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Doped YVO_4 crystals: growing, properties and applications

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Results of growing YVO_4 crystals doped with Nd, Er, Yb, Cr are given. Problems of obtaining crystals of high optical quality are discussed. Spectral and generating characteristics of these crystals are discussed. Spectral data of Cr^{5+} in YVO_4 are given. They suggest to create active laser medium with passive Q-switching in single Nd^{3+}, Cr^{5+}:YVO_4 crystal.

Приведены результаты выращивания кристаллов YVO_4, активированных Nd, Er, Yb, Cr. Обсуждаются вопросы получения кристаллов высокого оптического качества. Представлены их спектроскопические и генерационные характеристики. Приведены спектральные данные Cr^{5+} в YVO_4, которые предполагают создание в одном кристалле Nd^{3+}, Cr^{5+}:YVO_4 активной лазерной среды с пассивной модуляцией добротности.

YVO_4 crystal is an excellent birefringent material. It has a lot of advantages over such birefringent crystals as $LiNbO_3$, $CaCO_3$, and TiO_2. The advantages are a large birefringence Δn, a high damage threshold, a wide transparency range (400–5000 nm), a relative simplicity of machining. YVO_4 is widely used in optical communication circuits, optical insulators, light circulators, and polarizers. Doped YVO_4 crystals are very attractive for use in lasers with diode pumping. Compared with well-known Nd:YAG crystal [1], Nd:YVO_4 has 2.7 times larger laser emission cross-section at $\lambda = 1064$ nm and 18 times larger at $\lambda = 1.34$ μm. Moreover, doped YVO_4 crystal has a low generation threshold, good mechanical and chemical properties. First reports on growing YVO_4 crystals from melt have appeared in 1966 [2], however, till now, there is a problem of obtaining high-quality crystals and it is connected first of all with low melting point (680°C) and high vapor pressure of V_2O_5. In this work, we discuss problems of growing Nd:YVO_4, Er:YVO_4, Nd,Cr:YVO_4, Yb:YVO_4, Er,Yb:YVO_4 crystals using Czochralski technique and their spectral and generation characteristics.

To obtain high-quality YVO_4 crystals close to stoichiometric composition, the initial charge was synthesized at temperatures not exceeding 700°C. It allows to keep stoichiometry of the compound and to obtain crystals of high optical quality. Methods of the charge preparation are described in [3].

YVO_4 has the zircon structure (space group D_{4h}^{19} — 14_1/amd) that consists of yttrium-oxygen octahedra and vanadium-oxygen tetrahedra that makes it possible to dope the crystal with rare-earth ions which substitute yttrium as well as with tetra- and pentavalent ions which can substitute vanadium position. We obtained YVO_4 crystals doped with Nd, Er, Yb, Cr ions. The Czochralski technique, iridium crucibles (50–70 mm in diameter, 40–60 mm in height and 1–2 mm in thickness), and Ar + O_2 (0.3–1 vol. %) atmosphere were used for growth. Neodymium concentration was varied from 0.2 to 3.0 at. %, erbium concentration, from 0.5 to 5 at. %, ytterbium, from 0.5 to 12 at. %, chromium concentration was 0.4 wt. %. The rotation rate was 10–20 rpm, the pulling speed, 1–3 mm/h. Diameter of crystals obtained was about 32 mm and length, about 30 mm. Total optical loss in the crystals did not exceed 0.001 cm^{-1}.

The crystals were grown along (100), (001). The best results were obtained at (001) orientation. This is connected first of all with the fact that thermal expansion coefficient along c-axis (a_c = 11.37·10–6/K) is almost three times higher than those along a- and b-axes (a_c = 4.43·10–6/K). So the crystals grown along c-axis, are less subjected to cracking and have small wave front distortion. The optical quality of YVO_4 depends heavily on the activator type and its concentration in the crystal. At Nd concentration >3 at. %, an optical quality deterioration and increase of internal strains was observed in the crystal. When Yb was used as the dopant, the optical quality is not deteriorated at concentrations up to of 10 at. %. This is connected with ratio of ionic radii of Y and the dopant ion. Effective distribution coefficients for ions-dopants are as follows (according to our data): 0.63 for Nd, 0.73 for Er, 0.78 for Yb.

The spectral and generation characteristics of the crystals were investigated at the Institute of Laser Physics, Siberian Division of Russian Academy of Sciences, and International Laser Center (Minsk). The following results were obtained. An intense band with maximum cross-section of 1.3·10–19 cm^2 at 985.4 nm wavelength for π-polarization was observed in absorption spectra of Yb (1.63 at. %):YVO_4 crystal, that allows the use of commercial InGaAs laser diodes for pumping. The radiation lifetime of Yb^{3+} ions in Yb (1.63 at. %):YVO_4 crystal was about 250±5 μs. The maximum output power of 610 mW was achieved at 1020 nm wavelength with differential efficiency of 49 % with respect to the absorbed pumping power. The output emission showed π-polarization for which the stimulated emission cross-section is about 0.9·10–20 cm^2. To generate femtosecond pulses, an X-resonator with the output mirror transmission of 1.6 % was used. Pulses of 61 fs duration at 1021 nm wavelength with pulse frequency of 155 MHz and 10 kW peak power were obtained. A continuous generation with $\eta_{dif.}$ = 72 % and generation in modulated quality mode with η = 48 % were obtained on Nd:YVO_4 (Nd = 1 at. %) crystals. As to the crystals with Nd concentration of 0.4 at. %, the output power was 14 W at 27 W pumping power.

According to EPR data, chromium ions substitute tetrahedral coordinated vanadium ions in YVO_4 lattice and become pentavalent (Cr^{5+}) in the D_{2d} local symmetry [4]. The spectral parameters of chromium ions in YVO_4 crystals are typical of ions with $3d^1$ configuration of the electron shell. The absorption spectrum consists of two absorption bands connected with electron-oscillation transition $^2A_1$–$^2B_2$ and $^2A_1$–^2E of tetrahedrally coordinated Cr^{5+} ion. At room temperature, the absorption band corresponding to $^2A_1$–$^2B_2$ transition with maximum at 10970 nm is polarized along $E//c$ and the $^2A_1$–^2E band with maximum at 670 nm is polarized along $E\perp c$. The luminescence spectrum at liquid nitrogen temperature consists of an about 1500 cm^{-1} wide band peaked at about 14000 nm. The selection rules for absorption and luminescence spectra confirm the data of EPR spectra and coordination of chromium impurity ions in the YVO_4 lattice. The excited state lifetime measured by luminescence quenching was shorter than 20 ns that points to multi-phonon relaxation from excited $^2B_2$ state. At present, Nd^{3+}, Cr^{5+}:YVO_4 crystals are studied with the aim to obtain an active laser medium with passive quality modulation in one and the same crystal.

Thus, YVO_4 crystals doped with Nd, Er, Yb, Cr have been grown. The total optical loss therein was about 0.001 cm^{-1}. Spectral and generation characteristics of the crystals have been investigated. Their high efficiency in diode-pumped lasers has been demonstrated. Investigation of Nd^{3+}, Cr^{5+}:YVO_4 crystals are in progress to clarify their efficiency in passive mode lasers. Generation of Yb:YVO_4 with passive mode synchronization at pulse duration of 61 fs has been obtained, thus evidencing the suitability of these crystals for high-power lasers on the base of thin disk and for generation of ultrashort pulses.

References

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Активовані кристали, вирощування, властивості і застосування

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Приведено результати вирощування кристалів YVO_4, активованих Nd, Er, Yb, Cr. Обговорюються питання отримання кристалів високої оптичної якості. Представлено їх спектроскопічні і генераційні характеристики. Приведено спектральні дані Cr^{5+} в YVO_4, які припускають створення в одному кристалі Nd^{3+}, $Cr^{5+}:YVO_4$ активного лазерного середовища з пасивною модуляцією добротності.