GROWTH AND CHARACTERIZATION OF THE LiGd$_{0.25}$Lu$_{0.75}$F$_4$ CRYSTAL DOPED WITH NEODYMIUM

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Abstract. Mixed crystals based on scheelites type LiLnF$_4$ (Ln = lanthanides, Y) are an alternative in the development materials with better structural features to be doped with light rare earth ions. In this work a LiGd$_{0.232}$Lu$_{0.75}$Nd$_{0.018}$F$_4$ crystal was successfully grown using the Czochralski method in a commercial system with automated diameter control, under a mixed atmosphere of argon and CF$_4$. It was demonstrated that G25L75LF:Nd is an ideal solid solution that can be obtained with good optical quality from its stoichiometric composition. The spectroscopic studies showed that Nd presents larger bandwidth at 792 and 797 nm, which can be suitable to obtain a laser medium for mode-locking purposes.

1. Introduction

Crystals with the general formula LiLnF$_4$ or LnLF are isostructural to LiYF$_4$, which has the scheelite structure with space group $I4_1/a$. These crystals have high chemical stability with good mechanical and thermal properties and, in general, present high solubility to the incorporation of rare earth ions. In addition, as in the case of many fluoride crystals, they present a large transmission range from the ultraviolet (UV) to the infrared (IR), making them suitable for laser operation.

LiLuF$_4$ (LLF) has a congruent melting behavior, and its crystals present good optical quality. Since Lu$^{3+}$ effective radius is 0.977Å for coordination 8 [1], the smallest lanthanide, this matrix is the most compact in the LiLnF$_4$ family (Ln = Eu up to Lu) with lattice parameters: $a = 5.124$ (5) Å and $c = 10.54$ (1) Å [2]. This crystal presents laser action when doped with many lanthanides ions: cerium [3,4], holmium [5], thulium and praseodymium [6], for example. LLF:Nd$^{3+}$ crystals have also been investigated because of ultraviolet optical transitions resultant from 4f$^{n-1}$5d levels [7, 8].

The LiGdF$_4$ (GLF) compound has a strong incongruent melting behavior and, consequently, the growth of optical quality crystals from the melt is more difficult. Laser action has been reported for GLF:Pr and GLF:Nd, although laser performance was limited by the poor quality of the samples [9, 10].

The growth of mixed crystals proved to be a viable alternative in order to obtain crystals with better quality or new properties [11, 12]. Therefore, new laser materials were achieved: Nd:LiLu$_{0.75}$Y$_{0.25}$F$_4$ crystals exhibited a broader emission band compared to Nd:YLF [13], and LiGd$_{0.50}$Y$_{0.47}$Nd$_{0.03}$F$_4$ crystals could be grown with good optical quality [14]. The present paper is the first report of a solid solution crystal grown from the LiGdF$_4$-LiLuF$_4$ system. The LiGd$_{0.232}$Lu$_{0.75}$Nd$_{0.018}$F$_4$ (G25L75LF:Nd) crystal was obtained from its stoichiometric composition, and presented a nearly congruent melting behavior. Characterization regarding its optical properties, composition and lattice parameters was
performed. Optical characterization was focused on absorption; the composition of the crystal was determined using the ICP – OES technique and the lattice parameters of the crystal were calculated from X-ray diffraction patterns.

2. Experimental Setup

The starting materials were prepared from commercially available GdF$_3$ and LuF$_3$ (AC Materials, 99.99%). Commercial LiF (Aldrich, 99.9%) was previously purified using the zone melting technique. The compounds were mixed in the LiGd$_{0.232}$Lu$_{0.75}$Nd$_{0.018}$F$_4$ composition and placed into an open platinum boat, which was inserted in a sealed platinum reactor. The material was synthesized in a reactive atmosphere of HF + Ar.

The single crystal was grown through the Czochralski technique under a high purity CF$_4$ + Ar atmosphere, in a commercial system with automatic diameter control. The crystal was grown with a growth rate of 1 mm/h and a rotation rate of 15 rpm for a [1 0 0]-oriented boule; a seed of LiLuF$_4$ was used to achieve the crystallization process.

X-ray powder diffraction (XRD) analyses were performed at room temperature in a PANalytical MPD 1980 diffractometer. The diffraction patterns were taken in 2θ range from 18 to 70° in step scan mode, with steps of 0.02°, 1 s per point, using CuKα radiation and operating at 40 kV and 40 mA. Three samples were obtained from the top, middle and bottom of the crystal to determine the lattice parameter variation over the length of the boule. The diffraction patterns where treated with the Rietveld Method [15] using the GSAS program to calculate lattice parameters [16]. The rare-earth concentrations were determined by inductive coupled plasma with optical emission spectrometry (ICP-OES, IRIS Thermo Electron, USA). Absorption measurements were performed on a Cary 17D-Olis spectrometer and on a Thermo-Nicholet – 6750 spectrometer for the near and far-infrared regions respectively. Luminescence lifetime measurements were performed at room temperature, the samples were excited by pulsed laser radiation generated by a tunable optical parametric oscillator-infrared (OPO-IR) pumped by a second harmonic of a Q-switched Nd:YAG laser (Brilliant B from Quantel, France). Laser pulses (width = 4ns, frequency = 10 Hz and wavelength = 797 nm) were used to excite the $^4F_{5/2}$ excited state of Nd$^{3+}$. Luminescence lifetime was measured using a digital oscilloscope of 100 MS s$^{-1}$ model TDS from Tektronix interfaced to a microcomputer.

3. Results and discussion

The G25L75LF:Nd single crystal, with a length of 65 mm, a diameter of 20 mm and 65g, is shown in Fig. 1. The numbers on the figure identify the positions where the samples were extracted from to perform X-ray diffraction analyses.

The concentration determined by ICP-OES is shown in Table 1. The data show a wide variation in Gd concentration throughout the crystal. This variation is mostly due to the fact that this solid solution presents its liquidus line in a higher temperature than its solidus line, giving rise to segregation. In addition, the ionic radius of Gd is smaller than that of Nd, inhibiting the incorporation of the latter in favor of Gd ions.

![Fig. 1. The G25L75LF:Nd crystal grown using the Czochralski method.](image-url)
Table 1. Rare earth concentrations determined by ICP-OES.

| Solidified fraction | Gd       | Lu       | Nd       |
|---------------------|----------|----------|----------|
| 0.19                | 16.68(6) | 82.82(4) | 0.498(2) |
| 0.28                | 17.50(5) | 81.95(3) | 0.545(3) |
| 0.36                | 18.54(9) | 80.85(6) | 0.608(3) |
| 0.45                | 19.51(9) | 79.81(7) | 0.673(4) |
| 0.54                | 20.97(6) | 78.26(5) | 0.773(2) |
| 0.64                | 22.91(4) | 76.16(3) | 0.935(3) |

Rare earth segregation coefficients were estimated using the normal solidification equation, represented by Scheel’s law (Equation 1).

\[ C_g = C_0 k (1 - g)^{(k-1)} \]  

(1)

Where \( C_g \) is the dopant concentration in the crystal; \( C_0 \) is the initial dopant concentration in the melt; \( k \) is the segregation coefficient and \( g \) is the solidified fraction. It was determined that Nd segregation coefficient is 0.22(1) (Fig. 2). This value is smaller than expected, since 0.31 and 0.40 are Nd segregation coefficients in LiLuF\(_4\) and LiGdF\(_4\), respectively. The same determination was made for Gd (\( k = 0.61 \)) and Lu (\( k = 1.10 \)) ions. These values reflect the variation of these constituents along the crystal.

![Fig. 2. Distribution of neodymium ions along the G25L75LF:Nd crystal.](image)

The X-ray diffraction patterns obtained for the three assigned samples presented only a single phase, as expected for a single crystal (Fig.3). All reflections from the LiGd\(_{1-x-y}\)Lu\(_x\)Nd\(_y\)F\(_4\) phase can be indexed with the scheelite structure (\( I4_1/a, Z=4 \)). The additional peaks are due to Si, which was added as an internal standard.
Fig. 3. X-ray diffraction patterns of three samples taken from the grown crystal and their respective fitted curves. a) LiGd$_{0.167}$Lu$_{0.828}$Nd$_{0.005}$F$_4$ (sample 1); b) LiGd$_{0.195}$Lu$_{0.798}$Nd$_{0.007}$F$_4$ (sample 3); c) Sample LiGd$_{0.229}$Lu$_{0.762}$Nd$_{0.009}$F$_4$ (sample 6).

Table 2. Lattice parameters calculated from X-ray diffraction patterns.

| Sample | $a$ (Å)        | $c$ (Å)        | Vol. (Å³)    | Rp (%) | Rwp (%) | Goodness of fit |
|--------|----------------|----------------|--------------|--------|---------|-----------------|
| 1      | 5.1416(1)      | 10.6183(2)     | 280.707(8)   | 12.4   | 16.5    | 1.90            |
| 2      | 5.1442(1)      | 10.6314(2)     | 281.339(7)   | 10.6   | 14.4    | 1.69            |
| 3      | 5.1476(1)      | 10.6503(2)     | 282.210(8)   | 11.4   | 15.0    | 1.77            |

The lattice parameters calculated from X-ray diffraction patterns using the Rietveld Method [15] are shown in Table 2. The increase in lattice parameters along the crystal is mainly due to Gd incorporation during the process of crystallization. The data presented in Table 1 show that Gd...
concentration in the beginning of the process is 16.68 At.% and it rose to 22.91 At.% at the last solidified portion. Since the ionic radius of Gd$^{3+}$ is 7.8% larger than that of Lu$^{3+}$ [1], lattice parameters variation is strongly related to Gd content in the LiGd$_{1-x}$Lu$_x$F$_4$ matrix.

The infrared spectrum revealed no contaminants related to OH$^-$ or Me(OH)$_2$ (Me = divalent metals). The absorption bands in 4200 – 3700 cm$^{-1}$ and 2300 – 1800 cm$^{-1}$ are due to Nd transitions. Residual CO$_2$ present in the measurement chamber was detected by the absorption band in 2345 cm$^{-1}$ (Fig. 3). Thus, the CF$_4$ + Ar atmosphere used during growth was suitable for obtaining a crystal free of contamination.

![Graph]

Fig. 3. Absorption coefficient in the infrared of a G25L75LF:Nd sample 66.5 mm thick.

Absorption spectra were obtained in polarizations $\pi$ (E//c) and $\sigma$ (E⊥c) (Fig. 3). It can be observed that emission in the $\pi$ polarization is more efficient and, in general, the most commonly used to obtain laser action. This mechanism occurs when Nd$^{3+}$ levels $^4F_{5/2}$ and $^2H_{9/2}$ are pumped by a diode laser. There is a nonradiative decay to the upper laser transition $^4F_{3/2}$ that decays radiatively to level $^4I_{15/2}$, generating laser action around 1.047 and 1.053 nm.

![Graph]

Fig. 3. $\pi$ and $\sigma$ polarization absorption spectra from a sample with 0.5 mol% Nd.
Spectroscopic studies showed that the G25L75LF:Nd crystal presents intermediate properties when compared to LLF:Nd and GLF:Nd (Table 3). The absorption bandwidth for transitions $^{4}F_{5/2}$, $^{2}H_{3/2}$ and $^{4}F_{3/2}$ were obtained through multi-Lorentzian fittings. It can be observed that bandwidths increased proportionally to Gd content, and there is also some shifting to larger wavelengths. These properties reveal how gadolinium influences spectroscopic properties in this crystal. The lifetime calculated for the $^{4}F_{5/2}$ transition decreased proportionally to Nd content, given that the interactions between Nd ions increase with concentration. This phenomenon is known as concentration quenching [17] and it takes into account the energy transfer from excited Nd$^{3+}$ ions to centers Nd$^{3+}$ - Nd$^{3+}$ ion pairs through a dipole-dipole interaction. Since this process is competitive with luminescence radiation, it results in a decrease in luminescence efficiency and in luminescence lifetime (Table 3).

**Table 3.** Measured $^{4}F_{5/2}$ level lifetime and absorption bandwidth for the samples studied.

| Sample              | Lifetime ($\mu$s) | $\lambda_{\text{Peak}}$ (nm) | bandwidth (nm) |
|---------------------|-------------------|-------------------------------|----------------|
| LiLu$_{0.992}$Nd$_{0.008}$F$_{4}$ |                  | 791.67                        | 1.56           |
|                     |                   | 796.87                        | 0.93           |
|                     |                   | 797.59                        | 1.46           |
|                     |                   | 862.27                        | 2.55           |
| LiGd$_{0.167}$Lu$_{0.828}$Nd$_{0.005}$F$_{4}$ | 511 (1)       | 791.75                        | 1.66           |
|                     |                   | 796.83                        | 1.11           |
|                     |                   | 797.57                        | 1.90           |
|                     |                   | 862.28                        | 2.68           |
| LiGd$_{0.195}$Lu$_{0.798}$Nd$_{0.007}$F$_{4}$ | 496 (1)       | 791.78                        | 1.93           |
|                     |                   | 796.84                        | 1.24           |
|                     |                   | 797.62                        | 1.84           |
|                     |                   | 862.29                        | 2.63           |
| LiGd$_{0.229}$Lu$_{0.762}$Nd$_{0.009}$F$_{4}$ | 480 (1)       | 791.81                        | 2.26           |
|                     |                   | 796.84                        | 1.29           |
|                     |                   | 797.62                        | 1.94           |
|                     |                   | 862.33                        | 2.72           |
| LiGd$_{0.985}$Nd$_{0.015}$F$_{4}$ | 480 (5)        | 792.27                        | 2.47           |
|                     |                   | 796.72                        | 1.20           |
|                     |                   | 797.75                        | 2.27           |
|                     |                   | 862.91                        | 2.67           |
4. Conclusions
It was demonstrated that G25L75LF:Nd is a solid solution that can be obtained with good optical quality from its stoichiometric composition. It presents accentuated Gd segregation that is typical of solid solutions with a lens-type phase diagram. Of the two ions to be incorporated into the crystal during the growth process, Gd$^{3+}$ and Nd$^{3+}$, gadolinium proved more effective, since it has a smaller ionic radius than that of the neodymium ion. A mean Gd segregation coefficient of 0.22 was determined to the G25L75LF crystal. Nevertheless, the spectroscopic studies showed that due to the larger bandwidth of Nd at 792 and 797 nm in this matrix, it can be a suitable crystal to obtain a laser medium for mode-locking purposes, with advantages over Nd:YLF and Nd:LuLiF.

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