

Growth of YLF:Yb:Tm:Nd for optical applications

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Abstract The focus of this study is the behavior of Tm, Yb and Nd ions in the LiYF₄ (YLF) crystal. One YLF crystal was successfully grown by the Czochralski method; it was doped with 20 mol% Yb, 1.3 mol% Nd and 0.05 mol% Tm. The segregation coefficients of the dopants and lattice parameters were determined. The spectroscopic properties of samples with different amounts of Nd were obtained from absorption and emission studies.

Introduction

Crystals and glasses doped with rare earth ions such as Nd³⁺, Ho³⁺, Er³⁺, Tm³⁺ and Yb³⁺ are used to produce well-known lasers with near infrared emissions [1, 2]. Currently rare earth properties in the UV and visible regions have received more attention because of the following applications- infrared (IR) quantum counter detectors, temperature sensors, laser displays and compact visible or ultraviolet (UV) solid state lasers [3–6]. The availability of efficient near-IR and IR

pump lasers overcome the lack of suitable sources to pump these ions directly by sequential pumping, with two or three photon excitation or upconversion of the infrared pumped photons by different energy transfer processes. Among the rare earth elements, Pr³⁺, Nd³⁺, Ho³⁺, Er³⁺ and Tm³⁺ are more suitable for upconversion, as these ions also present long-lived highly excited 4fⁿ states that give strong green, blue or UV luminescence [3].

Further it is well-known that the use of Yb as a sensitizer enhances the efficiency of the process by one or two orders of magnitude [7, 8]. New results on glasses demonstrated enhancement of over two orders of magnitude of the upconverted emission around 480 nm when telluride glass were doped with Nd³⁺ and Tm³⁺ ions, and a 40-fold enhancement of the blue emission in a fluorozirconate glass [9]. Additionally, bright blue upconversion emission through sensitization of thulium ions in lead and cadmium germanate glass triply doped with Nd–Tm–Yb under excitation around 800 nm demonstrated that for the same excitation power, the triply -codoped sample generated ten times more 475 nm blue upconversion fluorescence than the Yb³⁺-sensitized Tm³⁺-doped samples [10]. The population of the Tm ions in the ¹G₄ emitting level was obtained by multi-ion interaction involving ground-state absorption of pumped photons around 800 nm by the Nd³⁺ (⁴I_{9/2} → ²H_{9/2}, ⁴F_{5/2}) and Tm³⁺ (³H₆ → ³F₄) ions, followed by energy-transfer processes involving the Nd³⁺–Yb³⁺ and Yb³⁺–Tm³⁺ pairs.

LiYF₄ crystals doped with Tm using Yb as sensitizer has been extensively studied and present two intense emission, around 450 and 475 nm, due to the transitions ¹D₂–³F₄ and ¹G₄–³H₆, respectively. Laser emission at 450 nm was obtained via two-photon pump

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mechanism at 780 and 650 nm, and laser emission in 475 nm was obtained using a single pump wavelength at 629 nm. The upconversion mechanism was by photon avalanche [11–14]. In this work the effect of Nd, used as a second sensitizer to pump Tm ions in an YLF:Tm:Yb:Nd crystal has been studied. An YLF crystal codoped with 0.5 mol% Tm, 20 mol% Yb and 1.3 mol% Nd in the melt was successfully grown by the Czochralski method, in a reactive atmosphere of CF₄ and Argon. The crystal was characterized using x-ray diffraction analysis to determine the lattice parameters, IR absorption to detect some moisture contamination, differential thermal analysis (DTA) to measure the crystal melting point. The segregation coefficient of neodymium was calculated from optical-absorption measurement data.

Experimental

The rare earth fluorides were prepared from pure oxide powders (Alpha-Johnson Matthey, 99.99%) by hydrofluorination at high temperature in HF atmosphere. The powder was contained in a cylindrical platinum boat, which was inserted in a sealed platinum tube. The LiF–LnF₃ (Ln = Y, Yb, Nd, and Tm) mixture was melted using an open platinum boat in the same atmosphere, with a composition of 1.02 LiF: 1 LnF₃. LiF powder (Alpha-Johnson Matthey, 99.9%) was zone-refined before it was added to the mixture.

The studied crystal was grown by the Czochralski method using automatic diameter control, with growth rate of 1.30 mm/h and rotation rate of 15 rpm for the <100>-oriented boule. During the process, the atmosphere inside the Czochralski furnace was composed by Ar (1.4 bar) and CF₄ (0.2 bar). Powder X-ray diffraction (XRD) measurements to determine lattice parameter were carried out on a Bruker AXS diffractometer, model D8 Advance, operated at 40 kV and 30 mA, in the 2θ range of 18–66°. The lattice constants were obtained by minimum square fittings. DTA curves were obtained in TGA-DTA equipment from TA Instruments, model 2960. Samples weighing around 50 mg were placed in open platinum crucibles without a reference material and the measurements were performed under a flux of purified helium and with a heating rate of 10 °C/min.

A Cary-17D was used for the absorption measurements, and an experimental arrange consisting of a 50 cm-monochromator from Spex, a chopper, a lock-in amplifier, a photomultiplier with an extended S-20 cathode and a germanium detector were used to obtain the emission spectra excited by a diode laser from SLD

emitting around 792 nm. Three samples 2 mm thick, from the top, middle and the bottom of the crystal were cut and polished to determine the effect of Nd-content on the emission properties and to calculate the segregation coefficient of the neodymium.

Results and discussion

The YLF:Yb:Tm:Nd crystal with 60 mm in length and 20 mm in diameter is shown in Fig. 1.

The infrared spectrum, revealed slight OH⁻ contamination, due to formation of Me(OH)² complexes (Me = divalent metals) resulting from the residual water moisture in the crystal growth atmosphere (Fig. 2).

The Neodymium segregation coefficient was determined, taking into account the maxima of the absorption coefficients (α) of the three samples, with unpolarized light at 805.5 nm (π polarization) or 806 nm (σ polarization), after fitting of the absorption spectra to multiple Lorentzian functions. These bands are transitions of the multiplets $^4F_{3/2} \rightarrow ^5H_{9/2}$ and are not sensitive to polarization (Fig. 3).

The absorption density (α) was obtained from :

$$\alpha = \sigma_a N \quad (1)$$

where σ_a is the absorption-peak cross section and N is the number absorbing centers in at.cm^{-3} , that is, the concentration of Nd ions in the sample. The segregation coefficient was determined by considering the normal solidification equation:

$$C_s = C_0 k(1 - g)^{k-1} \quad (2)$$

where C_s is the concentration of neodymium in the crystal, C_0 is the initial concentration in the melt, k is the segregation coefficient and g is the solidified fraction. Substitution of N from Eq. 1 into Eq. 2, results in:

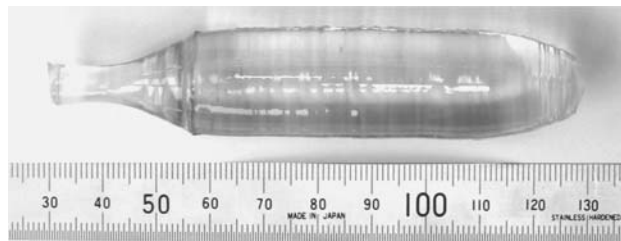


Fig. 1 The crystal of YLF:Yb:Tm:Nd grown by the Czochralski method

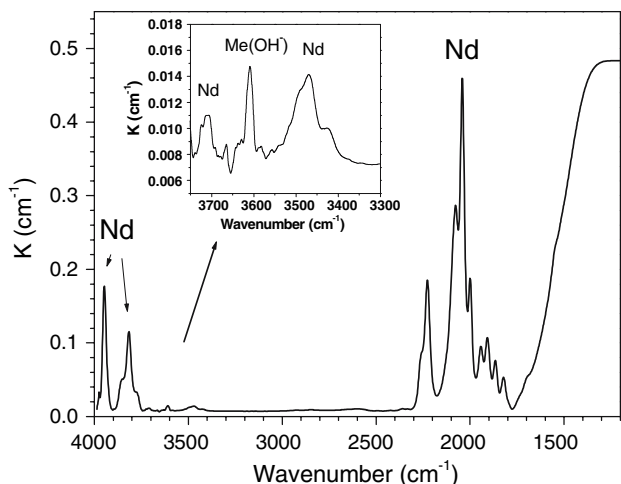


Fig. 2 Absorption coefficient in the infrared of a YLF:Yb:Tm:Nd sample with 20 mm thick

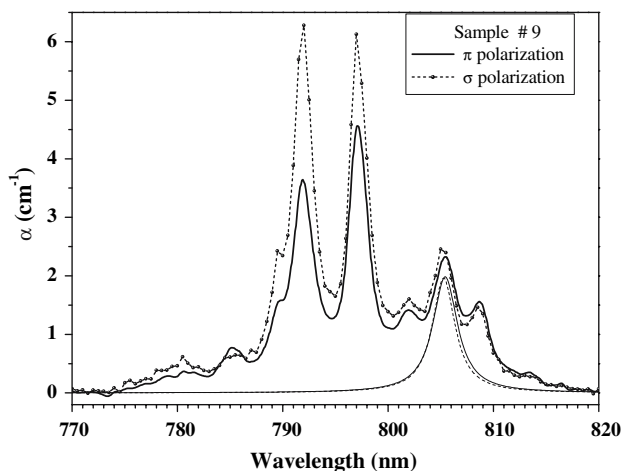


Fig. 3 Neodymium absorption coefficients of the ${}^4F_{3/2} \rightarrow {}^5H_{9/2}$ multiplets obtained with polarized light. It is also shown the resulting Lorentzians corresponding to the Nd absorption coefficients around 805.5 nm; and 806 nm, which are not sensitive to the sample orientation

$$\alpha_s = \alpha_0 k(1 - g)^{k-1} \quad (3)$$

Fitting of the peak intensities of the 806 nm-absorption band of the π and σ polarizations versus the solidified fraction with the equation (3) resulted in a value of 0.31(2) for the coefficient segregation and a value of $1.31(1) \times 10^{-20} \text{ cm}^{-2}$ for the absorption cross section (Fig. 4). The Nd segregation coefficient is similar to that obtained for fluoride crystals with the scheelite structure [15, 16], and the absorption cross section is of the same order of those cited in the literature for this wavelength [17, 18]. Thus, it was possible to obtain the Nd concentrations in the three samples, and these are 0.44, 0.63 and 1.08 mol%, respectively.

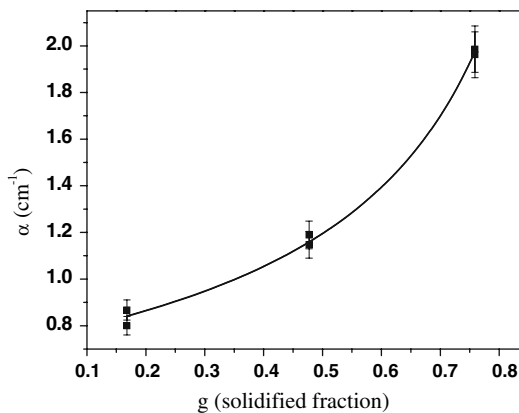


Fig. 4 Distribution of neodymium ions along the crystal considering the absorption coefficient peaks

There was no change in the melting point compared to YLF pure crystals, which presented an onset temperature of 806 °C in the heating mode. However this crystal presented smaller lattice parameters compared to YLF crystals, and this can be attributed to substitution of 20 mol% of Y by Yb, as the latter has a shorter atomic radius (1.019 and 0.985 Å, respectively) (Table 1). A slight increase in the lattice parameters is noticeable, due mainly to the higher neodymium concentration at the bottom of the crystal. No variations in the concentrations of thulium and ytterbium, along the crystal, were detected by optical absorption.

The polarized emission spectra of the three samples were obtained by excitation in the 792 nm band of the Neodymium and it is shown in the Fig. 5a. When this emission is compared with the polarized absorption of the excitation band it can be seen that the emission tends to saturate as the concentration of Nd increases. This can be attributed to a back transfer mechanism given by $\text{Yb} ({}^2F_{5/2}) + \text{Nd} ({}^4I_{3/2}) \rightarrow \text{Yb} ({}^2F_{7/2}) + \text{Nd} ({}^4I_{11/2})$.

The Yb emission around 1030 nm also presents an enhancement in intensity when Nd concentration is increased demonstrating the high efficiency of the

Table 1 Lattice parameters determined from x-ray diffraction analysis, using Si as an internal pattern

Sample	Lattice parameters (Å)
YLF:Yb:Tm:Nd (top)	a = 5.126 (1) c = 10.622 (3)
YLF:Yb:Tm:Nd (bottom)	a = 5.130 (1) c = 10.628 (5)
YLF	a = 5.167 (1) c = 10.729 (2)

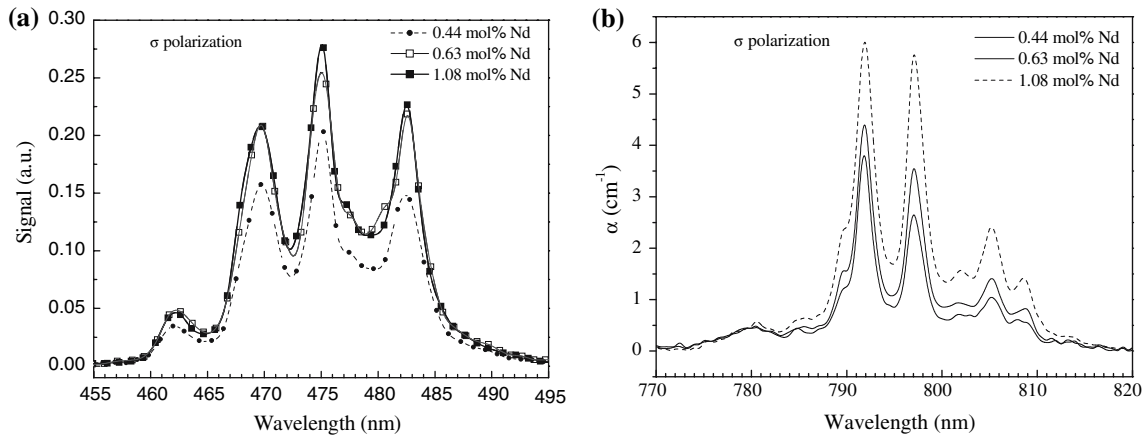


Fig. 5 (a) Tm blue emission intensity in three YLF:Yb:Tm:Nd samples containing different Nd concentrations; and (b) absorption coefficients of the same samples in the region of the excitation wavelength of the Nd (792 nm)

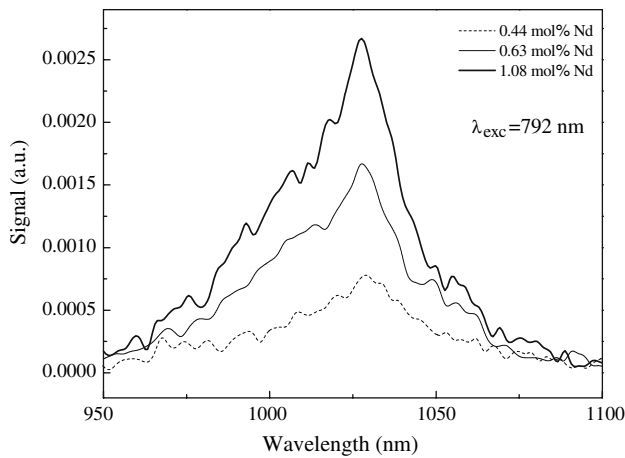


Fig. 6 Yb emission band in the three YLF:Yb:Tm:Nd samples

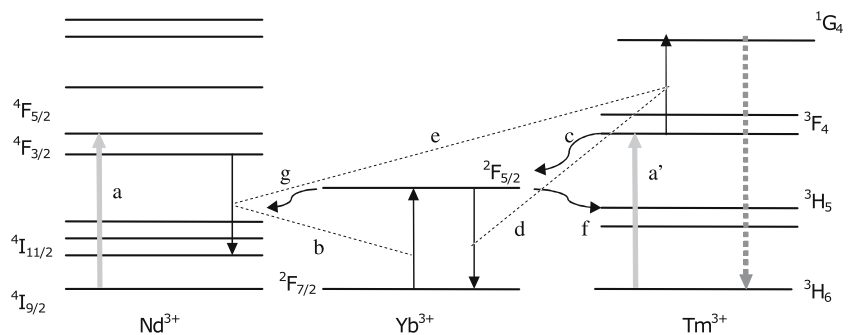
energy transfer from Nd to Yb via cross relaxation (Fig. 6).

The energy transfer mechanisms involved in the upconversion process resulting in the generation of the blue emission are presented in the Fig. 7. The following mechanisms can coexist: (a) Ground state absorption of Nd; (a') Ground state absorption of Tm; (b) Cross

relaxation between Nd and Yb: $\text{Nd}(^4\text{F}_{3/2}) + \text{Yb}(^2\text{F}_{7/2}) \rightarrow \text{Nd}(^4\text{I}_{11/2}) + \text{Yb}(^2\text{F}_{5/2})$; (c) Energy transfer from Tm to Yb: $\text{Tm}(^3\text{F}_4) + \text{Yb}(^2\text{F}_{7/2}) \rightarrow \text{Tm}(^3\text{H}_6) + \text{Yb}(^2\text{F}_{5/2})$; (d) Cross-relaxation between Yb and Tm: $\text{Yb}(^2\text{F}_{5/2}) + \text{Tm}(^3\text{F}_4) \rightarrow \text{Yb}(^2\text{F}_{7/2}) + \text{Tm}(^1\text{G}_4)$; (e) Cross relaxation between Nd and Tm: $\text{Nd}(^4\text{F}_{3/2}) + \text{Tm}(^3\text{F}_4) \rightarrow \text{Nd}(^4\text{I}_{11/2}) + \text{Tm}(^1\text{G}_4)$; (f) Back transfer from Yb to Tm: $\text{Yb}(^2\text{F}_{5/2}) + \text{Tm}(^3\text{H}_6) \rightarrow \text{Tm}(^3\text{H}_5) + \text{Yb}(^2\text{F}_{7/2})$; (g) Back transfer from Yb to Nd: $\text{Yb}(^2\text{F}_{5/2}) + \text{Nd}(^4\text{I}_{3/2}) \rightarrow \text{Yb}(^2\text{F}_{7/2}) + \text{Nd}(^4\text{I}_{11/2})$; (h) Energy transfer from Nd to Tm: $\text{Nd}(^4\text{F}_{5/2}) + \text{Tm}(^3\text{H}_6) \rightarrow \text{Nd}(^4\text{I}_{9/2}) + \text{Tm}(^3\text{F}_4)$; and (i) Energy transfer from Tm to Nd: $\text{Tm}(^3\text{F}_4) + \text{Nd}(^4\text{I}_{9/2}) \rightarrow \text{Tm}(^3\text{H}_6) + \text{Nd}(^4\text{F}_{5/2})$. The spectroscopic parameters for these mechanisms were calculated and is presented elsewhere [19].

The blue emission in the YLF:Yb:Tm:Nd was compared with that from another YLF crystal doped with 10 mol% Yb and 1%Tm. The triply codoped crystal presented a greater emission cross section compared with the doubly codoped one and a 5-fold enhancement on the blue emission was obtained (Fig. 8). This is because Nd ions absorb efficiently the 792 nm-excitation and transfer it to Yb ions, given that both blue and Yb emission enhance proportionally

Fig. 7 Energy levels scheme and energy transfer mechanisms of Yb/Tm/Nd system



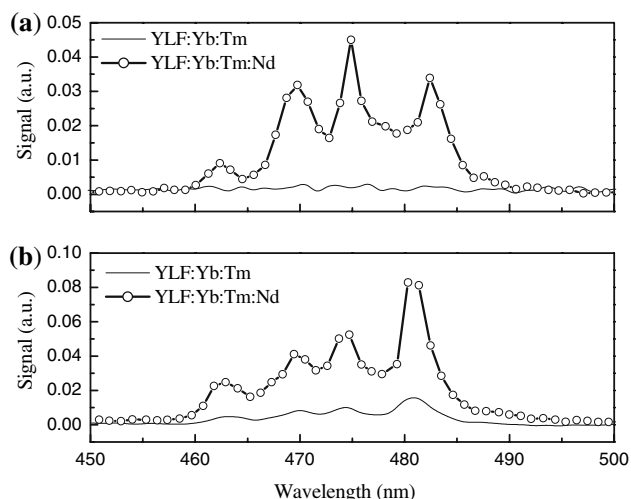


Fig. 8 Polarized emission spectra of YLF:Yb:Tm:Nd and YLF:Yb:Tm samples excited at 792 nm: **(a)** σ polarization ; and **(b)** π polarization

with the neodymium content in the sample. Nevertheless, it was observed that although the cross section of the 792-nm absorption band increases exponentially with Nd concentration the blue emission tends to saturate. This is a sign that back transfer between Nd and Yb ions is an important mechanism when the Nd concentration is greater than 1 mol%.

By comparing the results obtained for YLF:Yb:Nd:Tm crystals with some glasses such as ZBLAN and tellurite glasses [9] doped with Tm and Nd or lead and cadmium germanate glasses triply doped with Tm, Yb and Nd [10], it can be concluded that the enhancement of the blue emission intensity is more efficient in glasses, since it was obtained by increasing factors up to 200. In glasses, the larger inhomogeneous bands favor the energy transfer mechanisms.

Conclusions

This paper shows that good quality YLF:Yb:Tm:Nd crystals can be obtained, and that the utilization of Nd as a second sensitizer for YLF:Yb:Tm crystals improves the upconversion mechanism that gives rise to the Tm blue emission in 475 nm. As the increase in Tm blue emission and the Yb emission in the infrared

are proportional to the increase in Nd absorption, it can be concluded that there is an efficient mechanism for energy transfer from Nd to Yb and from Yb to Tm. Conversely the concentration of Nd in the crystal must be around 0.8 mol% to prevent back transfer from Yb to Nd, which is detrimental to the blue emission of Tm.

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