Lasing in slurry-like active medium on LiF:F$_2$ microparticles

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Abstract. Active media composed of the particles of solid-state laser-active material immersed in the liquid are the subject of research since this approach can provide new solutions to the problem of heat removal from the laser medium. Investigation of the active medium on microparticles of LiF crystal with F$_2$ color centers is presented. The technique of the preparation and characterization of the index-matched slurry-like mixture was developed. Powders of LiF crystal particles with F$_2$ color centers with size from 50 to 1000 $\mu$m immersed in various liquids and their mixtures were tested. Laser radiation of a compact cavity containing two flat dichroic mirrors and a glass cuvette with the LiF:F$_2$ slurry with grain size of 500 $\div$ 1000 $\mu$m and the mixture of heptane and vaseline oil was obtained under Coumarin 120 dye laser pumping. The pulses of the laser radiation with the beam divergence of 2 $\div$ 5 mrad at the wavelength of about 680 nm, duration of 10 ns and energy of 83 $\mu$J were obtained under pulsed pumping with the energy of 1.34 mJ. The real and slope efficiencies of the LiF:F$_2$ slurry laser reached 6.2% and 12.9% correspondingly.

1. Introduction

Active media based on particles of solid-state laser materials distributed in liquid or gas media have been the object of research, since such an approach can provide a new solution to the problem of the heat removal during the laser operation [1-6]. Suspensions of glass or crystal nanoparticles doped with Nd or Yb ions were considered as laser active media as the scattering losses from particles with the size of about 10 nm are negligible [4-6]. However nanoparticles may have some properties (emission lifetime, quantum yield) different from their bulk counterparts and so for laser action a surface modification of Nd$_2$O$_3$ nanoparticles was required [4, 5]. Particles of solid-state laser materials with dimensions over 1 $\mu$m are easier to manufacture, they do not need a complicated modification, as their properties are identical to those in the original single crystal or bulk glass samples. For such particles index-matching liquids may be used to suppress Fresnel reflection and scattering. A "slurry laser" with an active medium in the form of a mixture of LiF microparticles with F$_2$ color centers and an immersion liquid was demonstrated in [7]. The "slurry laser" concept may be attractive due to the possibility of receiving potentially higher laser output energy from a dense pulp, circulating through the laser active element. This report considers the method of fabrication of an active medium in the form of an index-matched slurry and testing of compact LiF:F$_2$ slurry laser.
2. Fabrication of a slurry-like active medium

Slurry-like laser is possible only with an active medium with high gain, because it is necessary to overcome the internal parasitic losses in the mixture of solid particles and liquid. Incomplete immersion of particles as well as various scattering centers at the surface and inside the particles can be the source of parasitic losses. LiF crystal with F₂ color centers (CC) is one of the most promising materials for preparing an active medium for the slurry laser. LiF:F₂ CC crystal have broad absorption (0.42-0.47 μm) and emission (0.56-0.84 μm) bands in the visible spectral region. F₂ CCs have high emission and absorption cross sections $\sigma \approx 7 \times 10^{-17}$ cm². Their intrinsic feature is very high concentration in LiF crystal which results in high gain up to tens of cm⁻¹ [8-11]. LiF crystal has high thermal conductivity (4 Wm⁻¹K⁻¹) and can be used in cw and pulse-periodic lasers. Its low refractive index $n_d \approx 1.39$ simplifies search and selection the immersion among various liquids.

F₂ CCs with the concentration of $10^{18}$ cm⁻³ were produced in the nominally pure oxygen-free samples of LiF crystal by irradiation at room temperature with $\gamma$-quanta from Co⁶⁰ source with the doze of $2 \times 10^7$ Rad. The grinded LiF:F₂ powder was sieved serially through the sieves with different mesh size for separation of the fractions from 200 μm to 1000 μm and over 1000 μm. Several pieces of transparent non-irradiated LiF crystal samples were subjected to grinding and fractionation by the similar procedure for comparison. Microphotographs of non-irradiated LiF powder fractions obtained using mortar with pestle and then sieved through 200-500 μm and > 1000 μm cells are shown in figure 1. Fractions of crushed material were placed and poured with the immersion liquid into rectangular glass cuvettes with dimensions of 24 × 40 × 8 mm³ and 3 mm gap between the walls (figure 2).

![Figure 1](image1.png)

**Figure 1.** Microphotographs of fractions of non-irradiated LiF crystal powder sieved through 200-500 μm (a) and > 1000 μm (b) cells.

![Figure 2](image2.png)

**Figure 2.** Photo of the glass cuvette containing the 3 mm thick slurry of 500 - 1000 μm LiF:F₂ granules in the immersion liquid heptane/vaseline oil.
The values of the refractive index of irradiated and non-irradiated LiF crystal are practically the same and equal to 1.3909 at 656.3 nm. The refractive indexes of common liquid chemicals are presented in table 1. All these liquids are transparent in the visible and near IR spectral range (400 - 1000 nm). One can see that there is no liquid with refractive index that equals to that in LiF. However, it is possible to use the mixture of two liquids with higher and lower refractive indexes to fit it. In this case the value of the particle refractive index $n_p$ equals to

$$n_p = x \cdot n_1 + (1 - x) \cdot n_2$$

where $n_1$ and $n_2$ are refractive indexes of the first and second liquids, $x$ is the mixing fraction. We had the following requirements for the immersion liquid: complete coincidence of its refractive index and LiF crystal, high hydrophilicity with LiF, insolubility of LiF in the liquid, high solubility of one component of immersion in another component, safety and non-toxic.

The index-matching liquid was prepared by mixing two components: the first one with higher refractive index was anise oil or vaseline oil and the second one with the lower index was acetone or heptane. Following equation (1) the mixture anise oil/heptane, vaseline oil/heptane and vaseline oil/acetone should be prepared as 16:1, 6:1 and 6:2.5, correspondingly. It is necessary to note that refractive index depends on the operating wavelength, temperature, on the manufacturer. That’s why the preparation of the index-matched slurry was carried out using the special laser set-up shown in figure 3. It used a diode and a He–Ne lasers as reference light sources operating at the wavelengths of 650 nm and 632 nm, that was close to the expected operating wavelength of LiF:F$_2$ CC laser. Their beam diameters were about 2 mm. To measure the power transmitted through a cuvette with slurry, a power meter was placed behind an iris aperture near the focus of the lens with a focal length of 85 mm. Liquids were added to the layer of powder (≈ 1 cm in height) in a cuvette using a syringe, drop-wise with stirring, so that a buffer layer of liquid was formed above the slurry.

**Table 1.** Refractive indexes of LiF and YLiF$_4$ crystals and investigated liquids.

| Material          | Refractive index (656.3 nm) |
|-------------------|----------------------------|
| Methanol          | 1.3241                     |
| Acetone           | 1.3567                     |
| Ethanol           | 1.3606                     |
| Heptane           | 1.3878                     |
| LiF               | 1.3909                     |
| Isobutyl alcohol  | 1.3959                     |
| Ethylene glycol   | 1.4283                     |
| Vaseline oil      | 1.45-1.46                  |
| YLiF$_4$          | 1.4523 (o), 1.4748 (e)     |
| Castor oil        | 1.47-1.48                  |
| Glycerine         | 1.4717                     |
| Benzene           | 1.4966                     |
| Benzyl alcohol    | 1.5396                     |
| Anise oil         | 1.54-1.57                  |

The optimum composition of the immersion liquid was achieved by recording the maximum of the reference beam transmission through the slurry and by the observations of the quality of transmitted laser beam spot at a remote screen. While adding the immersion liquid to the powder, a noticeable decrease of light scattering of the reference beam, the formation of a thin light channel in the slurry and a compact beam spot on the screen were observed. At the optimal composition, the transmission
of reference beam through the slurry of a fixed thickness depended on the size of granules. Reducing the thickness of the layer of particles in the cuvette, as well as the use of particles of larger size (500 ÷ 1000 µm and above) contribute to the reduction of the scattering in the medium. For 500 ÷ 1000 µm LiF or LiF:F₂ grains the fraction of the transmitted laser radiation in the angle of 0.01 rad reached 70%. For the particles of smaller sizes (200 ÷ 500 µm and < 200 µm), the transmission reduced to 30% ÷ 60%. All these observations correspond to the characteristics of the Christiansen filter – a well-known device in the form of a cuvette with a powder of passive (non-activated) particles of glass or crystal in immersion [12, 13].

![Figure 3. Scheme of the laser set-up for the preparation and testing of the index-matched LiF:F₂ slurry, where 1 – laser sources; 2 – cuvette with the slurry; 3 – components for preparing immersion liquids; 4 – lens; 5 – diaphragm; 6 – screen; 7 – power meter.](image)

Note that reduction in scattering losses in a cuvette is possible for particles of isotropic materials (glass, cubic crystals etc.). This circumstance is illustrated in figure 4, which shows the pictures of the spot of the He-Ne laser passed through the cuvette of 3 mm thickness containing a powder of the isotropic non-irradiated LiF crystal in an immersion mixture of heptane and vaseline oil and a powder from the anisotropic Nd:YLF crystal in an immersion mixture of isobutyl and benzyl alcohols. The composition of the mixture was chosen for the highest power transmission of the slurry. Comparison of beam profiles on the screen indicates extremely high scattering losses for the cuvette with Nd:YLF powder. The reason of these losses is the fundamental impossibility to fit the refractive index of the liquid to values of ordinary and extraordinary refraction indexes simultaneously.

The transmission spectra of LiF:F₂ slurries with 500 ÷ 1000 µm and 200 ÷ 500 µm granules are similar (in the region 300 ÷ 900 nm) to the spectrum of LiF:F₂ bulk plate (figure 5). The slurry spectra also reveal the absorption peak of the immersion liquid near 1200 nm. Comparing these spectra with the spectrum of the immersion liquid it was possible to estimate the particles’ filling factor in the slurry which was found to be about 0.5.

![Figure 4. Images of the He-Ne laser beam on the screen at a distance of 1 m from the stage with cuvettes: without the cuvette (a); cuvette with powder of isotropic LiF crystal (b); cuvette with powder of anisotropic Nd:YLF crystal (c). The size of the grains was 500 ÷ 1000 µm in both cases.](image)
Figure 5. Transmission spectra of LiF:F$_2$ bulk crystal 2.5 mm thick (1) and cuvettes 3 mm thick containing the slurry of LiF:F$_2$ crystal granules with dimensions of 500 ÷ 1000 μm (2) and 200 ÷ 500 μm (3) in the immersion liquid of heptane/vaseline oil.

3. LiF:F$_2$ slurry-like laser

The scheme of the experiment on LiF:F$_2$ slurry laser is shown in figure 6. The transversely pumped Coumarin 120 (C120) dye laser operating at the wavelength of about 0.45 μm was used as a pump source. The windows of the cuvette with the dye solution in the ethanol formed a resonator with the length of 30 mm. Windows were composed of two flat mirrors: one with high reflectivity $R \approx 99\%$ and an output coupler with $R \approx 30\%$ at $\lambda_p \approx 0.45$ μm. The C120 dye was pumped by the 3$^{rd}$ harmonic (354 nm) of a pulsed Nd:YAG laser LOTIS TII. The energy in a single 12 ns pulse of the 3$^{rd}$ harmonic was 8.7 mJ. Linear polarized 3$^{rd}$ harmonic radiation was focused through the side wall of the cuvette into the dye solution by a cylindrical lens, $f = 35$ mm. The length of the dye solution along the resonator axis was 8 mm. The C120 dye laser emitted linearly polarized pulses with the duration of 11 ns and energy up to 1.6 mJ at the wavelength of $\lambda_p = 446$ nm. The diameter of the output beam was 2 mm. This radiation was focused on the samples (LiF:F$_2$ plate or a cuvette with the LiF:F$_2$ slurry) by the lens $f = 172$ mm. The LiF:F$_2$ sample was placed into the resonator ($L \approx 40$ mm) formed by two flat mirrors. The diameter of the pump spot at the entrance of the active media was 0.5 mm, and the maximum pump intensity reached 60 MW·cm$^{-2}$. The dye laser radiation was focused along the resonator axis through the input mirror with 90% transmission at $\lambda_p$ and 99% reflection in the red spectral region. The pump radiation was absorbed almost completely (> 98%) in the LiF:F$_2$ active media. Mirrors with transmission from $T = 1\%$ to $T = 23\%$ at the wavelength near 0.68 μm were used as an output coupler (OC). The pulses of red collimated radiation were produced at the output of the resonator containing LiF:F$_2$ plates or cuvettes with LiF:F$_2$ granules. It is known that the parameters of LiF:F$_2$ laser under intensive pumping may degrade due to ionization of the F$_2$ active color centers in a two photon excitation process, F$_2 \rightarrow$ F$_2^*$ [8].

Figure 6. Scheme of the experiment on pumping the LiF:F$_2$ slurry active medium by the Coumarin 120 dye laser 1, where 2 – the beam of the 3$^{rd}$ harmonic of a pulsed Nd:YAG laser; 3 – focusing lens; 4 – cuvette with the LiF:F$_2$ slurry.
This process was observed at high pump power levels in our experiments as well. At 1 Hz pulse repetition rate and pump energy close to the generation threshold of 0.5-0.6 mJ per pulse, the LiF:F₂ laser output energy reduced by a factor of 2 after 3-4 shots for single crystal sample and after 6-7 shots for the slurry without stirring. At the maximum pump pulse energy of 1.4 mJ the generation degrades just after the first shot. Because of this, the measurements of LiF:F₂ laser generation parameters were carried out in a single shot regime. In the study of LiF:F₂ slurry, after each shot the medium in the cuvette was stirred to ensure the presence of fresh active granules in the pumped region. In the experiments with bulk plates, each new measurement was recorded at a neighbor place by shifting the active element.

Measurements of the pulse energy from all types of LiF:F₂ active elements were performed using a calibrated silicon photodiode FD24 connected to a digital oscilloscope. Figure 7 compares the dependences of the LiF:F₂ slurry laser output energy (for 2 compositions) and that of the LiF:F₂ single crystal laser on the pump. All measurements were carried out in the same resonator configuration with the OC with the transmission of 13%. From the graphs in figure 7 one can see that the efficiency of the slurry laser is only twice as less than that of single crystal laser. When comparing these data, one should take into account 0.5 filling factor of granules in the slurry and, also, the fact that the pump radiation at \( \lambda_p \) was noticeably scattered in the slurry, since the immersion in the cuvettes was balanced for the laser oscillation wavelength \( \lambda_e \). The maximum generation energy of slurry laser was about 83 \( \mu \)J at the pump energy of 1.34 mJ, the slope efficiency was 12.9\%. It was found that the lasing threshold is smaller and the laser output energy is higher for 500 \( \div \) 1000 \( \mu \)m granules as compared with 200 \( \div \) 500 \( \mu \)m granules. For the cuvettes with the slurry of 2 mm thickness, the laser output energy was weaker compared to the 3 mm thick cuvettes. For particles < 200 \( \mu \)m the lasing threshold was not achieved, even for the OC with the reflectivity of 99%.

**Figure 7.** The dependences of the LiF:F₂ laser output pulse energies on the pump pulse energy: LiF:F₂ bulk plates of 3.8 mm (1) or 2.5 mm (2) thickness in the resonator; LiF:F₂ slurry with 500 \( \div \) 1000 \( \mu \)m (3) or 200 \( \div \) 500 \( \mu \)m (4) granules in the resonator.

Time profiles of LiF:F₂ slurry laser pulses were recorded with a GW Instek GDS-2104 digital oscilloscope (100 MHz band, 1 G\( \text{s}^{-1} \)) using a fast MRD500 photodiode. Pulse duration of LiF:F₂ slurry-like laser was measured to be 10 ns. A diffraction spectrograph with a dispersion of 2.4 nm-mm\(^{-1}\) was used to measure the spectrum of the LiF:F₂ slurry laser. Due to nonselective cavity, the central wavelength of the generation spectrum may jump from shot to shot in the region 675 - 695 nm. The spectral width of the slurry laser output may extend for about 60 nm.

The intensity distribution in the LiF:F₂ slurry output beam was usually not reproduced from shot to shot. This can be apparently explained by the disordered internal structure of the active medium based
on particles of various dimensions and shapes, which somehow manifest themselves due to unavoidable particles and liquid small index-mismatch. Figure 8 illustrates the beam spot in the near field at the 6 cm distance from the OC and in the far field (in the focus of the lens with the focal length of 1 m) and intensity profiles. The most symmetrical and homogeneous beam profiles were obtained when a ‘fresh’ place of the slurry was pumped near the generation threshold. Beam divergence of LiF:F₂ slurry laser near the generation threshold was estimated to be about 2 mrad and increased up to 5 mrad at higher pump energies. The degree of linear polarization of the LiF:F₂ slurry radiation was about 75%.

Figure 8. Pictures of LiF:F₂ slurry laser beam spots (up) and their intensity profiles (below): (a) in the near field at the distance of 6 cm from the OC; (b) in the far field at the focus of the lens with the focal length of 1 m.

4. Conclusion
The observed collimated beams of LiF:F₂ slurry emission, the dependences of the beam energy on pump energy and other registered parameters of LiF:F₂ emission give grounds for the conclusion that the lasing action from an active medium based on microparticles from a solid-state laser material in an immersion liquid (a slurry laser) was demonstrated in our experiments. Further research is needed to improve the slurry laser characteristics. One of the important research objectives of such an active medium is the search for the solution to the problem of heat removal from the laser active medium by using a flow of dispersed laser material through the pumped region. In addition to the perspective in solving the problem of heat removal, the use of an active medium on the particles has a number of other advantages, such as an easy replacement of the active medium in case of damage, a possibility of combining several activators in one laser element, new capabilities for inversion profiling, new pumping schemes and some others. The continuation of the study into the generation and amplification of cw and pulsed laser radiation in active media of this type at LD and laser pumping seems to be reasonable. The technique of preparation and characterization of index-matched slurry containing solid-state particles and an immersion liquid was tested not only for fluoride crystals, but for laser glasses as well. It is of interest to conduct experiments with the slurry active media based on standardized particles, for example, those on glass beads highly doped by Nd or Yb ions.

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