

# Up-conversion luminescence of $\text{LaF}_3:\text{Pr}^{3+}$ crystal

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**Abstract.**  $\text{LaF}_3:\text{Pr}^{3+}$  crystal is proposed as a promising media for an infrared quantum counter in the mid-infrared spectrum range. In this paper it has been shown that this crystal can work as an infrared quantum counter in the range of spectra of about  $3\ \mu\text{m}$  at the temperatures 170 K and 210 K with the efficiency of about 5%.

## 1. Introduction

This paper is devoted to a problem of creating a solid-state infrared quantum counter (IRQC) based on  $\text{LaF}_3:\text{Pr}^{3+}$  crystal. The topic of IRQC creation is relevant due to a number of circumstances. Currently there are number of monographs about the up-conversion luminescence of rare-earth ions in crystals, one of them for example is the work of Chukova [1], which summarizes the results of work on the issue until 1980. Auzel in his paper [2] summarized the results of a similar orientation up to 2004. In addition there are several works in which close to practice results on IRQC were obtained on  $\text{LaCl}_3$  crystal with REI. Thus,  $\text{LaCl}_3$  crystal, activated by REI, occupies a special place in the study of up-conversion IRQC. This is due to its low phonon energy [3]. Transmittance of the crystal in the infrared spectrum region increases and probability of a nonradiative relaxation between closely spaced energy levels reduces. In the paper [4] it was directly demonstrated that energy levels and selection rules for REI in the anhydrous salt  $\text{LaCl}_3$  are best suited to implement IRQC. The article [5] disclosed the results of the IRQC realization on the basis of  $\text{LaCl}_3:\text{Pr}^{3+}$  for  $4.5\ \mu\text{m}$  spectrum range. It would seem that  $\text{LaCl}_3$  crystal is an ideal media for the problem of IRQC. However, it has a significant disadvantage – the crystal is extremely hygroscopic. This property restricts greatly of IRQC at its base. But  $\text{LaF}_3$  crystal hasn't got this disadvantage, and it has a phonon spectrum width close to  $\text{LaCl}_3$  crystal -  $350$  and  $260\ \text{cm}^{-1}$ , respectively.  $\text{LaF}_3$  crystal has a broad band of transparency up to  $9\ \mu\text{m}$  and a low phonon wing.

However, most works on IRQC based on  $\text{LaF}_3$  crystal contains information only about the possibility of such counters creation, which is based on authors theoretical assumptions of a simple transport phenomena from  $\text{LaCl}_3$  crystal to  $\text{LaF}_3$  crystal. In other works authors have implemented IRQC, but only in the infrared region from  $0.8$  to  $1.5\ \mu\text{m}$ . But we are interested in the region of  $2 - 6\ \mu\text{m}$ . Thus, this question still remains open.

## 2. Samples and research technique

The samples of  $\text{LaF}_3$  crystal were grown in the MRS laboratory, Institute of Physics, Kazan Federal University, using the method of directional solidification in graphite crucibles. Three samples of  $\text{LaF}_3$  crystal, doped by  $\text{Pr}^{3+}$  ions with concentration 0.1, 0.3 and 1 at. % were grown. The samples were cylinders of 6 mm diameter and 20 mm length. On the side surfaces of the boule two flattened areas

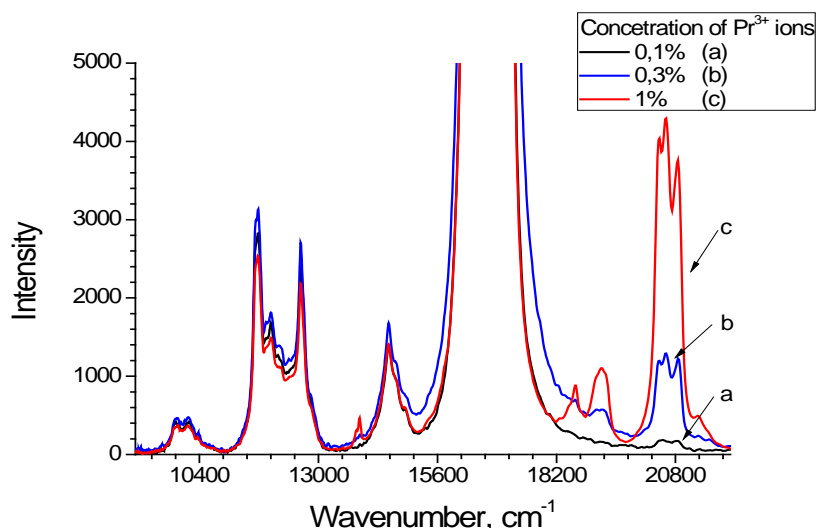


were polished. They were parallel to the axis of the crystal, as well as to each other. It allows us to perform experiments with  $\pi$ - and  $\sigma$ - polarized light.

Experimental setup for carrying out studies of up-conversion transitions properties in  $\text{LaF}_3:\text{Pr}^{3+}$  crystal contained several blocks. A block of tunable dye laser for sample pumping. A block of probe IR light for illumination of a sample, which consisted of removable positionally dependent filters and IR source "global". A block of temperature setpoint with a cryogenic nitrogen gas cooling system and a thermal insulated box with a sample holder and a temperature sensor. A block of luminescence registration with a CCD spectrometer. This setup allows us to record the luminescence spectra of the samples, as well as their temperature dependence from 77 K up to a room temperature.

## 2. Luminescence spectra of $\text{LaF}_3:\text{Pr}^{3+}$ crystal

During the experiments at a room temperature without IR illumination, it was found that the maximum luminescence intensity for  $\text{LaF}_3:\text{Pr}^{3+}$  crystal excited by  $\pi$ -polarized radiation was observed at an excitation wavelength -  $0.5985 \mu\text{m}$  ( $16708 \text{ cm}^{-1}$ ), and for  $\sigma$ -polarized – at a wavelength of -  $0.5945 \mu\text{m}$  ( $16820 \text{ cm}^{-1}$ ). The luminescence spectra of the samples with different concentration under excitation by a  $\sigma$ -polarized laser beam with a wavelength of  $0.5945 \mu\text{m}$  are shown in figure 1. From these spectra one can see that the luminescence is also caused by the transitions from levels lying higher than  $^3\text{P}_0$ , and occurs even in the absence of IR illumination. The mechanism of this up-conversion luminescence excitation was considered in details and described in [6].

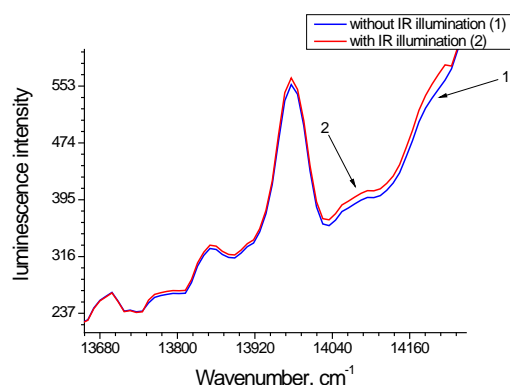


**Figure 1.** The luminescence spectra intensity of  $\text{LaF}_3:\text{Pr}^{3+}$  samples with different concentration of  $\text{Pr}^{3+}$  ions

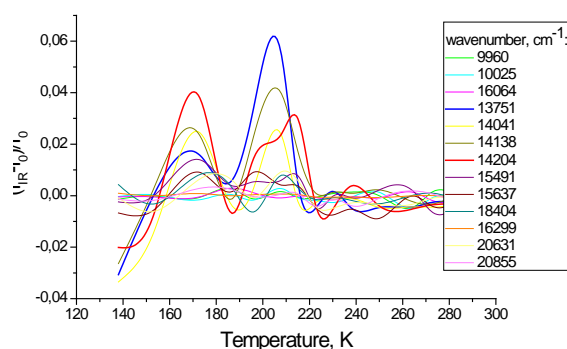
## 3. Properties of $\text{LaF}_3:\text{Pr}^{3+}$ (1%) crystal as IRQC

The luminescence spectra of the samples in the temperature range from 140 to 280 K at a constant value of the  $\sigma$ -polarized pumping radiation energy in the visible range of the spectrum -  $0.5945 \mu\text{m}$  with the illumination by IR radiation at  $3 \mu\text{m}$ , and without it as well was recorded. When the temperature changes in the range from 140 to 280 K under illumination with IR radiation, we observed the luminescence intensity increase of individual lines. Figure 2 shows fragments of two luminescence spectrum: with IR illumination and without it. On the figure, one can see an increase in the intensity of up-conversion luminescence with IR illumination. Such luminescence response on IR illumination was stable in all experiments.

For obtained data analyze we constructed temperature dependences of relative intensity  $(I_{\text{IR}} - I_0)/I_0$  versus a luminescence spectral lines of  $\text{LaF}_3:\text{Pr}^{3+}$  (1%) crystal, which is shown in figure 3. Here  $I_0$  - luminescence intensity of a pumped sample,  $I_{\text{IR}}$  - luminescence intensity of a pumped sample with additional illumination by IR radiation.



**Figure 2.** Luminescence spectra of LaF<sub>3</sub>:Pr<sup>3+</sup> (1%) crystal 1 - without IR illumination. 2 - with IR illumination

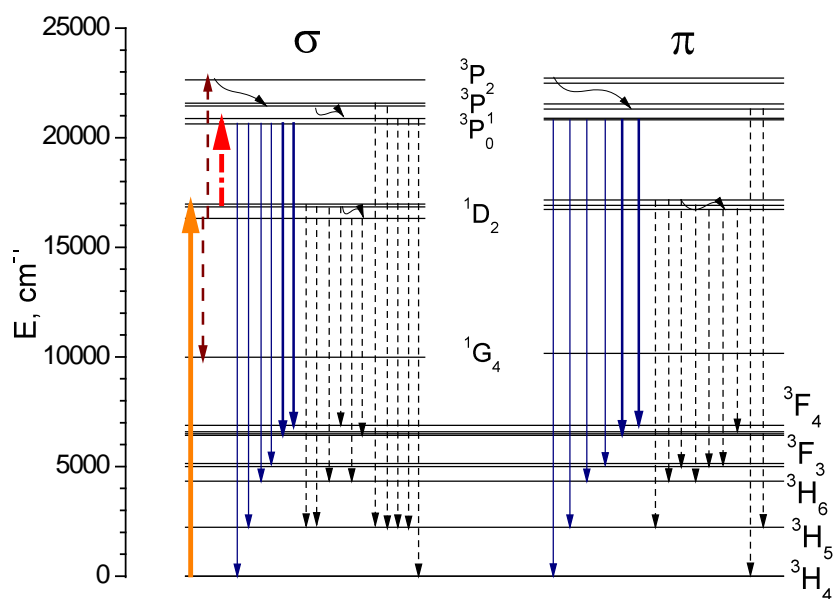


**Figure 3.** Dependencies of relative luminescence intensity  $(I_{IR}-I_0)/I_0$  for a number of spectral lines for LaF<sub>3</sub>:Pr<sup>3+</sup> (1%) crystal versus temperature

From the curves in the figure 3, one can see positive response to IR illumination from several spectral lines of luminescence, such as lines with wave numbers 13751 cm<sup>-1</sup>, 14204 cm<sup>-1</sup>, 14138 cm<sup>-1</sup> and 20631 cm<sup>-1</sup>. For other lines under illumination by an infrared radiation in the same conditions, there are no significant changes in their increase. It can also be seen from the figure that there are two temperature optima points, in which the response to IR illumination of some spectral lines has maxima. One of them corresponds to the temperature point of 170 K, and the other – 200 K.

#### 4. Energy levels diagram of Pr<sup>3+</sup> ions and electron transitions between them in LaF<sub>3</sub> crystal

For a better understanding of the processes occurring in LaF<sub>3</sub>:Pr<sup>3+</sup> crystal under IR illumination it is necessary to take a look at the energy levels diagram of Pr<sup>3+</sup> ions in this crystal and to transitions between them.



**Figure 4.** Energy levels diagram of Pr<sup>3+</sup> ions and transitions between them in LaF<sub>3</sub> crystal

The interpretation of luminescence spectra (as transitions between states) with IR illumination shown on the energy levels diagram of  $\text{Pr}^{3+}$  ions (figure 4). The dash-dot arrow pointing upward on the diagram indicates the transition with absorption of IR quantum and excitation of  $\text{Pr}^{3+}$  ion from the excited (by radiation  $0.5945 \mu\text{m}$ ) state - solid arrow pointing up  $^1\text{D}_2$  state to  $^3\text{P}_0$  state. IR photon energy is approximately  $3300 \text{ cm}^{-1}$  or about  $3 \mu\text{m}$ . It is evident that with IR illumination the intensity of individual lines of up-conversion luminescence corresponding to radiative transitions from  $^3\text{P}_0$  level to the lower energy levels increases based on the plots shown in the figure 3. These transitions are marked on the diagram by solid arrows pointing downwards. Thus, in these experiments with  $\text{LaF}_3:\text{Pr}^{3+}$  crystal pumped by  $0.5945 \mu\text{m}$  radiation at low temperatures an increase in intensity of the individual lines of up-conversion luminescence with additional IR illumination with a wavelength of about  $3 \mu\text{m}$  was observed and interpreted.

## 5. Conclusion

As a result of this work it has been shown that  $\text{LaF}_3:\text{Pr}^{3+}$  crystal can be used as a quantum counter in the mid-infrared spectrum range. For this purpose the increment of up-conversion luminescence of pumped  $\text{LaF}_3:\text{Pr}^{3+}$  crystal under IR illumination has been detected and interpreted.

The results are obtained under the following conditions: pumping was carried out with a pulsed laser with wavelength of  $0.5945 \mu\text{m}$  and IR illumination of the crystal with a wavelength of  $3 \mu\text{m}$  and power  $10^{-7} \text{ W}$ . Thus, at a low temperature 5% intensity increasing of the individual up-conversion luminescence lines was observed. Moreover, this effect occurred at two temperature optima 170 K and 210 K.

Increase of efficiency can be achieved by increasing of the interaction length of IR radiation with a pumped sample. For example, it can be done through the usage of crystalline optical fibers.

## Acknowledgements

This work was funded by the subsidy allocated to Kazan Federal University for the project part of the state assignment in the sphere of scientific activities.

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