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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

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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

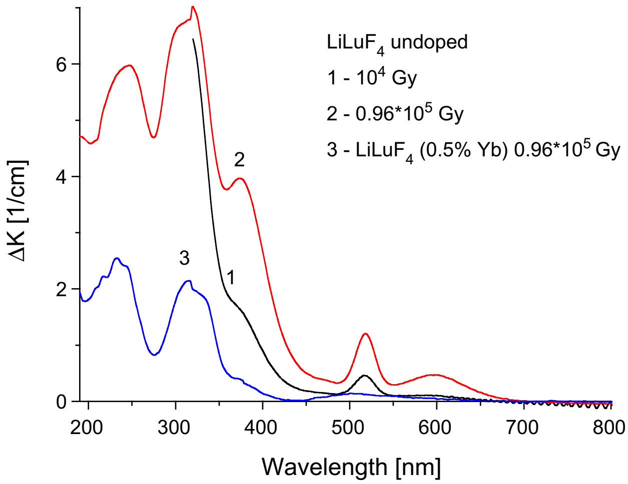

Fig. 1. Induced absorption of undoped and 0.5% Yb-doped $LiLuF_4$ obtained after γ-ray irradiation with doses: 10^4 Gy (1) and 0.96×10^5 Gy (2, 3)

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 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