ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 67–71

Journal of ALLOYS AND COMPOUNDS

Growth by liquid phase epitaxy and characterization of Nd:$YLiF_4$ layers

L. Douysset-Bloch[a], B. Ferrand[a,*], M. Couchaud[a], L. Fulbert[a], M.F. Joubert[b], G. Chadeyron[b], B. Jacquier[b]

[a]*LETI (CEA-Technologies Avancées) DOPT/SCMDO, 17 avenue des Martyrs, 38054 Grenoble Cedex 09, France*
[b]*LPCML, UMR 5620, CNRS Université Lyon I, 69622 Villeurbanne, France*

Abstract

We report the growth of Nd:$YLiF_4$ layers using liquid phase epitaxy. Fluorescence decays were measured at different temperatures, 1.05 μm laser performances have been investigated and photon avalanche up-conversion has been observed up to 60 K. © 1998 Elsevier Science S.A.

Keywords: Liquid phase epitaxy; YLF; Laser waveguide; Photon avalanche up-conversion

1. Introduction

Several recent demonstrations of up-conversion pumped solid state lasers have renewed the interest in excitation mechanisms that result in emission at wavelengths shorter than that of the pump light. Efficient up-conversion is possible in rare earth doped materials with metastable, intermediate levels that can act as a storage reservoir for pump energy. This metastable level exists for Nd^{3+} ions in $YLiF_4$ compounds. The photon avalanche mechanism was previously demonstrated in the bulk leading to a strong emission at 413 nm under CW excitation at 603.6 nm and up-conversion lasing was obtained up to 40 K [1]. Moreover, the development of rare earth doped crystalline waveguides, which combine high emission cross sections of crystal with confinement and guiding effects, is promising for future short wavelength microsources.

With this purpose, we have studied the growth by liquid phase epitaxy (LPE) and the characterization of Nd:$YLiF_4$ layers for application as up-conversion laser waveguides. Active layers have been grown on $YLiF_4$ oriented (100) and (110) substrates. Fluorescence decays were measured at different temperatures, 1.05 μm laser performances have been investigated and photon avalanche up-conversion has been observed up to 60 K.

2. Liquid phase epitaxy growth

The phase diagram of the LiF–YF_3 system shows that $YLiF_4$ (YLF) can be grown from melt solutions with compositions ranging in a molar ratio (LiF/YF_3) from 51:49 to 80:20 [2]. Whereas bulk crystals are usually grown at nearly stoichiometric compositions, a larger excess of LiF has been used in LPE experiments. Contrary to the LPE of oxide layers, YLF layers have been grown in an inert atmosphere. The LPE apparatus was equipped with two chambers, an upper chamber for the outgassing and a lower chamber for the growth, constituted by a resistively heated vertical tube furnace. The growth process was about the same as for oxide growth, but before introducing the substrate in the growth chamber, an outgassing in the upper part of the furnace was necessary in order to eliminate oxygen pollution. A platinum crucible was used and put in around the middle of the growth chamber in order to minimize the vertical temperature gradient. The growth was performed in a quartz chamber in an inert argon atmosphere (Fig. 1).

Active YLF layers doped with neodymium (1 to 3 at. %) were grown horizontally on (100) or (110) oriented YLF substrates from LiF rich melts in a molar ratio (LiF/YF_3) around 70:30. The growth temperature was near 730°C. Even for very low supersaturation (1°C), the deposition rates were larger than 3 $\mu m\ mn^{-1}$. So in order to avoid some nucleations on the substrate, it was necessary to control the growth temperature with a high precision better than 0.5°C. Before the growth, the melt was superheated at about 800°C in order to ensure complete melting. When the

*Corresponding author. Tel.: +33 47 6884047; fax: +33 47 6885157; e-mail: ferrand@chartreuse.cea.fr

PII: S0925-8388(98)00275-8

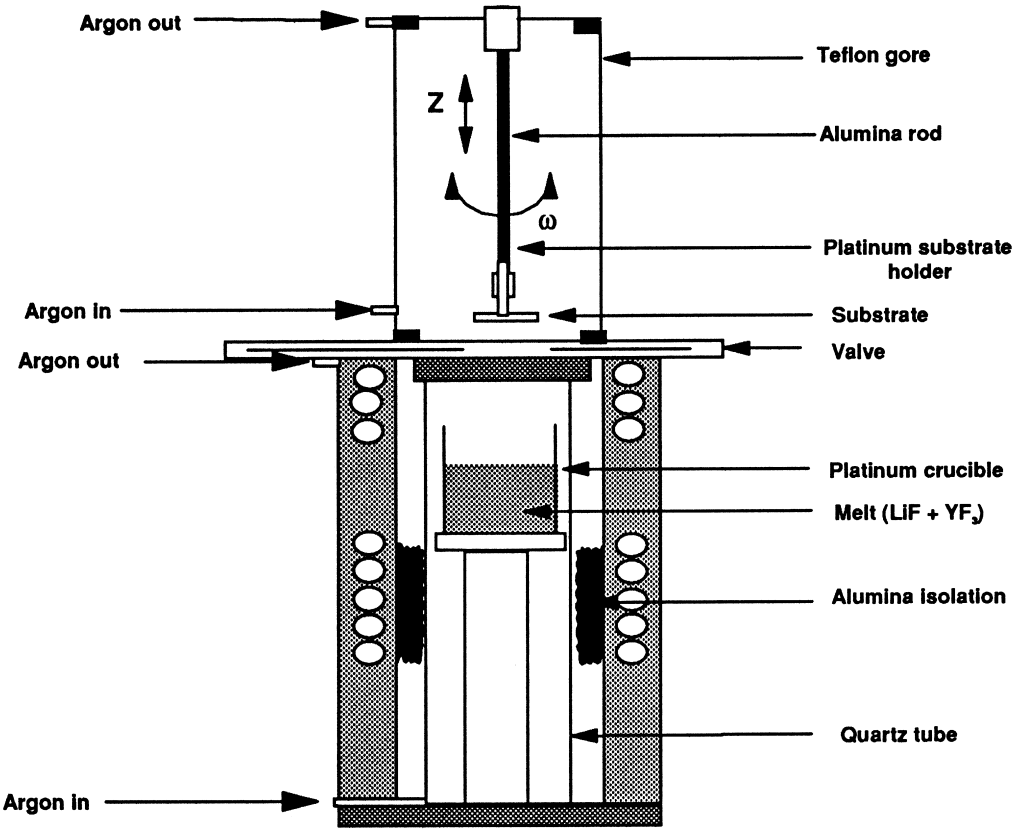

Fig. 1. Liquid phase epitaxy apparatus used for the growth of YLF layers.

layers were extracted out from the furnace, some contamination by oxygen could happen. In this case, formation of oxyfluoride was rapidly generated and the growth of YLF layers became impossible. As demonstrated by Rogin and Hulliger [3], we have also used gadolinium substitutions in order to increase the refractive index of the layers.

3. Layer characterization

Generally the layers exhibited some surface roughness, caused by an excess of LiF precipitated. Indeed upon extraction from the melt, a liquid LiF rich layer of a few micron thickness could not be completely removed. During cooling this layer crystallized, resulting in precipitation of excess LiF on the surface. Smooth faces were obtained by mechanical polishing. The layer quality was investigated by X-ray analysis and optical microscopy. The presence of the LiF phase, after the growth, was confirmed. After polishing only single crystal YLF phase remained on the substrate. The lattice mismatch was measured in the (100) plane. Due to increase of the lattice parameter by neodymium (or gadolinium), a Δa of -2×10^{-3} Å was obtained for a 3% neodymium doped YLF layer.

Spectroscopic measurements have been made in the visible and in the near infra-red range. In Fig. 2 typical absorption spectra of Nd:YLF layers for two different polarisations are presented. The behavior was about the same as for bulk crystals. We have confirmed the possibility to obtain by LPE, YLF material with high Nd concentration (up to 3 at. %). In order to fabricate waveguides, we have investigated the variation of the refractive index with rare earth substitutions. Refractive index measurements have been made on bulk crystals (undoped and with 1.5 at. % Nd) and have confirmed a slight increase in the index with neodymium. Direct measurements on the layers by M-lines technique are now in progress.

4. Lifetime measurements

Lifetimes of $^4F_{3/2}$, $^2P_{3/2}$ and $^4D_{3/2}$ Nd^{3+} levels, measured in a 100 μm thick Nd:$YLiF_4$ layer (with 3 at. % Nd^{3+} concentration) are given in Table 1. They have been recorded at 10, 56 and 260 K under selective pulsed laser excitation. $^4F_{3/2}$ population exhibits exponential decay with a time constant decreasing from 580 μs at 10 K to 280 μs at 260 K. It was observed that the $^4D_{3/2}$ fluorescence decay is exponential (t=1.3 μs) and independent of temperature and active ion concentration, as already mentioned in the literature for bulk $YLiF_4$: Nd^{3+} crystals [4]. The $^2P_{3/2}$ fluorescence decay is nonexponential at short time and the time constant of the exponential component decreases from 17 μs at 10 K to 11 μs at 260 K.

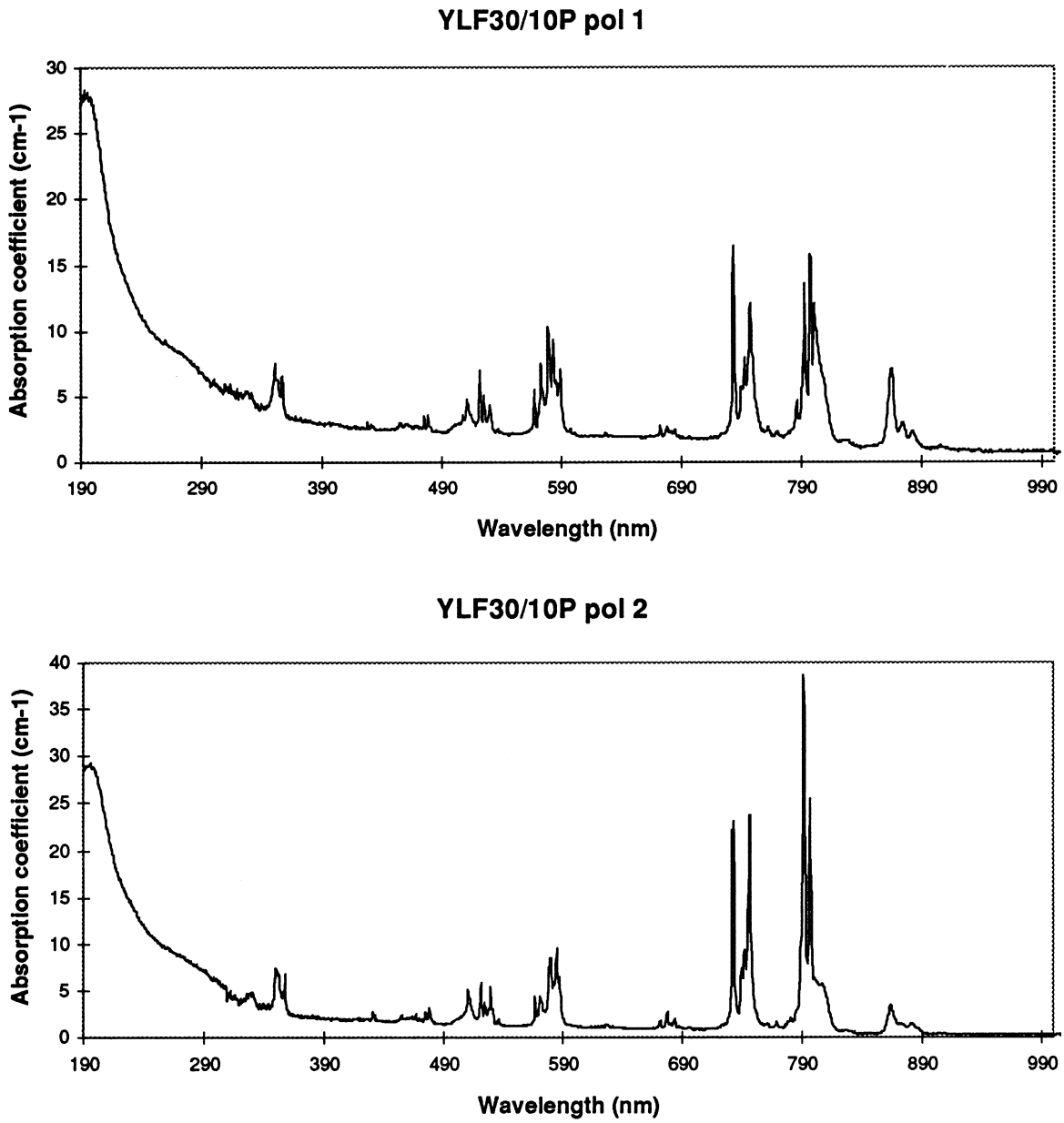

Fig. 2. Typical absorption spectra of a 3 at % Nd:YLF layers (sample YLF30/10P) for the two polarisations: σ (pol 1) and π (pol 2).

All these results are consistent with previously reported Nd^{3+} fluorescence decays in 0.1, 1, 1.5 and 2.2 at. % doped bulk $YLiF_4$ [4–7].

Table 1
Experimental values of luminescence decay times (in μs) for three emitting J states of Nd^{3+} ions in $YLiF_4$:Nd^{3+} (3 at %) as a function of temperature

		T (K)		
		10	56	260
J state	$^4F_{3/2}$	580	350	280
	$^2P_{3/2}$	17	15	11
	$^4D_{3/2}$	1.3	1.6	1.1

5. Photon avalanche up-conversion

In this section, we report the experimental power dependence of the transmitted laser intensity and of the violet up-converted emission intensity in the 1, 1.5 and 3% Nd doped $YLiF_4$ layers. The experimental equipment we used was described previously [8] and the excitation laser beam was sent perpendicular to the layer plane. We first recorded the time evolution of the violet fluorescence intensity and of the transmitted laser light during illumination of the sample. The laser beam, fixed at 603.6 nm, was resonant with the excited state absorption $^4F_{3/2} \rightarrow {}^4D_{3/2}$. The selected fluorescence was the intense $^2P_{3/2} \rightarrow {}^4I_{11/2}$ line located at 413 nm. Some of these experimental

transients recorded at 40 K in the 1% Nd doped layer are drawn on Fig. 3. With an excitation power of 36 mW, the up-converted fluorescence signal is very small and exhibits a relatively short risetime (see Fig. 3a). At higher excitation power, the behavior is quite different. Indeed, Fig. 3b shows that, for an excitation power of 40 mW, the establishment of the fluorescence is much longer and quite linear. Then by increasing the excitation density, the rise of the violet fluorescence intensity shortens and presents a bending point (see Fig. 3c).

We have reported on Fig. 4 the evolution of the stationary fluorescence emission and its time of establishment versus the excitation power in the 1% Nd doped layer. At the threshold power (40 mW corresponding to an excitation density of 3.9 kW cm^{-2}), the violet fluorescence signal increases by orders of magnitude and its time of establishment has a value of 107 ms which is much longer than the $^4F_{3/2}$ metastable state lifetime (500 μs). This value decreases from 107 ms for the 1% Nd doped layer to 38 ms for the 3% Nd doped layer. A maximum absorption of 3% is observed in the 60 μm thick 1% Nd doped layer for an excitation power of 230 mW.

In Fig. 5 the power dependence of the violet stationary fluorescence for different Nd concentrations is shown. The curves recorded for the 1 and 1.5% Nd doped layers are quite similar. However, the intensity of the violet fluorescence is slightly higher for the 1.5% Nd doped layer than for the 1% Nd doped layer. The threshold power increases with concentration from 40 mW for the 1% doped layer to 102 mW for the 3% Nd doped layer.

All this behavior is characteristic of an avalanche process and is analogous to the one previously described for $YLiF_4$:Nd^{3+} bulk crystals [1,8,9].

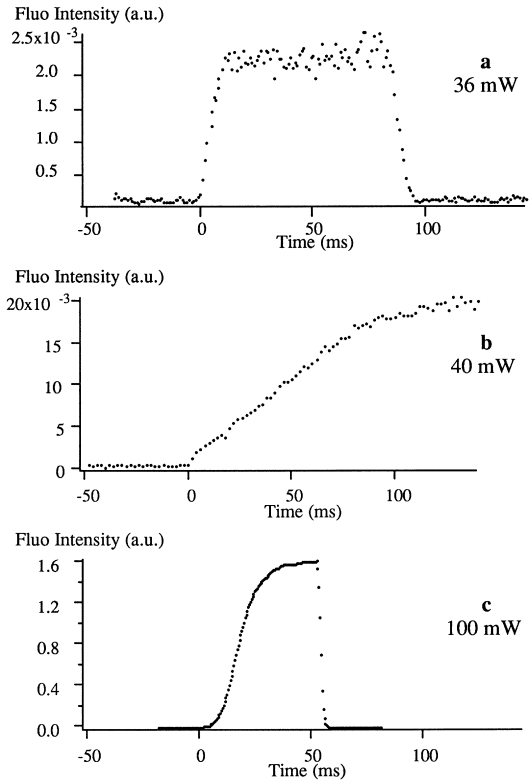

Fig. 3. Experimental anti-Stokes fluorescence (413 nm) intensity versus time during laser (603.6 nm) illumination at 40 K with an excitation power of (a) 36 mW; (b) 40 mW; (c) 100 mW focused on the sample with a 50 mm lens.

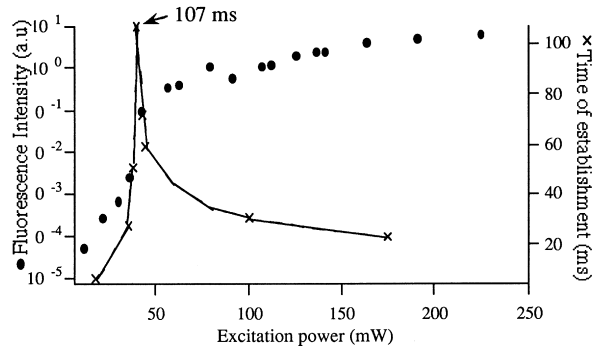

Fig. 4. Stationary intensity and time of establishment of the violet fluorescence emission at 413 nm versus the excitation power in $YLiF_4$: 1 at % Nd^{3+} at 40 K.

6. Laser performances at 1.05 μm

Preliminary laser experiments at 1.05 μm have been performed on some neodymium doped YLF layers in waveguide configuration with Ti:Sapphire pumping, (Fig. 6). We have tested a 40 μm thick layer with 3 at. % Nd concentration. This layer was cut in samples of 5 mm long and the endfaces perpendicular to the layer were polished. Using two plane mirrors butted directly on the polished endfaces of the layer to form the laser cavity and a 1.6% transmission output mirror, laser operation was achieved. Absorbed power threshold of 120 mW and slope efficiency of 30% were obtained for this 3 at. % Nd doped sample (Fig. 7). We have now to optimize the properties of the layers (dopant concentration, thickness, length, refractive

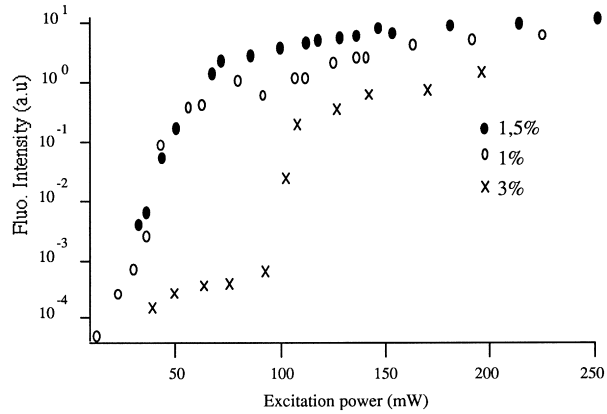

Fig. 5. Stationary fluorescence intensity at 413 nm versus the excitation power in $YLiF_4$: 1, 1.5 and 3 at % Nd^{3+} at 40 K.

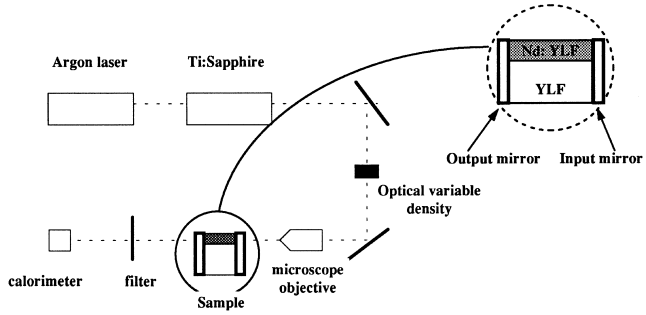

Fig. 6. Experimental set-up for YLF laser tests.

index difference...) in order to increase the laser performances. Layers with gadolinium substitutions will also be tested soon.

7. Conclusion

We have demonstrated the growth of rare earth doped YLF layers using liquid phase epitaxy from a solution with excess LiF. The layers were of good optical quality after polishing of the surface. Fluorescence decays were measured at different temperatures and photon avalanche up-conversion has been observed up to 60 K. Laser performances have been investigated at 1.05 μm.

Up-conversion laser experiments under photon avalanche pumping in these Nd^{3+}:YLF layers are in progress. Moreover, in order to achieve room temperature efficient waveguide up-conversion lasers, the growth of the rare earth doped layers must be investigated in more detail. In addition, we are expecting blue laser action in thulium doped waveguides.

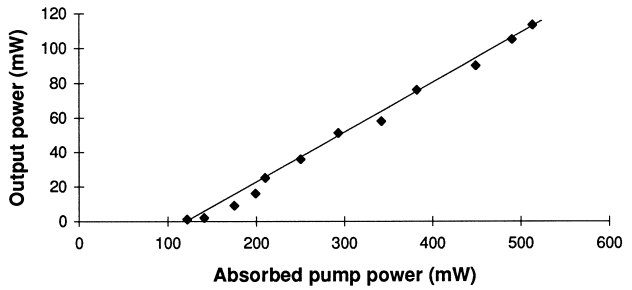

Fig. 7. Output power versus absorbed pump power for a Ti:Sapphire pumped Nd:YLF layer.

References

[1] W. Lenth, R.M. Macfarlane, J. Lumin. 45 (1990) 346.
[2] R.E. Thoma, C.F. Weaver, H.A. Friedman, H. Insley, L.A. Morris, H.A. Yakel, J. Phys. Chem. 65 (1961) 1096.
[3] P. Rogin, J. Hulliger, J. Cryst. Growth 179 (1997) 551.
[4] M. Malinowski, B. Jacquier, M. Bouazaoui, M.F. Joubert, C. Linares, Phys. Rev. B 41 (1990) 31.
[5] B. Jacquier, M. Malinowski, M.F. Joubert, R.M. Macfarlane, J. Lumin. 45 (1990) 357.
[6] A.L. Harmer, A. Linz, D.R. Gabbe, J. Phys. Chem. Solids 30 (1969) 1483.
[7] A.A. Kaminskii, V.S. Mironov, S.N. Bagaev, G. Boulon, N. Djeu, Phys. Status Solidi 185 (1994) 487.
[8] M.F. Joubert, S. Guy, B. Jacquier, Phys. Rev. B 48 (1993) 10031.
[9] M.F. Joubert, S. Guy, B. Jacquier, C. Linarés, Opt. Mat. 4 (1994) 43.