Powerful, room-temperature stable LiF:F$_2^{+**}$ tunable laser

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ABSTRACT

A powerful photo- and thermostable, LiF:F$_2^{+**}$ color center laser pumped by radiation at 740 nm (alexandrite laser) or at 683 nm (Raman shifted (H$_2$) second harmonic of a Nd:YAG laser) is described. This is the first time an average power as high as ~1.4 W and an energy per pulse as high as ~100 mJ, with record real efficiency of 53% (683 nm pumping) and 28% (740 nm pumping) were achieved for a room temperature LiF:F$_2^{+**}$ color center laser. Such color center laser, tunable in the 820 - 1210 nm range, features a number of important advantages over pulsed lasers based on Ti or Cr doped crystals.

Keywords: laser, color center, tunable laser, photostability, thermostability, powerful laser

1. OVERVIEW. COLOR CENTER CRYSTALS AS ACTIVE MEDIA FOR TUNABLE LASERS

In 1965, Fritz and Menke became the first to attain oscillation with a color center (CC) crystal [1]. They used a flashlamp to pump a KCL-Li crystal with F$_A$(II) centers, cooled to liquid nitrogen temperature. In the next decade color center lasers (CCL) virtually fell outside active research interests. Considerable efforts were devoted to the development of tunable lasers using solutions of organic dyes during this period. The availability of dyes and the simplicity of an active volume creation prompted a wide range of dye laser research. However, as early as the mid-1970s, when new application opportunities and requirements arose, and the merits and shortcomings of dye lasers were clearly understood, interest in tunable CCLs was renewed. The Bell Telephone group was the first to start the new era of CCL development [2]. It was shown that CC crystals featuring allowed vibronic transitions are of considerable interest in quantum electronics. Such media usually feature very wide, homogeneously-broadened, absorption and luminescence bands, as well as high stimulated transition probabilities[2]. As a result, these crystals can be used for achieving tunable laser action [2,3,4,5,6,7], as saturable filters for Q-switching [8,9,10,11] or mode-locking [12,13] of laser resonators, for temporal pulse shaping [14], and for spatial beam profiling[15].

Among alkali-halide, alkali-earth fluoride and oxide crystals with F-aggregate color centers, LiF (F$_2$, F$_2^+$, F$_3^+$, F$_2^-$), NaF (F$_2^+$*, F$_2^+$**), NaF-Li(F$_2^+$)$_A$, CaF$_2$ -Na(F$_2$)$_A$, SrF$_2$ -Na(F$_2$)$_A$, and Al$_2$O$_3$ are the most useful for providing tunable room temperature laser action. Major spectral characteristics of these aggregate color centers at room temperature are presented in reviews by Basiev et.al. [5,6]. These crystals feature vibronic transitions with large oscillator strengths, nanosecond lifetimes, broad absorption and luminescence bands, Stokes shifts which are sufficiently large for achieving four level laser oscillation at room temperature, and high luminescence quantum yield at ~300 K.

There are, however, several reasons why not all color centers lase. For many, laser oscillation is suppressed by competing processes such as optical bleaching and CC degradation by the pump beam [5,6]. Other factors are spontaneous thermal and/or thermooptical degradation of color centers at room temperature, optically induced parasitic absorption in the emission region, nonlinear losses due to the excited state and triplet state absorption, and absorption bands from different centers overlapping the emission region. Investigations performed for over 15 years (see ref. in reviews by Basiev et al. [5,6]) have shown that the above losses can either be completely eliminated or controlled. This was demonstrated for a number of the most important laser active color centers in LiF crystals.

At the end of 1980s CCLs started to fall outside active research interest for the second time. Considerable effort is devoted during this period to the development of efficient optical parametric oscillators (OPOs) [16,] and tunable lasers based on impurity doped crystals: Ti^{3+}:Al$_2$O$_3$ [17], Cr^{3+}:BeAl$_2$O$_4$ [18], Cr^{3+}:LiCAF [19], Cr^{3+}:LiSAF [20], Cr^{4+}:Mg$_2$SiO$_4$ [21], Cr^{4+}:YAG [22], etc.

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Some scientists engaged in this research began to consider OPOs and lasers based on impurity doped crystals as better choices for tunable pulsed radiation in the near IR.

One of the objectives of this paper is to renew an interest of scientific community in color center lasers. We hope that our recent research [23] and current studies demonstrate that LiF CCLs can serve as a reliable alternative to either dye, Ti and Cr activated crystalline laser systems, or OPOs. The advantages over dye lasers include: wider wavelength tunability, compactness, long operational lifetime, rigidity and ease of handling. Compared to OPOs and impurity based lasers, CCLs are relatively insensitive to the quality of the cavity optical elements, and to the spatial, angular and spectral characteristics of the pump source. They also exhibit virtually no temporal delay between pump and output pulses. This temporal overlap of pump and generated pulses in the entire tuning range allows for easy extension in the IR region (2-18 μm) through frequency difference mixing of pump and CCL output.

LiF color center active elements combine unique spectroscopic, oscillation, modulation, thermooptic, and operational properties [5-14, 24]. Room temperature LiF color center lasers yield very high conversion efficiencies (tens of % for nanosecond pump pulse duration)[5,6,24]. Furthermore, efficient operation is observed as in CW[25] so in sub-picosecond regimes[26]. Due to the quasi-homogeneous broadening of color center gain profile the CC lasers have narrow spectral widths, achievable virtually without power loss while preserving a wide region of continuous tuning (up to 2500 cm^{-1}).

LiF crystals are moisture resistant, mechanically durable, and easy to handle. The crystals are isotropic with a face centered cubic symmetry. High-quality crystals can be grown using the Kyropulos technique, which is a simple, fast and convenient technique for producing large (for instance, Ø 400x200 mm) commercial-grade crystal boules [6]. These large crystals are suitable for use in powerful laser systems as either laser active elements or Q-switches. Such large LiF CCL's have been used to achieve energy outputs exceeding 100 J per pulse, with peak powers of 1 GW [10]. In addition, LiF solubility in water of 0.1 g/100g H_2O is acceptable for most practical applications. LiF also has good thermooptic characteristics, with a temperature-derivative refractive index, $dn/dt = -1.2 \cdot 10^{-5}$ °C^{-1} and a high thermal conductivity coefficient $\alpha = 14$ W/m°C (at 300 K). This is even higher than that of YAG crystal (13 W/m°C). The critical thermal power of LiF (thermal power at which the value of thermal aberration becomes comparable with the laser wavelength) is $P_{cr} = \lambda \cdot \alpha \cdot |dn/dt|^{-1} = 1.25$ W at $\lambda = 1.06$ μm. This value is three to four orders of magnitude higher that of dye solutions [5,6], and very close to that of YAG (1.3 W). Therefore, LiF is a promising laser material for achieving high average power lasing at room temperature.

2. F_2^+ COLOR CENTERS IN CRYSTALS. ADVANTAGES AND SHORTCOMINGS

"Pure" (non-stabilized) F_2^+ CCs in alkali-halide crystals consist of a pair of neighboring anion vacancies (located along the [110] axis), with one captured electron [27]. The fact that the anion vacancies are equivalent was used by Aegerter and Luty [27] to compare the energy levels of the F_2^+ centers with those of the hydrogen molecular ion, H_2^+. Such an approach, though not very accurate, provides a satisfactory consistency for the energies of transitions [27]. At a distance R between the anion vacancies in a medium with dielectric constant ε, the values of the F_2^+ transition energies can be obtained from the equation

$$E_{F_2^+} = \varepsilon^{-2} \cdot E_{H_2^+}\left(R/\varepsilon\right), \qquad (2.1)$$

where the values ε and R are fitted to attain better agreement with experimental results.

The F_2^+ CC energy level diagram is presented in Fig. 1.

The levels are marked analogously with those of the H_2^+ molecular ion. The low-lying optical transition is the transition $1s\sigma_g \rightarrow 2p\sigma_u$. The two higher-energy transitions, $1s\sigma_g \rightarrow 2p\pi_u$, are in the region of the F absorption band. It should be noted that the
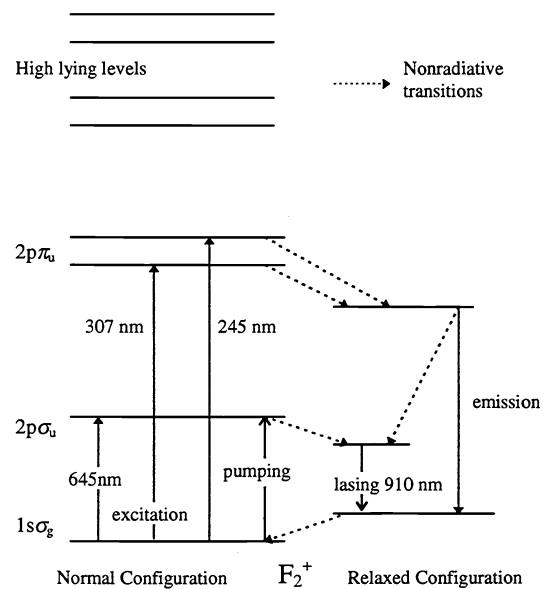

Fig. 1 Energy level diagram of the F_2^+ center in LiF

quantum yield of the radiational transition from the upper $2p\sigma_u$ level, presented in the diagram, decreases practically to zero with increasing temperature up to 100 K [28]. At temperatures above 100 K, only emission from the lower excited $2p\sigma_u$ level can be observed. The quantum yield of this F_2^+ emission, which is observed for all alkali-halide crystals is rather high. For instance, according to Parfianovich et al.[29], quantum yield for LiF:F_2^+ is equal to 0.52 at 90 K, and 0.15 at 300 K.

Some spectroscopic data for pure F_2^+ CCs in LiF are presented below. The first most comprehensive studies of the F_2^+ CCs optical properties were performed by Nahum [30]. A relative oscillator strength of the optical transition $1s\sigma_g \rightarrow 2p\sigma_u$ at λ_{max}=645 nm was determined experimentally to be [30]: $f_{F_2}/f_{F_2^+} = 1.1$. The temperature dependence of the absorption bandwidth, determined by measurement of excitation spectra, can be satisfactory described with the following formula [27,28]:

$$\Delta v(T) = \sqrt{8 \cdot \ln 2 \cdot S_0} \cdot \hbar\omega_o \sqrt{cth(\hbar\omega_o/2kT)} = \Delta v(0)\sqrt{cth(\hbar\omega_o/2kT)},$$ (2.2)

with parameters $\Delta v(0)$=2450 cm^{-1}, ω_b=2π·6.8·10^{12} s^{-1}, S_0=21.1, where $\Delta v(0)$ is the multiphonon bandwidth at O K, ω_b is the effective phonon frequency, and S_0 is the effective Huang-Rhys factor.

The luminescence band with λ_{max}=910 nm and bandwidth 1730 cm^{-1} corresponds to the radiational transition $2p\sigma_u \rightarrow 1s\sigma_g$ of the F_2^+ CCs in LiF at 77 K. The temperature dependence of the luminescence band half-width is determined by formula (2.2) with parameters $\Delta v(0)$=1720 cm^{-1}, ω_b=2π·7.4·10^{12} s^{-1}, S_0=8.74. The F_2^+ luminescence band shape in LiF is well described by the Gaussian curve. The measured lifetime of the relaxed excited at 77 K state equals 29 ns [31].

The ionic configurations of the F_2^+ and $F_A(II)$ CCs are identical in a relaxed excited state. This enabled F. Luty, who studied comprehensively properties of these color centers, to suggest to the Bell Telephone group in 1974, their use as a laser active center [32]. Lasing on F_2^+ CCs at liquid nitrogen temperature was done for the first time by Mollenauer[33]. Later, he reported on much higher efficiency (~60%) and average CW power (up to 1.8 W) for a LiF:F_2^+ laser[34], again when the laser crystal was kept at 77 K. Despite of very favorable laser characteristics of LiF:F_2^+ crystal (high gain, low losses, high optical quality) the problem of fast thermal degradation of active F_2^+ centers at higher temperatures has drastically limited possible application of such laser.

Room temperature lasing of F_2^+ CCs in LiF crystal was attained for the first time by Gusev et al. [35] under ruby laser pumping. The efficiency of the laser was not high (2÷6%), and the thermal degradation of F_2^+ CCs at 300 K with a half decay time of 12 h prevented the crystal from being used for more than 24 h.

To solve the problem of stability of LiF active media with unpertubed F_2^+ centers at room temperature, a new method for LiF:F_2^+ lasing due to nonlinear $F_2 \rightarrow F_2^+$ photoionization was suggested by Basiev et.al.[36].

A group at Irkutsk State University, Russia [29,37] doped the original crystals with impurities to stabilize F_2^+ CCs. The LiF crystals doped with hydroxyl ions enabled the formation of $F_2^+(OH)$ CCs that are thermostable up to a temperature of 380 K. However, besides the thermostabilizing effect of the hydroxyl ions, some decline of the laser output characteristics was observed. Since then, numerous publications related to the lasing of LiF crystals with unpertubed and stabilized F_2^+ CCs have appeared (see, for example, ref. in review by Basiev and Mirov [5]). Nevertheless, the problem of LiF:F_2^+ active element operational stability has been not solved completely.

Below we propose a method for efficient photo- and thermostable lasing of LiF:F_2^+ stabilized (LiF: F_2^+**) color center crystals. Our preliminary experimental results show that such LiF:F_2^+** color center laser demonstrates excellent room-temperature-stable performance.

3. TECHNOLOGICAL ASPECTS OF PHOTO- THERMOSTABLE LIF:F$_2^{+**}$ COLOR CENTER CRYSTAL DEVELOPMENT

One of the most important differences between the stabilized LiF:F$_2^{+**}$ crystals described in the current paper and LiF:F$_2^+$ like crystals known from the literature is a technology of multistage irradiation and thermal treatment of specially doped crystals. The proposed technology provides simultaneously the highest possible concentration of F$_2^+$ like centers in LiF at a small level of losses, efficient thermal stabilization of F$_2^+$ like centers, and significantly reduce the efficiency of formation of color centers - donors of electrons, what, in turn, dramatically improves the overall photostability of the crystal under powerful laser excitation.

3.1 Thermal stabilization

LiF crystals were grown by Kyropulos method in platinum crucibles under argon atmosphere from nominally pure raw materials, doped with LiOH, Li$_2$O, and MgF$_2$.

Infrared measurements of the absorption bands of the grown LiF crystals showed an intense band (absorption coefficient ~ 1.2 cm^{-1} at v_m=3730 cm^{-1}) of valent vibrations of OH$^-$ ions, substituting fluoride in the anion node of the crystalline lattice, and intense bands with frequency maxima at 3560 and 3610 cm^{-1}, corresponding to complexes Mg^{++}OH$^-$ OH$^-$V$_c^-$. UV absorption spectra of the grown LiF crystals exhibit some strong absorption bands in the region 200-270 nm that are due to the O^{2-}-V$_a^+$ as well as O^{2-}-Mg^{2+} dipoles.

The formation of aggregate color centers in alkali-halide crystals under ionizing radiation is a complicated process. It involves emergence, separation, and recombination of primary Frenkel defects, association into aggregate F$_2$, (F$_2$)$_A$, F$_2^+$, (F$_2^+$)$_A$, F$_2^-$, F$_3$, F$_3^+$, F$_3^-$ and other color centers and recharging of color centers by electrons and band holes. The defect formation may run fast or slow. Decomposition of self-localized excitons into primary radiational defects and recharging of color centers are relatively fast processes (10^{-12} -10^{-7} s). Slow processes run either due to spatial diffusion of the defects and their associates, or due to diffusion of self-localized holes (resulting in color centers recharging).

The efficiency of formation of any type of color centers is determined by all the above processes. These processes depend upon the temperature of irradiation and storage of the crystal, impurity composition of the initial material, ionizing radiation dose power and irradiation dose.

Separated electrons and holes, free and self-localized excitons are generated in alkali-halide crystals under ionizing irradiation. Self- localized excitons decompose with the emergence of pairs of F-centers and interstitial halogen atoms (H). A fast recharging of these pairs under flux of electrons gives rise to actually simultaneous formation of the anion vacancies V$_a^+$ and interstitial halogen ions I$_a^-$ [38]:

$$e_s^o \Rightarrow F + H,$$ (3.1)

$$e_s^o \Rightarrow V_a^+ + I_a^-$$ (3.2)

The mechanisms of formation of aggregate centers through migration of anion vacancies have been studied by Delbecq.[39] According to this paper, charged F$_2^+$ centers first appear, and then capture electrons to produce neutral F$_2$ centers:

$$V_a^+ + F \Rightarrow F_2^+,$$ (3.3)

$$F_2^+ + e \Rightarrow F_2$$ (3.4)

Simultaneously with a fast process of electron capture, F$_2^+$ centers may take part in a slow temperature-dependent migration process. Colliding with the F, F$_2^+$ and F$_2^-$ CCs, they form more complex CCs - F$_3^+$, F$_4^+$, and F$_4$, respectively:

$$F_2^+ + F \Rightarrow F_3^+,$$ (3.5)

$$F_2^+ + F_2 \Rightarrow F_4^+,$$ (3.6)

$$F_2^+ + F_2^- \Rightarrow F_4,$$ (3.7)
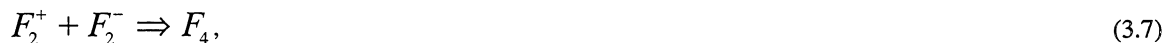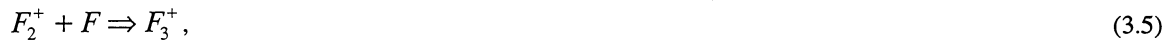
whose further aggregation leads to the appearance of colloid particles in the crystal. The processes of F_2 CCs formation by scheme (3.4) are competing with the processes of their ionization due to a fast capture of free electrons:

$$F_2 + e \Rightarrow F_2^-, \tag{3.8}$$

or holes

$$F_2 + h \Rightarrow F_2^+, \tag{3.9}$$

or due to diffusion processes involving mobile anion vacancies

$$V_a^+ + F_2 \Rightarrow F_3^+, \tag{3.10}$$

and self-localized holes

$$F_2 + V_k \Rightarrow F_2^+. \tag{3.11}$$

The processes of the type 3.4, 3.8, 3.9, 3.11, leading to recharging in the group of F_2, F_2^+, and F_2^- CCs, are also inherent in the group of F_3, F_3^+, and F_3^- CCs.

The ratio of the contributions of different reactions depends on the irradiation procedure and impurity composition in the irradiated crystal. The optimization of irradiation treatment to create F_2^+ stabilized color centers in doped LiF crystals is discussed below.

<u>1 stage</u>

The crystals are subjected to an ionizing treatment at temperatures lower than temperature $T(V_a^+)$ of anion vacancy (V_a^+) mobility in LiF crystals.

Ionizing treatment creates a great number of divided electron and holes, which after thermalization can form self-localized excitons. These excitons localized near a specific anion node of the crystalline lattice may annihilate and the released energy can be used for shifting anion from its node to the interstitial position causing formation of anion vacancy and F center according to the schemes (3.1) and (3.2).

Simultaneously with primary defect formation according to (3.1) and (3.2), two processes of (OH)⁻ ions dissociation are taking place under ionizing treatment:

$$2(OH^-) \Rightarrow O_2^- + e + V_a^+ + 2H_i^o, \tag{3.12}$$

and

$$2(OH^-) + V_a^+ + e \Rightarrow O^{--}V_a^+ + O^- + 2H_i^o, \tag{3.13}$$

where "O_2^-" is a molecular ion of oxygen, "O^-" is a single ionized atom of oxygen, and "H_i^o" is an interstitial atom of hydrogen.

It is very important that there is no formation of the aggregate color centers during the irradiation of the crystal at temperatures below the temperature of mobility of anion vacancies. $O^{--}V_a^+$ dipoles are accumulated in a high quantity, since they are photo- and thermostable under γ-irradiation. In addition to this, ionizing treatment creates a high concentration of single ionized oxygen atoms and molecules due to a hydroxyl group dissociation. It is noteworthy to mention that one of the products of OH⁻ radiolysis --interstitial H_i^o atoms are efficient traps of electrons:

$$H_i^o + e \Rightarrow H_i^-, \tag{3.14}$$

which prevent the electrons from being captured by the F_2^+ center, thereby increasing the efficiency of accumulation of stable F_2^{+**} centers on the following stages of the crystal preparation.

The role of Mg dopant is very important, too. According to the process (3.1) the F center formation is likely to occur near impurity-cation vacancy dipole Mg^{++}- V_c^-. The F center gives its electron to the divalent metal forming Mg^+ and a pair of vacancies:

$$Mg^{++}V_c^- + F \Rightarrow Mg^+ + V_a^+V_c^-. \tag{3.15}$$

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Anion-cation dipoles are important components of F_2^+ pertubed color centers that are formed at the second stage of the crystal preparation. At the same time superfluous concentration of Mg dopant may play a negative role due to decreasing concentration of the useful O^- V_a^+ dipoles by bonding with oxygen and formation of the $Mg^{++}O^{--}$ dipoles that do not take part in F_2^+ like center formation.

<div align="center">2nd stage</div>

At the second stage of the technological process the crystals are heated up to $T(V_a^+)$ <T <T(mobility of F_2^+, $V_a^+V_c^-$ and O^- V_a^+ dipoles) and stored at this temperature for some time. During this time an important process of formation of unpertubed F_2^+ color center takes place due to diffusion of mobile anion vacancies and their association with F centers:

$$V_a^+ + F \Rightarrow F_2^+ .$$ (3.16)

In a result the concentration of F centers is decreased due to their association with anion vacancies. It is a useful process helping to increase at the following stages the concentration of F_2^+ stabilized centers and decrease concentration of other aggregates and colloids. Note that the above mentioned temperature interval is chosen within these borders since anion vacancies are mobile in the crystal and F_2^+ centers as well as $V_a^+V_c^-$ and O^- V_a^+ dipoles are frozen and can not diffuse in the crystalline lattice.

<div align="center">3-d stage</div>

At the third stage the crystals are re-irradiated at the temperature T< $T(V_a^+)$ and then subjected to the procedure described in the stage two. The main idea of this treatment is to increase the amount of pure F_2^+ centers by means of increasing of the amount of anion vacancies (by the neutral F centers ionizing) that have been exhausted at the second stage due to process (3.16).

<div align="center">4-th stage</div>

At the fourth stage the crystals heated up to the room temperature and are stored for some period of time, after which the crystal exhibit a stable concentration of the color centers of interest and is ready for utilization as active medium for tunable laser. The processes that take place at this stage are as follows.

First of all at room temperature the O^- V_a^+ complexes are mobile and their migration leads to the development of F_2^{+**} centers stabilized with the O^{--} ion ($F_2^+O^{--}$)

$$O^{--}V_a^+ + F \Rightarrow F_2^+O^{--} .$$ (3.17)

Another very important reaction occurs due to the intrinsic mobility of F_2^+ centers at room temperature. The migration of these centers may lead to a useful process of association of F_2^+ centers with a single ionized oxygen atoms O^- with $F_2^+O^{--}$ centers formation

$$F_2^+ + O^- + e \Rightarrow F_2^+O^{--} .$$ (3.18)

Since at room temperature bi-vacancy dipoles $V_a^+V_c^-$ are mobile too ($V_a^+V_c^-$ start to be mobile at temperature about 273 K) they may associate with F centers and a pertubed F_2^+ centers occur:

$$V_a^+V_c^- + F \Rightarrow F_2^+V_c^- .$$ (3.19)

In a result of the described LiF crystal multistage treatment we provided the optimal conditions for useful processes (3.17-3.19) of F_2^+ stabilized color center formation and suppressed the efficiency of the parasitic processes (3.4-3.10) responsible for formation of other aggregate and colloid centers.

3.2. How the problem of photostability is solved.

Formation of thermostabilized active color centers provides only half of the success in achieving stable lasing of the color center crystal. In addition to solving the problem of thermostability it is necessary to realize photostability of the active color center as well as other color centers that may be ionized by the powerful excitation of a pump laser.

In our case, in addition to F_2^{+**} color centers, LiF color center crystal also contains a significant concentration of neutral F_2 centers. The investigations performed in [36] have demonstrated that photodestruction of F_2 centers by the radiation

overlapping with its absorption band occurs via a two-step ionization process. As a result free electrons are localized at the other aggregate color centers (see process 3.8).

Therefore, the proposed method for photo-thermostable lasing of LiF: F_2^{+**} color center crystals is based on three important considerations.

1) The technology of active medium formation should provide a highest possible concentration of the working optical centers. In this case the pump radiation will be predominantly absorbed by the photostable F_2^+ like centers.

2) From one hand, pump radiation should match the absorption band of F_2^{+**} color centers to provide a population of inversion and lasing of these centers, and from the other, its wavelength should be longer than the threshold wavelength determining the process of two step ionization of the neutral F_2 centers. For the LiF crystals this wavelength is about 590 nm.

3) The wavelength of the pump radiation should not match the absorption bands of the parasitic aggregate color centers that may occur in the crystal and result in decreasing of the efficiency of lasing. For LiF crystal these parasitic color centers exhibit absorption in the region 500-600 nm. Taking in consideration the above-mentioned circumstances, the optimal spectral region for wavelength for LiF: F_2^{+**} color center laser pumping is about 590-750 nm.

4. SPECTROSCOPIC AND LASER CHARACTERIZATION OF LiF:F_2^{+**} CRYSTALS

4.1 Experimental details

Absorption measurements were made with a Shimadzu 3401UVPC spectrophotometer.

For measurement of luminescence spectra we used a spectroscopic set-up based on Acton Research 750 monochromator with R406 Hamamatsu photomultiplier or InGaAs detectors. Spectral sensitivity of the spectroscopic detection system in 700-1500 nm was measured with the help of calibrated tungsten halogen lamp (Oriel). These data were used for correction of measured luminescence spectra. Luminescence decay curves were measured with a fast sampler module SR255 (Stanford Research). Radiation at 683 nm (Raman shifted second harmonic of a pulsed Nd:YAG laser) was used as an excitation source for measurements of luminescence spectra and luminescence decay curves of F_2^{+**} color centers in LiF.

4.2 Absorption and luminescence measurements

The results of spectroscopic evaluation of the laser crystals used are illustrated in Fig.2 and Fig.3. F_2^{+**} color centers feature quasi-homogeneously broadened absorption ($\lambda_{max} \sim 620$ nm, $\Delta v \sim 3550$ cm^{-1}) and luminescence ($\lambda_{max} \sim 890$ nm, $\Delta v \sim 2300$ cm^{-1}) bands. The luminescence decay curves measured at 77 and 300 K are shown in Fig.3. Short width (6 ns) of the excitation pulse allowed for accurate measurement of short F_2^{+**} luminescence lifetime (20 ns at 300 K and 37.5 ns at 77 K, see Fig.3). Using the data for the luminescence lifetime at 77 and 300 K we estimated the quantum efficiency of luminescence to be ~55% at 300 K.
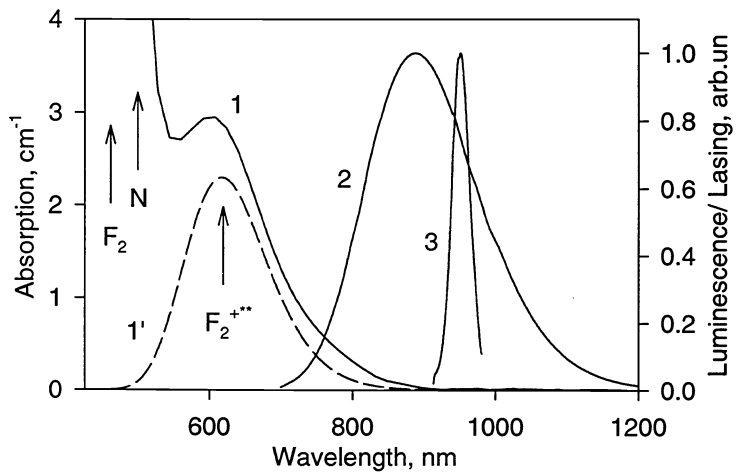

Fig. 2 Absorption (1 and 1'), luminescence (2) and lasing (3) spectra (in non-selective resonator) for F_2^{+**} color centers in LiF laser crystal at 300 K

Developed LiF:F_2^{+**} crystals feature a high concentration of the active F_2^{+**} centers ~4-8x10^{16} cm^{-3} (absorption coefficient ~2.3 cm^{-1} at 620 nm) at a low level of losses (contrast ~40), and high emission cross section (σ_e=5.7x10^{-17} cm^2 at 890 nm).

The F_2^{+**} concentration was determined with the help of a well known Smakula's equation:

$$N_F = 0.87 \cdot 10^{17} \cdot \frac{n}{\left(n^2 + 2\right)^2} \cdot \frac{1}{f} \cdot \alpha(cm^{-1}) \cdot \Delta v(eV)$$ (4.1)

where $\alpha = 2.3$ cm^{-1} - absorption coefficient, $\Delta v = 3577$ cm^{-1} or 0.4435 eV - HWFM for absorption, n = 1.39 - refractive index at 620 nm, f = 0.1 - 0.2 - oscillator strength.

As can be seen in Fig.2, the absorption range (i.e. suitable pumping range) of F_2^{+**} laser crystals is between 500 and 800 nm. The threshold wavelength for F_2 centers two-step photoionization in LiF is about 590 nm. For example, pumping of the LiF:F_2^{+**} crystals by powerful radiation of the second harmonic of a Nd:YAG laser (532 nm) results in significant fading of the color center laser output [40], although, at low levels of pumping (several tens of millijoules), the color center laser will operate relatively well [41]. The fading under high power excitation is caused by the photo-chemical process in the pumping channel of the crystal, which involves two-step photoionization of neutral F_2 centers and trapping of the released electron by the positively charged F_2^{+**} centers. In principal, this problem can be solved by complete elimination of F_2 centers from a LiF crystal, while preserving the concentration of F_2^{+**} centers. However, technologically this is not a simple task. Therefore in order to decrease absorption by F_2 and N centers (Fig.2, curve 1) and avoid photoionization of F_2 centers, it is necessary to shift the excitation to the long wavelength part of the F_2^{+**} absorption band (590-750 nm). Thus the wavelength range of an alexandrite laser, which emits in the 700-800 nm range, or the 1st Stokes component at 683 nm of a Raman shifted (H_2) frequency doubled Nd:YAG laser makes them very attractive pumping sources for a LiF:F_2^{+**} laser.
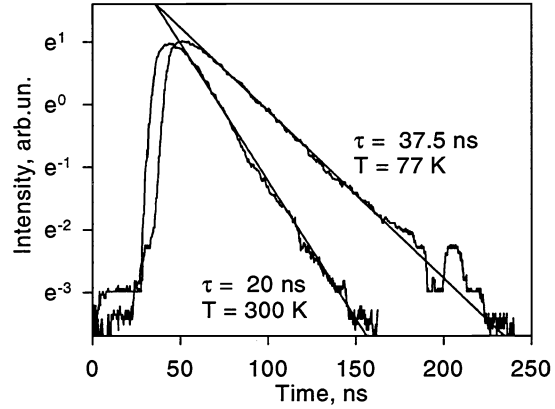

Fig.3 Luminescence decay curves of F_2^{+**} color centers in LiF crystal ($\lambda_{ex} = 683$ nm, $t_{pulse} \sim 6$ ns)

In our experiments LiF:F_2^{+**} crystals did not exhibit any photodegradation when pumped by radiation in 680-750 nm spectral region at energy densities of up to 5-10 J/cm^2 (this value is limited by optical damage of the crystal host). We estimated the lifetime of these color center crystals to exceed 10 years at room temperature.

4.3 Stable room-temperature lasing of LiF:F_2^{+**} crystals

Initial laser experiments were performed in a simple flat-flat resonator, set to a length of about 20 cm. The active element, with Brewster faces, had 40 mm length and clear aperture of 8x8 mm. The input dichroic mirror transmitted $\geq 93\%$ at 683 and 740 nm and reflected $\geq 99\%$ in the 875-1040 nm range. An unfocused pumping beam was introduced into a crystal through this dichroic mirror. The output coupler transmitted about 50% in the 800-1100 nm range. Parameters of the pumping laser sources used in our experiments are given in the Table 1.

Pumping laser	Wavelength, nm	Energy per pulse, mJ	Pulse width, ns	Repetition rate, Hz
Alexandrite laser PAL-101 (Light Age, Inc.)	740	up to 250	~ 60	20
Raman shifted (H_2) SH of Nd:YAG laser GCR-230 (Spectra Physics, Inc.)	683	up to 250	~ 6	10

Table 1. Main parameters of the pumping lasers used

Experimentally, it was determined that for alexandrite laser pumping the optimum wavelength was ~740 nm. Because the alexandrite laser has the maximum output energy around 750 nm, with a sharp drop to 720 nm, the pumping wavelength of 740 nm is a compromise at which the output energy of alexandrite laser is high enough and the absorption of F_2^{+**} centers is still sufficient for effective lasing. It is necessary to point out that some laser properties of F_2^+-like centers
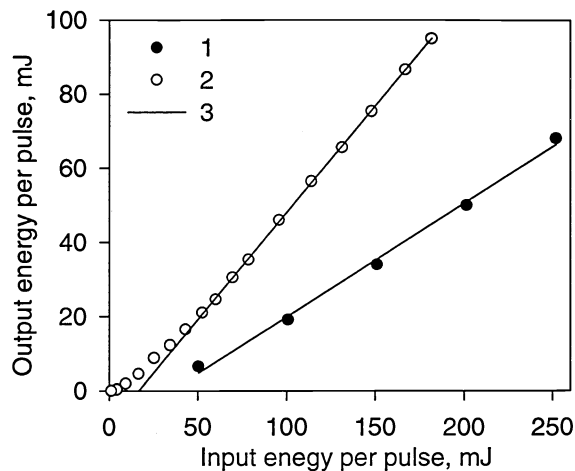
Fig.4 Input/output dependence for LiF:F_2^{+**} laser at 300 K with nonselective resonator: (1) λ_{pump}=683 nm, and (2) λ_{pump}=740 nm. Line (3) is linear fit.
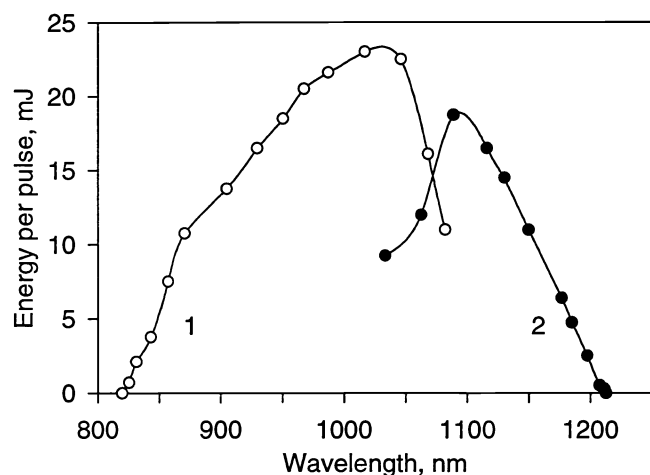
Fig. 5 Tuning curve for room temperature LiF:F_2^{+**} laser under alexandrite laser pumping (λ_p=740 nm, E_p ~ 145 mJ)

under alexandrite laser pumping were briefly reported by Lobanov and Kostyukov [42].

The lasing spectrum for the LiF:F_2^{+**} laser with a non-selective resonator under alexandrite laser pumping (740 nm) is shown in Fig.2 (curve 3) with maximum at 950 nm and bandwidth of about 30-40 nm (FWHM). The input-output curve for this laser with a 50% output coupler is shown in Fig.4 (curve 1) with slope efficiency of ~31%. The lasing threshold was estimated to be ~150 mJ/cm². A maximum output average power of 1.4 W was achieved with 5 W of input power at 740 nm incident onto the crystal (real efficiency ~ 28%).

The same resonator arrangement was used for 683 nm pumping radiation, but the output coupler had 10% reflectivity. A much higher slope efficiency of 58% and real conversion efficiency of ~ 53% were obtained (see Fig. 4, curve 2). The efficiency was higher than for alexandrite laser pumping because (1) the 683 nm wavelength is closer to the absorption peak (620 nm) of F_2^{+**} centers (k_{683nm}/k_{740nm}=2.9), and (2) temporal relationship between the laser pulsewidth and luminescence decay time (τ_{lum} =20 ns) is different: t_{pulse}=6 ns < τ_{lum} for the 683 nm pumping and t_{pulse}=60 ns > τ_{lum} for alexandrite laser. The lasing threshold of 7-8 mJ/cm² under 683 nm pumping was also lower (even with 10% reflectivity of output coupler). The maximum output power of the LiF:F_2^{+**} laser was limited by the available capabilities of the pumping lasers used.

In order to measure the tuning range, the output coupler was replaced with a diffraction grating with 1200 grooves/mm. The experimental tuning curve extended from 820 to 1120 nm and is shown in Fig.5 (curve 1). By replacing the input dichroic mirror, optimal for 875-1040 nm range, with a mirror which had high reflectivity in 1000-1300 nm and low reflectivity in 800-1000 nm ranges the tuning range was extended up to 1212 nm. By using LiNbO₃ crystal for second harmonic generation, the spectral output of the color center laser was extended in 410-606 nm visible range.

Due to the fact that the emission band of LiF:F_2^{+**} crystals partially overlaps with the emission band of commonly used Ti:sapphire lasers, it is of interest to compare these two materials. Their main spectroscopic and thermo-optical properties are given in the Table 2.

As one can see, the luminescence bandwidth is similar for both materials but the luminescence peak for F_2^{+**} centers is shifted toward longer wavelengths. The main difference lies in the value of emission lifetime and cross-section. Ti:sapphire has relatively low emission cross-section as compared with LiF:F_2^{+**} crystal. The consequences of that for Ti:sapphire are a high lasing threshold (~1 J/cm²) and a lack of temporal overlapping of pump and generated pulses in pulsed regime. The latter makes it very difficult to perform nonlinear frequency mixing of pump and generated laser beams.

A LiF:F$_2^{+**}$ laser combines the advantages of a dye laser, such as high quantum efficiency, large emission cross sections, and wide tuning ranges, with the advantages of solid state laser media: crystalline host, high thermal conductivity, easy handling and high optical damage threshold. The other very important feature, almost unreachable for dye lasers and OPOs, is the possibility for easy scaling of the LiF:F$_2^{+**}$ laser. Crystal sizes as large as $\varnothing$ 400x200 mm can easily be achieved for LiF.

Material	LiF:F$_2^{+**}$	Ti:sapphire
Luminescence maximum, nm	890	760
Luminescence halfwidth, nm	**185**	**175**
Emission cross-section, cm^2	**5.7x10^{-17},**	**2.7x10^{-19}**
Laser threshold, J/cm^2	**2.5x10^{-3}**	1
Quantum efficiency	0.55	0.80 .
Damage threshold, J/cm^2	~ 10	~ 10
Coefficient of heat conductivity, W/mK	14.2	35.0
Luminescence lifetime at 300 K, ns	20	3150

Table 2. Comparison of main spectroscopic properties of LiF:F$_2^{+**}$ and Ti:sapphire laser media

An alexandrite-color center laser combination may be an excellent alternative for pulsed Ti:sapphire tunable laser and even surpass it in a region of continuous wavelength tuning (0.7-1.20 μm). The fact that the LiF:F$_2^{+**}$ laser pulses have almost no temporal delay relative to the pump laser pulses makes the alexandrite - color center laser combination a very attractive source of coherent radiation tunable in 2.5-7.5 μm IR range by nonlinear mixing of pump and generated beams.

LiF:F$_2^{+**}$ color center laser can be a good alternative for OPOs and pulsed tunable lasers based on impurity doped crystals in 800-1200 nm range. Compared to OPOs and impurity based lasers, LiF:F$_2^+$** lasers feature high gain and low threshold, and are relatively insensitive to the quality of the cavity optical elements as well as the spatial, angular and spectral characteristics of the pump source. Also color center lasers are free of such difficulties, common to OPOs, as spectral line stability and high threshold of a narrow-linewidth generation. Moreover, application of frequency mixing of the pump radiation and tunable radiation of the color center laser in a nonlinear crystal will allow for extension of the laser tuning range in the middle and far infrared regions of the optical spectrum.

In conclusion, a highly efficient tunable room temperature LiF laser, based on F$_2^{+**}$ color center crystals, was developed. A LiF:F$_2^{+**}$ room-temperature-stable color center laser with an output power of ~1.4 W and output energy per pulse of ~100 mJ with real efficiency of about 28% under alexandrite laser pumping and 53% under 683 nm pumping has been demonstrated as a first effort. This is the highest known average output power/ energy per pulse reported for a room temperature LiF:F$_2^+$ laser. A photo- and thermostable regime of operation was realized due to an advanced approach in the technology of LiF crystals with stabilized F$_2^+$ color centers as well as a new method of lasing.

ACKNOWLEDGMENTS

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