Growth and characterization
of urea-doped KDP crystals

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Potassium dihydrophosphate single crystals were grown from aqueous solutions onto a point seed using temperature reduction method by doping with different molar values of Urea. The characterization of the grown crystals was made by visible and fourier transform infrared spectroscopy, Vicker's hardness studies, X-ray powder diffraction, nonlinear optical and laser damage threshold measurements. By comparing these crystals with the ones grown from the pure solution, it is shown that 0.2÷2.0 M of the Urea additive enhances the laser damage threshold and the second harmonic efficiency more than by 25 and 20 %, respectively. The Vicker's hardness studies carried out on (100) and (001) crystallographic planes show an increased hardness of the doped crystals (grown in the presence of Urea additive) on the plane (001) in comparison with that of pure potassium dihydrophosphate crystal.

Методом снижения температуры на точечной затравке выращены монокристаллы дигидрофосфата калия (KDP) из водных растворов с различной концентрацией карбамида. Выращенные кристаллы исследованы методами стандартной спектрофотометрии, ИК спектроскопии, прецизионной рентгеновской дифрактометрии. Изучено влияние примеси карбамида на нелинейно-оптические свойства, лазерную прочность и микротвердость кристаллов KDP. Показано, что для кристаллов, выращенных из растворов с содержанием карбамида 0.2÷2.0 M, наблюдается увеличение порога лазерной прочности на 25 % и эффективности генерации второй гармоники более чем на 20 % по сравнению с чистыми кристаллами. На основе сравнительного анализа значений микротвердости для кристаллографических плоскостей (100) и (001) установлено увеличение механической прочности допированных кристаллов (выращенных в присутствии карбамида) на плоскости (001) по сравнению с чистым кристаллом KDP.

During recent few years the scope for the creation of new non-linear optical media based on complex combinations of water-soluble inorganic matrixes with organic and inorganic impurity is being actively discussed in the scientific literature. Thereat, special consideration is given not only to the possibility of changing significant functional characteristics of the crystals, but also to the creation of new properties which are not peculiar to the pure crystals [1].

Undoubtedly, KDP belongs to those crystals which are successfully used as a model system for studying the mechanism of crystal growth from the solution, as well as for finding out a relation between non-linear optical properties and crystal structure. This is caused, first of all, by rather simple growth set-up, high structure perfection of water-soluble crystals, the possibility to essentially vary the crystallization conditions, i.e. the temperature, the solution acidity,
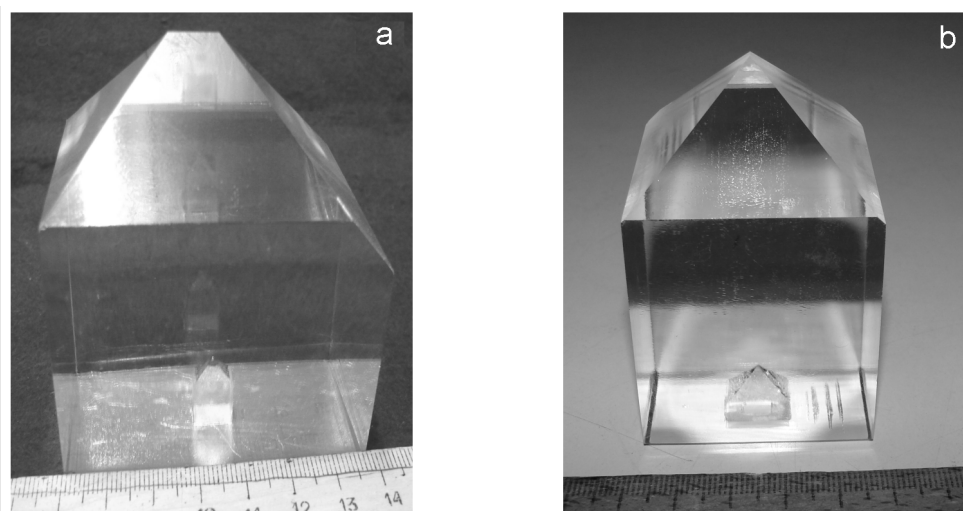
Fig. 1. As grown crystals: the KDP crystal grown from the mother liquor with 0.2 M Urea additive (a), the KDP crystal grown from the mother liquor with 2 M Urea additive (b).

the types of the introduced impurities (e.g. organic molecules [1–3]). As shown in [1, 4, 5–8], KDP crystals can absorb a variety of organic molecules, such as chicago sky blue, amaranth, sunset yellow, trypan blue, direct blue, fast red extra, stilbene, xylenol orange, methylthymol blue, urea, ethylenediamine tetra acetic acid (EDTA), ethanol, 1-propanol, etc. The mechanism of the incorporation of organic molecules into the crystal lattice of KDP is discussed in [9, 10] where an essential role of local stereochemical affinity between the impurities and the matrix is considered. The study of the kinetics of KDP crystal growth in the presence of some organic molecules (Urea, Ethanol, 1-Propanol) [8] shows that the addition of Urea to the mother liquor practically does not influence the growth rate for the faces.

By analyzing the influence of Urea on the optical, non-linear and strength characteristics of KDP crystals, Podder [11] showed Urea-doped KDP crystals to have a higher mechanical strength in comparison with the pure crystals. Indeed, for the growth sectors {001} the Vickers hardness of the doped crystals increased by approximately 10 % at applied indenter loads ranging between 15 g and 100 g. It is interesting to note that, by introducing Urea into KDP solution the author of the mentioned paper managed to obtain KDP crystals with a higher efficiency of the second harmonic generation.

The present paper reports the new results of studying the structural, optical and strength (laser damage threshold, microhardness) characteristics of KDP crystals

grown from the solutions doped with Urea (CH_4N_2O).

KDP single crystals were grown from water solution onto a point seed by the temperature reduction method in $30 \div 50$°C range. There were obtained both pure KDP crystals and those with different molar values of Urea in the mother liquor (0.2; 1.0; 2.0; 5.0 and 10 M; the solubility of Urea at the water at 25°C exceeds 20 M/L). The crystals were grown from stoichiometric solutions with pH = $4.0 \div 4.1$. As a raw material, we used potassium dihydrophosphate salt with a content of micro-impurities not higher than $1 \cdot 10^{-4}$ mass. %. The content of micro-impurities in the raw material and in the grown crystals was determined by inductively coupled plasma-atomic emission spectrometry [12].

The physical characteristics of the crystals were investigated using $10 \times 10 \times 10$ mm^3 satellite samples obtained from the growth sectors {101} and {100} with working surfaces subjected to grinding and optical polishing. The grown crystals are shown in Fig. 1.

The transmission spectra in the region of 200–1100 nm wavelengths were measured by means of automated UV-Vis-NIR Perkin-Erlmler spectrophotometer; for IR-measurements (400–4000 cm^{-1} region) Fourier spectrometer of Brucker IFS 66 type was used (the samples were mixed with KBr and pressed into pellets, 2 mg of the studied sample per 9 mg of KBr). The value of Vickers microhardness H_V was measured by PMT-3meter at loads ranging within $10 \div 200$g interval. The laser damage threshold was determined using single-mode
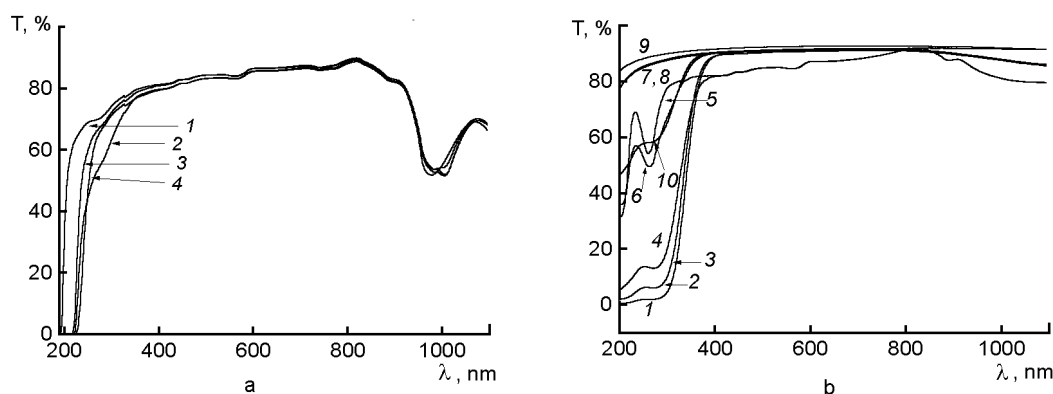
Fig. 2. a) UV-Vis-NIR absorption spectra of the solutions: pure KDP (*1*), KDP+10 M Urea (*2*), KDP+5 M Urea (*3*), Urea (*4*); b) UV-Vis-NIR absorption spectra of the crystals: KDP+2 M Urea {100} (*1*), KDP+1 M Urea {100} (*2*), KDP+5 M Urea {100} (*3*), KDP+10 M Urea {100} (*4*), KDP+10 M Urea {101} (*5*), KDP+5 M Urea {101} (*6*), KDP+1 M Urea {101} (*7*), KDP+2 M Urea {101} (*8*), pure KDP {101} (*9*), pure KDP {100} (*10*).

$YAG{:}Nd^{3+}$ laser working in modulated Q-factor regime. X-ray diffraction analysis of the samples was realized by means of DRON-3M diffractometer in monochromatized CoK_β radiation (with asymmetric flat LiF monochromator, the reflection {200}). For high-precision determination of the crystal lattice parameters by the Bond method there was used a multipurpose three-crystal X-ray diffractometer [13].

To study possible influence of Urea impurity on the transmission of the grown KDP crystals, we measured the spectra of the initial KDP solutions, of KDP solutions with 5 and 10 M Urea concentrations, as well as of pure Urea solution. The obtained data show (Fig. 2) that, due to the introduction of Urea into the solution, the absorption edge is shifted towards the long-wavelengths region by 30 nm (Fig. 2a, curves *2* and *3*). The long-wavelengths region of the spectrum is characterized by the presence of the absorption band at $\lambda = 976$ nm typical of KDP water solutions and connected with oscillations of OH-ions of water. An additional band at $\lambda = 1000$ nm caused by oscillations of NH group of Urea is observed for Urea water solution.

The transmission spectra of pure and Urea-doped crystals are shown in Fig. 2b. As is seen, in the region of 300–1100 nm all the crystals are transparent, irrespective of the content of Urea in the initial KDP solution. At wavelengths shorter than 300 nm UV absorption with a maximum at 270 nm sharply increases for all the samples made from the growth sectors {100} (Fig. 2b, curves *1–4*, 10). For the growth sectors formed by the pyramid faces {101}

the mentioned absorption band is observed only for the samples grown from KDP solutions with 5 and 10 M contents of Urea.

According to the literature data [14], the main cause of UV-absorption in KDP crystals is the presence of impurities of polyvalent metals (their segregation coefficient for the prismatic sector is ~1, for the pyramidal sector it is by an order lower). The chemical analysis of the grown crystals for the content of micro-impurities (Table 1) shows that the presence of Al^{3+} in the prismatic and pyramidal sectors differs by an order. Thus, the absorption band at $\lambda = 270$ nm in the prismatic growth sectors {100} may be caused by the incorporation of Al^{3+} into the crystal.

KDP crystal belongs to the tetragonal-scalenohedral symmetry $\bar{4}2m$; its unit cell dimensions are $a = b = 7.452$ Å and $c = 6.974$ Å [15, 16].

Powder X-ray diffraction analysis performed for nominally pure KDP crystals and for the ones grown from the solution containing Urea (10 M) does not reveal the presence of other phases (Fig. 3), the sensitivity of the method being ≤2 mass. %. The diffraction patterns show an insignificant rise of the parameter *c* of the lattice of the crystals grown from Urea containing solutions.

To determine the lattice parameters of the grown crystals more precisely, the parameter *c* depending on the concentration of Urea in the solution was measured and calculated by the Bond method using a three-crystal diffractometer in $Cu\ K_{\alpha 1}$-radiation.

As seen from Fig. 4, the crystal lattice parameter c ($\Delta c = 1.4 \cdot 10^{-3}$) essentially increases with the addition of 0.2÷2 M of
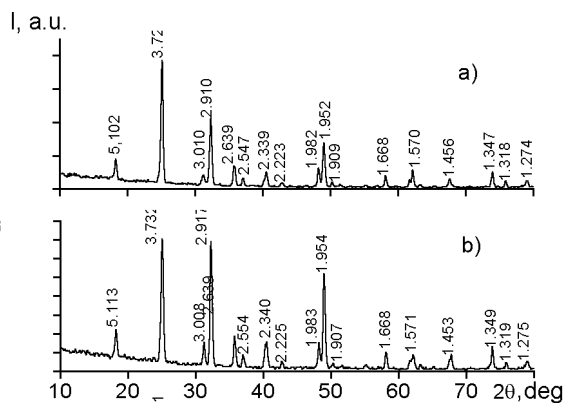
Fig. 3. Diffraction patterns of the samples: nominally pure KDP crystal (a), KDP crystal grown from the solution containing 10 M of Urea (b).

Fig. 4. Dependence of KDP lattice parameter c on Urea concentration in the solution.

Urea to the solution. At Urea concentrations exceeding 2 M the observed increase in the lattice parameter is insignificant. Such a behavior of the parameter c depending on the concentration of Urea in the solution testifies to an intricate character of the incorporation of different complexes into the crystal lattice of KDP. The behavior of the lattice parameter a is by an order less sensitive to the changing Urea concentration in the solution and is on the level of the error of the experiment.

FTIR spectra of powdered samples of KDP crystals grown from the pure solution and from the solutions containing Urea (0.2 M and 10.0 M) are shown in Fig. 5. Table 2 presents the wavenumbers of the absorption maxima in these spectra.

The obtained results testify that all the IR spectra are practically identical and agree with the available literature data, e.g.
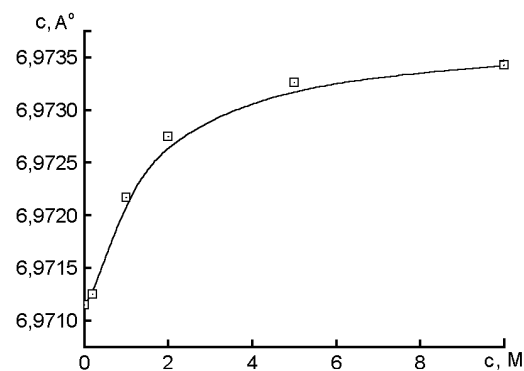
[17]. The comparative analysis of IR-absorption in the pure crystals and in those containing Urea does not show essential features of the spectrum related to the presence of Urea in the lattice of KDP. Nevertheless, it should be assumed that the band with the maximum $\nu = 900$ cm^{-1} (Fig. 5, curves *2* and *3*) is connected with an out-of-plane bending of (N_2CO) group whereas the band with $\nu = 1640$ cm^{-1} is caused by the C–O stretching of Urea. Finally, the wide weakly pronounced band at about 3450 cm^{-1} is evidently due to the overlapping peaks of the asymmetric stretching of NH_2 of Urea and OH stretch of KDP. In our opinion, the mentioned indirectly testifies to the presence of functional Urea groups in the crystals and to some extent it agrees with the results of the measurements of the crystal lattice parameter c.

The microhardness (H_V) was measured at room temperature. The typical descent rate of the indenter is ~1 mm/min., the time of

Table 1. The amount of the inorganic impurities in KDP crystals, mass. %

| Sample	Fe	Al	Mg	Si	Cu	Mo/Ni	Co/Cd
Raw material	$<5{\cdot}10^{-5}$	$7{\cdot}10^{-5}$	$5{\cdot}10^{-5}$	$<1{\cdot}10^{-3}$	$2{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
Mother liquor after growing	$1{\cdot}10^{-4}$	$2.7{\cdot}10^{-4}$	$5{\cdot}10^{-5}$	$<1{\cdot}10^{-3}$	$2{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+0.2 M Urea, {101}	$2{\cdot}10^{-4}$	$1{\cdot}10^{-4}$	$<2{\cdot}10^{-5}$	$1{\cdot}10^{-3}$	$3{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+0.2 M Urea, {100}	$5{\cdot}10^{-4}$	$4.1{\cdot}10^{-3}$	$<2{\cdot}10^{-5}$	$3{\cdot}10^{-3}$	$3{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+1.0 M Urea, {101}	$1{\cdot}10^{-4}$	$2{\cdot}10^{-4}$	$<2{\cdot}10^{-5}$	$3{\cdot}10^{-3}$	$2{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+1.0 M Urea, {100}	$2{\cdot}10^{-3}$	$5{\cdot}10^{-3}$	$<2{\cdot}10^{-5}$	$1{\cdot}10^{-3}$	$2.4{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+2.0 M Urea, {101}	$5{\cdot}10^{-5}$	$3.6{\cdot}10^{-4}$	$<2{\cdot}10^{-5}$	$1{\cdot}10^{-3}$	$2{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+2.0 M Urea, {100}	$2.1{\cdot}10^{-4}$	$4{\cdot}10^{-3}$	$<2{\cdot}10^{-4}$	$1{\cdot}10^{-3}$	$2{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+5.0 M Urea, {101}	$<5{\cdot}10^{-5}$	$1{\cdot}10^{-4}$	$<2{\cdot}10^{-4}$	$1{\cdot}10^{-3}$	$2{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+5.0 M Urea, {100}	$5.6{\cdot}10^{-4}$	$3{\cdot}10^{-3}$	$<2{\cdot}10^{-4}$	$1{\cdot}10^{-3}$	$2{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+10.0 M Urea, {101}	$<5{\cdot}10^{-5}$	$2{\cdot}10^{-4}$	$<2{\cdot}10^{-4}$	$1{\cdot}10^{-3}$	$2{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
KDP+10.0 M Urea, {100}	$3.7{\cdot}10^{-4}$	$4.6{\cdot}10^{-3}$	$<2{\cdot}10^{-4}$	$1{\cdot}10^{-3}$	$2{\cdot}10^{-4}$	$<5{\cdot}10^{-5}$	$<5{\cdot}10^{-5}$
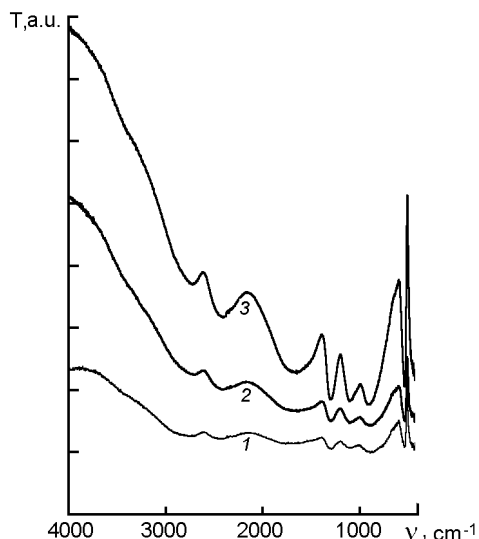
Fig. 5. IR-spectra of KDP crystals: pure KDP (*1*); KDP crystal grown from the solution with 0.2 M Urea content (*2*), KDP crystal grown from the solution with 10 M Urea content (*3*).

Fig. 6. Microhardness as a function of loading of the plane (001): KDP+10 M Urea (*1*); KDP+5 M Urea (*2*); KDP+0.2 M Urea (*3*); KDP+2 M Urea (*4*); KDP+1 M Urea (*5*); pure KDP (*6*) — the concentration of Urea is given for solution.

Fig. 7. Microhardness as a function of loading of the plane (100): KDP+5 M Urea (*1*); KDP+10 M Urea (*2*); KDP+1 M Urea (*3*); KDP+0.2 M Urea (*4*); KDP+2 M Urea (*5*); pure KDP (*6*) — the concentration of Urea is given for solution.

indentation being 10 s. For each sample H_V was calculated by taking the average of the results of 10 measurements on the planes (100) and (001); the root-mean-square fluctuation of H_V did not exceed 4 %. The microhardness value was estimated from the formula $H_V = 1.81544P/D^2$ (g/μm^2). In this expression H_V is the Vicker's microhardness, P is the applied load, D is the average value of the measured diagonal lengths.

Presented in Fig. 6, 7 is the dependence of the microhardness on the applied load. As is seen, with the increase in the load, the hardness value diminishes. At high loads the law of geometric similarity of the impressions is fulfilled, and the value of hardness is practically load-independent. At low loads the microhardness sharply increases or diminishes due to an elevated measurement error at small impression dimensions and to the influence of the damaged surface layer caused by treatment of the crystal. Fig. 6 testify that the doped samples acquire strengthening on the plane
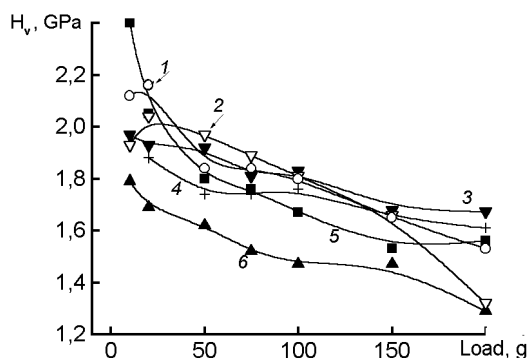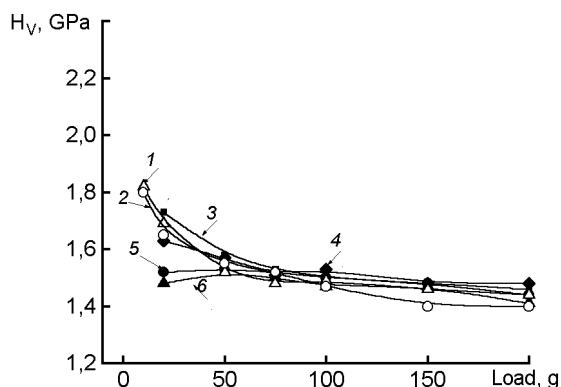
(001) in comparison with pure KDP crystal. Its value makes approximately 15–20 % taking into account a measurement error of 4–5 %. At the same time on the plane (100) (Fig. 7) strengthening is absent. Moreover, we observed different character of the formation of cracks and damage on the planes

Table 2. Wavenumbers of the absorption band maxima in the FTIR-spectra of KDP crystals

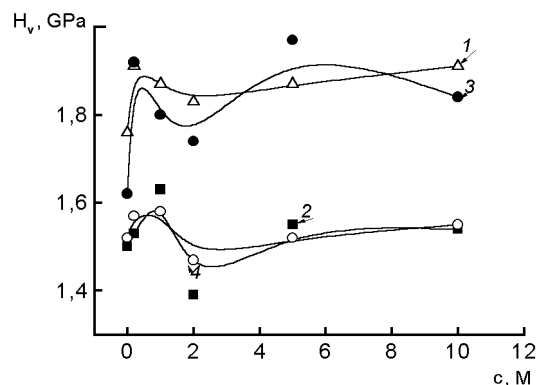| Urea concentration in the mother liquor, M	ν, cm^{-1}							
0	540	910	1107	1300	1700	2440	2749	3450
0.2	534	900	1107	1300	1650	2433	2699	3450
10.0	534	900	1107	1300	1640	2401	2706	3450

Fig. 8. Microhardness of KDP crystals depending on the concentration of Urea in the solution for the load $P = 50$ g: the sector {100} of the plane (001) (*1*); the sector {100} of the plane (100) (*2*); the sector {101} of the plane (001) (*3*); the {101} of the plane (100) (*4*).

Fig. 9. Efficiency of SHG for the crystals: KDP+2 M Urea (*1*); KDP+1 M Urea (*2*); KDP+0.2 M Urea (*3*); pure KDP (*4*) — the concentration of Urea is given for solution.

(001) and (100) caused by anisotropy of the mechanical properties of the crystal.

As seen from Fig. 8, the value of microhardness slightly varies at essentials changes in the concentration of Urea. In particular, for all the samples H_V increases at Urea concentrations up to 1 M, irrespective of the growth sector and the indentation plane. Thus, in contrast to the results reported in the paper [11], these data testify to the absence of explicit dependence of the microhardness value on the concentration of Urea.

The laser damage threshold of pure KDP samples and of those containing Urea was investigated at the wavelength of the first harmonic of neodymium laser. In the course of the measurements the energy of one-mode laser radiation pulse was 2.75 µJ, the frequency of pulse repetition equaled 1 Hz, the pulse duration $\tau = 10$ ns, $\lambda = 1.064$ µm. The 1/e-radius of the focused spot was estimated to be 45 µm. The investigated samples were located in such a way that the focus of the optical system should lie in the crystal bulk.

The preformed measurements show that the laser damage threshold of the doped samples is by 20–25 % higher than that of the pure samples, taking into account the experimental error equal to ±15 %. The average threshold value for the pure and doped crystals is ~25 J/cm^2 and ~32 J/cm^2, respectively. The crystals grown from the solution with Urea concentrations up to 1 M have the highest values of radiation strength, and this correlates with the data
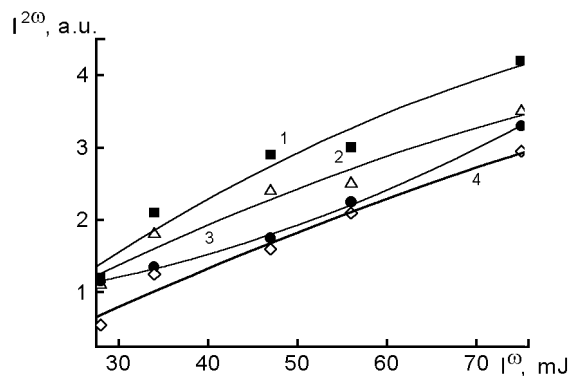
on mechanical strengthening of the crystals.

The non-linear optical (NLO) properties of the crystals were studied using the process of second-harmonic generation of YAG:Nd^{3+} laser at $\lambda = 1.064$ µm (with 5 Hz pulse frequency, 10 ns pulse duration, 1 mm laser beam diameter, the pulse energy instability being ±3.5 %). The samples of pure and doped KDP crystals were cut out at the synchronism angle $\theta = 59°$ (Type II, oe→e) and contained only the prism sectors {100}.

The data on the non-linear properties of the crystals are presented in Fig. 9. According to the obtained results, for the crystals grown from the solution with 0.2÷2 M Urea content the efficiency the second harmonic generation (SHG) increases in comparison with that of the pure crystal by ~20 % (taking into account a measurement error of ±7 %) and reaches the maximum value at 2 M Urea concentration. At Urea concentrations exceeding 2 M the efficiency of SHG insignificantly differs from its value for the pure crystal.

Single crystals of pure KDP and those with different molar values of Urea in the mother liquor (0.2; 1.0; 2.0; 5.0 and 10 M) were grown. The grown crystals were found to be transparent in the visible region. It was revealed that in the Urea concentration range 0.2÷2.0 M the change of the unit cell volume (obviously caused by the incorporation of the additive into KDP crystal lattice) was the most significant. The lattice parameter c ($\Delta c = 1.4 \cdot 10^{-3}$) of the grown crystals essentially increased with the addition of 0.2÷2 M of Urea to the solution. Preliminary measurements indicated that the second harmonic generation efficiency

increased in comparison with that of the pure crystal by ~20 %. It was found that the doped samples (grown in the presence of Urea) acquire a strengthening of approximately 15–20 % on the plane (001) as compared with pure KDP crystals. Single-shot laser damage at 1.064 μm wavelength showed that the LDT of the doped samples was by 20–25 % higher than that of the pure samples.

Finally, further studies are required to explain the relationship between the measured NLO and the structural properties of the grown KDP crystals and the concentrations of Urea additive in the mother liquor.

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Вирощування та властивості монокристалів KDP, легованих карбамідом

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Методом зниження температури на точковій затравці вирощено монокристали дигідрофосфату калію (KDP) із водних розчинів з різною концентрацією карбаміду. Вирощені кристали досліджено методами стандартної спектрофотометрії, ІЧ спектроскопії, прецизійної рентгенівської дифрактометрії. Вивчено вплив домішки карбаміду на нелінійно-оптичні властивості, лазерну міцність і мікротвердість кристалів KDP. Показано, що для кристалів вирощених із розчинів із вмістом карбаміду 0.2÷2.0 М спостерігається збільшення порогу лазерної міцності на 25 % і ефективності генерації другої гармоніки більш ніж на 20 % у порівнянні з чистими кристалами. На основі порівняльного аналізу значень мікротвердості для кристалографічних площин (100) й (001) встановлено збільшення механічної міцності допованих кристалів (вирощених в присутності карбаміду) на площині (001) відносно чистого кристала KDP.