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Characteristics of lasers based on binary vanadate and orthoborate single crystals with disordered structure

M.B.Kostyna, B.P.Nazarenko, I.O.Radchenko, A.N.Shekhovtsov

Institute for Single Crystals, STC "Institute for Single Crystals" National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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Characteristics of lasers based on the binary orthovanadates $Ca_{10}Li(VO_4)_7$:Nd, $Ca_9La(VO_4)_7$:Nd and the orthoborates $Ca_3RE_2(BO_3)_4$:Nd (RE = Y, Gd) crystals with disordered structure were investigated. For $Ca_3Y_2(BO_3)_4$:Nd crystals laser oscillations was observed for the first time. The obtained slope efficiencies of vanadate-based lasers are comparable with the one of the lamp-pumped laser based on commercial $Y_3Al_5O_{12}$:Nd crystal. The optical breakdown threshold of binary vanadate crystals is higher than that of the orthoborate crystals. For $Ca_{10}Li(VO_4)_7$:Nd and $Ca_9La(VO_4)_7$:Nd crystals the values of optical breakdown threshold are approximately the same — 80 J/cm^2. The optical breakdown thresholds of $Ca_3Y_2(BO_3)_4$:Nd and $Ca_3Gd_2(BO_3)_4$:Nd crystals is approximately twice as low.
Keywords: binary orthovanadates,laser oscillations,optical breakdown.

Исследованы и проанализированы характеристики лазеров на основе кристаллов двойных ортованадатов $Ca_{10}Li(VO_4)_7$:Nd, $Ca_9La(VO_4)_7$:Nd и ортоборатов $Ca_3RE_2(BO_3)_4$:Nd (RE — Y, Gd) с разупорядоченной структурой. На кристалле $Ca_3Y_2(BO_3)_4$:Nd лазерная генерация получена впервые. Полученные КПД для лазеров на основе ванадатов сопоставимы с КПД лазера с ламповой накачкой на основе коммерческого кристалла $Y_3Al_5O_{12}$:Nd. Кристаллы двойных ванадатов характеризуются более высоким порогом оптического пробоя, чем кристаллы ортоборатов. Величина порога оптического пробоя кристаллов $Ca_{10}Li(VO_4)_7$:Nd и $Ca_9La(VO_4)_7$:Nd примерно одинакова и составляет 80 Дж/см^2. Порог оптического пробоя кристаллов $Ca_3Y_2(BO_3)_4$:Nd и $Ca_3Gd_2(BO_3)_4$:Nd примерно в два раза ниже.

Характеристики лазерів на основі монокристалів подвійних ванадатів і ортоборатів з розупорядкованою структурою. *М.Б.Космина, Б.П.Назаренко, І.О.Радченко, О.М.Шеховцов.*

Досліджено та проаналізовано характеристики лазерів на основі кристалів подвійних ортованадатів $Ca_{10}Li(VO_4)_7$:Nd, $Ca_9La(VO_4)_7$:Nd і ортоборатів $Ca_3RE_2(BO_3)_4$:Nd (RE — Y, Gd) з розупорядкованою структурою. На кристалі $Ca_3Y_2(BO_3)_4$:Nd лазерну генерацію отримано вперше. Отримані ККД для лазерів на основі ванадатів співставні з ККД лазера з ламповим накачуванням на основі комерційного кристала $Y_3Al_5O_{12}$:Nd. Кристали подвійних ванадатів характеризуються більш високим порогом оптичного пробою, ніж кристали ортоборатів. Величина порога оптичного пробою кристалів $Ca_{10}Li(VO_4)_7$:Nd і $Ca_9La(VO_4)_7$:Nd приблизно однакова і становить 80 Дж /см^2. Поріг оптичного пробою кристалів $Ca_3Y_2(BO_3)_4$:Nd і $Ca_3Gd_2(BO_3)_4$:Nd приблизно в два рази нижче.

1. Introduction

Interest in lasers with active nonlinear medium (ANM lasers) is due to the fact that they possess a number of advantages over those lasers containing two crystals: active elements and nonlinear crystals. Nonlinear optical losses in ANM restrict the density of the power of the main radiation and, consequently, reduce the influence of amplification saturation that raises the efficiency of laser pumping. Calculations show that in the said lasers the optimum value of the the nonlinear coupling coefficient is approximately by 3–5 times lower than the one for the lasers containing active element (AE) and nonlinear converter (NC). This makes it possible to use crystals with lower values of the nonlinear coupling coefficient. For ANM lasers radiation focusing is not required, therefore, the bulk of nonlinear crystals can be used more effectively. Moreover, an essential drawback of AE+NC lasers is time instability of their radiation at the second harmonic wavelength [1, 2].

The use of ANM has a number of operational advantages. In particular, the use of one element in the resonator instead of two elements raises the reliability of the device, facilitates its adjustment, promotes reduction of the Fresnel losses. Moreover, in this case wave phasing in the gaps between the elements is not required, etc [1].

As concerns materials for effective nonlinear transformation of radiation (frequency doubling), complex oxides with asymmetric spatial arrangement of oxygen bonds with polyvalent metals, such as Ti, V, Nb, Ta are considered to be promising [3]. These compounds are inorganic polymers with chain-like or cyclic arrangement of anionic complexes.

The binary orthovanadates $Ca_9RE(VO_4)_7$ (RE is Y and REE) $Ca_{10}M(VO_4)_7$ (M is alkali metal) have the structure of "whitlockite" type, and are isostructural to calcium orthovanadate $Ca_3(VO_4)_2$. The latter has 5 non-equivalent crystallographic positions of Ca, one of them (Ca(4)) being half-occupied. This structure makes it possible to obtain phase with different compositions at heterovalent substitution of Ca by M^+ and RE^{3+}. So, the use of cations with different charges, ionic radii and polarizability permits to regulate their distribution over the crystallographic positions, to influence deformation of their electron cloud and, consequently, to control the second-order nonlinearity of the material [4].

For creation of compact diode-pumped lasers crystalline matrices with several cations are preferable. Many of such crystals are characterized by crystal structure disordering. At RE^{3+} ion doping they show spatial isolation of the rear-earth cations and, consequently, weak exchange interaction. This causes an essential reduction of concentration quenching of $f-f$ luminescence of the cations and, as a consequence, the possibility to obtain the crystals with a high impurity concentration without worsening of spectroscopic characteristics. In this connection, the binary orthoborate $Ca_3RE_2(BO_3)_4$ (RE =|Y, Gd) crystals seem to be promising.

The values and quantity of the components of the Stark splitting, the strength of the oscillators of induced electric dipole transitions of RE ions will be defined by the local symmetry of the crystal lattice site where the RE cation is located, and by the crystalline field value. Thus, by changing the local symmetry and the crystalline field value one can influence the width of the spectra of RE^{3+} ions (Nd^{3+}, Yb^{3+}), the $f-f$ transition oscillator strength and, consequently, the absorption and luminescence cross-sections [5], as well as to vary the quadratic nonlinearity of vanadates with a structure of "whitlockite" type [4].

Moreover, crystal structure disordering must lead to widening of the spectral bands of the activator ions. In this case temperature stability of the wavelength of a diode laser at pumping of the crystals containing ions with narrow absorption bands, becomes not so critical.

The aim of the present study was determination and analysis of the laser characteristics of the binary orthovanadates $Ca_{10}Li(VO_4)_7$:Nd, $Ca_9La(VO_4)_7$:Nd and the orthoborates $Ca_3RE_2(BO_3)_4$:Nd (RE — Y, Gd). These crystals which possess disordered structures and belong to different systems are believed to be promising for laser engineering.

2. Experimental

In view of high melting temperatures of vanadates (~1500°C) and borates (~1450°C), the crystals were grown in argon atmosphere. Ir crucibles and the "Crystal 3M" type setup with induction heating and automated system of crystal diameter control were used. The direction of the growing crystal coincided with the crystallographic axis [001]. Neodymium was added to the raw material in the form of preliminarily

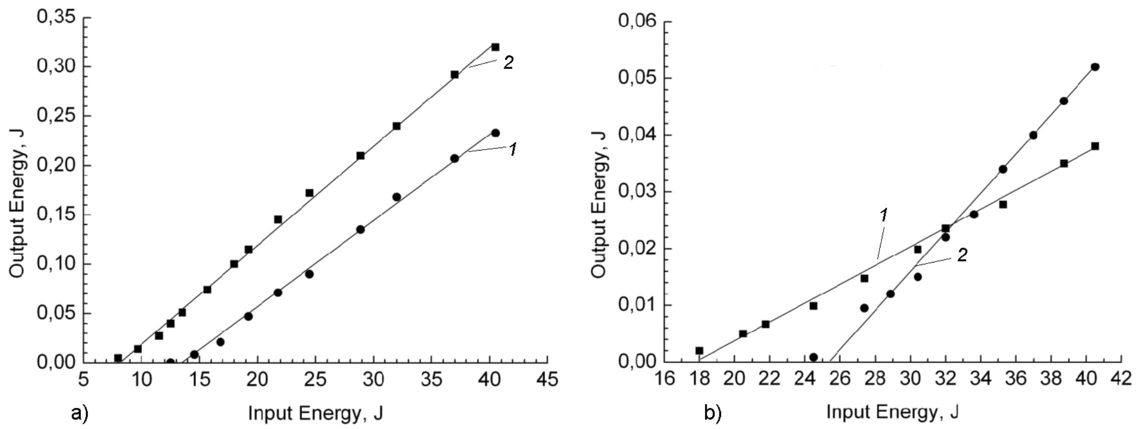

Fig. Laser output vs. the electrical flash-lamp energy: a) — $Ca_{10}Li(VO_4)_7$:Nd (*1*) and $Ca_9La(VO_4)_7$:Nd (*2*); b) — $Ca_3Gd_2(BO_3)_4$:Nd and $Ca_3Y_2(BO_3)_4$:Nd (*2*).

synthesized compounds $Ca_9Nd(VO_4)_7$ and $Ca_3Nd_2(BO_3)_4$, respectively. The conditions of the growth of the vanadate and borate single crystals are described in details in [6, 7].

Under the mentioned conditions there were obtained $Ca_{10}Li(VO_4)_7$:Nd, $Ca_9La(VO_4)_7$:Nd and $Ca_3RE_2(BO_3)_4$:Nd (RE — Y, Gd) single crystals free of bubbles and cracks. According to the data of chemical analysis, the total concentration of uncontrolled impurities in each crystal was not higher than $2–5\cdot10^{-3}$ wt. %. The crystals had a diameter up to 25 mm and a length up to 80 mm.

Laser oscillation in the considered crystals was experimentally studied at lamp pumping in the regime of free generation. The transmission of the output mirror was 37 %. The laser elements were 5 in diameter and 40 mm long.

The laser damage threshold was measured using YAG:Nd^{3+} laser (λ = 1.06 μm) at single-mode generation. Thereat, the pulse repetition frequency was 1 Hz at pulse duration of 10 ns, the spot diameter amounted to 45 μm and the Gaussian distribution of the intensity over the cross-section. The dimensions of the samples for determination of the optical breakdown were 10×10×10 mm^3.

3. Results and discussion

The luminescence spectra of Nd^{3+} ions in binary vanadate and borate crystals contain non-uniformly broadened lines in the region of 900 nm, 1060 nm and 1350 nm corresponding to the transitions $^4F_{3/2} \to {}^4I_{9,11,13/2}$ of Nd^{3+} ion. The spectral and kinetic characteristics of these crystals are studied in detail in [8, 9]. Laser oscillation was obtained using the most effective transition $^4F_{3/2} \to {}^4I_{11/2}$.

As seen from Table 1, the best was achieved for the laser based on $Ca_9La(VO_4)_7$:Nd crystal. The slope efficiency was 0.99 % [10]. The said laser had the minimal generation threshold equal to 8 J. The slope efficiency of $Ca_{10}Li(VO_4)_7$:Nd — based laser was somewhat lower — 0.87 % [11]. Thereat, its generation threshold was by approximately by 1.5 times higher (Fig. 1a). The obtained values of slope efficiency of the vanadate-based lasers are comparable with the one of lamp-pumped $Y_3Al_5O_{12}$:Nd laser [12].

The slope efficiency of $Ca_3Y_2(BO_3)_4$:Nd-based laser was twice as high in comparison with that of $Ca_3Gd_2(BO_3)_4$:Nd-based laser. However, for latter laser the generation

Table. Parameters of lamp pumping lasers based on binary vanadate and orthoborate crystals

Crystal	$Ca_{10}Li(VO_4)_7$	$Ca_9La(VO_4)_7$	$Ca_3Y_2(BO_3)_4$	$Ca_3Gd_2(BO_3)_4$
Concentration C_{Nd}, mass. %	1	2.5	1	2
Luminescence ($^4F_{3/2} \to 4I_{11/2}$) λ_{max}, nm	1068	1067	1062	1062
Generation threshold E_{th}, J	13.5	8	25.5	18
Slope efficiency η_{sl}, %	0.87	0.99	0.34	0.16
Optical breakdown threshold J, J/cm^2	78	80	36	21

threshold was approximately by 30 % lower. It should be also mentioned that the efficiency and generation threshold achieved for $Ca_3Gd_2(BO_3)_4$:Nd-based laser essentially exceeded the corresponding characteristics reported in [13] for the said laser at lamp pumping. The authors of [13] reported 0.04 % and ~50 J, respectively. Note that laser oscillation in $Ca_3Y_2(BO_3)_4$:Nd crystal was achieved for the first time (Fig. 1b).

The concentration of neodymium in the studied vanadate and borate crystals varied in the 1–3 wt. % range. However, the slope efficiency and generation threshold of the binary vanadates and borates were practically independent of the concentration of neodymium.

4. Conclusion

The binary vanadate crystals were found to have a higher optical breakdown threshold in comparison with that of the orthoborate crystals. Thereat, the values of optical breakdown of $Ca_{10}Li(VO_4)_7$:Nd and $Ca_9La(VO_4)7$:Nd crystals were approximately the same (are about 80 J/cm^2). The optical breakdown thresholds for $Ca_3Y_2(BO_3)_4$:Nd and $Ca_3Gd_2(BO_3)_4$:Nd crystals were found to be 36 and 21 J/cm^2, respectively.

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