Violet–blue emissions due to frequency up-conversion in Nd^{3+}-doped fluoroindate glasses

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Abstract

We report the observation of intense frequency up-conversion in Nd^{3+}-doped fluoroindate glasses pumped by the second harmonic of a cw mode-locked Nd:YAG laser. Mechanisms for generating the observed emissions are discussed.

Keywords: Rare-earth; Blue–violet emission; Fluoroindate glasses

1. Introduction

The study of rare-earth (RE)-doped fluoride glasses has been a subject of increasing interest because of their successful application as optical amplifiers, frequency up-converters, sensors and lasers. One of the reasons for this success is that the phonon energy in these materials (typically $\leqslant 510\,cm^{-1}$) is smaller than for silicate glasses ($E_{ph} \approx 1000\,cm^{-1}$), which reduces non-radiative decay rates, in general.

Among the new glasses available the fluoroindate glasses are promising materials because of their transparency window (250 nm to 8 μm), small sensitivity to atmospheric moisture and capability of incorporating large concentrations of RE ions. Recently, we have shown that these materials present large efficiency as light frequency up-converters from the infrared to visible [1], from infrared to ultraviolet [2], and from orange to blue [3] using Er^{3+}, Nd^{3+} and Pr^{3+} as the doping ions, respectively.

2. Experimental results and discussion

We report the observation of intense violet and blue emissions from a Nd^{3+}-doped fluoroindate glass sample pumped with the second harmonic of a mode-locked Nd:YAG laser at 532 nm (76 MHz pulse repetition rate, and ≈ 80 ps pulse duration). The sample composition is (mol%): $36InF_3$–$20ZnF_2$–$16BaF_2$–$20SrF_2$–$2GdF_2$–$2NaF$–$1GaF_3$–$3NdF_3$, prepared following the procedure described in Refs. [1, 3]. The observed up-converted fluorescence spectrum is illustrated in Fig. 1, which

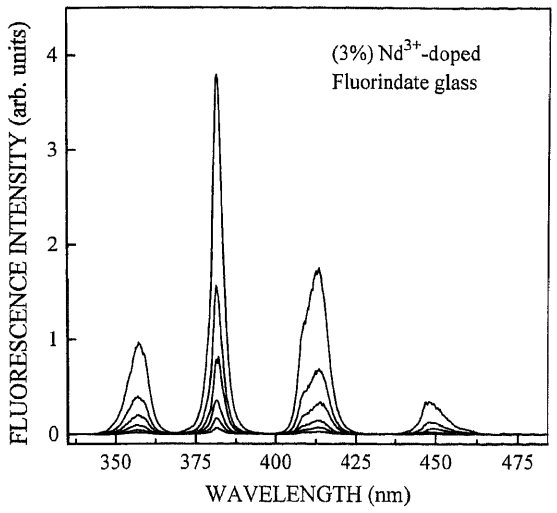

Fig. 1. Fluorescence spectra for Nd^{3+}-doped (3 mol%) fluoroindate glass pumped at 532 nm. The pump powers are: 180, 290, 450, 740, 1080 mW.

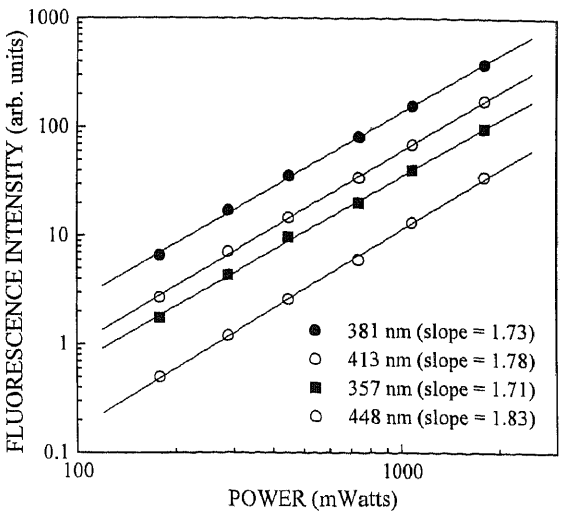

Fig. 2. Power dependence of the fluorescence. The slope for all emissions is close to 2 indicating that two photons are involved in the process.

corresponds to transitions $^4D_{3/2} \rightarrow {}^4I_{9/2}$ ($\approx$357 nm); $^4D_{3/2} \rightarrow {}^4I_{11/2}$ and $^2P_{3/2} \rightarrow {}^4I_{9/2}$ ($\approx$381 nm); $^4D_{3/2} \rightarrow {}^4I_{13/2}$ and $^2P_{3/2} \rightarrow {}^4I_{15/2}$ ($\approx$413 nm); $^4D_{3/2} \rightarrow {}^4I_{15/2}$ and $^2P_{3/2} \rightarrow {}^4I_{13/2}$ ($\approx$448 nm).

The violet–blue emissions are clearly visible to the naked eye for the average pump powers used (180–1800 mW). The behavior of the fluorescence signal with the laser pump power was observed to be quadratic indicating that two photons participate in the process (Fig. 2). The excitation mechanisms which originate the violet–blue emissions are excited state absorption (ESA) and energy transfer (ET) among pairs of Nd^{3+} ions. In the first case, the most probable pathway is: $^4I_{9/2} + \hbar\omega \rightarrow {}^4G_{7/2} \rightarrow$ (non-radiative relaxation) $\rightarrow {}^4F_{3/2} + \hbar\omega \rightarrow {}^4D_{7/2} +$ (non-radiative relaxation) $\rightarrow {}^4D_{3/2}$, as previously observed by Fan and Byer in Nd:YLF [6]. In the case of energy transfer the pathway is less clear but a strong possibility is: $^4I_{9/2} + {}^4I_{9/2} + 2\hbar\omega \rightarrow {}^4G_{7/2} + {}^4G_{7/2} \rightarrow$ (non-radiative relaxation) $\rightarrow {}^4F_{3/2} + {}^4G_{5/2} \rightarrow$ (energy transfer) $\rightarrow {}^4I_{9/2} + {}^4D_{3/2}$. A similar process has been previously identified in these samples, using a pulsed dye laser to resonantly pump the Nd^{3+} ions at the transition $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$ [7]. In this case the analysis of the temporal behavior confirms that the dominant mechanism is ET.

The high efficiency of the ultraviolet up-conversion mechanism leads to the question of the possibility of operation of an up-converted laser emitting at 413 nm, corresponding to the transitions $^4D_{3/2} \rightarrow {}^4I_{13/2}$ and $^2P_{3/2} \rightarrow {}^4I_{15/2}$. Temporal decay measurements of the level $^4F_{3/2}$ at low concentrations of Nd^{3+} (0.5 mol%) show that this level has relatively long lifetime (950 μs), compared to Nd:BaY_2F_8 [5]. To investigate the amplified spontaneous emission at 413 the line width behavior of this fluorescence has been measured as a function of the pump power. For the range of powers and sample lengths ($\approx$12 nm) employed, however, there are no observable changes, but this is not enough to exclude the possibility of obtaining gain in our samples. Further experiments are underway.

Acknowledgements

This work was supported by the Brazilian Agencies CNPq. CAPES, FINEP, and FACEPE. We also thank Blenio J.P. da Silva for polishing the samples.

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