

Synthesis and spectroscopy of YVO₄ crystals activated by Yb³⁺ ions.**СИНТЕЗ И СПЕКТРОСКОПИЯ КРИСТАЛЛОВ АКТИВИРОВАННЫХ
ИОНАМИ**

Voronko J.K., Kochurichin V.V., Sobol A.A., Ushakov S.N., Shukshin V.E.
/Воронько Ю.К., Кочурихин В.В., Соболев А.А., Ушаков С.Н., Шукшин В.Е.

*Laser materials and technology research center IOFAN, Moscow/ Научный центр лазерных
материалов и технологий ИОФАН, г. Москва*

Come into the edition. /Поступила в редакцию

Abstract.

Absorption and luminescence spectrum of Yb³⁺ in Yttrium Vanadate crystals as well as attenuation kinetics of luminescence level of ²F_{5/2} Yb³⁺ ion have been studied. (Absorption and luminescence spectrum of Yb³⁺ in Yttrium Vanadate crystals as well as kinetics of Yb³⁺ ion ²F_{5/2} level luminescence decay have been studied - переводчик). The luminescence profile of ²F_{5/2}→²F_{7/2} Yb³⁺ ion transition in the given crystal was calculated by Fuhtbauer-Ladenburg method. The value of a radiation lifetime Yb³⁺ in YVO₄ is found.

Introduction.

The Vanadate crystals of rare earth elements have essential properties for their usage as laser mediums, therefore they are of great interest for a long time. For the first time Yttrium Orthovanadate monocrystals were obtained more than thirty years ago [1]. It was shown, for example, that YVO₄: Nd³⁺ crystals have higher radiation profile in

comparison with other crystal matrixes. But availability of laser mediums with better thermomechanical properties (in particular, YAG) and the technological problems of commercial laser quality crystal production have greatly restricted the application of YVO₄. The problems of growth were connected mainly with vanadium valence disturbance at YVO₄ matrix entering. Owing to the indicated imperfections, the Yttrium Vanadate spectroscopic properties, activated by different rare-earth ions, were insufficiently studied in the scientific literature. YVO₄ crystals, activated by Nd³⁺, Tm³⁺, Eu³⁺, Ho³⁺ ions of rare earth elements, are mentioned in the monograph of Kaminsky [2]

The spectroscopic study of YVO₄ – 5% Tm³⁺ crystal have been carried out in [3]. The values of absorption and luminescence profiles were obtained, the amplification profile for ³F₄→³H₆ Tm³⁺ ion transition was calculated. The radiation lifetime of Tm³⁺

ion 3F_4 level was measured. The laser radiation during ${}^3F_4 \rightarrow {}^3H_6$ Tm^{3+} ion transition was found at continuous laser pumping on sapphire with titanium. At that the efficiency reached 48 %.

After diode pumping occurrence, the lack of attention to YVO_4 crystals was replaced by a heightened interest, because crystals thermomechanical properties are not so critical at diode pumping usage as at lamp pumping. Moreover, in the present time the technology of crystals growth is considerably improved in comparison with the sixties of past century, for example, now it is possible to get $YVO_4: Nd^{3+}$ crystals of laser quality not by one, but by several methods, including Czochralski method [4].

The spectroscopic investigations of such crystals as $YVO_4: Er^{3+}$, $YVO_4: Tm^{3+}$, $YVO_4: Ho^{3+}$ were carried out in [5,6]. Absorption, luminescence, kinetics of luminescence decay were studied. The radiation profiles of Er^{3+} ion ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$, Ho^{3+} ion ${}^5I_7 \rightarrow {}^5I_8$, Tm^{3+} ion ${}^3F_4 \rightarrow {}^3H_6$ transitions were calculated by adequacy method. As a result the conclusions on possibility of $YVO_4: Tm^{3+}$ and $YVO_4: Ho^{3+}$ crystals usage are drawn for laser radiation generation in the area of about 2 microns.

In a number of works [7,8] the spectroscopy of YVO_4 crystals, activated by Er^{3+} , Tm^{3+} , and coactivated by Yb^{3+} , is studied. At that

the Yb^{3+} ion is considered as sensitizing agent. The comparison of $YVO_4: Tm^{3+}$ 5% and $YVO_4: Tm^{3+}$ 4%: Yb^{3+} 2% crystals is made in [7]. On the basis of Djadd-Ofelt theory the values of phenomenological parameters of Ω_2 , Ω_4 , Ω_6 oscillator forces are received. As a result the authors have drawn a conclusion that the crystal, coactivated by Yb^{3+} , has advantages in comparison with "net" $YVO_4: Tm^{3+}$, since the absorption of non-coactivated crystal in accessible spectral region of pumping is insignificant, and the additive of Yb^{3+} allows to avoid this disadvantage. The authors examined three crystals -- $YVO_4: Er^{3+}$ 0,5%, $YVO_4: Er^{3+}$ 1% and $YVO_4: Er^{3+}$ 1%: Yb^{3+} 2 % in [8]. The laser radiation in continuous operation at ambient temperature was received for all these crystals. Thus, it was possible to achieve discrete radiation wave length reorganization in the area of 1531 - 1604 nm. The maximal efficiency was 19 %. The best results were achieved for a crystal, coactivated by Yb^{3+} .

The considerable number of works, for example, [9-10], dedicated to $YVO_4: Nd^{3+}$ lasers with semiconductor pumping, has appeared during the last years. So, the authors in [10] were able to achieve an average power of 16 W, working in a mode of cavity dumping, with the efficiency of 54%.

Generally speaking, now $\text{YVO}_4:\text{Nd}^{3+}$ crystal is one of the most efficient laser mediums in solid lasers with diode pumping [11].

Along with wide spreading of diode pumping, Yb^{3+} ion attracts increasing attention as the activator, and owing to rather simple (only two levels) scheme of electronic states it has series of advantages over widely used Nd^{3+} : the lack of such negative effects, as absorption in an excited state, up-conversion, cross-relaxation, that can reduce efficiency of laser medium. Besides, during introduction of the activator in YVO_4 crystalline matrix, Yb^{3+} ion is more preferable than Nd^{3+} , as its ion radius is closer to ion radius of Y^{3+} , which is replaced by the activator. And, at last, Yb^{3+} ion absorption band is in a spectral interval of 940-980 nm, i.e. the laser diodes can be used for excitation, and the best technology is developed for such laser diodes to the present time.

The Yb^{3+} lasers mode can be considered as quasi-three-dimensional (including Stark sublevels). It leads to minimum Stokes shift of laser frequency in relation to pumping rate and, consequently, to a minimum heat liberation in laser active element, by that a rather low-level thermal conductivity of YVO_4 crystal is leveled. That makes it possible to create large average power lasers with compact cooling systems and good

quality performances of emanating beam. There is no data in the scientific literature about $\text{YVO}_4:\text{Yb}^{3+}$ crystal spectroscopy.

Crystal growth. The subject of investigation.

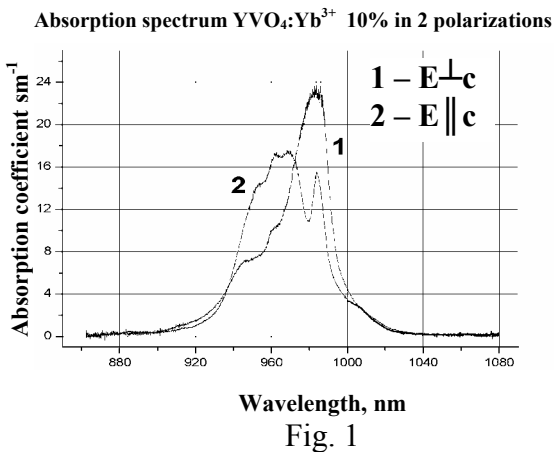
$\text{YVO}_4:\text{Yb}$ crystals were grown by Stepanov method. Yttrium Vanadate is characterized by high growth instability, that considerably complicates obtaining of high-quality crystals with uniform cross section by Czochralski method. At the same time the use of profiled growth technique allows to receive YVO_4 crystal of a given section. Moreover, this method allows to grow several monocrystal cores simultaneously. 4 monocrystal cores of a square section with the side of 3 mm had been simultaneously grown in the present work. The detailed technique of simultaneous crystal growth is described in [12]. The growth was carried out in Ar atmosphere with 1 at % (technical atmosphere %) of O_2 addition. The elongation rate was 1,5 mm per hour. The Yb^{3+} concentration in crystal was 10 at % ($1,2 \cdot 10^{21} \text{ cm}^{-3}$). The grown crystals were annealed in the air at the temperature of 1300°C . Two most qualitative cores of four ones were used for spectroscopic investigations.

Spectroscopic investigations.

We have made a cycle of spectroscopic examinations of Yb^{3+} ion in YVO_4 : the absorption, luminescence spectrums were

recorded, the kinetics of luminescence decay for lifetime definition of an excited state was measured. YVO_4 crystal (D_{4h}^{19} space group, symmetry of D_{2d} cation position) is anisotropic (monoaxial) crystal, that's why the measurements were conducted at different exciting light polarizations, and the geometry of shooting was varied. For luminescence excitation the laser diodes with a tunable wave length (about 988 nm and about 965 nm) were used. The measurements were made on CDL-1 double monochromator with a series of nominal polarizers and light filters. The signal was registered by the cooled photomultiplier of FEU - 83 and was digitized by C 9-8 oscillograph.

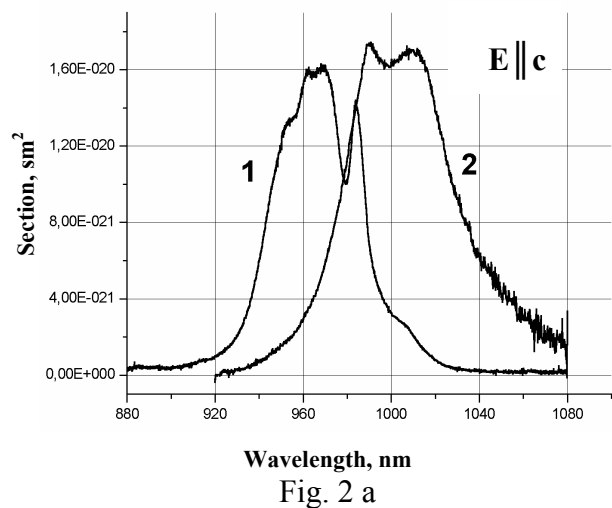
Samples of YVO_4 crystals with Yb^{3+} 10 at % concentration, oriented in such a way, that an axis "c" was positioned in a plane of investigated plates, were studied. The radiation was registered at normal slope on a plate plane in two polarizations ($E \parallel c$ and $E \perp c$). Absorption spectrum of $\text{YVO}_4: \text{Yb}^{3+}$ 10 at % sample is presented in a fig. 1.



The significant discrepancy in spectrums for polarizations $E \parallel c$ and $E \perp c$ can be seen. The similar discrepancies were shown in other classes of monoaxial crystals, for example, KGW and KYW tungstates [13,14], activated by Yb^{3+} . Absorption spectrum consists of broad absorption bands, the long-wave maximum of absorption is in 982 nm wave length. It is necessary to mark the very high absorption factor in comparison with other crystals classes, which can reach $17\text{--}23 \text{ cm}^{-1}$ in absorption maximum at spectrum half-breadth of 57 nm and 26 nm transition, respectively, depending on polarization,. Such spectrum half-breadth considerably exceeds a half-breadth of crystal YAG: Yb^{3+} (11 nm) spectrum.

The luminescent spectrums as well as absorption ones differ depending on polarization and look like very broad bands. Luminescent spectrums of $\text{YVO}_4: \text{Yb}^{3+}$ 10% sample in different polarizations are presented in a fig. 2 (a, b).

Absorption (1) & luminescent (2) spectrums
 $\text{YVO}_4: \text{Yb}^{3+}$ 10%



Absorption (1) & luminescent (2) spectrums

YVO₄:Yb³⁺ 10%

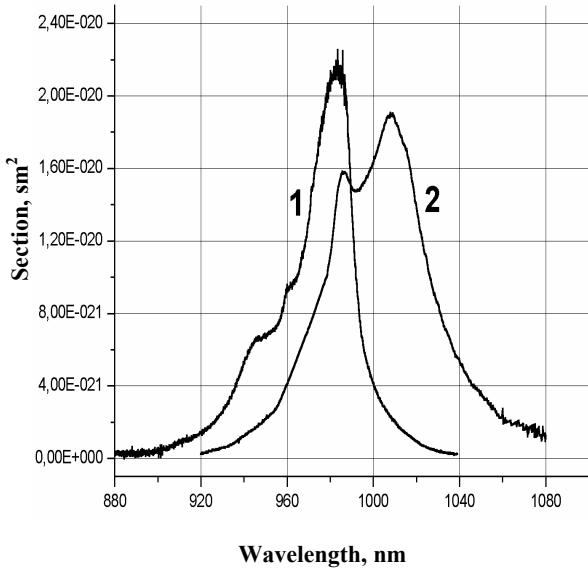


Fig. 2 b

The excitation was made by semiconductor diode with $\lambda = 965$ nm. To minimize the influence of reabsorption effect at luminescence recording, the geometry of luminescence recording at the angle close to 0° towards exciting radiation was used. The luminescence profile was calculated according to the Fuhtbauer-Ladenburg formula:

$$\sigma(\lambda) = \frac{\lambda^5}{8\pi c n^2} * \frac{1}{\tau_R} * \frac{I(\lambda)}{\int \lambda I(\lambda) d\lambda}$$

Where t_R - radiation lifetime, n - index of medium refraction, λ - wave-length, I - intensity, c - light speed. The luminescence maximum is in 1,01 microns wave length. The value of luminescence profile in σ_{em} ($\lambda=1,01$ micron) = $(1,75 - 1,9) * 10^{-20}$ cm² maximum was estimated depending on

polarization by Fuhtbauer-Ladenburg method.

It is necessary to know radiation lifetime for these calculations. For its estimation we have studied luminescence attenuation kinetics of available monocrystal samples. The ²F_{5/2} level lifetime registered in an experiment with volumetric samples was 0,85 ms. As the concentration of the activator is great, the lifetime can be vastly "delayed" due to reabsorption. The reabsorption effect plays sufficiently important role and can greatly influence on the results of experiments. So, in [14,15] works Yb³⁺ ion lifetime in KYW tungstate with small (0,5 at %) activator concentration was estimated in 300-354 mcs depending on sample width, i.e. the results difference can reach 15-17 %.

The method of lifetime measuring on small particles of a sample, suspended in a fluid with index of refraction, close to lifetime of studied crystal refraction is usually applied to reabsorption effect decrease and elimination of complete internal reflection. τ_{rad} was measured by such method in KYbW crystal [16]. By available crystals fragmentation we obtained fine-dispersed YVO₄ powders. The obtained powders were placed in a fluid with refractive index, close to refractive index of YVO₄, and kinetics of Yb³⁺ luminescence decay was measured in powders. The radiation was recorded at

$\lambda=983$ nm wave length at excitation of $\lambda_{exc}=961$ nm.. The kinetics is well described by exponential functions. The lifetime has appeared to be close to 255 mcs for investigated samples, that is likely to be a true value of radiation lifetime. A kinetics of luminescence decay is given in a fig. 3.

The suitable laser medium characteristics working according to quasi-three-dimensional scheme is σ_g value (amplification section), that is calculated according to the formula [17,18]:

$$\sigma_g(\lambda) = \beta\sigma_e(\lambda) - (1 - \beta)\sigma_a(\lambda),$$

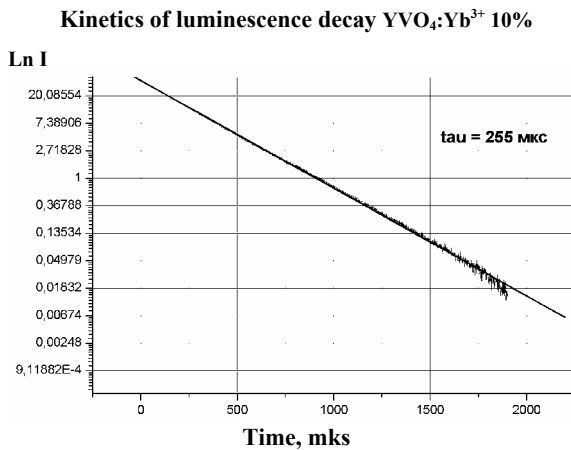
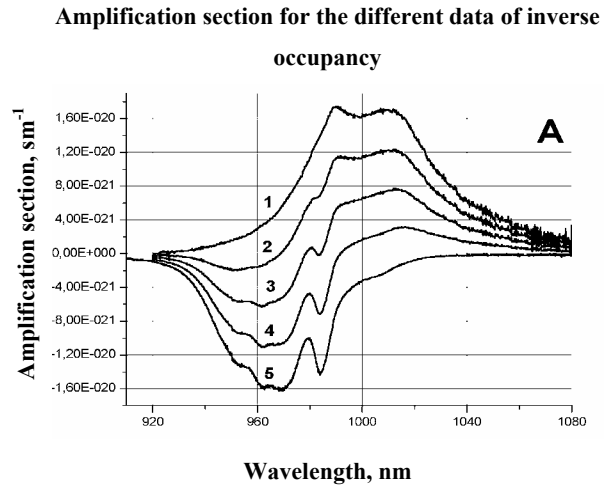


Fig. 3

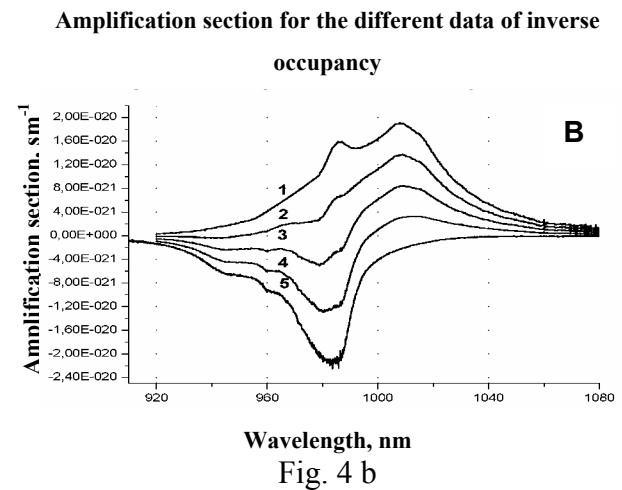
Where σ_e is a luminescence section at selected wave length, σ_a is a section of absorption at the same wave length,

$\beta = \frac{N_e}{N_e + N_f}$ - is the ratio of high level occupancy (N_e) to total number of particles (N_e+N_f). Thus, we at once can get at a given value the inverse occupancy β as an area of possible reorganization of a wave length generation, and value of section of

amplification at selected wave length. The values of σ_g for crystals under investigation in different polarizations are presented in a fig. 4.



Wavelength, nm
Fig. 4 a



Wavelength, nm
Fig. 4 b

Conclusions.

The obtained value of a radiation lifetime in YVO₄: Yb³⁺ 10 at % ($\tau_{rad} = 255$ mcs), that is rather low for Yb³⁺ ion, indicates the large allowance of $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition in this crystal in comparison with other laser crystals. The similar lifetime value is even less, that is observed in other crystal classes, for example, in KGW and KYW tungstates, garnets etc.

The value of luminescence profile in its maximum can reach $1,9 \cdot 10^{-20} \text{ cm}^2$, that is a little less than in YAG: Yb^{3+} ($\sigma_e = 2,2 \cdot 10^{-20} \text{ cm}^2$) crystal, however it poorly differs from peak in a major spectral range, due to large spectral line width and high integral profile of this transition in the given crystal.

One more positive result of band broadening Yb^{3+} in YVO_4 crystal is the broad and smooth amplification contour in the area of 1,0-1,06 microns, that will allow to realize laser radiation wave length reorganization inside a contour or to get impulses of subpicosecond duration in a synchronization state of modes.

At present such laser elements have been produced in which generation production is planned.

Bibliography.

1. J. J. Rubin and L.G. Van Uitert, **“Growth of Large Yttrium Vanadate Single Crystals for Optical Maser Studies”** // Journal of Applied Physics 1966, v. 37, p. 2920-2921
2. А.А. Каминский, Б.М. Антипенко **«Многоуровневые функциональные схемы кристаллических лазеров»** // М., «Наука», 1989, 270 с.
3. K. Ohta, H. Saito, M. Obara et al. **‘Characterization of a longitudinally pumped CW, room-temperature operation of $\text{Tm}^{3+}:\text{YVO}_4$ laser’** // Journal of Applied Physics, vol. 32, No 4, 1993, pp 1651-1657.

4. M.G. Hur, W.S. Yang, S.J. Suh et al. **“Optical properties of EFG grown $\text{Nd}:\text{YVO}_4$ single crystals dependent on Nd concentration”** // Journal of Crystal Growth, 2002, v. 237-239, pp. 745-748.
5. S. Golab, P. Solarz, G. Dominiak-Dzik et al. **“Optical properties of YVO_4 crystals singly doped with Er^{3+} , Ho^{3+} , Tm^{3+} ”** // Journal of Alloys and Compounds, 2002, N 341, pp 165-169.
6. S. Golab, P. Solarz, G. Dominiak-Dzik et al. **“Spectroscopy of $\text{YVO}:\text{Ho}^{3+}$ crystal”** // Applied Physics B, vol.74, 2002, pp.237-241.
7. L. Zhang, G. Wang, S. Lin. **“Synthesis, growth and spectral properties of $\text{Tm}^{3+}/\text{Yb}^{3+}$ -codoped YVO_4 crystal”** // Journal of Crystal Growth, 2002, v. 241, pp. 325-329.
8. L. Sokolska, E. Heumann, S. Kuck et al. **“Laser oscillation of $\text{Er}^{3+}:\text{YVO}_4$ and $\text{Er}^{3+}, \text{Yb}^{3+}:\text{YVO}_4$ crystals in the spectral range around 1,6 μm ”** // Applied Physics B, 2000, vol.71, pp.893-896.
9. P. Li, Q. Wang, X. Zhang et al. **“Analysis of a diode-pumped $\text{Nd}:\text{YVO}_4$ laser passively Q-switched with GaAs”** // Optics and laser technology, 2001, vol. 33, pp. 383-387.
10. J.H. Garcia-Lopez, V. Aboites, A.V. Kir'yanov et al. **“High repetition rate Q-switching of high power $\text{Nd}:\text{YVO}_4$ slab laser”** // Optics communications, 2003, vol. 218, pp. 155-160.
11. H. Zhang, L. Zhu, C. Wang et al. **“Growth, morphology and laser performance of $\text{Nd}:\text{YVO}_4$ Crystal”**// Journal of Crystal Growth, 1999, v.200, pp.199-203.

12. V.V. Kochurikhin, A.E. Borisova, M.A. Ivanov et al. **“Edge-defined film-fed growth of Yb:YVO₄ single crystals: approaches to produce a few crystals simultaneously”**// Journal of Ceramic Processing Research, 2003, v.4, No.3, pp.1-3
13. Brenier A., Metrat G., Muhlstein N. et al. **Growth by the top nucleated floating crystal method and spectroscopic properties of Yb³⁺-doped KGd(WO₄)₂.** // Opt. Mat. 2001. №16. C.189-192.
14. Metrat G., Boudelle M., Muhlstein N. et al. **Nucleation, morphology and spectroscopic properties of Yb³⁺-doped KY(WO₄)₂ crystals growth by the top nucleated floating crystal method.** // Journal of Crystal Growth, 1999. №197. C.883-888.
15. Demidovich A.A., Kuzmin A.N., Ryabttsev G.I. et al. **Influence of Yb concentration on Yb: KYW laser properties.**// Journal of alloys and compounds, 2000, №300-301.P.238-241.
16. Klopp P., Griebner U, Petrov V. et al. **“Laser operation of the new stoichiometric crystal KYb(WO₄)₂”** // Applied Physics B, 2002, v. 74. pp. 185-189
17. Haume R., Haumesser P. H, Viana B. et al. **“Spectroscopic properties and laser performances of Yb³⁺:Y₂SiO₅, a new infrared laser material.”** // ASSL, 2000, v 34. pp. 469-474.
18. Obaton A.F., Parent C, Flem G. et al. **“Yb³⁺-Er³⁺-codoped LaLiP₄O₁₂ glass: a new eye-safe laser at 1535 nm.”**// Journal of Alloys and Compounds. 2000, v. 300-301. pp.123-130.