Synthesis and characterization of KY$_3$F$_{10}$:Yb:Nd:Tm crystals

H M Silva$^1$, L C Courrol$^2$, L Gomes$^3$, R Bertram$^3$, S L Baldochi$^1$, I M Ranieri$^1$

$^1$ Instituto de Pesquisas Energéticas e Nucleares IPEN/CNEN – SP
Av. Prof. Lineu Prestes, 2242- CEP:05508000 - São Paulo-SP - Brasil
$^2$ Universidade Federal de São Paulo
Rua Prof. Artur Riedel, 275- CEP: 09972-270 - Diadema – SP - Brasil
$^3$ Institut für Kristallzüchtung (IKZ)
Max-Born-Strasse 2, D-12489, Berlim – Germany

E-mail: iranieri@ipen.br

Abstract . Energy transfer processes that generate thulium blue and ultraviolet emissions by upconversion were studied in KY$_3$F$_{10}$:Tm (KY3F:Tm), using Nd$^{3+}$ and Yb$^{3+}$ as sensitizers of Tm$^{3+}$. The upconversion mechanisms were determined by exciting into the Nd and Tm absorption bands with a diode laser at 797nm. It was observed that the intensity of the Tm$^{3+}$ blue and ultraviolet emissions in 484, 453, 366 and 350 nm were very dependent of the Yb$^{3+}$ concentration in the samples, confirming that the main energy transfer processes involve Nd$^{3+}$ and Yb$^{3+}$ ions. KY$_3$F$_{10}$:Nd (1.3 mol%):Tm (0.5 mol%) crystals codoped with 5, 10, 20 and 30 mol% Yb were prepared by slow cooling from the melt, to establish the optimal Yb concentration that maximizes the Nd$^{3+}$→Yb$^{3+}$→Tm$^{3+}$ energy transfer.

1.Introduction

Infrared to visible frequency upconversion (UC) in rare-earth (RE) doped materials has been extensively investigated due to its potential applications in UC lasers, high-density memories and solid-state color displays. Fluoride compounds in particular have been receiving special attention for UC applications owing to their low phonon energy, which means that nonradiative quenching of emission is limited and then higher efficiencies can be reached [1]. Also, they have good mechanical and thermal properties, lower melting temperatures than the oxides and are less hygroscopic than bromides, sulfides and chlorides. Some rare earth elements such as Pr$^{3+}$, Nd$^{3+}$, Ho$^{3+}$, Er$^{3+}$ and Tm$^{3+}$ are especially suitable for UC because these ions exhibit long-lived high excited 4f$^n$ states that lead to strong green, blue or UV luminescence [2]. Furthermore, it is already well-known that the use of Yb$^{3+}$ as a sensitizer enhances the efficiency of the process in one or two orders of magnitude [3,4].

The KY$_3$F$_{10}$ (KY3F) is a cubic optically isotropic material with a 2x2x2 superstructure of fluorite, space group Fm-3m (Z=8), and melts congruently at 990 °C [5]. This feature allows KY3F to be grown either as bulk crystals through the Czochralski method or as fibers through the micro-pulling-down method [6]. These crystals have low phonon energy (400cm$^{-1}$) and the yttrium ion occupies sites
with tetragonal symmetry ($C_{4v}$) [7, 8]. Previous studies have shown that this matrix exhibits high blue emission efficiency when KY3F:Tm is codoped with Yb and pumped with 975 nm-laser diode [1]. Blue emission enhancement of up to two orders of magnitude was also achieved, when Nd$^{3+}$ was added as a second sensitizer in LiYF$_4$:Yb:Tm (YLF:Yb:Tm) crystals [9, 10, 11] and glasses [12, 13, 14]. In these materials, the population of the Tm ions in the $^5G_4$ emitting level was obtained by multi-ion interaction involving ground state absorption of pumped photons around 800 nm by the Nd$^{3+}$($^4I_{9/2}$→$^2H_{9/2}$, $^4F_{5/2}$) and Tm$^{3+}$($^3H_6$→$^3F_4$) ions, followed by energy-transfer processes involving the Nd$^{3+}$–Yb$^{3+}$ and Yb$^{3+}$–Tm$^{3+}$ pairs.

In this work the effect of Nd used as a second sensitizer to pump Tm ions in KY3F:Tm:Yb:Nd crystalline samples has been studied. Nd$^{3+}$($^4I_{9/2}$→$^2H_{9/2}$, $^4F_{5/2}$) and Tm$^{3+}$($^3H_6$→$^3F_4$) ions were pumped by a 797nm-laser diode and the energy-transfer processes involved in the upconversion mechanism were determined. Monocrystalline samples doped with 0.5 mol% Tm, 1.3 mol% Nd and diverse concentrations of Yb (5, 10, 20 and 30 mol%) were synthesized through slow cooling from the melt under a HF+Ar atmosphere.

2. Experimental Setup
The rare earth fluorides were synthesized from pure oxide powders (Alpha-Johnson Matthey or Aldrich, 99.99%) through hydrofluorination at high temperature (around 800ºC) under an HF + Argon atmosphere. The powders were contained in a cylindrical platinum boat, which was inserted in a sealed platinum tube. The transformation from oxide to fluoride occurs as follows: RE$^2$O$_3$ + 6 HF $\leftrightarrow$ 2 REF$_3$ + 3 H$_2$O (RE=Y, Tm, Nd or Yb).

The bars of KY3F:Tm (0.5mol%) and KY3F:Tm (0.5mol%): Nd (0 or 1.3mol%) codoped with 0, 5, 10, 20 and 30 mol% Yb were synthesized using the same system and atmosphere. Fluorides react strongly with oxygen and moisture, when these impurities are present during the synthesis process, oxygen complexes are formed in the crystals. They are responsible for scattering centers that greatly influence the optical properties of the crystals causing losses in the laser media. The use of hydrofluoric acid as reactive atmosphere prevents the degradation of the materials. Mixtures of the rare earths fluorides and KF powder (99% -Johnson Mattey) were melted in an open platinum boat and slowly cooled with rates of 7.2, 10, 15 or 25ºC/h. Resulting material always presented transparent crystalline regions. Powder X-ray diffraction (XRD) measurements were carried out in the 2$\theta$ range of 12.5-72.5$^\circ$ on a Bruker AXS model A8 Advanced diffratometer, in the step scan mode, with 0.02º/step and step time of 5s. The lattice parameters were calculated using the LCLSQ program [15]. The rare earth concentrations in the samples were determined via inductively coupled plasma (ICP-OES). Absorption spectroscopy was carried out on a Cary 17-D Varian. An experimental arrange consisting of a chopper, a 50cm-monochromator from Spex, and photomultiplier with an extended S-20 cathode were used to obtain the emission spectra excited by a diode laser from SLD emitting around 797 nm. The signal was amplified with a lock-in and finally processed by a computer.

3. Results and Discussions
KY3F crystalline samples were successfully obtained directly from the synthesized bars. X-ray diffraction analysis demonstrated that only the desired phase is present in all samples. The triply codoped samples X-ray patterns are presented in Figure 1 and the lattice parameters are shown in table 1.
Figure 1. Powder diffraction patterns of KY3F doped with 0.5 mol% Tm, 1.3 mol% Nd and different concentrations of Yb: a) 30 mol% Yb; b) 20 mol% Yb; c) 10 mol% Yb; d) 5 mol% Yb; and e) undoped KY3F according the ICSD pattern Nr. 155135.

Table 1. RE concentrations and calculated lattice parameters

| Nominal concentration (mol %) | Measured concentrations (mol%) | Lattice parameters (Å) |
|-------------------------------|--------------------------------|------------------------|
| KY3F:Tm(0.5 mol%):Nd(1.3mol%) | 0.47 (1) 1.26 (1) 11.545(1) |                        |
| KY3F:Tm(0.5 mol%):Yb(10mol%)  | 0.48 (1) 9.48 (2) 11.523(4) |                        |
| KY3F:Tm(0.5 mol%):Nd(1.3mol%):Yb(5mol%) | 0.493 (4) 1.180 (1) 5.41 (8) 11.546 (2) |        |
| KY3F:Tm(0.5 mol%):Nd(1.3mol%):Yb(10mol%) | 0.492 (5) 0.871 (4) 9.30 (1) 11.539 (2) |        |
| KY3F:Tm(0.5 mol%):Nd(1.3mol%):Yb(20mol%) | 0.481 (1) 0.909 (1) 18.49 (1) 11.5271(1) |        |
| KY3F:Tm(0.5 mol%):Nd(1.3mol%):Yb(30mol%) | 0.493 (2) 1.520 (1) 29.60 (2) 11.5052(9) |        |

The concentrations of the samples presented in Table 1, show that measured concentrations are very close to the nominal values for the heavy rare earths. Different Nd concentrations could be obtained along the bars due to its segregation coefficient of approximately 0.7.

The KY3F:Tm:Nd sample present an absorption band with the most intense peak at 802 nm, due to transitions $^4I_{9/2} \rightarrow ^4F_{5/2}$ of Nd$^{3+}$. In the same region, other four bands peaked at 773 and 778.5, 796 and
802 nm correspond to transitions $^3\text{H}_6 \to ^3\text{H}_4$ of Tm$^{3+}$ (Figure 2). The excitation wavelength is highlighted in the figure. No blue emission was detectable when a sample of KY3F:Tm was excited at 797 nm; KY3F:Nd:Tm and KY3F:Yb:Tm samples presented smaller emissions when compared to KY3F:Yb:Nd:Tm (Figure 3).

![Figure 2](image2.png)  
**Figure 2.** Nd$^{3+}$ and Tm$^{3+}$ absorption bands in the pumping region.

![Figure 3](image3.png)  
**Figure 3.** Blue emission of KY3F:Tm codoped with Yb and/or Nd

![Figure 4](image4.png)  
**Figure 4.** Luminescence of KY3F:Yb(10mol%):Nd:Tm crystal under 797 nm excitation.

In KY3F:Yb:Nd:Tm samples strong blue emission was always observed under 797 nm excitation (Figure 4); the emission bands peaked at 453nm and 484nm correspond to the $^1\text{D}_2 \to ^3\text{F}_4$ and $^1\text{G}_4 \to ^3\text{H}_6$ transitions of Tm$^{3+}$ respectively [16].

The study of the dependence of the blue luminescence intensity upon the Yb$^{3+}$ concentration revealed that the blue emission was dependent of the ytterbium concentration (Figure 5). The emission intensity of the 484 nm band grows considerably when the Yb concentrations changes from 5 to 10 mol% and then decreases for larger concentrations. The intensity of the 453 nm emission band is proportional to the concentration of Yb up to 20 mol%, and probably tends to saturate with increasing ytterbium concentration (Figure 6). It was concluded that the energy transfer between Nd$^{3+}$ and Yb$^{3+}$ is the main mechanism in the process to provide Tm upconversion excitation.
Figure 5. Blue emission in KY3F:Tm:Nd:Yb

Figure 6. Blue emission intensity related to Yb concentration in KY3F:Tm:Nd:Yb.

Figure 7. UV emission in KY3F:Tm:Nd:Yb

Figure 8. Yb$^{3+}$ concentration dependence of the UV emission in KY3F:Tm:Nd:Yb

All tripled doped samples exhibited emission bands around 350 nm and 366 nm involving Tm$^{3+}$ ions in $^3H_4$ and $^1D_2$ levels respectively (Figure 7). The intensities of these peaks are proportional to Yb concentration (Figure 8).

From the absorption and emission spectra of doped and codoped samples, as well as earlier YLF spectroscopy studies [9,10,11, 17], were constructed the energy level schemes which show the most probable mechanisms of energy transfer (Figure 9). The emission around 484nm including bands with smaller wavelength (460 and 470nm) are originated from $^1G_4 \rightarrow ^3H_6$ transitions, and two pump photons participate in the upconversion excitation mechanism as they excite both Nd$^{3+}$ and Tm$^{3+}$ through ground-state absorption in the follow sequence:

(a) Tm$^{3+}$: $^3H_4$ + one photon $\rightarrow$ Tm$^{3+}$: $^3H_4$

Nd$^{3+}$: $^4I_{9/2}$ + one photon $\rightarrow$ Nd$^{3+}$: $^4F_{9/2}$

(b) Nd$^{3+}$: $^4F_{5/2}$ + Yb$^{3+}$: $^2F_{7/2} \rightarrow$ Nd$^{3+}$: $^4I_{9/2}$ + Yb$^{3+}$: $^2F_{5/2}$

Yb$^{3+}$: $^2F_{5/2}$ + Tm$^{3+}$: $^3H_4 \rightarrow$ Yb$^{3+}$: $^2F_{7/2}$ + Tm$^{3+}$: $^1G_{4}$
Once its $^1G_4$ level is populated, the Tm$^{3+}$ ion absorbs the energy from another excited Yb$^{3+}$ ion and has its $^1D_2$ level populated:

\[(a) + (b)\]

\[(c) \text{Tm}^{3+}:^1G_4 + \text{Yb}^{3+}:^2F_{5/2} \rightarrow \text{Tm}^{3+}:^1D_2 + \text{Yb}^{3+}:^2F_{7/2}\]

If the decay comes from $^1D_2$ to $^1H_6$ ground state, Tm$^{3+}$ emits at 350 and 366nm. If the transition is from $^1D_2$ to $^3F_4$ level, the 453nm emission occurs.

**Figure 9.** Energy levels scheme and energy transfer mechanisms of the Yb/Tm/Nd system related to the 484 nm emission.

**Figure 10.** KY3F and YLF spectra – both pumping at 797 nm

**Figure 11.** KY3F and YLF spectra supposing KY3F pump ed at 802 nm
Comparison between LiYF₄ (YLF) and KY3F crystals results in a higher blue emission in YLF crystals when compared with KY3F, both excited at 797nm (Figure 10). Conversely, taking into account a resonant absorption at 802 nm for the KY3F, a correction can be made resulting in a 4-fold enhancement on the blue emission when compared to YLF (Figure 11).

4. Conclusions
KY3F samples of good quality were obtained using a simple synthesis method consisted by the slow cooling of the liquid charges. This method reduced the time to produce samples with sufficient transparency and free of macroscopic defects. Analysis of the Tm³⁺ blue emission for KY3F:Yb:Tm:Nd crystals indicates that Nd³⁺ ions contribute significantly to enhance the population of ¹G₄ excited level. It was demonstrated that energy transfer between Nd³⁺ and Yb³⁺ is the main mechanism of the upconversion process when these crystals are pumped with 797 nm. The blue-emission intensity was enhanced around 30 times when compared to a KY3F:Yb:Tm crystal.

5. Acknowledgements
The authors thank CNPq for financial support.

6. References
[1] Rapaport A, Milliez J, Szipocs F, Bass M, Cassanho A and Jenssen H 2004 Applied Optics 43(35) 6477-80.
[2] Joubert M-F 1999 Opt. Mat. 11 181 – 203.
[3] Auzel F, 1969 Ann. Telecom. (Paris) 24(9-10) 363-76.
[4] Geusic J E, Ostermayer F W, Marcos H M, Van Uitert L G and van der Ziel J P, 1958-1960 J. Appl. Phys. 42(5).
[5] Grzechnik A, Nuss J, Friese K, Gesland J Y and Jansen M 2002 Z. Kristallogr. 217 460-3
[6] Yoshikawa A, Kamada K, Nikl M, Aoki K, Sato H, J Pejchal and Fukuda T 2005 Journal of Crystal Growth 285(4) 445-9.
[7] Porcher P and Caro P J 1976 Chem. Phys. 65(1) 89.
[8] Porcher P and Caro P J 1978 Chem. Phys 68, 4183–7.
[9] Courrol L C, Tarelho L V G, Baldoco S L, Gomes L and Vieira Jr N D 2005 J. Applied Physics 98 13504.
[10] Ranieri I M, Courrol L C, Carvalho A F, Gomes L and Baldoco S L 2007 4th Brazilian mrs Meeting 42 2309-13.
[11] Courrol L C, Tarelho L V G, Baldoco S L, Gomes L and Vieira Jr 2007 Journal of Luminescence 122-123 474-7.
[12] Qiu J, Mukai A, Makishima A and Kawamoto Y 2002 J. Physics Condensed Matter 14 13827–34.
[13] Gouveia-Neto A S, Costa E B, Santos P V, Bueno L A and Ribeiro S J L 2003 Journal of Applied Physics 94(9) 5678-81.
[14] Chen D, Wang Y, YuY, Liu F, Huang P 2007 Optics Letters 32(21) 3068-70.
[15] Burnham C 1991 Least squares refinement of crystallographic lattice parameters (LCLSQ), version 8.4, Harvard University.
[16] Dif M, Braud A, Labbé C, Doualan J L , Girard S, Margerie J, Moncorgé R and Thaua M, 1999 Can. J. Phys. 77 693–7.
[17] Zhang X X, Hong P, Bass M and Chai B H T 1995 Physical Review B 51 (14) 9298-9301.