Laser Physics II
PH482/582-VT (Mirov)
Color Center Lasers
Lecture 4
Spring 2014
OUTLOOK

1. Types of color centers in ionic crystals and principles of operation
2. Crystal hosts for active elements of color center lasers
3. Color center formation in ionic crystals
   3a. Additive coloration
   3b. Electrolytic coloration
   3c. Color center formation in alkali-halide crystals under ionizing irradiation
      LiF:F$_2^-$ active element optimization
      LiF:F$_2^+$ active element optimization
4. Major spectroscopic characteristics of color centers
5. CW and quasi-CW color center laser operation (T=77K)
6. Pico and femtosecond quasi-CW color center laser operation (T=77K)
7. Room temperature CCL operation
   7a. CW and quasi-CW
   7b. High peak power room temperature CCL operation in mode-locked regime
   7c. High energy and power color center lasers
   7d. Color center energy and power amplifier
   7e. Narrowline tunable color center lasers
8. Practical applications
Major Literature


1. Types of Color Centers

In general, the major crystals where laser active CCs can be developed are pure and impurity-doped fluorides and chlorides of Li, Na, K, and Rb alkali metals [i], [ii], [iii], [iv], as well as CaF2 and SrF2[v]. Laser oscillation has also been reported using CCs in Al2O3[vi],[vii], diamond[viii], MgF2[ix], and the compound fluorides KMgF3 [x] and YLiF4 [xi]. In the primal state these crystals are optically transparent. Under irradiation with high-energy electrons, neutrons, γ-rays, X-rays, or hard UV, or calcination in alkali metal vapor (additive coloration), anionic vacancies appear in the crystal lattice and serve to localize free electrons. The absorption bands of these (F) centers (vacancy + electron) give a typical coloring to the crystals.

1. Structure of the simplest color centers in LiF crystals

![Diagram of color centers in LiF crystals]

- **F**
- **F<sub>2</sub>**
- **F<sub>2</sub><sup>+</sup>**
- **F<sub>2</sub><sup>-</sup>**

**Legend:**
- F<sup>-</sup>-ions
- Li<sup>+</sup>-ions
- Anion Vacancy
- e<sup>-</sup>-electron
1. Ionic configurations of other simple F type color centers

$F_A(I)$ centers in the ground and excited states

$F_A(II)$ centers in the ground and excited states

$F_B(I)$ centers in the ground and excited states

$F_B(II)$ centers in the ground and excited states
1. Models of (a) $F_2$ CCs in alkali-halide crystals; (b) $(F_2)_A$ CCs in alkali-earth fluorides
1. Two possible arrangements of four F centers to form N centers. These arrays are either a tetrahedron or a parallelogram.
1. Principles of CCL operations

1. Pump radiation is absorbed in the wide band of the electric-dipole electron-vibrational transition $1 \rightarrow 2$.

2. In a time on the order of $10^{-12}-10^{-13}$ s, radiationless relaxation to the minimum of potential curve of the excited electronic state, $2 \rightarrow 3$ occurs, accompanied by a mutual rearrangement of the neighbouring ions and by phonon emission.

3. Then a radiative electron-vibrational transition $(3 \rightarrow 4)$ occurs with a probability of $A = 10^7-10^8$ s$^{-1}$, followed by

4. another rapid vibrational relaxation $(4 \rightarrow 1)$ to the potential curve minimum of the ground electronic state with resetting of the spatial ion configuration. Disregarding the details, one may consider this scheme as the four levels laser scheme of oscillation.
1. Principles of CCL operations

The principles of CCL operation can be accounted for using the Frank-Condon configuration diagram, which describes the optical properties of an electron system interacting with molecular or lattice vibrations: in particular, the optical transition of CCs.

The total energy of the defect is plotted versus the abscissa, which represents the movement of the and electrons from the equilibrium position. The depth to which each well is populated will depend on the temperature and density of available states. Only vertical transitions are allowed, which the electronic transitions are rapid compared with any lattice relaxation.
1. Two different groups of CCC. 
a) operating at RT; b) operating at T<77K
1. Major Defects Classification

LINE IMPERFECTIONS

DEFECTS

Point Defects

Impurity

Cation: Cr$^{3+}$; Ti$^{3+}$; Nd$^{3+}$; Er$^{3+}$; Ho$^{3+}$

Anion: OH$^-$; $O_2^-$

Impurity-Vacancy Dipoles

Cation-Vacancy: $F_A$; $F_B$; $(F_2^+)A_i$; Me$^+$$-$$F$; Me$^{++}$$-$$F_2^-$

Zcenters: $F$$-$$Me^{++}V_c$

Anion-Vacancy: $O^-V_a^+$

Intrinsic defects

Anion Vacancies

Electron centers (Color Centers): $F_2$; $F_2^+$; $F_2^{2+}$; $F_3$; $F_3^+$; $F_3^{2+}$; $F_4$

Simple $F$

Cation Vacancies

Laser active optical centers

Hole Trapping Centers
2. Main physicochemical, mechanical and optical characteristics of the most promising crystal hosts with CCs

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$d_0$ (Å)</th>
<th>$H$ (kg/mm$^2$)</th>
<th>Solubility (g/100g H$_2$O)</th>
<th>$T_m$ (K)</th>
<th>$K$ (W/mK)</th>
<th>$R_f^*$ (W/m)</th>
<th>$n$</th>
<th>$dn/dT \times 10^5$ (K$^{-1}$)</th>
<th>$I_{th} \times 10^{-12}$ (W/m$^2$)</th>
<th>Transparency range at $\alpha=1$cm$^{-1}$ level</th>
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</thead>
<tbody>
<tr>
<td>LiF</td>
<td>2.64</td>
<td>4.03</td>
<td>99-102</td>
<td>0.12</td>
<td>1121</td>
<td>14.2</td>
<td>43-143</td>
<td>1.387</td>
<td>-19</td>
<td>3600</td>
<td>0.11-6.6</td>
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<tr>
<td>NaF</td>
<td>2.79</td>
<td>4.62</td>
<td>60</td>
<td>4.2</td>
<td>1270</td>
<td>9.2</td>
<td>-</td>
<td>1.321</td>
<td>-18</td>
<td>1400</td>
<td>0.16-11.2</td>
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<tr>
<td>NaCl</td>
<td>2.17</td>
<td>5.64</td>
<td>15.2-18.2</td>
<td>36.0</td>
<td>1074</td>
<td>6.4</td>
<td>-</td>
<td>1.53</td>
<td>-13</td>
<td>200</td>
<td>0.17-18.0</td>
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<tr>
<td>KF</td>
<td>2.50</td>
<td>5.35</td>
<td>-</td>
<td>94.9</td>
<td>1130</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KCl</td>
<td>1.99</td>
<td>6.29</td>
<td>7.2-9.3</td>
<td>37.4</td>
<td>1049</td>
<td>6.0</td>
<td>-</td>
<td>1.48</td>
<td>-11</td>
<td>700</td>
<td>0.18-23.0</td>
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<tr>
<td>KBr</td>
<td>2.75</td>
<td>6.60</td>
<td>6-7</td>
<td>70.9</td>
<td>1007</td>
<td>4.8</td>
<td>-</td>
<td>1.54</td>
<td>-8</td>
<td>500</td>
<td>0.21-28.0</td>
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<tr>
<td>KI</td>
<td>3.13</td>
<td>7.07</td>
<td>5</td>
<td>144.0</td>
<td>959</td>
<td>2.1</td>
<td>-</td>
<td>1.64</td>
<td>-4.5</td>
<td>200</td>
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<td>RbCl</td>
<td>2.76</td>
<td>6.58</td>
<td>-</td>
<td>94.2</td>
<td>717</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>MgF$_2$</td>
<td>3.18</td>
<td>a=4.64 c=3.06</td>
<td>576</td>
<td>0.0076</td>
<td>1,536</td>
<td>21⊥c</td>
<td>30∥c</td>
<td>470</td>
<td>$n_0=1.373$</td>
<td>$n_c=1.385$</td>
<td>11.2</td>
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<td>CaF$_2$</td>
<td>3.18</td>
<td>5.46</td>
<td>120-163</td>
<td>0.0016</td>
<td>1,676</td>
<td>9.7</td>
<td>-</td>
<td>1.429</td>
<td>-1.05</td>
<td>&gt;1000</td>
<td>0.13-9.4</td>
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<tr>
<td>SrF$_2$</td>
<td>4.24</td>
<td>5.79</td>
<td>144</td>
<td>&lt;0.1</td>
<td>1,190</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1-9.0</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>3.974</td>
<td>a=4.76 c=13.0</td>
<td>2100</td>
<td>0</td>
<td>2,313</td>
<td>35.0</td>
<td>10,000</td>
<td>$n_0=1.765$</td>
<td>$n_c=1.757$</td>
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<tr>
<td>Diamond</td>
<td>3.515</td>
<td>3.57</td>
<td>8820</td>
<td>0</td>
<td>3,770</td>
<td>900.0</td>
<td>-</td>
<td>2.40</td>
<td>0.4</td>
<td>12000</td>
<td>0.24-2.7</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$</td>
<td>4.55</td>
<td>12.0</td>
<td>1350</td>
<td>0</td>
<td>2,223</td>
<td>13.0</td>
<td>790</td>
<td>1.815</td>
<td>1.05</td>
<td>2000</td>
<td>0.21-5.3</td>
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<tr>
<td>ED-2 glass</td>
<td>2.539</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>582</td>
<td>1.4</td>
<td>140</td>
<td>1.56</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
3. Methods of Color Center Formation

1. IONIZING IRRADIATION

\[ \gamma - \text{RAYS, } X - \text{RAYS, HARD UV, ELECTRONS, NEUTRONS} \ldots \]

\[ \begin{array}{ccc}
\bar{e} + \bar{e} & \rightarrow & \bar{e} \\
\text{Va} + \text{I} & \rightarrow & \text{Va}^- + \text{I} \\
F + H & \rightarrow & \text{F}^- , \text{H}^- \\
\end{array} \]

\[ \begin{array}{c}
\text{F}_2^+ + e^- \rightarrow \text{F}_2^0 ; \text{F}_2^- + e^- \rightarrow \text{F}_2^- \\
\text{F}_2^- + F_2^+ \rightarrow \text{F}_3^+ ; \text{F}_2^- + \text{F}_2^- \rightarrow \text{F}_4^+ ; \text{F}_2^+ + \text{F}_2^- \rightarrow \text{F}_4^- \\
\end{array} \]

2. ADDITIVE COLORATION

\[ \gamma \rightarrow + + + + + + + + + + + + + + \rightarrow + + + + + + + + + + + + + + \]

3. ELECTROLYTIC COLORATION

\[ T \text{ is optimised for high anion mobility} \]

\[ \text{KCl} \rightarrow \text{K}^+ \text{Cl}^- \rightarrow \text{K}^+ \text{Cl}^- \text{K}^+ \]

\[ \text{Na} \]

\[ 400 \text{ C} \]

\[ \text{ionic current} \]
3a. Formation of F centers by Additive Coloration (AD)

AC involves bringing the crystal in equilibrium with a bath of alkali vapor. The F-centers are formed at the crystal surfaces and fill up the body of the crystal through diffusion. Assume that $N_0$ – equilibrium density of F centers; $N'$ - the metal vapor density. Usually $N_0 = \alpha N'$, where $\alpha = 2-3$ for alkali-halides. At the beginning of coloration the F centers are concentrated at the crystal surfaces. For a thin slab, the behavior at later times ($t > \tau_D$) is

$$N(x,t) = N_0 \left[ 1 - \frac{4}{\pi} \sin \frac{\pi x}{l} \exp \left( -\frac{t}{\tau_D} \right) \right]$$

Where $D$-diffusion constant; $\tau_D$-diffusion time

$$\tau_D = \frac{l^2}{\pi^2 D} \quad D(T) = D_0 \exp \left( -\frac{T_0}{T} \right)$$

For KCl: $T_0 = 14,400K$; $D_0 = 1.22 \times 10^2 cm^2/s$

For $T = 600^\circ C$; $D = 8 \times 10^{-6} cm^2/s$

For $l = 2 mm$; $\tau_D = 8.4$ min and $t = 30$ min for practically uniform coloration
3b. Electrolytic coloration

- a. Thermal insulation cap
- b. Quartz tube
- c. Crystal sample (ZnSe)
  thickness = 4.0mm
- d. Chromium (Cr) foil
  thickness = 1.0mm
- e. Electrode stage
- f. Adjustment spring assembly
- g. Ceramic base
- h. Cathode connection
- i. Anode connection
- j. Gas inlet port
- k. Threaded assembly rod
- l. Thermal insulation wrapping
- m. Anode plate nut
- n. Inert/evacuated atmosphere
- o. Gas exhaust port
- p. Cover plate and stand bracket
- q. Cover plate nut
- r. Steel support stand and base
3c. Color center formation in alkali-halide crystals under ionizing irradiation

- The formation of aggregate color centers in alkali-halide crystals under ionizing radiation is a complicated process involving 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).

- All the above processes determine the efficiency of formation of any type of color centers. 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.
3c. Color center formation in alkali-halide crystals under ionizing irradiation

- 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 \( I_a^- \)

\[
e^o_s \Rightarrow F + H \quad (1)
\]

\[
e^o_s \Rightarrow V_a^+ + I_a^- \quad (2)
\]

- The mechanisms of formation of aggregate centers through migration of anion vacancies are mainly going through the following route: charged \( F_2^+ \) centers first appear, and then capture electrons to produce neutral \( F_2 \) centers

\[
V_a^+ + F \Rightarrow F_2^+ \quad (3)
\]

\[
F_2^+ + e \Rightarrow F_2 \quad (4)
\]
3c. Color center formation in alkali-halide crystals under ionizing irradiation

- 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:

\[
F_2^+ + F \Rightarrow F_3^+ \quad (5)
\]
\[
F_2^+ + F_2 \Rightarrow F_4^+ \quad (6)
\]
\[
F_2^+ + F_2^- \Rightarrow F_4^- \quad (7)
\]

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:

\[
F_2 + e \Rightarrow F_2^- \quad (8)
\]

or holes

\[
F_2 + h \Rightarrow F_2^+ \quad (9)
\]

or due to diffusion processes involving mobile anion vacancies

\[
V_a^+ + F_2 \Rightarrow F_3^+ \quad (10)
\]

and self-localized holes

\[
F_2 + V_k \Rightarrow F_2^+ \quad (11)
\]
3c. LiF:F$_2^-$ active element optimization

- The LiF:F$_2^-$ crystals combining unique modulation, thermal, and operational characteristics, are now widely used as active media in tunable lasers and as nonlinear elements with saturable absorption for neodymium laser Q-switches. However, available techniques of such laser crystals preparation fail to produce optically dense, high-contrast media required for a series of applications. Usually, the value of active absorption at the working wavelength does not exceed 0.4-0.6 cm$^{-1}$ at a contrast (ratio of the active absorption coefficient to the loss coefficient at 1.06 µm) of 10-20. Under the action of $\gamma$-quanta commonly used for producing LiF:F$_2^-$ laser crystals, the F$_2^+$ CCs emerging by reaction (3) may be involved in three processes: a) fast process of electron capture to produce F$_2$ CCs (reaction 4) and F$_2^-$ CCs (reaction 8); b) slow diffusion processes of aggregation of the type 5, 6, 7; c) dissociation on the F center and anion vacancy F$_2^+ \rightarrow$ F + Va$^+$.  

- The rates of the processes and final concentration of CCs depend on the impurity composition of the initial material, irradiation dose, power, and crystal temperature. Varying the ratio of these parameters, one can essentially influence the processes of F$_2^-$ CC formation in LiF.

- When we optimized the procedure of LiF crystal treatment under ionizing irradiation so, that the processes 3, 4 were efficient and 5-7 – negligible, maximum active absorption of F$_2^-$ CCs at the wavelength 1.064 µm exceed 1.5 cm$^{-1}$ at a contrast as high as 20 – 40.
3c. Optically Dense Electron Irradiated LiF:F$_2^-$ crystals

\[ e^- + e^+ \Rightarrow e^0 \Rightarrow F + H \rightarrow V^+_A + I^- \]

\[ kT_1 \]

\[ V_A + F \Leftrightarrow F_2^+; \quad F_2^+ + e \Rightarrow F_2^-; \quad F_2^- + e \Rightarrow F_2^- \]

\[ kT_2 \]

\[ F_2^+ + F \Rightarrow F_3^+; \quad F_2^+ + F_2 \Rightarrow F_4^+; \quad F_2^- + F_2 \Rightarrow F_4^+ \]

Absorption at 1.06 cm$^{-1}$

Electron Accelerator: $E_e = 10$ MeV; $I_p = 1$ A; $f = 10$ Hz; $W_p = 20$ J

Result: $K_{1.06} = 1.8$ cm$^{-1}$; $\beta = K_{1.06}/K_{\text{losses}} = 30$
3c. LiF($F_2 \rightarrow F_2^+$) crystals optimization

<table>
<thead>
<tr>
<th>LiF</th>
<th>PHOTOSTABILITY</th>
<th>THERMOSTABILITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2^+$</td>
<td>+</td>
<td>- (10 hours at RT)</td>
</tr>
<tr>
<td>$F_2$</td>
<td>-(2 step ioniz)</td>
<td>+ (&gt; 10 years at RT)</td>
</tr>
</tbody>
</table>
### 3c. Efficient, RT Stable LiF:F$_2$** Crystals

| Formation Of The Thermostabilized F$_2$** Active Color Centers | $e^o_s \Rightarrow F + H$; $e^o_s \Rightarrow V_a^+ + I_a^-; V_a^+ + F \Rightarrow F_2^+; F_2^+ + e \Rightarrow F_2$
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2^+ + F \Rightarrow F_2^+$; $F_2^+ + F \Rightarrow F_2^+$; $F_2^+ + F \Rightarrow F_2^+$; $V_a^+ + F \Rightarrow F_3^+$</td>
<td></td>
</tr>
</tbody>
</table>

1. LiF crystals doped with LiOH, Li$_2$O and MgF$_2$ can be grown by any method which assures good optical quality.

2. Crystals are subjected to $\gamma$-irradiation, X-ray or electron irradiation with a dose of $2.5 \times 10^3$ - $1.5 \times 10^4$ Q/kg at a temperature lower than $T_V$ - temperature of $V_a^+$ mobility in LiF crystals.

3. Crystals are heated up to $T_{O-V} < T_F$ and stored in the refrigerator for a period up to one month ($T_F$ corresponds to mobility of F$_2^+$CC and $T_{O-V}$ to $O^-V_A^+$ dipoles).

4. Crystals may be reirradiated at the temperature $T < T_V$ with a dose of 25-250 Q/kg and then subjected to the procedure described in 3.

5. Crystals heated up to RT and are stored for a period of some months. $O^-V_a^+ + F \Rightarrow F_2^+O^-$; $V_a^+V_c^- + F \Rightarrow F_2^+V_c^-; F_2^+ + O^- + e \Rightarrow F_2^+O^-$; $F_2^+ + F \Rightarrow F_3^+$ low efficiency since $N_F$ is small.
3c. Efficient, RT Stable LiF:F$_2$** Crystals

<table>
<thead>
<tr>
<th>Photostability Of Active CC As Well As Other CC That May Be Ionized By The Powerful Pump Laser Excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The technology of LiF should provide a highest possible concentration of the active CC. The pump radiation will be predominantly absorbed by the photostable F$_2^+$ like centers.</td>
</tr>
<tr>
<td>2. Pump radiation from one hand should match the absorption band of F$_2^{+**}$ color, and from another, should be longer than the threshold wavelength determining the process of two step ionization of the neutral F$_2$ centers (590 nm)</td>
</tr>
<tr>
<td>3. the wavelength of the pump radiation shouldn’t match the absorption bands of the parasitic aggregate CC (500-600 nm) that may occur in the crystal and result in decreasing of the efficiency of lasing</td>
</tr>
</tbody>
</table>
3c. Novel LiF:F$_2$$^{**}$ Crystals

(U.S. Patent No. 5,796,762)
3c. Proposed model of $F_2^{**}$ stabilized CC in LiF

Four defect configurations with different symmetries are possible for closest (110) neighboring positions of the F center vacancy site (labeled 1 to 4) with respect to the charge compensating vacancy.

1) $O^- V_{a}^{+} + F \xrightarrow{RT} F_{2}^{+} O^{--}$

2) $OH^{-} \xrightarrow{\gamma} O^{-} + H_{i}^{o}$

$O^{-} + e + V_{a}^{+} \xrightarrow{RT} O^{-} V_{a}^{+}$

$O^{-} V_{a}^{+} + F \xrightarrow{RT} F_{2}^{+} O^{--}$

2) $(OH^{-}) \xrightarrow{\gamma} O_{2}^{-} + e + V_{a}^{+} + 2H_{i}^{o}$

$2(OH^{-}) + V_{a}^{+} + e \xrightarrow{\gamma} O^{-} V_{a}^{+} + O^{-} + H_{i}^{o}$

$H_{i}^{o} + e \xrightarrow{} H_{i}^{-}$

3) $F_{2}^{+} + O^{-} + e \xrightarrow{R_{i}} F_{2}^{+} O^{--}$

4) $Mg^{++} V_{c}^{-} + F \xrightarrow{RT} Mg^{+} + V_{a}^{+} V_{c}^{-}$

$V_{a}^{+} V_{c}^{-} + F \xrightarrow{RT} F_{2}^{+} V_{c}^{-}$
3c. Key Advantages of the Optically Dense Color Center Active Media

- The key advantages of the optically dense active media are the high efficiency of the pump energy conversion into the output generation and an opportunity for further miniaturization of the laser devices on their basis. The aforesaid advantageous are undeniably true and for the ionic color center crystals. However, high-concentrated color center crystals exhibit some new special features.
- light to light efficiency increasing
- color center crystal photostability may be essentially improved
- it is possible to reach high gain coefficients and laser threshold conditions on the colored layers with a thickness of about 0.01 1m
- such a thin colored films of dielectric crystals are semicanductor in character. This fact provides a theoretical reason enough to develop principally new lasers based on the dielectric crystals with an electrical pumping
3c. LiF:F\textsubscript{2} ultimately high concentrated media

A highly-concentrated (k = 400 cm\textsuperscript{-1}) LiF:F\textsubscript{2} crystal with a 90 m thickness of coloration was developed under low energy electron irradiation. This enables the threshold of generation of the LiF:F\textsubscript{2} crystals to be significantly decreased to such a low level of pump radiation (3 \textmu J), that the probability of the F\textsubscript{2} color centers two step photoionization started to be negligible.
A new method of radiational coloring of the LiF crystals with quanta of soft X-ray radiation, generated with the use of a laser (1.06 μm) plasma source. The absorption coefficient in the F₂ band was about 1500 cm⁻¹, thickness of coloration - 4 μm.
4. Major spectroscopic characteristics of color centers

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Type of CC</th>
<th>λ_{max} (nm)</th>
<th>Δν_{0.5} (cm⁻¹)</th>
<th>λ_{max} (nm)</th>
<th>Δν_{0.5} (cm⁻¹)</th>
<th>τ (ns)</th>
<th>η (%)</th>
<th>σ_{max}^{max} (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>F₂</td>
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<td>F₃</td>
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<td>NaF:OH</td>
<td>F₂(OH)</td>
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<td>95</td>
<td>2.0 · 10⁻¹⁷</td>
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4. Luminescence bands of (a) $F_A$(II) and $F_B$(II) centers; (b) $F_2^+$ centers, and (c) $F_A$(Tl) centers in alkali-halides at 77K
4. Absorption (solid lines) and luminescence (dashed lines) bands of CCs in Al₂O₃ crystal at 4.2 and 300 K, respectively. Numbers near the bands are wavelengths of zero phonon lines.
5. CW and quasi-CW color center laser operation (T=77K)

- The pump density of several kW·cm$^{-2}$ is needed to reach the threshold of CCL oscillation. This is easily achieved for pulsed pumping by a flash lamp emitting few tens of joules during a millisecond pulse. In this case the lasing volume of color center crystal can be as large as 1 cm$^{-3}$ or even more.

- In order to get the same pump densities for cw laser pumping with power of 0.1-10 W, one have to use strong focusing of the pump radiation and put the CCL crystal at the focal point or cavity waist of 0.1-1 mm in diameter. The crystal length is limited by the confocal parameter of focused beam and usually does not exceed 1 cm (typically it is a few mm).
5. CW and quasi-CW color center laser operation (T=77K)

- The most popular optical scheme used now for cw CCL operation is the Kogelnik scheme with a Brewster cut active element and with V-shape or Z-shape folded cavity to compensate spherical lens or mirror astigmatism.[i]

  ![Schematic of the Burleigh laser](image)

  \[ \sin \theta \cdot \tan \theta \cdot \frac{n^4}{(n^2 - 1)(n^2 + 1)^{1/2}} = \frac{t}{f} \]

  The beam waist diameter \( W_0 \) and confocal length \( b \) can be found from the formulas

  \[ W_0 = f \sqrt{\frac{\lambda}{2\pi l_2}} \quad t \leq b = \frac{f^2}{l_2} \]

  \[ \left( \frac{b}{l_2} = \frac{f}{l_2} \right) \]

5. Cavities of CW CCL

Schematic of cw color center laser capable of single-frequency, single-knob tuning

Schematic of a typical ring laser
5. CW and quasi-CW color center laser operation (T=77K)

• There are two sets of the most popular regimes of operation in cw mode.
  1. The first one is the narrow line (single frequency) broadly tunable CCL oscillation for visible and IR spectroscopy, analytical application, and fundamental metrology.
  2. The second is the mode-locked pico- and femtosecond pulse operation regime for time resolved transient spectroscopy, high peak power nonlinear conversion, and fast telecommunication systems.
5. CW and quasi-CW color center laser operation (T=77K)

- Single-mode, single-frequency operation of a KCl:Li F_A(II) CCL under krypton ion laser pumping at 647 nm with linewidth less than 260 KHz and tunability in 2.5-2.9 $\mu$m spectral range realized with the pair of birefringent plates and an intracavity solid etalon was obtained in Ref. [i]. By the active frequency stabilization, linewidth as low as 2 KHz was realized later in [ii]. To obtain a single mode operation and to improve linewidth and wavelength stability, the ring cavity operation can be also applied [iii], [iv]. Typical output power of FA(II) CCL varies from tens to hundreds milliwatts in 2.3 - 3.5 mm spectral region.

5. CW and quasi-CW color center laser operation (T=77K)

• With the Kr laser pump source, LiF:F$_2^+$, CCL operation with a very high slope efficiency of 60%, close to the physical limit (output to pump photon energy ratio) 70%, was obtained. A wide tuning range 0.84÷1.04 µm was covered with the cw output power up to 1.1 W in pure cw regime and under synchronous picosecond pumping 6. In the last case, 25 times shortening from 100 ps pump to 4 ps CCL output was demonstrated [i].

5. CW and quasi-CW color center laser operation (T=77K)

- One of the main problems of the LiF(F$_2^+$) CCL is fast optical bleaching due to orientational diffusion of F$_2^+$ CCs. The maximum cw lasing output (2.7 W) was recorded in the KF(F$_2^+$) CCL under 1.064 µm Nd$^{3+}$:YAG pumping with the tuning range of 1.22÷1.5 µm. [i]

- In the case of (F$_2^+$)$_A$ color center, the KCL:Li crystal showed a very good performance: Pout=400 mW under 1.32 µm cw Nd laser pumping and Eout=2.3 mJ under 1.41 µm pulsed pumping with the tuning range from 2 to 2.5 µm. [i]

5. CW and quasi-CW color center laser operation (T=77K)

• The operation of \((F_{2}^{+})_{H}\) color centers in NaCl crystals doped by OH ions looks very promising. For the first time it was reported in [i].

• Output power as high as 3.05 W at the slope efficiency of 33% was reported in [ii] under 9W pumping at 1.064 \(\mu\)m and 200 mW collinear auxiliary light of 514 nm.

• A very wide tuning range, 1.4÷1.92 \(\mu\)m, important for telecommunication study and test with output up to 1.3 W was obtained in [iii] at 6 W 1.064 \(\mu\)m laser pumping and only 2 mW of 532 nm collinear auxiliary light. This laser can also easily operate in the mode-locked regime with picosecond pulses as short as 5 ps.

5. CW and quasi-CW color center laser operation (T=77K)

- A stable cw laser operation without using the auxiliary light was also obtained with the help of $F_A(Tl)$ color centers in KCl:Ti$^+$, KBr:Ti$^+$, and KF:Ti$^+$ crystals. The first of these crystals provides about 1.4 W output at the maximum of the tuning curve with tunability from 1.4 to 1.6 $\mu$m at the absorbed pump power $\sim$ 3.5 W of 1.064 $\mu$m Nd:YAG pump laser). [i]


Tuning curves of $F_A(Tl)$ color center laser in KCl:Ti$^+$ (solid lines) and KBr:Ti$^+$ (dashed lines) pumped by Nd:YAG laser radiation (1.064 mm).
6. Pico and femtosecond quasi-CW color center laser operation (T=77K)

- One of the most interesting and important regimes of CCL operation is the mode-locked regime, when many longitudinal modes of a broadband laser radiate with «coordinated phase». According to the Fourier transformation, this multifrequency cw laser operation leads to a short pulse high peak power quasi-CW lasing with the pulse-to-pulse temporal interval equaling to the laser cavity round trip time and pulse duration being inversely proportional to the number of longitudinal mode operating in mode-locking regime.

- All types of the mode-locking techniques developed for dye lasers are applicable for developing mode-locked CCL. Color center mode-locked operation is quite similar to the dye laser mode-locking regime with the only one distinction: the excited state lifetime of CC is about $\tau_{CC} = 15\text{−}1500$ ns and is usually larger than the laser cavity round trip time, $t_{cavity} = 6\text{÷}10$ns, while for the dyes it is smaller ($\tau_{dye} = 3\text{÷}5$ns).
6. Pico and femtosecond quasi-CW color center laser operation (T=77K)

- One of the most popular and effective techniques for realization of pico- and femtosecond lasing is synchronous pumping, when the pump laser mode-locking regime is transferred to CCL. In this case, the cavity round trip times of both pump and CCLs should be synchronized and the synchronized CCL gain modulation results in pulsed CCL lasing and pulse shortening to duration much shorter than the pump pulse duration.
- Expression for the pulse width \([i]\) shows that it should be proportional to the pump and CCL cavities mismatch parameters \(\Delta\) and inversely proportional to the logarithmic gain loss product.
- This means that the shortest pulse duration of CCL can be realized at the highest gain, pump energy, and power. When using 90 ps pulsed krypton laser synch-pumping, the LiF:F\(_2^+\) CCL pulses had duration of 2-3 ps in linear cavities and 0.7 ps in ring cavities\([ii]\).
- Similar results were obtained in linear cavities of KF(F\(_2^+\)), NaCl(F\(_2^+\)), and KCl:F\(_A^+(\text{Tl}^+)\) lasers under Nd:YAG synch-pumping and for KCl:Li(F\(_A^+\)) and RbCl:Li(F\(_A^+\)) CCL under modelocked argon laser pumping).

6. Pico and femtosecond quasi-CW color center laser operation (T=77K)

• In the passive mode-locking regime with a dye saturable absorber, pulse duration of 180 fs was achieved in a LiF:F$_2^+$ CCL ring cavity at the lasing bandwidth of about 60 cm$^{-1}$.[i] Using a multiple quantum well saturable absorber, a NaCl(F$_2^+$) CCL demonstrates 260 fs pulse operation with 50 cm$^{-1}$ bandwidth.[ii]

• By developing new additive pulse mode-locking technique for pulse shortening, 127 fs pulse duration instead of 23 ps from KCl:Tl CCL was realized.[iii] In a similar regime 50fs pulses have been generated by so-called «soliton laser» on KCL:Tl at 1.5 μm. [iv]

7. Room temperature CCL operation
7a. CW and quasi-CW

- Room temperature tunable CCLs color center lasers have special importance in comparison with dye and cryogenic CCLs due to their compactness, simplicity and easy to use both for laboratory and field conditions. Lithium fluoride with F$_2^-$ CCs is one of the most reliable active media for room temperature tunable operation.

- During last two decades only several papers were dedicated to the study of CW and quasi-cw laser operation on LiF:F$_2^-$ crystals at T=300 K [i],[ii] Most of them used neodymium solid state lasers as a pumping source.


7. Room temperature CCL operation
7a. CW and quasi-CW

- For the first time, pure cw LiF:F$_2^-$ lasing has been attained using the crystals with $k_{\text{abs}}$ = 1.3 cm$^{-1}$ at a pump wavelength of 1.064 mm and low losses ($K_L = 0.01\text{cm}^{-1}$) in the lasing region of 1.1-1.2 μm [i]. A ring cavity with 1 m base and astigmatism compensation incorporated two plane mirrors (2 and 3) with 99.7% and 99% reflectance in the lasing region and two 100% reflectance spherical mirrors (1) with the curvature radius of 10cm. For a pump power of 3 W, the lasing output power was 60 mW. These results were further improved: the maximum output CW power of LiF:F$_2^-$ laser exceeded 100 mW at a pump power of 5 W. The LiF:F2- active element preserved all its properties after a 30 h performance.

7. Room temperature CCL operation
7a. CW and quasi-CW

• The first results on frequency tuning and picosecond generation at room temperature of CW LiF:F$_2^-$ laser were obtained under synchronous pumping with a continuous train of picosecond pulses of CW-pumped Nd$^{3+}$:YAG laser. The use of a ring cavity and Lyo filter as a dispersive element provided lasing over 1.1-1.2 µm spectral region. LiF:F$_2^-$ oscillation under Nd$^{3+}$:YAG laser synchronous pumping provided picosecond pulses with duration of 10 ps and 7 ns axial interval for continuous train of pulses [i]

7. Room temperature CCL operation
7a. CW and quasi-CW

Tuning curves of quasi-cw oscillation of LiF:F$_2$· CCL pumped by Nd$^{3+}$:YAG (1) and Nd$^{3+}$:YLF (2) lasers.
7b. High peak power room temperature CCL operation in pico and femtosecond regime.

• Since middle 70th there were a lot of studies on picosecond operation of $F_2^+$; $F_2^+$ $O^-$; $F_2^-$ and $F_3^-$ color centers in LiF and NaF crystals at room temperature. Synchronous pumping by the train of picosecond pulses of ruby, Nd:YAG or Nd:glass lasers was used as the most effective scheme of CCL pulse shortening. Fast CC gain switching (modulation) leads to the effective CCL pulse shortening depending on degree of pump power exceeding threshold, number of pulses and length of the train.
7b. High peak power room temperature CCL operation in pico and femtosecond regime.

Experimental setup of picosecond LiF:F$_2$- CCL. (1, 2, 3) – end, spherical and cavity mirrors, (4) active element (LiF:F$_2$- crystal), (5) prism compensator of the group velocity dispersion, (6) aperture, (7) Lyo filter, (8) streak camera, (9) -PC.

7b. High peak power room temperature CCL operation in pico and femtosecond regime.

- A precise matching of resonator's lengths gave rise to \( \text{LiF:F}_2^- \) femtosecond oscillation with a pulse duration of less than 500 fs, at a full train duration of 300-400 ns and a train energy of 250 mJ [i].

- The durations of the subpicosecond pulses were measured directly on the screen of the streak camera (2) with a resolution of 0.6-0.7 ps as well as with an autocorrelator which provided an average pulse duration in the \( \text{LiF:F}_2^- \) train of less than 0.5 ps. A conservative estimation of the peak power for 0.5 ps output pulses gives a minimum power of 10 MW, which greatly (by 3-4 orders) exceeds the standard peak power generated by ordinary quasi-CW dye and CC lasers.

7c. High energy and power color center lasers

- Success in the growth of big size and good quality alkali-halide optical crystals and in the development of homogeneous, high contrast coloration technique gives rise to a unique opportunity to design a large scale high power lasers and amplifiers based on CCCs.

- Developing a large scale homogeneously colored LiF:F$_2^-$ CC active crystals with a size up to 40×80×200 mm$^3$ with 4 large polished faces allowed utilization of a huge (700 J in 120 ns pulse duration) pump energy from a multistage Nd-glass laser system. In a two pass pumping scheme with the 5 J/cm$^2$ pump energy density a transversely directed lasing of F$_2^-$ CCs was realized in the nonselective 300 mm long Fabri-Perot cavity with 50% output coupling. Under these conditions we were able to reach the record output energy of 100 J and peak power of 1 GW at 1.12 - 1.16 μm and 100 ns pulse duration.[i]

7c. High energy and power color center lasers

- For smaller (40×40×20 mm³) LiF:F₂⁻ crystal in transversal LiF and Nd:glass coupled cavity arrangement the Nd laser pump to CCL output conversion efficiency was increased up to 80 % with the CCL output energy of 8 J at 1.15 μm [i].

7c. Dependence of LiF:F2- Laser Output Energy on Mirror (R4) Reflectivity for Different LiF Crystal Optical Densities, Measured in a Transverse-Oriented Coupled Cavity Scheme
7c. Dependence of LiF:F2- Laser Output Energy on Mirror (R4) Reflectivity for Different LiF Crystal Optical Densities, Measured in a Longitudinal Coupled Cavity Scheme

glass Φ 3 x 50 mm small aperture

\[ R_{1.06} = 1\% \quad R_{1.15} = 72\% \quad R_{1.15} = 85\% \]

\[ \eta_{eff} = \frac{E(1.15\,\mu m)}{E(1.06\,\mu m)} = 75\% \]
7d. Color center energy and power amplifier

- In many cases it is necessary and convenient to amplify a weak laser radiation with special spectral, spatial or temporal properties to a high energy or peak power values. The four-level energy diagram describing electronic-vibrational transitions of CCs together with a considerable Stokes shift and quasi-homogeneous nature of their wide absorption and fluorescence bands, as well as a high quantum efficiency and a large amplification cross section are very favorable factors for tackling this amplification task. CCC can be effectively used in master oscillator power amplifier (MOPA) schemes or for pico- and femtosecond pulse amplification in near IR spectral region.

- High emission cross section ($\sigma_{em} = 7 \cdot 10^{-17} \text{ cm}^2$) and lifetime ($t = 100 \text{ ns}$) of F$_2$- CCs allows to predict a high amplification gain and efficiency of LiF:F$_2$- amplifier. Comparing to dye solutions the concentration of F$_2$- CCs in LiF crystal is rather low. Due to this the longitudinally pumped amplifier scheme is preferable for good spatial overlapping of the pump and probe radiation in the bulk CCC with 40÷80 mm length.
7d. Color center energy and power amplifier
Energy dependencies of amplification gain and output energy of LiF:F$_2^-$ single-pass CCL amplifier with 40 mJ pump pulse.
7d. Energy dependencies of amplification gain and output energy of LiF:F$_2^-$ two-pass amplifier with 40 mJ pump pulse.
7d. LiF:F$_2^{+}$ Color center energy and power amplifier

- The feasibility of amplification of broadband radiation of diode lasers and LEDs with the aid of LiF:F$_2^{+}$ CCCs was demonstrated in [i]. Single-pass amplifier configuration was used. The active centres were excited by the second harmonic (532 nm) of a multimode pulsed Nd$^{3+}$:YAG laser emitting pulses of 10 ns duration. A GaAs laser diode generated 85 ns radiation pulses with linear polarization at the wavelength 900 nm (close to the maximum of the fluorescence spectrum of F$_2^{+}$ CCs) with the spectral width was about 55 cm$^{-1}$.

- In this experiment a single-pass gain G=5 in the short crystal (l = 0.8 cm) and gain G=20 in the long crystal (l = 2 cm) was reached with the pump pulse energy 1 mJ. No saturation of the gain relative to the energy of the amplified radiation from the laser diode was observed. The optical gain was constant when the pump energy was in the range 0.1-1 mJ and the energy of the amplified IR radiation was 0.4-33 nJ.

7e. Narrowline tunable color center lasers

- The main advantage of CCL is the possibility to obtain a coherent radiation tunable over a wide near IR spectral range. Rough selection of the oscillating wavelength can be made by choosing appropriate color center active medium. In the nondispersive cavity the oscillation occurs at the wavelengths near the maximum of fluorescence curve. The width of the oscillating spectra can be up to several hundreds of cm⁻¹. Tunable radiation of CCLs in dispersive cavities is obtained when prisms, diffraction gratings, Fabri Perrot etalons, Lyo filters and other wavelength selective elements are utilized.
7e. A Schematic diagram of the commercial tunable color center lasers MALSAN-201 (bottom) and MALSAN-203 (top)
7e. Dependencies of the efficiency of MALSAN laser on the wavelength of tunable radiation:

1. the active medium is LiF:F$_2^-$ - fourth harmonic;
2. LiF(F$_2$ → F$_2^+$) - second harmonic;
3. LiF:F$_2^-$ - third harmonic;
4. LiF:F$_2^{++}$(Mg);
5. LiF(F$_2$ → F$_2^+$);
6. LiF:F$_2^-$;
7. NaF:F$_2^{++}$;
8,9. LiF:F$_2^-$ - first and second Stokes components, respectively.
7e. The dependence of the conversion efficiency of the LiF:F$_2^-$ laser crystal in the non selective cavity versus the reflectivity of the output mirror.
7e. Dependence of the LiF:F$_2^-$ laser efficiency on the wavelength of tunable radiation: 1,2-for a grazing incidence schemes, 1. - two gratings, 2. - one grating and a mirror as an end reflector for its first order diffraction; 3,4 in a scheme of the MALSAN laser, 3.-for the usual pump source and active element; 4. - for the optimized one.
Alexandrite laser pumped LiF:F$_2^-$ laser
Summary

For the first time to our knowledge LiF:F$_2^-$ lasing in 1-1.3 $\mu$m spectral region was realized under 740-795 nm alexandrite laser pumping. Experimental data on LiF:F$_2^-$ lasing are reported and peculiarities of mechanism of F$_2^-$ excitation via F$_3^-$ centers are studied.
MOTIVATION

1. Broadening of LiF:F$_2^-$ Color Center tuning range.
2. Development solid state system continuously tunable in 0.2-1.3 $\mu$m spectral range.
Shortcoming of the LiF:F$_2^-$ lasing under 1.064 $\mu$m excitation

\[
\frac{\partial N_2}{\partial t} = (\sigma_{12}(v_p)I_p + \sigma_{12}(v_g)I_g)N
- \left\{((\sigma_{21}(v_g) + \sigma_{12}(v_g))I_g + (\sigma_{21}(v_p) + \sigma_{12}(v_p))I_p + \tau_2^{-1})N_2
\right\}
\]

\[
\frac{\partial I_g}{\partial t} = \frac{t_{\text{cav}}^{-1}I_g}{2} (2\ln N_2 (\sigma_{21}(v_g) + \sigma_{12}(v_g))
- 2\ln \sigma_{12}(v_g) - \beta_{\text{act}} - \beta_{\text{pass}}))
\]
Effective $F_2^-$ Color Center Cross Section

\[ \sigma_{\text{eff}}^* = \frac{\sigma_{\text{em}}(\lambda_{os})\sigma_{\text{ab}}(\lambda_p) - \sigma_{\text{em}}(\lambda_p)\sigma_{\text{ab}}(\lambda_{osp})}{\sigma_{\text{ab}}(\lambda_p) + \sigma_{\text{em}}(\lambda_p)} \]

\[ N_{2\text{sat}} = N \frac{\sigma_{\text{ab}}(\lambda_p)}{\sigma_{\text{ab}}(\lambda_p) + \sigma_{\text{em}}(\lambda_p)} \]

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$\lambda_1$=965 nm
$\lambda_2$=1029 nm
$\lambda_3$=1047 nm
$\lambda_4$=1064 nm
$\lambda_5$=1079 nm
Comparison of main spectroscopic properties of LiF:F$_2^-$, LiF:F$_3^-$, LiF:F$_2^+$ and Ti-S laser media

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</table>
Structure of Color Centers in LiF crystals

- $F_2^-$ center
- $F_3^-$ center

- $\text{Li}^+$
- $F^-$
- Vacancy
- Electron

Diagram showing the structure of color centers in LiF crystals.
Idea of the lasing mechanism of the LiF:F$_2^-$ crystal under alexandrite laser pumping

Absorption and Emission spectra of F$_2^-$ Color Center

Absorption and Emission spectra of F$_3^-$ Color Center

\[ F_3^- + h\nu_{793} \rightarrow F_3^-^* \]

\[ F_3^-^* \rightarrow F_3^- + h\nu_{920} \]

\[ F_2^- + h\nu_{920} \rightarrow F_2^-^* \]

\[ F_2^-^* \rightarrow F_2^- + h\nu_{100-1300} \]
Absorption spectrum of the LiF active medium

![Absorption spectrum graph]

- Wavelength, nm: 600, 700, 800, 900, 1000, 1100, 1200, 1300
- Absorption, cm$^{-1}$: 0, 1, 2, 3, 4, 5, 6

D = 10$^8$ rad

$F_3^-$ $F_2^-$
LiF:F$_2^-$ Dispersive Cavity
Experimental Results

- Normalized Tuning Curves of LiF:F$_2^-$ Color Center Laser under different pumping wavelength
  1- $\lambda=1064$nm YAG:Nd$^{3+}$ laser
  2- $\lambda=1047$nm YLF:Nd$^{3+}$ laser
  3- $\lambda=793$nm Alexandrite laser

- LiF:F$_2^-$ tuning Curve under 793 nm Alexandrite laser pumping
Photostability of LiF:F$_2^-$ Laser

Spectral Dependence of Photoionization Probability (W) of F$_2^-$ and F$_3^-$ Color Centers in LiF at RT

Alexandrite Laser
two photon/ two step excitation

$F_2^-$

$F_3^-$
The kinetics of $F_3^-$ color center destruction under 740 nm excitation

$$F_3^- + 2h\nu_{740} \rightarrow F_3^{*-} + h\nu_{740} \rightarrow F_3 + e$$

$$\Delta K \sim \sigma I^2$$

Rate of $F_3^-$ concentration change

Intensity @ 740 nm (MW/cm$^2$) vs. $\Delta K/dt$ (cm$^{-1}$ s$^{-1}$)
LiF:F$_2^-$ Oscillation Efficiency Decay under different pumping wavelength
Conclusion

• For the first time to our knowledge a direct alexandrite laser pumping of LiF:F$_2^-$ laser was realized
• Tunable oscillation of LiF:F$_2^-$ laser in 1-1.3 µm spectral range with maximum efficiency 10% was achieved
• Two-step mechanism of photoionization of F$_3^-$ Color Center under λ=740 nm excitation was demonstrated experimentally.
• Stable Oscillation of LiF:F$_2^-$ laser at RT under λ=793 nm excitation was predicted and shown experimentally
All-Solid-State System Based On Alexandrite - LiF:F₂⁺⁺ Lasers For Deep UV (196 nm) And Mid-IR (4000 nm) Spectral Ranges

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OUTLINE

1. Motivation  
2. Introduction  
3. Room Temperature Stable LiF:F₂⁺⁺ Lasers  
   * Optical properties of LiF:F₂⁺⁺ crystals, ultrabroadband tuning capability (>400 nm)?  
   * Nonselective cavity, dispersive cavity, operational characteristics  
4. Alexandrite-CCL System Design, Frequency up-conversion (CLBO); Down-conversion (LiNbO₃, Ag₃AsS₃)  
5. Conclusions

Highlights of Current Findings

- We present a novel all solid-state laser system that exploits the best features of the high gain, “dye-like” LiF:F₂⁺⁺ medium and the high energy storage alexandrite laser. It is ideal for efficient deep UV (196-204 nm, η=23%) and mid-IR (2.2-5.5 μm, η=10%) lasing.

2002 OSA Annual Meeting and Exhibit/LS-XVIII
Motivation

• Pulsed Laser sources with deep UV (below 200 nm) and mid IR (3-5 μm) output radiation have attracted significant attention for use in integrated circuit processing, medicine, molecular spectroscopy, and remote sensing.

• CCL with frequency up- and down conversion are very attractive candidates: easy to scale up, high efficiency (tens of %), wide amplification band (hundreds of nm), high wavelength stability, extremely narrow oscillation spectral width, achievable virtually without power loss, low threshold, high gain, short oscillation built-up time, and absence of temporal delay between pump and output pulses.

• Our goal was to demonstrate that Alexandrite - LiF:F₂⁺⁺ CCL combination exploits the best features of both the high gain, “dye-like” CCL and the high energy storage alexandrite laser and is a promising drive source for a number of efficient nonlinear processes, including harmonic, sum-frequency and difference-frequency generation that offers simple and economical way to achieve widely tunable narrow-linewidth performance in the UV-middle IR spectral range.
Novel LiF:F$_2^{***}$ Crystals
(U.S. Patent No. 5,796,762)
# Major physicochemical and mechanical properties of LiF crystal

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$, melting point ($^\circ$C)</td>
<td>870</td>
<td>$E$, Young’s modulus (kg/mm$^2$)</td>
<td>8820</td>
</tr>
<tr>
<td>Solubility, (g/100g H$_2$O)</td>
<td>0.14</td>
<td>$\mu$, Poisson’s coefficient</td>
<td>0.28</td>
</tr>
<tr>
<td>$H$, Knupp hardness (kg/mm$^2$)</td>
<td>99</td>
<td>$S$, compression (tension) or bending strength (kg/mm$^2$)</td>
<td>1.2-4.0</td>
</tr>
<tr>
<td>$d$, lattice constant (Å)</td>
<td>4.03</td>
<td>$R$, thermal shock parameter (W/m)</td>
<td>43-143</td>
</tr>
<tr>
<td>$\rho$, density (g/cm$^3$)</td>
<td>2.64</td>
<td>$n$, refractive index</td>
<td>1.38</td>
</tr>
<tr>
<td>$K$, coefficient of thermal conductivity (W/m $^\circ$C)</td>
<td>14.2</td>
<td>$n_2$, nonlinear index ($10^{-22}$ m$^2$/V$^2$)</td>
<td>2.7</td>
</tr>
<tr>
<td>$\alpha$, coefficient of linear expansion ($10^{-6}$/°C)</td>
<td>32.0</td>
<td>$dn/dT$, temperature derivative refractive index ($10^{-5}$/°C)</td>
<td>-1.2</td>
</tr>
<tr>
<td>Transparency region (µm)</td>
<td>0.1-7.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Input/output dependence for LiF:F\textsubscript{2}** laser at 300 K with nonselective resonator under pumping with:

(1) $\lambda_{\text{pump}}=740$ nm, ($\eta_{\text{real}}=31\%; \eta_{\text{diff.}}=28\%$)

(2) $\lambda_{\text{pump}}=683$ nm, ($\eta_{\text{real}}=53\%; \eta_{\text{diff.}}=58\%; \eta_{\text{quant.}}=81\%$)

(3) is linear fit.

![Graph showing input/output dependence](image_url)
Alexandrite laser pumped tunable LiF:F$_2$*** laser
Fundamental, SHG, THG, and SFG conversion efficiency with respect to alexandrite laser pump energy as a function of wavelength for LiF:F\textsubscript{2}*** laser.
Typical temporal shapes and delays between the pump and the LiF:F$_2$ oscillating pulses
Optical arrangement for sum frequency generation of deep-UV radiation
Theoretically calculated angular tuning curves in CLBO crystal for different wavelengths of the pump radiation 240 nm, 243 nm, and 246 nm versus the SFG spectral output.

SFG Phase matching for CLBO. Alexandrite laser radiation (3w) is mixed (type 1, ooe interaction) with the tunable radiation of alexandrite laser pumped LiF:F2++ laser.
Deep UV Frequency Upconversion in CLBO

$233.66 \text{ nm}(701 \text{ nm}/3) + 1110 \text{ nm} = 193 \text{ nm (900)}$
FREQUENCY DOWNCONVERSION
(40-60 ns pump pulse duration)

Digital Oscilloscope

Joulemeter J4-10

Ge Filter (16)

λ₁=2.2-5 μm

LiNbO₃

M₁₁

M₂

Beam exp. 3:1 (12)

Slit

Input mirror (M₇)

HR M₆

LiF:F₂⁺⁺⁺ (8)

M₁₀

Grating (9)

M₁₁

Beam compressor 5:1 (12)

Ge filter-Spectrograph-InSb

Joulemeter

Ge Filter (16)

λ₁=2.2-5 μm

LiF:F₂⁺⁺⁺ (8)

E=80 mJ at λ₃=740 nm

τ=60 ns; f=10 Hz

Alexandrite Laser

Ee interaction
Experimental and theoretical DFG quantum efficiency versus DFG wavelength for LiNbO$_3$ (Li/Nb=1) nonlinear crystal. Power density of alexandrite laser was about 3 MW/cm$^2$. Power density of LiF:F$_2^+$ laser was not constant. It varied from 6MW/cm$^2$ for 3$\mu$m DFG output to 0.3 MW/cm$^2$ for spectral regions around 2.2 and 5 $\mu$m.
The external phase matching angle for Ag$_3$AsS$_3$. Inset: DFG wavelengths as a function of LiF:F$_2^{**}$ wavelengths at a pump wavelength, $\lambda_3$ of 736.7 nm.
FREQUENCY DOWNCONVERSION
500-600 ns pump pulse duration obtainable with Light Age, Inc. pulsed stretched 101PAL

Results
- Pulsewidth: 500 ns
- Pump wavelength: 737 nm
- LiF wavelength: 919 nm
- DFG wavelength: 3.7 μm
- Pump energy: 440 mJ

Mixed pulses:
- LiF energy: 27 mJ
- Residual pump: 76 mJ

Nonlinear material:
- Two 24 mm LiNbO₃ with walk-off compensation

DFG 3.7 μm energy: 1.04 mJ

Temporal overlapping of LiF:F₂⁺⁺⁺ color center laser oscillation (red) and oscillation of the Alexandrite laser (black).
FREQUENCY DOWNCONVERSION
(500-600 ns pump pulse duration)

η = 0.25%

η = 4%

η = 6.2%

η = 1.5%
CONCLUSIONS

1. Photo and thermostable regime of LiF:F$_2$+* lasing was realized due to a novel technology of LiF:F$_2$+ stabilized crystal formation.

2. We demonstrated solid-state laser system for deep UV and mid IR spectral range.

3. The tunable radiation in 196- 204 nm with 23 % efficiency and up to 0.5 mJ pulse energy has been realized.

4. The difference frequency generation between radiation of alexandrite and LiF:F$_2$+** lasers in 2.2 –5.5 µm was achieved with 10% efficiency in LiNbO$_3$ crystal at 3 µm for 50 ns pulses.

5. Output energies of 1.04 mJ at wavelength of 3.7 µm for a long, 600 ns, pulse duration was obtained in LiNbO$_3$ crystal.
Tunable Room Temperature Stable Color Center Distributed Feedback Laser

Jason G. Parker, Mentor: Sergey B. Mirov
Collaborators: Dmitri Martyshkin, Vladimir V. Fedorov

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**Introduction**

Tunable room temperature distributed feedback color center lasers were studied.

**Motivation**

• Current tunable lasers: utilize external cavities with dispersive elements that provide tunability across the amplification band. However, utilization of an external cavity makes the overall system not compact and bulky. It is very advantageous to combine inside laser crystals all laser elements (gain medium and positive feedback – mirrors and/or dispersive elements).

• The distributed feedback (DFB) phenomenon makes it possible to do this while still achieving tunable oscillation.

• Newly discovered LiF:F$_2$** crystals combine the thermal- and photo-stability of impurity doped laser crystals with the high absorption and emission cross-sections of laser dyes.

• Until now, no tunable room temperature stable DFB lasers had been created using color center crystals (CCC).
Distributed feedback (DFB) lasers

• The DFB laser uses a periodic modulation of its medium to attain selective oscillation. This means that this modulation acts as a diffraction grating and thus follows the grating equation.

\[ \Lambda \left( \sin \theta_i - \sin \theta_m \right) = m \lambda_l \]

\( \Lambda \) = period, \( \theta_i \) = angle of incident beam from surface normal, \( \theta_m \) = angle of reflected beam from normal, \( m \) = order of diffraction, \( \lambda_l \) = lasing wavelength

Which in our case (\( \theta_i=90^\circ \), \( \theta_m=-90^\circ \)) reduces to:

\[ 2\Lambda = m \lambda_l \]
Grating construction by interference

• The interference of two equal laser beams creates a fringe normal to the point of intersection and sinusoidal in nature. Our setup uses this fringe to penetrate the crystal periodically and create our (dynamic) grating.
Spectroscopic analysis

• Spectroscopy was used to know if DFB was realized. Typical lasing with LiF:F$_{2}^{+}$ produces a spectrum approximately 15 nm in width. However, because feedback is selective in the DFB laser, DFB lasing should occur at a very specific wavelength, determined by the grating equation. The graph below shows one instance of DFB lasing transposed over one instance of typical LiF:F$_{2}^{+}$ broadband lasing. The linewidth of DFB lasing was measured and found to be less than 0.2 cm$^{-1}$ (0.017 nm).
Proof of lasing due to DFB

• If a particular peak is due to DFB, it should completely disappear when either shoulder is blocked.

DFB lasing at 945 nm
Right shoulder blocked
Left shoulder blocked

This technique was employed in all instances in which DFB occurred.
Tuning results

• The LiF DFB laser was fully tunable from 962 to 882 nm. This is a large range of tuning for any laser, and we suspect this range can grow considerably. The following figure shows instances taken throughout a tuning run from 962 to 882 nm. The small hump centered around 940 nm is due to normal LiF:F$_2^+$ broadband lasing (with oscillation from the crystals faces).
Power relationship

•The following graph shows the relationship between pumping power and output power for our laser. A linear dependence of output energy on pumping energy was determined. The maximum efficiency reached was 3%. Also, the optical threshold of pumping was found to be 1.2 mJ.
Conclusion

• For the first time, tunable room temperature stable color center DFB lasing has been realized.

• A dynamic grating was constructed inside the CCC using interference.

• The laser showed a large tuning range and we believe this range can grow considerably.

• A linear relationship between pump power and output power was determined, with a maximum pumping efficiency of 3%. Also, the optical pumping threshold was found to be 1.2 mJ.

• The results were prepared for presentation in the Photonics West LASE 2004 conference and publication in the physics journal Applied Physics Letters.
Persistent photon-gated spectral hole burning in LiF:F$_2^-$ color center crystal (V. Fedorov, S. Mirov Appl. Phys. Lett. 79, 2318-2320 (2001)).

LiF:F$_2^{++}$ Color Center laser

Alexandrite laser, Light Age, Inc.

The Q-switched alexandrite laser
$\lambda$=720-800 nm, $f$= 25, Hz,
$\tau$=80ns, $E$=80 mJ

ARC-750 spectrometer ($\Delta v=0.2$ cm$^{-1}$)

Close Cycle helium refrigerator,

LiF:F$_2^-$ crystals was $\gamma$-irradiated by a $^{60}$Co source with a dose $D=10^7$rad
Persistent photon-gated spectral hole burning in LiF:F$_2^-$ color center crystal

\[
F_2^- + h\nu \overset{1.04\mu m}{\longrightarrow} F_2^{*-} + h\nu \overset{0.52\mu m}{\longrightarrow} F_2 + e
\]

- Optical Density
  - E$\parallel E_{2\omega}$
  - E$\perp E_{2\omega}$

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1038</td>
<td></td>
</tr>
<tr>
<td>1039</td>
<td></td>
</tr>
<tr>
<td>1040</td>
<td></td>
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<tr>
<td>1041</td>
<td></td>
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<tr>
<td>1042</td>
<td></td>
</tr>
</tbody>
</table>

- P$_{1.04\mu m} =$ 5 MW/cm$^2$
- P$_{0.52\mu m} =$ 0.1 MW/cm$^2$
- time = 20 min, T = 14K
- $\Delta v_{\text{laser}} =$ 0.2-0.3 cm$^{-1}$

$\Delta v = 1.7\text{cm}^{-1}$
LASER ATOMIC FLUORESCENCE SPECTROSCOPY

- **RESEARCH GOAL:** Develop novel laser atomic fluorescence instrument for heavy metal detection at sub-ppt level for biomedical and industrial applications.

![Diagram of laser atomic fluorescence setup]

LAF detection of Cu atoms in water sample (Cu-10μg/L), distilled water, and deionized water (prepared using reverse osmosis at 18 megohm resistance)

- $\lambda_{ex} = 324.754\ nm$
- $\lambda_{reg1} = 510.554\ nm$
- $\lambda_{reg2} = 570.024\ nm$
Application of LiF laser in Opto-acoustic medical imaging

![Graph showing absorption coefficient vs. wavelength. Peaks at 757 nm, 800 nm, 920 nm, and 1060 nm are labeled for Hb and HbO2.](image-url)