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Growth of large-size KDP single crystals with high laser damage threshold

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It is shown that the developed method of solvent re-circulation which provides the obtaining of the crystals under optimum growth conditions at a constant temperature (T_{cr} = 80°C, V_{growth} ~ (0.8 ÷ 1.6) · 10^{-6} cm/s, pH = 4) allows to grow KDP crystals with a cross-section up to 300 × 300 mm^2 and a bulk laser damage threshold of ~60 J/cm^2.

Показано, что разработанный метод рециркуляции растворителя, обеспечивающий рост кристаллов при постоянной температуре и оптимальных условиях кристаллизации ($T_{кр.}$ = 80°C, $V_{кр}$ ~ (0.8 ÷ 1.6) · 10^{-6} см/с, pH = 4), позволяет получать монокристаллы KDP сечением до 300 × 300 $мм^2$ с величиной объемной лучевой прочности ~60 Дж/$см^2$.

Large-size KDP single crystals, i.e. those with a cross-section of 300 × 300 mm^2 and more, are widely used as volumetric electro-optical devices (optical modulators, deflectors) for solid-state optical media. They are meant for transformation of the frequency of coherent radiation of powerful picosecond lasers such as generators of 2–5 harmonics of YAG:Nd^{3+} lasers, optical parametric oscillators for the IR region of the spectrum, integral optical waveguides. However, effective use of KDP single crystals is often limited by their low laser damage threshold. At present it is generally recognized that, besides the fundamental physical damage mechanisms [1], the value of breakdown essentially depends on the defects of different nature present in the crystals. In its turn, the presence of defects in the crystals is known to be functionally connected with the growth technique [2, 3].

Investigated in the present paper is the influence of the crystallization conditions (solution acidity, crystallization temperature, solution purification degree) on the laser strength of the grown KDP crystals. A correlation between the density of scattering centers and the laser damage threshold is established.

KDP crystals were grown by the method of solvent re-circulation which provides constancy of the crystallization conditions during the whole of the crystal growth cycle. For growing the crystals, there was used potassium dihydrophosphate containing controllable impurities (Fe, Cr, Al, Sb, Bi, Cu, Hg, Ag, Pb) on the level of 5 · 10^{-5} mass %. The crystals were grown along the direction [100] on a prismatic seed. The temperature of the mother liquor was maintained to an accuracy of ±0.05°C. All the solutions were subjected to micro-filtration by polymer membrane filters with a pore diameter of 0.05 μm. Prior to filtration, the solutions were overheated up to a temperature higher than the saturation point by 30°C, and then kept at this temperature for 24 hours. The process of filtration was carried out under a low pressure (~0.8 kg/cm^2). To maintain a constant growth rate at raising the crystallization temperature up to 70–80°C, the area of evaporation surface was diminished by a diaphragm fixed on the central crystal-carrier shaft. The values of optical homogeneity and bulk radiation strength were determined using the samples measuring 20 × 20 × 20 mm^3 with polished surfaces perpendicular to the axes c and a. The absorption spectra were registered on a SF-56 (LOMO) spectrophotometer at room tem-

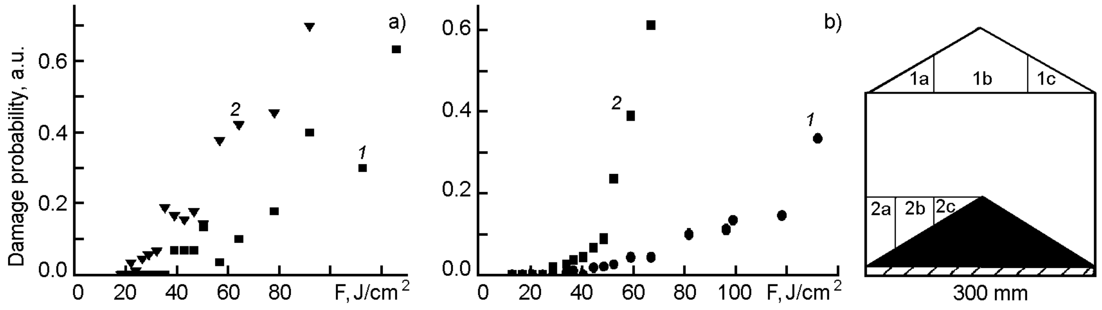

Fig. 1. Damage probability curve for samples: a — pH = 3, b — pH = 2 (*1* — region of the upper pyramid, *2* — region near the seed, crystallization temperature — 60°C).

perature without reference to the Fresnel reflection.

While investigating the laser damage threshold there was used the radiation of single-mode YAG:Nd^{3+} laser ($\lambda = 1.064$ μm, $\tau = 10$ ns), the radiation beam diameter being 1 mm. The radiation was focused on the crystal by a lens with 5 cm focus distance, and this provided a caustic diameter of about 45 μm. Each point of the sample was affected by a single radiation pulse. For any level of radiation intensity I the probability of damage P was defined as the ratio of the quantity of the obtained breakdowns n to the total quantity of the irradiation pulses N. In order to reduce the experimental error of the damage threshold determination, the threshold value was averaged over 90 points. The damage threshold was calculated from the standard formula: $W_{E_i} = 4TE_u/\pi d_f^2$. Here W_{E_i} is the maximum fluence of laser radiation energy for individual sample (J/cm^2), E_u is the energy of laser radiation (J), T is the focusing system transmission, d is the laser beam diameter (cm). The relative error of laser damage threshold determination for each sample was defined by the relative determination error for the incident radiation energy fluence and run into ±15 %.

For visualization of scattering centers in the crystals there was used a unit based on a CCD camera matched with an optical microscope, which allowed to obtain high-quality images at different magnification. The samples were placed on a stand that provided their displacement in the directions perpendicular to the incident radiation. Illumination of the samples was realized by He–Ne laser with an output power of 30 mW. The standard program Live 2000 was used for the capture and treatment of the obtained micro-images.

Variation of the solution pH and, consequently, of the solution composition is one of the methods which allow to control the crystal growth process and the structure perfection of the crystals [3]. There were investigated the values of laser damage threshold (LDT) for KDP single crystals with 300 × 300 mm^2 cross-section grown from the solution with different pH values (2, 3, 4). The results of studying the influence of the solution acidity on the laser damage threshold of the crystals grown from these solutions are shown in Fig. 1a, b. The crystals obtained from non-stoichiometric solutions (pH = 2–3) were found to be characterized by non-uniform distribution of the values of laser damage threshold over the crystal volume. Thereat, the probability of the onset of laser damage abruptly increased in the vicinity of the seed and reached 50 % at ~70 J/cm^2 energies, the maximum values of laser damage (corresponding to the appearance of the first breakdown) being 28 J/cm^2 (pH = 2) and 20 J/cm^2 (pH = 3). In the region of the upper pyramid the threshold value did not exceed 35 J/cm^2. It should be noted that the samples cut out of the upper pyramid (pH = 2 and pH = 3) differed in the character of the increase of breakdown probability with the growth of the incident radiation fluence. For the crystals grown at pH = 3 such a dependence was practically linear, whereas for those grown at pH = 2 the breakdown probability increased slowly and did not reach 50 % even with fluences of the order of 140 J/cm^2.

Study of the samples grown at pH = 4 showed that, irrespective of relatively non-uniform distribution of the values of laser damage threshold over the crystal bulk, even the region of the seed vicinity (sample *2c*) was characterized by high value of the threshold (42 J/cm^2); for the samples cut

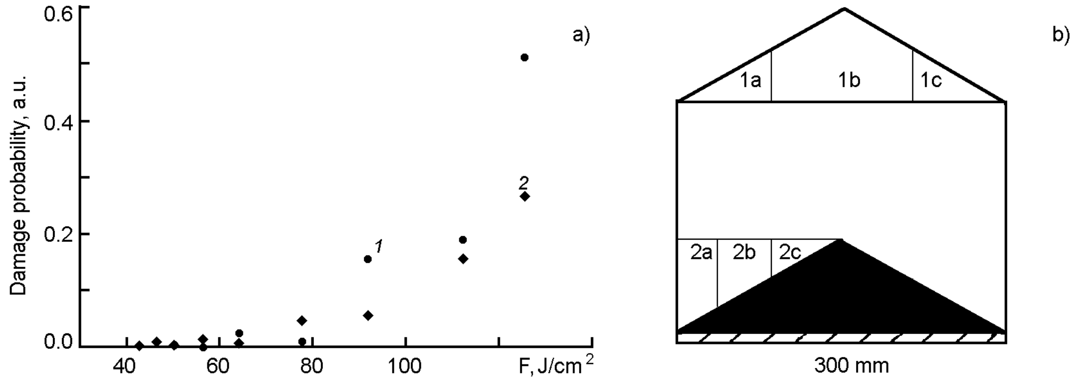

Fig. 2. Damage probability curve for samples: a — pH = 4, b — schematic view of rapidly grown crystal KDP and cut position for the samples.

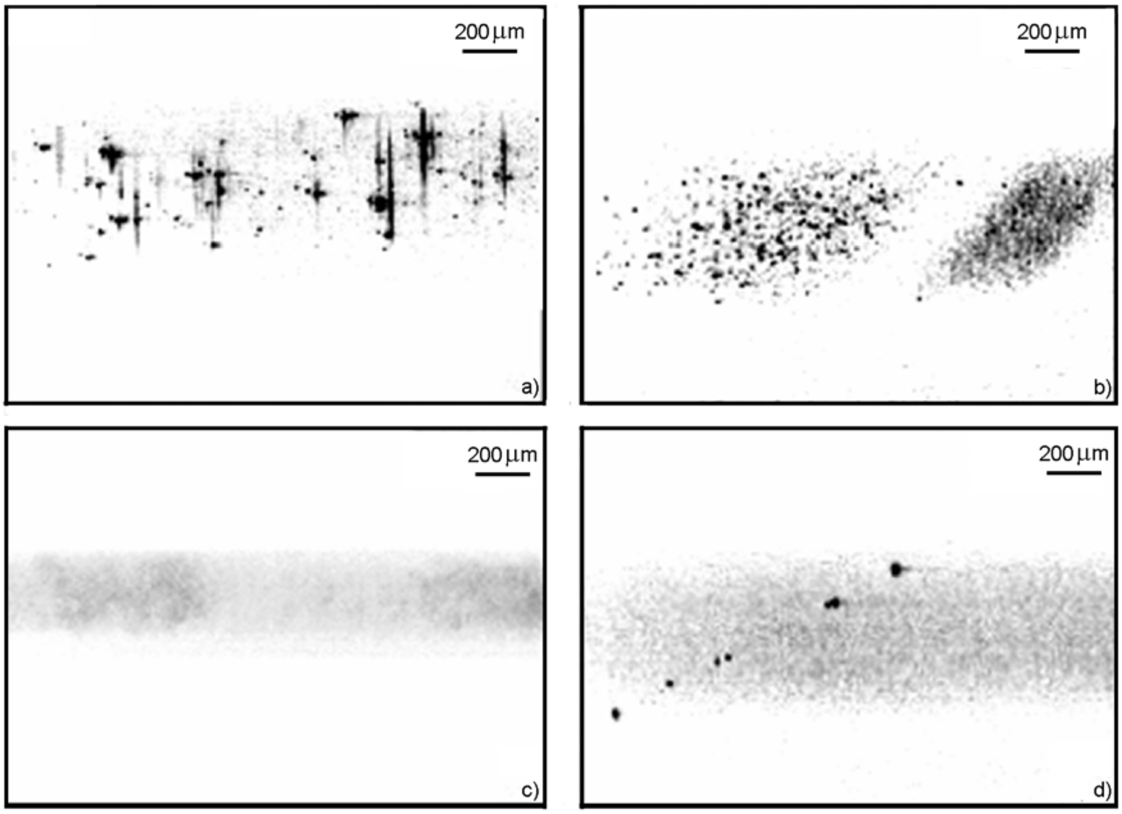

Fig. 3. Light scatter in KDP crystals which was grown with different pH: a — pH = 3; b — pH = 2; c — pH = 4; d — pH = 2÷3.

out of the upper part of the crystal the average threshold value was 48 J/cm^2 (Fig. 2a, b). It should be emphasized that 50 % breakdown probability for the seed vicinity region was achieved at fluences of about 130 J/cm^2; for 1a, 1b and 1c samples such a probability was not obtained at the fluences used.

Analysis of the data on light scattering testified that the crystals grown from non-stoichiometric solutions (pH = 2–3) had a large number of defects such as growth layers, individual defects (Fig. 3a, pH = 3), impurity-streaky structure (Fig. 3b, pH = 2), oriented liquid-phase inclusions (Fig. 3d, pH = 2–3). For the crystals grown at pH = 2, non-uniform distribution of the said effects was characteristic, thereat, their concentration was ~10^4 cm^{-3}. The crystals grown at pH = 3 had rather uniform distribution of different kinds of inhomogeneities measuring 10–50 μm with an average density of

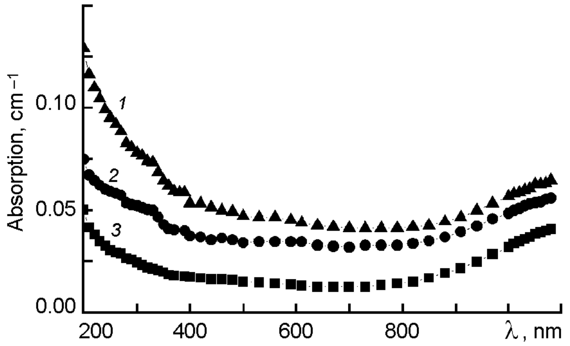

Fig. 4. Variation of absorption spectra in KDP crystals, which was grown with different pH: *1* — pH = 3; *2* — pH = 2; *3* — pH = 4.

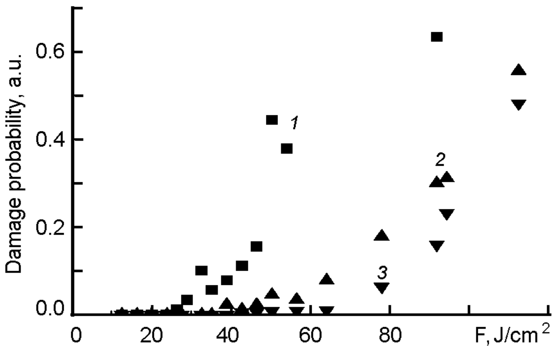

Fig. 5. Damage probability curve for the KDP crystals, which was grown at the different crystallization temperature: *1* — 50°C, *2* — 70°C, *3* — 80°C.

10^6 cm^{-3}. The crystals grown from stoichiometric solutions were characterized by the presence of individual inclusions (Fig. 3c).

As seen from the presented data, deviation from the stoichiometry of the initial solutions (pH < 4) noticeably influences the crystallization process and, consequently, the defect structure of the crystals. This is due to the fact that, in accordance with the phase diagram [4], the excessive acidic component which accumulates in the process of crystal growth in front of the growing crystal face, locally acidifies the solution in close proximity to the growing surface. In its turn, local change of pH in front of the growing face leads to local over-saturation decrease, since KDP solubility is the lowest at pH = 4 and sharply increases when pH changes. Such processes seem to cause inherent inhomogeneity of the crystals grown from non-stoichiometric solutions.

Inherent inhomogeneity of the crystals essentially manifests itself in the absorption spectra, too. In particular, for the crystals (pH = 3) with a high micro-defect density (10^6 cm^{-3}) the absorption in the UV-region of the spectrum increases. The minimum absorption value ($<3 \cdot 10^{-2}$ cm^{-1} at $\lambda = 260$ nm) is characteristic of the crystals with the concentration of scattering centers ~10^2 cm^{-3}, pH = 4 (Fig. 4).

To compare the crystals' non-linear properties there was used the process of generation of the second harmonic of YAG:Nd^{3+} laser radiation ($\lambda = 1.064$ μm (τ=15 ns, at a beam diameter of 3 mm and an initial pulse energy of 30 mJ).

The energy of the second harmonic radiation was measured by a pyroelectric detector, the non-transformed part of the pumping laser radiation being cut off by light filters. The measurements were realized on the samples shaped as plane-parallel parallelepipeds cut out of the crystals at the angle of synchronism for the interaction oe → e (Type II): $\theta = 59^\circ$. The measurement results are presented in Table 1.

Table 1. Efficiency of the conversion of laser radiation into the second harmonic

Sample number (part of the crystal used for cutting it out)	Solution pH	P_1, mJ (λ =1064 nm)	P_2, mJ (λ =532 nm) (conversion efficiency, %)
1 (top)	4	33	7.0 (~22 %)
2 (center)	4	33	6.8 (~20 %)
3 (bottom)	4	33	6.9 (~20 %)
4 (top)	4	33	8.4 (~25 %)
5 (top)	2	33	6.1 (~18 %)
6 (center)	2	33	6.2 (~18 %)
7 (bottom)	2	33	5.9 (~17 %)
8 (top)	3	33	5.9 (~17 %)
9 (center)	3	33	4.9 (~15 %)
10 (bottom)	3	33	4.6 (~14 %)

Table 2. Chemical analyses of KDP single crystals grown at different temperatures

Sample	Crystallization temperature, °C	Content of elements, ppm											
		Ti	Mn	Fe	Co	Ni	Cu	Zn	Bi	Ca	Mg	Ba	Si
14-77	50	0.58	0.024	0.86	<0.01	0.021	0.025	0.022	<0.01	2.00	9.00	5.02	10.00
12-63	50	0.37	0.025	0.93	<0.01	0.021	0.037	0.011	<0.01	1.00	5.00	4.01	20.00
15-23	50	0.35	0.032	1.67	0.02	0.021	0.030	0.045	0.02	3.00	1.00	6.02	15.00
63-65	50	0.34	0.025	0.89	<0.01	0.018	0.028	0.066	<0.01	1.00	1.00	1.00	10.00
1-10	50	0.30	0.029	0.81	0.01	0.018	0.029	0.034	<0.01	5.00	1.00	2.00	10.00
16-27	80	<0.03	0.011	<0.03	<0.01	0.003	0.010	0.028	<0.01	0.10	0.10	0.10	1.00
77-28	80	<0.03	0.012	<0.03	<0.01	0.007	0.010	0.026	<0.01	0.10	0.10	0.10	1.00
17-50	80	<0.03	0.014	<0.03	<0.01	0.007	0.010	0.011	<0.01	0.10	0.10	0.10	1.00
Initial solution		0.11	0.022	0.55	<0.01	0.019	0.021	0.025	<0.01	5.00	5.00	5.00	2.00

The goal of the measurements was to estimate the efficiency of the conversion of laser radiation into the second harmonic in KDP crystals grown at different pH of the solution. Since the energy of the second harmonic proportional to the square of the length of the nonlinear crystal measured under the same conditions, the energy of the second harmonic had to be normalized to the square of the samples' length. The conversion efficiency measured in different crystals varied from 14 to 25 %.

The absolute magnitudes of the obtained values and their spread show that the efficiency of light frequency doubling essentially differs for the studied samples; to a large measure it is defined by the density of the scattering centers. The highest transformation efficiency value is obtained for the crystals which have the least quantity of the light-scattering centers lowest ($\leq 10^2$ cm^{-3}) and the lowest absorption at the working wavelength (≤ 0.03 cm^{-1}).

We analyzed the influence of the crystallization temperature on the laser damage threshold of the crystals. The performed measurements allow to establish that the threshold value increases from 40 J/cm^2 to 60 J/cm^2 as the crystallization temperature changes from 50°C to 80°C, respectively (Fig. 5). As seen from the chemical analysis results, the KDP crystals grown at 80°C the quantity of the impurities Ti, Ni, Fe, Mg, Ba, Ca, Si is by an order lower in comparison with that in the crystals grown at 50°C, the chemical composition of the raw material being the same (Table 2).

Analysis of the data on light scattering shows that the increase of the crystallization temperature from 50°C to 80°C leads to the decrease of the density of scattering centers in the crystals. For instance, in the crystals grown at 80°C scattering centers are practically absent in the whole of the crystal bulk, and only individual micro-defects which size is ~5–10 μm are observed. At the same time, in the crystals obtained at 50°C the concentration of scattering centers is high.

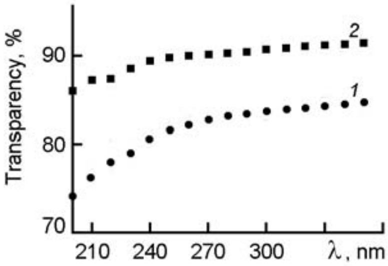

Fig. 6. UV-absorption spectra in KDP crystals which was grown at the different crystallization temperature: *1* — $T_{cryst.}$ = 50°C, *2* — $T_{cryst.}$ = 80°C.

The influence of the crystallization temperature is also seen in the transmission spectra, especially near the fundamental absorption edge. For instance, the characteristic transmission values are 70 % and 86 % at λ = 260 nm for the crystals obtained at 50°C and 80°C, respectively (Fig. 6). The positive influence of the temperature may be caused by several factors [5–8] such as changes in the structure and properties of the growth solution itself (e.g. density, viscosity, thermal motion and degree of ion hydration, formation of nuclei), changes in the structure of the crystal surface, in particular, in the concentration of slopes on the steps [6], diminution of the intensity of inter-sectorial boundary formation [7], decrease of impurity adsorption on the surface due to shift of the equilibrium "adsorption <–> desorption to the right" [8]. At lower temperatures effective capture of impurities by the growing crystal results in the formation of different kinds of defects.

In conclusion, the performed investigations allow to establish a correlation between the values of laser damage threshold and UV-absorption. The existence of certain correlation between the data on the value of laser strength, the concentration of scattering centers and the absorption spectra permits to assume that there exist a single physical nature of the centers responsible for both the decrease of laser strength and the changes in the absorption spectra. Unfortunately, the nature of absorption centers was not established in the present research. It will be the object of further investigations.

References

1. 1. A.A. Manenkov, *Kvantovaya elektronika*, **33**, 639, (2003).
2. H. Yoshida, T. Jitsuno, H. Fujita, M. Nakatsuka et. al, *Appl. Phys. B*, **70**, 195 (2000).
3. N.Zaitseva, L.Carman, *Prog. in Cryst. Growth and Charact.*, **43**, 1 (2001).
4. V.S.Veintemillas, C.R.Rodrigues, *J. Cryst. Growth*, **23**, 243 (1974).
5. I.V.Gavrilova, in: Crystal Growth, Nauka, Moscow, **79**, 198 (1986) [in Russian].
6. S.S.Fridman, N.S.Stepanova, A.V.Beluatin, in: Crystal Growth, Nauka, Moscow, **9**, 79 (1972) { in Russian].
7. Yu.N. Velikhov, I.M. Pritula, M.I. Kolybaeva, V.I.Salo, *Neorg. Mat.* **36**, 880 (2000).
8. E.B. Treyvus, *Krystallographiya*, **34**, 1053 (1989).

Вирощування крупногабаритних монокристалів KDP з високим порогом променевої стійкості

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Показано, що розроблений метод рециркуляції розчинника забезпечує ріст кристалів при постійній температурі і оптимальних умовах кристалізації ($T_{кр.}$ = 80°C, $V_{кр}$ ~ $(0.8 \div 1.6) \cdot 10^{-6}$ см/с, pH = 4), дозволяє одержувати монокристали KDP перерізом до 300 × 300 мм^2 з величиною об'ємної променевої міцності ~60 Дж/см^2.