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Effective Upconversion in Alkaline Earth Fluorides Activated by Yb^{3+}–Ho^{3+} Ions

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Abstract—A study is performed of optical spectra (absorption, excitation, luminescence, energy yield) associated with the upconversion of infrared excitation of 980 nm into visible radiation in crystals of alkaline–earth fluorides CaF_2, SrF_2, and BaF_2, co-doped with YbF_3 (0.01–10 mol %) and HoF_3 (0.01–0.3 mol %). In the 0.1–10 W cm^{-2} range of excitation power densities, the intensity of the upconversion bands at 542, 650, and 752 nm grows as the square of the power. A quadratic dependence of the intensity of upconversion on the concentration of Yb^{3+} (0.03–3 mol %) and a weak dependence on the Ho^{3+} concentration (0.01–0.3 mol %) with a maximum at 0.1–0.15 mol % are observed. It is assumed that the upconversion is due to consecutive energy transfer from two closely spaced excited ytterbium ions to the holmium ion.

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INTRODUCTION

The search for effective phosphors that convert near infrared radiation into visible light remains of great relevance [1]. The growing field of upconversion phosphor application, including protective labels on securities and banknotes, biological labels [2], optical thermometry [3], solar energy [4] and new laser media [5], demands that we seek more effective materials. Of the known mechanisms of upconversion, the one most effective is the mechanism of sensitizied energy transfer upconversion [1, 6].

For example, at a low lighting density of 0.4 W cm^{-2} and an excitation wavelength of 1500 nm, the internal yield of energy in the integrated upconversion spectrum of $NaYF_4$–25% Er is 12% [4]. At the same time, the greatest intensity of upconversion lies in the band around 1000 nm; this can be used to increase the efficiency of silicon solar cells [4]. High efficiency in the upconversion of 750 nm emissions into 550 nm emissions (8.1% at a high pumping power of 2.2×10^3 W cm^{-2}) was achieved in CaF_2–1% Ho crystals and could be used to develop an upconversion laser [5].

Due to its large absorption cross section around 980 nm and the effective transfer of the energy of excitation to activators, the Yb^{3+} ion is an effective sensitizer for Ho^{3+}, Tm^{3+}, and Er^{3+} ions [1, 7]. The upconversion of a pair of lanthanide impurities (sensitizer Yb and activator Ho^{3+}) has been studied in a variety of fluorides and oxides [7–10]. This pair seems to be the one most promising for converting 900–1000 nm radiation into visible light. The reverse transfer of excitation from Ho^{3+} ions (sensitizers) to Yb^{3+} ions (activators) to improve the efficiency of solar cells was studied in [11].

Although the basic mechanisms of upconversion are known [1, 13], details of the energy transfer mechanisms and the structure of defects require additional research. In this work, we studied efficient upconversion in CaF_2 , SrF_2, and BaF_2 crystals activated by YbF_3–HoF_3 with concentrations in the range of 0.01 to 10 mol %.

EXPERIMENTAL

MeF_2 (Me: Ca, Sr, Ba) crystals were grown according to Stockbarger inside three-barreled graphite crucibles in a vacuum [12]. Several percents of CdF_2 was added to the initial material to purify it of oxygen impurities. Crystals of alkaline-earth fluorides were grown, into which, in addition to YbF_3 impurity (concentration of 0.01–10%), a second lanthanide was added. A small proportion of Yb^{3+} ions (10%) were converted to the bivalent form in some crystals as they grew.

Anti-Stokes luminescence was excited by a 980 nm semiconductor laser with a measured power of 69 mW. Of our investigated Yb–RE lanthanide pairs (RE: Pr, Nd, Sm, Dy, Ho, Er, Tm), only crystals activated by Yb–Ho, Yb–Er, and Er had effective visible upconversion luminescence.

Absorption spectra in the region of 190–3000 nm were measured on a PerkinElmer Lambda-950 spectrophotometer. The emission spectra in the region of 200–850 nm were measured using a H6780-04 Hamamatsu photomodule. The emission spectra in the long wavelength region were measured with an FUU83 photomultiplier (up to 1200 nm), an FPU-FDG LOMO-PHOTONICS photodetector equipped with a cooled Ge-photodiode (up to 1600 nm), and a cooled PbS-FSW19AA photoresistor (up to 2500 nm).

The upconversion energy yield in alkaline earth fluorides MeF_2–3% YbF_3–0.1% HoF_3 was measured using an integrating sphere. The detector was a TSL237 silicon photosensor. The intensity of the exciting beam was measured using both the sphere and an IMO-2M thermocouple laser power meter. The intensity of upconversion was measured through a SZS25 filter, which blocked the infrared radiation of the 980 nm laser. The TSL247 signal was converted into radiation power (W) using a 536 nm laser beam of measured power, passed through a HC13 power density filter.

RESULTS AND DISCUSSION

Luminescence Spectra

Upon the excitation of MeF_2–Yb–Ho crystals with 980 nm laser light (which falls into the Yb^{3+} ($^2F_{7/2}$–$^2F_{5/2}$) band), we observed anti-Stokes luminescence bands of Ho^{3+} at 542 nm ($^5S_2$,$^5F_4$–$^5I_8$), 650 nm ($^5F_5$–$^5I_8$), and 752 nm ($^5S_2$,$^5F_4$–$^5I_7$). Stokes bands were visible at 1150–1180 nm ($^5I_6$–$^5I_8$) and 1950–2050 nm ($^5I_6$–$^5I_8$) (Fig. 1). Due to the splitting of Ho^{3+} levels by the crystal field, the luminescence bands had a developed structure.

Since the probability of resonance energy transferring from Yb^{3+} to Ho^{3+} depends on the distance between them as R^{-6}, we would expect perturbations of Ho^{3+} ions by nearby Yb^{3+}ions. We therefore compared the Ho^{3+} spectra of MeF_2–Yb–Ho crystals when Yb^{3+} and Ho^{3+} were excited by laser emissions of 980 nm and 532 nm, respectively (Fig. 2). The structure of the Ho^{3+} bands excited by the 980 nm laser (upconversion) and the 532 nm laser (on the edge of the Ho^{3+} band) differed considerably.

Absorption and Excitation Spectra

The absorption spectra of alkaline earth fluoride crystals with double activation show the $^2F_{7/2}$–$^2F_{5/2}$ band of Yb^{3+} at around 1000 nm$^+$ and Ho^{3+} bands in the range of 400–800 nm (Fig. 3a). Intense broad bands at 360 and at 220 nm belonged to Yb^{2+} ions partially reduced from Yb^{3+} during crystal growth (see Fig. 3a).

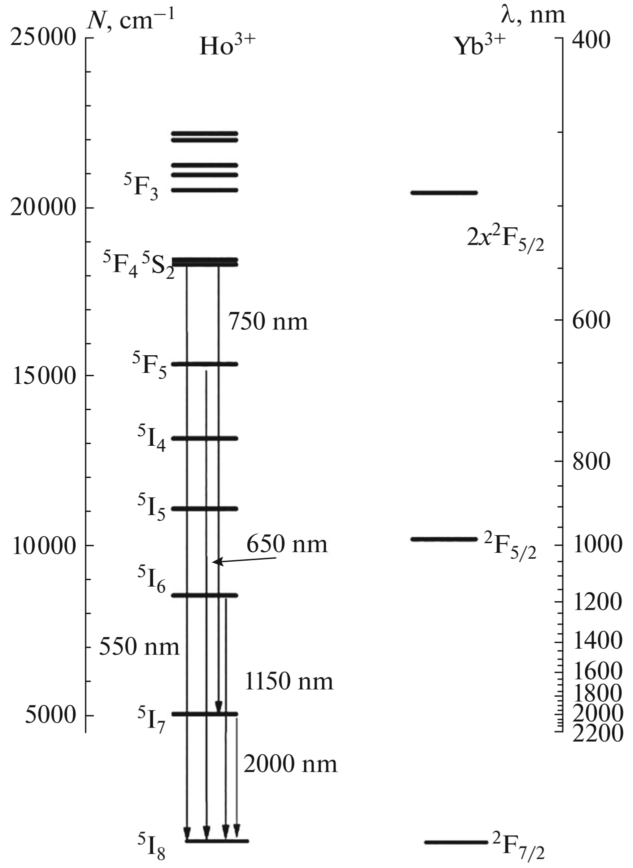

Fig. 1. Level scheme of the Ho^{3+} and Yb^{3+} ions and observed transitions in MeF_2–Yb–Ho crystals. The doubled energy of the $^2F_{5/2}$ Yb^{3+} level is also indicated.

Excitation spectra were measured using the emissions of a DKSSh-200 xenon lamp, passed through a MDR-2 monochromator. The spectrum of the xenon lamp was measured with a germanium photodiode and a PbS photoresistance, and then adjusted for the spectral sensitivity of the photodetectors. The excitation spectrum of the green luminescence of Ho^{3+} in BaF_2 correlates with the absorption spectrum (Fig. 3b). The large width of the excitation bands relative to the absorption bands is due to the greater spectral width of the monochromator slit (see Fig. 3b).

Efficiency of Upconversion

The intensities of the anti-Stokes emission bands of Ho^{3+} are proportional to the square of radiation power of the 980 nm laser (Fig. 4a), indicating a two-photon mechanism of excitation. The Stokes infrared bands at 1180 and 2000 nm grow linearly along with the excitation power.

The intensity of upconversion crystals has a weakly pronounced maximum at HoF_3 concentrations in the range of 0.1–0.15 mol % and a constant concentration

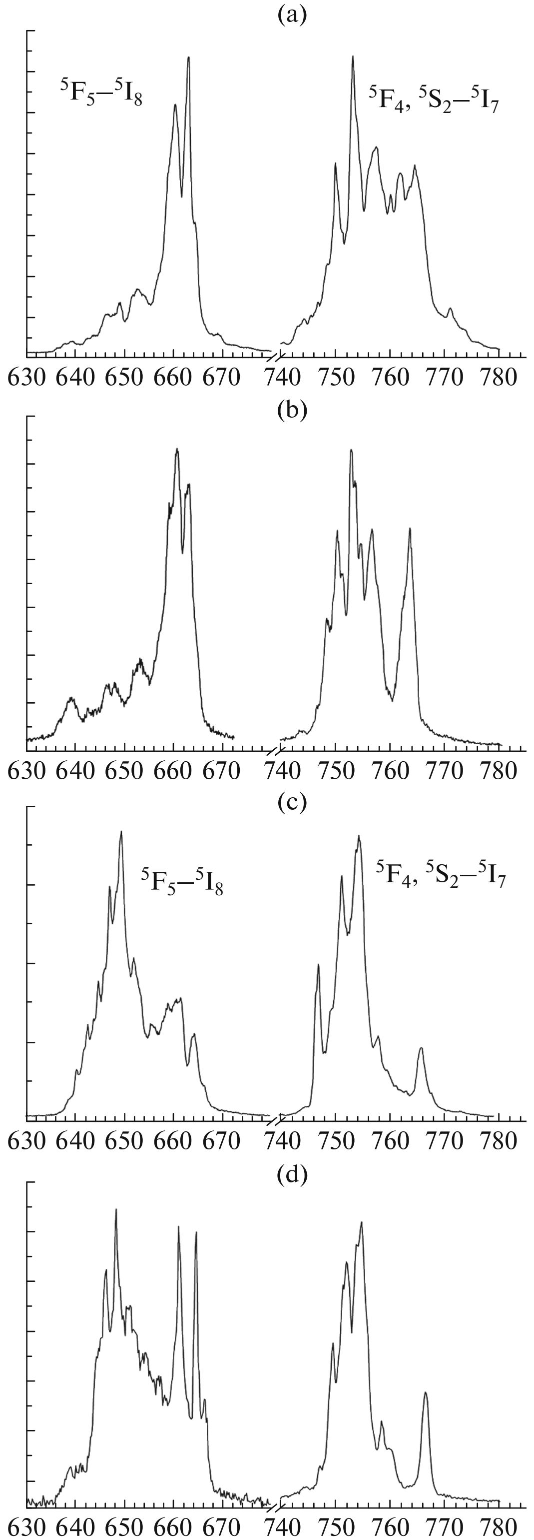

Fig. 2. Luminescence spectra of BaF_2 and SrF_2 crystals with an admixture of 0.1 mol % YbF_3 and 0.1 mol % HoF_3 upon excitation of (a) BaF_2, (b) SrF_2 at 532 nm, (c) BaF_2, and (d) SrF_2 at 980 nm. Temperature was 80 K.

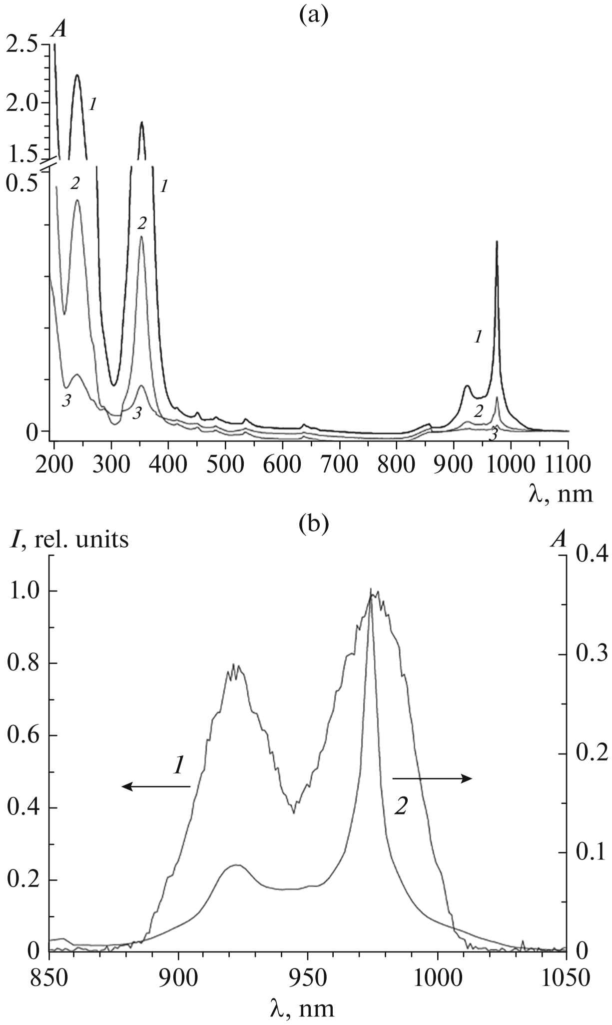

Fig. 3. (a) Absorption spectra of BaF_2 crystals with an admixture of 0.1 mol % HoF_3 and the specified concentration of YbF_3: (*1*) 3% Yb, d = 2.21 mm, (*2*) 1% Yb, d = 2.37 mm, and (*3*) 0.1% Yb, d = 2.49 mm. (b): (*1*) Excitation spectrum of the green luminescence of Ho^{3+} in BaF_2 crystals with admixture of 3 mol % YbF_3 and 0.1 mol % HoF_3, T = 80 K, and (*1*) absorption spectrum of this crystal at T = 295, shown for comparison.

of YbF_3. The intensity of upconversion increases quadratically when the concentration of YbF_3 is increased to 3 mol % (Fig. 4b), indicating the center of upconversion includes two Yb^{3+} ions.

The phosphor's yield of energy was determined as the ratio of the energy's emitted and absorbed power. The yield of energy for upconversion phosphors grows along with the absorbed power. To characterize n-photon upconversion, we therefore propose using the normalized efficiency, obtained by dividing the output energy by the emitted (or absorbed) energy in the power of $(n - 1)$. With a two-photon process, the normalized efficiency is measured in units of $cm^2 W^{-1}$ [1].

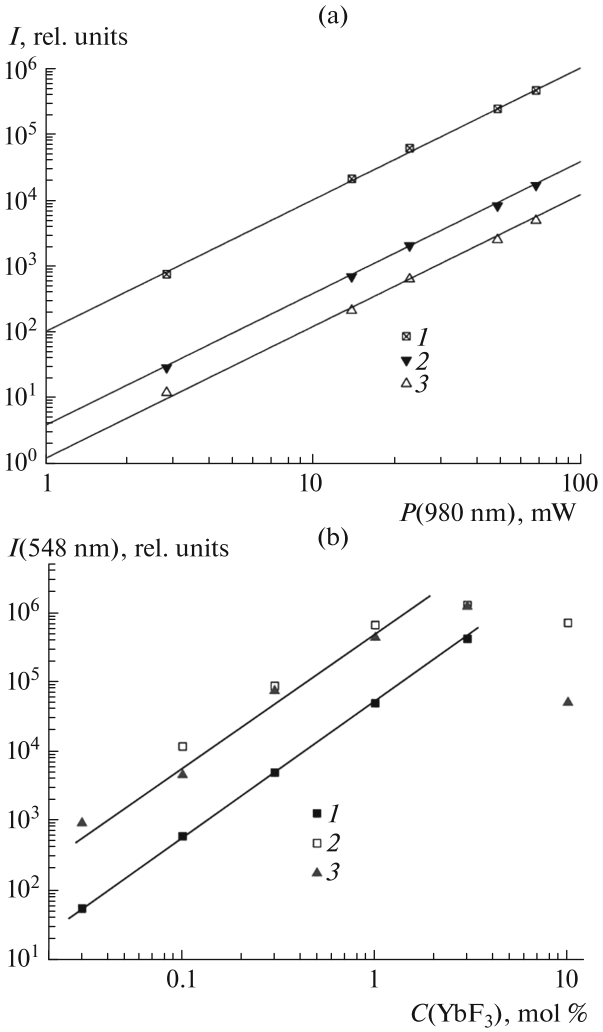

Fig. 4. (a) Dependence of the intensity of anti-Stokes luminescence bands at (*1*) 542, (*2*) 650, and (*3*) 752 nm on the power of 980 nm exciting radiation in SrF_2 crystals with a mixture of 0.3 mol % YbF_3 and 0.1 mol % HoF_3. (b) Dependence of the intensity of Ho^{3+} green luminescence on the concentration of Yb^{3+} in BaF_2 and SrF_2 crystals: (*1*) BaF_2 with 0.1% HoF_3–YbF_3, (*2*) SrF_2 with 0.1% HoF_3–YbF_3, and (3) SrF_2 with 0.03% HoF_3–YbF_3.

At the same time, it should be noted that in efficient powder materials $NaYF_4$–Er, Gd_2O_2S–Er, the output is saturated as the emitted power increases, which means a drop in the normalized efficiency as power increases [4]. Deviation of the upconversion output from the $(n - 1)$ power dependence on the density of the excitation power has also been observed in other works [14].

Table 1. Yield of energy (in %) for MeF_2–YbF_3 (3%)–HoF_3 (0.1%) crystals upon excitation by 980 nm laser light

Crystal	Yield of upconversion in the visible range at an excitation power density of 0.9 W cm^{-2}, %
CaF_2	0.04
SrF_2	0.10
BaF_2	0.09

The quadratic dependence of the intensity of visible upconversion (and thus the linear growth of the energy yield) was in our case observed throughout the range of measurement, from 0.1 to 10 W cm^{-2}. Data on the upconversion efficiency of single crystals MeF_2–3% YbF_3–0.1% HoF_3 are given in Table 1.

We may assume the number of upconversion centers is much less than the total number of Ho^{3+} ions. As a result, the structure of the Ho^{3+} luminescence bands in the upconversion center and all other holmium ions different considerably (see Fig. 2), due to short distance between the Yb–Ho ions in the upconversion center, which perturbs transitions in a holmium ion.

In CaF_2–Ho and CaF_2–Ho, Er crystals, high-resolution study of the excitation and luminescence spectra revealed there were two types of centers with single Ho^{3+} ions and three types of aggregate centers with two or more holmium ions [15]. Upconversion was observed only for aggregate centers Ho–Ho, Ho–Er [15], and Er–Er [16] in CaF_2, and was a consequence of energy transfer between neighboring ions. A similar conclusion was drawn in [17], in which a quadratic dependence of the intensity of the blue luminescence bands of CaF_2–Ho (upon excitation by green light at 532 nm) on the concentration of holmium was observed.

The quadratic dependence of the upconversion bands on the Yb concentration and the weak dependence on the Ho concentration observed in this work clearly indicate that the upconversion center in crystals of alkaline earth fluorides is a complex of two ytterbium ions and one holmium ion. Such complexes form at a concentration of the $YbF_3 + HoF_3$ impurity of around 0.03 mol %.

CONCLUSIONS

Ho^{3+} bands were observed in luminescence spectra at 542 nm ($^5S_2$,$^5F_4$–$^5I_8$), 650 nm ($^5F_5$–$^5I_8$), and 752 nm. Due to the interaction between Ho^{3+} and the crystal's field, these bands had a developed structure. Ho^{3+} bands excited by a 980 nm laser (upconversion), and by 532 nm light incident on the edge of the Ho^{3+} band, had very different structures, due to perturbation of the holmium ions in the upconversion center.

The center of upconversion in crystals of alkaline earth fluorides MeF_2–Yb–Ho is a complex of two ytterbium ions and one holmium ion, as is confirmed by the quadratic dependence of the upconversion bands on the concentrations of Yb and the weak dependence on the concentration of Ho.

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