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Growth and characterization of $LiGd_{1-x-y}Y_xNd_yF_4$ single crystals

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Abstract

$LiGdF_4$ (GLF) crystals co-doped with yttrium concentrations up to 50 mol% and neodymium have been grown by the Czochralski method, under argon and CF_4 atmospheres. The best conditions for crystal growth were achieved using carbon-free chemicals and CF_4 atmosphere, and one good-quality crystal of $LiGd_{1-x-y}Y_xNd_yF_4$ ($x = 50$ mol%, $y = 2.7$ mol%) was obtained. The segregation coefficients measured for gadolinium and yttrium were close to 1 and for neodymium is 0.40, independent of the Gd/Y ratio. From the point of view of the application of these crystals as laser media there is the possibility to use two crystals with advantage over the Nd:YLF (Nd:YLF) the Nd:GLF and the Nd:GLF co-doped with 50 mol% Y. The characterization of these crystals is presented.

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Keywords: $LiYF_4$; $LiGdF_4$; Crystal growth from the melt; Laser crystals

1. Introduction

$LiGdF_4$ (GLF) is isostructural to $LiYF_4$ (YLF), which has the scheelite structure, space group $I4_{1a}$. As it is a positive uniaxial crystal, the natural birefringence compensates the birefringence induced by heating during the laser operation, and this crystal can be used for high-power lasers when doped with rare-earth ions. The site symmetry for the lanthanide ion is S_4. This site presents no inversion symmetry, so the mixture of the terms with even parity in the wavefunctions of the multiplet 4f makes the optical transitions permitted and of suitable intensity for laser emission. Nevertheless, crystals with good optical quality have not yet been reported [1–3]. A new application for Eu^{3+}-doped gadolinium fluorides is as a luminescent material: in Eu^{3+}:GLF an efficient photon cascade emission through down-conversion with a visible quantum efficiency of 190% has been reported. Elimination of non-radiative losses by improvement of material

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synthesis can result in a visible quantum efficiency of 200% [4].

Laser action has been reported for neodymium [5] and praseodymium [6,7] in GLF, but the laser performance was limited by the poor quality of the samples. In the case of Pr : GLF in continuous wave operation, this resulted in a fading of the laser. The fading was probably caused by the presence of lead ions incorporated into the crystal during growth, since lead fluoride was used as an oxygen scavenger. Up-conversion processes also impose drastic limitations in the maximum achievable population inversion for Nd : YLF or GLF laser media used as amplifier or Q-switched systems [8]. For both crystals, the maximum inverted population is of the order of one-tenth of the total population, so higher Nd concentrations allow for higher gain coefficients.

The motivation for this work was to investigate the possibility of obtaining optical-quality GLF crystals doped with higher concentrations of neodymium. The growth of GLF crystals is difficult because of a strong incongruent melting behavior. The LiF–GdF_3 phase diagram presents two invariant points: a eutectic at 25 mol% GdF_3 and 700°C, and a peritectic at 34 mol% GdF_3 and 750°C [9]. GLF is a unique intermediary compound [1,10]. The addition of yttrium was done to investigate its influence on the incongruent behavior and on the neodymium segregation coefficient. As shown previously, it is possible to obtain solid solutions for the system $LiYF_4$–$LiLuF_4$ [11], where both compounds are nearly congruent, so that the mixture of a nearly congruent and with an incongruent compound was studied.

In this work, crystals of $LiGd_{1-x-y}Y_xNd_yF_4$ were grown by the Czochralski technique using argon or a reactive atmosphere (CF_4) to obtain crystals with better optical quality. The influence of these atmospheres on the crystal quality and also the influence of the yttrium concentration in the GLF crystals were investigated.

2. Experimental procedure

The raw materials were prepared in two ways: (1) GdF_3, NdF_3, and YF_3 were prepared from pure oxide powders (Alpha–Johnson Matthey, 99.99% or better) 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–GdF_3 mixtures, with or without YF_3, were melted using an open platinum boat in the same atmosphere, with a composition of 0.66 LiF : 0.34 GdF_3. LiF powder (Alpha–Johnson Matthey, 99.9%) was zone-refined before it was added to the GdF_3; and (2) GdF_3, YF_3, NdF_3 and LiF pure commercial powders (rare metallic 99.99% or better), were added in the crucible and melted in CF_4 atmosphere prior to the growth.

Single crystals were grown by the Czochralski technique under high-purity argon or CF_4 atmosphere. The crystal-pulling rates were 0.6–0.8 mm/h for $\langle 1\,0\,0\rangle$-oriented boules, with 8–10 rpm rotation rates. $LiGd_{1-x-y}Y_xNd_yF_4$ crystals with concentrations in the melt of $x = 0$ and 28 mol% and $y = 0$ and 2 mol% were grown in argon atmosphere (99.999%). $LiGd_{1-x-y}Y_xNd_yF_4$ crystals with concentrations in the melt of $x = 0.29$ and 47.3 mol% and $y = 1$ and 2.7 mol% were grown in CF_4 atmosphere (99.9999%). The crystals henceforth will be designated always by their nominal concentrations.

Powder X-ray diffraction (XRD) measurements for the lattice parameter determinations were carried out on a Rigaku diffractometer, model RINT, operated at 40 kV and 40 mA in the 2θ range of 15–80°. The crystals were sectioned longitudinally to measure the composition over the length of the boule. The rare-earth compositions were determined using an electron microprobe analyzer (EPMA) model JXA-8900R from JEOL.

Lifetime measurements were performed at room temperature, by exciting the spectroscopic samples with an OPO laser, pumped by a second harmonic of a pulsed Nd : YAG laser. The polarized Nd emission was analyzed using a 1-m Spex spectrometer, an S-1 photo-multiplier and a boxcar averager. The absorption and emission spectra were obtained using a 4W GaAlAs diode laser (SDL2382P1) for the pumping excitation at 792 nm.

3. Results and discussion

GdF_3 synthesized from the oxide powder presented an external gray layer, due to carbon, which probably resulted from the organic phase used in the oxide purification process. Calcination of the material at 1000°C in an oxygen atmosphere yielded no substantial reduction in the amount of carbon. The synthesis of the starting material resulted in a black layer of carbon on the bar surface which could be only partially cleaned.

Crystals grown in argon atmosphere, with raw materials prepared in HF atmosphere, were very difficult to obtain. The melt surface presented the same carbon scum, making the seeding process sometimes impossible. The carbon layer produces a supercooling of the melt near the seed, and the temperature must be increased by up to 20°C to start the seeding. After the carbon was consumed, the temperature had to be decreased rapidly to continue the crystallization process, or the crystal detached from the melt. The initial part of the seed was always composed of a polycrystalline mass and the crystal detached very easily from the seed. The crystals possessed good optical quality only for small diameters [12]. Cones of macro-bubbles and planes of micro-bubbles parallel to the growth axis appeared when the diameter increased.

A noticeable improvement of the crystal quality was achieved by co-doping with 28 mol% Y. The seeding was easy but the melt did not wet the seed and promptly detached from the crystal. Instead of a better appearance, the crystal presented inclusions when the diameter increased.

Crystals grown in a CF_4 atmosphere, with the compounds in the fluoride form, presented no problems in seeding. The better chemical quality, the absence of carbon, and the reactive atmosphere were responsible for this improvement (Figs. 1 and 2).

Nevertheless, the un-doped and the 29 mol% yttrium-doped crystals also presented the same kind of inclusions, as can be seen in Fig. 3. Inspection by an optical microscope revealed three types of defects: (A) randomly distributed macro-defects, similar to bubbles; (B) some planes of micro-defects parallel to the (0 1 1) plane were present in crystals co-doped with yttrium (Fig. 3a) and (C) a cloud

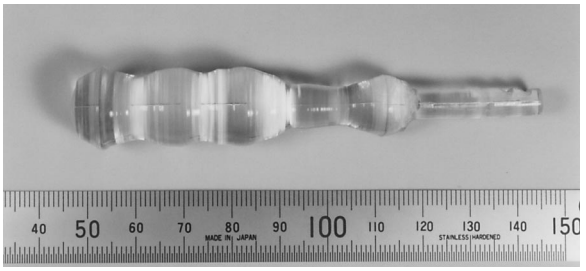

Fig. 1. Crystal of $LiGd_{1-x-y}Y_xNd_yF_4$ ($x = 0.29$, $y = 0.01$) grown in CF_4 atmosphere using carbon-free starting material.

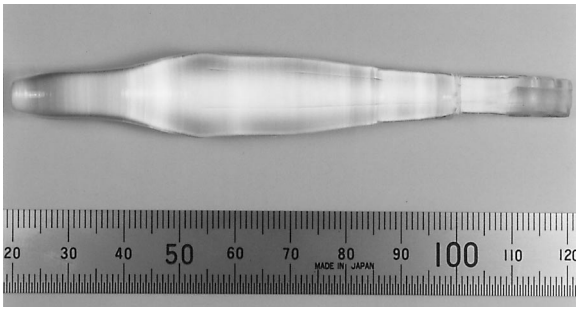

Fig. 2. Crystal of $LiGd_{1-x-y}Y_xNd_yF_4$ ($x = 0.473$, $y = 0.027$) grown in CF_4 atmosphere using carbon-free starting material.

composed of many planes of submicroscopic defects parallel to the (1 1 0) plane. The macro-defects were seen to be elongated when inspected using the microscope, and were in larger quantity in the center of the crystal (Figs. 3a and b). These inclusions seemed to be filled with a segregated foreign phase (Figs. 3c and d). Other authors [13,14] have observed the formation of voids in YLF crystals when the growth rate is too fast compared with the time required for any segregated component to diffuse away from the boundary near the liquid–solid interface. Therefore, a more detailed inspection of these defects is necessary, as are new experiments optimizing the pulling and rotation rates.

On increasing the amount of yttrium to 47.3 mol%, a crystal of good quality with fine planes of micro-defects near the seed that disappeared as the diameter increased was obtained. The crystal was free of scattering centers under

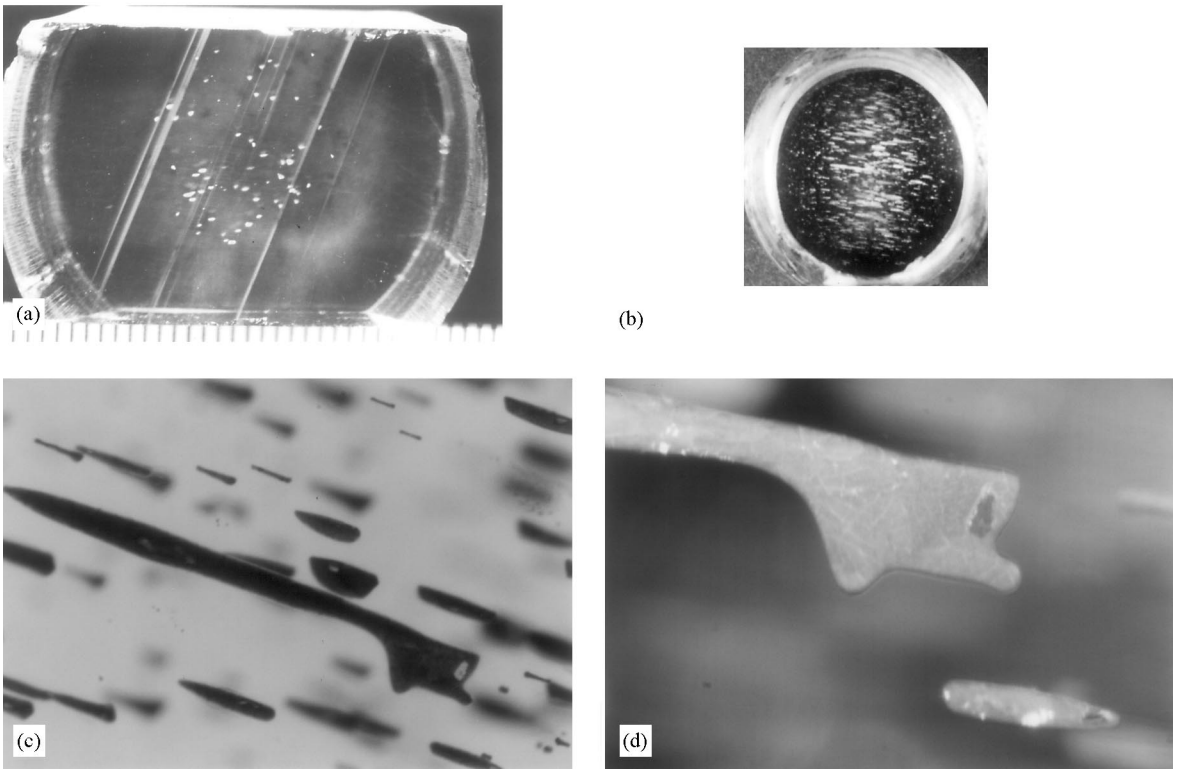

Fig. 3. (a) $LiGd_{1-x-y}Y_xNd_yF_4$ ($x = 0.29$, $y = 0.01$) crystal showing inclusions, planes of micro-defects and a cloud formed by planes of submicroscopic defects; (b) $LiGd_{1-x}Nd_xF_4$ ($x = 0.027$) crystal showing only inclusions; (c) and (d) details of an inclusion in a $LiGd_{1-x}Nd_xF_4$ ($x = 0.027$) crystal observed by optical microscopy.

inspection with a He–Ne laser (Fig. 4). The co-doping with yttrium apparently decreased the liquid viscosity, making the convective flow in the melt appropriate to the diffusion of the major component, that is LiF, and neodymium.

As the solidified fraction in all grown crystals was not greater than 10%, the rare-earth segregation coefficients were obtained from the mean value of the concentrations in the crystals. For gadolinium and yttrium, the segregation coefficients were very close to 1, and for neodymium, it was 0.4. The segregation coefficient for neodymium is half of the only value reported in the literature [1].

The lattice parameters obtained by XRD are presented in Table 1. As expected, the lattice parameters decreased for yttrium-co-doped crystals. Further DTA measurements, to determine possible alterations in the melting behavior of the crystals,

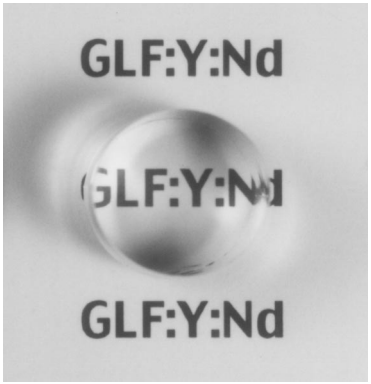

Fig. 4. Transparency of the $LiGd_{1-x-y}Y_xNd_yF_4$ ($x = 0.473$, $y = 0.027$) crystal.

related to the YLF–GLF solid solutions, are presently in progress.

The variations of the lattice parameters with the Y concentration designated in mol% are expressed

by the following linear equations:

$$a(\text{Å}) = 5.215(1)–0.5(2)10^{-3}\ Y, \quad (1)$$

$$b(\text{Å}) = 10.972(5)–2.4(1)10^{-3}\ Y. \quad (2)$$

The spectroscopic studies showed that the emission and absorption spectra of $LiGd_{1-x-y}Y_xNd_yF_4$ crystals are similar to those of Nd:YLF. Thus, the most suitable wavelengths for diode-laser pumping are 797 and 792 nm. The absorption and emission cross-sections for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions (π and σ polarizations) were obtained by using the method of McCumber [15] (Table 2). The measured $^4F_{3/2}$ level lifetimes increased proportionally to the Y content and the emission cross sections increased as well. The bandwidths decreased with the addition of Y, but surprisingly the measured bandwidth for Nd:GLF has the emission linewidth broadened by 39% compared with that of the Nd:YLF sample, under this high-intensity diode laser pumping. This value is also higher than the value obtained for Nd:LuLiF crystals [11] which had been supposed to present the broadest bandwidth for neodymium.

Table 1
Lattice parameters and density

Sample	Lattice constant (Å)	Density (g/cm^3)
$LiGdF_4$	$a = 5.214$ (1) $c = 10.965$ (3)	5.351 (3)
$LiGd_{0.70}Y_{0.29}Nd_{0.01}F_4$	$a = 5.202$ (1) $c = 10.903$ (3)	4.947 (3)
$LiGd_{0.50}Y_{0.473}Nd_{0.027}F_4$	$a = 5.192$ (3) $c = 10.854$ (2)	4.647 (2)
$LiYF_4$	$a = 5.167$ (1) $c = 10.729$ (1)	3.984 (1)

4. Summary

In conclusion, it was shown that the use of CF_4 and carbon-free starting materials resulted in an improvement in the growth of $LiGd_{1-x-y}Y_xNd_yF_4$ crystals. It is also possible that with good-quality chemicals and a CF_4 atmosphere during the crystal growth, the incongruent behavior of the systems $LiF–GdF_3$ and $LiF–GdF_3–YF_3$ can be shifted towards stoichiometry as demonstrated for the system $LiF–YF_3$ [16], and the LiF excess can be minimized. Further DTA studies can test this hypothesis. Nevertheless, further experiments should be performed to obtain crystals with good quality, by changing the growth parameters (pulling and rotation rates), melt composition and having a more suitable diameter control.

Nd:GLF crystals seem to be the most promising laser media for mode-locking purposes, with advantages over Nd:YLF and Nd:LuLiF if the optical quality is improved. Crystals with optical quality were obtained only by co-doping with 47.3 mol% Y and this new crystal also presented a bandwidth broadening of 9% when compared

Table 2
Measured $^4F_{3/2}$ level lifetime, calculated peak absorption and emission cross-sections (for σ and/or π polarization), and emission bandwidth for the samples studied

Crystal	Lifetime (10^{-6} s)	Cross-section (absorption) ($10^{-19}/cm^{-2}$)	Cross-section (emission) ($10^{-19}/cm^{-2}$)	Bandwidth (nm)
$LiGd_{0.973}Nd_{0.027}F_4$	480 (5)	π: 0.73 (7)	π: 2.22 (22) σ: 1.69 (17)	2.06 (21)
$LiGd_{0.70}Y_{0.29}Nd_{0.01}F_4$	510 (5)	π: 1.34 (13)	π : 2.55 (26) σ: 1.78 (18)	1.61 (16)
$LiGd_{0.50}Y_{0.473}Nd_{0.027}F_4$	520 (5)	π: 1.13 (11)	π: 2.02 (20) σ: 1.46 (15)	1.56 (16)
$LiY_{0.977}Nd_{0.023}F_4$	525 (5)	π: 1.09 (11)	π: 2.23 (22) σ: 1.67 (17)	1.48 (15)

with Nd:YLF. Laser testing of these crystals is necessary to check these new possibilities.

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References

[1] A. Pham, J. Lefaucheur, G. Lutts, B. Chai, J. Nicholls, OSA Proc. Adv. Solid State Lasers 15 (1993) 178.
[2] I.A. Ivanova, A.M. Morozov, M.A. Petrova, I.G. Podkolzina, P.P. Feofilov, Inorg. Mater. 11 (1975) 1868.
[3] B.M. Walklyn, J. Mater. Sci. 10 (1975) 1487.
[4] R.T. Wegh, H. Donker, K.D. Oskam, A. Meijerink, J. Lumin. 82 (1999) 93.
[5] X.X. Zhang, A.B. Villaverde, M. Bass, B.H.T. Chai, Appl. Phys. 74 (2) (1993) 790.
[6] T. Danger, T. Sandrock, E. Heumann, G. Huber, B.H.T. Chai, Appl. Phys. B 57 (1993) 239.
[7] T. Sandrock, T. Danger, E. Heumann, G. Huber, B.H.T. Chai, Appl. Phys. B 58 (1994) 149.
[8] L.C. Courrol, E.P. Maldonado, L. Gomes, N.D. Vieira Jr., I.M. Ranieri, S.P. Morato, Opt. Mater. 14 (2000) 81.
[9] I.M. Ranieri, S.P. Morato, in preparation.
[10] R.E. Thoma, G.D. Brunton, R.A. Penneman, T.K. Keenan, Inorg. Chem. 9 (1970) 1096.
[11] I.M. Ranieri, S.P. Morato, L.C. Courrol, H.M. Shihomatsu, A.H.A. Bressiani, N.M.P. Moraes, J. Crystal Growth 209/4 (2000) 906.
[12] E.P. Maldonado, I.M. Ranieri, S.P. Morato, N.D. Vieira Jr., in: C.R. Pollock, W.R. Bosenberg (Eds.), Trends, Optics and Photonics Series, TOPS, Advanced Solid State Lasers, Vol. 10, Optical Society of America, Washington, DC, 1997, pp. 444–447.
[13] B. Cockaine, K.H. Lloyd, J.S. Abell, I.R. Harris, J. Crystal Growth 36 (1976) 205.
[14] P. Rogin, J. Hulliger, J. Crystal Growth 172 (1997) 200.
[15] D.E. McCumber, Phys. Rev. 136 (1964) 954.
[16] R.C. Pastor, M. Robinson, W.M. Akutagawa, Mater. Res. Bull. 10 (1975) 501.