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# Luminescence properties of Yb:Nd:Tm:$KY_3F_{10}$ nanophosphor and thermal treatment effects

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ABSTRACT

In this work, we present the spectroscopic properties of $KY_3F_{10}$ (KY3F) nanocrystals activated with thulium and codoped with ytterbium and neodymium ions. The most important processes that lead to the thulium upconversion emissions in the blue region were identified. A time-resolved luminescence spectroscopy technique was employed to measure the luminescence decays and to determine the most important mechanisms involved in the upconversion process that populates $^1G_4$ ($Tm^{3+}$) excited states. Analysis of the energy-transfer processes dynamics using selective pulsed-laser excitations in Yb:Nd:Tm, Nd:KY3F nanocrystals shows that the direct energy transfer from $Nd^{3+}$ to $Tm^{3+}$ ions is the mechanism responsible for the 78% of the blue upconversion luminescence in the Yb:Nd:Tm:KY3F when compared with the Yb:Nd:Tm:KY3F bulk crystal for an laser excitation at 802 nm. An investigation of the $^1G_4$ level luminescence kinetic of $Tm^{3+}$ in Yb/Nd/Tm system revealed that the luminescence efficiency ($^1G_4$) starts with a very low value (0.38%) for the synthesized nanocrystal (as grown) and strongly increases to 97% after thermal treatment at 550 °C for 6 h under argon flow. As a consequence of the thermal treatment at $T=550$ °C, the contributions of the (Nd × Tm) ($Up_1$) and (Nd × Yb × Tm) ($Up_2$) upconversion processes to the $^1G_4$ luminescence are 33% ($Up_1$) and 67% for $Up_2$. $Up_2$ process represented by $Nd^{3+}$ ($^4F_{3/2}$)→$Yb^{3+}$ ($^2F_{7/2}$) followed by $Yb^{3+}$ ($^2F_{5/2}$)→Tm ($^3H_4$)→$Tm^{3+}$ ($^1G_4$) was previously reported as the main mechanism to produce the blue luminescence in Yb:Nd:Tm:$YLiF_4$ and $KY_3F_{10}$ bulk crystals. Results of X-ray diffraction analysis of nanopowder using the Rietveld method reveled that crystallite sizes remain unchanged (12–14 nm) after thermal treatments with $T \leq 400$ °C, while the $^1G_4$ luminescence efficiency strongly increases from 0.38% ($T=25$ °C) to 12% ($T=400$ °C). Results shown that the $Nd^{3+}$ ions distribution has a concentration gradient increasing towards the nanoparticle surface allowing the direct (Nd × Tm) ($Up_1$) (78%) in competition with the (Nd × Yb × Tm) ($Up_2$) (22%) upconversions for the synthesized nanocrystals (11 nm).



## 1. Introduction

With the oncoming of the nanoscience and nanotechnology in the past few decades, this new field has exerted great impact on upconversion materials, then studies on the synthesis and properties of upconversion nanophosphors [1] have received intense research interest due to their application as luminescent labels in bioimaging, and as donors in energy transfer systems [2,3]. Within this aim, fluoride crystals doped with trivalent rare earth ions has extensively studied due to generation of efficient multicolor emission lines in the visible when excited by infrared diode laser near 800 and 970 nm (the optical window for biological samples from 700 to 1200 nm). In particular, $KY_3F_{10}$ (KY3F) crystal has been studied as luminescent materials when activated by several $RE^{3+}$ ions, which can easily substitute $Y^{3+}$ ions in a non-center-symmetrical site [$C_{4v}$ symmetry] [4,5–8]. KY3F is the only compound in the KF–$YF_3$ system that melts congruently without any phase transition. It crystallizes in the cubic fluorite-type structure (Fm3m) with a lattice parameter $a=11.553$ Å [8], which constitutes an isotropic crystal. In particular, Yb:Nd:Tm:$KY_3F_{10}$ can be synthesized as nanocrystals able to efficiently emit at 482 nm when excited at 802 nm due to its relatively low phonon energy (cut off ~500 $cm^{-1}$) that is an important point in avoiding energy loss by non-radiative relaxation involving the $^1G_4$ and $^3H_4$ excited levels of $Tm^{3+}$ [9,10].

In this paper, nanocrystals of Yb:Nd:Tm:KY3F sizing 11 nm were synthesized by co-precipitation method in aqueous solution. The multiple processes of energy transfer that occur when this material

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is excited around 800 nm were inspected and the transfer rates constants were determined. The upconversion luminescence transient at 482 nm of $^1G_4$ excited state of $Tm^{3+}$ was measured for Yb (10 mol%): Nd(1.3 mol%):Tm(0.5 mol%):KY3F nanocrystals induced by pulsed laser excitation at 802 nm. The luminescence efficiency of $^1G_4$ excited state was determined and its dependence on the thermal treatment temperature and crystallite size were determined.

## 2. Experimental procedure

The nanopowders were obtained by the coprecipitation method [11,12,13], boiling aqueous solution of potassium fluoride (KF – Merck, 99%) was slowly added in a hot $RECl_3$ aqueous solution (RE=Y, Yb, Nd and Tm), followed by slow addition of an ammonium bifluoride boiling aqueous solution ($NH_4HF_2$ – Aldrich, 98%). Rare earth fluorides were obtained from $ReO_3$ (Aldrich, 99.9%) dissolved in concentrated hydrochloric acid. After the addition of the $NH_4HF_2$ solution a white precipitate was formed, and the resulted solution was maintained at 80 °C and stirring for 3 h. The initial molar proportion was of 1 $KF+(1-x)$ $YCl_3+x$ $LnCl_3+3$ $NH_4HF_2$, where Ln=Yb, Nd, and Tm. The nanocrystals were separated by centrifugation ($G_{max}=3800$) and the fine powder was collected, washed with Milli-Q water several times and dried in air in a hot plate at 40 °C for 48 h. Thermal treatments at different temperatures were carried out at a resistive oven for 6 h under argon flow (White Martins, 99.995%), using an amount of the synthesized nanopowder and extracting aliquots of it at every interest temperature, to perform the spectroscopic studies.

Samples were characterized by X-ray diffraction (XRD) on a Panalytical X´PERT diffractometer and by transmission electronic microscopy (TEM) on a JEOL JEM 200C microscope with accelerating voltage of 200 kV. Lattice parameters were obtained by Rietveld refinement method using a GSAS-EXPGUI program [14,15] and the mean crystallite diameters (MCD) using Rietveld or the single line methods [16].

The following nanocrystals were synthesized for the luminescence measurements performed in this work: *i*) Yb(10 mol%):Nd (1.3 mol%):Tm(0.5 mol%):KY3F, and *ii*) Nd(1.3 mol%):KY3F.

The absorption spectra of all samples were measured in the range 400–1200 nm at room temperature using a Varian Cary 5000 spectrophotometer working in the diffuse reflection mode. In the luminescence lifetime measurements, the samples were excited by pulsed laser radiation generated by a tunable OPO-IR pumped (Rainbow from OPOTEK, USA) by the second harmonic of a Q-switched Nd:YAG (yttrium aluminum garnet) laser (Brilliant B from Quantel, France). Laser pulse widths of 4 ns at 802 nm were used to directly excite the $^4F_{3/2}$ and $^3H_4$ excited states of $Nd^{3+}$ and $Tm^{3+}$, respectively. Luminescence signals were analyzed by the 0.25 m Kratos monochromator, detected by the EMI S-20 (or S-1) PMT (response time of 10 ns) or InSb 77 K infrared detector from Judson (response time ~0.5 μs) or using a charge coupled device (CCD) spectrometer coupled to the sample holder containing the nanopowder via optical fiber. Luminescence lifetime was measured using a digital oscilloscope of 100 MS $s^{-1}$ model TDS 410 from TEKTRONIX interfaced to a microcomputer.

## 3. Experimental results

The synthesized nanopowders have shown the cubic phase ($Fm\bar{3}m$) of $KY_3F_{10}$ corresponding to the fluorite crystalline structure, however with the diffraction peaks wider due to the crystalline planes distortions and defects as seen in Figs. 1 and 2. Nevertheless, X-ray diffraction peaks become narrow after thermal treatment at $T=550$ °C due to the particles growth and increasing of

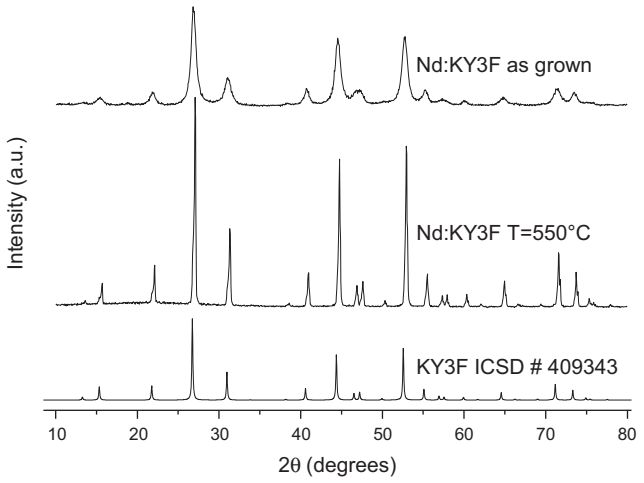


**Fig. 1.** X-ray diffraction pattern for Nd:KY3F synthesized nanopowder before (as grown) and after thermal treatment ($T=550$ °C). Lowest diffratogram was obtained for a bulk crystal (KY3F) for comparison.

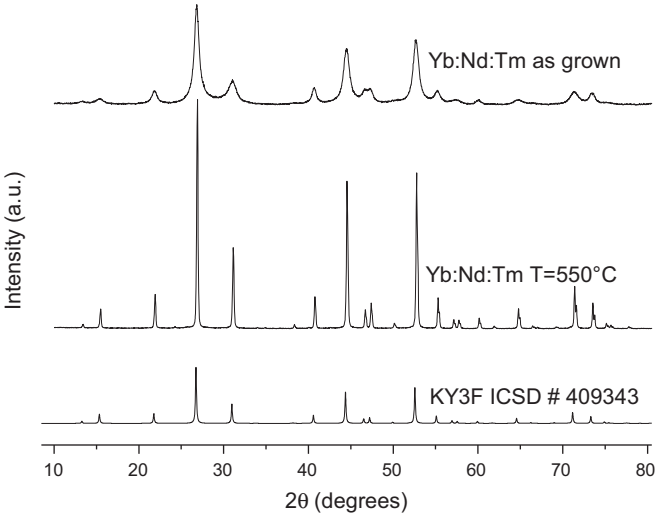


**Fig. 2.** X-ray diffraction pattern of Yb:Nd:Tm:KY3F synthesized nanopowder before (as grown) and after thermal treatment ($T=550$ °C). Lowest diffratogram was obtained for a bulk crystal (KY3F) for comparison.

crystallinity (Figs. 1 and 2). The synthesized nanocrystals were approximately spherical with a mean diameter of 11 nm as shown by TEM photograph (Fig. 3). After thermal treatment at $T=550$ °C the crystallite grows exhibiting a mean diameter of 198 nm as shown by TEM photograph (Fig. 4) for Nd:KY3F.

Rietveld refinement of the XRD patterns considering the cubic structure with space group $Fm\bar{3}m$ (ICSD 409643) and spherical particles yielded lattice parameters of 11.560 (1) Å and 11.499 (1) Å, and mean crystal size of 11 and 12 nm for the synthesized Nd:KY3F and Yb:Nd:Tm:KY3F nanocrystals, respectively. The smaller cell parameter for the tri-doped sample is due to the codoping with Yb and Tm ions, which have smaller ionic radii than the yttrium one. TEM analysis confirmed the results obtained for the particles sizes. After thermal treatments, the XRD peaks were narrowed due to particles growth and the increasing of crystallinity (Figs. 1 and 2). The changes in the mean crystallite sizes ($d$) after heating of the samples at diverse temperatures are given in the following:

i) Nd:KY3F
$d=12$ nm (as grown −25 °C); $d=12$ nm ($T=150$ °C); $d=11$ nm