# Blue emission in $KY_3F_{10}$:Yb:Nd:Tm crystals

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## Abstract

*The results related with the addition of Neodymium as a second sensitizer to pump Tm ions in $KY_3F_{10}$:Yb:Tm crystals will be presented. The Nd efficiency in the upconversion mechanism was determined pumping the crystals with a diode laser in 797nm. Samples of $KY_3F_{10}$:Nd:Tm codoped with 5, 10 and 20 mol% Yb were also prepared. The enhancement in Tm blue emission is proportional to the Yb concentration in the samples, showing that the main energy transfer process involves Nd and Yb ions.*

## Introduction

Near IR and IR pump lasers are suitable sources to pump directly rare earth ions, by use of sequential pumping with two or three photon excitation or upconversion of the infrared pump photons by different energy transfer processes. Among the rare earth elements, $Pr^{3+}$, $Nd^{3+}$, $Ho^{3+}$, $Er^{3+}$ and $Tm^{3+}$ are the most suitable for upconversion, because these ions also present long-lived high excited $4f^n$ states that give rise to strong green, blue or UV luminescence [1]. Besides that it is already well-known that the use of Yb as a sensitizer enhances the efficiency of the process in one or two orders of magnitude [2, 3]. Recently, rare earth properties in the UV and visible regions have received more attention, due to applications such as infrared (IR) quantum counter detectors, temperature sensors, laser displays and compact visible or ultraviolet (UV) solid state lasers [4,5,6].

$KY_3F_{10}$ (KY3F) has high chemical stability, good mechanical properties, melts congruently and is suitable for doping with rare earth ions. It is a cubic optically isotropic material with a 2x2x2 superstructure of fluorite, space group Fm3m (Z=8) [7]. $KY_3F_{10}$ crystals present low fonon energy and the Yttrium ion occupies sites with tetragonal symmetry ( $C_{4_v}$ ) that make them a good laser host to be doped with rare earth ions. Blue emission have been cited in $KY_3F_{10}$:Yb:Tm crystals with higher efficiency in the energy transfer mechanism between $Yb^{3+}$ and $Tm^{3+}$ when compared with the well known YLF:Yb:Tm [8, 9]. In this work it is studied the effect of Nd used as a second sensitizer to pump Tm ions in an KY3F:Tm:Yb:Nd crystal using a 797nm excitation.

## Experimental Setup

Fluorides react strongly with oxygen and moisture. When these impurities are present during the synthesis process there is the formation of oxygen complexes in the crystals. The optical properties of the crystals are greatly influenced by the presence of these complexes, as they are responsible for scattering centers that causes losses in the laser media. The use of a HF reactive atmosphere prevents the degradation of the material. Then rare earth fluorides were prepared from pure oxide powders (Alpha-Johnson Matthey or Aldrich, 99.99%) by hydrofluorination at high temperature in HF + Ar atmosphere. The powder was contained in a cylindrical platinum boat, which was inserted in a sealed platinum tube. KF commercial powder of 99% purity (Johnson Mattey) was utilized. In the same system were synthesized samples of $KY_3F_{10}$:Tm(0,5mol%) and $KY_3F_{10}$:Tm(0,5mol%):Nd(1,3mol%) codoped with 0, 5, 10 and 20 mol% Yb, using an open platinum boat in the same atmosphere. The samples were obtained by slow cooling of the melt and the synthesized material had always transparent crystalline regions.

The rare earth concentrations in the samples were obtained using inductively coupled plasma (ICP). The emission spectra were obtained by exciting the samples, with a 797 nm laser diode and were analyzed with a 0.5 m monochromator and a S-20 photomultiplier tube. The signal was amplified with a lock-in and processed by a computer.

## Results and Discussions

When KY3F sample containing $Tm^{3+}$ co-doped with $Yb^{3+}$ and $Nd^{3+}$, is excited at 797 nm, a strong blue emission is observed with maximum at 480 nm, due to the transition $^1G_4 \rightarrow {}^3H_6$. Analysis of this strong emission showed that it is dependent of the Yb concentration in the sample. In crystals of KY3F:Tm and KY3F:Nd:Tm no blue emission was detected, but it grows considerably when the Yb concentration changes from 5 to 10 mol% and have a tendency to saturate with 20 mol% Yb (Figure 1). It was concluded that the energy transfer between $Nd^{3+}$ and $Yb^{3+}$ is the main mechanism and responsible for the blue up-conversion.

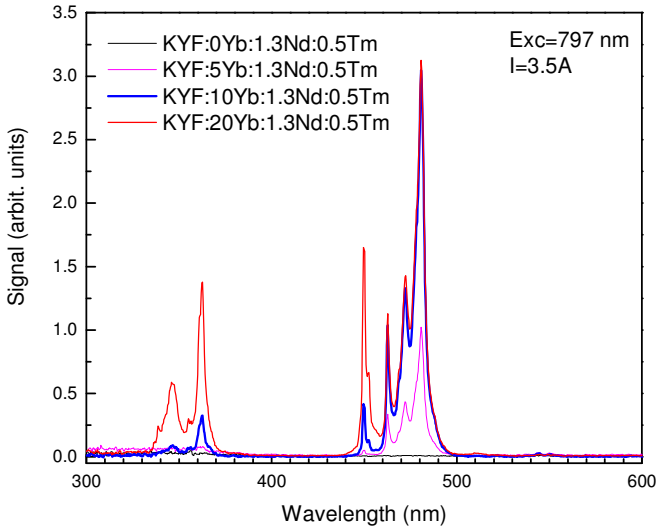


**Figura 1**: $KY_3F_{10}$ emission from samples doped with Nd, Tm and Yb

Nevertheless, all samples presented an emission band around 350 nm involving ions in $^3H_4$ level, this broad band changes features depending on the codopant. In KY3F:Tm it is composed by almost three bands, around 270, 300 and 350 nm, when Nd is added to the host the 270 nm band disappears and when Yb is present it becomes more intense and narrow. This band is composed by two peaks at 340 and 360 nm. In the Figure 2 it is presented the 350nm-emission for KY3F:Tm and for KY3F:Nd:Tm.

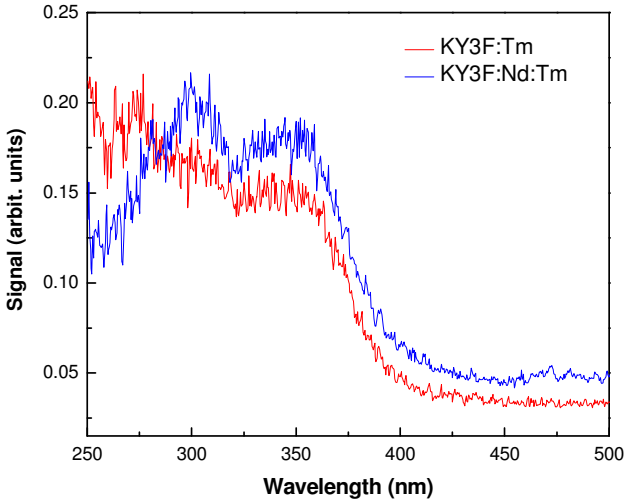


**Figure 2**- Emissions bands from KY3F:Tm and for KY3F:Nd:Tm with excitation in 797 nm.

The intensity of the bands varies with the laser current with a third-order polynomial function resulting in processes that involves the interaction of three photons (Figure 3-a and b).

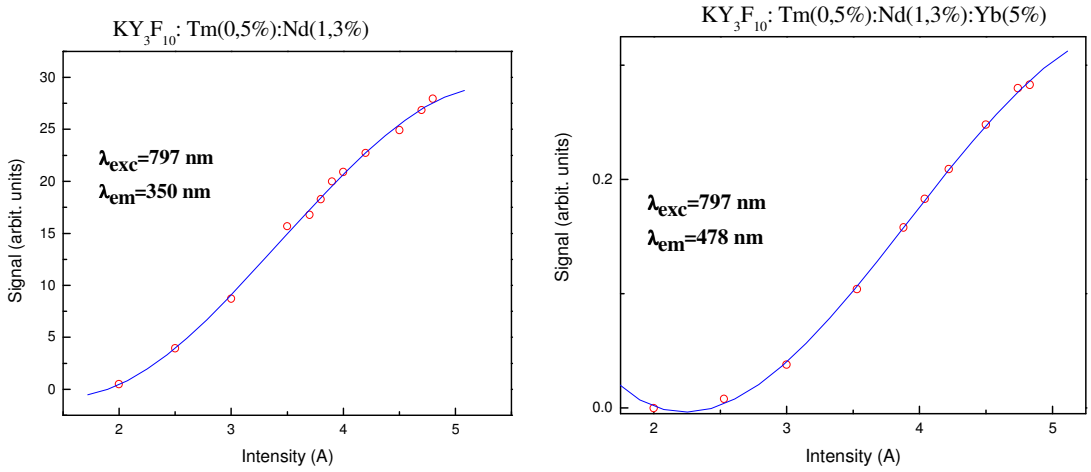


Figure 3- Dependence of the emissions in 350 and 480 nm with the laser pumping current.

## Conclusions

Samples KY3F with good quality have been obtained using a simple synthesis method, which reduced the time to produce spectroscopic samples. Analysis of the Tm blue emission for KYF:Yb:Tm:Nd crystals indicates that Nd ions contributes significantly to enhance the population of $^1G_4$ excited level. It was showed that energy transfer between $Nd^{3+}$ and $Yb^{3+}$ is the main mechanism in the upconversion mechanism, when these crystals are pumped with 797 nm.


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## References


[1] M.-F. Joubert, Opt. Mat. 11 (1999) 181 – 203.
[2] F. Auzel, Ann. Telecom. (Paris) **24**(9-10), 363-376 (1969).
[3] J. E. Geusic, F. W. Ostermayer, H. M. Marcos, L. G. Van Uitert, and J. P. van der Ziel, J. Appl. Phys. **42**(5), 1958-1960 (1971).
[4] L. van Pieterson, M. F. Reid, G. W. Burdick, and A. Meijerink, Phys. Rev. B 65 (2002) 045114
[5] L. van Pieterson, M. F. Reid, R. T. Wegh, S. Soverna, and A. Meijerink, Phys. Rev. B 65 (2002) 045113.
[6] A. F. H. Librantz, L. Gomes, L. V. G. Tarelho, and I. M. Ranieri, J. Applied Phys 95 (4) ( 2004) 1681-1691.
[7] A. Grzechnik, J. Nuss, K. Friese, J.Y. Gesland, M. Jansen, Z. Kristallogr. 217 (2002) 460-463.
[8] A. Rapaport, J. Milliez, F. Szipocs, M. Bass, A. Cassanho, H. Jenssen, Applied Optics 43 (35) (2004) 6477-6480
[9] A. Braud, S. Girard, J.L. Doualan, M. Thuau, R. Moncorge, Phys. Review 61 (8) (2000) 5280