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γ-Ray induced color centers in pure and Yb doped $LiYF_4$ and $LiLuF_4$ single crystals

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Abstract

γ-Ray irradiation was used to carry out a comparative study of the induced optical absorption phenomena and color center creation in the ultraviolet and visible spectral regions. The F-center absorption band at 315 and 330 nm in $LiLuF_4$ and $LiYF_4$, respectively, is the dominating induced absorption feature. The amplitude of the induced absorption is reduced by more than a factor of 3 in Yb-doped crystals compared to the undoped ones. Comparison was made with other fluorides, such as CaF_2, KY_3F_{10} and BaY_2F_8. In Yb-doped CaF_2, $LiLuF_4$, $LiYF_4$, BaY_2F_8 and KY_3F_{10} we observed arising of two possible types of Yb^{2+} centers after γ-ray irradiation. For the entire materials exclude KY_3F_{10} we found Yb^{2+} centers related to Yb^{3+}, as an effect of recharging one of Yb^{3+} ion from pair, while for KY_3F_{10} we found mainly Yb^{2+} centers related to isolated Yb^{3+} ions, as an effect of Compton electron capturing by isolated Yb^{3+} ion.

Keywords: Color centers; $LiYF_4$; $LiLuF_4$; BaY_2F_8; KY_3F_{10}; Induced absorption

1. Introduction

Single crystals of $LiLuF_4$ (LLF) and $LiYF_4$ (YLF) with suitable dopants have been recently considered for solid-state laser or scintillated applications [1,2]. The study of color center creation is a useful approach, which can be applied to understand the relevance of degradation processes due to e.g., pumping radiation and/or external radiation, and, their microscopic mechanisms. In this paper we focus particularly on the gamma irradiation-induced defects in Yb-doped LLF and YLF as candidates for high power lasers. In fluoride crystals, irradiation by X or gamma ray or UV light occasionally creates color centers systematically studied for example in LiF and CaF_2 [3,4]. In LLF and YLF these characteristics have already been partially studied, but their interpretation is somewhat contradictory [5–7].

The aim of the paper is to provide a systematic overlook of γ-induced color centers in LLF and YLF, including also the influence of Yb^{3+} dopant. We describe γ-ray induced radiation damage in the undoped and Yb-doped LLF and YLF single crystals using optical absorption measurements in the UV/VIS/NIR spectral regions. For comparison we analyze color centers in other fluorides, such CaF_2, BaY_2F_8 and KY_3F_{10}.

2. Experimental

High quality LLF ($LiLuF_4$, scheelite, tetragonal, space group: $I4_1/a(C_{4h}^6)$, lattice parameters: $a = 5.150$ Å, $c = 10.47$ Å), YLF ($LiYF_4$, scheelite, tetragonal, space group $I4_1/a(C_{4h}^6)$, lattice parameters:

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$a = 5.155$ Å, $c = 10.68$ Å), BYF (BaY_2F_8, monoclinic, space group: $C_{2h}3$–$C2/m$, lattice parameters: $a = 0.6972$ Å, $b = 1.0505$ Å, $c = 0.4260$ Å, $\beta = 99°45'$) and KYF (KY_3F_{10}, cubic O_h^5, space group $Fm3m$, lattice parameter: $a = 11.535$ Å) single crystals were grown by the Czochralski method under CF_4 atmosphere in the Institute for Materials Research, Tohoku University, Sendai, Japan. The CF_4 atmosphere ensures an efficient suppression of oxygen-related impurities in the material [1]. Doping with Yb was also pursued. Growth procedure of fluoride single crystals was fully described in Ref. [1,8].

Moreover, $Ca_{1-x}Yb_xF_{2+x}$ ($x = 0.005$, 0.02, 0.05, 0.15 and 0.3) crystals were prepared in Tohoku University, Japan, by simply melting mixtures of commercially available powders of CaF_2 and YbF_3 with the purity of 4N. The crystal size was a few cm, but actually they were poly-crystals consisted of some grains and some cracks. Nevertheless, each grain was quite large from a few mm to a few cm. So, we believe it has high quality as same as single crystal.

Room temperature γ-ray irradiations of 2 mm thick plates cut from the crystal boules were accomplished with the doses up to 120 kGy. The gamma source of ^{60}Co with efficiency of 1.5 Gy/s was used. The effect of irradiation was investigated by room temperature (RT) optical absorption measurement before and after γ-irradiation in the 190–3200 nm range using LAMBDA-900 spectrophotometer.

The annealing in hydrogen was performed in case of the irradiated LLF, YLF, BYF and KYF samples at a temperature of 903 K for 1 and 5 h. Subsequent irradiation with gammas with a dose of 10^5 Gy we applied after the annealing process.

The induced absorption by γ-rays and hydrogen was calculated according to the following formula for the additional absorption:

$$\Delta K = \frac{1}{d} \ln \frac{T_1}{T_2}, \qquad (1)$$

where d denotes the sample thickness, and T_1 and T_2 are transmissions of the sample before and after a given treatment.

Photoluminescence (PL) was measured after exciting of the investigated crystals with $\lambda_{ex} = 442$ nm (laser excitation), and, $\lambda_{ex} = 225$ nm and $\lambda_{ex} = 342$ nm light using a SS-900 Edinburgh Inc. spectrophotometer in the Institute of Optoelectronics, MUT, Poland.

3. Results and discussion

As in the case of other complex fluorides [9,10], induced absorption spectrum of undoped LLF (Fig. 1) support the idea that several kinds of color centers are created under γ-irradiation. The most frequent induced

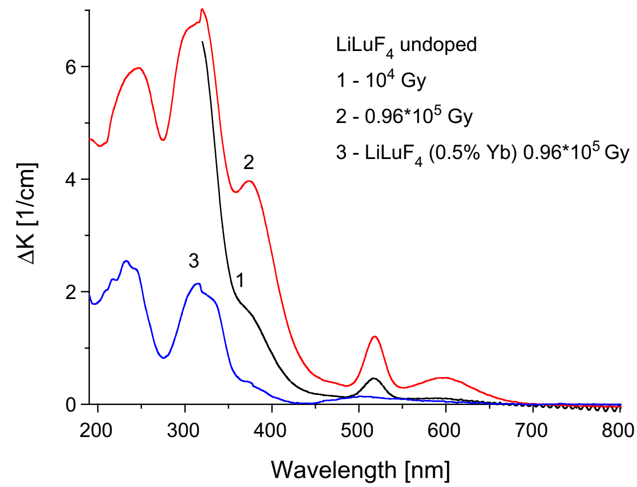

Fig. 1. Induced absorption of undoped and 0.5% Yb-doped $LiLuF_4$ obtained after γ-ray irradiation with doses: 10^4 Gy (1) and 0.96×10^5 Gy (2, 3)

absorption bands in the UV–visible spectral region in high quality alkali halides are related to F-centers, i.e., electrons localized in anion vacancies. The position of the F center absorption band is determined by the structure of the material, namely by the distances between the fluorine site and surrounding cations (Molvo-Iwey relation). By taking into account the position of the F-center band in LiF (245 nm) and the F–Li distance (2.013 Å), it is reasonable to ascribe the intense absorption band peaking around 315 nm in LLF to an F center, since the mean F-to-nearest-cations distance is 2.183 Å. Additional absorption bands were produced: they are localized around 240, 380, 520 and 600 nm. The two bands around 240 and 380 nm correspond probably to perturbed V_k centers [5]. The induced absorption band at 520 nm can be most probably related to the F_2 (F_2^+) centers considering its considerably lower amplitude and the long wavelength shift (e.g., in $KMgF_3$, F and F_2 centers are absorbing at 280 and 445 nm, respectively [10,11]). The induced absorption band at 600 nm may be of N_2 type center as 550 nm band in LiF or generally coming from higher order F centre aggregates.

It was shown that rare-earth trivalent dopant ions substitute preferentially, both for LLF and YLF, at the Lu^{3+} or Y^{3+} site, respectively [12]. In the case of 0.5% Yb-doped LLF, the induced absorption spectrum is also given in Fig. 1 (curve 3). The presence of Yb^{3+} with concentration of 0.5% did not significantly alter the optical absorption bands positions. However, the intensity of the total induced absorption is considerably reduced; especially the amplitude of the F-absorption band is lowered by almost a factor of 3.5 for the 0.5% Yb-doped LLF compared to the undoped crystal. Moreover, a new band one can recognize peaked at about 340 nm and some changes in the shape of the 240 nm band. As Yb^{3+} can easily change to Yb^{2+}, the most probable explanation of the changes is the competition of Yb^{3+} with F vacancies in capturing free electrons arising after γ-ray irradiation.

In the case of X-ray irradiation, conclusions made on Yb doping influence on the shape of the induced absorption were generally the same, but the total induced absorption was reduced by almost a factor of 15 for 0.5% Yb-doped LLF compared to the undoped crystals [7].

Fig. 2a and b shows induced absorption bands in 0.5% and 5% Yb-doped LLF single crystals, respectively. As one can see from the figures, the higher is Yb- concentration, the lower is induced absorption. Moreover, the intensity of F-center significantly decreases with the increase of Yb^{3+} concentration showing clear 340 nm band we assigned to Yb^{2+}.

YLF has the same scheelite structure as LLF, with somewhat larger lattice constants ($a = 5.155$ Å (5.150 Å), $c = 10.68$ Å (10.47 Å) for YLF (LLF)) and similar induced absorption behavior is observed for YLF crystals with respect to LLF. The radiation-induced absorption spectrum after γ-ray irradiation for undoped YLF is shown in Fig. 3. Similarly to LLF and contrary to CaF_2, no radiation induced absorption bands were found above 800 nm. Four bands pattern was found within 200–650 nm similarly to Ref. [5]. Comparing with the LLF induced absorption, the same bands are observed just shifted towards longer wavelengths (260, 330, 440, 505 and 640 nm).

This is in good accordance with the lattice constants relation. For the same structure, larger lattice constants induce the low energy shift of the bands. F-center band in YLF is thus located around 330 nm while it is placed around 315 nm in LLF.

Yb doping has the same effect on the induced absorption for YLF as for LLF crystals, resulting in a considerable lowering of the induced absorption amplitude by a factor of about 50—see curves 1 and 4 in Fig. 3. Nd-doped YLF (5) show higher susceptibility to γ-irradiation as compare to Yb-doped but lower then pure YLF.

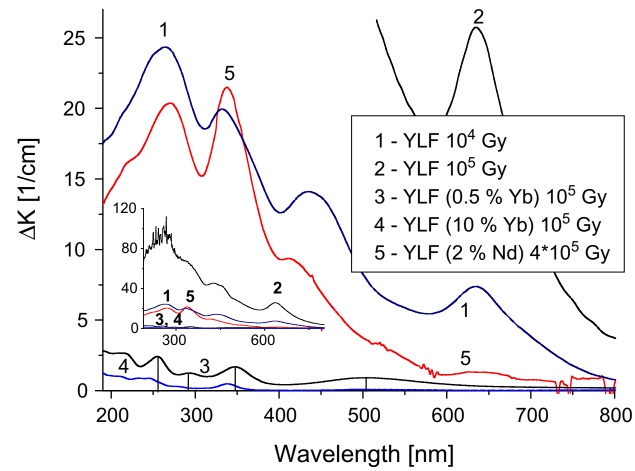

Fig. 3. Induced absorption of undoped (1, 2), 0.5% Yb-doped (3), 10% Yb-doped (4) and 2% Nd-doped $LiYF_4$ (5) obtained after γ-ray irradiation with doses: 10^4 Gy (1), 0.96×10^5 Gy (2–4) and 4×10^5 Gy (5).

Fig. 4a and b shows the induced absorption bands in 0.5% and 10% Yb-doped YLF single crystals, respectively. As one can see from the figures, the higher is Yb-concentration, the lower is induced absorption. There is almost not observed the 640 nm band. Beside 330 nm band assigned to F-center one can recognize also 340 nm band assigned to Yb^{2+}. Moreover some shifting in the position of the bands is observed towards shorter wavelengths for higher Yb-doped crystals.

Unexpectedly, induced absorption spectrum has extremes in the same positions as previously for LLF crystal.

Very similar pattern we observed for induced absorption of CaF_2:Yb (30%) crystal (see Fig. 5). The addi-

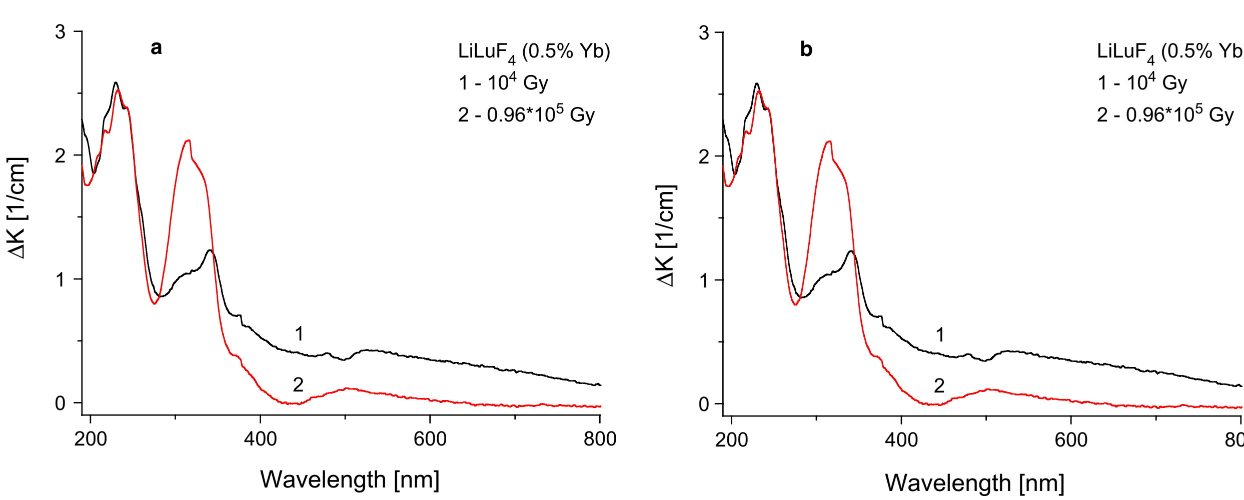

Fig. 2. Induced absorption of: (a) 0.5% Yb-doped $LiLuF_4$ and (b) 5% Yb-doped $LiLuF_4$.

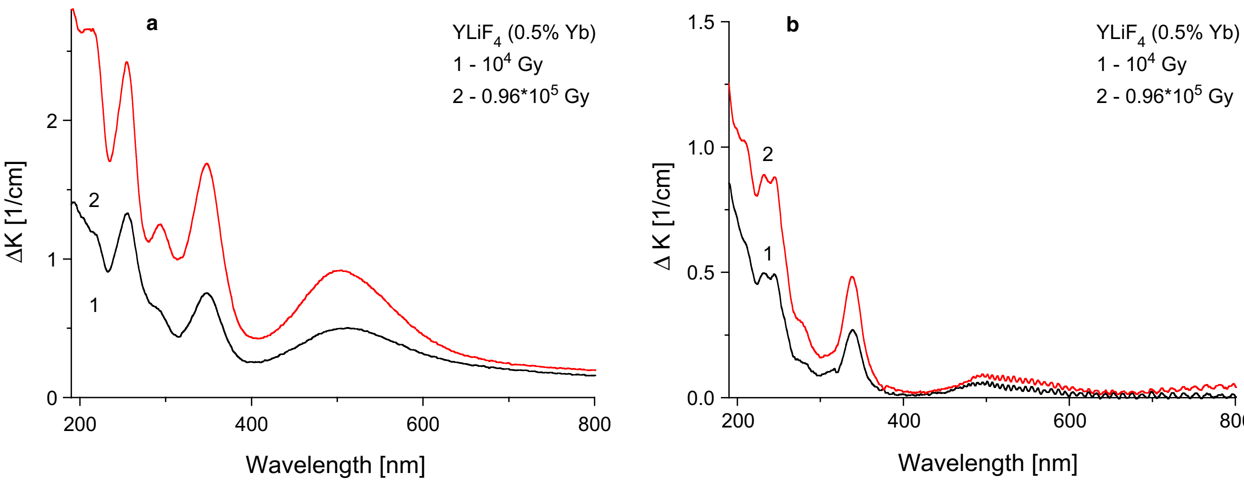

Fig. 4. Induced absorption of: (a) 0.5% Yb-doped $LiYF_4$ and (b) 10% Yb-doped $LiYF_4$.

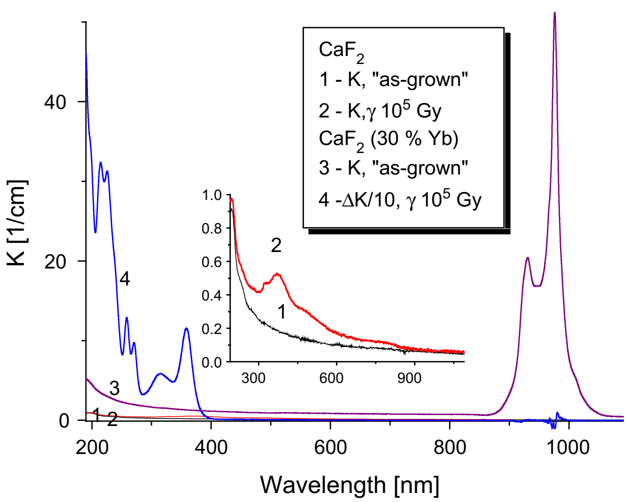

Fig. 5. Absorption (1), induced absorption after gamma dose of 10^5 Gy of pure CaF_2 crystal (2), absorption (3) and induced absorption after gamma dose of 10^5 Gy, $\Delta K/10$, of Yb (30 wt.%) doped CaF_2 crystal (4).

tional absorption bands after γ-irradiation with a dose of 10^5 Gy may be interpreted as Yb^{2+} absorption bands. Comparing Figs. 2, 4 and 5 one can distinguish only 520 nm band, as additional band in the induced absorption spectrum of Yb-doped YLF and LLF crystals with respect to CaF_2. Moreover the intensity of the induced absorption for CaF_2:Yb crystal is about 10 times higher than for LLF:Yb and YLF:Yb crystals and does not depend on the Yb concentration.

In Fig. 5 one can compare the induced absorption in pure CaF_2 (inset) and CaF_2 doped Yb (30 wt.%) single crystals. Pure CaF_2 crystals reveal the same type of the induced absorption as we observed for other fluorides but significantly lower in the intensity. In case of CaF_2:Yb the induced absorption bands are observed at 360, 315, 271, 260, 227 and 214 nm, which are called A, B, C, D, F and G bands, respectively. Such UV absorption bands have been observed by several investigators and they were attributed to Yb^{2+} and Yb^{2+}-associated centers (see e.g., 13) as the cases in various host materials [14,15].

To check validity of the assumption on Yb^{2+} origin of the induced absorption bands obtained for LLF:Yb and YLF:Yb crystals, we performed gamma ray irradiations of the fluorides more complex in the structure. We have chosen BaY_2F_8:Yb (0.5%), (BYF) and KY_3F_{10}:Yb (5%), (KYF) crystals. They belong to wide band gap materials. Doped with trivalent rare-earth ions they have recently a lot of attention because of their potential applications as VUV scintillators, as media for solid state lasers in VUV, as new efficient phosphors for plasma display panels and luminescent lamps based on rare gas discharges.

As in case of $LiYF_4$ substituting ion may occupy Y^{3+}site.

Fig. 6a and b present induced absorption spectra after γ-ray irradiation with doses 10^4 Gy (curves 1) and 10^5 Gy (curves 2) of BYF:Yb (0.5%) and KYF:Yb (5%) crystals, respectively. Curve 3 in both figures illustrates induced absorption of CaF_2:Yb (30%) crystal (10^5 Gy dose) for comparison. As in case of the induced absorption for LLF:Yb and YLF:Yb crystals, we observe induced absorption bands very similar to that recorded for CaF_2:Yb crystal. The induced absorption spectrum of KYF:Yb crystal differs from all others presented here by presence of a characteristic negative absorption band near IR Yb^{3+} ion transition range (980 nm). It suggests that Yb^{2+}centers created by γ-irradiation arise in the crystal at the expense of Yb^{3+} centers. Yb^{2+} centers that respond for the induced absorption spectra in Yb doped LLF, YLF and BYF crystals favors Yb^{2+} centers related to Yb^{3+} because Compton electrons can be easy captured by Yb^{3+} pairs usually present in highly doped with Yb^{3+} crystals. The induced absorption spectrum in KYF:Yb crystal

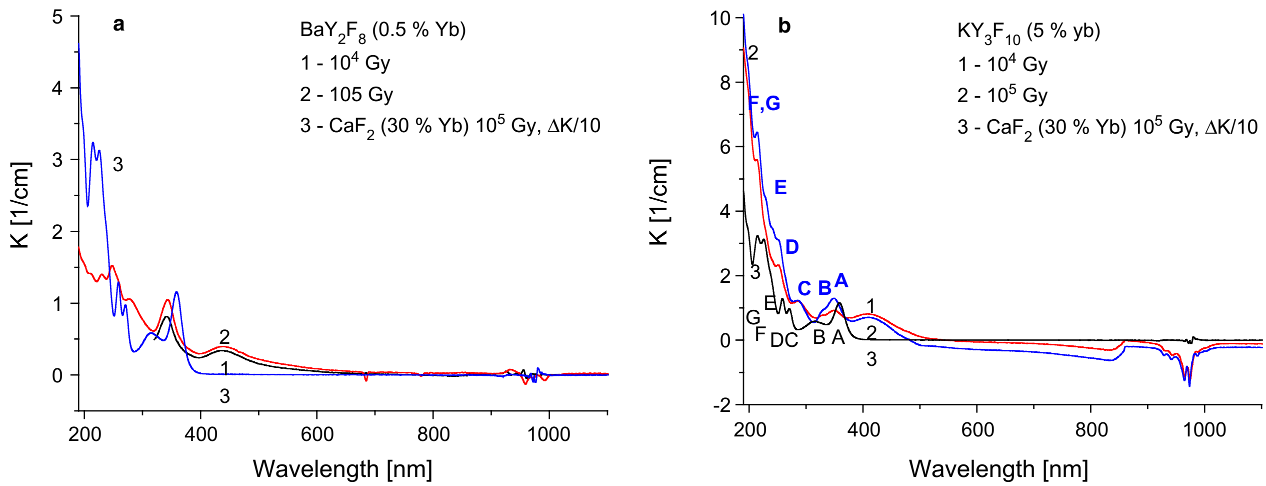

Fig. 6. (a) RT induced absorption spectra of BYF:Yb (0.5%); (b) RT induced absorption spectra of KYF:Yb (5%); curves 1–10^4 Gy dose; curves 2–10^5 Gy dose; curves 3 in both figures illustrate induced absorption of CaF_2:Yb (30%) crystal (10^5 Gy dose).

seem to be related to recharging phenomenon of the isolated Yb^{3+} ions. Generally gamma irradiation (near room temperature) results in the attachment of the secondary electrons to the preexisting Yb^{3+} clusters—which remain intact.

To check which is a mechanism of Yb^{2+} creation in the YLF:Yb, LLF:Yb, BYF:Yb and KYF:Yb crystals we performed annealing of the crystals in hydrogen and subsequent gamma irradiation. The annealing in hydrogen leads to lowering the intensity of Yb^{3+} absorption (near 980 nm) in all the cases and to disappearing of the induced by gammas bands we associated with Yb^{2+} centers. So heating in H_2 at elevated temperature reduces the Yb^{3+} ions, but also the high temperature, allowing for diffusion, results in preponderance of ytterbium centers. Oppositely to the above mentioned crystals, annealing in the hydrogen of the CaF_2:Yb crystal leads to creating of Yb^{2+} centers at the expense of Yb^{3+} centers [15]. Moreover, in case of LLF:Yb, YLF:Yb, BYF:Yb and KYF:Yb crystals, some bleaching effect is observed in short range absorption edge, depending on the time of the annealing. It means curing influence of the annealing on point growth defects present in the crystals. Subsequent gamma irradiation performed after the annealing leads to arising of the same shape of the induced absorption but in the case of KYF:Yb crystal we observe negative induced absorption near 980 nm (as in case of the induced absorption for γ-irradiated "as-grown" the crystals). It means creating of Yb^{2+} centers at the expense of Yb^{3+} ones.

To confirm the presence of Yb^{2+} centers in γ-irradiated LLF:Yb, YLF:Yb, BYF:Yb and KYF:Yb samples we performed excitation of the samples with 225 and 342 nm light. The emission spectrum of the LLF:Yb crystal reveals presence of the bands related to uncontrolled Tb^{3+} dopant and Yb^{2+} ion. The emission spectra of YLF:Yb, BYF:Yb and KYF:Yb crystals show the presence of the same type PL bands peaked at about: 260, 280, 300, 330, 360 and 550 nm but the relative intensity of the bands is different for different compounds. These are charge transfer bands (from oxygen ion to Yb^{3+} ion) and Yb^{2+} bands. So, in all the crystals underwent to γ-irradiation, we found the presence of Yb^{2+} centers in PL spectra.

4. Conclusions

γ-Ray irradiation was used for a comparative study of induced absorption phenomena and color center creation within UV/VIS/NIR spectral regions in the undoped and Yb-doped $LuLiF_4$ and $YLiF_4$ single crystals grown by Czochralski method under CF_4 atmosphere.

Induced absorption spectra are governed by the F-center absorption at 315 and 330 nm in LLF and YLF, respectively, and no induced absorption was observed above 800 nm. Position of the induced absorption bands of pure LLF and YLF shift towards longer wavelengths in YLF crystals comparing to LLF, which is coherent with larger lattice constants in the former. Yb^{3+} doping reduces the induced absorption by more than a factor of 3 in both materials but does not shift the positions of induced absorption bands. The higher is Yb- concentration, the lower is induced absorption. Moreover, the intensity of F-center significantly decreases with the increase of Yb^{3+} concentration showing clear 340 nm band we assigned to Yb^{2+}. Yb^{2+} centers that respond for the absorption spectra induced with gammas in LLF, YLF and BYF crystals favors Yb^{2+} positions related to Yb^{3+}. Only in the case of KYF:Yb induced absorption we found that Yb^{2+}centers created by γ-irradiation arise in the crystal at the expense of isolated Yb^{3+} centers (as in case of the annealing in hydrogen of CaF_2:Yb crystal [15]).

General conclusion on the influence of gamma rays onto the absorption spectrum of LLF:Yb, YLF:Yb and BYF:Yb crystals is: Yb^{3+} ions could compete with F-centers in capturing of the free electrons created after γ-ray irradiation in the crystals and so change to Yb^{2+}. The annealing of the LLF:Yb, YLF:Yb and BYF:Yb crystals in hydrogen does not introduce new Yb^{2+} centers but in distinct manner decrease the content of Yb^{3+} centers.

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