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$Er,Yb:ReGa_3(BO_3)_4$ (Re = Y, Gd) LASER CRYSTALS

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Abstract. Phase relationships in the $Er_xYb_yY_{1-x-y}Ga_3(BO_3)_4$-$Bi_2O_3$-$B_2O_3$-$(Y,Er,Yb)_2O_3$–$Ga_2O_3$ and $Er_xYb_yGd_{1-x-y}Ga_3(BO_3)_4$-$Bi_2O_3$-$B_2O_3$-$(Gd,Er,Yb)_2O_3$ – Ga_2O_3 (x = 0.02, y = 0.11 at.%) system were studied in the temperature range from 1000 to 900 °C. Multicomponent melt Bi_2O_3-Ga_2O_3-B_2O_3-$(Y,Gd)_2O_3$ were used as reasonable fluxes for high-temperature solution growth of $Er_xYb_yR_{1-x-y}Ga_3(BO_3)_4$ (*R* = Y, Gd) spontaneous crystals. The segregation coefficients of Yb and Er impurities in the obtained crystals are determined. The unit cell parameters for the grown crystals were studied, also showing the micromorphology characteristics of the crystals. The luminescence kinetics were investigated, and the lifetimes of the $^4I_{13/2}$ energy level of Er^{3+} ions for $Er,Yb:ReGa_3(BO_3)_4$ crystals were determined.

Key words: erbium; ytterbium; gallium borate; growth; luminescence kinetics.

ЛАЗЕРНЫЕ КРИСТАЛЛЫ $Er,Yb:ReGa_3(BO_3)_4$ (Re = Y, Gd)

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Аннотация. Изучены фазовые соотношения в системах $Er_xYb_yY_{1-x-y}Ga_3(BO_3)_4$-$Bi_2O_3$-$B_2O_3$-$(Y,Er,Yb)_2O_3$–$Ga_2O_3$ и $Er_xYb_yGd_{1-x-y}Ga_3(BO_3)_4$-$Bi_2O_3$-$B_2O_3$-$(Gd,Er,Yb)_2O_3$ – Ga_2O_3 (x = 0,02, y = 0,11 ат.%) в температурном диапазоне 1000-900°С. Выращивание спонтанных кристаллов $Er_xYb_yR_{1-x-y}Ga_3(BO_3)_4$ (*R* = Y, Gd) из высокотемпературного раствора-расплава проводилось с использованием сложного растворителя состава Bi_2O_3-Ga_2O_3-B_2O_3-$(Y,Gd)_2O_3$. Определены коэффициенты распределения ионов Yb и Er, оценены параметры кристаллической решетки, а также определены морфологические особенности полученных кристаллов. Исследованы кинетики затухания люминесценции и определены времена жизни уровня $^4I_{13/2}$ ионов Er^{3+} в кристаллах $Er,Yb:ReGa_3(BO_3)_4$.

Ключевые слова: эрбий, иттербий, кристалл галлиевого бората, рост, кинетики люминесценции.

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A great attention to $RM_3(BO_3)_4$ orthoborate crystals co-doped with Er and Yb is associated with their potential as efficient active media solid-state lasers emitting in the spectral range 1.5–1.6 µm. Due to high phonon frequencies (more than 1000 см$^{-1}$) efficient energy transfer from Yb to Er ions take place in these crystals that is one of the crucial conditions for efficient laser action in Er-Yb co-doped materials. The lasers sources in this spectral range are of high interest due to specific features of this radiation. First of all, laser emission in this spectral range is eye-safe since it is absorbed by cornea and does not reach retina. Secondly, it has low losses in atmosphere and quartz fibers, and thirdly, room temperature sensitive detectors exist in this spectral range. The use of diode-laser pumping with high brightness and efficiency and long lifetime gives opportunities for the development of compact laser sources with unprecendent out parameters in different modes of operation for practical applications. Mode-locked lasers emitting in the spectral range 1.5–1.6 µm with high repetition rate are especially useful as pulse generators for high bit rate optical networks.

Most of these studies were focused on the rare earth aluminum borates $YAl_3(BO_3)_4$ and $GdAl_3(BO_3)_4$, methods for growing single crystals and studying their spectroscopic and laser properties, for example [1; 2]. One of the present work tasks is synthesis of the $YGa_3(BO3)_4$ and $GdGa_3(BO_3)_4$ borates co-doped with Er and Yb ions and investigation of their compositional and optical properties. In contrast to the above borates, orthoborates with gallium $ReGa_3(BO_3)_4$ have been studied relatively little.

For crystal growth process a vertical resistance-heated furnace equipped with a Proterm-100 precision temperature controller and a set of Pt/Rh-Pt - thermocouples was used. A Pt crucibles of 15 ml volume was used in the growth experiments. For the melt crystallization solution $Er_xYb_yY_{1-x-y}Ga_3(BO_3)_4$: ($Bi_2O_3$ - B_2O_3 - R_2O_3 - Ga_2O_3), the following reagents were used: R_2O_3 (R = Y, Gd, Yb, Er) (99.996 %), Ga_2O_3, Bi2O3, B_2O_3 (all A.C.S. grade). The size of the isometric or slightly alongated crystals formed is about 2–3 mm (Figure 1). The crystals are transparent and have a typical for the huntite-type habit.

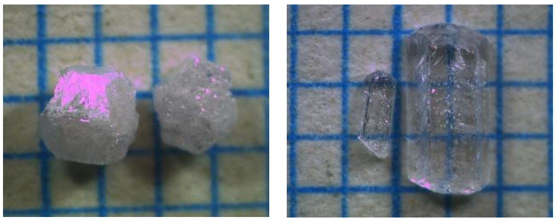


Figure 1 – The $YGa_3(BO_3)_4$ and $GdGa_3(BO_3)_4$ single crystals

The morphological features and elemental analysis were studied by analytical scanning electron microscopy (SEM) technique using JSM-5300 + Link ISIS. Microprobe analysis of unpolishing samples was performed within the accuracy of 0.2–0.3 wt.% using a Cameca analyzer. The micromorphology of the crystal faces is shown in Figure 2. The unusual structure as the characteristic small cracks on the edges of the crystal, are probably associated with the entry of Bi into the YGB structure in an amount of up to 3.5 wt.%.

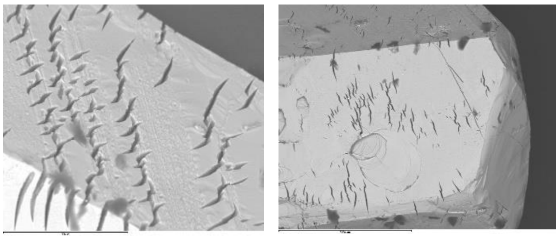


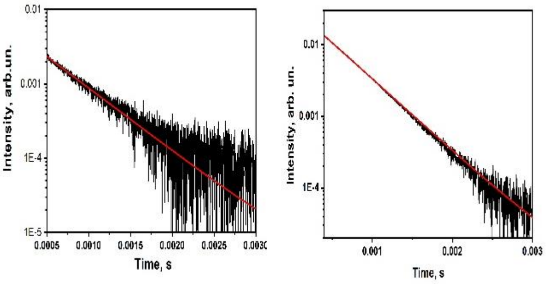
Figure 2 – Micromorhphology of the $YGa_3(BO_3)_4$ and $GdGa_3(BO_3)_4$ crystal faces

For the $Er_xYb_yY_{1\text{-}x\text{-}y}Ga_3(BO_3)_4$ and $Er_xYb_yGd_{1\text{-}x\text{-}y}Ga_3(BO_3)_4$ (x = 0.02, y = 0.11 at.%) crystals, the real impurity segregation coefficients were for yttrium-gallium orthoborate are $Ks_{Er} = 1.0$, $Ks_{Yb} = 0.72$ for the composition-averaged formula $Er_{0.02}Yb_{0.08}Y_{0.89}$ $Ga_3(BO_3)_4$ and, respectively, for gadolinium-gallium orthoborate $Ks_{Er} = 3.0$, $Ks_{Yb} = 1.45$ for the composition-averaged formula $Er_{0.06}Yb_{0.16}Gd_{0.78}Ga_3(BO_3)_4$.

Powder X-ray diffraction (PXRD) studies were carried out on a Rigaku MiniFlex-600 powder diffractometer (Rigaku Corp., Japan). PXRD datasets were collected in continuous mode at room temperature (CuK$_\alpha$ radiation) in the range of 2θ = 3–90°, scan speed of 4° per minute. Phase identification was performed using the ICSD database. Unit cell parameters of $ReGa_3(BO_3)_4$ single crystals obtained by least-squares refinement are as follows $a = b = 9.4367(5)$ Å, $c = 7.4343(5)$ Å, $V = 573.34$ Å^3 for $Er_{0.02}Yb_{0.08}Y_{0.89}Ga_3(BO_3)_4$ and $a = b = 9.4568(3)$ Å, $c = 7.4569(4)$ Å, $V = 577.54$ Å^3 for $Er_{0.06}Yb_{0.16}Y_{0.78}Ga_3(BO_3)_4$.

The lifetime measurements were performed using the optical parametric oscillator based on a β-$Ba_2B_2O_4$ crystal and pumped by the third harmonic of the Q-switched Nd:YAG laser. The fluorescence from the sample was collected on the entrance slit of the monochromator MDR-12 and registered by the InGaAs photodiode with preamplifier coupled with a 500 MHz digital oscilloscope.

The decay curves of 1.5 μm emission ($^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} ions) were single exponential (Figure 3) for both crystals, and the luminescence decay times of the $^4I_{13/2}$ energy level of Er^{3+} were measured to be about 480±20 μs and 450±20 μs for Er,Yb:$YGa_3(BO_3)_4$ and Er,Yb:$GdGa_3(BO_3)_4$ crystals, respectively. The obtained values are close to those presented before for Er,Yb:$ReAl_3(BO_3)_4$ crystals.



a *b*

Figure 3 – Kinetics of luminescence decay of Er,Yb:$YGa_3(BO_3)_4$ (*a*) and Er,Yb:$GdGa_3(BO_3)_4$ (*b*) crystals

The phase relations in this temperature range for the systems $Er_xYb_yY_{1\text{-}x\text{-}y}Ga_3(BO_3)_4$-$Bi_2O_3$-$B_2O_3$-$(Y,Er,Yb)_2O_3$ – Ga_2O_3 and $Er_xYb_yGd_{1\text{-}x\text{-}y}Ga_3(BO_3)_4$-Bi2O3-$B_2O_3$-$(Gd,Er,Yb)_2O_3$ – Ga_2O_3 (x = 0.02, y = 0.11 at.%) were studied. The lifetimes of $^4I_{13/2}$ Er^{3+} energy level were measured for Er,Yb:$YGa_3(BO_3)_4$ and Er,Yb:$GdGa_3(BO_3)_4$ crystals.

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