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# Visualiser of two-micron laser radiation based on Ho : $CaF_2$ crystals

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***Abstract.*** **The anti-Stokes luminescence spectra of Ho : $CaF_2$ crystals corresponding to the $^5G_4 \to {}^5I_8$, $^5G_5 \to {}^5I_8$, $^5F_3 \to {}^5I_8$, $^5F_4(^5S_2) \to {}^5I_8$, $^5F_5 \to {}^5I_8$, $^5S_2 \to {}^5I_7$, $^5I_4 \to {}^5I_8$, $^5I_5 \to {}^5I_8$, $^5F_5 \to {}^5I_7$, $^5F_3 \to {}^5I_6$, $^5I_6 \to {}^5I_8$, $^5F_5 \to {}^5I_6$, and $^5I_5 \to {}^5I_7$ transitions upon excitation of the $^5I_7$ level of $Ho^{3+}$ ions are studied. A method for visualisation of IR radiation in the two-micron range using Ho : $CaF_2$ crystals is proposed. The energy efficiency of conversion of two-micron laser radiation to radiation in the red spectral range 620 – 690 nm by a 1 mol % $HoF_3$ : $CaF_2$ crystal is estimated to be no higher than 0.02 %.**

***Keywords:*** *Ho : $CaF_2$ crystals, anti-Stokes luminescence, visualisation of IR radiation.*

## 1. Introduction

One of the topical problems of modern photonics is the search for materials for visualisation of IR laser radiation. From available information sources, it is known that the currently used commercial visualisers can convert to the visible light only the IR radiation with wavelengths not exceeding 1.7 μm. For example, the working spectral range of visualisers produced by Roithner Lasertechnik (Germany) is 0.7 – 1.7 μm [1]. At the same time, for practical applications, it is desired to have visualisers that convert to visible light the radiation with wavelengths longer than 1.7 μm. These materials are of interest for visualisation of radiation of two-micron lasers, which are efficiently developed today for medicine and lidar systems [2 – 5].

The conversion of IR radiation to visible light by most available visualisers is based on anti-Stokes luminescence from the $^4S_{3/2}$ and $^4F_{9/2}$ levels of $Er^{3+}$ ions in various Er-doped materials upon excitation to the $^4I_{13/2}$ level of $Er^{3+}$.

At the same time, beginning from the 1960s, the anti-Stokes luminescence of $Ho^{3+}$-doped fluorite-type crystals (Ho : $MF_2$, where M = Ca, Sr, Ba) in the visible and near-IR wavelength regions has been extensively studied. The specific features of these materials are the low phonon energy, the inhomogeneous impurity distribution, and the tendency to formation of clusters of dopant ions at certain dopant concentrations [6].

In 1964, Brown and Shand [7] observed anti-Stokes luminescence in Ho : $CaF_2$ crystals in the red, green, and blue spectral regions under lamp excitation and proposed to use the Ho : $CaF_2$ crystals as quantum counters and IR visualisers. Work [8] is devoted to anti-Stokes luminescence at the $^5F_5 \to {}^5I_8$ transition of $Ho^{3+}$ ions in $CaF_2$ crystals upon excitation of the $^5I_6$ level ($\lambda_{ex}$ = 1.16 μm). The authors of [9] propose to use the Ho : $CaF_2$ crystals for creating upconversion lasers. It should be noted that lasing in the Ho : $CaF_2$ crystal at a wavelength of 551.2 nm ($^5S_2 \to {}^5I_8$ transition of $Ho^{3+}$ ions) at a temperature of 77 K was obtained for the first time by Osiko with co-authors in 1965 [10].

Concerning the specific features of the growth technology of Ho : $CaF_2$ crystals, it is necessary to note the $HoF_3$ distribution coefficient during the $CaF_2$ melt crystallisation is close to unity [11], which simplifies the growth of Ho : $CaF_2$ crystals with a high optical quality.

Analysis of works on the anti-Stokes luminescence of $Ho^{3+}$ ions in Ho : $CaF_2$ crystals [7 – 10, 12 – 20], among which there are recently published papers, shows that the mechanisms of anti-Stokes luminescence in these crystals are of great interest for researchers. However, we have found no studies of anti-Stokes luminescence in Ho : $CaF_2$ crystals excited by two-micron radiation to the $^5I_7$ level of $Ho^{3+}$ ions. The goal of the present work is to study the anti-Stokes luminescence in Ho : $CaF_2$ crystals under excitation of the $^5I_7$ level of $Ho^{3+}$ ions and to evaluate the possibility of using this material as a visualiser of two-micron laser radiation.

## 2. Experimental technique

The 1 mol % $HoF_3$ : $CaF_2$ and 3 mol % $HoF_3$ : $CaF_2$ single crystals were grown by the vertical directed crystallisation method (Bridgman method) in vacuum in graphite crucibles, with a graphite resistance heater and graphite heat shields [21]. The samples for investigations were made in the form of plane-parallel plates 0.55 and 5 mm thick.

The absorption spectra of $Ho^{3+}$ ions in the Ho : $CaF_2$ crystal were recorded using a PerkinElmer Lambda 950 double-beam, double-monochromator spectrophotometer.

For excitation of the $^5I_7$ levels of $Ho^{3+}$ ions in Ho : $CaF_2$ crystals, we used a solid-state cw Tm : $LiYF_4$ laser operating at a wavelength of 1912 nm. The focused pump beam diameter on the crystal was 230 μm. The luminescence of $Ho^{3+}$ ions in Ho : $CaF_2$ crystals excited by the two-micron laser was recorded using an automated setup based an MDR-23 monochromator. The luminescence signal was synchronously

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detected by an SR-810 synchronous amplifier. As radiation detectors, we used a FEU-79, a FEU-83, and an FD-7G photodiode depending on the spectral region. The dependence of the anti-Stokes luminescence intensity on the pump radiation power was measured with the use of a set of neutral optical filters for attenuation of the pump radiation. All measurements were performed at room temperature.

The spectral intensity of luminescence in the range 620–680 nm were measured using an OL IS-670-LED integrating sphere and an OL-770 UV/VIS (Gooch & Housego) spectroradiometer. The two-micron pump power absorbed in the Ho : $CaF_2$ crystal was measured with an 11 PMK-30H-H5 (Standa) power meter.

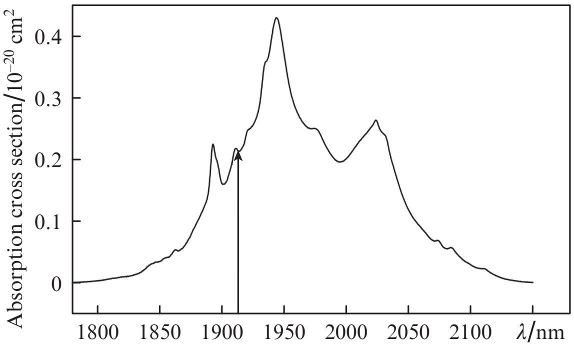


**Figure 1.** Absorption spectrum for the $^5I_8 \rightarrow {}^5I_7$ transition of $Ho^{3+}$ ions in the 1 mol % $HoF_3$ : $CaF_2$ single crystal at $T = 300$ K.

## 3. Results and discussion

Figure 1 shows the absorption spectrum of the $^5I_8 \rightarrow {}^5I_7$ transition of $Ho^{3+}$ ions in Ho : $CaF_3$ crystals. To record the anti-Stokes luminescence, we excited the $^5I_7$ level of $Ho^{3+}$ ions by the radiation of a Tm : $LiYF_4$ laser at a wavelength of 1912 nm (the excitation wavelength is shown by the arrow).

The anti-Stokes luminescence spectra in the visible and near IR regions corresponding to the $^5G_4 \rightarrow {}^5I_8$, $^5G_5 \rightarrow {}^5I_8$, $^5F_3 \rightarrow {}^5I_8$, $^5S_2(^5F_4) \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$, $^5S_2(^5F_4) \rightarrow {}^5I_7$, $^5I_4 \rightarrow {}^5I_8$, $^5I_5 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_7$, $^5F_3 \rightarrow {}^5I_6$, $^5I_6 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_6$, and $^5I_5 \rightarrow {}^5I_7$ transitions of $Ho^{3+}$ ions recorded upon the mentioned excitation are shown in Figs 2a–2i.

These spectra were measured at identical laser excitation intensities. For recording each individual spectrum, we chose the optimal monochromator slit width and the optimal gain coefficient of the receiving system. The luminescence intensity $I_{lum}$ was normalised to the intensity in the spectral maximum.

The existence of intense anti-Stokes luminescence in Ho : $CaF_2$ crystals in the range 630–670 nm allowed us to propose a method of visualisation of IR radiation in the two-micron region. We demonstrated the possibility of visualisation using a display in the form of an aluminium substrate coated, with the help of a binder, by a powder milled from

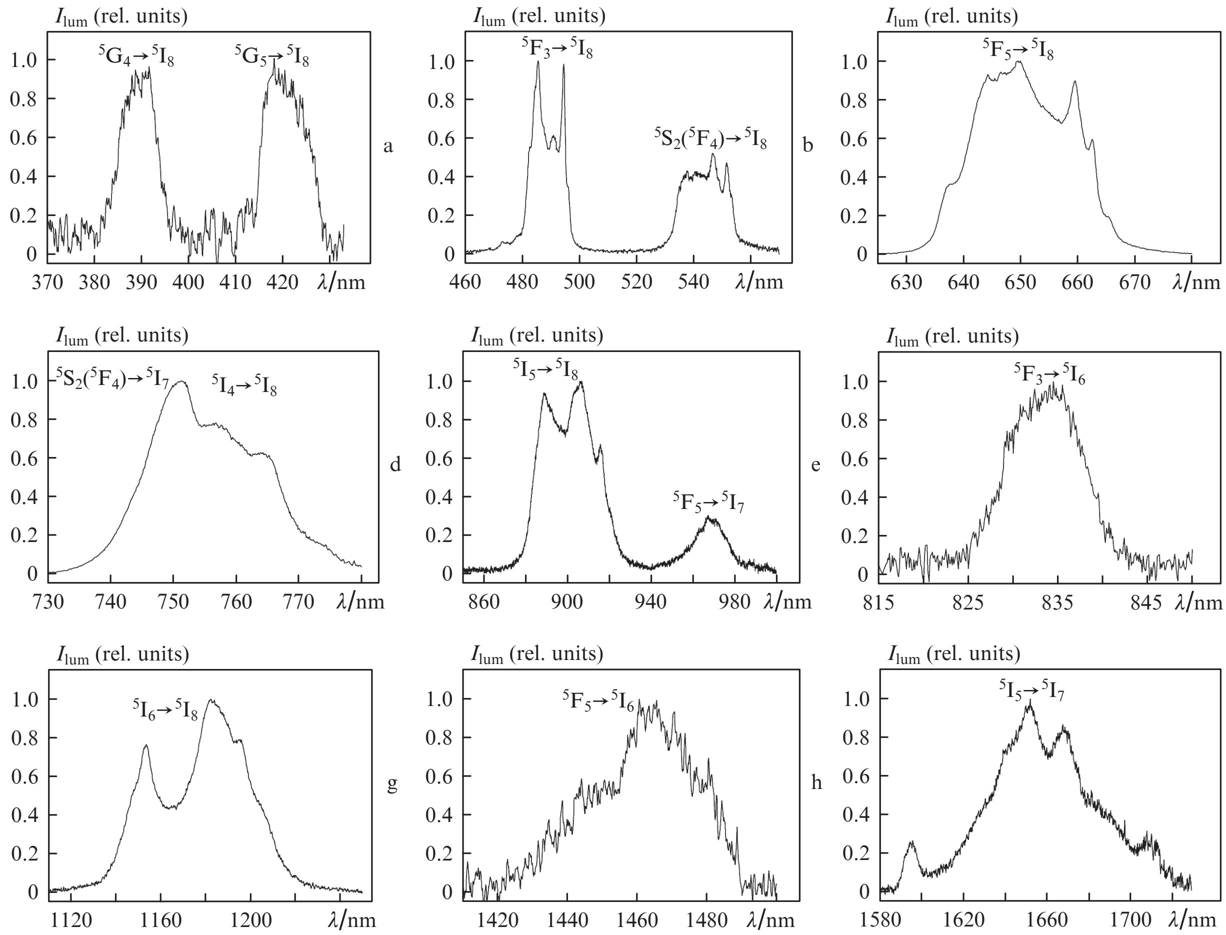


**Figure 2.** Normalised luminescence spectra of $Ho^{3+}$ ions in the 1 mol% $HoF_3$ : $CaF_2$ single crystal for the transitions (a) $^5G_4 \rightarrow {}^5I_8$, $^5G_5 \rightarrow {}^5I_8$, (b) $^5F_3 \rightarrow {}^5I_8$, $^5S_2(^5F_4) \rightarrow {}^5I_8$, (c) $^5F_5 \rightarrow {}^5I_8$, (d) $^5S_2(^5F_4) \rightarrow {}^5I_7$, $^5I_4 \rightarrow {}^5I_8$, (e) $^5I_5 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_7$, (f) $^5F_3 \rightarrow {}^5I_6$, (g) $^5I_6 \rightarrow {}^5I_8$, (h) $^5F_5 \rightarrow {}^5I_6$, and (i) $^5I_5 \rightarrow {}^5I_7$ at $T = 300$ K.

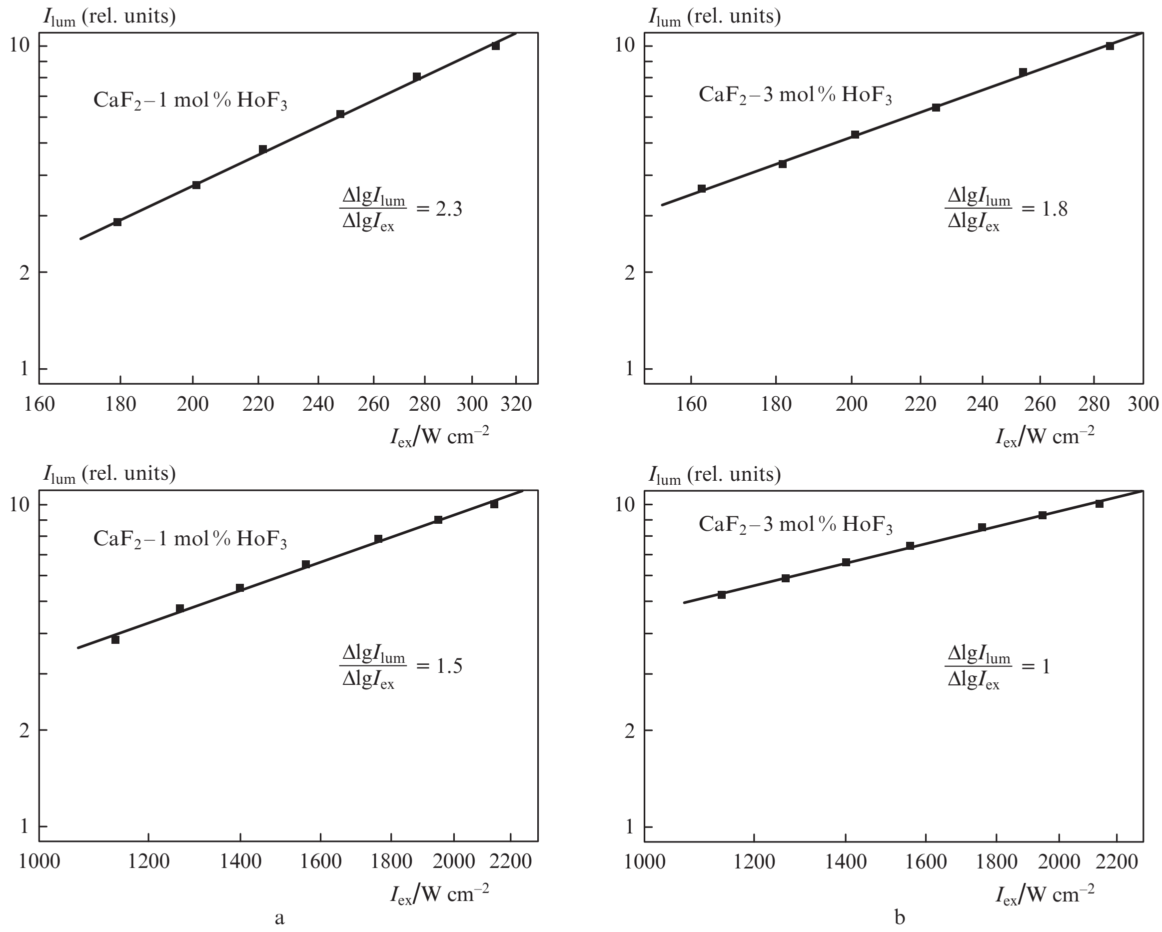


**Figure 3.** Dependences of the intensity of the anti-Stokes luminescence at the $^5F_5 \rightarrow {}^5I_8$ transition of $Ho^{3+}$ ions on the pump $LiYF_4$ laser intensity for (a) 1 mol % $HoF_3:CaF_2$ and (b) 3 mol % $HoF_3:CaF_2$ crystals.

$Ho:CaF_2$ crystals. When illuminating this visualiser by the radiation of a $Tm:LiYF_4$ laser, we observed a bright red spot.

In the present work, we also studied the dependences of the intensity of anti-Stokes luminescence at the $^5F_5 \rightarrow {}^5I_8$ transition of $Ho^{3+}$ ions on the excitation intensity. These dependences are shown in Fig. 3.

As is known from the literature, the dependence of the anti-Stokes luminescence intensity $I_{lum}$ on the long-wavelength excitation intensity $I_{ex}$ in the absence of saturation is expressed by the formula [22]

$$I_{lum} \propto (I_{ex})^n, \quad (1)$$

where $n$ is the number of absorbed photons needed for populating the upper energy level of the transition. The population of the $^5F_5$ level of $Ho^{3+}$ ions in the case of excitation at a wavelength of 1912 nm occurs with participation of three photons. According to formula (1), the slope of the dependence of the intensity $I_{lum}$ of the anti-Stokes luminescence from the $^5F_5$ level to the $^5F_8$ level of $Ho^{3+}$ ions on the excitation intensity $I_{ex}$ on a log-log scale must be equal to 3. However, our experiments show that the slope of the dependence of $\log(I_{lum})$ on $\log(I_{ex})$ for the 1 mol % $HoF_3:CaF_2$ crystal is 2.3 in the excitation intensity range 180–310 W cm$^{-2}$ and 1.5 in the range 1.14–2.14 kW cm$^{-2}$ (Fig. 3). The reason for the decrease in the slope of this dependence in the case of anti-Stokes luminescence in different compounds with rare-earth ions was studied in [22]. The authors of [22] suggest that this decrease is caused by competition of the processes of radiative and multiphonon relaxation from the luminescent level with the processes of interionic interaction depopulating this level. In our opinion, it is the interaction between $Ho^{3+}$ ions on intermediate levels in 1 mol % $HoF_3:CaF_2$ crystals that is responsible for the fact that the slope of the dependence of $\log(I_{lum})$ on $\log(I_{ex})$ differs from 3. The occurrence of these processes in $Ho:CaF_2$ crystals is evidenced by the luminescence spectra shown in Fig. 2. The decrease in this slope from 2.3 to 1.5 with increasing excitation intensity for the 1 mol % $HoF_3:CaF_2$ crystal indicates that the interaction between $Ho^{3+}$ ions at the $^5F_5$ level become more intense at higher excitation intensities.

The decrease in the slope of the dependence of $\log(I_{lum})$ on $\log(I_{ex})$ for the anti-Stokes luminescence of $Ho^{3+}$ ions from the $^5F_5$ level with increasing concentration of $Ho^{3+}$ ions (in 3 mol% $HoF_3:CaF_2$ crystals, Fig. 3b) is explained by an increase in the absorbed pump power with increasing $Ho^{3+}$ concentration.

We estimated the energy efficiency of the conversion of two-micron laser radiation to radiation in the red spectral range 620–680 nm by the 1 mol% $HoF_3:CaF_2$ crystal. A beam of a two-micron $Tm:LiYF_4$ laser was focused on a 1 mol % $HoF_3:CaF_2$ sample positioned in an OL IS-670-LED integrating sphere. The power of the anti-Stokes luminescence of $Ho^{3+}$ ions in the range 620–680 nm measured by an OL-770 UV/VIS spectroradiometer was $2\times10^{-5}$ W. The radiation power absorbed in the crystal was measured by an 11

PMK-30H-H5 power meter to be 0.1 W. The energy efficiency of the conversion of two-micron laser radiation to radiation in the red spectral range 620–680 nm by the 1 mol% $HoF_3$ : $CaF_2$ crystal does not exceed 0.02%.

## 4. Conclusions

In this work, we measured the anti-Stokes luminescence spectra of $Ho^{3+}$ ions in Ho : $CaF_2$ crystals corresponding to the $^5G_4 \to {}^5I_8$, $^5G_5 \to {}^5I_8$, $^5F_3 \to {}^5I_8$, $^5S_2(^5F_4) \to {}^5I_8$, $^5F_5 \to {}^5I_8$, $^5S_2(^5F_4) \to {}^5I_7$, $^5I_4 \to {}^5I_8$, $^5I_5 \to {}^5I_8$, $^5F_5 \to {}^5I_7$, $^5F_3 \to {}^5I_6$, $^5I_6 \to {}^5I_8$, $^5F_5 \to {}^5I_6$, and $^5I_5 \to {}^5I_7$ transitions in the case of excitation $Ho^{3+}$ ions the $^5I_7$ level. The occurrence of intense anti-Stokes luminescence of Ho : $CaF_2$ crystals in the range 630–670 nm can be used for visualisation of IR two-micron radiation. The energy efficiency of the conversion of two-micron laser radiation to radiation in the red spectral range 620–680 nm by the 1 mol % $HoF_3$ : $CaF_2$ crystal does not exceed 0.02%.

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