Study of point defects created by high-intensity ultrashort pulse laser in YLF crystals

Lilia Coronato Courrol[*a], Everson Bragança dos Santos[a] , Ricardo Elgul Samad, Izilda Marcia Ranieri, Laércio Gomes, Anderson Zanardi de Freitas, Nilson Dias Vieira Jr

[a]Laboratório de Espectroscopia Óptica, FATEC-SP, Praça Coronel Fernando Prestes 30, São Paulo, SP, Brazil.
Centro de Lasers e Aplicações, IPEN-CNEN, São Paulo,SP, Brazil

ABSTRACT

In this work we report the creation of color centers in LiF and YLF crystals by high intensity, ultrashort laser pulses. We used pure and Tm^{3+} and Oxygen doped samples, all irradiated with a Ti:Sapphire CPA laser system and also with electron beam, at room temperature. In both kinds of irradiations the production of photochromic damages and color centers that have absorption bands in UV and visible range was observed. A comparison between the two kinds of irradiation was done and the involved processes are described in this paper. F_2^+ stable centers were produced by the ultrashort laser pulses irradiation in contrast to the well-known, short lived centers produced by electron beams, and a mechanism was proposed to explain the observed stability.

Keywords: laser, YLF, thulium, fluorescence, color centers, ultrashort pulse.

I. Introduction

Doped $YLiF_4$ (YLF) crystals are well known laser materials with scheelite structure, excellent optical quality, low values of non-linear refractive index and thermo-optical constants, and a very large optical transmission range from 0.12 μm to 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, naturally polarized oscillation and long lifetime makes Nd:YLF an excellent material for CW and mode locked operation. YLF host allows growing various laser mediums for generation at numerous wavelengths from UV to NIR[2].

When pure or doped YLF crystals are exposed to high intensities of UV/visible radiation or ionizing particles, degradation of the application-related characteristics and performance can occur, due to the creation of color centers defects. The study of these produced color centers is then a useful approach, which can be applied to understand the relevance of such degradation processes and their creation mechanisms.

Color centers are lattice vacancies defects trapping electrons or holes, and can be easily created in single crystals by ionizing radiation[3], at room temperature. These color centers can be used as active laser media, and also, if created with controlled spatial dimensions, as photonic devices or waveguides[4].

Recently, the creation of color centers by high-energy ultrashort laser pulses in fluoride crystals has been reported, as for example in LiF[5] and Na_2F[6]. To our knowledge, color centers in YLF crystals have only been created by ionizing radiation[7].

In this work we show that is possible to produce color centers inside YLF crystals with dimensional control, by focusing a high-intensity ultrashort laser pulses in the material and to discuss the basic formation mechanisms of these centers.

* lcourrol@fatecsp.br; phone 55-11-33222200-extension 2276; fax 55-1133158498; www.fatecsp.br

Nonlinear Frequency Generation and Conversion: Materials, Devices, and Applications IV, edited by Peter E. Powers, Proceedings of SPIE Vol. 5710 (SPIE, Bellingham, WA, 2005) · 0277-786X/05/$15 · doi: 10.1117/12.588407

II. Experimental Setup

We studied pure and doped LiF and YLF crystals. The pure samples were grown by the zone refine (zf) method, and the doped ones were grown by Czochralski technique under Argon atmosphere. The doped samples have 15mol% Tm (3+) concentration, and 10^{18}atoms/cm^3 of Oxygen. The LiF samples were cleaved and the YLF samples were oriented, cut and polished to 2 mm thickness.

The absorption spectra of the samples were measured in the range 200 nm-800 nm, at room temperature, using a Varian Spectrometer Cary 17 D.

To irradiate the samples, a Ti:Sapphire CPA system (coherent Mira-Seed pumping a Quantronix Odin amplifier) was used, producing a 1kHz train of pulses, centered at 830nm, with 640μJ of energy and 60fs of duration (FWHM), in a M^2 = 1.6 beam. The beam was focused by a 200mm lens, producing a converging beam with a waist of 25 μm. The samples were placed before the beam waist in such way that the color center creation threshold was achieved inside the crystals. The sample was then moved transversely to the beam, for 2 mm, to produce a plane of color centers. Three planes were created in each sample in order to enhance the optical density for the absorption measurements. A scheme of this irradiation can be seen in figure 1a. In a second experiment represented in the figure 1b, the sample was kept motionless, with the beam impinging on it for 1 minute, creating a track inside the sample. After irradiation, the samples were stored at liquid nitrogen temperature up to the experimental measurements.

The samples were also irradiated with electron beam, at room temperature (18 s, 2.8KGy/s, 0.7 mA, 1.5MeV), in regions that did not overlap the color centers produced by the ultrashort laser pulses.

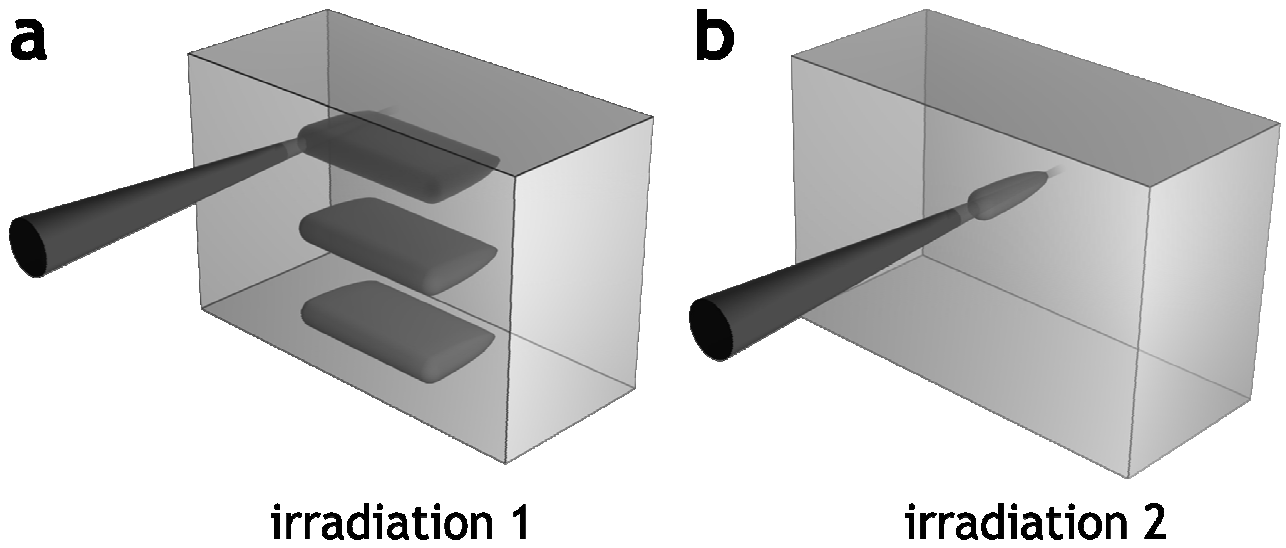

Figure 1. Scheme of the color centers production by ultrashort laser pulses. a) Three planes of color centers were created by dislocation the sample for 2 mm across the beam, during 200 s, for the optical absorption measurements. The vertical distance between the planes is 0.5 mm; b) color center track created inside the sample by 1 minute irradiation without moving the sample.

II. Results

Figure 2 shows several photographs with details of color centers created in LiF crystals by ultrashort laser pulses by the methods described. LiF crystals were chosen for this experiment due to its simple structure, what helps to

understand the basic principles governing the creation of the centers. Understanding why and how these defects are created is important to control its production. Similar induced absorption behavior is observed for YLF crystals with respect to LiF and figure 3 shows pictures of the produced defects in YLF crystals

The microscopic photographs show that the tracks produced (irradiation 2) have cylindrical symmetry, but are not homogeneous, presenting many filaments with periodic structure. Looking across the trace formed inside the LiF and YLF crystals is possible to see a filamented structure. The same structure is seen in the planes produced when the sample were moved laterally (irradiation 1). In LiF crystals, a higher concentration of color centers (red color) is observed in the micro-tracks. In YLF (figure 3) a periodic structure is observed in a homogeneous color region (blue-green color).

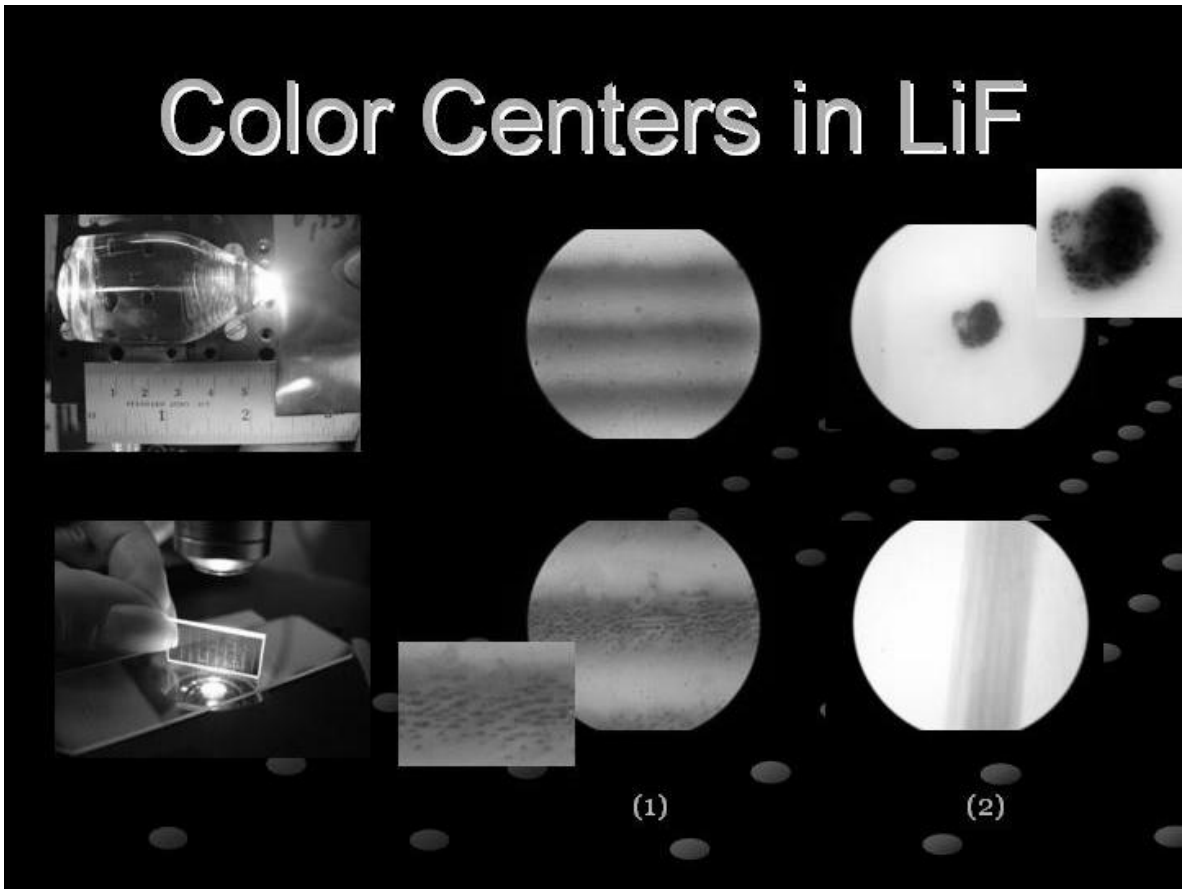

Figure 2. Photos of F_3^+ color centers emission in LiF produced by high intensity ultrashort laser pulses when excited by white light and images of traces observed in an optical microscope. (1) Traces produced and micro-tracks (zoom) by irradiation 1 and (2) track produced mby irradiation 2 in frontal and lateral views.

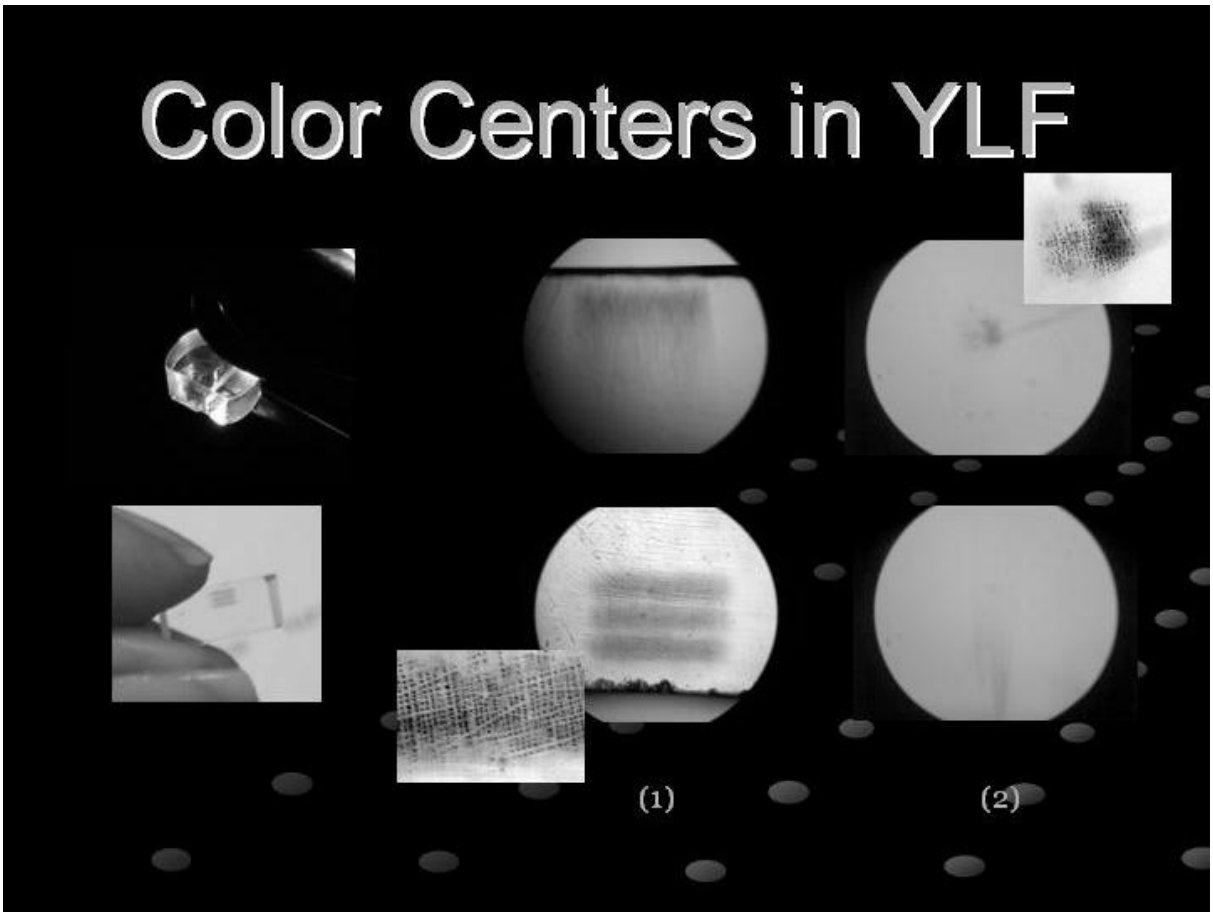

Figure 3. Characteristics of the YLF:O crystals irradiated with femtosecond laser pulses. (1) Traces produced and micro-tracks (zoom) by irradiation 1 and (2) track produced mby irradiation 2 in frontal and lateral views.

Figure 4 shows the spectra of the electron beam and ultrashort pulses irradiated LiF and YLF samples, measured shortly after the irradiation. Comparing the absorption spectra of the electron beam and ultrashort pulses irradiated LiF samples (continuous line in figure 4 a and 4b), we notice that both spectra show that the basic F center (electron bounded to a vacancy) was created (absorption band at UV region). F_3^+ and F_2 centers (two electrons bound to three and two neighboring anion vacancies, respectively), that are responsible for the almost overlapping absorption band, generally called M band, around 448 nm (F_3^+) and 440 nm (F_2) were also observed in both spectra. Besides the main M absorption band, other types of aggregate defects have been detected in electron beam irradiated samples: we observed the 520nm and 545nm bands, attributed to N_1 and N_2 transitions of four associated F centers (N center), and the 632 nm band due to F_2^+ center (ionized F_2 center). Comparing the spectra for electron beam and laser irradiation, we see that the laser produces smaller absorption bands evidencing that the formation of neutral aggregate defects is strongly reduced under ultrashort laser irradiation with respect to electron beam irradiation, probably due to the non-thermal interaction of femtosecond pulses resulting in low vacancies dislocation. Similarly to LiF, no radiation induced absorption bands were found above 800 nm in YLF samples (line + symbol in figure 4 a and 4b). Comparing with the LiF induced absorption, the same bands are observed in YLF:O but shifted. The secondary oxygen defects produced with irradiation (O_2^-), play an important role in stabilization of color centers as F_2^+ and F_2^- [8]. The absorption bands correspondents to these centers generally disappear some days after electron beam irradiation in the pure samples irradiated by electron beam.

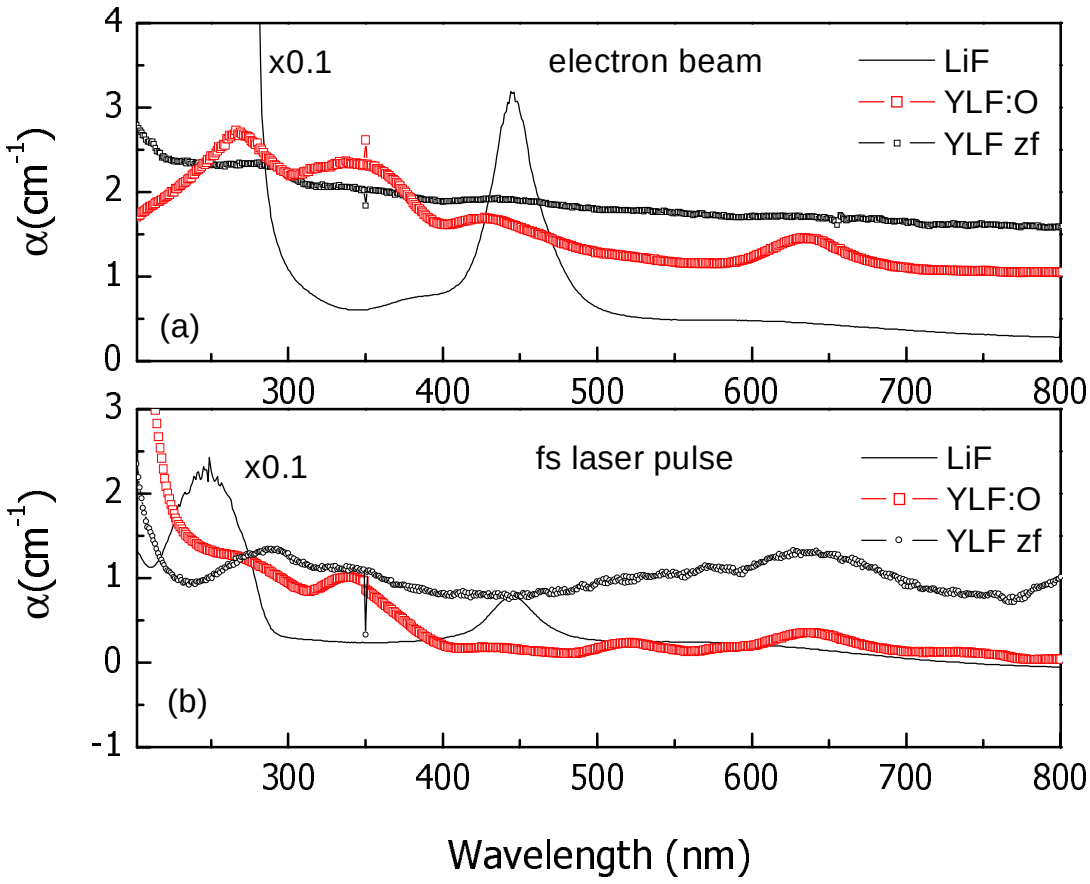

Figure 4. Absorption spectra of LiF, YLF and YLF:O samples measured after irradiation by: (a) electron beam (b) ultrashort laser pulses irradiation.

In figure 5 it is possible to see that the centers created by fs laser in pure YLF crystals are more stable than that ones produced in YLF. In these case we see that the oxygen centers are not responsible for centers stabilization. Another kind of process should occurs. Differently from LiF crystals, in pure and Tm^{3+} doped YLF crystals, photochromic centers were produced. These centers consist of one or two electrons bound to an anion vacancy adjacent to a trivalent impurity cation. Curiously, YLF:Tm shows a mix of color centers and photochromic centers (Figure 6). These kind of centers interfere with optical properties of rare earth ion.

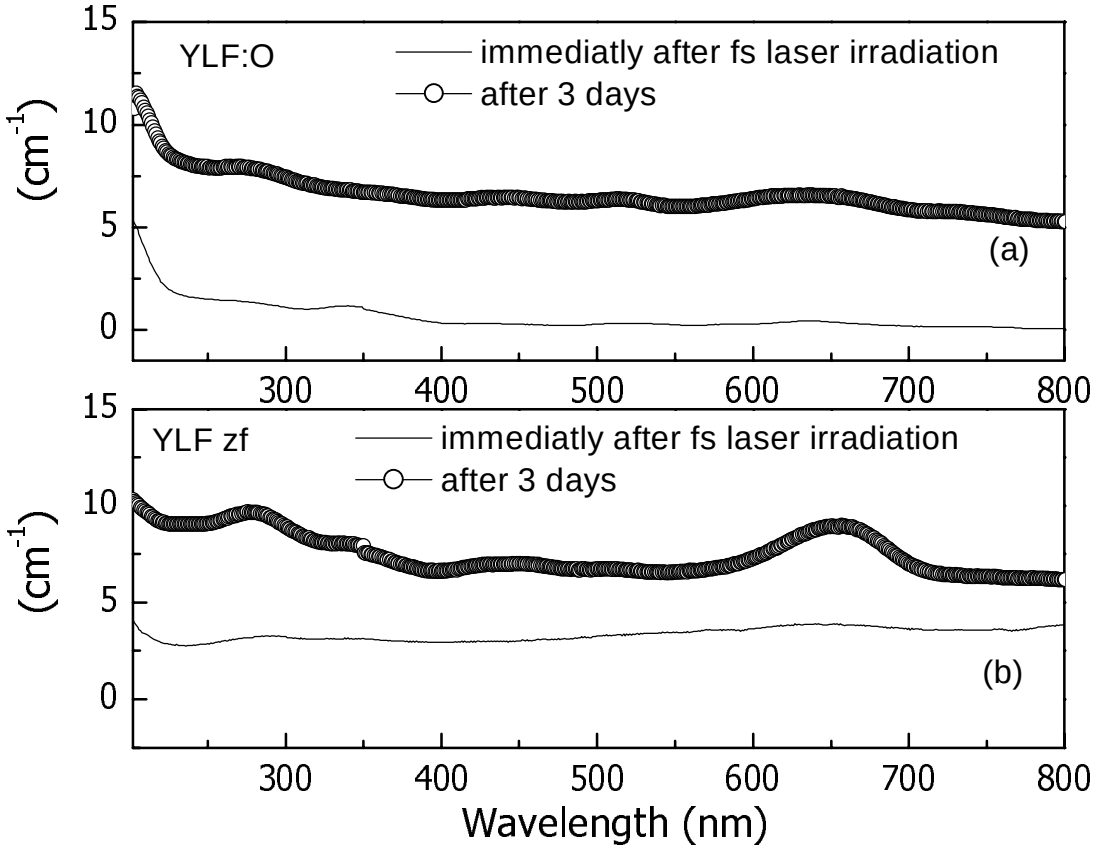

Figure 5 . Absorption spectra of pure YLF and YLF:O samples measured three days after irradiation by: (a) electron beam (b) after ultrashort pulses laser irradiation.

In ultrashort high intensity regime, a strong non-linear multiphoton absorption generates electron avalanche. If an electron can achieve energy equal to the band gap, subsequent impact ionization promotes another valence electron into the conduction band. An anion vacancy with trapped electrons that neutralize the vacancy charge is an F center. The second step in 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 suppose that the creation and destruction processes occur simultaneously, since the fundamental and the harmonics of pumping laser can be absorbed by the defects. This effect can explain the presence of F_2^+ and F_3^+ centers immediately after irradiation of LiF crystals.

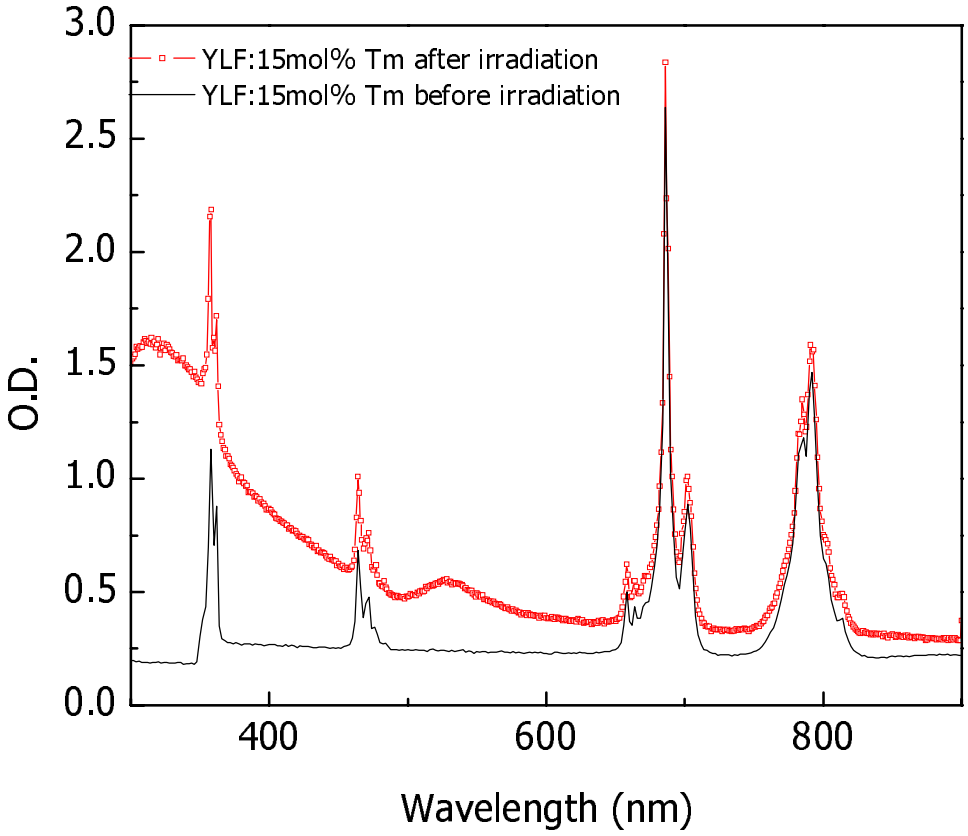

Figure 6. Absorption spectra of a high concentrated YLF:Tm sample (15 mol%) before and after electron irradiation.

Observing the produced traces under a microscope we can see micro tracks regularly separated. These tracks probably correspond to clusters created by the laser beam that trap the color centers and consequently stabilize than. These trapped color centers have a little shift in the maximum of F_2^+ absorption band. 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 optics devices[9 10]

IV. Conclusions

We observed for the first time to our knowledge, the formation of color centers in YLF crystals by high intensity, ultrashort laser pulses. We propose that the mechanism responsible for the centers creation is a multiphotonic process depending on the gap energy. Microscopic observation of the produced tracks showed filamentation of the color centers, and we propose that these filaments are responsible for the color center stabilization. Also, when produced in a controlled way, these color center tracks could be used to manufacture photonic devices.

Acknowledgments

The authors thank the “Fundação de Amparo à Pesquisa do Estado de São Paulo”, FAPESP, for the support under the grant 00/15135-9 and 04/06261-1.

References

[1] Chemical Rubber, Handbook of Chemistry and Physics, 53 ed., Ohio (1972).

[2] A. BENSALAH, K.SHIMAMURA, V. SUDESH, H. SATO, K. ITO, AND T. FUKUDA, J. Cryst. Growth, 223, 539. (2001).

[3] A. M ESPÍRITO, L. C. COURROL, I. M. RANIERI, N. U WETTER, N. D. VIEIRA JUNIOR, S. L. BALDOCCHI, Optical Materials.27,3, pp.487-490, (2004).

[4] G. BALDACCHINI, R. M. MONTEREALI, Optical Materials, 16, 53-61, (2001).

[5] L. C. COURROL, R. E. SAMAD, L. GOMES, I. M. RANIERI, S. L. BALDOCHI, A. Z. DE FREITAS, N. D. VIERA JR, Optics Express, v.12, pp. 288 - 293, (2004).

[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, 213404 (2002).

[7] A. BENSALAH, M. NIKL, A. VEDDA, K. SHIMAMURA, T. SATONAGA, H. SATO, T. FUKUDA and G. BOULON, Radiation Effects & Defects in Solids, Vol. 157, pp. 563–567, (2002).

[8] L. C. COURROL, L. GOMES, I. M. RANIERI, Physical Review B, 42, 7, (1990).

[9] H. Sun, Y. Xu, S. Juodkazis, K. Sun, M. Watanabe, S. Matsuo, H. Misawa and J. Nishii, Opt. Lett. 26, 325-27 (2001).

[10] JIANRONG QIU, The Chemical Record, 4, 1 , 50 – 58, (2004).