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Growth of $LiY_{(1-x-y)}Lu_xNd_yF_4$ crystals for optical applications

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Abstract

Crystals of $LiY_{1-x}Lu_xF_4$ ($x = 9$, 31, 47.3 and 100 mol%) doped with neodymium were successfully grown by the Czochralski technique. The influence of the lutetium concentration in the YLF crystals was verified by measuring the melting temperature, the crystal lattice parameters and the spectroscopic properties. The segregation coefficients measured for yttrium and lutetium are close to one and for neodymium is 0.33, which remained by the Y/Lu ratio unchanged. It was found that there was a proportional increment in the emission bandwidth up to 24% (for $x = 47.3$ mol%) when compared to only neodymium doped YLF without lutetium. This value is comparable to the bandwidth of the $LiLuF_4$: Nd. The characterization of these mixed crystals is presented.

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Keywords: $LiYF_4$; Crystal growth from the melt; Laser crystals

1. Introduction

$LiYF_4$: Nd (YLF : Nd) crystals are widely used for diode-pumped solid-state lasers [1,2]. For such systems it is necessary to produce crystals with high optical quality to support high-density pumping power. When using passive mode locking techniques, Nd-doped crystals with broad emission bands will favor the production of ultra short laser pulses.

The $LiLuF_4$ (LuLF) crystal is the host isostructural to YLF that has the broader bandwidth for neodymium [3]. Although the LuLF has a congruent melting behavior and presents good optical quality, there are drawbacks like the high cost of the lutetium compounds and the small segregation coefficient for neodymium.

In this work the distortion caused by the substitution of part of Y^{3+} sites by an ion having a smaller ionic radius was studied. The codoping with lutetium was a natural choice because this ion does not present optical transition bands in the energy

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gap, so there is no problem with energy transfer between the dopants.

Crystals of $LiY_{1-x-y}Lu_xNd_yF_4$ were grown by the Czochralski method. A proportional increment in the emission bandwidth up to 24% (for $x =$ 47.7 mol%) was found when compared with the Nd-doped YLF. This value is comparable with the bandwidth of the LuLF : Nd. The characterization of these mixed crystals is presented.

2. Experimental procedure

2.1. Crystal preparation

LuF_3, NdF_3, and YF_3 were prepared from pure oxide powders by hydrofluorination at high temperature in a HF atmosphere. The YLF and the LuLF were synthesized in the same atmosphere with compositions of 1 : 1.02 YF_3 : LiF, and 1 : 1 LuF_3 : LiF. LiF powder was zone-refined before it was added to the YF_3 or LuF_3. Zone refining purification was done by a single pass cycle performed along the material at a transverse rate of 7 mm/h. Details of this procedure are described in Ref. [4]. Due to the YLF incongruent melting behavior, a characteristic three-zone bar was usually obtained [5]. The LuLF bar was completely transparent. The purity was of 3N for LiF and rare earth oxides and 4N for Y oxide.

Single crystals were grown by the Czochralski technique under a purified argon atmosphere. The crystal-pulling rate was 1 mm/h for [1 0 0] or [0 0 1]-oriented boules, and 20–25 rpm rotation rates, YLF seeds were used for the codoped crystals. The crystal diameter was controlled visually. $LiY_{1-x-y}Lu_xNd_yF_4$ crystals with $x = 9$, 31, 47.3 and 100 mol% and $y = 2.3$ or 2.7 mol% were grown. Small crystals of good optical quality weighing around 50 g were obtained, except for the LuLF where only a 10 g crystal was obtained. The crystal with 50 mol% Lu was more fragile presenting some fractures on handling.

2.2. Crystal characterization

The variation in the melting temperature related to the addition of lutetium in the YLF crystal melt was monitored by differential thermal analysis. A model 2100 DTA-TGA equipment, from TA Instruments, under a helium atmosphere was utilized. The samples were placed in open platinum crucibles weighing around 50 mg without a reference material. Quantitative analysis were carried out by high-performance liquid chromatography (HPLC) using a liquid chromatograph model 625LC, from Waters Instruments. Microfusions were obtained from a fine YLF : Lu : Nd powder and lithium metaborate, and then dissolved in nitric acid. After evaporation of the acid the precipitate is easily diluted in water. The limpid aqueous solution was utilized to determine the rare-earth concentrations. A shift in the onset temperature was found with the increase of lutetium concentration (Table 1). The linear fitting of the data results in an increase of 1°C in the onset temperature per 12.5 mol% Lu.

The mixed crystals were sectioned transversally to measure the composition over the length of the boule. The rare-earth compositions were determined using a scanning electron microscope (SEM) model XL30 from Philips with an energy-dispersive spectrometer model eDXAUTO from EDAX. As the measurements for neodymium concentration showed a large amount of scattering it was decided to use the concentrations obtained by optical absorption. Then the neodymium segregation coefficients were determined taking into account the maximum of the absorption coefficient (K) with unpolarized light at 805.5 nm (π polarization) or 806 nm (σ polarization) which were obtained from the fitting of the absorption spectra to multiple Lorentzian functions. These bands are transitions of the multiplets $^4F_{3/2}$–$^5H_{9/2}$ and not sensitive to

Table 1
Variation of the melting temperature with lutetium concentration in YLF crystals

Composition	T_{onset} ($\pm$ 1°C)
$LiYF_4$	818
$LiY_{0.943}Lu_{0.044}Nd_{0.013}$	818
$LiY_{0.71}Lu_{0.279}Nd_{0.011}$	821
$LiY_{0.512}Lu_{0.478}Nd_{0.010}$	822
$LiLuF_4$	826

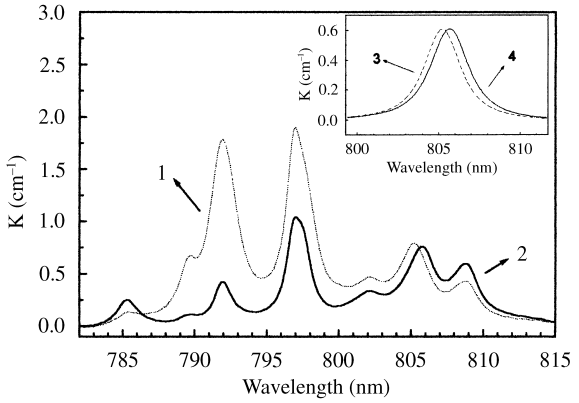

Fig. 1. Neodymium absorption coefficients of the $^4F_{3/2}$–$^5H_{9/2}$ multiplets obtained with unpolarized light for (1) samples with (1 0 0) orientation; and (2) samples with (0 0 1) orientation. The inset shows the resulting Lorentzians corresponding to the Nd absorption coefficients around (3) 805.5 nm; and (4) 806 nm, which are not sensitive to the sample orientation.

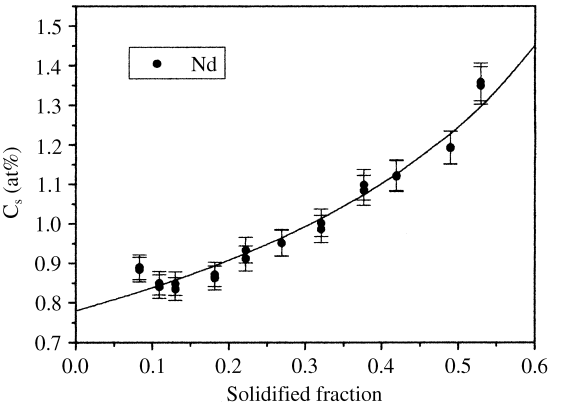

Fig. 2. Distribution of neodymium ions along the $LiY_{0.500}Lu_{0.473}Nd_{0.027}$ crystal considering the absorption coefficient peaks.

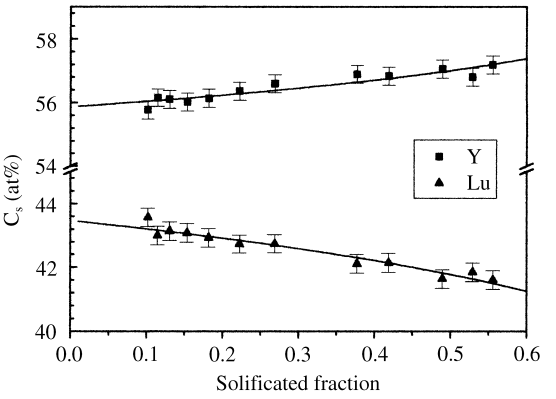

Fig. 3. Distribution of lutetium and yttrium ions along the $LiY_{0.500}Lu_{0.473}Nd_{0.027}$ crystal considering EDS measurements.

polarization (Fig. 1). Four samples have been taken from the top and four from the bottom of the crystals with $x = 9$ and 31 mol% Lu and the crystal with $x = 47.3$ mol% Lu was entirely sectioned. The optical absorption spectra were recorded on a Varian-Cary 17 spectrophotometer.

The concentration in atomic percent can be obtained from

$$C_{Nd}(\text{at\%}) = 100K/\sigma N, \quad (1)$$

where σ is the absorption-peak cross section and N is the Nd concentration (atoms/cm^3). The neodymium concentrations values obtained by EDS were used to determine the mean cross section for each crystal. The segregation coefficients were determined using the well-known normal solidification equation. The fitting for the $LiY_{0.500}Lu_{0.473}Nd_{0.027}$ crystal is presented in Figs. 2 and 3. These results are summarized in Table 2.

It was expected that the presence of an ion with smaller ionic radius in the vicinity of one yttrium site could enhance the volume to be occupied by a neodymium ion, increasing the neodymium segregation. However, the distribution coefficients for neodymium remained unchanged showing that the presence of lutetium did not cause the desired effect.

The segregation coefficients of the heavy rare earth in YLF are very close to 1 and it was expected that for the YLF–LuLF mixture no problems in seeding would be present, but there was an initial rejection of the dopant in the three growth runs. Differently from erbium, thulium and holmium [4] in YLF, the seeding for 31 and 47.3 mol% Lu was dependent more on the crystal rotation and the homogeneity of the melt. Once the seeding was established, the behavior of the distribution of lutetium as expected, was shown to be around 1.

Powder X-ray diffraction (XRD) measurements were carried out in the 2θ range of 18–56° on

Table 2
Absorption cross sections and fitting results for neodymium, lutetium and yttrium distribution in the mixed crystals

Concentration in the melt	$\sigma\ 10^{-20}$ (cm^{-2})	Neodymium		Lutetium		Yttrium	
		C_0 (at%)	K	C_0 (at%)	K	C_0 (at%)	k
$LiY_{0.883}Lu_{0.090}Nd_{0.027}$	1.32 (2)	3.0 (2)	0.30 (2)	5.3 (1)	1.00 (3)	92.9 (1)	1.01 (1)
$LiY_{0.667}Lu_{0.310}Nd_{0.023}$	1.29 (3)	2.2 (1)	0.33 (2)	28.6 (1)	1.03 (1)	70.1 (1)	0.99 (1)
$LiY_{0.500}Lu_{0.473}Nd_{0.027}$	1.19 (3)	2.4 (2)	0.33 (3)	41.1 (2)	1.06 (9)	57.6 (2)	0.97 (1)

Table 3
The values obtained for the lattice parameters, unit-cell volume and density

Sample	Lattice constant (Å)	Volume ($Å^3$)	Density (g/cm)
$LiY_{0.99}Nd_{0.01}F_4$	$a = 5.168$ (1) $c = 10.741$ (2)	286.888 (119)	3.991 (2)
$LiY_{0.936}Lu_{0.053}Nd_{0.011}$	$a = 5.170$ (1) $c = 10.733$ (2)	286.843 (116)	4.098 (2)
$LiY_{0.700}Lu_{0.288}Nd_{0.012}$	$a = 5.156$ (1) $c = 10.694$ (4)	284.292 (239)	4.609 (4)
$LiY_{0.568}Lu_{0.420}Nd_{0.012}$	$a = 5.150$ (1) $c = 10.659$ (3)	282.653 (160)	4.902 (3)
$LiLuF_4$	$a = 5.130$ (1) $c = 10.550$ (3)	277.668 (0.181)	6.169 (4)

a Phillips diffractometer, type PW1710 operated at 40 kV and 40 mA. Silicon was used as an internal standard to assess the solubilities of the dopants into the YLF. The determination of the lattice constants were performed using the peaks in the 2θ range, after making corrections for errors caused by misalignments of the apparatus and sample displacement. Lattice parameters were calculated using a least-squares refinement [6] (see Table 3), and found to decrease linearly with the Lu concentration (Fig. 4). The relations of the lattice parameter with the Lu concentration are expressed by the following equations:

$$a(\text{Å}) = 5.169\ (2)–0.0040\ (3) \times (\text{mol\%}), \quad (2)$$

$$b(\text{Å}) = 10.742\ (2)–0.0193\ (3) \times (\text{mol\%}). \quad (3)$$

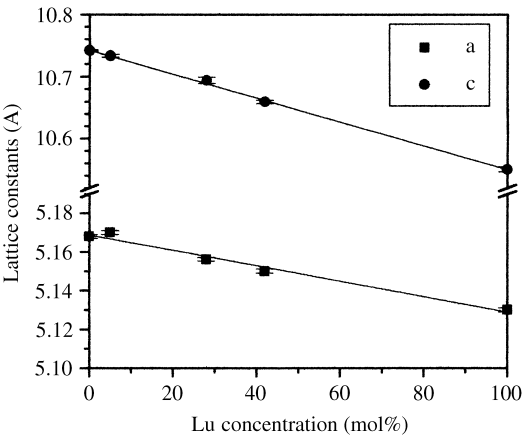

Fig. 4. Dependence of the lattice constants with Lu concentration.

A diode laser beam at 792 nm, pumped the crystals for emission measurements. The light beam chopped at 40 Hz was focused on the sample with a 10-cm focal length lens. The π polarized 1047 nm emission was detected with a Ge detector and was analyzed with a high resolution 1 m Spex monochromator.

The spectroscopic studies showed that there were no significant changes in the emission cross

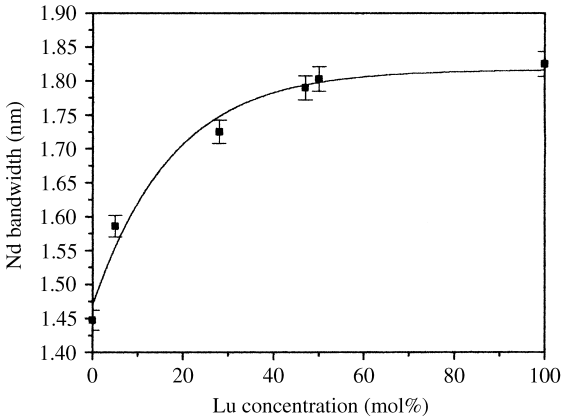

Fig. 5. Measured spectral bandwidths at the 1047-nm emission, for Nd : LuYLF crystals with different Lu concentrations.

sections at 1047 nm, but there was an enlargement of emission bandwidths with the increase of lutetium concentration in the crystals. The emission bandwidth for 42 mol% of Lu is almost the same emission bandwidth as that of LuLF and was broadened approximately by 24% compared with that of the Nd : YLF (Fig. 5). Thus, Nd : Lu : YLF crystals with this composition can be used for mode locking purposes having advantages over Nd : YLF [7].

3. Conclusions

The incorporation of Nd in crystals of YLF codoped with Lu was investigated. It was demonstrated that it is possible to grow crystals of $LiY_{(1-x-y)}Lu_xNd_yF_4$ with Lu concentrations up to 50 mol%, maintaining the YLF characteristic to form solid solution with the heavy rare earth.

The Lu segregation coefficient in YLF, once the seeding was established, was found to be around 1, as expected. The seeding for 31 and 47.3 mol% Lu was highly dependent on the crystal rotation and the homogeneity of the melt. The neodymium segregation coefficient remained unchanged, but the interaction with the lattice, due to the decrease in the lattice parameters and consequently a larger electron–phonon interaction, resulted in an enlargement of its emission bandwidth.

The physical properties of these crystals, as melting temperature and lattice parameters changed linearly with the Lu concentration as expected, since the LuLF is isostructural to YLF. The major advantage in the utilization of the Nd : YLuLF crystals is that one can obtain crystals with higher Nd concentration having the same bandwidth as in the LuLF, with lower cost.

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