Upconversion processes in Er^{3+}:KPb_2Cl_5 laser crystals

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Abstract

Energy transfer and dynamics of excited levels population were studied in erbium doped potassium–lead chloride crystals Er^{3+}:KPb_2Cl_5 under direct impurity excitation in UV (at 355 nm) and IR (975–980 nm) spectral ranges. It was shown that emission spectrum of Er^{3+}:KPb_2Cl_5 crystals strongly depends on excitation spectral range. Under direct UV selective excitation of Er ions the population of lower energy levels goes via cascade schemes. Under upconversion IR continuous-wave or pulsed excitation at $^4I_{11/2}$ level the population of upper energy levels goes via excited state absorption and upconversion nonradiative energy transfer. The efficiency of upconversion processes at room temperature is demonstrated. The different ways of Er excited level population are discussed.
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1. Introduction

Potassium–lead double chloride crystals KPb_2Cl_5 (KPC) are known as extremely low phonon energy crystalline matrices, which incorporate rare earth (RE^{3+}) ions. These hosts have low nonradiative relaxation rates and RE doped KPC crystals have been demonstrated to be very advantageous for lasers with upconversion pumping by IR laser diodes (LD), currently they attract large attention of the researchers.

In low phonon energy hosts the upconversion of the excitation energy arising due to excited state absorption (ESA) or nonradiative energy transfer upconversion (ETU) become more effective and govern the population inversion on the working laser levels to a great extent. In such crystals greater number of levels takes part in upconversion processes. The understanding of the processes responsible for creation of the population on the RE levels which can be considered as promising for laser action is of great importance, especially in a case of laser hosts having extremely low multiphonon relaxation rates like Er^{3+}:KPC crystals.

The KPC crystal was found to exhibit superior spectroscopic and mechanical properties desirable for practical solid-state lasers: high chemical resistance, satisfactory mechanical properties, and low hygroscopicity unlike the known simple tri-chlorides. RE ions in KPC crystals demonstrate intense absorption bands and high radiative probabilities [1–3]. All these properties together with extremely narrow phonon spectrum of the host (maximal phonon energy is $h\omega_0 \sim 203\,cm^{-1}$), leading to low multiphonon relaxation rates, make RE doped KPC crystals promising for use as active media for mid-IR and VIS solid-state lasers. Crystals can be grown in a quite-large size with high optical quality for applications in solid-state lasers.

Direct pump laser action in Er^{3+}:KPC at both 1.7 and 4.5 μm on transitions originating from the erbium $^4I_{9/2}$ manifold have been demonstrated in Ref. [4]. Specrtoscopic properties of Er^{3+}:KPC crystals are under study up to now. The absorption and luminescence spectra, Judd–Ofelt intensity parameters, calculated radiative transition

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probabilities, lifetimes and branching ratios of Er ions in KPC crystal are reported in Refs. [2,5,6]. The intense luminescent bands in UV, visible, and near IR spectral regions show that all excited levels of Er^{3+} ions separated by energy gap of $\Delta E > 1400\,cm^{-1}$ in KPC host are radiative, including $^4I_{9/2}$ [6] which is considerably quenched in oxides and fluorides. In Refs. [4,7] it is supposed that erbium doped KPC crystals are promising candidates for mid-IR lasers directly pumped with commercial high-power LDs at 0.67, 0.80 and 0.98 μm.

Erbium-doped crystals are of great interest for lasers with InGaAs LD upconversion pumping at $\lambda = 960$–980 nm, because of peculiar structure of Er energy levels and efficient absorption of LD emission. To predict efficiency of laser action in the mid-IR, visible and UV spectral regions in the Er^{3+}:KPC crystals, information about efficiency of energy transfer processes such as ESA and nonradiative upconversion excitation is required.

In the present work we report on the results of the spectroscopic studies of Er:KPC crystals. Room temperature upconversion spectra and dynamics of Er^{3+} level population were investigated under UV and IR direct impurity excitation, different ways of Er excited level population are discussed.

2. Crystal growth, structure and physical properties

The Er^{3+}:KPC crystals were grown by the Bridgman–Stockbarger technique from a mixture of stoichiometric composition. Starting high purity K and Pb chlorides were multiple purified by zone melting in the presence of chlorine agent $ErCl_3$ that had been synthesized from the Er oxide by high-temperature chlorinating in a CCl_4 flow. The Er^{3+}:KPC crystals were grown in evacuated quarts ampoules. Growth setup was a vertical two-zone furnace with a temperature gradient of about 30 °C/cm. The crystal growth rate was 2–4 mm/d.

The KPC crystals belong to the KCl–$PbCl_2$ system [8–11], they are biaxial and their structure is characterized by a monoclinic space group $P2_1/c$ (C_{2h}^5). Unit cell parameters are: $a = 0.8854$ nm, $b = 0.7927$ nm, $c = 1.2485$ nm, $\beta = 90.05°$ and $Z = 4$ [8].

The peculiarities of substitution of cations by RE ions in RE^{3+}:MPb_2Cl_5 (M = K, Rb) crystals are reflected in optical absorption and photoluminescence spectra. The optical spectra at room temperature exhibit weakly structured bands of inter-multiplet transitions. Stark component structure was determined for the ground and first four excited erbium states in the Er:KPC crystals using spectroscopic measurements performed on oriented single crystals at room and low (10 K) temperature [5]. The quantity and positions of the energy levels were consistent with a single erbium site in the host material. The conclusion was made that the erbium ion replaces only one of the two nonequivalent lead ion sites in the crystal host, with the assumption that a potassium vacancy compensates for the charge difference.

Er^{3+}:KPC crystals with average erbium concentration from 0.6 to 3 mol% and up to 15 mm in diameter and 30 mm long were grown. Oriented samples were prepared for spectroscopic measurements.

Estimates of the erbium entering coefficient in Er^{3+}:KPC gave average value $K_{Er} \sim 0.5$. KPC crystals are transparent in a wide spectral region—from 330 nm up to 20 μm. The average refractive index in the visible region (630 nm) is $n = 2.016 \pm 0.001$ [1] ($n_z = 2.019 \pm 0.001$ and $n_x = 1.982 \pm 0.001$) [6].

3. Experimental methods

Composition of the grown crystals was controlled by chemical and X-ray microanalysis. The erbium concentration in KPC crystals was monitored by X-ray spectral analysis with an electron-probe microanalyzer, as well as by spectral photometric method similar to that reported in Ref. [12].

The absorption spectra are recorded with a PERKIN-ELMER Lambda-900 spectrophotometer at room temperature. The luminescence spectra of Er:KPC crystals were recorded on a spectrometric setup with computer data processing built on the double monochromator DFS-32. Emission of a mercury lamp or an InGaAs LD was used for steady-state excitation.

The luminescence kinetics of Er:KPC were detected at radiation wavelengths corresponding to transitions from excited Er^{3+} levels: $^4F_{9/2}$, $^4S_{3/2}$, $^4F_{7/2}$, $^2G_{9/2}$ and $^4G_{11/2}$ upon short pulse UV laser excitation into $^2G_{7/2}$ level at 355 nm or under short pulse IR laser excitation into $^4I_{11/2}$ level at 980 nm. For luminescence kinetics measurements we used two different selective excitation sources: (i) the third-harmonic generation of Nd:YAG pulsed laser (pulse length 15 ns, < 50 mJ in a pulse at 355 nm, repetition rate 10 Hz), (ii) the second-harmonic generation of Nd:YAG pulsed laser combined with a dye laser (pulse length 15 ns, < 3 mJ in a pulse at 980 nm, repetition rate 10 Hz, linewidth $0.1\,cm^{-1}$). Sample fluorescence was analyzed with a 1 m Hilger & Watts monochromator with dispersion 8 A/mm and detected with a RCA GaAs photomultiplier. Luminescence decay kinetics was measured with a 500 MHz Lecroy oscilloscope. Registration dynamic range exceeded 3 decimal orders. Time-resolved upconversion luminescence spectra were analyzed by an Andor CCD camera combined with ORIEL monochromator.

4. Results and discussion

Room temperature absorption cross-section and emission spectra of Er:KPC crystals were studied in details in Ref. [6]. Intensity parameters, radiative transition probabilities, branching ratios, and nonradiative relaxation rates were estimated by Judd–Ofelt method. Lifetimes of the radiative levels $^4G_{11/2}$, $^2G_{9/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ upon selective excitation were studied. In the Er:KPC absorption spectrum the most intensive band is a narrow