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Journal of Crystal Growth 217 (2000) 151–156

JOURNAL OF **CRYSTAL
GROWTH**

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Crystal growth of Ce:LiLuF₄ for optical applications

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Received 4 April 2000; accepted 10 April 2000

Communicated by M. Schieber

Abstract

High-quality Ce:LiLuF₄ (Ce:LLF) crystals were grown by the Czochralski technique using CF₄ as reactive atmosphere. The segregation coefficient of Ce³⁺ was determined to be 0.066 (3). No changes in the lattice parameters due to the presence of the Ce³⁺ in the lattice were observed. Laser action in the ultraviolet region was obtained by pumping this active medium with a KrF excimer laser in 248 nm. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 81.10; 42.70.H; 78.47

Keywords: LiLuF₄; Crystal growth; Laser crystals; UV laser

1. Introduction

LiLuF₄ (LLF) crystals are isostructural to LiYF₄, they have a congruent melting behavior, and present good optical quality. The lutetium effective ionic radius for coordination number 8 is 0.977 Å [1], the smallest of the lanthanides, so this matrix is the most compact in the LiREF₄ family (RE = Eu to Lu), having lattice parameters: $a = 5.124$ (5) Å and $c = 10.54$ (1) Å [2]. When doped with cerium ions (ionic radius of 1.143 Å),

these crystals exhibit six broad absorption bands in 130, 186, 196, 206, 244 and 292 nm, due to an inter-configurational optical transition 5d \leftrightarrow 4f. Excitation of these bands gives rise to two broad emission bands at 309 and 328 nm that are used for laser generation.

Cerium-doped fluoride crystals including LuLiF₄ (LLF) [3,4] and LiCaAlF₄ [5,6] have been identified as efficient and convenient ultraviolet (UV) solid-state laser media. In particular, Ce:LLF crystals have a wider potential tunability in the UV spectral region from 305 to 340 nm [7], which is attractive for the spectroscopy of wide band-gap semiconductors such as GaN used for blue laser diodes [8]. Other applications are in medicine, biology and environmental sciences where the use of ultra-short pulses is necessary, requiring a broad-band laser emission.

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Improvement of the laser performance of cerium-doped fluorides and oxides can be achieved with proper dopant concentration to minimize losses by polarized excited-state absorption (ESA) and solarization effects. The ratio between the cerium and lutetium ionic radii in this case has the maximum value among the rare-earth ions, 1.17. In view of the fact that low concentrations of Ce^{3+} are required, lattice distortions due to the difference of ionic radius are minimized. Another advantage is the LiLuF_4 congruent melting behavior requiring only a mass compensation of the LiF fluoride vaporization.

As reported previously, the growth of optically clear fluoride single crystals depends not only on the growth process, but also on the purity of the starting materials and on the oxygen complex free atmosphere during the process [9–12]. Oxygen-related impurities have absorption bands in the VUV and can act as radiation traps that interfere in the Ce^{3+} transfer mechanisms, constituting a source of losses during the laser generation. In this work, high optical-quality $\text{Ce}:\text{LuLiF}_4$ crystals have been grown by the Czochralski method under CF_4 atmosphere. The cerium segregation coefficient, ultraviolet and infrared spectra, and lattice parameters were measured. Laser generation and tunability were investigated using this active medium.

2. Experimental

Crystal growth was performed in a vacuum-tight Czochralski system equipped with an automatic diameter control system. The resistive heater and thermal insulators were made of high-purity graphite. The starting material was prepared from commercially available LiF (> 99.99%, Rare Metallic Co., Ltd.), CeF_3 (99.9%, Rare Metallic Co., Ltd.) and LuF_3 (99.999%, AC Materials, Inc.). The starting material was mixed prior to the growth run with composition 1 mol% LiF -enriched from the stoichiometric one and conditioned in a platinum crucible. The Ce^{3+} concentration in the starting materials was 1 mol%. The growth run started after a thermal treatment of the material at high vacuum (10^{-4} Torr) from room temperature up to approx-

imately 700°C in a period of 12 h. Then the system was filled with high-purity CF_4 gas (99.9999%) and the material heated up to melting point. The crystals were grown with a pulling rate of 1 mm/h and a rotation rate of 15 rpm for $[100]$ -oriented boules.

Powder X-ray diffraction (XRD) measurements for 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 crystal samples were sectioned transversally in four locations to measure the composition over the length of the boule. The rare-earth composition was determined by inductively coupled plasma technique. An absorption spectrum was measured in the range 120–230 nm with a model 789A VUV spectrometer from McPherson from S.I. Corp. In the range 200–330 nm, a JASCO model V-530 spectrometer was used. The fluorescence was recorded between 290 and 400 nm with a spectrofluorimeter, JASCO model FP-750.

3. Results and discussion

Clear crystals as shown in Figs. 1 and 2 were grown, with typical dimensions 18 mm in diameter and 50 mm in length. The crystals presented no inclusions, scattering centers or cracks, although there was sometimes a segregation of a foreign phase in the end of the boule, as can be seen in Fig. 2.

Taking five samples along the crystal growth axis the uniformity of Ce^{3+} -doping distribution along the crystal was inspected. The distribution coefficient of Ce^{3+} was estimated as 0.066 (3) by fitting the experimental data with the well-known normal freezing equation (Fig. 2). This value is approximately one-third of that determined for $\text{Ce}:\text{YLF}$ crystals [9]. However, the scattering in the concentration data is large and new measurements using electron microprobe analysis and crystalline samples are necessary.

The lattice parameters of a and c are almost independent of the solidification fraction along the crystal as can be seen in Fig. 3. As both the nominal concentration and the Ce^{3+} segregation coefficient were low, the amount of cerium in the crystal was not sufficient to introduce significant macroscopic

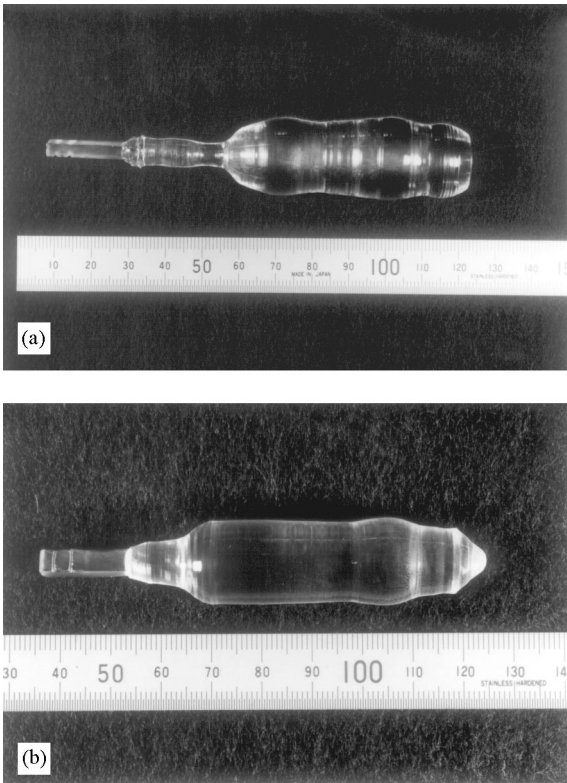


Fig. 1. (a) Undoped LLF, and (b) Ce:LLF crystal grown under CF_4 atmosphere.

alterations. The mean values obtained for the lattice parameters were $a = 5.127(1) \text{ \AA}$ and $c = 10.546(1) \text{ \AA}$. These values are in accordance with those cited in the literature.

The optical absorption of an undoped LLF and a Ce:LLF sample, and Ce^{3+} emission spectra, obtained by excitation at 248 nm, are presented in Figs. 4 and 5. The undoped LLF crystal showed no absorption bands, and the VUV absorption edge is around 130 nm. This value is smaller than the value of 160 nm cited in the literature [13], probably due to the superior starting material and growth atmosphere purity. The broad absorption bands exhibited in the Ce:LLF crystal are due to the $5d \leftrightarrow 4f$ intraconfigurational transitions. The absorption bands at 206, 244 and 292 nm can be used for laser pumping with the fifth harmonic of an Nd:YAG laser (212 nm), a KrF excimer laser ($\lambda = 248 \text{ nm}$) or

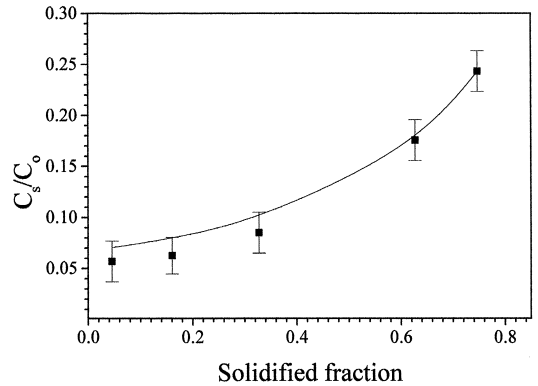


Fig. 2. Distribution of cerium in a Ce:LLF along the growth crystal.

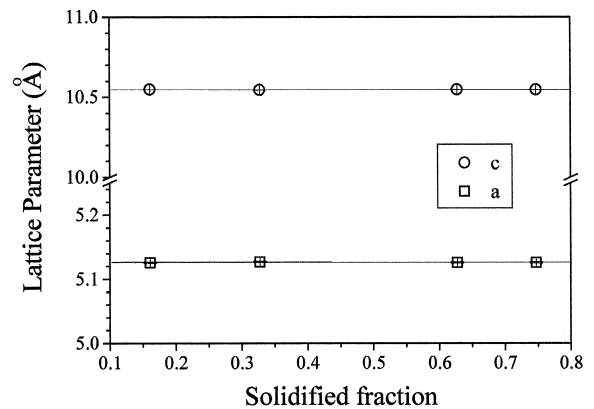


Fig. 3. Dependence of the lattice parameters on solidified fraction for the Ce:LLF crystal.

a Ce:LiSAF laser ($\lambda = 290 \text{ nm}$). The two emission bands in 309 and 328 nm can be tuned and this is the most important characteristic of this laser material.

The crystals showed no scattering by incidence of a He-Ne laser, but three small impurity bands appeared in the Ce:LLF infrared spectra. Fig. 6 shows the infrared transmission spectra for an undoped LLF and a Ce:LLF sample. The undoped LLF and the Ce:LLF crystals presented an impurity band at 3615 cm^{-1} , that was attributed to $\text{Me}(\text{OH})_2$ complexes, where Me is a transition metal. It is one of a group of narrow absorption

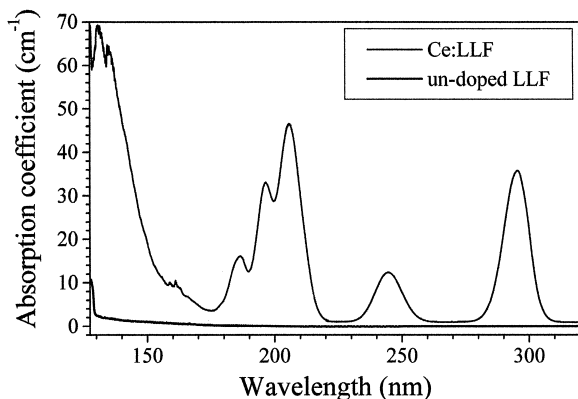


Fig. 4. Absorption spectra of an undoped LLF and a Ce:LLF sample in the VUV-UV range.

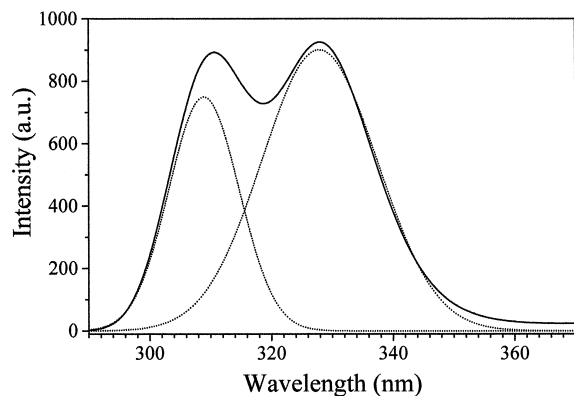


Fig. 5. Emission spectrum of Ce^{3+} for excitation at 248 nm. Dashed lines are the result of the curve fitting by multiple Gaussian peaks.

bands attributed to these complexes that appear in the range of $3650\text{--}3550\text{ cm}^{-1}$ [14]. The main source of this contamination is the LiF, because it is difficult to eliminate the transition metals in this compound since the ionic radius of these ions are very close to the lithium ionic radius. Traces of moisture were also present. The band around 2350 cm^{-1} in both spectra is due to the CO_2 present in the spectrometer during the spectrum measurements.

The Ce:LLF spectrum exhibited additional bands at $2350, 2850, 2920, 3060$ and 3210 cm^{-1} .

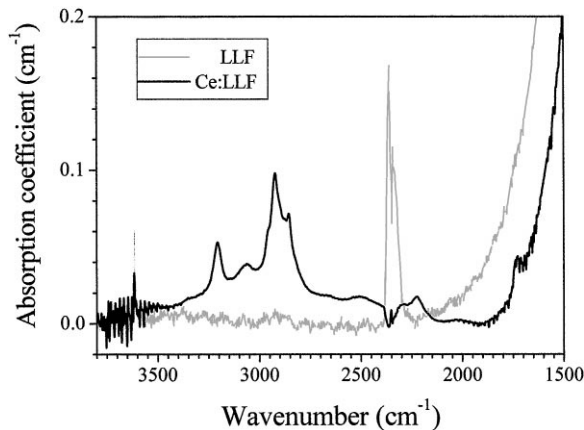
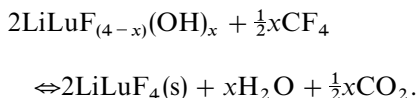
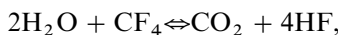


Fig. 6. Transmission spectra in the infrared of an undoped LLF and a Ce:LLF sample.

Bands around 3060 and 3210 cm^{-1} are due to $4f\text{--}5d$ optical transitions of the Ce^{3+} [15]. Bands around 2850 and 2920 cm^{-1} are probably due to the presence of a small amount of carbon and oxygen or moisture in the furnace or in the starting material, and have been associated with HCO^- [12]. This band also appeared in Ce:LiYF₄, where the same CeF_3 powder was used for doping [9]. It was assumed that the source of carbon contamination was the CeF_3 powder, since the purity was only 99.9% and it was absent in the undoped LLF spectrum. Substitution of chemicals with higher purity should eliminate these contaminations. The efficacy of the CF_4 and HF gases to eliminate OH^- and O^{2-} impurities has been studied in Ref. [16]. During the LLF growth, by analogy, the following reactions can occur:



All possible reactions are dependent on the compound and on temperature, CF_4 reacts more efficiently with water at temperatures greater than 800°C , and HF with oxygen and hydroxyl ions.

Since only traces of moisture contamination have been detected one can presume that the equilibrium of the reactions is slightly towards the left. Elimination of the oxygen complexes in the furnace chamber could be achieved empirically growing the crystal in a flux of CF_4 . As the main absorption bands for cerium are in the ultraviolet there are almost no possibilities of losses by absorption in this region during the Ce^{3+} energy transfer processes.

In the laser experiments, the resonator was established by a flat high reflector and a flat output coupler. The 10 mm Ce:LLF active medium was cut from the as-grown boule in the middle along its axis (a half-cut cylinder). The side window and the two end surfaces were polished, but no dielectric coatings were used. The pumping pulses of a randomly polarized KrF excimer laser, which operated at 248 nm with a 1 Hz frequency, were softly focused on the Ce:LLF side window by a spherical lens with 50 cm focal lens in normal incidence (Fig. 7).

The best results were obtained with a 6 cm cavity and output coupler with 45% transmission. The maximum output power at 309 nm was 27 mJ with a pumping pulse energy of 230 mJ; the corresponding pumping fluency was approximately 0.6 J/cm^2 . The slope efficiency was approximately 17% (Fig. 8). This is the highest output power obtained directly from a Ce:LLF laser reported until now. Ce:LLF tunability was investigated by replacing

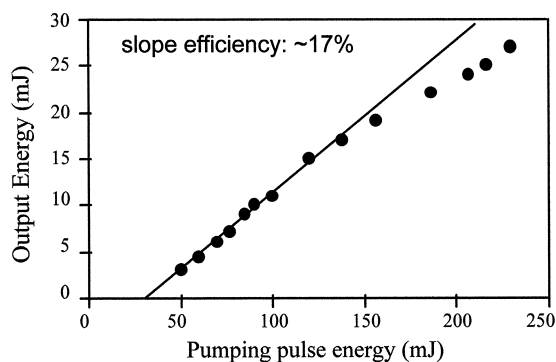


Fig. 8. Input–output relation for the Ce:LLF laser.

the output mirror with a Littrow prism and an output coupler with 10% transmission. Laser tunability was obtained in the ranges 307.8–311.7 and 323.5–326.5 nm when the pumping energy reached 100 mJ. This tuning regime was similar to that obtained in Ref. [17] where a Ce:LLF was pumped by the fifth harmonic of an Nd:YAG laser.

4. Summary

In this work, it was demonstrated that high-quality Ce:LLF crystals could be grown using CF_4 as reactive atmosphere. The segregation coefficient of Ce^{3+} was determined to be 0.066 (3). The lattice parameters remained unchanged along the crystal, so the presence of the Ce^{3+} in the lattice induced no macroscopic changes in the structure at these low concentrations. Finally, generation of 27 mJ at 309 nm was obtained by pumping with a KrF excimer laser at 248 nm. The laser was tunable in the ranges 307.8–311.7 nm and 323.5–326.5 nm.

Acknowledgements

The authors would like to express their sincere thanks to Associate Prof. S. Durbin of the Institute for Materials Research, Tohoku University, for his critical reading of the manuscript and fruitful discussions.

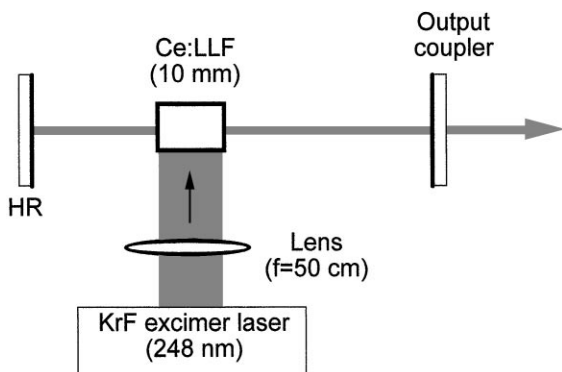


Fig. 7. Experimental setup of the high-power Ce:LLF laser pumped by a randomly polarized KrF laser operating at 1 Hz.

References

- [1] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751.
- [2] C. Keller, H. Schmutz, *J. Inorg. Chem.* 27 (1965) 900.
- [3] M.A. Dubinski, V.V. Semashko, A.K. Naumov, R.Y. Abdulsabirov, S.L. Korableva, in: A.A. Pinto, T.Y. Fan (Eds.), *OSA Proceedings on Advanced Solid State Lasers*, Vol. 15, 1993, p. 195.
- [4] M.A. Dubinski, V.V. Semashko, A.K. Naumov, R.Y. Abdulsabirov, S.L. Korableva, *J. Mod. Phys.* 40 (1993) 1.
- [5] Z. Liu, S. Izumida, H. Ontake, N. Sarukura, K. Shimamura, Na Mujilat, S.L. Baldochi, T. Fukuda, *Jpn. J. Appl. Phys.* 37 (1998) L1318.
- [6] M.A. Dubinski, R.Y. Abdulsabirov, S.L. Korableva, A.K. Naumov, V.V. Semashko, *Laser Phys.* 4 (1994) 480.
- [7] Z. Liu, N. Sarukura, M.A. Dubinski, R.Y. Abdulsabirov, S.L. Korableva, A.K. Naumov, V.V. Semashko, *Jpn. J. Appl. Phys.* 37 (1998) L36.
- [8] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sigimoto, H. Kiyoku, *Appl. Phys. Lett.* 69 (1996) 3034.
- [9] S.L. Baldochi, K. Shimamura, K. Nakano, Na Mujilat, T. Fukuda, *J. Crystal Growth* 205 (1999) 537.
- [10] K. Shimamura, S.L. Baldochi, Na Mujilat, K. Nakano, Z. Liu, N. Sarukura, T. Fukuda, *J. Crystal Growth*, in press.
- [11] K. Shimamura, Na Mujilat, S.L. Baldochi, K. Nakano, Z. Liu, H. Ontake, N. Sarukura, T. Fukuda, *J. Crystal Growth* 197 (1999) 896.
- [12] I.M. Ranieri, S.L. Baldochi, A.M.E. Santo, L. Gomes, L.C. Courrol, L.G. Tarelho, W. de Rossi, J.R. Berreta, F.E. Costa, G.E.C. Nogueira, N.U. Wetter, D.M. Zzell, N.D. Vieira Jr., S.P. Morato, *J. Crystal Growth* 166 (1996) 423.
- [13] A. Ivanova, A.M. Morozov, M.A. Petrova, I.G. Podkollzina, P.P. Feofilov, *Inorg. Mater.* 11 (1975) 1868.
- [14] K. Guckelsberger, *J. Phys. Chem. Solids* 41 (1980) 1209.
- [15] G.H. Dieke, H.M. Crosswhite, *Appl. Opt.* 2 (7) (1963) 675.
- [16] R.C. Pastor, *J. Crystal Growth* 200 (1999) 510.
- [17] N. Sarukura, Z. Liu, S. Izumida, M.A. Dubinskii, R.Y. Abdulsabirov, S.L. Korableva, *Appl. Opt.* 37 (1998) 6446.