Kinetics of accumulation and excitation of F_2^+ centers in LiF(F_2) crystals

T. T. Basiev, Yu. K. Voron'ko, S. B. Mirov, V. V. Osiko, and A. M. Prokhorov
P.N. Lebedev Physics Institute, USSR Academy of Sciences

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In this paper we propose a mechanism for the accumulation of F_2^+ color centers and their excitation in a LiF crystal with stable, neutral F_2 centers. The practical realization of this made it possible to build tunable lasers ($\lambda_E = 0.84$–1.1 μm) operating at room temperature with a high efficiency and a high pulse repetition rate.

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Lasers using color centers in alkali-halide crystals are a new class of tunable, solid state optical lasers whose emission spectrum covers a wide range of wavelengths of the near infrared and visible light. Lately, therefore, their development has attracted considerable attention (see for example, Refs. 1–5).

Usually, the excited color centers in the existing lasers (for example, F_2^+ in LiF and NaF crystals[2,5] and $F_B(\pi)$ in KCl-Na and RbCl-Na crystals[6]) are unstable at room temperature and break down in several days or hours after their formation. Stability of the active centers is achieved by storing and using the crystals at liquid nitrogen temperatures, which greatly complicates and limits the range of application of the lasers using these centers.[1–3]

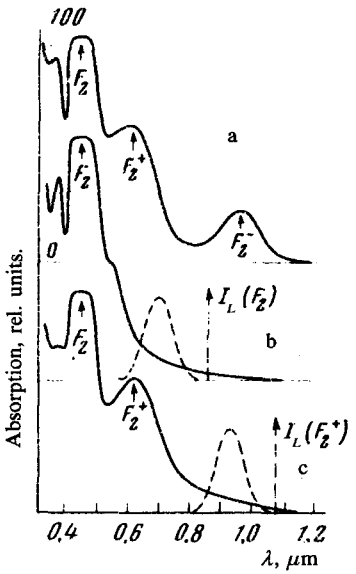

FIG. 1. Absorption spectra of a pure, γ-ray irradiated LiF crystal: a, photographed 4 hours after γ-ray irradiation; b, photographed after additional treatment of the crystal by uv radiation (---, luminescence spectrum of the F_2 centers produced as a result of their excitation by light $\lambda = 0.53$ μm); c, photographed in the active zone of the crystal, which is subjected to an intensive exposure to light with $\lambda = 0.53$ μm (---, luminescence spectrum of the F_2^+ centers produced as a result of their excitation by light with $\lambda = 0.53$ μm).

One way to eliminate these deficiencies is to stabilize the excited centers by introducing in the crystal additional impurities (for example, oxygen ions[4]). It is difficult, however, to stabilize large concentrations of excited centers by using this method, because of the appearance of large quantities of other aggregation centers whose nucleation efficiency is high.[1,5]

In this paper we propose a new method of color-center excitation, which makes it possible to produce selectively a high concentration of excited centers and thus secure a stable excitation without preliminary stabilization, a high efficiency, and a high pulse repetition rate at room temperature.

Let us examine the conversion processes of the color centers in a pure LiF single crystal colored by $\sim 10^7 p$ γ-radiation dose from a Co^{60} source. Figure 1a shows an absorption spectrum of pure LiF, taken 4 hours after its irradiation. It has three characteristic bands. As shown in Refs. 3 and 7, the F_2 centers—pair anion vacancies that have captured two electrons each—are responsible for the band with $\lambda_{max1} = 450$ nm, the F_2^+ centers are responsible for the band with $\lambda_{max2} = 645$ nm, and F_2^- centers, which are pair anion vacancies with one and three electrons, respectively, are responsible for the band with $\lambda_{max3} = 960$ nm. Of the aggregate of centers examined the most stable are the neutral F_2 centers whose concentration is much higher than that of the ionized F_2^+ and F_2^- centers. The lifetime of the F_2^+ and F_2^- centers at room temperature is estimated to be many months; however, the half-life of the F_2^+ centers is only 12 hours.

In this work we were interested primarily in the excitation of the F_2^+ centers which overlap the important region of pumping wavelengths from 0.84 to 1.1 μm.

The important conditions for efficient excitation of the F_2^+ centers are selective establishment of their high concentration and the absence of parasitic centers that are absorbed at the laser-transition frequency. The F_2^- centers are in the latter category. The F_2^- color centers can be easily eliminated in the crystal either by irradiating the crystal by ultraviolet radiation or by annealing it. After such procedure we obtain a crystal that contains only stable neutral F_2 centers that do not change their properties with time. The absorption spectrum of such a crystal is shown in Fig. 1b. It turns out that the F_2 centers, which can be effectively excited in the long-wave part of the absorption spectrum by the second harmonic of the neodymium laser, generate a wide-band radiation with $\lambda_{max} = 0.69$ μm, as shown by the dashed line in Fig. 1b.

As a result of the action of high power density radiation on the crystal, nonlinear photoionization of the F_2 centers in addition to their excitation begins to develop in it. The 0.532-μm radiation quantum transfers one electron from the excited level of the neutral F_2 center to the conduction band, thereby producing an ionized F_2^+ center. The mechanism of such a process can be described as a two-step photoionization of the F_2 centers $F_2 + h\nu \rightarrow F_2^* + h\nu \rightarrow F_2^+ + \bar{e}$.

Figure 1c, in which the absorption spectrum was photographed in the active zone of the crystal (which is subjected to an intensive exposure to light with $\lambda = 0.53$ μm), demonstrates such a process. It can be seen that the concentration of the F_2^+ centers increases sharply in the active zone (a band with $\lambda_{max} = 0.645$ μm appears) and the

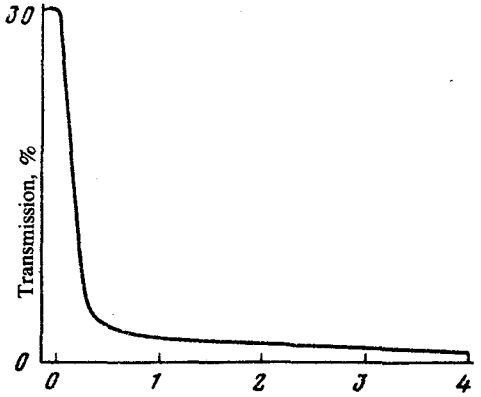

FIG. 2. Kinetics of transmission of radiation $\lambda = 0.632$ μm by the active zone of the crystal from the moment the pump laser is turned on.

concentration of the neutral F_2 centers decreases. Visually, this is expressed by the change of color of the active zone from red to green.

The kinetics of formation of the F_2^+ centers can be traced by measuring the transmission of the active zone of the crystal at the radiation frequency of the helium-neon laser $\lambda = 0.6328$ μm, which is close to the maximum of the absorption band of the F_2^+ centers. The curve for the dependence of transmission on the time required to pump the crystal when the laser is operating in the pulsed-periodic mode with frequency $f = 12.5$ Hz is shown in Fig. 2. It can be seen in Fig. 2 that during several tens of seconds (the time depends on the power density of pumping) the absorption at $\lambda = 0.63$ μm increases by a factor of four to five and reaches 1.5 cm^{-1}. The concentration of the ionized centers is sufficiently large, so that a large part of the pumping radiation is now absorbed by the F_2^+ centers which in turn convert it efficiently to radiation. The luminescence spectrum of the F_2^+ center, which represents the shape of the amplification curve, is denoted by a dashed line in Fig. 1c.

The use of LiF crystals as an active medium with residual or specially introduced impurities obtained at the Irkutsk State University[1)] showed that in this case the laser with a pumping radiation at $\lambda = 0.53$ μm operates according to the mechanism described above.[8] There are not enough oxygen-stabilized F_2^+ centers to obtain generation with pumping at $\lambda = 0.53$ μm, since greater than 95% of the pumping radiation power is initially absorbed by the F_2 centers. Infrared generation is observed only after selective photoionization of the F_2 centers to F_2^+, i.e., after establishment of a higher photoionization than that produced as a result of stabilization of the concentration of the F_2 centers. This is indicated by a strong change of color in the active zone and a delay of generation at 10^2–10^3 pulses after the pulsed-periodic pumping is first switched on. Thus, we can produce directly and maintain in the laser system a necessary concentration of active F_2^+ centers and invert the population in them by selecting a pumping-radiation wavelength in the region in which the absorption spectra of the neutral F_2 and the ionized F_2^+ centers overlap.

By using the method described above we were able to obtain for the first time at

room temperature a pulsed-periodic excitation mode with a high pulse repetition frequency in a narrow directional pattern and at high excitation efficiency. Thus, a wide-band excitation of F_2^+ centers with $\lambda_{max} = 0.93\ \mu m$, a power of 2.4×10^4 W per pulse, a divergence of 10^{-3} rad, and 42% quantum conversion efficiency of pumping radiation to infrared generation was obtained for a frequency of 50 Hz in a plane-parallel Fabry-Perot cavity with a 10% output mirror at a duration of the pump pulse $t_i = 1.5\times10^{-8}$ sec of peak power $P_p = 3.4\times10^5$ W. The photostability of the color centers obtained as a result of γ-ray irradiation is confirmed by the fact that the laser worked stably in the $f = 12.5$ Hz mode for more than three hours ($\sim2\times10^5$ pulses) without a noticeable decrease of generating power. To obtain a tunable generation, we used dispersion cavities which are frequently used in lasers based on organic-dye solutions.[9] The crystal, which was placed in a cavity with a diffraction lattice or with three prisms, was excited almost according to the longitudinal scheme. The generated frequencies were in the range of 0.84 to 1.1 μm when the width of the generation line was about 2 Å. By doubling the frequency of the tunable laser with the help of a nonlinear $LiIO_3$ crystal, we were able to obtain a tunable generation of the second harmonic in the range of 0.42 to 0.55 μm.

Thus, the crystal laser produced by us covers a range in its tunable radiation in which dye lasers are least effective and reliable. The compactness and simplicity of such laser, the much wider range of generated frequencies, the high power characteristics, and the narrow directional radiation pattern, together with a suitable pumping source having a high pulse repetition rate, will enable it to find a wide application in scientific research and technology.

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