Nature of Centers with Yellow-Orange Emission in Gamma-Irradiated LiF Crystals

L.I. Shchepina, L.I. Ruzhnikov, K.V. Cherepanova

Applied Physics Institute of Irkutsk State University. Blvd Gagarina 20, Irkutsk, 664003, Russia,
E-mail: schepina@api.isu.ru

Abstract – The nature of defects in LiF crystals grown by the Stockbarger technique in vacuum and colored by γ- radiation on special technology was found by using optical spectroscopy and polarization methods. The absorption band at 420 nm and emission band at 600 nm are interpreted as electron transitions in $F_2V_c^-Me^{2+}$center.

1. Introduction

The interest in given object is caused by their practical applications: from optical material for producing of prisms in spectrophotometers to integral optics and quantum electronics. The solid state reconfigurable lasers, with emission in yellow-orange range of spectrum give significant interest for quantum electronics and its medical applications. The lithium fluoride crystals with F_2 and F_3^+- color centers are perspective for these aims. The first gratifying results were received by using color centers emitting in yellow-orange range of spectrum as active centers. The model of optical stable color centers was offered (F_2 V_c^-) … Me^{2+} [1]. Recently, the works [2, 3] have appeared, in which it is reported that generation in this range of spectrum is stipulated by F_3^+- color centers. Their statement is based on the fact that the quantum efficiency, optical gain and opto- and thermo-stability of these new centers were much the same as those of F_3^+-centers. The aim of this work was to determine nature of defects emitting in yellow-orange range of spectrum in γ-irradiated LiF crystals. In this connection the purpose present paper is to install a nature of defects, radiating in the given range of spectrum in the gamma-irradiated LiF crystals.

We studied γ- irradiated ($D=10^7$–$4x10^8$ R) LiF crystals grown by the Kyropoulos method in air and by the Stockbarger method in vacuum. The crystals were exposed to the integrated emission of xenon lamp in a "kvantron" type laser head of a Kvant-17 laser (1MW) and to the fourth harmonic of an Nd:YAG laser (λ = 266 nm; ν = 12,5 Hz, τ = 10 ns, n $=10^4$ pulses, P=0,03 W at 78 K) and second harmonic (λ=532 nm; ν = 12,5 Hz, τ = 10 ns, n = 10^4 pulses) for the study of color centers (CC) phototransformation. The absorption spectra were measured on an MPS-50L spectrophotometer at 78 and 300 K in range 200–2500 nm. The emission and excitation spectra were measured on the standard installation.

2. Experimental results

The normalized spectrums of luminescence at excitement by second harmonica of Nd:YAG laser for two types of samples are given in Fig. 1. The maximum of emission band is observed on the wavelength 600 nm (Fig. 1, curv. 1) in crystals grown by the Kyropoulos method in air. The maximum of radiation is changed in long wave region of spectrum for crystals grown by the Stockbarger method in vacuum. This can be stipulated by either different encirclement, or that we observe electronic transition in different types of centers.

The emission spectrum is shown in Fig. 2, measured at T = 78 K, in LiF- Me, O, OH crystals. The luminescence is extinguished in yellow-orange range unlike similar spectrum for crystal vacuum melting (Fig. 3). We observed imposition an luminescence of molecular ion O_2^- with vibratory constant 1210 cm^{-1} (within inaccuracy of measurements complying with the value ω=1170 cm^{-1} [4]) on the emission band of F_3^+. Consequently, we register a phosphorescence of different centers in two types of crystals.

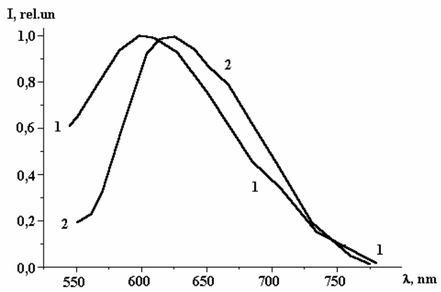

Fig. 1. Normalized spectrums of emission at excitement by second harmonica of Nd:YAG laser for LiF crystals grown by the Kyropoulos method (1) and by the Stockbarger method in vacuum (2). T=300 K

Therefore, it is necessary to take into account composition of impurity and technology of creation of lasing centers.

The charge state of the research centers was determined by using optical bleaching in the F band at 78 K under action of the fourth harmonic (4ω) of a Nd:YAG laser in sample grown by the Stockbarger method in vacuum. The concentration of F centre was valued on formula Smakula:

$$N_F\,[cm^{-3}] = 0{,}87\cdot10^{17}\cdot[n/(n^2–2)^2]\cdot1/f\cdot K_m\cdot H= =1{,}3\cdot10^{16}\cdot K_m\,,$$

where f – oscillator power, Km- absorbing factor in maximum of band, N (eV) – half-width of band of absorption. The concentration of broken F centers reached ~ $2{,}5\cdot10^{17}$ cm^{-3}.

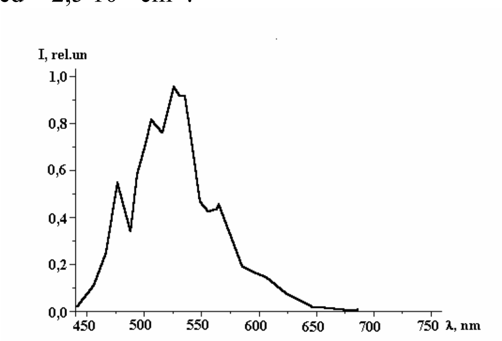

Fig. 2. Normalized spectrum of emission at excitement by forth harmonica of Nd:YAG laser for LiF crystals grown by the Kyropoulos method. T=78 К

Consequently, the electrons appear in lattice of crystal, which will interact with positively charged defects, for instance F_3^+-centres, in process of influence. Fig. 3 demonstrates a result of the optical bleaching F-centers. We observed the destruction of F_3^+(Fig. 3, curv. 2) and manifestation of a band with $\lambda_{m.ex}$=420 nm and $\lambda_{m.em}$= 600 nm. Therefore, these results indicate that investigated defects possess a neutral charge and do not interact with electrons of the F centers. This explains their high optical stability.

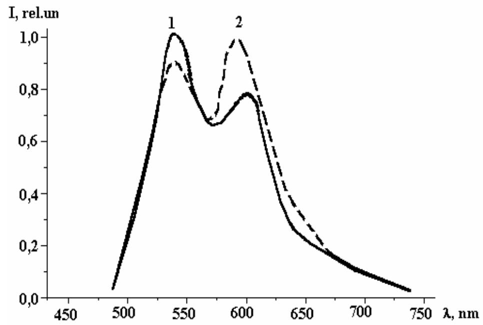

Fig. 3. Normalized spectrums of emission at excitement by forth harmonica of Nd:YAG laser for LiF crystals grown by the Stockbarger method in vacuum. T=78 К: 1 – before, 2 – after the influence $1{,}5\text{x}10^4$ pulses of 4ω harmonica of laser at T=78 K

The phototransformation of defects will be considered under the action of coherent radiation of Nd: YAG laser in LiF(F_2, F_3^+) active element channel**.** The destruction of positively-charged defects: F_3^+ with emission band λ_m=540 nm, F_2^+(λ_m=910 nm), magnesiums impurity centers ($\lambda_{mex.}$=670 и $\lambda_{m.em.}$= 740 nm) and ($F_2^+V_c^-$) …Me^{2+} ($\lambda_{m.ex=}$=580; λ_{mem}=840 нм [5]) is observed at first stage (n=10^3 pulses) optical influence 2ω harmonica of Nd:YAG laser (λ=532 nm). The band with maximum of 620 nm reveals itself, belonging to investigated defects (Fig. 4), in emission spectrum measured at 300 K.

The photoionization of color centers takes place at second stage of optical influence, when electron traps are devastated. The concentration of F_2^+($\lambda_{m.em}$.= 910 nm); ($F_2^+V_c^-$)…Me^{2+}-centres ($\lambda_{m.em}$=840 nm) and magnesium impurity centers ($\lambda_{m.em}$=740 nm) increases. We observe the displacement of maximum of emission band until λm= 650 nm, is observed when increasing a dose of optical influence with $2\text{x}10^4$ to $2{,}25\text{x}10^4$ pulses (Fig. 5).

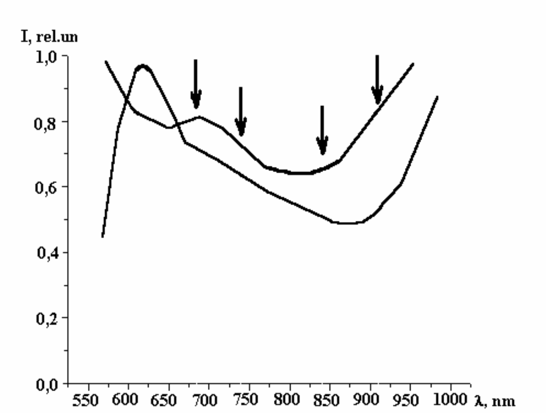

Fig. 4. Normalized spectrums of emission at excitement by second harmonica of Nd:YAG laser for LiF crystals grown by the Stockbarger method in vacuum. T=300 K. The spectrums measured in the channel of lazer element $2{,}4\text{x}10^3$ pulses(1), $5{,}4\text{x}10^3$ (2)

The optical stable F_2-centres [6] are formed in the channel. It is reasonable to conduct This experiment to conduct it is reasonable under low temperature for division of overlaying bands. Herewith we could exclude alternative mechanism of destroying F_2-centres, offered in work [7]:

$$F_2 \rightarrow F + F \quad (1);$$

$$F + V_a^+ \rightarrow F_2^+ \quad (2).$$

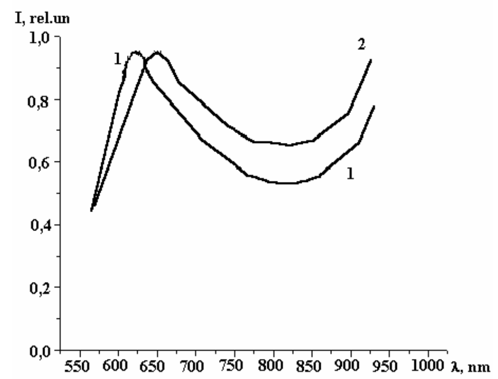

Fig. 5. Normalized spectrums of emission at excitement by second harmonica of Nd:YAG laser for LiF crystals grown by the Stockbarger method in vacuum. T=300 K. The spectrums measured in the channel of lazer element $2\text{x}10^4$ pulses(1), $2{,}25\text{x}10^4$ (2)

The anion vacancy is motionless and signifies F_2^+-centers will not be formed on reactions (2) under low temperature (T<240 K). A temperature does not play essential role at photoionization and we must to observe phototransformation of defectes: $(F_2V_c^-)$ …$Mg^{2+}\rightarrow$ $(F_2^+V_c^-)$…Mg^{2+} $F_2\rightarrow$ F_2^+. Really, the concentration of F_2^+ centers is increased in emission spectrum of active element, measured at 78 K, and F_2 centers are formed in channel after the action 3,6x10^4 pulses of coherent radiating of Nd:YAG laser (4ω).

A calculation of azimuth dependency of degree polarization of luminescence color centers are conducted in work [8] on the base classical of the model of oscillators in cubic crystals. The comparison of accounting and experimental data will allow to determine the nature and the center orientation. Calculated dependences of degree polarizations of luminescence color centers from azimuth are submitted in Fig. 6, curves 1,2,4 [8] for the plates sliced in planes (100). The experimental dependency is shown as curve 3 for LiF crystals grown by the Stockbarger method in vacuum. The analysis of curves shows that character of the dependency of degree polarizations of luminescence researched color centers from azimuth mainly corresponds to a calculated curve for oscillator with axis of C_2 symmetry [$P = 1/3(1 + \sin^2 2\alpha)$]. Consequently, kernel of luminescence centers is F_2. Really, the orientation F_2 -center must be defined by direction from given anion point to nearby, that is to say co-ordination anion to anion in crystalline lattice.

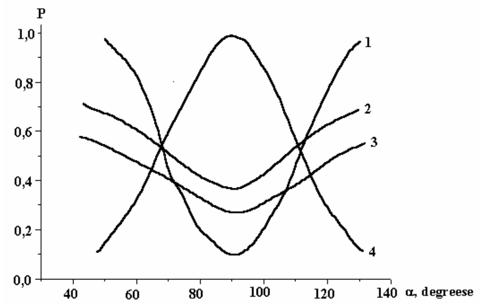

Fig. 6. The dependencies of degree to polarizations of luminescence color centers from azimuth: calculated curve for oscillator with axis of C_3 symmetry (1);-C_2(2);-C_4(4). The experimental curve for $\lambda_{m.em}$= 600 nm in LiF crystal grown by the Stockbarger method in vacuum (3)

It is easy to understand that these directions comply with C_2 axis of symmetry. There are six axes of second order, which get through mediums of ribs cube at elementary cell. The presence of cation vacancy does not change symmetry of centre. If yellow-orange luminescence observed in crystals LiF vacuum melting belonged to F_3^+ – centers, that with F_3 – a centre in analogy, radiating oscillator would possess trigonal symmetry. Consequently, radiating oscillator must have own axis of symmetry, stipulated its geometric structure, and complying with one of four axis of third order ($4C_3$). Thus a comparison of accounting and experimental data allowed to determine the nature and of emitting center orientation in yellow-orange range of spectrum as follows along axis of second order that characteristic for $(F_2V_c^-)$ – centers.

The analysis of conditions of forming the investigated centers has shown that their appearance under repeated γ -irradiation the crystals LiF vacuum melting is connected with presence of $(F_2^+ V_c^-)$ … Me^{2+} – centers ($\lambda_{m.ex=}$=580; λ_{mem}=840 nm) in samples. Thereby new band ($\lambda_{m.ex=}$=420; λ_{mem}=600 nm) belongs to F_2-centres, formed as aresult the capture of electrons by stable $(F_2^+ V_c^-)$… Me^{2+}. This conclusion is made on the grounds of vicinity of bands of excitement and emission to corresponding to features F_2 -centers, and also that

anisotropic absorption is observed in bands 410 and 435 nm under the same conditions, as band 445 nm (F_2). The possible mechanism of perturbed F_2-centres formation was offered:

$$(F_2^+ V_c^-)\ldots Me^{2+} + e^- \rightarrow (F_2 V_c^-)\ldots Me^{2+}.$$

on the basis of the facts that it was managed to observe the reverse transformation under optical bleaching from range of highenergy transition F_2-centre. A bivalent metal ion does not enter in structure of center. Otherwise the shift of maximum of band emission would be observed in more long-wave region of spectrum for radiation F_2 center (650 nm). Consequently, the defect of lattice: $(F_2 V_c^-)$ is nucleus of perturbed F_2 centers, but not impurity, as authors of work [2] stated. Thus, taking into account the experiment on determination of charge state of investigated defects and orientation of radiating oscillators along axis C_2 we prefer the last model in gamma – irradiated crystals, grown by Stockbarger method among the offered ones: F_3^+; $(F_2V_c^-)$…Me^{2+}.

References

[1] L.I.Shchepina, B.D.Lobanov, N.T.Maksimova, V.M.Kostukov, Rus. Optics and Spectroscopy **57**, 222 (1984).

[2] T. Morolo, G.Baldacchini, V.S.Kalinov, R.M.Monterali, Phys. Stat. Sol. **2**, 367 (2005).

[3] Hong – En GU, Lan QI, Liang – Feng Wan, Optics Communication. **67**, 237 (1988).

[4] J.Rolfe, Journal of Chemistry Phys. **40**, 1664 (1964).

[5] B.D.Lobanov, N.T.Maksimova, V.M.Khulugurov, I.A.Parfianovich, Bel. Journal Applied Spectroscopy. **32**, 1079(1980).

[6] B.D.Lobanov, N.T.Maksimova, Yu.M.Titov, E.I.Shuraleva, Rus. Optics and Spectroscopy **62**, 1315 (1987).

[7] E.F.Martynovich, *Color centers in lazing crystals,* Irkutsk, ISU, 2004, p 227.

[8] P.P.Feofilov, Rus. Journal Exper. Theor. Phys. **26,** 609 (1954).