Short-wavelength luminescence in Ho^{3+}-doped KGd(WO$_4$)$_2$ crystals

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ABSTRACT

Emissions from the high-lying excited states, energy transfer and upconversion processes are investigated in Ho^{3+}-activated KGd(WO$_4$)$_2$ crystal. The spectral assignment based on time-resolved emission spectra allowed to identify various near ultra-violet (UV), blue and green emissions starting from the excited $^3H_5$, $^5G_4$, $^5G_5$, $^5F_3$ and $^5S_2$ levels. The temporal behavior of these transitions after pulsed excitation was analyzed as a function of temperature and holmium ions concentration. The shortening and nonexponentiality of the decays, observed with increasing activator concentrations, indicated cross-relaxation (CR) among the Ho^{3+} ions. Cross-relaxation rates were experimentally determined as a function of activator concentration and used to evaluate the values of the nearest-neighbor trapping rates X_{01} and to model the decays. It was observed that KGW, despite higher than in YAG maximum phonon energy of about $900\,cm^{-1}$, is more efficient short-wavelength emitter than YAG. Examples of the excited-state absorption (ESA) and energy transfer (ET) mechanisms responsible for the upconverted, short-wavelength emissions were identified by analyzing fluorescence dynamics and possible energy resonances.

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1. Introduction

Trivalent holmium (Ho^{3+})-doped matrixes have been the subject of extensive investigation for the development of mid infra-red (IR) lasers [1]. Holmium ion has also several high-lying metastable levels that can give rise to transitions at various wavelengths in the visible and ultra-violet (UV) region [2]. However, these short-wavelength transitions are much less investigated. Interest in studying these transitions is further stimulated by the rapid growth of applications requiring visible lasers, such as full-color displays, optical data storage and biomedical instruments.

The potassium gadolinium tungstate KGd(WO$_4$)$_2$ (KGW) single crystal is monoclinic with the space group C_2/c and the cell parameters $a = 10.652\,\text{Å}$, $b = 10.374\,\text{Å}$, $c = 7.582\,\text{Å}$, $\beta = 130.8°$ and $Z = 4$.

Rare-earth (RE) activators entering the KGW lattice, substitute equivalent Gd^{3+} positions having C_2 local symmetry and eightfold coordination. KGW crystal is optically biaxial with the C_2-axis parallel to the crystallographic [0 1 0] b-axis. RE-activated KGW crystals are successfully used as a host for infra-red wavelengths solid-state lasers [3,4]. Recently, Kaminski et al. [5] reported on visible lasing, at green and at red wavelengths, in Dy^{3+}:KGW. Also, these crystals have large value of the third-order nonlinear optical

susceptibility $\chi^{(3)}$ which makes them suitable for stimulated Raman scattering (SRS) frequency self-conversion lasers [6].

Ho^{3+}:KGW crystal has been investigated as a potential 2 and 3 μm laser material [7,8] and its optical and spectroscopic properties in this range are well described. The purpose of this work was to characterize in detail and extend our knowledge on the short-wavelength emission properties of this system crystal.

2. Experimental

Samples used in our study were grown by means of top-seeded solution growth method from K$_2$W$_2$O$_7$ solvent, as described in details elsewhere [9] and had nominal concentrations of 0.05, 0.5, 1, 3 and 8 at% of Ho^{3+}. For spectroscopic investigations Ho^{3+}-doped KGd(WO$_4$)$_2$ crystals were oriented, cut and polished in the form of cubes of $5 \times 5 \times 4\,mm^3$ sizes with faces perpendicular to the a, b and c directions. Most of the emission spectra were registered for π polarization.

Emission spectra were measured using CVI-480 grating monochromator followed by a PMT and SR-400 photon counting system. The samples were excited by pulsed (10 ns pulse-width, repetition rate 10 Hz) Continuum Surelite Nd:YAG laser with third harmonic generator, followed by an optical parametric oscillator or by c.w. Coherent Innova 300, 10 W argon ion laser. Fluorescence dynamics profiles were recorded with SR-430 multi-channel analyzer controlled with a PC computer. The best temporal resolution of the experimental apparatus was 5 ns. Sample cooling

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was provided by a closed cycle He optical cryostat which allowed the temperature to be varied between 10 and 300 K.

3. Results and discussion

A generic holmium energy level scheme in a KGW matrix is shown in Fig. 1. Holmium 4f10 levels extend in the KGW band-gap of 4.52 eV [10]. The intrinsic optical absorption edge is at about 275 nm (36,370 cm^{-1}). Narrow absorption bands around 32,000 and 32,600 cm^{-1} have been ascribed to Gd^{3+} intraconfigurational transitions [11]. After selective UV excitation in the 27,500–33,500 cm^{-1} range, various emission lines, from UV to visible and IR, were observed as shown in a low-resolution, room-temperature spectrum in Fig. 2. As seen from Fig. 2, the main visible emission channel of Ho^{3+} is in the green part of the spectrum (550 nm) and corresponds to the $^5S_2 \rightarrow {}^5I_8$ transition. On the short-wavelength side, less intense blue line centered at 488 nm ($^3F_3 \rightarrow {}^5I_8$) and several UV transitions; 420 nm ($^5G_5 \rightarrow {}^5I_8$), 390 nm ($^5G_4 \rightarrow {}^5I_8$) and 365 nm ($^3H_5 \rightarrow {}^5I_8$) could be observed. Details of these emissions measured at 10 K in the 8 at% Ho^{3+} sample are presented in the higher part of the figure. It should be noted that, contrary to YAG, YAP and ZBLAN glass investigated earlier [2,12], no UV emission originating from the $^3D_3$ state is observed in KGW. As shown in Fig. 1, $^3D_3$ state is situated between the Gd^{3+} levels and close to the bottom of the host absorption which may influence $^3D_3$ quantum efficiency.
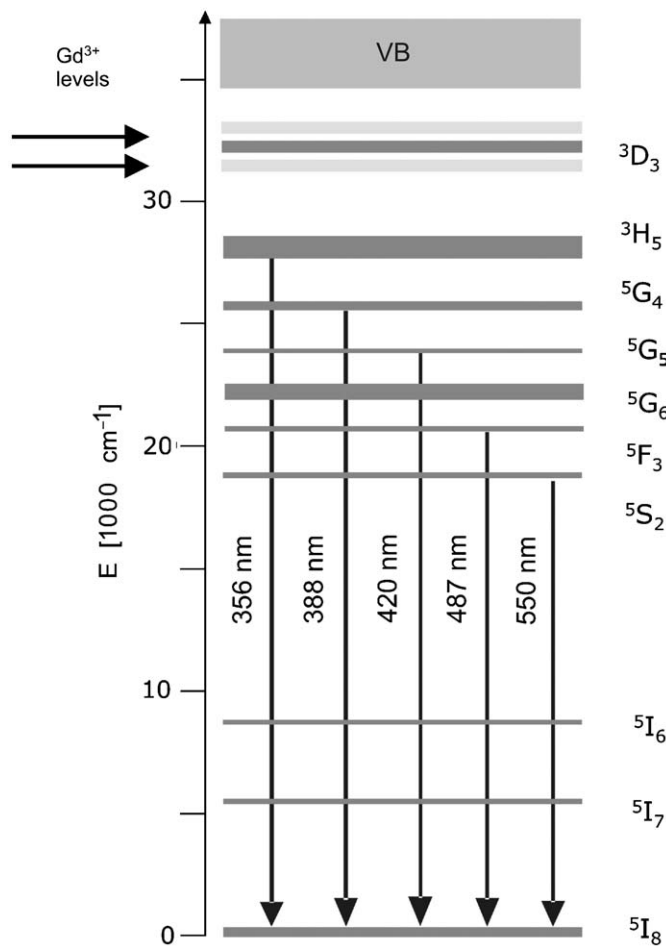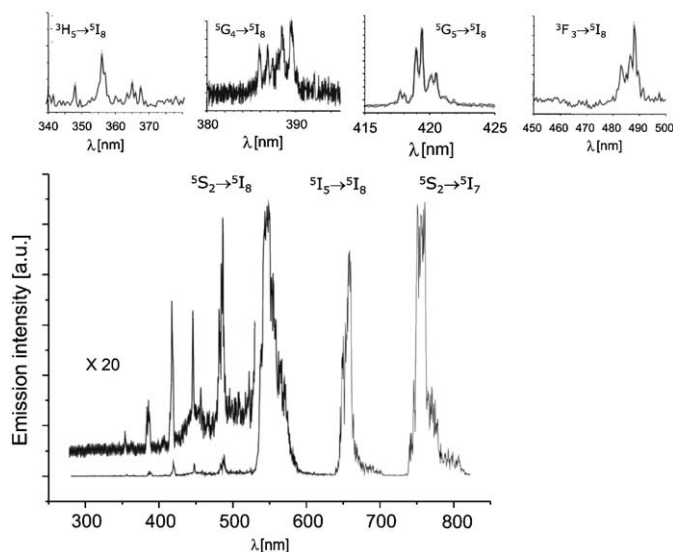

Fig. 2. UV-excited emission spectrum of 8 at% Ho^{3+}:KGW, in the upper part of the figure details of the short-wavelength transitions are shown.

We measured the lifetimes of the emitting levels at different concentrations and temperatures after pulsed, selective laser excitation. It was observed that $^5S_2$ decay profiles vary only slightly with concentration and are nearly exponential except for the highly doped samples. The $^5S_2$ lifetime measured in the low-concentrated crystal is strongly temperature dependent it is 17.5, 5.4 and 2.3 μs at 10, 300 and 620 K, respectively. Decays of the $^5G_5$ level at 420 nm clearly show concentration dependence and keep the single exponential character only for the lowest dopant level. The nonexponentiality and shortening of decays with increasing concentration of the activator is an indication of efficient energy transfer cross-relaxation (CR).

The next step in our investigation was to determine the CR rates and their concentration dependence. When the fluorescence decay is exponential cross-relaxation transfer rates could be defined as $X = 1/\tau - 1/\tau_0$, where τ is the fluorescence decay time and τ_0 is the isolated ion lifetime measured in the low-concentration sample. For nonexponential decay X could be defined as

$$X = \frac{I(0)}{\int_0^\infty I(t)\,dt} - \frac{1}{\tau_0} \tag{1}$$

The quenching rates X, for the $^5S_2$, $^5F_3$ and $^5G_5$ states calculated according to Eq. (1) are plotted as a function of holmium concentration in Fig. 3 in double-logarithmic representation. In these calculations, τ_0 lifetimes of levels $^5S_2$, $^5F_3$ and $^5G_5$ were taken to be 5.8, 6.11 and 0.15 μs, respectively, at room temperature. Values of calculated CR rates for the $^5S_2$ level in KGW:Ho^{3+} are in a reasonable agreement with our results for holmium-doped YAG and YAP crystals [2]. At room temperature, and over the range of investigated concentrations, close to linear dependence of X is clearly visible for all luminescences. This is an indication that the weak quenching approximation is still valid, and is consistent with the model presented in Ref. [13] which guarantees linear dependence of a transfer rate on N for times shorter than X_{01}^{-1}, that is when $\tau_0 \leqslant X_{01}^{-1}$. It could be also noted that the higher lying states are characterized by stronger concentration quenching. This could be explained by the large number of resonant and quasi-resonant cross-relaxation channels, namely $^3H_5 \rightarrow {}^5G_6 + {}^5F_1 \cong {}^5I_8 \rightarrow {}^5I_7$, $^3H_5 \rightarrow {}^5S_2 \cong {}^5I_8 \rightarrow {}^5I_6$, $^3H_5 \rightarrow {}^5F_5 \cong {}^5I_8 \rightarrow {}^5I_5$, $^3H_5 \rightarrow {}^5I_4 \cong {}^5I_8 \rightarrow {}^5F_5$, $^5G_4 \rightarrow {}^5F_3 \cong {}^5I_8 \rightarrow {}^5I_7$, $^5G_4 \rightarrow {}^5F_5 \cong {}^5I_8 \rightarrow {}^5I_5$, $^5G_4 \rightarrow$

Fig. 1. Generic energy level diagram of Ho^{3+}:KGW, analyzed emission transitions are indicated by arrows.