On the Distribution Coefficient of Ce$^{3+}$ Ions in LiF–LuF$_3$–YF$_3$ Solid-Solution Crystals

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The optimum ratio of the numbers of the Y$^{3+}$ and Lu$^{3+}$ ions in LiF–LuF$_3$–YF$_3$ solid solutions at which the distribution (introduction) coefficient of Ce$^{3+}$ ions is three to five times larger than that in LiYF$_4$ and LiLuF$_4$ crystals has been determined by the EPR and optical spectroscopy methods.

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INTRODUCTION

Double fluoride crystals LiYF$_4$ (LYF) and LiLuF$_4$ (LLF) with a scheelite structure activated by Ce$^{3+}$ ions are active media of ultraviolet lasers [1–3]. It is known that the distribution coefficient of trivalent rare-earth ions of the cerium subgroup in these crystals is much smaller than unity [4]. Attempts to noticeably increase the content of these ions (up to 3–5 at %) increase the number of defects of the crystal structure and worsen the optical quality and photochemical stability of activated crystals with respect to ultraviolet radiation.

This paper presents the results of the investigations demonstrating the possibility of increasing the distribution coefficient of Ce$^{3+}$ ions in the LiF–LuF$_3$–YF$_3$ crystals by varying their chemical composition.

SAMPLES AND INVESTIGATION METHODS

In this work, we investigated the samples of LiYF$_4$ and LiLuF$_4$ crystals and LiF–LuF$_3$–YF$_3$ solid solutions activated by Ce$^{3+}$ ions grown at Kazan State University.

It was previously found [5] that LiY$_{1-x}$Lu$_x$F$_4$Ce$^{3+}$ ($x = 0.1–0.9$) solid solutions have the structure of scheelite and a tetragonal crystal lattice with the space group $C_{4h}^2$. The Lu$^{3+}$ and Y$^{3+}$ ions are statistically distributed in the crystal lattice.

It is known that the activation of crystals by a small amount of Ce$^{3+}$ ions (up to 3–5 at % in the initial mixture) is accompanied by the crystallization of a melt, but the real content of activator ions in the crystallized part of the grown material is one tenth to one third of the initial amount of the CeF$_3$ reagent in the mixture. The distribution coefficients of Ce$^{3+}$ ions are different for the LLF and LYF crystals [4].

We grew a series of LiY$_{1-x}$Lu$_x$F$_4$Ce$^{3+}$ crystals with $x$ from 0 to 1 with a step of 0.1. The content of Ce$^{3+}$ ions in the initial mixture was 0.1 at % in all of the crystals per the total amount of the substituted matrix cations Lu$^{3+}$ and Y$^{3+}$. The crystals were grown by the Bridgman–Stockbarger method in graphite crucibles in a fluoridizing atmosphere at an excess argon pressure. The samples with the known direction of the optical axis were manufactured from the grown crystals to investigate them by optical spectroscopy methods. The samples were processed in the same unit in order to ensure the same optical quality of the bloomed surfaces (windows) and their optical axes were parallel to these surfaces. For EPR measurements, the manufactured samples were the same in volume and shape.

The EPR spectra of LiF–LuF$_3$–YF$_3$ crystals were detected by an ESP-300 Bruker spectrometer at a frequency of 9.43 GHz and a temperature of 20 K.

The photometric investigations were performed on a laboratory spectrometer based on a MDR–23 monochromator. The absorption coefficients were determined with an accuracy of 0.01 cm$^{-1}$. The absorption spectra are detected in the range of 220 to 320 nm, which corresponds to the $4f$–$5d$ transitions in Ce$^{3+}$ ions.

INVESTIGATION OF THE DISTRIBUTION COEFFICIENT OF CE$^{3+}$ IONS IN THE CRYSTALS

An intense EPR spectrum of Ce$^{3+}$ ions was observed for all of the samples and was axisymmetric. The EPR spectra were detected under the same conditions in the magnetic field $H$ perpendicular to the optical axis of the samples.
The spectra for LiYF₄:Ce³⁺ and LiLuF₄:Ce³⁺ crystals are described by the g factors that coincide within the experimental accuracy with those presented in [6, 7]. The EPR spectra for LiY₁₋ₓLuₓF₄ solid solutions remain axial; the linewidth increases; and the g factors have intermediate values and, which during an increase in the content of Lu³⁺ ions, vary monotonically from $g = 1.475$ for LiYF₄:Ce³⁺ [6] to $g = 1.467$ for LiLuF₄:Ce³⁺ [7]. Thus, the symmetry of the crystal lattice of solid solutions holds despite the appearance of the strongly nonuniform distribution of local fields in the position of Ce³⁺ ions.

The relative content of Ce³⁺ ions in the samples was determined by calculating the double integrals of the EPR lines normalized to the volume of the samples. The resulting value is proportional to the number of paramagnetic ions. The figure shows this quantity as a function of the number of Lu³⁺ ions in the samples of LiF–LuF₃–YF₃ solid solutions at 0.1 at % of Ce³⁺ ions in the initial mixture. As is seen in the figure, the content of Ce³⁺ ions at the 60–80% content of Lu³⁺ ions is more than five times larger than the content in YLF and LLF samples.

A similar property was determined by the absorption spectroscopy method: the absorption coefficient of Ce³⁺ ions in LiY₁₋ₓLuₓF₄:Ce³⁺ solid solutions with $x = 0.6–0.8$ is several times larger than that for the YLF:Ce and LLF:Ce samples (see figure).

Since the radiative lifetime of the 5d–4f luminescence of Ce³⁺ ions is independent of the chemical composition of LiF–LuF₃–YF₃ solid solutions [8], the cross sections for these transitions are also constant according to the known formulas relating the Einstein coefficients. Therefore, using the Buger–Lambert–Beer law, it is possible to determine the absolute content of activator ions in LiY₁₋ₓLuₓF₄:Ce³⁺ compounds by comparing the absorption coefficients at the wavelengths of the 4f–5d transitions of Ce³⁺ ions with similar absorption coefficients for YLF:Ce and LLF:Ce crystals in which the content of Ce³⁺ ions was determined by chemical analysis methods [9]. The resulting values of the absolute content and distribution coefficient of Ce³⁺ ions for the crystals under consideration are presented in the table.

### CONCLUSIONS

The EPR and optical spectroscopy studies indicate that the distribution coefficient of Ce³⁺ ions depends on the chemical composition of LiF–LuF₃–YF₃ solid solutions. It has been revealed that the isomorphic capacity of LiY₁₋ₓLuₓF₄ (with $x = 0.6–0.8$) with respect to Ce³⁺ ions is much larger than that of LiYF₄ and LiLuYF₄ crystals and the content of Ce³⁺ ions in the LiLu₀.₇Y₀.₃F₄:Ce³⁺ crystal is about five times larger than that in the LiLu₀.₇Y₀.₃F₄:Ce³⁺ crystal for the same amount of Ce³⁺ ions in the initial components of the mixture. The solid solutions maintain their high optical quality; basic spectroscopic parameters; and, according to [9, 10], high photochemical stability with respect to intense ultraviolet radiation.

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### REFERENCES


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