Continuous wave ultraviolet frequency upconversion due to triads of Nd^{3+} ions in fluoroindate glass

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We have observed ultraviolet upconversion fluorescence from the $^4D_{3/2}$ and $^2P_{3/2}$ levels of Nd^{3+} in fluoroindate glass under infrared pumping. It was found that the excitation of a large population in the $^4F_{3/2}$ metastable level allows to achieve strong upconversion emissions at 354 and 382 nm. A simple rate equation model reproduces the temporal behavior of the upconverted emission and allows us to estimate the energy transfer rate among three Nd^{3+} ions participating in the process.

The subject of frequency upconversion by resonantly pumped rare-earth (RE) doped solids has received increasing attention in recent years.[1,2] From the fundamental point of view, the study of frequency upconversion processes is important to understand the mechanisms of interaction between the RE ions in different hosts. On the other hand, from a practical point of view, these studies may lead to the discovery of new laser systems based on energy transfer (ET) processes among RE ions.

The study of frequency upconversion processes associated to atom pairs was initiated long ago[1,2] and the selection of appropriated hosts led to the operation of an efficient cw pair upconversion laser based on a Er^{3+}:CaF_2 crystal operating at 2.8 μm.[3] The operation of a trio-upconversion laser based on the same crystal host was obtained at 0.85 μm,[4] also based on an upconversion process previously reported for Pr^{3+}:LaF_3 crystal.[5] The laser of Ref. 4 has an efficiency of $\approx$30% but has to be operated at low temperatures (<77 K).

Clearly the characterization of an efficient trio-upconversion process occurring at room temperature and emitting in the blue-UV region is highly desirable and such spectroscopic studies may help to identify appropriate hosts for laser operation.

Among the new materials available to date, the fluoroindate glasses are especially interesting, since they present large transparency from ~250 nm to ~8 μm, are resistant to atmospheric moisture, and are capable of incorporating large concentrations of RE ions to the matrix.[6] As far as the nonradiative properties are concerned, fluoroindate glasses show multiphonon relaxation rates lower than those of fluorozirconate glasses, and their spectroscopic[7,8] and laser properties[9] have been characterized in details. Moreover, our recent studies have shown their large potential to be used as optical upconverters.[10]

In this letter, we report, for the first time to our knowledge, the observation of efficient cw pumped UV trio upconversion in Nd^{3+}-doped fluoroindate glass.

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The samples used have the following compositions (mol %): (39-x) InF_3-20 ZnF_2-20 SrF_2-16 BaF_2-2 GdF_3-2 NaF-1 GaF_3-$x$$NdF_3$ (x=1,3). They were obtained following the procedure given in Refs. 8 and 10, having good optical quality and volumes of a few cubic centimeters.

The absorption spectra measured are similar to the spectra shown in Ref. 8 except for the bands' intensities and their linewidths, which are dependent on the Nd^{3+} concentration. The fluorescence measurements were made using a cw Ti:sapphire laser as the excitation source. The fluorescence signal was dispersed by a 0.25 m spectrometer and detected by a photomultiplier using either a lock-in or a digital oscilloscope. All measurements were done at room temperature.

Figure 1 shows the upconversion fluorescence in the 325–400 nm region for a sample with x=1 when the laser wavelength was tuned to 866 nm, in resonance with the transition $^4I_{9/2} \rightarrow {}^2F_{3/2}$. Two peaks at 354 and 382 nm are observed and attributed to the $^4D_{3/2} \rightarrow {}^4I_{9/2}$; $^4D_{3/2} \rightarrow {}^4I_{11/2}$, and $^2P_{3/2} \rightarrow {}^4I_{9/2}$ transitions of the Nd^{3+} ion, respectively. The dependence of both lines on the pump power is summarized in Fig. 2 and the nearly cubic slope indicates that three laser photons participate in the UV generation process. Three blue lines, at 414, 426, and 449 nm were also observed, and their

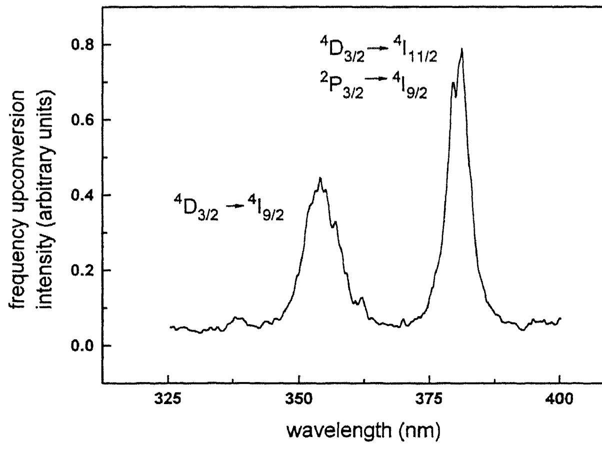

FIG. 1. Room temperature upconversion fluorescence spectrum (sample with x=1).

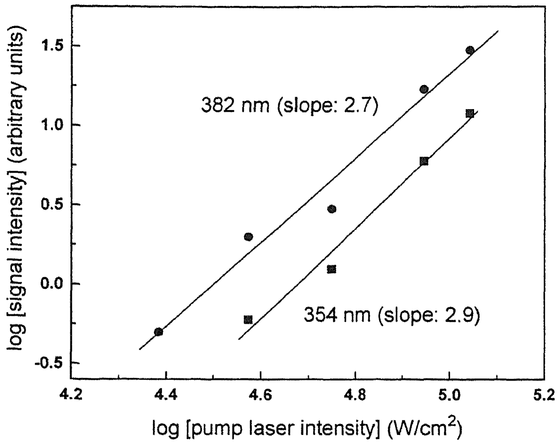

FIG. 2. Dependence of the upconversion fluorescence intensity as a function of the excitation intensity (sample with $x=1$).

power dependence is the same as that of the UV lines. Other upconversion emissions were detected at 522, 587, and 654 nm, but their quadratic dependence with the laser intensity indicates processes involving Nd^{3+} pairs. The upconversion efficiency is so high that a white fluorescence is readily observed by the naked eye. The emissions at 354 and 382 nm are 40 times smaller than that observed at 522 nm for the sample with $x=3$.

Because the energy of the UV photons is greater than twice the energy of the laser photons and because of the cubic dependence of the fluorescence intensity with the pump laser intensity, we conclude that the upconversion process observed is a result of ET between three ions in the metastable ${}^4F_{3/2}$ level.[11] With the use of similar excitation conditions, the fluorescence intensity was compared for both samples. The sample with $x=1$ presents an UV fluorescence approximately 3 times larger than the signal obtained from the sample with $x=3$, indicating a stronger quenching of the fluorescence in the sample with larger Nd^{3+} concentration. We also observed that the lifetime of the ${}^4F_{3/2}$ level for a sample with $x=0.05$ was 0.95 ms, while for the samples with $x=1$ and $x=3$ the values obtained were 186 and 167 μs, respectively.[12] This is strong evidence that ET processes are efficient for the concentrations investigated. Figure 3 shows the energy levels which participate in the process and the proposed upconversion pathway. It is important to note

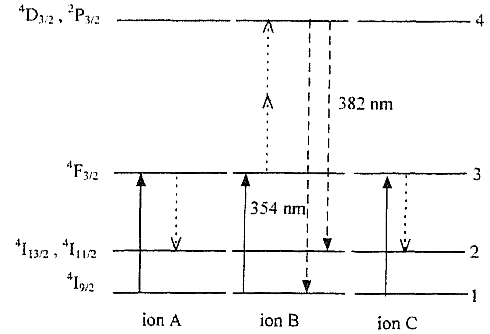

FIG. 3. Simplified energy level scheme considered to describe the trio-upconversion process. The solid lines indicate the radiative transitions induced by the pump laser, and the arrows with dotted lines indicate the resonant energy transfer process.

TABLE I. Rise (τ_r) and decay (τ_d) times observed for the ultraviolet upconverted signals.

Emission wavelength	$x=1$		$x=3$	
	τ_r (ms)	τ_d (ms)	τ_r (ms)	τ_d (ms)
354 nm	0.86	0.63	0.56	0.60
382 nm	0.97	0.73	0.64	0.64

that for the concentrations used the process in which an excited ion transfers its energy to an already excited neighbor is one of the most efficient mechanisms for frequency upconversion, because it depends on the ion–ion separation. Thus, for the large Nd^{3+} concentrations used, ET processes are expected to play a dominant role. Also, the possibility of ions clustering in our samples[10] may favor the three-body ET process.

The temporal evolution of the UV fluorescence was also studied. For this experiment, the laser beam was chopped at 8 Hz and the fluorescence was analyzed with a time resolution better than 0.1 ms. The results obtained are indicated in Table I. From the data, we conclude that the contribution of the ET process is dominant because the UV fluorescence decay times are longer than the lifetimes of the emitting levels $[\tau({}^4D_{3/2})=3\ \mu s$ and $\tau({}^2P_{3/2})=50\ \mu s]$ as measured under direct pumping.[13] Also, the similar temporal behavior of the emissions at 354 and 382 nm indicates that the same upconversion pathway is related to both emissions.

To understand the dynamical behavior of the UV signals, we compared the time resolved data to a rate equation model for a 4-level system which takes into account the contributions from levels ${}^4D_{3/2}$, ${}^2P_{3/2}$, ${}^4F_{3/2}$, ${}^4I_{13/2}$, ${}^4I_{11/2}$, and ${}^4I_{9/2}$. The equations for the levels' populations can be written observing that three ions are initially excited to the ${}^4F_{3/2}$ metastable state (level 3). Due to the cross relaxation process, two ions decay transferring energy to the third ion which is promoted to the level ${}^4D_{3/2}$. Because of the fast nonradiative decay (${}^4D_{3/2}\rightarrow{}^2P_{3/2}$), these two levels were grouped together in level 4. The same procedure was used concerning levels ${}^4I_{11/2}$ and ${}^4I_{13/2}$ which correspond to level 2. The relaxation of levels ${}^4D_{3/2}$ and ${}^4F_{3/2}$ to other levels were also considered. Therefore, the system of rate equations assumes the form:

$$\dot{n}_1=-W_p n_1+\gamma_{41}n_4+\gamma_{31}n_3+\gamma_{21}n_2, \tag{1}$$

$$\dot{n}_2=2W_{\mathrm{ET}}n_3^3+\gamma_{42}n_4-\gamma_{21}n_2, \tag{2}$$

$$\dot{n}_3=-3W_{\mathrm{ET}}n_3^3+\gamma_{43}n_4-\gamma_{31}n_3+W_p n_1, \tag{3}$$

$$\dot{n}_4=W_{\mathrm{ET}}n_3^3-(\gamma_{41}+\gamma_{42}+\gamma_{43})n_4, \tag{4}$$

where n_i denotes the population density of level i ($i=1-4$) as indicated in Fig. 3, γ_{ij} is the decay rate from level i to level j, W_p is the pump rate, and W_{ET} represents the energy transfer rate.

To estimate the values of γ_{ij}, we first note that the only possibility of having emission at 354 nm is due to the transition ${}^4D_{3/2}\rightarrow{}^4I_{9/2}$. However, the lifetime of level ${}^4D_{3/2}$ is determined by nonradiative decay ${}^4D_{3/2}\rightarrow{}^2P_{3/2}$ with a large transition rate ($\sim10^6$ Hz) due to the small energy gap ($\sim1930\ \mathrm{cm}^{-1}$) between the two levels.[14] The γ_{41} value, due to radiative decay, is expected to be in the range 10^2-10^3 Hz and the values of γ_{43} and γ_{42} were taken in the same range because the radiative transitions $^2P_{3/2}\rightarrow{}^4I_{13/2}$ at 449 nm, $^2P_{3/2}\rightarrow{}^4I_{11/2}$ at 414 nm, and $^4D_{3/2}\rightarrow{}^4F_{3/2}$ at 587 nm are relatively strong. Concerning level $^4F_{3/2}$, the large energy gap $E(^4F_{3/2})-E(^4I_{15/2})\approx 5700$ cm^{-1} suggests that its lifetime is mainly due to cross relaxation. Then, with basis on the results of Ref. 9, we considered $\gamma_{32}=3.4\times 10$ and $\gamma_{31}=2\times 10^3$ Hz. The lifetime of levels $^4I_{13/2}$ and $^4I_{11/2}$ are mostly due to nonradiative decay with $\gamma_{21}=3\times 10^5$ Hz, estimated using the energy-gap law.[14] The pump rate $W_p=\sigma I/h\nu_p$ was determined considering a pump intensity $I=1.1\times 10^5$ W/cm^2, laser frequency $\nu_p=3.46\times 10^{14}$ Hz and absorption cross section $\sigma(^4I_{9/2}\rightarrow{}^4F_{3/2})=5.2\times 10^{-20}$ cm^2.[15]

The time evolution of the levels' populations was not very strongly dependent on the variation of the relaxation rate parameters, and slightly different results could be obtained. The best-fitting results correspond to an energy transfer rate $W_{ET}=10^4$ Hz (sample with $x=3$) and illustrate the good agreement with the experimental results, corroborating the assumption of a trio-upconversion process.

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