Abstract—The spectroscopic properties of Ho$^{3+}$ laser channels in KGW($\text{WO}_4$)$_2$ crystals have been investigated using optical absorption, photoluminescence, and lifetime measurements. The radiative lifetimes of Ho$^{3+}$ have been calculated through a Judd–Ofelt (JO) formalism using 300-K optical absorption results. The JO parameters obtained were $\Omega_2 = 15.35 \times 10^{-20}$ cm$^2$, $\Omega_4 = 3.79 \times 10^{-20}$ cm$^2$, $\Omega_6 = 1.69 \times 10^{-20}$ cm$^2$. The 7–300-K lifetimes obtained in diluted (8 $\times 10^{-4}$ cm$^{-3}$) KGW : 0.1% Ho samples are: $\tau(\text{F}_2) \approx 0.9 \, \mu$s, $\tau(\text{F}_4) \approx 19–36 \, \mu$s, and $\tau(\text{F}_6) \approx 1.1 \, \mu$s. For Ho concentrations below $1.5 \times 10^{-30}$ cm$^{-3}$, multiphonon emission is the main source of non-radiative losses, and the temperature independent multiphonon probability in KGW is found to follow the energy gap law $\tau_{\text{mp}}^{-1}(0) = \beta \exp(-\alpha \Delta E)$, where $\beta = 1.4 \times 10^{-7}$ s$^{-1}$, and $\alpha = 1.4 \times 10^{3}$ cm$^{-1}$. Above this holmium concentration, energy transfer between Ho impurities also contributes to the losses. The spectral distributions of the Ho$^{3+}$ emission cross section $\sigma_{\text{EM}}$ for several laser channels are calculated in $\sigma$- and $\tau$-polarized configurations. The peak $\sigma_{\text{EM}}$ values achieved for transitions to the $6 \text{I}_8$ level are $\approx 2 \times 10^{-20}$ cm$^2$ in the $\sigma$-polarized configuration, and three main lasing peaks at 2.02, 2.05, and 2.07 $\mu$m are envisaged inside the $\text{F}_4 \rightarrow \text{I}_8$ channel.

Index Terms—Crystals, holmium, rare-earth compounds, solid lasers, spectroscopy.

I. INTRODUCTION

The present development trend of rare-earth solid-state lasers requires media with low excitation thresholds and high impurity admittance, suitable to be excited by the emission of diode lasers. Ho$^{3+}$ has 13 laser channels ranging from $\lambda = 0.55 \text{ to } 3.9 \, \mu$m and it is prone to multi-wavelength emission by cascade de-excitation [1]. The $\text{F}_4 \rightarrow \text{I}_8$ emission near $\lambda = 2 \, \mu$m is of particular interest because of its use in eye-safe systems, medical applications involving coagulative cutting, and welding. The $\text{F}_4 + \text{S}_2 \rightarrow \text{I}_8$ holmium laser emission near $\lambda = 0.5 \, \mu$m is of interest to the present requirement for short-wavelength-emitting solid-state lasers. Moreover, green and blue up-conversion holmium emissions have been observed in several hosts upon excitation in red or infrared regions suitable for diode pumping [2]–[4]. This offers new excitation paths for lasing.

Potassium gadolinium tungstate KGW($\text{WO}_4$)$_2$ (KGW) has achieved outstanding relevance as a frequency self conversion laser host by using the stimulated Raman scattering effect because of its very high cubic nonlinearity, $\chi^{(3)} \approx 10^{-13}$ esu [5], [6]. KGW($\text{WO}_4$)$_2$ belongs to the monoclinic system with C$2/c$ symmetry space group, having four unit formula per unit cell. Trivalent rare earth ions substitute for Gd$^{3+}$ at an eight-coordinated site with C$2$ site symmetry, in which the $C_2$-axis is parallel to the crystallographic [010] axis. The high rare-earth admittance of KGW would allow codoping with several impurities, helping to reduce the laser threshold of Ho$^{3+}$ by sensitizing with several ion combinations: Cr$^{3+}$, Fe$^{3+}$, Tm$^{3+}$, Er$^{3+}$, Dy$^{3+}$, or Er$^{3+}$/Tm$^{3+}$/Yb$^{3+}$ [7].

The Ho$^{3+}$ laser channels so far demonstrated at 300 K in KGW are only $\text{S}_7 \rightarrow \text{I}_8 \lambda = 2.072 \, \mu$m [8] and $\text{I}_6 \rightarrow \text{I}_7 \lambda = 2.934 \, \mu$m [9]. Therefore, more work is required to realize lasing in other channels and to optimize the system performance in these two.

Despite the interest in KGW: Ho as a laser medium, the spectroscopic knowledge and lasing demonstrations reported so far are scarce, and most of the previous information is limited to temperatures at or above 77 K. This makes difficult a detailed understanding of Ho$^{3+}$ optical properties, especially because of the rather low energy splitting ($\lesssim 200$ cm$^{-1}$) of the fundamental $\text{I}_8$ level, the final level for 0.55- and 2-$\mu$m laser transitions. This low splitting allows an efficient electronic population of $\text{I}_8$ Stark sublevels different to the fundamental one, and therefore it influences the laser dynamics to a given temperature. In a previous study of optical absorption and photoluminescence (PL) measurements at 10 K, we have provided a detailed list of the Ho$^{3+}$ energy levels and their assignments have been confirmed by crystal field calculations [10]. The aim of this paper is to provide a survey of the Ho$^{3+}$ PL in KGW, serving as a reference for the analysis of lasing properties and the design of the associated optical elements. Experimental studies as a function of the holmium concentration and temperature, as well as the JO formalism, have been used to estimate radiative and non-radiative probabilities, quantum efficiencies and emission cross sections for the transitions responsible for laser channels.

II. EXPERIMENTAL TECHNIQUES

Inclusion-free KGW$_{1-x}$Ho$_x$(WO$_4$)$_2$ single crystals were obtained by a top-seeded solution growth slow-cooling technique using K$_2$W$_2$O$_7$ as the solvent. The growth procedure is described with more details elsewhere [11]. Crystals of typical size 10–15 $\times$ 8–11 $\times$ 4–4.5 ($c \times a^3 \times b$) mm$^3$
were pulled using b-oriented seeds from 88.5 K2W2O7–11.5
KGd1-xHo2(WO4)2 solutions with four compositions: x = 0.001 (0.1%), 0.01 (1%), 0.03 (3%), and 0.049 (5%).

The level of Gd3+ substitution by Ho3+ was analyzed by
electron probe microanalysis (EPMA) using a CAMECA Camebax SX 50 system. The Ho concentrations obtained in the
crystal were 0.59 × 1020 cm–3 (1%Ho), 1.65 × 1020 cm–3 (3%Ho), and 3.06 × 1020 cm–3 (5%Ho). These results yield a
distribution coefficient of KHo = 0.85–1. The holmium con-
centration in the 0.1% Ho-doped KGW sample was estimated
from a comparison of the optical absorption intensity to be
0.08±0.2 × 1020 cm–3.

The unit cell parameters of the KGd0.951Ho0.049(WO4)2
crystal have been determined by powder X-ray diffraction.
In comparison to undoped KGW, the unit cell volume of 5%
Ho-doped KGW is decreased less than 0.05%. This result
is foreseeable, since the ionic radii of Ho3+ and Gd3+ are
1.015 and 1.053 Å, respectively. Due to its low magnitude,
the Ho-induced lattice contraction has been ignored in the
calculation of the Ho concentrations above.

Optical absorption was measured at room temperature in a
Varian 5E spectrophotometer. Continuous-wave (CW) PL was
excited using ultraviolet (UV) and visible multiline emissions
of a Coherent 5-W Ar+ laser, model Innova 300. The UV excitation
regime partially resembles that achieved under pumping
by a high-current-operated Xe-lamp. The excitation light inten-
sity was in the 10–200-mW range. The emission was analyzed
with a Spex 340E spectrometer (f = 34 cm) and detected with a
cooled R928 Hamamatsu photomultiplier (λ = 185–1060 nm),
or an InSb photovoltaic detector [model Hamamatsu P5968-060
(λ = 1.1–5.5 μm)]. The latter two were cooled to 77 K.
The detector signals were recorded by using a lock-in amplifier.
A nitrogen-excited pulsed dye laser was used for CW-PL measure-
ments with resonant excitation and for lifetime measurements.
In the lifetime measurements, the emissions were monitored
by using the same spectrometer described above and detected
with a GaInAs photomultiplier (λ = 185–1060 nm, fall time
2 ns) connected to a Tektronix TDS520 digital oscilloscope.
The sample temperature was varied in the 7–300 K tempera-
ture range by using flowing liquid-He or closed-cycled cryostats
and the required temperature controllers.

III. EXPERIMENTAL RESULTS

A. Optical Absorption

Following the selection rules imposed by group theory for the
local C2 symmetry of Ho3+ in KGW and taking into account
that the fundamental level belongs to an A irreducible representa-
tion [10], electronic transitions yield polarized spectra, both
in absorption and PL. Transitions between levels with same ir-
reducible representation will be observed with light polariza-
tion parallel to the C2-axis (σ-spectra), while transitions be-
tween levels with different irreducible representation are polar-
ized perpendicular to it (τ-spectra).

This difference with light polarization has, indeed, been ob-
served in the room-temperature optical absorption spectra of
KGW:Ho. Fig. 1 shows an average between optical absorp-
tion σ- and τ-spectra. The inset of Fig. 1 sketches for reference
the energy positions of Ho3+ levels inferred from 7-K measure-
ments [10] and the laser channels of Ho3+.

The experimental oscillator strengths fexp are calculated as

\[ f_{\text{exp}} = \frac{4\varepsilon_0\hbar c^2}{N e^2 \lambda^2} \Gamma_{j,j'} \]  

(1)

where

- c vacuum speed of the light;
- ε0 dielectric constant;
- m, e electron mass and charge, respectively;
- \( \lambda \) average wavelength of the \( J \rightarrow J' \) transition;
- N holmium concentration;

Fig. 1. Unpolarized 300-K optical absorption of KGW:1%Ho. Inset: potential laser channels of Ho3+. 
Table I summarizes the measured oscillator strengths for the 2S + 1L multiplets observed in the σ- and π-spectra.

B. JO Calculations

JO theory [12], [13] is often used to determine the radiative rates of the manifold 2S + 1L levels. The oscillator strength for an electric dipole (ED) transition between 4fᵐ[L, S]J and 4fᵐ[L', S']J' states is

\[ f_{ED} = \frac{8\pi^2mc}{3h(2J+1)} S_{J,J'} \tag{2} \]

where \( \chi = (n^2 + 2)^2/9n \) (n is the refractive index), \( h \) is Planck’s constant, and the line strengths are \( S_{J,J'} = \sum_{m,J,J'}(-1)^m \Omega_R[4f^m[L, S]J][|U|^2]|4f^m[L', S']J'|^2 \). \( \Omega_R \) are the adjustable JO parameters and the reduced matrix elements corresponding to the \( J \rightarrow J' \) transition of Ho³⁺, \(|U|^2\), have been tabulated previously [14], [15]. The Ho³⁺ ⁵S₁ → ⁵I₇ transition also has some magnetic dipole (MD) character. In that case, the MD oscillator strength is given by

\[ f_{MD} = \frac{nh}{6mc(2J+1)} \times |(4f^m[L, S]J)[|L + 2S||4f^m[L', S']J'||^2. \tag{3} \]

The matrix elements of the \([L + 2S]\) MD operator were calculated [16], [17], and the total oscillator strength is given by \( f_T = f_{ED} + f_{MD} \).

Since the JO theory does not consider the crystal field of the lattice, its application to anisotropic solids requires an average of the experimental optical properties. For this reason and following previous works [18]–[20], we have measured separately the absorption of each polarization configuration and the average \( f_{exp} \) set has been calculated as \( f_{exp} = (f_{exp, \pi} + 2f_{exp, \sigma})/3 \). In this calculation, we have used the proper refractive indices of KGW at the corresponding \( \lambda \) of the multiplet [21]. The \( \Omega_R \) set has been obtained for minimizing the \( \sum_{J,J'}(f_{exp} - f_{ED})^2 \) differences. Table I shows the \( \Omega_R \) values obtained for Ho³⁺ in KGW. The quality of the fit is described by the root-mean-square (RMS) deviation, \( \text{RMS} = \sqrt{\frac{\sum_{i=1}^{q}(\Delta f_i)^2}{q-3}} \), where \( \Delta f_i \) are the residuals between the experimental \( f_{exp} \) and calculated \( f_{cal} \) oscillator strengths, and \( q \) is the number of transitions. In spite of a relatively low number of transitions taken into account for the calculations, the RMS deviation in the case of Kgd(WO₄)₂:Ho³⁺ is equal to 4.3 x 10⁻⁷, being similar to the values obtained for other hosts [19], [20].

The \( \Omega_R \) parameters were further used to calculate the radiative rates \((A_{J,J'})\) of the luminescent transitions according to the formula

\[ A_{E_{DJ'}} = \chi \left( \frac{16\pi^3e^2}{3h\varepsilon_0\lambda^3} (2J+1) \right)^2 \times \sum_{k=2,4,6} \Omega_R [(4f^m[L, S]J)|[U]|^2|4f^m[L', S']J'|^2 \tag{4} \]

\[ A_{MD_{DJ'}} = \frac{2mn^2e^2}{\varepsilon_0 mc^2} f_{MD} \tag{5} \]

\( f_{MD} \) is given by (2) for ED and MD transitions, respectively.

The \( A_{E_{DJ'}} \) values of the radiative transition rates calculated for Ho³⁺ transitions related to laser channels in the KGW crystal are summarized in Table II. From the whole \( A_{E_{DJ'}} \) set (not given for the sake of brevity), it is possible to obtain the branching ratios \( \beta_{J,J'} = A_{J,J'}/\sum_{J} A_{J,J} \) and the radiative lifetimes \( \tau_r = 1/\sum_{J} A_{J,J'} \), also given in Table II.

C. PL

Fig. 2 shows an overview of the 7-K Ho³⁺ CW-PL excited by the UV or visible multiline emissions of the Ar⁺ laser. In the first case, ³H₅ and ³F₄+³K₀ Ho³⁺ multiplets are simultaneously excited through 27 548 cm⁻¹ (\( \lambda = 363 \) nm) and 29 895–29 976 cm⁻¹ (\( \lambda = 334.5–333.6 \) nm) laser lines, while in the second, the excitation takes place at the ⁵F₂ multiplet via the 21 008 cm⁻¹ (476 nm) laser emission. The PL emissions observed arise from the de-excitation cascade to levels of lower energy. Under these conditions, the spectral assignments are not straightforward due to the great level number of the Ho³⁺ electronic configuration and the possible overlap of emissions.
TABLE II

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<tr>
<th>λ (nm)</th>
<th>A_{ED,μ} (s^{-1})</th>
<th>β_{μ} (%)</th>
<th>τ_{rad} (μs)</th>
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corresponding to different transitions. In order to eliminate ambiguities in the assignment of the PL bands to electronic transitions, further PL measurements were performed with resonant excitation to energy levels below 5F_{2}. For this purpose, a tunable dye laser was used. The correspondence between the observed emission bands and the electronic transitions is given in Fig. 2.

These assignments deserve some comments.

1) The very narrow energy gap between 5F_{4} and 5S_{2} levels makes difficult to distinguish their contributions to the green emission at about 545–555 nm. At 7 K by resonant excitation into the 5S_{2} level the shape of the emission is very similar to that shown in Fig. 2, therefore most of the emission likely arises from this multiplet. However, it is well known that, at higher temperatures, thermalization of the 5S_{2} population occurs and 5F_{4} \rightarrow 5I_{8} emission, having a higher radiative probability than that for 5S_{2} \rightarrow 5I_{8}, is observed [22].

2) The emission located in the red, λ = 650–665 nm, could correspond to the overlapping of 5F_{3} \rightarrow 5I_{8} and 5F_{3} \rightarrow 5I_{7} transitions. This latter contribution was neglected since the emission shape does not change when the 5S_{2} multiplet is excited.

3) The emission in the near-infrared region λ = 750–770 nm arises from the 5F_{4} + 5S_{2} \rightarrow 5I_{7} transition with thermal considerations similar to those mentioned before. Contribution from the 5I_{4} \rightarrow 5I_{8} transition were neglected in view of the lacking emission excitation at the 5F_{3} multiplet.

D. Up-Conversion

PL from the 5S_{2} level has been also obtained by up-conversion exciting the 5I_{4} multiplet. The emission spectral distribution obtained at 7 K (not shown for the sake of brevity) is similar to that shown in Fig. 2(b). Fig. 3 shows a comparison between the excitation spectra of this IR-excited 5S_{2} PL and the ground state absorption (GSA) of the 5I_{4} multiplet. It is worth remarking that the excitation peaks matching the 5I_{4} GSA spectrum have very weak intensities.

E. Lifetime Measurements

Lifetimes of several multiplets were obtained by resonant excitation on the high-energy side of 5F_{3} (λ_{exc} = 484.5 nm), 5F_{4} + 5S_{2} (λ_{exc} = 540.5 nm) and 5F_{3} (λ_{exc} = 642 nm) multiplets. At the lowest Ho concentration available, namely 0.1%, the intensity decays obtained were single exponential, independently of the sample temperature (7–300 K). This single exponential law was also observed for 1% and 3% Ho-doped samples; however, some departure from the exponential law is observed for 5% Ho doping. Fig. 4(a) shows this behavior for the intensity decays of the 5S_{2} multiplet in 0.1%, 1%, 3%, and 5% Ho-doped samples. The decays of 0.1%–3% Ho-doped samples overlap, giving a τ_{exp}(5S_{2}, 7 K) \approx 19 μs.

The experimental lifetime τ_{exp} is related to the radiative lifetime τ_{rad} of the level and its nonradiative probability τ_{NR} by
The nonradiative probability is expressed as \( \tau_{\text{NR}}^{-1}(T) = \tau_{\text{ph}}^{-1}(T) + \tau_{\text{ET}}^{-1}(T) \), where \( \tau_{\text{ph}}^{-1}(T) \) is the multiphonon emission probability and \( \tau_{\text{ET}}^{-1}(T) \) is the energy transfer probability. For a sufficiently large Ho–Ho distance, \( \tau_{\text{ET}}^{-1}(T) \) is negligible and the light intensity decay becomes single exponential; therefore, the results of Fig. 4(a) suggest that at the 0.1% Ho doping level, energy transfer can be ignored.

Lifetime shortening related to electron relaxation by phonon emission has a probability \( \tau_{\text{rad}}^{-1}(T) = \tau_{\text{ph}}^{-1}(0) \prod_i \left(1 + n_i \right)^{\text{ph}_i(T)} \), where \( n_i = \left[ \exp \left( \frac{h \omega_i}{k_B T} \right) - 1 \right]^{-1} \), \( k_B \) is Boltzmann’s constant, and \( \text{ph}_i(T) \) is the number of phonons with energy \( h \omega_i \) created in the nonradiative transition between levels separated by \( \Delta E = \Sigma h \omega_i \).

The expected \( \tau_{\text{rad}} \) values for Ho\(^{3+}\) multiplets were provided in Table II. The experimental lifetimes of the \( ^5\text{F}_3 \) and \( ^5\text{F}_5 \) multiplets have been found to be nearly temperature independent in the 7–300 K range, and the values obtained have been included in Table II. However, a temperature dependent lifetime was obtained for the emission starting in the \( ^5\text{F}_4 \) and \( ^5\text{S}_2 \) multiplets [see Fig. 4(b)]. For these levels, another source of temperature dependence for the lifetime is the thermal redistribution of the \( ^5\text{S}_2 \) electronic population with the \( ^5\text{F}_4 \) multiplet lying only \( \Delta E = 57 \text{ cm}^{-1} \) above [10]. In that case, the radiative probability becomes \( \tau_{\text{rad}}^{-1}(T) = \left( g_4 \tau_{\text{rad}}^{-1}(0) \right) \prod_i \left(1 + n_i \right)^{\text{ph}_i(T)} + g_2 \tau_{\text{rad}}^{-1}(0) \prod_i \exp \left( -\Delta E/k_B T \right) + g_2^{-1} \exp \left( -\Delta E/k_B T \right) + g_2^{-1} \), \( g_4 \) and \( g_2 \) being the degeneracies of the \( ^5\text{F}_4 \) and \( ^5\text{S}_2 \) multiplets, respectively.

Fig. 4(b) shows the fit of the experimental \( ^5\text{F}_4 + ^5\text{S}_2 \) lifetimes, taking into account the electron population redistribution and phonon emission. The assumption of 3 phonon \( (h \omega = 901 \text{ cm}^{-1}) \) emission is not able to reproduce the temperature lifetime dependence. Emission of phonons with lower energy is required to roughly reproduce the thermal behavior of this lifetime.

The temperature independent multiphonon probability follows the energy gap law \( \tau_{\text{ph}}^{-1}(0) = \beta \exp( -\alpha \Delta E) \), where \( \beta \) and \( \alpha \) are characteristic of the host. A previous attempt to characterize \( \alpha \) and \( \beta \) parameters in KGW was based only on three lifetimes of Er\(^{3+}\) [21]. Fig. 5 shows a recalculation of these parameters on the base of Pr\(^{3+}\) [23], Ho\(^{3+}\) (this work), Er\(^{3+}\) [21], and Tm\(^{3+}\) [24] lifetimes, which cover a broad range in \( \Delta E \). The best fit of the results of Fig. 5 yields \( \beta = 1.4 \times 10^7 \text{ s}^{-1} \) and \( \alpha = 1.4 \times 10^{-3} \text{ cm} \).
Fig. 6. Emission cross sections $\sigma_{\text{EMI}}$ of Ho$^{3+}$ in KGW. (a) $^{5}F_{4} \rightarrow ^{5}I_{8}$ laser channel. (b) $^{5}I_{6} \rightarrow ^{5}I_{6}$ laser channel. (c) $^{5}I_{7} \rightarrow ^{5}I_{8}$ laser channel. Continuous and dashed lines: $\pi$- and $\sigma$-polarized configurations.

IV. DISCUSSION

The laser efficiency of a rare earth-doped solid-state material is related to the intrinsic radiative properties of the rare earth ion and to the losses due to nonradiative processes. Fig. 2 has identified the relevant electronic transitions contributing to a particular emission band of Ho$^{3+}$ in KGW. Once the initial and final Ho$^{3+}$ levels of the transition are known and ignoring the nonradiative processes, it is possible to estimate the emission cross sections for the three Ho$^{3+}$ laser channels terminating on the ground $^5I_8$ multiplet. To this purpose, we use the experimental GSA cross section $\sigma_{\text{GSA}}(\lambda)$ for the three Ho$^{3+}$ laser channels terminating on the ground $^5I_8$ multiplet. To this purpose, we use the experimental GSA cross section $\sigma_{\text{GSA}}(\lambda) = \alpha(\lambda)/N$ and the reciprocity principle [25]

$$\sigma_{\text{EMI}} = \frac{Z_d}{Z_u} C(E_{ud}-h\nu)/k_B T \quad (6)$$

where $Z_u$ and $Z_d$ are the partition functions of the upper and lower multiplets, respectively, and $E_{ud}$ is the energy difference between the lowest Stark levels of these two multiplets.

Fig. 6 shows the spectral dependence of the room temperature $\sigma_{\text{EMI}}$ for $^{5}F_{4} \rightarrow ^{5}I_{8}$ ($\lambda \approx 5.50$ nm), $^{5}I_{6} \rightarrow ^{5}I_{8}$ ($\lambda \approx 1.2$ $\mu$m), and $^{5}I_{7} \rightarrow ^{5}I_{8}$ ($\lambda \approx 2$ $\mu$m) laser channels.

As a first approximation, light amplification could be expected when the emitted light counterbalances the absorption losses. If $P$ is the population fraction of the excited state, this condition can be described as $P\sigma_{\text{EMI}} = (1-P)\sigma_{\text{GSA}} > 0$.

Fig. 7 shows this condition for different polarization configurations in the 2-$\mu$m laser channel. Three emission maxima can be expected at about 2020, 2051, and 2071 nm and, in all cases, the selection of $\sigma$-polarized emission is favored. It is worth remarking that the maximum at 2071 nm agrees very well with the $\lambda = 2072$-nm laser emission actually found in KGW : Ho [8]. This builds confidence in the simulation of Fig. 7 and should encourage further search of the other possible lasing peaks in this channel.

The peak $\sigma_{\text{EMI}}$ obtained for Ho$^{3+}$ in KGW is $\approx 2 \times 10^{-20}$ cm$^2$ (see Fig. 6). This value compares well to those reported in other laser hosts, namely, $\sigma_{\text{EMI}} \approx 1.84 \times 10^{-20}$ cm$^2$ for LiYF$_4$ to $\sigma_{\text{EMI}} \approx 0.28 \times 10^{-20}$ cm$^2$ for KCaF$_3$ [26]. Therefore, efficient laser operation appears possible. However, the nonradiative processes also limit the laser efficiency. In this respect, the KGW lattice has a large energy value of the highest Raman phonon ($\hbar\nu \approx 901$ cm$^{-1}$) and a rich phonon spectrum. In fact, it is clear from Fig. 4 that multiphonon emission is rather relevant, decreasing the radiative emission efficiency. The $^{5}F_{4} \rightarrow ^{5}S_{2}$ luminescence quantum yield at room temperature, $\eta = \sigma_{\text{EMI}}/\sigma_{\text{GSA}} \approx 0.02$, is rather low; therefore, codoping with sensitizing ions should be relevant for efficient laser action. In this respect, the KGW crystal is a good host due to its high rare-earth acceptance level. Generally, 5% rare-earth doping has been achieved without losing optical quality [11]. According to the results of Fig. 4(a), the holmium concentration can be increased up to about 3% without significant enhancement of the Ho–Ho energy migration losses and, therefore, the crystals can be co-doped with a further 2% of other sensitizing ions, Tm$^{3+}$ being the most commonly used.

Another source of losses which may particularly influence the $^{5}I_{7} \rightarrow ^{5}I_{8}$ ($\lambda \approx 2$ $\mu$m) emission yield during optical pumping with diodes is up-conversion. Fig. 3 has evidenced this process in our KGW : Ho samples. The up-conversion excitation may arise from different processes, such as ESA, energy transfer from Ho neighbors (ETU), or photon avalanche [27]. In view of the poor matching between GSA and the up-conversion excitation, the ETU process seems to be less relevant than is excited-state absorption by intermediate levels.
V. CONCLUSION

The relevant electronic transitions contributing to Ho\(^{3+}\) PL in KGW single crystals have been identified in the 7–300 K temperature range. The radiative lifetimes of the \(^5F_3\), \(^5S_2\), and \(^2F_5\) levels of Ho\(^{3+}\) are about two orders of magnitude larger than those measured. This difference has been associated mainly with strong multiphonon de-excitation due to the relatively small energy gaps between holmium multiplets and the large energy of KGW phonons. Energy transfer between Ho impurities becomes important for impurity concentrations above \(3 \times 10^{20} \text{cm}^{-3}\). The peak emission cross sections for the laser channels terminating on the ground \(^1I_8\) multiplet are \(2 \times 10^{-20} \text{cm}^2\). This suggests three main laser-tuning regions (\(\lambda \approx 2.02, 2.05, 2.07 \mu \text{m}\)) inside the \(^1I_7 \rightarrow ^1I_8\) laser channel.

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Dr. Zaldo is a member of the OSA and E-MRS societies.