrive at an expected time constant for the ETU emission of 13.7 μs, which conforms excellently with the experimental value of 14 μs.

The faster decay at short times and for the 0.44 μm band, determined to be approximately 8 μs, however, cannot be related to ETU in a similar way, as there is no corresponding behavior in the $^4F_{3/2}$ population decay. It therefore must be due to the second mechanism, ESA from the $^4F_{3/2}$ level populating the $^2P_{1/2}$ level during the laser-on time. This population decays quickly after the laser's switch-off causing both, 0.44 μm fluorescence and a transient population of the $^4G_{7/2}$ level, the upper level for the other three upconversion bands. Thus all upconversion bands just after laser switch-off reflect the total lifetime of the $^2P_{1/2}$ level.

To be sure that the $^4G_{7/2}$ population has only transient character, we determined its lifetime directly by pumping it

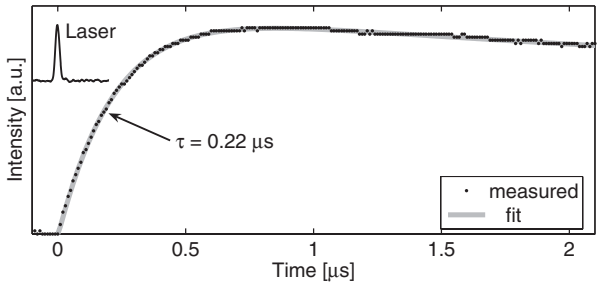

Figure 4 Onset of the 0.88 µm fluorescence in Nd^{3+}-doped bismuth–borate glass after pumping with a short 0.53 µm laser pulse.

with a short 0.53 µm laser pulse and measuring the onset of the 0.88 µm fluorescence [16]. The result is shown in Fig. 4, a fit to the measured data yields a lifetime of 0.22 µs, short compared to all other times.

During laser-on time (1 ms, large compared to all other time constants) steady-state occupations of all levels are reached, which then decay with their respective time constants. Thus an extrapolation of the measured decay curves to the laser switch-off time allows to determine the contributions of the two mechanism to the total upconversion emission during pumping. Energy-transfer upconversion turns out to be dominating with an approximate ratio ETU : ESA = 2 : 1 for the three bands arising from the $^4G_{7/2}$ level.

4 Conclusion Upconversion luminescence in Nd^{3+}-doped bismuth–borate glass, excited by 0.8 µm light, was demonstrated to cause four distinct emission bands in the visible spectral region. An accurate evaluation of their decay kinetics allowed to determine the relevant lifetimes of the levels involved and to identify the mechanisms responsible for upconversion in this material. For the 0.4 µm band, excited-state absorption is responsible. For the other three bands, it could be shown that energy-transfer upconversion is the dominating mechanism – about twice as probable as excited-state absorption during continuous-wave pumping. For pulsed applications, energy-transfer upconversion might be a hampering factor, as it is still present after pump-light switch-off.

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