



ELSEVIER

15 January 1998

OPTICS  
COMMUNICATIONS

Optics Communications 146 (1998) 163–166

# Efficient and stable pulsed laser operation of Ce:LiLuF<sub>4</sub> around 308 nm

P. Rambaldi <sup>a</sup>, R. Moncorgé <sup>b,1</sup>, J.P. Wolf <sup>a</sup>, C. Pédrini <sup>b</sup>, J.Y. Gesland <sup>c</sup><sup>a</sup> *Laboratoire de Spectroscopie Ionique et Moléculaire (LASIM), UMR 5579 CNRS, Université de Lyon 1, F-69622 Villeurbanne, France*<sup>b</sup> *Laboratoire de Physico-Chimie des Matériaux Luminescents, UMR 5620 CNRS, Université de Lyon 1, F-69622 Villeurbanne, France*<sup>c</sup> *Université du Maine – Cristallogénèse, URA 807 CNRS, F-72085 Le Mans, France*

Received 4 June 1997; accepted 9 September 1997

## Abstract

Very efficient and stable laser operation of Ce<sup>3+</sup>-doped LiLuF<sub>4</sub> (Ce:LLF) single crystals longitudinally pumped with a Ce:LiSAF pulsed laser is demonstrated for the first time. At the peak operating wavelength of 308 nm, laser thresholds as low as 250 mJ cm<sup>-2</sup> and laser slope efficiencies and output energies as high as 55% and 2 mJ, respectively, have been obtained at a pulse repetition rate of 20 Hz. © 1998 Elsevier Science B.V.

*Keywords:* Solid-state lasers; UV lasers

## 1. Introduction:

As emphasized in a recent article [1], there is an increasing interest on lasers operating in the near UV (200–350 nm) and more particularly on those based on solid state materials and which can be tuned continuously in a certain wavelength domain. Indeed, these lasers will likely become very important tools for many applications. They already find applications in the fields of medicine and biology (cornea shaping, angioplasty, measurements of ADN sequences, biological micromanipulation) for which one can take advantage of the broad-band laser emissions for production of ultra-short laser pulses. They are also more and more used in environmental sciences [2]. Some of them were recently used in LIDAR systems to make measurements and analyze atmospheric molecules related with the ozone layer question and for various climatic problems [3].

Now, to obtain an efficient and reliable UV tunable solid state laser, one of the most attractive solutions is to take advantage of the interconfigurational optical transitions 5d ↔ 4f of some rare-earth ions such as Ce<sup>3+</sup> in crystalline environments such as fluorides and oxides [1,4–8]. In fact, it is probably the only solution which can give a good-quality laser beam, which allows for easy control of the spectral linewidth of the laser and which allows multi-wavelength operation from only one oscillator. However, because of serious problems of solarization, induced by the formation of transitory or permanent color centers due to absorptions of the pump radiation and/or the laser emission from the emitting state of the rare-earth active ion (excited-state absorption phenomenon) [7,9], this type of solid state laser has been discarded for many years; it was only recently, with Ce<sup>3+</sup>-doped colquiriite crystals LiCaAlF<sub>6</sub> (LiCAF) then LiSrAlF<sub>6</sub> (LiSAF) discovered by Dubinskii et al. [10], that these laser systems have been reconsidered. In particular it has been evidenced that spectacular improvements in the laser performance of materials could be obtained, first from a very careful study of their spectroscopic properties [11] such as polarized excited-state absorption (ESA) but also by using adequate pump wavelength and polarization conditions and by codoping the

<sup>1</sup> Present address: Laboratoire de Spectroscopie Atomique, Université de Caen – ISMRA – UPRESA 6084 CNRS, 6 Blvd Marechal Juin, 14050 Caen, France.

crystals by charge compensating ions [7]. It has been shown that solarization problems could be further significantly reduced and laser performance increased by exposing the laser crystals simultaneously to the pump radiation of a frequency-quadruple YAG:Nd laser at 266 nm and to the residual green radiation at 532 nm of the same frequency doubled laser. Now, laser efficiencies as high as 45% with respect to the UV pump radiation and of about 10% with respect to the IR radiation of the Nd:YAG laser can be obtained, which is excellent, especially when considering the good quality of the resulting laser beam. The wavelength tunability domain of Ce:LiSAF remains modest, between 285 and 300 nm, but already allows numerous applications.

The present paper is devoted to the description of the laser performance of another  $\text{Ce}^{3+}$ -doped fluoride crystal,  $\text{LiLuF}_4$  (or LLF). This crystal as well as its isotype  $\text{YLiF}_4$  (or YLF) were already considered a number of times in the past both for their spectroscopic and their laser properties, the most important results being the following: (i) peak laser wavelength of 311 nm, threshold pump energy of about 5 mJ and laser slope efficiency of about 18.5% (for an output mirror transmission of 90%) in the case of Ce:LLF, for transverse pumping with randomly polarized radiation at 248 nm of a KrF excimer laser; (ii) better laser performance and photochemical stability for Ce:LLF than for Ce:YLF; and (iii) appearance of color center absorptions above 325 nm due to KrF excimer laser pumping. In contrast to Ce:LiSAF, Ce:YLF and Ce:LLF lasers are pumped with an excimer laser so that they cannot be fully considered as all solid-state tunable UV lasers.

## 2. Experimental conditions

The crystals used were grown by using the Czochralski technique, using a seed oriented along the [110] crystallographic direction. They were pulled from  $\text{Li}(\text{Y}$  or  $\text{Lu})_{0.99}\text{Ce}_{0.01}\text{F}_4$  melts (i.e., 1%  $\text{Ce}^{3+}$ ) but due to the low segregation coefficient of Ce in these materials, the actual cerium concentration is probably between 0.1% and 0.2%  $\text{Ce}^{3+}$ . Chemical analyses are in progress to clarify this point. Samples were cut in the form of platelets with polished and parallel faces. The  $c$  crystallographic axis is contained in the plane of the faces and the Ce:YLF and Ce:LLF platelets used for the laser experiments are 3.65 mm thick.

These platelets were pumped longitudinally with the aid of a home-made horizontally polarized and tunable Ce:LiSAF pulsed laser operating at around 290 nm. This pump laser was already described in detail elsewhere [3]; it consists of two mirrors and an intracavity prism, the Ce:LiSAF crystal being pumped longitudinally with frequency quadrupled radiation at 266 nm of a Nd:YAG pulsed laser (pulse duration equal to 4 ns). The platelets

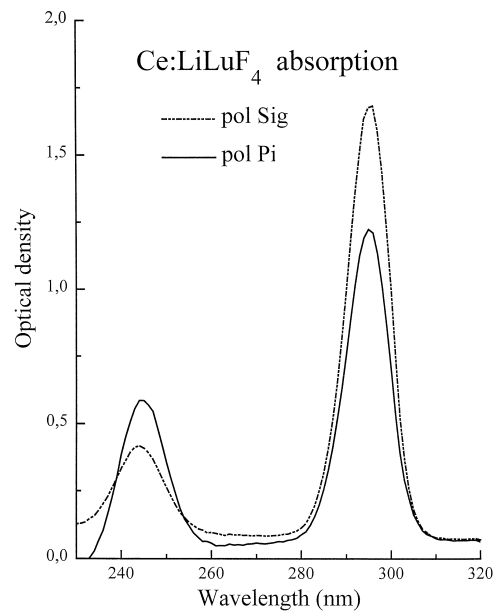


Fig. 1. Room-temperature  $\sigma$  (*sig*) and  $\pi$  (*pi*) polarized absorption spectra of Ce:LiLuF<sub>4</sub> (sample thickness 1 mm).

could be pumped with their  $c$ -axis placed horizontally or vertically, which corresponds to  $\pi$  and  $\sigma$  polarization conditions, respectively. According to the absorption spectra reported in Fig. 1 (the optical density  $D$  is related to the absorption coefficient  $\alpha$  by the expression  $D \ln 10 = \alpha x$ ,  $x$  being the sample thickness), Ce:LLF absorbs more in  $\sigma$  than in  $\pi$  polarization around 290 nm, and more than 99% of the excitation pump energy at this wavelength was absorbed in the 3.65 mm thick laser crystals. The same result is found in the case of Ce:YLF, in good agreement with Ref. [1]. The laser crystals were placed inside a laser cavity made of two flat-flat mirrors separated by about 25 cm. The input mirror was a dichroic mirror which was highly reflective ( $R > 99\%$ ) between 300 and 370 nm and highly transmissive ( $T > 95\%$ ) at the pump wavelength. The pump beam was focused behind the crystal with a spherical lens of 18.5 cm focal length placed at about 5 cm from the input dichroic mirror, and the pump beam spot diameter onto the crystal was of the order of 0.5 mm.

## 3. Experimental results and analysis

The best laser performance was obtained with Ce:LLF, thus confirming the results already obtained in the past [1]. The best laser performance was also obtained when the  $c$  axis of the crystals was placed horizontally, that is for  $\pi$  polarized excitation and emission conditions. According to the absorption spectra reported in Fig. 1 and the emission spectra reported in Fig. 2, these conditions correspond, in principle, to a lower absorption coefficient and a lower

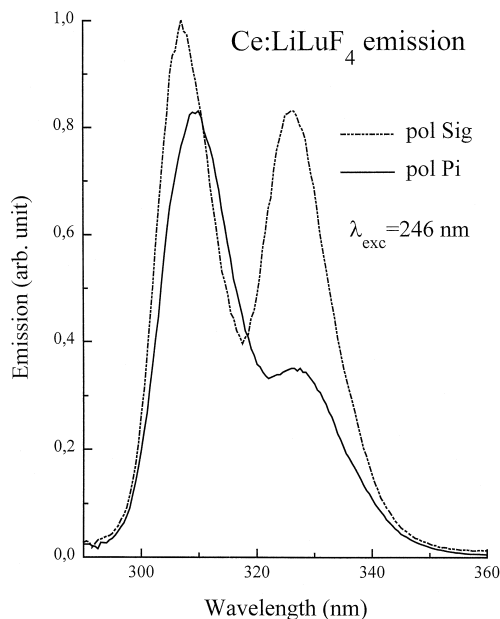


Fig. 2. Room-temperature  $\sigma$  (*sig*) and  $\pi$  (*pi*) polarized emission spectra of Ce:LiLuF<sub>4</sub>.

emission intensity than in  $\sigma$  polarization. It did lase under  $\sigma$  polarization conditions but with much lower performance. The choice of the polarization and the wavelength conditions (290 nm with a Ce:LiSAF laser or 248 nm with a KrF laser) thus appears to be very important, as in the case of Ce-doped colquiriites. This is certainly related to excited-state absorption and UV-induced solarization loss phenomena. We do not discard either reabsorption effects since our crystals were probably too thick to lase at the shortest wavelengths. These reabsorption effects probably occurred even more severely in the experiments reported in Ref. [1]. Indeed, the authors worked with a 1 cm long laser rod; on the other hand, they reported emission spectra in which the short-wavelength emission peak occurs around 311 nm (in fact the wavelength at which their crystal lased) instead of 307–311 nm, depending on the polarization (see Fig. 2).

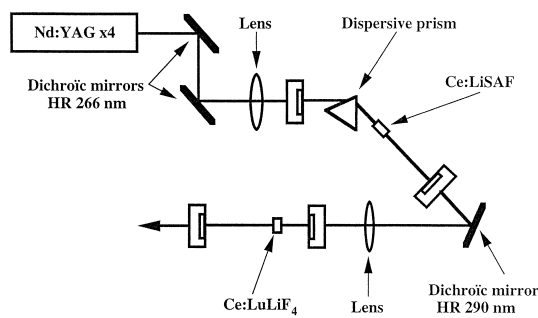


Fig. 3. Laser set-up.

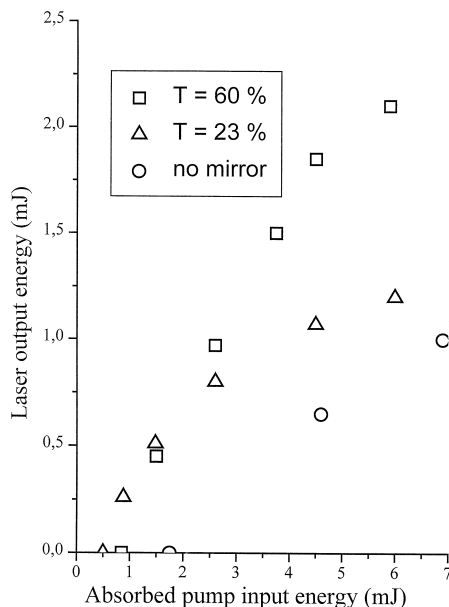


Fig. 4. Input/output laser curves of Ce:LiLuF<sub>4</sub> for two output coupler transmissions and without any cavity mirrors.

Fig. 3 shows a schematic of the overall experimental set-up and Fig. 4 the input–output laser curves obtained with Ce:LLF for  $\pi$  polarized pumping and by using output couplers with transmissions of about 23–60% around 308 nm. The best performance was thus obtained with the one having about 60% transmission. The laser threshold was very low, of the order of 0.5 mJ for the  $T = 23\%$  output coupler, which corresponds to about  $250 \text{ mJ cm}^{-2}$ , and of 0.85 mJ for the  $T = 60\%$  output coupler. This is much lower than reported previously. This threshold was so low that the laser could be operated without cavity mirrors (see Fig. 4): laser oscillation occurred between the sample faces above a threshold of about 1.8 mJ ( $900 \text{ mJ cm}^{-2}$ ). The laser efficiency was very high with a maximum value, with respect to the input absorbed energy, of about 55%. This is the highest efficiency ever reported for such a UV solid state laser. Tuning was possible by misaligning the laser crystal and inserting a quartz (Suprasil 1) prism inside the cavity. The laser wavelength could be tuned between 307.6 and 313.5 nm and between 324 and 328.5 nm, so around the two emission peaks. The laser linewidth at half maximum was typically 0.35 nm.

To have more insight into these laser results, we have tried to use the values of the laser thresholds and of the laser slope efficiencies obtained with the different output couplers to have an idea of the nature and amount of losses due to the laser crystal, knowing that [12]:

$$\rho_{\text{diff}}^a = \frac{h\nu_p}{h\nu_L} \eta_p \frac{\sigma_e - \sigma_{\text{esa}}}{\sigma_e} \frac{T}{T + L + 2(\sigma_{\text{esa}}/\sigma_e)A_g}, \quad (1)$$

and

$$E_{\text{th}}^{\text{a}} = \frac{\pi h \nu_{\text{p}} (\bar{\omega}_{\text{p}}^2 + \bar{\omega}_{\text{c}}^2)}{4 \eta_{\text{p}} (\sigma_{\text{e}} - \sigma_{\text{esa}})} \frac{\tau_{\text{p}}}{\tau_{\text{f}} [1 - \exp(-\tau_{\text{p}}/\tau_{\text{f}})]} \times (T + L + 2 A_{\text{g}}), \quad (2)$$

where  $\sigma_{\text{e}}$  and  $\sigma_{\text{esa}}$  are the stimulated emission and the excited-state absorption cross-sections at the laser frequency  $\nu_{\text{L}}$ , respectively,  $A_{\text{g}}$  is the ground state absorption (GSA) per pass in the crystal,  $\eta_{\text{p}}$  is the pump efficiency,  $T$  is the transmission of the output coupler and  $L$  the round trip intracavity losses other than GSA.  $\tau_{\text{p}} = 4$  ns and  $\tau_{\text{f}} = 40$  ns [1] are the pump pulse duration and the fluorescence lifetime, respectively.

According to expression (1), for 290 nm pumping and 308 nm lasing, the quantum limit for the differential slope efficiency should be equal to about 94%. Assuming  $\eta_{\text{p}} = 1$  and  $\sigma_{\text{esa}} = 0$ , which is probably optimistic, and using our highest slope efficiency of 55% for  $T = 60\%$  output transmission, losses  $L$  of about 42% can be estimated. This is much higher than the simple Fresnel reflection losses. These round-trip reflection losses on the crystal faces were measured separately and estimated to be about 25%.

Let us now consider the expression (2) for the absorbed pump energy at the laser thresholds. Using the above given threshold values, it is found, without particular assumptions, that  $L + 2 A_{\text{g}} \approx 45\%$ . Knowing that the round-trip reflection losses on the crystal faces are of the order of 25%, this might indicate single pass reabsorption losses  $A_{\text{g}} \approx 20\%$ . The thickness of the laser crystal being equal to 3.65 mm, this means an absorption coefficient around 308 nm, the laser wavelength, of about  $0.6 \text{ cm}^{-1}$ . Considering the absorption spectra of Ce:LiLuF<sub>4</sub> reported in Fig. 1 for a 1-mm-thick sample, this result is quite possible.

Consequently, though losses due to excited-state absorptions at the pump (reduction of  $\eta_{\text{p}}$ ) and at the laser ( $\sigma_{\text{esa}}$  term) wavelengths, and due to color-center induced residual absorption cannot be disregarded, especially on the longer-wavelength side of the emission spectrum, the losses due to reabsorption might be the most important effect.

#### 4. Conclusions

A significant improvement of the laser performance of Ce:LiLuF<sub>4</sub> is found by pumping in its lowest absorption

band around 290 nm. The studied crystal seems to be more resistant than Ce:LiSAF. Indeed, it could support pump energy densities of about  $4 \text{ J cm}^{-2}$  without damage nor apparent solarization effect, whereas damage usually occurred around  $1 \text{ J cm}^{-2}$  with our Ce:LiSAF samples. In addition, the thermal effects in Ce:LiLuF<sub>4</sub> also seem more reduced than in Ce:LiSAF. Thus, Ce:LiLuF<sub>4</sub> is a very attractive laser material. Lasing could not be obtained, however, over its whole emission domain, only around the peaks, between about 307.5 and 313.5 nm and between 324 and 328.5 nm. This means that further improvements can be expected by working first with thinner crystals or with less doped crystals to reduce reabsorption losses, then by addressing more specifically the excited-state absorption processes and the solarization effects which we did not see by eye but which certainly exist since they have been already evidenced in the past [1].

#### References

- [1] N. Sarukura, M.A. Dubinskii, Z. Liu, V.V. Semashko, A.K. Naumov, S.L. Koableva, R.Y. Abdulsabirov, K. Edamatsu, Y. Suzuki, T. Itoh, Y. Segawa, IEEE J. Quantum Electron. QE 1 (1995) 792, and references therein.
- [2] E.V. Browell, in: Advanced Solid State Lasers, OSA Tech. Digest (Opt. Soc. Am., Washington, DC, 1995), paper MA1, p. 2.
- [3] P. Rambaldi, M. Douard, J.P. Wolf, Appl. Phys. B 61 (1995) 117.
- [4] K.H. Yang, J.A. Deluca, Appl. Phys. Lett. 31 (1977) 594.
- [5] D.J. Erlich, P.F. Moulton, R.M. Osgood Jr., Optics Lett. 4 (1979) 184.
- [6] D.J. Erlich, P.F. Moulton, R.M. Osgood Jr., Optics Lett. 5 (1980) 339.
- [7] A.J. Bayramian, C.D. Marshall, J.H. Wu, J.A. Speth, S.A. Payne, G.J. Quarles, V. Castillo, in: S.A. Payne, C. Pollock (Eds.), OSA TOPS on Advanced Solid-State Lasers, 1996, vol. 1, p. 60, and references therein.
- [8] J.L. Pinto, L. Esterowitz, G.J. Quarles, Electron. Lett. 31 (1995) 2009.
- [9] D.S. Hamilton, in: Tunable Solid State Lasers, Springer, Berlin, 1985, p. 80.
- [10] M.A. Dubinskii, V.V. Semashko, A.K. Naumov, R.Yu. Abdulsabirov, S.L. Korableva, J. Mod. Phys. 40 (1993) 1.
- [11] C.D. Marshall, J.A. Speth, S.A. Payne, W.F. Krupke, G.J. Quarles, V. Castillo, B.H.T. Chai, J. Opt. Soc. Am. B 11 (10) (1994) 2054.
- [12] S.A. Payne, L.L. Chase, H.W. Newkirk, L.K. Smith, W.F. Krupke, IEEE J. Quantum Electron. QE-24 (1988) 2243.