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ScienceDirect
Journal of Luminescence 122–123 (2007) 318–321
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Stabilized color centers created by high-intensity ultra-short pulse laser in pure YLF crystals

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Available online 29 March 2006

Abstract

In this work, we show that it is possible to produce stable color centers inside $YLiF_4$ crystals with dimensional control, by focusing a high-intensity ultra-short laser pulses in the material. In particular, it is possible to determine the center creation intensity threshold and therefore to discuss the basic formation mechanisms of these centers.

Keywords: Ultra-short pulse laser; Color centers; Waveguide

1. Introduction

The $YLiF_4$ (YLF) crystals are well-known laser materials with scheelite structure, excellent optical quality, low values of non-linear refraction index and thermo-optical constants and a very large optical transmission range 0.12–7.5 μm [1]. The yttrium ions can be replaced by other rare-earths ions and the most popular dopant is neodymium. The combination of weak thermal lensing, large fluorescence line width and naturally polarized oscillation makes Nd:YLF an excellent material for CW and mode-locked operation. YLF host allows growing various laser media for generation at numerous wavelengths from UV to NIR [2].

When the YLF crystal is exposed to high intensities of pumping radiation in the UV/visible spectral regions or ionizing particles, degradation of the application-related characteristics and performance is implied. The study of defects like color centers is then a useful approach, that can be applied to understand the relevance of such degradation processes and their microscopic mechanisms.

Color centers are lattice vacancy defects trapping electrons or holes. The simplest color center, formed by an electron trapped in an anion vacancy, is the F center. When two, three and four F centers are aggregated, F_2, F_3 and F_4 centers are formed, respectively. When ionized or an electron is additionally trapped by these centers, positively or negatively charged color centers are formed (F_2^+ or F_2^- centers in the case of F_2 center). They are easily created in single crystals at room temperature, by irradiation with ionizing radiation [3]. Color centers have some important optical characteristics, if created with particular spatial dimensions, it can modulate the material refraction index, creating waveguides or photonics devices [4].

In fluoride crystals, ultra-short pulse laser creates color centers, for example in LiF [5] and Na_2F [6]. In LLF and YLF, these characteristics have been studied only for ionizing radiation [7]. In this work, we show that it is possible to create stable color centers in YLF by interaction of ultra-short pulse laser in the material. Optical properties of created color centers are studied.

2. Materials and methods

In this paper, we study pure and oxygen-doped YLF crystals grown by Czochralski technique under argon atmosphere.

The absorption spectra of all samples were measured at room temperature in the range 200—900 nm using a Varian

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doi:10.1016/j.jlumin.2006.01.157

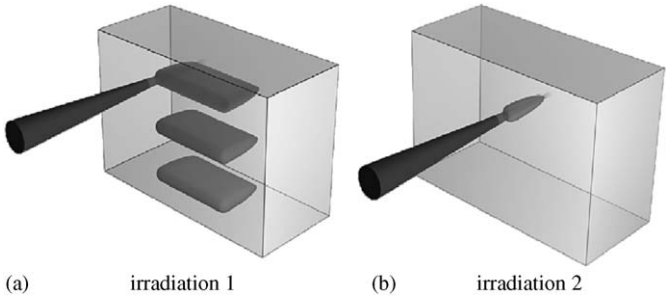

Fig. 1. Ultra-short pulse laser excitation scheme.

Spectrometer Cary 17 D. The emission spectra were obtained by exciting the samples with a 150 W xenon lamp. The emissions of the samples were analyzed with a 0.5 m monochromator (Spex) and a PMT detector. The signal was amplified with an EG&G 7220 lock-in and processed by a computer. A time-resolved luminescence spectroscopy technique was employed to measure the luminescence decay at 710 nm decay induced by resonant laser excitation. The excitation system consists of a tunable optical parametric oscillator (OPO from OPOTEK) pumped by the second harmonic of a Q-switched Nd–YAG laser from Quantel. This laser system delivers pulses of 10mJ with time duration of 4 ns and repetition rate of 10 Hz. The time-dependence luminescence of the color centers was detected by S-20 Hammamatsu PMT and analyzed using a 200 MHz Tektronix TDS 410 digital oscilloscope. The relative errors in the emission measurements are estimated to be $<5\%$, while errors in the lifetime measurements are $<10\%$.

Ti:sapphire CPA laser system operating at 830 nm was used, producing a train of 640 J, 60 fs pulses at 1 kHz, in a beam with an $M^2 = 1.6$ and a peak power of 12.5 GW. The beam was focused by an 83 mm lens to a radius of 12 μm, in the low-power limit (no self-focusing). The samples were placed in such a way that the beam waist was inside the crystals. A scheme of the experimental setup is shown in Fig. 1. The irradiation was done at room temperature.

3. Results

To determine the effects of the ultra-short pulse irradiation in the YLF crystals, the absorption spectra of the samples were measured. In Fig. 2 the absorption spectra obtained for the YLF and YLF:O crystals are shown. Absorption bands prevented by Mollwo–Ivey [8] relations in YLF can be observed in the spectra of: $F = 296$ nm, $F_2 = 473$ nm, $F_3 = 343$ nm. Absorption peaks at 515 nm and 650 nm are also observed. Between YLF and YLF:O absorption spectra, we observe some differences in the intensity of bands and changes in wavelength and width of centers absorbing around 650 nm. We suppose this absorption allowing F_2^+ color centers and changes in width and maximum is probably due to perturbation of oxygen in color centers neighborhood.

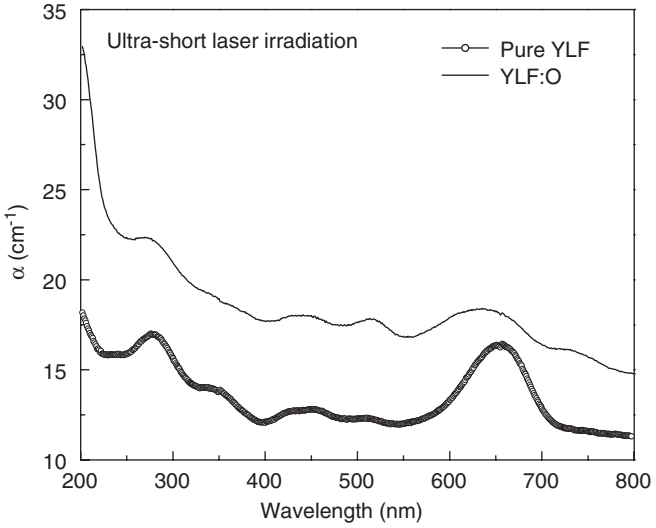

Fig. 2. Absorption spectra of the tracks created in YLF and YLF:O crystals by 640 μJ, 60 fs laser pulses.

The emission spectra obtained exciting the samples around 650 nm are shown in Fig. 3 for both the crystals. We can observe two peaks in both samples, at around 710 and >900 nm (cut in the spectra is due to limitations of the emission system). Fixing emission at 710 nm, we obtained excitation spectra. Two bands were observed at 430 and 650 nm, probably due to F_2 and F_2^+ absorptions, respectively. YLF:O and YLF crystals have the same emission and excitation bands but with differences in the signal intensities. In YLF:O, the secondary oxygen defects produced with irradiation (O_2^- and O^{2-}), play an important role in the stabilization of color centers as F_2^+ .

The pursuit for the stable F_2^+ centers in crystals was an important issue in the past for building resonators. If both thermal-and photo-stable are present, this center can have high energy output and good efficiency [9]. Also, the spectral output is shown to be very wide. We believe the stable centers produced in YLF can be useful to make ultra-fast color center lasers.

For YLF crystals, the calculated emission cross section for 710 nm emission band was approximately $2 \times 10^{-17}\text{cm}^2$ (lifetime of 90 ns).

In order to determine the color center creation intensity threshold, the samples were placed in the focused laser beam before the waist, in a position where no color centers were formed, and were moved towards the waist until color centers were observed, by naked eye, to be formed by the laser pulses. The sample position relative to the lens was measured, and the pulse intensity was calculated at the sample position. Considering the laser spot size w, given by the laser beam propagation law [10]

$$w = w_0\sqrt{1 + \left(\frac{M^2\lambda(z - z_0)}{\pi w_0^2}\right)^2}, \quad (1)$$

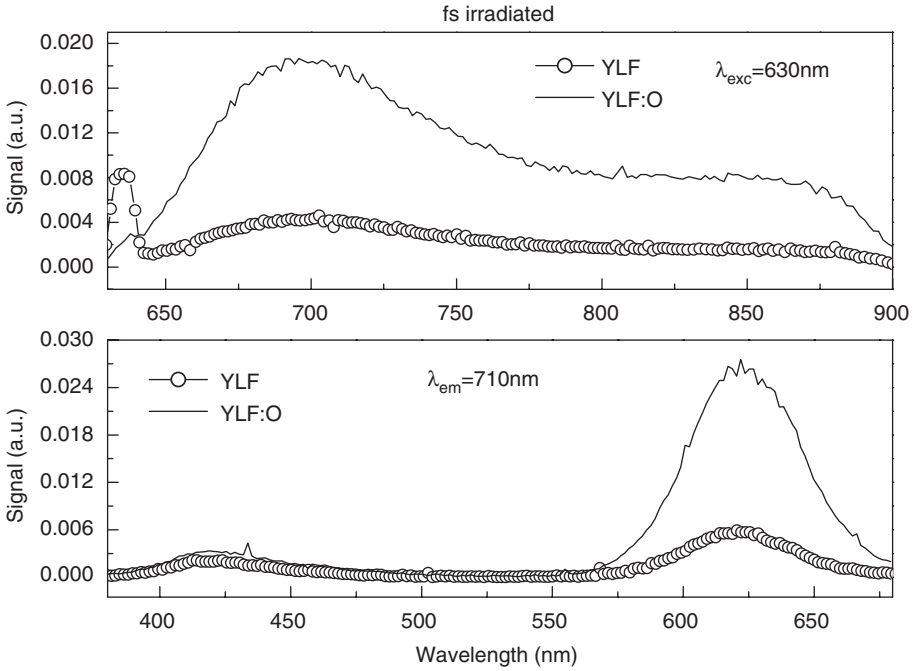

Fig. 3. Emission spectra obtained in YLF and YLF:O crystals with excitation at 630 nm (upper graphic) and excitation spectra obtained fixing the emission at 710 nm (lower graphic).

where $\lambda = 830\,\text{nm}$ is the laser wavelength, $z_0 = 19.8\,\text{cm}$ is the beam waist position relative to the lens, $w_0 = 25\,\mu\text{m}$ the beam waist, $M^2 = 1.6$ the beam quality factor and $z = 17.5\,\text{cm}$ the sample position where color centers were observed to be formed by the laser pulses, resulting in $w = 390\,\mu\text{m}$. In this measure the pulse energy was 547 μJ and the pulse width 60 fs, resulting in a color center creation threshold of $1.9\,\text{TW/cm}^2$ for YLF.

To explain the color center production by the ultra-short pulses, we propose a mechanism based on the non-linear multi-photon absorption [11,12]. This process promotes free electrons to the conduction band, where they acquire kinetic energy from the laser field and create vacancies by impact with the fluorine ions. When this anion vacancy traps an electron (neutralizing the vacancy charge), an F center is created. The second step in the production of defects involves the migration of primary defects and the formation of complex defects. These secondary processes are temperature-and intensity rate-dependent. We propose that creation and destruction processes occur simultaneously, during the ultra-short pulse irradiation, since the fundamental and the harmonics [13] of pumping laser can be absorbed by the defects.

The production of stable color centers in pure YLF samples was obtained as a consequence of the interaction of ultra-short laser pulse with the material. We think that a controllable refractive index change can be achieved by adjusting femtosecond laser irradiation parameters and subsequent annealing conditions. In this way, one can induce refractive index change for the crystals to fabricate internal diffraction gratings or optical waveguide, etc. for three-dimensional integrated optic devices.

4. Conclusions

We created, color centers in YLF crystals by high intensity ultra-short laser pulses, for the first time to our knowledge, and measured its absorption and emission spectra. YLF:O and YLF crystals have the same emission and excitation bands but with differences on signal intensities. We propose that the mechanism responsible for the center creation is a multi-photon process depending on the crystal energy gap as well as higher color center density formation that induces aggregation of them.

Stable color centers with emission at 710 nm were produced in YLF and its emission cross section was calculated to be approximately $2 \times 10^{-17}\text{cm}^2$.

Acknowledgments

The authors thank the ''Fundação de Amparo à Pesquisa do Estado de São Paulo'', FAPESP, for the support under the Grants 00/15135-9 and 05/50437-0.

References

[1] Handbook of Chemistry and Physics, in: R.C. Weast (Eds.), 53 ed., Chemical Rubber Company, Ohio, 1972.
[2] A. Bensalah, K. Shimamura, V. Sudesh, H. Sato, K. Ito, T. Fukuda, J. Cryst. Growth 223 (2001) 539.
[3] A.M. Espírito, L.C. Courrol, I.M. Ranieri, N.U. Wetter, N.D. Vieira Jr., S.L. Baldocchi, Opt. Mater. 27 (3) (2004) 487.
[4] G. Baldacchini, R.M. Montereali, Opt. Mater. 16 (2001) 53.
[5] L.C. Courrol, R.E. Samad, L. Gomes, I.M. Ranieri, S.L. Baldochi, A.Z. de Freitas, N.D. Viera Jr., Opt. Express 12 (2004) 288.

[6] S. Vajda, C. Lupulescu, A. Merli, F. Budzyn, L. Worste, M. Hartmann, J. Pittner, V. Bonacic-Koutecky, Physical Review Letters, Phys. Rev. Lett. 89 (2002) 213404.
[7] A. Bensalah, M. Nikl, A. Vedda, K. Shimamura, T. Satonaga, H. Sato, T. Fukuda, G. Boulon, Radiat. Eff. Defects Solids 157 (2002) 563.
[8] H. Yvey, Physical Review 72 (4) (1947) 341.
[9] S.B. Mirov, A.Yu. Dergachev, Proc. SPIE 2986 (1997) 162.
[10] D.R. Hall, P.E. Jackson, *The Physics and Technology of Laser Resonators,* IOP Publishing, Amsterdam, 1989 Chapter 1.
[11] N. Bloembergen, IEEE J. Quant. Electron 10 (1974) 375.
[12] D. Du, X. Liu, G. Korn, J. Squier, G. Mourou, Appl. Phys. Lett. 64 (1994) 3071.
[13] A. Brodeur, S.L. Chin, Band-Gap Dependence of the Ultra-fast White-Light Continuum, Phys. Rev. Lett. 80 (1998) 4406.