

Frequency upconversion in Nd³⁺-doped fluoroindate glass

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Abstract

We report the observation of frequency upconversion in fluoroindate glasses with the following compositions: (mol%) (39 - x)InF₃-20ZnF₂-20SrF₂-16BaF₂-2GdF₃-2NaF-1GaF₃-xNdF₃ (x = 0.05, 0.1, 0.5, 1, 2, 3). The excitation source was a dye laser in resonance with the ⁴I_{9/2} → (²G_{5/2}, ²G_{7/2}) transition of the Nd³⁺ ions. The upconverted fluorescence spectra show emissions from ~ 350 to ~ 450 nm, corresponding to transitions ⁴D_{3/2} → ⁴I_{9/2}; ⁴D_{3/2} → ⁴I_{11/2}; ²P_{3/2} → ⁴I_{9/2}; ⁴D_{3/2} → ⁴I_{13/2}; ²P_{3/2} → ⁴I_{11/2}; ⁴D_{3/2} → ⁴I_{15/2}; and ²P_{3/2} → ⁴I_{13/2}. The dependence of the fluorescence signals on the laser intensity indicates that two laser photons participate in the process. The temporal behavior of the signal indicates that energy transfer among the Nd³⁺ ions is the main mechanism which contributes to upconversion at 354 and 382 nm.

1. Introduction

Rare-earth (RE) doped glasses capable of efficient frequency upconversion, have received great attention due to the possibilities of using these materials to achieve solid state lasers operating in the blue-green region, as well as for developing infrared display devices and sensors. Accordingly, in the past years, extensive investigations have been directed towards the characterization and use of RE doped heavy-metal fluoride glasses.

The fluorozirconate glass ZBLAN is the most important representative of this class of materials [1]. So far, upconversion fluorescence has been observed in ZBLAN (bulk and fiber) doped with RE trivalent ions [2]. However, difficulties such as small mechan-

ical and chemical stabilities, along with the small intensity damage threshold are common problems when using ZBLAN fibers.

Recently, a new interesting InF₃-based glass was reported [3,4]. This fluoroindate glass is *chemically* and *mechanically more stable* than ZBLAN, and can also be fabricated into various shapes, such as optical fibers and planar waveguides [5]. From the basic point of view, one of the major interests of fluoroindate glasses lies in their small multiphonon absorption, which enlarges the infrared transmission window up to ~ 8 μm. Furthermore, because of the small multiphonon emission rate, the nonradiative relaxation between close levels is reduced and some RE fluorescence transitions, which are not observed in ZBLAN glass, can be active in this new host. Altogether, these characteristics make the fluoroindate glasses, a promising material for a variety of photonic applications and as a host for RE ions.

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Therefore, we report here an investigation of up-conversion fluorescence in Nd^{3+} -doped fluoroindate glass. The Nd^{3+} concentration dependence of the upconverted emissions in the violet-blue region (300–450 nm) and their related dynamical characteristics have been investigated.

2. Experimental

The samples were prepared following the procedure given in Ref. [3,4] and have the following compositions: (mol%) $(39 - x) \text{InF}_3 - 20\text{ZnF}_2 - 20\text{SrF}_2 - 16\text{BaF}_2 - 2\text{GdF}_3 - 2\text{NaF} - 1\text{GaF}_3 - x\text{NdF}_3$ ($x = 0.05; 0.1; 0.5; 1; 2; 3$). The polished samples are transparent from ~ 250 nm to $\sim 8 \mu\text{m}$ and are resistant to atmospheric moisture reactions. Previous optical studies with this material doped with Nd^{3+} [6], Pr^{3+} [7], and Er^{3+} [8] have been reported recently.

Optical absorption measurements in the 200–800 nm range were made with a double-beam spectrophotometer. For all measurements the spectral resolution was much larger than the observed linewidths.

For the excitation of the upconverted fluorescence spectra, a dye laser, consisting of an oscillator plus one stage of amplification, transversely pumped by the second harmonic of a pulsed NdYAG laser, delivering pulses of ~ 10 ns and ~ 20 kW peak power, was used. The oscillator was operated with a grazing incidence grating, tunable in the range 560 to 600 nm, with a linewidth of $\leq 0.5 \text{ cm}^{-1}$. The linearly polarized excitation beam was focused into the sample with a 10 cm focal length lens and the upconverted fluorescence was collected along a direction perpendicular to the incident beam. The signal spectrum was analyzed with a 0.25 m spectrometer, equipped with a photomultiplier and a boxcar. The temporal behavior of the upconverted fluorescence was measured using a fast digital oscilloscope. All measurements were made at room temperature.

3. Results

Fig. 1 shows the absorption spectra in the 200 to 800 nm range obtained for one pure and one of the Nd^{3+} -doped samples studied. The broad features with several Angstroms bandwidth in the doped sample can be identified with transitions from the ground

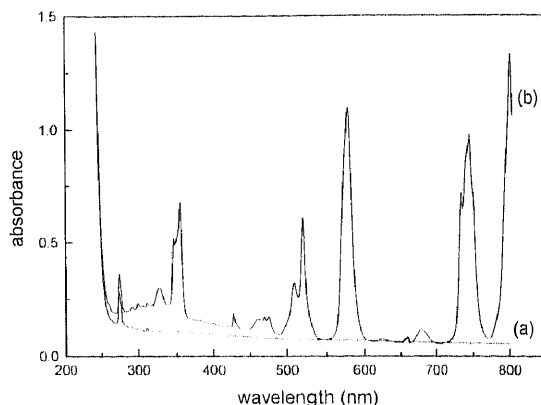


Fig. 1. Absorption spectra of fluoroindate glass: (a) pure matrix; thickness: 2.75 mm; (b) sample with $x = 2$; thickness: 3.37 mm.

state ($^4I_{9/2}$) to the excited states of the Nd^{3+} ion. The positions of the Nd^{3+} bands shown in Fig. 1 are tabulated in Table 1. The feature observed at 274 nm and the smaller one at 312 nm are due to electronic transitions in the Gd^{3+} ions present in the glass matrix. The spectra obtained for the other samples are similar, except for the band intensities, which increase with the Nd^{3+} concentration. For all transitions observed the linewidths are inhomogeneously

Table 1

Energy, in cm^{-1} , of the Nd^{3+} absorption bands (sample with $x = 2$) and the corresponding electronic levels reached from the ground state

Level	Energy (cm^{-1})
$^2D_{5/2}$	34364
$^2D_{3/2}$	33445
$^4D_{7/2}$	30395
$^4D_{15/2}$	29326
$^4D_{1/2}$	28818
$^4D_{3/2}$	28249
$^2P_{3/2}$	26316
$^2P_{1/2}, ^2D_{5/2}$	23416
$^4G_{11/2}$	21787
$^2D_{3/2}$	21322
$^4G_{9/2}$	21053
$^2K_{15/2}$	20576
$^2G_{9/2}$	19608
$^4G_{7/2}$	19194
$^2G_{7/2}, ^2G_{5/2}$	17361
$^2H_{11/2}$	16051
$^4F_{9/2}$	14749
$^4S_{3/2}$	13661
$^4F_{7/2}$	13477
$^2H_{9/2}, ^4F_{5/2}$	12547

broadened, due to the site-to-site variation of the crystalline-field strength.

Fig. 2 shows the upconverted fluorescence spectrum obtained for the sample with $x = 0.1$. The spectra recorded for the other samples exhibit the same features, but the intensities of the lines depend on the Nd^{3+} concentration: to record the spectra, the dye laser was fixed at 577 nm and the spectrometer was scanned in the region from 300 nm to 450 nm. The upconverted emissions observed are due to radiative transitions of the 4f electrons in the Nd^{3+} ion from the high energy excited states to the ground state and to some intermediate states. The emissions correspond to transitions: ${}^4\text{D}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ (~ 354 nm); ${}^4\text{D}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ and ${}^2\text{P}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ (~ 382 nm); ${}^4\text{D}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ and ${}^2\text{P}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ (~ 414 nm); and ${}^4\text{D}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^2\text{P}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ (~ 449 nm).

To understand the mechanisms which contribute for each upconversion emission band, we measured the dependence of the signal with the laser intensity. It is well known [9] that for unsaturated upconversion processes the fluorescence signal, I_s , is proportional to some power, n , of the excitation intensity, such that $I_s \propto I^n$, where n ($= 2, 3, \dots$) is the number of photons absorbed per upconverted photon emitted. In the present experiments, measurements of the upconverted fluorescence intensity were made on the samples and the data for the four emission bands are

illustrated in Fig. 3. The intensities of the upconverted emissions follows a quadratic dependence with the laser intensity indicating that two incident photons are required to generate each photon of the upconverted signal. The deviations from the value $n = 2$ are mainly due to the strong absorption at 577 nm and reabsorption of the upconverted emission.

To determine the temporal evolution of the upconverted signal another set of experiments was performed. The laser beam was fixed at 577 nm, the spectrometer was tuned at the peak of each upconverted emission band and the signal was observed using a fast digital oscilloscope. The time-resolution of the detection system was better than 10 ns and the results obtained for the emissions at 354 and 382 nm are illustrated in Fig. 4. In general, for all samples, the signals grew to their maxima in $\tau_r < 0.33$ μs and the maximum decay times is $\tau_d = 3.06$ μs . In general, both characteristic times (τ_r and τ_d) decrease for increasing Nd^{3+} concentrations.

4. Discussion

The upconverted emissions observed are analogous to those found in ZBLAN [2] and fluoride crystals [9–11], and the band shifts are due to the different structures and coordination numbers of the

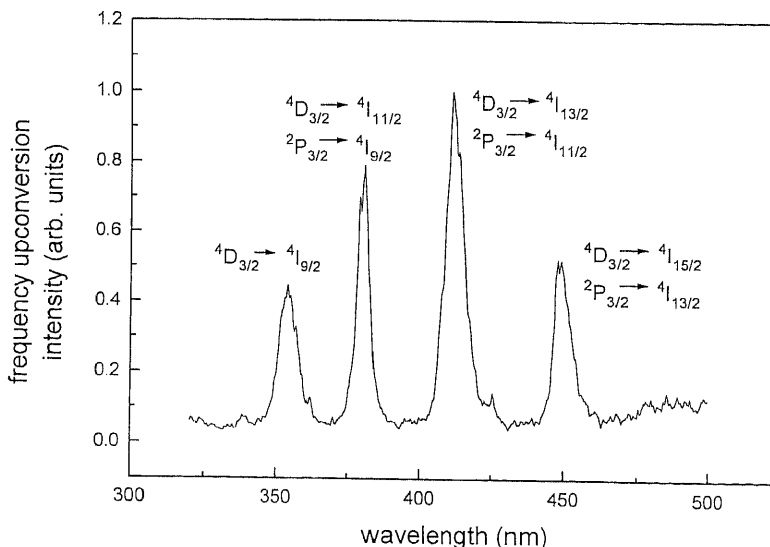


Fig. 2. Upconverted fluorescence spectra for the sample doped with 0.1 mol% Nd^{3+} . The excitation wavelength was 577 nm in resonance with the transition ${}^4\text{I}_{9/2} \rightarrow ({}^2\text{G}_{5/2}, {}^2\text{G}_{7/2})$.

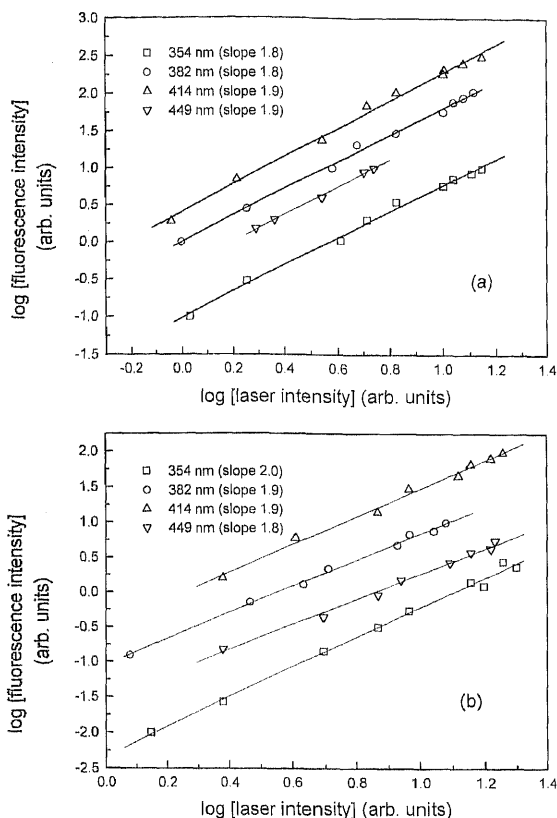


Fig. 3. Upconverted fluorescence intensity as a function of the input laser intensity: (a) Sample with $x = 0.05$; (b) $x = 0.1$. Straight lines with slope $1.8 < n < 2.0$ are obtained for the four emission bands.

Nd^{3+} ions. The intensities of the upconverted lines are dependent on the Nd^{3+} concentration and a quenching is observed for concentrations larger than $\sim 0.5\%$ as illustrated in Fig. 5. This effect may be due to reabsorption of the upconverted fluorescence, energy migration and cross-relaxation processes which become important for large Nd^{3+} concentrations.

To identify the upconversion pathway corresponding to each emission band, we first note that the signals observed may result from excited state absorption (ESA) or energy transfer (ET) among two ions. By either process the emission intensities would depend quadratically on the laser intensity. On the other hand, a study of the upconversion transient evolution may be useful to identify which process, ESA or ET, are dominant in each case. In the present

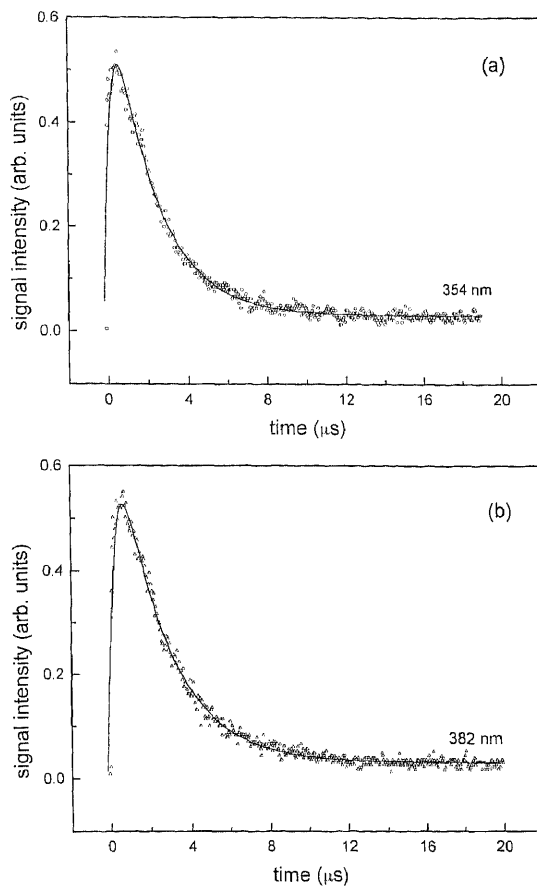


Fig. 4. Temporal behavior of the upconverted fluorescence at 354 and 382 nm (sample with $x = 0.05$). The solid lines is a theoretical fittings with a double exponential curve as described in the text.

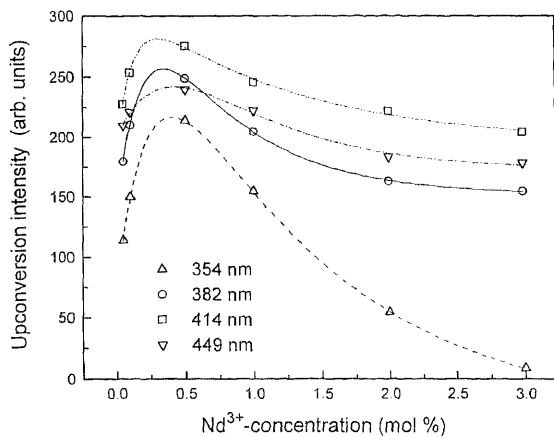


Fig. 5. Upconverted emission intensities as a function of the samples' concentrations. The lines are guides for the eye.

Table 2

Parameters used to reproduce the temporal behavior of the upconverted signal at 354 and 382 nm shown in Fig. 4

x	354 nm		382 nm	
	τ_r (μ s)	τ_d (μ s)	τ_r (μ s)	τ_d (μ s)
0.05	0.29	2.12	0.33	2.40
0.1	0.23	2.62	0.17	3.06
0.5	0.07	2.42	0.10	2.59
1.0	0.07	1.76	0.09	1.77
2.0	0.03	0.93	0.02	1.25
3.0	0.02	0.50	0.02	0.55

work the transient signals were fitted using the expression, $S(t) \propto (e^{-t/\tau_d} - e^{-t/\tau_r})$. For the emissions at 354 and 382 nm a fit with the parameters shown in Table 2 reproduces the experimental data while the emissions at 414 and 449 nm can not be described by a double exponential function. However, a linear combination of three exponentials describes their temporal dependence. We recall that the behavior of $S(t)$ corresponds to that expected for an upconversion process mediated by ET between two ions [7,9]. The observed deviation from this temporal dependence could be due to contributions of one-atom intermediate state relaxations and it may indicate that ESA and ET are contributing simultaneously for the upconversion process, which was first suggested for $\text{Nd}^{3+}:\text{LaF}_3$ [10]. This kind of analysis has proven to be useful for studies of upconversion processes in a number of RE-doped systems [9,11]. A possible extension of the present work is to exploit the dependence of the relative efficiency of ESA and ET as a function of excitation wavelength. As in Ref. [12], ESA may be suppressed for appropriate energy mismatches between the laser frequency and the ion levels, while ET may still be efficient for much larger energy mismatches. This point will be the subject of further work and a detailed study using a rate-equation model, assuming the simultaneous contribution of ESA and ET processes, will be performed.

5. Conclusion

We have presented the first report of efficient red-to-violet and blue upconversion in Nd^{3+} -doped fluorindate glass. The process has been studied for samples with different Nd^{3+} concentrations which

present a large efficiency. Excited state absorption and energy transfer are the mechanisms in which originate the upconverted fluorescence and their contribution are dependent on the excitation wavelength and Nd^{3+} concentrations. The results herein may open the way for the development of efficient wavelength conversion devices based in Nd^{3+} -doped fluorindate glass.

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