Distribution coefficient of Pr$^{3+}$ ions in crystals of solid solutions LiF-LuF$_3$-YF$_3$-PrF$_3$

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Abstract. Aim of this work was to investigate the possibility of increasing the distribution coefficient of Pr$^{3+}$ ions in fluoride crystals with scheelite structure. As a result of investigations by XRF and optical absorption spectroscopy the absorption cross section for $3H_0 \rightarrow 3P_0$ transitions Pr$^{3+}$ ions was clarified and segregation coefficient of Pr$^{3+}$ ions in LiY$_{0.3}$Lu$_{0.7}$F$_4$ mixed crystals was estimated.

1. Introduction
In recent years a considerable interest in the development of efficient laser sources emitting in the visible spectral range with laser diode pumping occurred. Prospects for such devices lay in development of color displays, projectors, as well as biomedical and quantum-optical applications and industry [1, 2]. Development of laser diodes technology provides increase of number of works on Pr$^{3+}$ based active media [3, 4, 5]. One of the most promising materials for such active media is LiYF$_4$ crystal, activated with Pr$^{3+}$ ions. For example, in the work [6] two InGaN laser diodes emitting at $\lambda_p$=443.9 nm were used to excite the $3H_4-3P_2$ transition of Pr$^{3+}$ in LiYF$_4$. The differential efficiency of 54% has been demonstrated in the green region of the spectrum at 522.6 nm. The laser oscillation at wavelengths 523, 546, 604, 607, 640, 698, and 720 nm was achieved in Pr:LiYF$_4$ as described in the work [7] and the output power of 2.9 W and slope efficiency of 72 % have been shown for 532 nm lasing with 5 W frequency doubled optically pumped semiconductor laser pump at 479 nm.

In present work we investigate the possibility of increasing the distribution coefficient of Pr$^{3+}$ ions in fluoride crystals with scheelite structure, which is an actual problem [8]. Earlier in Kazan Federal University it was found that the transition from LiYF$_4$ and LiLuF$_4$ crystals to their solid solutions LiY$_{1-x}$Lu$_x$F$_4$ increases sharply the distribution coefficient of rare-earth ions (REI), which leads to increased concentrations of rare-earth ions and improvement the optical quality of the material [8].

2. Object of research, scheme and experimental techniques
Objects of the study were solid solutions LiF-LuF$_3$-YF$_3$-PrF$_3$. Three series of crystals with chemical compositions LiLu$_{0.5}$Pr$^{3+}$ (0.5 at. %), LiLu$_{0.5}$Y$_{0.3}$F$_4$:Pr$^{3+}$ (0.5 at. %) and LiLu$_{0.7}$Y$_{0.3}$F$_4$:Pr$^{3+}$ (1 at. %) were synthesized. The crystals were grown in carbon crucibles by the Bridgman-Stockbarger method. Because of irregular distribution of impurities in the samples along the crystal boule different groups of samples were prepared for X-ray fluorescence and optical spectroscopy studies: 3 plane-parallel plate samples of LiY$_{1-x}$Lu$_x$F$_4$: Pr$^{3+}$ (0.5%) cut from different places of the crystal boule with respect to the start of crystallization and the same series were prepared for the sample LiY$_{1-x}$Lu$_x$F$_4$: Pr$^{3+}$ (1%). Also plane-parallel plate sample was prepared from the middle of LiLuF$_4$ boule. For all cases the
optical e-axis was oriented in the plane of polished windows. The experimental scheme for the absorption spectra detection is shown in Figure 1.

Figure 1. Experimental setup: 1 - source of the continuous spectrum; 2 - Glan prism; 3 - diaphragm and the sample; 4 - monochromator MDR-23; 5 - photomultiplier tube; 6 - luminous flux modulator (chopper); 7 – optomechanical shutter; 8 - stepper motor for scanning the spectrum range; 9 - selective amplifier; 10 - ADC and computer.

3. Research Methods

Information on the actual concentration of the impurity ions in the synthesized single crystals can be obtained by X-ray fluorescence analysis (XRF) and optical absorption analysis.

XRF method is based on detection of transitions between the deep-lying energy levels of the atom, when electrons are always localized at the inner shells of the atom and give the information on real concentration of the given chemical element. Absorption spectroscopy method is characterized by detection of transitions between the outer energy levels of the atom and it is used to evaluate the perspective of new materials.

The investigated fluoride crystals with scheelite structured crystal lattice are characterized by low isomorphic capacity in respect to rare-earth ions of the first half of the row due to significant mismatch of ionic radii of cations substituting each other. This means that segregation coefficient of these ions will be less than unity, e. i. not all the PrF$_3$ component we put to the charge appears in the crystal lattice of synthesized material. The resulting solid concentration $C_s(x)$ was measured by means of XRF spectroscopy. Knowing the real concentration of the impurity ions and absorption coefficient we can obtain the cross section of the transition value.

Thus the absorption cross section could be estimated according to the following expression:

$$\sigma(\lambda) = \frac{k(\lambda) \cdot \mu}{C_s \cdot \rho \cdot Na}$$

(2)

Where $k$ - the absorption coefficient, $\mu$ - the molar mass of the crystal, $\sigma$ - the absorption cross section, $\rho$ – density, $Na$ - Avogadro's number, $C_s$ - Pr$^{3+}$ ions solid concentration (at. %).

4. Experiment Results

The X-ray diffraction was studied from grown crystalline material in order to investigate the phase composition of the mixed crystals.
Figure 2. X-ray diffraction results of the samples: LiLuF$_4$:Ce$^{3+}$ and LiY$_{0.3}$Lu$_{0.7}$F$_4$: Ce$^{3+}$

The diffraction pattern obtained for Ce$^{3+}$: LiY$_{0.3}$Lu$_{0.7}$F$_4$ (Fig. 2) corresponds to scheelite structure. For transition from LiLuF$_4$ to LiY$_{0.3}$Lu$_{0.7}$F$_4$ data the shift is observed towards bigger angles due to larger lattice constant, as it was expected.

The measured concentration of Pr$^{3+}$ ions C$_s$ dependent on place at the crystal boule is presented in Table 1. The data for LiLuF$_4$:Pr$^{3+}$ sample corresponds to the hat of the boule. It is seen that real concentration of Pr$^{3+}$ ions is slightly higher for mixed crystal than that for LiLuF$_4$ at the same level of concentration in the initial charge.

Table 1. Concentration of the samples: a) LiLuF$_4$:Pr$^{3+}$(0,5%); b) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$(0,5%); c) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$(1%).

| Sample                      | C$_s$, at. % (from XRF data) | L, mm (point from crystallization start) |
|-----------------------------|-----------------------------|-----------------------------------------|
| a) LiLuF$_4$:Pr$^{3+}$      | 0,25                        | 23                                      |
| b) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$ (HAT) | 0,31                        | 40                                      |
| b) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$ (MID) | 0,2                         | 23                                      |
| b) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$ (NOSE) | 0,16                        | 6                                       |
| c) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$ (HAT) | 0,38                        | 40                                      |
| c) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$ (MID) | 0,3                         | 23                                      |
| c) LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$ (NOSE) | 0,24                        | 6                                       |
In order to determine segregation coefficient of Pr$^{3+}$ ions in mixed crystal LiY$_{0.3}$Lu$_{0.7}$F$_4$ the dependence of $\ln[1-C_s/C_0]$ on length of the crystal was plotted (see Fig. 3). Slope of the dependence gives the value of segregation coefficient.

![Figure 3](image)

**Figure 3.** Longitudinal distribution of the resulting solid concentration $C_s(x)$ of praseodymium ions in the samples of crystals of solid solutions LiY$_{0.3}$Lu$_{0.7}$F$_4$:Pr$^{3+}$.

The Figure 3 shows that, as crystals are grown in a closed type crucible, the concentration of rare earth ions increases in the melted part during crystal growth. For the middle part of the boule that is usually associated with higher optical quality of the synthesized crystalline material real Pr$^{3+}$ ions concentration was $0.4 \times 10^{20}$ cm$^{-3}$. It is seen that segregation coefficient decreases with increase of concentration of Pr$^{3+}$ in the initial charge $C_0$. This is the evidence of finite isomorphic capacity of LiY$_{0.3}$Lu$_{0.7}$F$_4$ host lattice. For the cases of $C_0$ levels of 1.5 at. % and 2 at. % the dependence on point at the crystal is almost vanished and this can lead to formation of significant amount of defects inside the crystal.

Registered absorption spectra in the middle of Pr:LiY$_{0.3}$Lu$_{0.7}$F$_4$ crystals boules in $\pi$-polarization are presented in Figure 2. The observed line at 479.2 nm corresponds to the $^3H_4 \rightarrow ^1P_0$ transition of praseodymium ions. The absorption coefficient at the maximum has value of $3.5$ cm$^{-1}$ for crystal with 1 at. % of Pr$^{3+}$ in the initial charge and this line is prospective for pumping the Pr$^{3+}$ ions by means of laser diode light. Knowing the real value of Pr$^{3+}$ concentration in the crystal we have obtained the value of absorption cross section at the wavelength of 479.2 nm which has value of $12 \pm 3 \times 10^{-20}$ cm$^2$. 
Figure 2. The absorption spectra of crystals and solid solutions of LiLu\textsubscript{0.7}Y\textsubscript{0.3}F\textsubscript{4}: Pr\textsuperscript{3+} (0.5\%) and LiLu\textsubscript{0.7}Y\textsubscript{0.3}F\textsubscript{4}: Pr\textsuperscript{3+} (1\%).

5. Conclusion
Here we have investigated the segregation coefficient of solid solutions of scheelite structure LiF-LuF\textsubscript{3}-YF\textsubscript{3}-PrF\textsubscript{3} in respect to Pr\textsuperscript{3+} ions. It has been shown that segregation coefficient decreases with increase of concentration of Pr\textsuperscript{3+} in the initial charge. Low isomorphic capacity of the investigated host lattice in respect to Pr\textsuperscript{3+} ions leads to saturation of segregation coefficient at the 1.5 at. \% and 2 at. \% of Pr\textsuperscript{3+} in the initial charge. Thus in order to obtain crystals of good optical quality by growing with Bridgeman technique it is proposed to use 0.5 or 1 at. \% of Pr\textsuperscript{3+}. The real concentration of Pr\textsuperscript{3+} for such charges appears to be 0.3 at. \% (0.4*10\textsuperscript{20} cm\textsuperscript{-3}) which is slightly higher than that for Pr:LiLuF\textsubscript{4} crystal. Also we were able to clarify the absorption cross section of \textsuperscript{3}H\textsubscript{0} \rightarrow \textsuperscript{3}P\textsubscript{0} transitions of Pr\textsuperscript{3+} ions in investigated crystals which has the value of 12 \pm 3 \times 10\textsuperscript{-20} cm\textsuperscript{2}. Thus, the new crystals are promising as active media for diode-pumped laser.

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