

Effect of L-arginine on the optical properties, crystalline perfection and laser damage threshold of KDP crystals

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Potassium dihydrogen phosphate (KDP) single crystals doped with L-arginine amino acid were grown from aqueous solutions onto a point seed using the temperature reduction method. The incorporation of L-arg molecules into the crystal was verified by the methods of UV-vis-IR and FTIR spectroscopy. It was shown that the entering of L-arg into the matrix was accompanied with the increase of the volume of KDP:L-arg elementary cell by $\sim 2 \cdot 10^{-2} \text{ \AA}^3$ with respect to the one of the pure crystal. There was analyzed the influence of L-arg molecules on the value of laser damage threshold for different growth sectors of KDP crystal. The laser damage threshold of KDP:L-arg crystal was found to rise for the growth sector {101} and to diminish for the growth sector {100} with respect to the corresponding parameter of the pure crystal.

Keywords: dihydrogen phosphate, L-arginine amino acid, laser damage.

Монокристаллы дигидрофосфата калия (KDP), допированные аминокислотой L-аргинином (L-arg), выращены из водных растворов на точечной затравке методом снижения температуры. Вхождение молекул L-arg в кристалл подтверждено методами видимой и ИК спектроскопии. Показано, что вхождение молекул L-arg в матрицу сопровождается увеличением объема элементарной ячейки кристалла KDP:L-arg относительно чистого кристалла на величину $\sim 2 \cdot 10^{-2} \text{ \AA}^3$. Проанализировано влияние молекул L-arg на величину порога лазерного разрушения различных секторов роста KDP. Установлено увеличение порога лазерного разрушения для сектора роста {101} и уменьшение лазерной прочности для сектора роста {100} в кристалле KDP:L-arg относительно чистого кристалла.

Вплив L-аргініну на оптичні властивості, досконалість кристалічної структури та лазерну міцність кристалів KDP. *Е.І.Костенюкова, О.М.Безкровна, В.Ф.Ткаченко, М.І.Колібаєва, Д.С.Софронів, О.Ф.Долженкова, А.В.Лопін, І.М.Притула.*

Монокристали дигідрофосфату калію (KDP), допованого амінокислотою L-аргініном (L-arg), вирощено з водних розчинів на точечній затравці методом зниження температури. Вхідження молекул L-arg у кристал підтверджено методами видимої та ІЧ спектроскопії. Показано, що вхідження молекул L-arg у матрицю супроводжується збільшенням обсягу елементарної комірки кристала KDP:L-arg щодо чистого кристала на величину $\sim 2 \cdot 10^{-2} \text{ \AA}^3$. Проаналізовано вплив молекул L-arg на величину порога лазерного руйнування різних секторів росту KDP. Встановлено збільшення порогу лазерного руйнування для сектора росту {101} і зменшення лазерної міцності для сектора росту {100} у кристалі KDP:L-arg щодо чистого кристала.

1. Introduction

Potassium dihydrogen phosphate (KDP) is a traditional nonlinear optical crystal widely used for creation of optical converters of laser radiation, optical parametric generators, optical gates [1]. KDP crystals have become popular due to their transparency in the UV spectral region, high structure perfection, relatively high laser damage threshold and low cost of the fabrication of optical elements. However, one of the main functional restrictions for these crystals is relatively low value of quadratic susceptibility.

In KDP group crystals hydrogen bonds essentially contribute to nonlinear optical phenomena such as quadratic electrooptical effect and generation of higher harmonics. The increase of the number of hydrogen bonds and optimization of their spatial location in the crystals make it possible to control the nonlinear optical characteristics of the crystals [2]. For raising the quadratic susceptibility and, consequently, the efficiency of the three-wave processes, there have been made many attempts to incorporate organic molecules into KDP group crystals. In particular, such molecules include amino acid molecules which possess high polarizability due to the processes of internal charge transfer between the donor (COO^-) and acceptor (NH_2^+) groups [3–5]. KDP crystals doped with amino acids such as α -alanine, β -alanine, α -leucine, α -histidine, α -cystine and α -valine are reported in [6]. In [5, 7, 8] it has been found that incorporation of a number of amino acids (L-arginine (L-arg), L-valil, L-proline) into the structure of KDP group crystals raises the efficiency of the second harmonic generation (SHG). As shown by Parikh K.D. et al. [5], the efficiency of SHG in KDP: L-arg, grown with the addition of 0.3 wt. % and 0.4 wt. % of L-arg increases by a factor of 1.33 and 1.74, respectively, in comparison with that of pure KDP. For KDP crystal doped with L-threonine (0.4 wt % L-threonine in the solution) the efficiency of SHG exceeds the one of the pure crystal by 1.24 times [4].

Despite a variety of experimental data which testify to the possibility of the obtaining of efficient nonlinear optical materials on the base of KDP group crystals doped with organic molecules [9–11], the processes of physico-chemical interaction of the impurities with KDP matrix remain insufficiently studied. In particular, a number of papers report the presence of functional groups corresponding to amino acids in the IR spectra of

KDP:L-arg crystals which testifies to the entering of L-arg molecules into KDP crystal [10, 11].

It should be noted that the process of the entering of L-arg molecules into different growth sectors ($\{100\}$ and $\{101\}$), as well as the form of the molecule in the crystal (amino acid or L-arginine phosphate) are still being discussed.

The present work is aimed at studying peculiarities of the entering of L-arg into KDP crystal growing by the temperature reduction method onto a point seed. The influence of organic molecule on the optical properties, structure perfection and laser damage threshold of KDP crystal is investigated, too.

2. Experimental

Nominally pure KDP single crystals and the ones with incorporated L-arginine amino acid (Fig. 1) were grown by the temperature reduction method [1] onto $5 \times 5 \times 10 \text{ mm}^3$ point seed. The initial KH_2PO_4 salt was synthesized from the high-purity reagents H_3PO_4 and KOH , the content of the impurities (Fe, Al, Cr, Mg, Mn, etc.) in KH_2PO_4 salt did not exceed 10^{-5} wt.%. KDP and KDP:L-arg crystals were grown from aqueous solution in a 6 liter crystallizer the rate of temperature reduction was $0.4^\circ\text{C}/\text{day}$, the crystal growth rate being $1.3 \text{ mm}/\text{day}$. The duration of the growth was 40 days. The growth solutions were prepared by dissolving KH_2PO_4 salt in redistilled water according to the solubility curve at a saturation temperature of 50.9°C (at $\text{pH } 4.0 \pm 0.1$). Prior to the experiment, the solutions were overheated at 70°C . The solutions were passed through filters with a pore diameter of $0.05 \mu\text{m}$. To provide dynamic crystal growth conditions, the solution in the crystallizer was stirred at a velocity of 70 rpm. For the present study there were manufactured $10 \times 10 \times 10 \text{ mm}^3$ samples cut out from the growth sectors $\{100\}$ and $\{101\}$, the faces were oriented along the crystallographic axes. All the surfaces of the samples were finished by optical polishing.

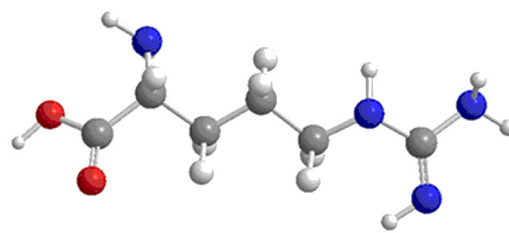
L-arg and orthophosphoric acid (85 %, ultra high purity) were mixed in equimolar proportions in the aqueous solution for the preparation of the crystalline powder L-arginine phosphate. The obtained powder was filtered, washed and air dried in an oven at 50°C .

The Fourier transform infrared spectra of the crystals and of the powders were recorded at room temperature in $400\text{--}4000 \text{ cm}^{-1}$ region by means of a Spectrum One Perki-

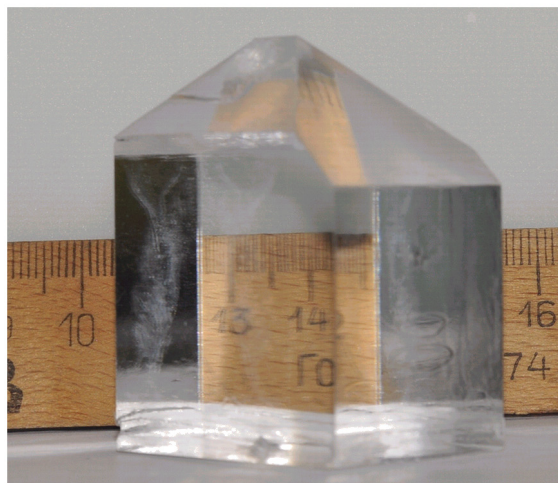
nElmer spectrophotometer using KBr pellet (~0.16 wt. % sample for all specimens). To measure IR spectra of the sample we used crushed samples of the pure and doped crystals, as well as L-arg powder and crystalline L-arginine phosphate powder. The UV-vis-IR absorption spectra for all the samples were registered by a Lambda 35 PerkinElmer spectrophotometer (200–1100 nm).

The influence of L-arg molecules on the matrix structure perfection was established on the base of the intensity data collected using a High Resolution Three-Crystal X-ray Diffractometer (germanium-monochromated, $\text{CuK}\alpha$ -radiation ($\lambda = 1.54051 \text{ \AA}$) at 300 K [12–14]. The width of incident monochromatic beam was ~50 μm , the height run into 2–8 mm, the horizontal divergence being $\ll 0.1''$. As the structure-sensitive parameters being measured by High Resolution Three-Crystal X-ray Diffractometer, the following were selected the diffraction reflection curve shape, the rocking curve half-width, β , the width at 10 % of rocking curve shape maximum intensity, β' , the integral reflection power, R_B [14]. The error of the measurement of the crystal lattice parameters was $\Delta a \pm 2 \cdot 10^{-6} \text{ \AA}$, $\Delta c \pm 2 \cdot 10^{-6} \text{ \AA}$, $\Delta V \pm 2 \cdot 10^{-4} \text{ \AA}^3$. Taking into account the mechanism of layer-by-layer crystal growth the measurements were realized for different reflections $\langle hkl \rangle$ at parallel ($\langle hkl \rangle_{\parallel}$) and perpendicular ($\langle hkl \rangle_{\perp}$) incidence of X-ray beam on the investigated sample with respect to coherent boundaries conjugation of the growth layer stacks in the crystal.

The laser-induced damage threshold (LIDT) of the samples was investigated at the wavelength of the first harmonic of Nd:YAG³⁺ laser. During the measurements the energy of single-mode laser radiation pulse was 2.75 μJ , the frequency of pulse repetition equaled 1 Hz, the pulse duration $\tau = 10 \text{ ns}$, $\lambda = 1.064 \mu$. The 1/e-radius of the focused spot was estimated to be 45 mm. The investigated samples were located in such a way that the focus of the optical system lay in the crystal bulk. The samples were irradiated by laser pulses at each point according to the scheme $n-1-n$ (90 positions were radiated at the same energy with the light propagating in the Z-direction, the samples were moved in the plane perpendicular to the laser beam). The criterion for laser damage was a spark of high-temperature glow visually observed at the crystal breakdown. The measurements were carried out on $10 \times 10 \times 10 \text{ mm}^3$ samples



a)



b)

Fig. 1. Photo of KDP:L-arg (a) and L-arg molecule structure (b). The computer model of L-arg molecule was built using ChemOffice.

cut out from the crystal growth sectors $\{100\}$ and $\{101\}$.

3. Results and discussion

KDP and KDP:L-arg (1.4 wt. %) crystals were grown from aqueous solutions by the temperature reduction method at the relative supersaturation $\sigma \sim 2 \%$ (Fig. 1). Both crystals had well developed growth sectors $\{100\}$ and $\{101\}$.

The UV-vis-IR transmission spectrum is very important for any optical material because a nonlinear optical material is of practical use only if it has a wide transparency window. The spectral transmission of the samples of pure and doped KDP was on the order of ~83–87 % in the visible region of the spectrum for both growth sectors ($\{101\}$ and $\{100\}$). Shown in Fig. 2 are the absorption spectra of the samples of KDP and KDP:L-arg crystals cut out from the prismatic $\{100\}$ and pyramidal $\{101\}$ growth sectors. As is seen, the spectrum of KDP:L-arg crystal contains absorption bands with maxima at 5.66 eV (219 nm) and 4.59 eV (270 nm) which seem to be caused by the entering of L-arg molecules into the matrix.

Such an assumption is confirmed by the fact that the observed position of the absorption maxima coincides with the one of the absorption bands in the UV region of the spectrum which are caused by the electron transitions of L-arg molecule in the aqueous solution [10]. In the samples obtained from the growth sector {101} of KDP crystal the said bands are absent (Fig. 2, spectrum 1). For the growth sector {100} the absorption band at 4.4 eV (280 nm) is obviously caused by the entering of ions of polyvalent metals into the crystal [15–17]. In our opinion, the presence of intense absorption bands in the UV region of the spectrum for KDP:L-arg crystal observed in both growth sectors {101} and {100} is connected with the entering of the amino acid molecules into the matrix.

The effect of L-arg and L-arginine phosphate on the vibration frequencies of the functional groups of pure KDP crystal has been identified by FTIR-spectroscopy. Shown in Fig. 3 are the FTIR spectra of KDP and KDP:L-arg crystals (the growth sectors {101} and {100}), as well as of L-arg and L-arginine phosphate powders. The IR spectrum of pure KDP crystal (Fig. 3, spectrum 2) contains the absorption bands with maxima at 1302, 1100 and 905 cm^{-1} corresponding to the vibrational modes of PO_4^{3-} (the stretching vibrations of P–OH), as well as the absorption band at 536 cm^{-1} corresponding to the deformational vibrations of PO_4^{3-} [18]. Analogous absorption bands at the wavenumbers 1099.4 cm^{-1} and 910.3 cm^{-1} , as well as at 536.2 cm^{-1} are reported in [4]. The IR spectrum of KDP:L-arg crystal (Fig. 3, spectrum 1) has additional absorption peaks with maxima at 617, 702, 872, 955, 1068, 1125, 1456, 1558, 1633 and 1658 cm^{-1} , as well as weak absorption peaks (observed as a shoulder) at 550 and 513 cm^{-1} . The position of such additional bands in KDP:L-arg crystals coincides with the position of the bands characteristic of the absorption spectrum of L-arginine phosphate molecules. As seen from Fig. 3 (spectrum 4), the IR spectrum of L-arginine phosphate contains characteristic absorption bands at wavenumbers of about 872, 1068, 1658 cm^{-1} . These bands reveal themselves in the spectrum of KDP:L-arg crystal, but in the spectrum of pure L-arg (Fig. 3, spectrum 3) they are absent.

The band at 955 cm^{-1} is present in the spectra of KDP:L-arg crystal, L-arginine phosphate and pure L-arg. The band in the vicinity of 872 cm^{-1} which is characteristic

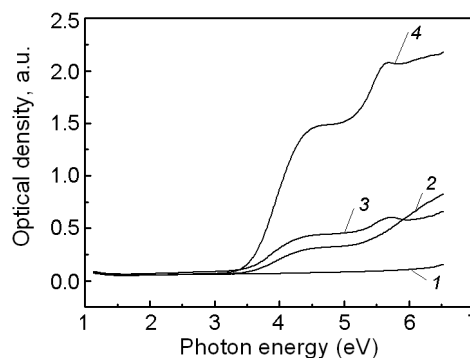


Fig. 2. Dependence of the value of optical density on the photon energy: the growth sector {101} of KDP (1); the growth sector {100} of KDP (2); the growth sector {101} of KDP:L-arg (3); the growth sector {100} of KDP:L-arg (4).

of KDP:L-arg crystal and L-arginine phosphate powder may be caused by C–C stretching vibration and P–OH stretching vibration [11]. The analysis of the spectrum shows that the absorption band at 1658 cm^{-1} in KDP:L-arg may be related to deformational vibrations of the group $=\text{NH}_2^+$ at $\nu = 1654 \text{ cm}^{-1}$ (L-arginine phosphate), the band at $\sim 1125 \text{ cm}^{-1}$ is connected with wagging vibration of the group $-\text{NH}_2$, whereas the band at 623 cm^{-1} corresponds to flat deformational vibration of $-\text{OH}$ (from the group $-\text{COOH}$) [11]. The absorption band with a maximum at 1560 cm^{-1} is characteristic of symmetric vibrations of COO^- , the band at 1380 cm^{-1} is connected with planar deformational vibration of C–C–H, the band at $\sim 702 \text{ cm}^{-1}$ corresponds to $-\text{NH}_2$ out of plane bending [11]. The fact that the position of absorption maxima in a number of bands characteristic of the spectrum of L-arg and L-arginine phosphate molecules coincides with the one of the absorption bands observed for KDP:L-arg testifies that the amino acid enters into both growth sectors. This may be explained by peculiarities of the charge state of KDP crystal faces [19]. L-arg molecule obviously enters into KDP crystal by means of coordination with its phosphate groups.

KDP crystals are characterized by a contrast between covalent chemical binds within the anionic groups and relatively weak ionic bonds between the cation and the corresponding anionic group. Depending on their direction and distribution in the crystal lattice, all chemical bonds in KDP crystal may be divided into three types: the ionic K–O (with a length of 2.897 Å) practically parallel to the axis z ; the ionic K–O (with a length of 2.824 Å) directed practi-

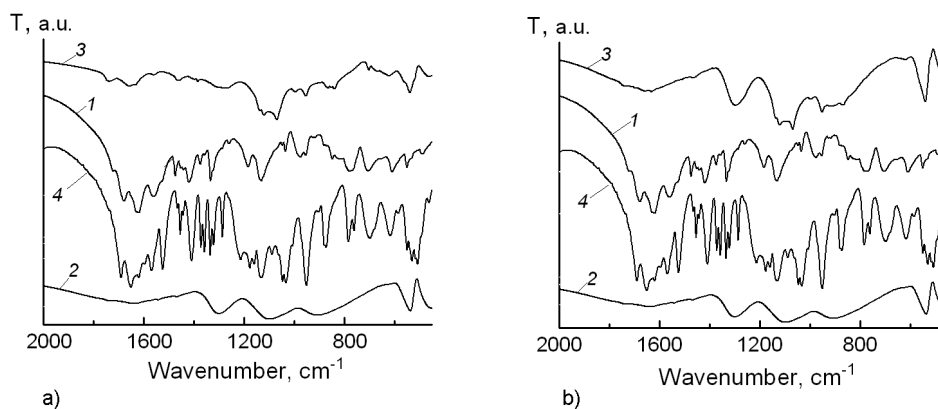


Fig. 3. FTIR spectra for the samples cut out from the growth sectors $\{101\}$ (a) and $\{100\}$ (b): KDP:L-arg (1) and KDP (2), L-arginine (3) L-arginine-phosphate (4).

cally perpendicular to the axis z ; the hydrogen bonds O–H...O (with a length of 2.495 Å) between two adjacent PO_4^{3-} groups perpendicular to the axis z [20]. Note that the hydrogen bonds play a significant role in the processes of migration of electronic excitations and energy transfer between the anionic groups of the crystal. As shown in [21–23], the pyramidal $\{101\}$ faces terminate in K^+ atoms rather than in H_2PO_4^- groups, while the prismatic $\{100\}$ faces terminate in alternating rows of K^+ and H_2PO_4^- ions. Thus, the prismatic $\{100\}$ faces can adsorb both ions of polyvalent metals and organic molecules (in particular, amino acids) able to form hydrogen bonds with the matrix. Evidently, L-arg molecules may enter into the growth sector $\{100\}$ since they contain carboxyl and amino groups due to the formation of hydrogen bonds with the prismatic $\{100\}$ faces, and be incorporated into the pyramidal sector owing to the Coulomb interaction between the negatively charged COO^- groups and the positively charged pyramidal $\{101\}$ faces.

Good functional properties of the material are closely related to its crystal structure. KDP crystal has a tetramolecular unit cell with the dimensions $a = b = 7.453$ Å and $c = 6.959$ Å [24]. The results of the study of the structure perfection of KDP and KDP:L-arg crystals for the growth sectors $\{101\}$ and $\{100\}$ are presented in Table. As is seen, on the whole there are no essential distinctions in the structure perfection of KDP:L-arg and KDP crystals. One can note only insignificant increase of the value of the structure-sensitive parameters β and β' — up to 3 % and up to 8 %, respectively, as well as the rise of the value of the parameter R_B in the geometry in which in-

cident X-ray beam is parallel to the coherent boundaries between the growth layer stacks. The analysis of the change of the crystal lattice periods shows an essential rise of the crystal lattice parameters by the value $\Delta a = 2.45 \cdot 10^{-4}$ Å for KDP:L-arg samples cut out from the growth sector $\{100\}$, and by the value $\Delta a = 2.42 \cdot 10^{-4}$ Å for the samples obtained from the growth sector $\{101\}$. While comparing KDP:L-arg and KDP crystal, in the former one can observe uniaxial "extension" of the elementary cell along the direction $[100]$ and "compression" along the direction $[001]$ for the samples obtained from both growth sectors. In KDP:L-arg, due to the increase of the lattice parameter a and less essential diminution of the parameter c , the volume of the elementary cell increases (see Table). This may lead to the appearance of elastic stresses in the lattice.

One of decisive criteria for a crystal material meant for nonlinear optical applications is the resistance to laser damage, since high optical intensities are involved during nonlinear processes. Multi-photon ionization is one important mechanism of free carrier generation when a KDP crystal is irradiated by the laser [25]. In [26] the effect of neutral and charged H-interstitial and H-vacancy on the laser damage of KDP crystals is reported. It is shown that the bandgap of KDP due to the existence of the neutral H-interstitial and positively charged H-vacancy are greatly reduced to 2.6 and 2.5 eV, respectively. The authors assume that these two types of defects may be responsible for lowering the damage threshold in KDP crystal [27].

The measurement of the value of laser strength of the grown crystals makes it possible to determine the average LIDT values for the pure and doped crystal. The obtained

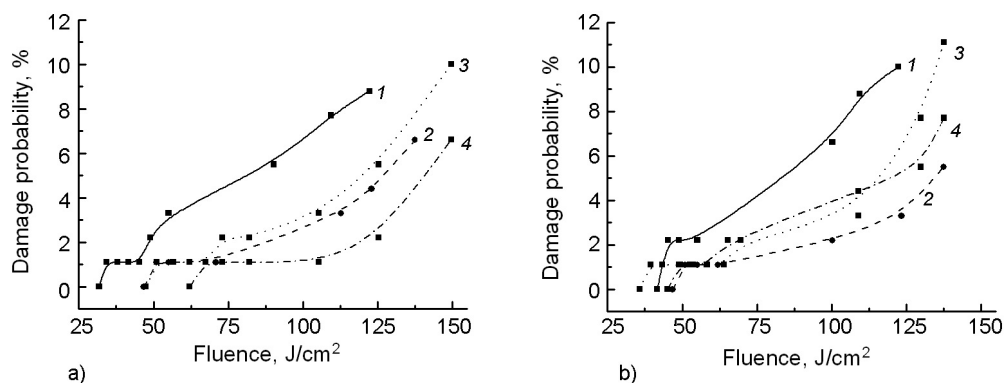


Fig. 4. The dependences of the probability of damage on the fluence of the incident laser radiation for samples cut out of the growth sectors {101} (a) and {100} (b): in the directions [100] (1) and [001] (2) for pure KDP, and in the directions [100] (3) and [001] (4) for KDP:L-arg crystal.

Table. Structure perfection characteristics of KDP and KDP:L-arg (1.4 wt. % L-arg) crystals

Crystal	Growth sector	<hkl> reflection	β	β'	$R_B \cdot 10^6$	$\Delta a (\pm 2 \cdot 10^{-6})$	$\Delta c (\pm 2 \cdot 10^{-6})$	$\Delta V^{**} (\pm 2 \cdot 10^{-4})$
KDP:L-arg	{100}	<800> _{II}	6.3	13.9	4.47	$+2.45 \cdot 10^{-4}$	$-8.0 \cdot 10^{-5}$	$+2.0 \cdot 10^{-2}$
		<800> _⊥	6.2	12.0	4.47			
		<080> _{II}	6.8	15.2	5.81			
		<080> _⊥	6.5	14.8	5.59			
		<008> _{II}	6.9	15.7	8.83			
		<008> _⊥	6.8/6.58	13.9	8.08			
	{101}	<800> _{II}	6.2	12.8	4.57	$+2.42 \cdot 10^{-4}$	$-9.5 \cdot 10^{-5}$	$+2.07 \cdot 10^{-2}$
		<800> _⊥	5.7	12.1	4.04			
		<080> _{II}	6.2	13.6	4.57			
		<080> _⊥	5.9	12.1	4.57			
		<008> _{II}	7.2	15.4	8.08			
		<008> _⊥	6.3/6.25	13.6	8.08			
KDP pure	{100}	<800> _{II}	6.2	13.8	4.46	$V = 387.1674$		
		<800> _⊥	6.1	12.0	4.45			
		<080> _{II}	6.8	18.4	5.05			
		<080> _⊥	6.6	12.6	5.00			
		<008> _{II}	6.2	13.9	8.77			
		<008> _⊥	6.1/6.33	13.7	8.51			
	{101}	<800> _{II}	6.2	13.4	4.67			
		<800> _⊥	5.9	12.6	4.47			
		<080> _{II}	5.9	12.6	4.57			
		<080> _⊥	5.7	11.6	4.70			
		<008> _{II}	6.2	13.6	8.72			
		<008> _⊥	5.7/5.93	12.5	8.30			

β, β' — arcsec, R_B — rad, $\Delta a, \Delta c$ — Å, ΔV — Å³.

values are the following: for the growth sector {100} in the direction [001] — 42.1 and 40.52 J/cm², respectively; in the

direction [100] — 37.24 and 32.1 J/cm²; for the growth sector {101} in the direction [001] — 42.1 and 55.92 J/cm²,

and in the direction [100] — 28.62 and 42.7 J/cm² (Fig. 4), taking into account the experimental error equal to $\pm 15\%$. The measured LIDT values testify that the doping of KDP crystal with the amino acid L-arg is accompanied with the rise of the laser damage threshold for the growth sector {101} in the directions [001] [100]. The observed effect may be caused by the fact that the formation of additional hydrogen bonds due to the presence of L-arg the lattice of KDP crystal can reduce the concentration of H defects which act as optical absorption centers in KDP. Thereat, it should be noted that the problem of the character of organic impurities on the value of laser damage threshold in KDP is not completely clarified and requires further investigations.

4. Conclusions

KDP crystals and KDP doped with L-arginine were grown by the temperature reduction method. Investigated were the effects of L-arg additives on the optical properties, crystalline perfection and laser-induced damage threshold of KDP. The optical transmission spectrum of KDP:L-arg showed very low absorption in the entire visible with a UV cut-off of 4.59 eV. The authors confirmed the interaction between KDP and amino acid by additional peaks in FTIR -spectra corresponding to the functional groups of L-arginine. L-arg molecules were found to enter in the growth sectors {100} and {101} of KDP crystal, either due to the fact that the carboxyl and amino groups formed hydrogen bonds with the face (100) in the former case, or, in the latter case, owing to the electrostatic interaction of the negatively charged carboxyl groups with the positively (101) face. By means of the Bond method using a multi-purpose three-crystal X-ray diffractometer it was shown that the presence of L-arg additive increased the crystal lattice parameter a of the grown crystals, and diminished the crystal lattice parameter c . The laser damage threshold was found to rise for the growth sector {101}, and to decrease for the growth sector {100} of KDP:L-arg with respect to the corresponding values for the pure crystal.

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