Study of UV fluorescences induced from $4f^3 \rightarrow 4f^25d$ multistep absorptions of Nd^{3+} ions in $YLiF_4$ and $LuLiF_4$ crystals [1]

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Nd^{3+} ultraviolet (UV) fluorescence induced by multiphotonic laser excitations was studied in doped Nd:$YLiF_4$ (YLF) and Nd:$LuLiF_4$ (LLF) crystals by using the time resolved spectroscopy technique. The UV luminescences are due to transitions between the $4f^25d$ and the $4f^3$ electronic configurations of Nd^{3+} ions. The $4f^25d$ configuration can be reached by direct pumping or by multiphotonic excitation, both processes give rise to the UV band emission with structure due to the strong phonon coupling expected for 5d orbital involvement in the transition. The multiphotonic excitation process is due to three photons (532 nanometers [nm]) sequential absorptions by metastable levels of the $4f^3$ configuration split by crystalline local field. The sequential excitation of Nd by the laser excitation is attributed to the $4I_{9/2}$ + 532 nm $\rightarrow$ $4G_{7/2}$ ground state absorption followed by the $4G_{7/2}$ + 532 nm $\rightarrow$ $2F_{5/2}$ and $2F_{5/2}$ + 532 nm $\rightarrow$ $4f^25d$ excited state absorptions. The UV emissions due to $4f^25d$ configuration are parity allowed, having lifetime of 35 nanoseconds (ns) in contrast to UV emissions from $4f^3$ configuration which are induced by two absorption steps and are parity forbidden showing longer lifetime of 8 microseconds (μs) and narrow lines. The polarization effects of the UV emissions were studied and their behaviors are dependent on the excited state configuration involving or not involving the 5d orbital. The allowed UV emission positions were affected by the host variation more than the ones originated from the $4f^3$ configuration as expected. The electronic energy of the $4f^25d$ configuration shifts to lower energy for increasing the crystal field.

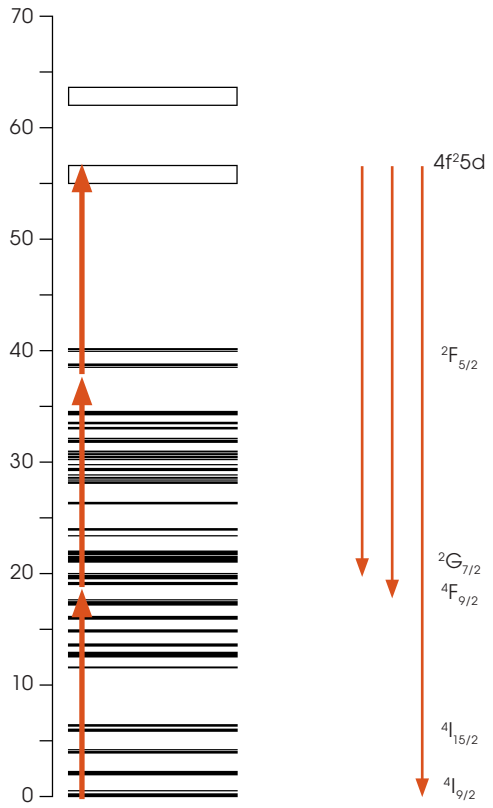
Key words: Multiphotonic excitation process. Ultraviolet radiation. UV transition.

1 Introduction

Rare earth ions-doped crystals are very useful laser media for generating laser radiation in the visible and infrared region. Solid state materials doped with Nd are very promising for using as laser medium for ultraviolet (UV) region (THOGERSEN; GILL; HAUGEN, 1996). The excitation can be performed directly to the level of interest or sequentially pumped. The most interesting pumping mechanism is the three steps excitations at 532 nanometers (nm) which has the advantage of matching the second harmonic of Nd:YAG laser which is one of the most disseminated laser for optical pumping systems (THOGERSEN; GILL; HAUGEN, 1996; VENIKOUAS et al., 1984). The $4f^n \rightarrow 4f^{n-1}5d$ transitions are characterized by a strong environmental interaction and they are responsible for high oscillator strength and broad band absorption and emission spectra in the UV range. Otherwise, the intraconfigurational $4f^n \rightarrow 4f^n$ transitions are parity forbidden and they are sharp and weak because they take place only due to the crystal field configuration mixing (KOLLIA et al., 1998; POWELL, 1998[1]).

The spectrum characterization of the $4f^3 \rightarrow 4f^25d$ and $4f^3 \rightarrow 4f^3$ transitions provides information about the local level structure and electron-phonon coupling differences between $4f^3$ and the $4f^25d$ configurations (KOECHNER, 1986).

The pumping scheme used in this work is illustrated in Graphic 1. The main UV emissions originated form the $4f^25d$ configuration are indicated in this illustration.



Graphic 1: Energy level diagram of Nd:YLF showing the three-photon excitation scheme and the observed transitions from decay of the $4f^25d$ configuration[2] (1 nm= 250 cm^{-1})

Source: Toghersen and collaborators (1996).

2 Experimental setup

YLF and LLF samples were cut and polished properly with the c-axis parallel to the longest side of the rectangular samples. The absorption spectra were performed using a Cary-Olis 17 D double-beam spectrophotometer interfaced to a computer. Using a time resolved spectroscopy system of 10 nanoseconds (ns) of resolution the emission spectra and decay time determination were provided. The laser pumping system consists of a frequency doubled Nd:YAG pulsed laser whose beam intensity is reduced and focused on the samples. The emission of the samples is focused into the monochromator that disperses and directs the light to the EMI S-20 photomultiplier tube. The detection system is connected to the 200 megahertz (MHz) Tektronix oscilloscope and a Box-Car gated integrator coupled to a microcomputer as showed in the Illustration 1.

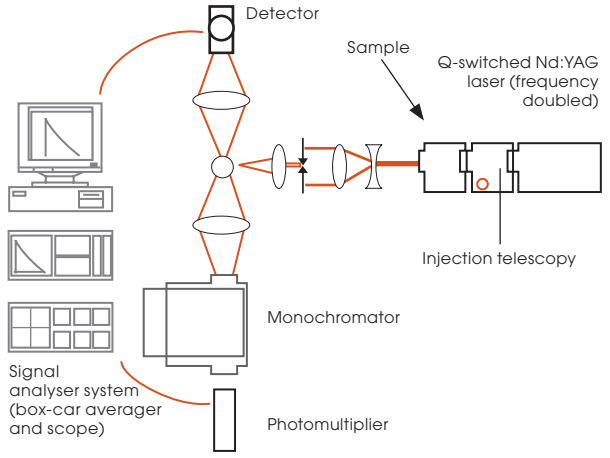


Illustration 1: Experimental setup for luminescence measurements

Source: The authors.

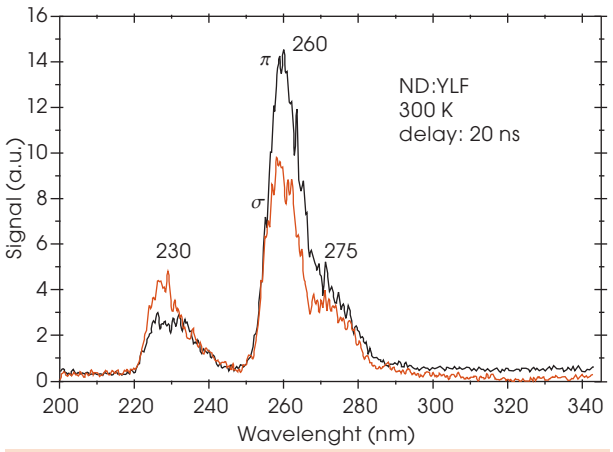
The reduction of laser energies to hundred of microjoules (μJ) is necessary to avoid the self focusing and thermal lens problems in the millijoule (mJ) energy range which can destroy the samples (KOLLIA et al., 1998). The thermal lens effects produce a strong signal decrease and a bad signal-noise ratio, which can disguise the UV emission signal. A non-divergent beam and energies ranging from 4 to 100 μJ can be used to improve UV fluorescence performance.

3 Results and discussion

In order to obtain a time resolved spectroscopy of the emissions and to investigate polarization effects they were measured both UV emissions from $4f^3$ and $4f^25d$ excited states, which follow in the sub-sections.

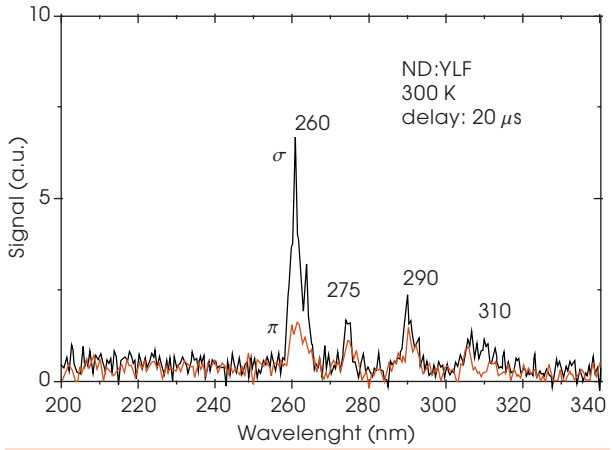
3.1 UV Emissions and the Polarization Effects

The frequency doubled Nd:YAG-Q-switched laser operating at 532 nm with a repetition rate of 10 hertz (Hz) was used in all the investigations of UV fluorescences. The lower energy limit of the $4f^25d$ band of Nd^{3+} in YLF lies at ~ 55,000 cm^{-1} so, the three-photon sequential absorptions of 532 nm, can excite Nd ion to this configuration. The UV fluorescence spectra of Nd in YLF crystal are exhibited in Illustrations 3 and 4. The emission spectrum of $4f^25d \rightarrow 2G_{7/2}$ at 230 nm and $4f^25d \rightarrow 4F_{9/2}$ at 260 nm are exhibited by Illustration 3. They were discriminated by using a narrow static gate (2 ns) and a delay time of 20 ns, in order to detect only the allowed UV emissions. The two-photon that induced emissions from $4f^3$ configuration are also present in the experiment and were optically discriminated by using a narrow static gate of 2 ns using a longer delay time of 2 microseconds (μs) in the box-car averager. By the comparison of both integrated emission signals from distinct electronic configurations, we must say that UV emission from $4f^25d$ is about ten times stronger than the one from $4f^3$ configuration, besides having an absorption process of order two. The emission spectrum of Illustration 4 exhibits the following transitions: $2F_{5/2} \rightarrow 4I_{15/2}$ at 310 nm, $2F_{5/2} \rightarrow 4I_{13/2}$ at 290 nm, $2F_{5/2} \rightarrow 4I_{11/2}$ at 275 nm and $2F_{5/2} \rightarrow 4I_{9/2}$ at 260 nm. The measured lifetime of $2F_{5/2}$ state is 8 μs in contrast with the measured lifetime of 35 ns found for the $4f^25d$ configuration. By comparing these results one concludes that the $4f^25d$ configuration has an emission spectra larger than the emission from $4f^3(2F_{5/2})$ state. This comes from the fact that $4f^3$ configuration produces inner states shielded by the closed $5p^6$ orbital thus producing optical transitions with very small phonon coupling. As a consequence, the polarization effects in the UV emissions from each configuration must have different effects. The strongest polarization effects are observed for the internal $4f^3$ transitions, while the $4f^25d$-mixed configuration is slightly polarized.



Graphic 2: Polarized emission spectrum of the $4f^25d$ configuration of Nd:YLF crystals, after three photons absorptions of 532 nm

Source: The authors.

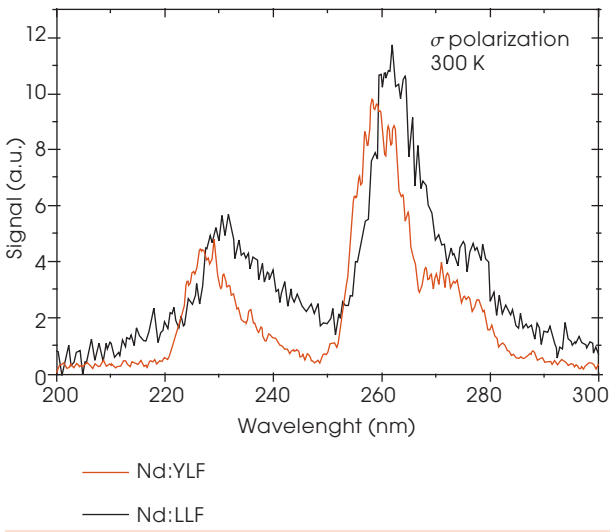


Graphic 3: Polarized emission spectrum of the $4f^3$ configuration after two photons absorption of 532 nm in Nd:YLF crystal

Source: The authors.

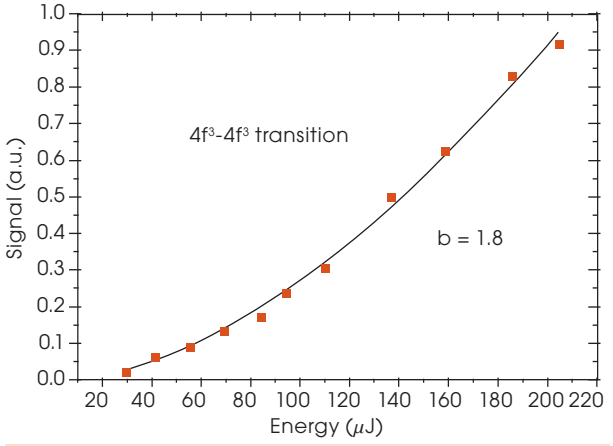
3.2 Host lattice effects

UV emissions were induced in both Nd-doped crystals of YLF and LLF with laser pulsed excitation at 532 nm. Graphic 4 shows the measured $4f^25d$-emission spectrum of both crystals for comparison. The spectrum shape of both UV emissions is similar. However, a strong shift of main peaks by 180 and 200 cm^{-1}, towards the lowest energy, was observed for LLF crystal. This suggests that the total energy of the bottom of the $4f^25d$ mixed configuration of Nd ions in LLF crystal is diminished by approximately 180-200 cm^{-1} in comparison with the position of this level in YLF, due to the strongest crystal field felt by Nd ions in LLF crystal when Y^{3+} neighbors are substituted by Lu^{3+} ions which have smallest ionic radius. On the other hand, the $4f^3$ configuration has UV emissions showing a very small shifting caused by the local field increasing. As observed, the $2F_{5/2} \rightarrow 4I_{9/2}$ emission showed a 20 cm^{-1} peak shift.



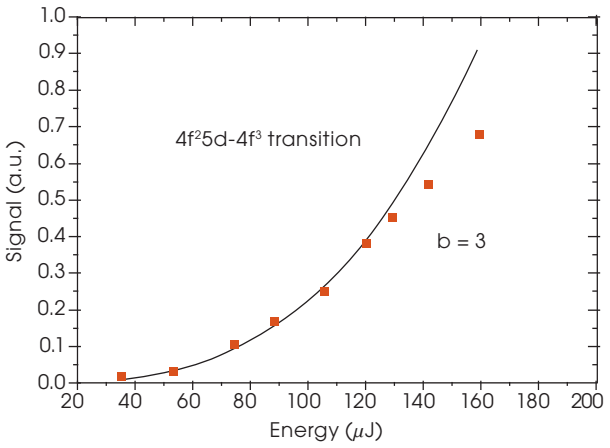
Graphic 4: Emission spectrum of the $4f^25d$ configuration showing the differences between the host lattices

Source: The authors.



Graphic 5: Process order of the excitation mechanism of the $4f^3$ configuration. The fit is $S = cE^{1.8}$

Source: The authors.



Graphic 6: Process order of the excitation mechanism of the $4f^2 5d$ configuration. The fit is $S = cE^3$

Source: The authors.

Graphics 5 and 6 show the behavior of the 260 nm UV emissions intensities *versus* the laser pumping energy at 532 nm. Illustration 6 a shows the behavior of $2F_{5/2}$ state emission at 260 nm from the $4f^3$ configuration, giving an energy power dependence of second order (c = 1,8) for a pumping energy varying from 30 to 200 μJ. The UV emission at 260 nm from the $4f^2 5d$ configuration exhibits power law dependence according to the three order process (Graphic 7). In this case, it is seen a luminescence decrease for pumping energy higher than 130 μJ.

4 Final considerations

The Nd:LLF crystal shows a three photon multistep absorption at 532 nm allowing the population of a $4f^2 5d$ configuration, similar as it was previously observed in Nd:YLF crystal. This observation validates the use of LLF crystal as a promising system for UV laser operation near 260 nm. The spectral discrimination of a long lived UV emission of $4f^3$ configuration from the UV fast emission component allowed us to clarify the multistep excitation mechanism involved in neodymium UV fluorescence for laser applications.

Notes

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2 See chapter 10.

3 This transformation is related to the equation $c = \lambda \times f$, where c is the light speed, λ is the wavelength and f is the frequency that is proportional to the photon energy.

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