Refractive index of fluoride crystals doped with rare earth ions with low concentration

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Abstract. Refractive indices of SrF$_2$ crystals doped with low concentrations of holmium, erbium, and thulium ions are investigated. These crystals are attractive as active laser media for developing planar waveguides for near and mid-IR spectral regions. It is shown that, by varying the concentration of impurity rare-earth ions in SrF$_2$ crystals, it is possible to increase and control the refractive index of the medium. This allows one to develop planar waveguides with the core and shell of the same fluoride and control their numerical aperture and the number of excited modes. The design of single mode planar waveguide is calculated and proposed for the wavelength of 2 $\mu$m.

1. Introduction
Development of integral and fiber optics and optical computers requires compact solid state laser oscillators and amplifiers operating in a broad spectral range from near UV to mid IR. There are optical glass fibers doped with rare earth ions that satisfy these requirements. Due to their long length, they provide high gain and can control the radiation intensity. Meanwhile, the transparency range of glass fibers, which is 0.4÷1.8 $\mu$m, is narrower than that of fluoride materials (0.16÷11 $\mu$m). This considerably limits their possible applications in the near and mid-IR spectral region. The small core and low concentration of active dopants in fibers limit the efficiency of fiber amplifiers. Crystalline planar waveguides similar to bulk crystals can be doped with high concentration of impurities in the core area [1-5]. Planar waveguides have very small diffraction losses, which allows one to increase the length of interaction between the laser and pump radiation and thus to achieve higher amplification gain comparable with that in crystalline media. At the same time, planar waveguides conserve the linear polarization of the radiation and exhibit good thermal physical properties. In a simple planar waveguide, one can excite a large number of spectrally and spatially split channels which can increase the amplification efficiency via further coherent summation [6, 7].

During two decades, one observes a strong increase in the number of investigation on development, characterization, and application of planar waveguides [1-3]. Optimization of active media and cavity design allowed creating a great number of compact highly efficient laser sources. Planar waveguide lasers can operate in various spectral regions, in cw and pulsed temporal regimes with pulse durations up to tens of femtosecond. The research of planar waveguides is mostly restricted to oxide crystals which are usually produced by the molecular-beam epitaxial technique. It provides a very thin waveguide structure with dimensions of several microns. Recently, irradiation of crystals by femtosecond lasers was proposed as an efficient technique of planar waveguide production [4]. Such technique allows creating structures with various sizes and shapes. It was shown that highly effective
waveguide lasers can also be prepared from oxide ceramics [5]. In contrast to oxide crystals, ceramics can be prepared with required shape, high concentration of doped ions, high distribution coefficient, and good physical and optical properties [8].

Since the invention of the first laser, optical materials based on fluorides doped with rare earth ions attracted great interest as solid state laser active materials [9, 10]. They have some advantages compared with oxides, specifically for developing of a wide range of lasers and amplifiers [11]. Fluoride crystals can be doped with high concentrations of rare earth ions up to $10^{21}$ cm$^{-3}$ without considerable nonradiative quenching. They exhibit shorter phonon spectra than oxides, which allows one to reduce the probability of multiphonon relaxation processes, considerably diminish the nonradiative losses, and obtain laser radiation in mid-IR spectral region with high efficiency and low thermal losses [12, 13]. Fluoride materials have lower linear and nonlinear refractive indexes, which makes it possible to reduce the probability of various nonlinear processes, such as SRS, Brillouin scattering, etc., at high pump intensity [14]. In addition, fluorides have high mutual solubility in systems like Me$^{(1)}$F$_2$-Me$^{(2)}$F$_2$, as well as in Me$^{(1)}$F$_2$-Me$^{(2)}$F$_3$, which allows one to have different spectral properties of rare earth ions due to different local surrounding fields in more complex systems Me$^{(1)}$F$_2$-Me$^{(2)}$F$_2$-Me$^{(3)}$F$_3$ [15]. It is important to note that solid solutions Me$^{(1)}$F$_2$-Me$^{(2)}$F$_3$ keep a cubic structure for concentrations of Me$^{(2)}$F$_3$ up to 20%, which allows obtaining nanoceramic samples [16]. Fluoride nanoceramics has some advantages over similar single crystals due to its higher mechanical strength and fracture toughness [17]. Recently, four-component BaF$_2$–ZnF$_2$–CdF$_2$–YbF$_3$ fluoride nanoceramics was synthesized [18].

A larger relaxation lifetime of rare earth ions in fluorides allows them to accumulate a high population inversion, which simplifies the development of laser amplifiers excited by longer laser pulses. The thermal conductivity of fluoride materials is also rather high. It is necessary to note that, even at low concentrations, rare earth ions in fluorides create different optical centers with various luminescence properties [19, 20]. This proves that the local surrounding of rare earth ions can differ from center to center.

The refractive indices of nanostructured crystals composed of solid solutions Me$^{(1)}$F$_2$-Me$^{(2)}$F$_3$ (where Me$^{(1)}$ is Ca, Sr, Ba, Cd, or Pb ion and Me$^{(2)}$ is a rare-earth ion with the fraction from 10 to 50%) were recently investigated [21, 22]. It was shown that the refractive indices of two-component solid solutions linearly depend on the concentration of rare earth ions and can be calculated using a method of molecular refraction additivity for components with a rather high accuracy. The value can be determined by separating crystals into the components related to Me$^{(1)}$F$_2$, for which refractive indices are known, and Me$^{(2)}$F$_3$, for which the impact in refractive index linearly depends on the atomic number of Me$^{(2)}$ in the periodic table. Doping of the fluoride crystal with rare earth ions results in the change of the lattice constant due to various sizes of Me$^{(1)}$ and Me$^{(2)}$ ions. The authors of [21, 22] investigated considerable changes of the refractive index in highly doped solid solutions. In Me$^{(1)}$F$_2$-Me$^{(2)}$F$_3$ crystals with a low doping concentration, due to unequal ionic charges, rare earth ions can create double and triple optical centers, which are clearly registered by site-selective laser spectroscopy [23]. Thus, due irregular positions of Me$^{(2)}$ ions, the concentration dependence of the refractive index can not be linear.

The aim of this research was to investigate the concentration dependence of the refractive index of SrF$_2$ crystal doped with Tm, Ho, and Er ions with concentrations as low as 0.5 ± 5% and to analyze the possibility of preparing single-mode planar waveguides composed of the shell of undoped SrF$_2$ crystal and the core of SrF$_2$ crystal doped with a low concentration of rare earth ions.

2. Investigation of the refractive index of SrF$_2$ crystal doped with Tm, Ho, and Er ions

In this paper, we present the results on measurement of the refractive indices of strontium fluoride crystals containing small concentrations of rare earth ions, which are usually used for laser-active media. Tm, Ho, and Er ions were chosen as they are active impurities used in lasers operating in the near-infrared spectral region 1.5 ± 3 μm. The refractive indices were measured using an URL-2 refractometer, which allows one to measure refractive indices of liquids and solids at the Fraunhofer line D ($\lambda = 589$ nm) with an accuracy up to 0.0002 [24].
The high-quality SrF₂ crystals were grown by the Bridgman technique from the melt in a fluoride atmosphere of CF₄. The impurity ions were added in the form of rare-earth fluorides. The raw materials were prepared by appropriate mixture of initial fluoride powders with the purity of 99.99% and put into a graphite crucible heated up to the melting temperature of 1465°C. After complete melting, which was controlled visually, the crucible was pulled out with a speed of 5-6 mm per hour. Annealing of the crystal continued during 4 hours. Up to seven single crystal samples were obtained during one crystal growth process. For refractive index measurements, we made samples in the form of parallelepipeds with a length of 20 mm and transverse dimensions of 5 x 5 mm. All surfaces of the samples were polished.

Table 1. Refractive indices of SrF₂ crystals doped with Ho, Er, and Tm, their differences from that of undoped SrF₂, and ratio of the core size and the oscillation wavelength for a single-mode waveguide.

| Material          | Refractive index, n (589 nm) | Δn  | d/λ |
|-------------------|------------------------------|-----|-----|
| SrF₂              | 1.4380±0.0002                | 0   | -   |
| SrF₂+2 mol.% TmF₃| 1.4416±0.0002                | 0.0036 | 4.9 |
| SrF₂+4 mol.% TmF₃| 1.4453±0.0002                | 0.0073 | 3.4 |
| SrF₂+2 mol.% ErF₃| 1.4411±0.0002                | 0.0031 | 5.3 |
| SrF₂+4 mol.% ErF₃| 1.4451±0.0002                | 0.0071 | 3.5 |
| SrF₂+0.5 mol.% HoF₃| 1.4389±0.0002               | 0.0009 | 10  |
| SrF₂+1 mol.% HoF₃| 1.4401±0.0002                | 0.0021 | 6.4 |

The refractive index of the SrF₂ crystal at a wavelength of 589 nm was measured to be $n = 1.4380±0.0002$, which agrees well with the results published in [22]. Doping of the rare-earth fluoride as a second component in the SrF₂-Me²⁺F₃ crystal leads to an increase in the refractive index. The measured refractive indices for SrF₂ crystals with different molar concentrations of Me²⁺F₃ fluorides, where Me²⁺ stands for Ho, Er, Tm, are shown in table 1 and presented in figures 1-3. The dashed curves present the linear dependencies calculated according to the results described in [21]. One can see that the refractive index exhibits a rather linear behaviour in SrF₂ crystals with low concentrations of rare-earth impurities. However, the investigated samples have slightly lower values of refractive indexes than those calculated by the method of molecular refraction additivity for the components. This can be attributed to the presence of double and triple optical centers recently discovered in fluorides [18-20].

![Figure 1](image1.png)  
**Figure 1.** Dependence of the refractive index of SrF₂ – TmF₃ crystal on the molar concentration of TmF₃.

![Figure 2](image2.png)  
**Figure 2.** Dependence of the refractive index of SrF₂ – ErF₃ crystal on the molar concentration of ErF₃.
Figure 3. Dependence of the refractive index of SrF$_2$–HoF$_3$ crystal on the molar concentration of HoF$_3$.

The obtained data show that the refractive index of SrF$_2$–Me$^{(2)}$F$_3$ crystal can be controlled by changing the Me$^{(2)}$ concentration, which makes it possible to develop planar waveguides with the core and reflective cladding made of one and the same fluoride. This opens the possibility of controlling the properties of planar waveguides, namely, numerical aperture and number of excited modes, which is demonstrated below.

3. Planar waveguide

The laser operation of planar waveguide based on a LaF$_3$:Nd$^{3+}$ layer grown on a CaF$_2$ substrate by molecular-beam epitaxy was demonstrated for the first time in 1999 [25]. Recently, laser operation of a hot-pressed planar waveguide based on SrF$_2$ ceramics with a neodymium-doped core was described [26]. However, these researches used multimode waveguides. One of the key problems of waveguide development is to develop a single-mode planar waveguide with a maximum size of the core. This allows working with a high laser energy and a good divergence of the output beam. If we consider a one-dimensional case, the number of modes of a symmetrical planar waveguide is determined by parameter $p$, which is determined as [2]:

$$ p = \frac{2d \cdot NA}{\lambda} , $$

where $d$ is the waveguide thickness, $\lambda$ is the operation wavelength, and $NA$ is the numerical aperture. The $NA$ of a waveguide with a simple step-index structure in air is

$$ NA = \sqrt{n_2^2 - n_1^2} , $$

where $n_2$ is the refractive index of the core and $n_1$ is the refractive index of the waveguide shell. For a single-mode waveguide, parameter $p$ should be $p \leq 1$. Thus, from (1) and (2) we find that the ratio of the maximal core size of a single-mode waveguide to the operation wavelength is determined by the difference of refractive indices of the core and the shell $\Delta n$ as

$$ \frac{d}{\lambda} = \frac{1}{2\sqrt{2n \cdot \Delta n}} , $$

Figure 4 presents the dependence of the ratio $d/\lambda$ on $\Delta n$ for a SrF$_2$ single-mode waveguide. This ratio calculated for investigated samples used as a core material is presented in table 1. It is clear that, the core dimension for a single-mode waveguide can be increased by using the core and shell made of materials with close values of refractive indices. In this paper, we propose to use SrF$_2$ crystal as a shell material and SrF$_2$-Me$^{(2)}$F$_3$ solid solution (where Me$^{(2)}$ stands for Tm, Ho, and Er ions with the low
concentration of 0.5 ± 5%). These laser active ions oscillate in the wavelength region of 2-3 μm. As an example, we can consider a waveguide with the core made of a SrF₂ – HoF₃ crystal with a HoF₃ concentration of 0.5 mol %, which provides the difference between the refractive indices of 0.0009 and the ratio $d/\lambda$ equals to 10. This gives the thickness of the core of a single-mode planar waveguide with a step-index structure operating at 2 μm to be about 20 μm. Due to the large thickness of the waveguide core, it is easier to fabricate it and it can amplify laser radiation to a higher output power due to a lower thermal load. It is necessary to note that further increase of the core size can be made by further reduction of the concentration of rare-earth fluorides and shifting the operation radiation to longer wavelengths. By varying the concentration of doping rare-earth ions in SrF₂ crystals, it is possible to control the refractive index of the medium and to develop single-mode planar waveguides with the core and the shell of the same fluoride.

![Graph](image-url)

**Figure 4.** Dependence of the ratio of the core size of a SrF₂ single-mode waveguide to the operation wavelength on the difference between the refractive indices of the core and the shell.

4. Conclusion

The refractive indices of SrF₂ crystals doped with small concentrations of impurities of Ho, Er, and Tm ions were investigated. These crystals are well known as active media of lasers operating in the spectral region of 2-3 μm. It was shown that, by varying the concentration of impurity rare-earth ions in SrF₂ crystals, it is possible to precisely control the refractive index of the medium. The concentration dependences of the refractive index exhibit a linear behavior in SrF₂ crystals for all Ho, Er, and Tm impurities. However, they exhibit a slightly lower slope than those calculated by the method of molecular refraction additivity for the components for high doping levels. It was shown that these materials can be used for fabrication of planar waveguides with the core and shell of the same fluoride and for control of its numerical aperture and the number of excited modes. The design of SrF₂ single-mode planar waveguides with the core of the SrF₂ – HoF₃ crystal was calculated and proposed for a waveguide laser emitting at a wavelength of 2 μm.

References

[1] Mackenzie J I 2007 IEEE J. Sel. Topics Quantum Electron. 13 626
[2] Grivias C 2011 Progress Quantum Electronics 35 159
[3] Grivias C 2016 Progress Quantum Electronics 45 3
[4] Chen F and V'azquez de Aldana J R 2014 Laser Photonics Review 8 251
[5] Salam G, Jipa F, Zamfirescu M and Pavel N 2014 Optics Express 22 5177
[6] Thielen P A, Ho J G, Burchman D A, Goodno G D, Rothenberg J E, Wickham M G, Flores A, Lu C A, Pulford B, Robin C, Sanchez A D, Hult D and Rowland K B 2012 Optics Letters 37 3741
[7] Pyrkov Yu N, Trikshev A I and Tsvetkov V B 2012 Quantum Electronics 42 790
[8] Ikesue A 2002 Optical Materials 19 183
[9] Batygov S K, Kulevskii L A, Prokhorov A M, Osiko V V, Savel'ev A D and Smirnov V V 1975 Sov. J. Quantum Electronics 4 1469
[10] Moncorge R, Braud A, Camy P, Doualan J L 2013 *Handbook of solid-state lasers: materials, systems and applications*, eds B Denker and E Shklovsky (Amsterdam: Elsevier) p 28
[11] Lucca A, Jacquemet M, Druon F, Balembois F, Georges P, Camy P, Doualan J L and Moncorge R 2004 *Optics Letters* **29** 1879
[12] Basiev T T, Dergachev A Y, Kirpichenkova E O, Orlovskii Y V and Osiko V V 1987 *Sov. J. Quantum Electronics* **17** 1289
[13] Orlovskii Y V, Basiev T T, Pukhov K K, Vorobiev I N, Papashvili A G, Pelle F and Osiko V V 2001 *J. Luminescence* **94** 791
[14] Joubert M F and Moncorgé R 2003 *Optical Materials* **22** 95
[15] Basiev T T, Doroshenko M E, Fedorov P P, Konyushkin V A and Osiko V V 2007 *Quantum Electronics* **37** 934
[16] Fedorov P P, Osiko V V, Basiev T T, Orlovskii Yu V, Dukel’skii K V, Mironov I A, Demidenko V A and Smirnov A N 2007 *Russian Nanotechnologies* **2** 95
[17] Doroshenko M E, Demidenko A A, Fedorov P P, Garibin E A, Gusev P E, Jelinkova H, Konyshkin V A, Krutov M A, Kuznetsov S V, Osiko V V, Popov P A and Shule J 2013 *Phys. Stat. Solids C* **10** 952
[18] Alimov O K, Doroshenko M E, Pierpoint K A, Komandin G A, Nozdrin V S, Buchinskaya I I, Popov A I and Fedorov P P 2019 *Optical Materials* **94** 113
[19] Doroshenko M E, Pierpoint K A, Alimov O K, Papashvili A G, Konyushkin V A and Nakladov A N 2019 *J. Luminescence* **208** 475
[20] Doroshenko M E, Papashvili A G, Konyushkin V A, Nakladov N A, Martynova K A and Osiko V V 2018 *J. Luminescence* **199** 331
[21] Konstantinova A F, Krivandina E A, Karimov D N and Sobolev B P 2010 *Crystallography Reports* **55** 990
[22] Glushkova T M, Karimov D N, Krivandina E A, Zhmurova Z I and Sobolev B P 2009 *Crystallography Reports* **54** 603
[23] Alimov O K, Doroshenko M E, Konyushkin V A, Papashvili A G and Osiko V V 2016 *Quantum Electronics* **46** 68
[24] Karasik A Y, Konyushkin V A, Nakladov A N and Chunaev D S 2018 *Quantum Electronics*, **48** 854
[25] Daran E, Shepherd D P, Bhutta T and Serrano C 1999 *Electron. Lett.* **35** 398
[26] Konyushkin V A, Nakladov A N, Konyushkin D V, Doroshenko M E, Osiko V V and Karasik A Y 2013 *Quantum Electronics* **43** 60